ORIGINAL PAPER

EVALUATION OF HEAVY METALS LEVELS IN *EVERNIADIVARICATA* THALLUS, GROWING ON SPRUCE AT DIFFERENT ALTITUDES IN BUCEGI MOUNTAINS, BY EDXRF SPECTROMETRY

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Abstract. *The study presents the researches concerning the dominant lichen species which are in a large expansion on conifers in many regions of the world, as well in Romania. We take in study one of the dominant lichen species Everniadivaricata, which is colonizing the conifers in Bucegi, because of the damages caused to trees, till a drying process. So, we have to establish the mainly heavy metals content of thallus in correlation with altitude. It is well known that the lichens are bioindicator for heavy metals pollution. The arboreal lichens were sampled from 900, 1200, 1500 and 1800 m altitude. The iron was found in the highest quantities in all samples collected from all four altitudes, between 526 ppm and 1824 ppm in lichen thallus. The other heavy metals investigated were in much lower quantities than iron (between 1 ppm and 73 ppm), at all four sampled stations. The metal content was different from one altitude to other.*

Keywords: *EDXRF, Everniadivaricata, heavy metals, altitude.*

1. INTRODUCTION

Everniadivaricata is a rare lichen species, which is registered in Red Data Books of Sweden and Lithuania and in the Lists of endangered lichens species in Finland, Austria and Poland [1]. It is a lichen species which is growing especially on branches of conifers and only occasionally on deciduous branches from mixed forests. *Everniadivaricata*was registered for the first time in Latvia in Vecpiebalga region by A. Bruttan, in 1869 [2-4] and later in Serbia [5]. Their habitat is on conifers in mesic forests [6]; it is spread in Rocky Mountains from Alberta to New Mexico and Arizona [7], rare in OR and WA. So, in spite of *Everniadivaricata* is spread all over the continents of the world, there are very few information on its physiological characteristics indicated in the Report of United States Forest Service National Lichens & Air Quality Database and Clearinghouse [6]. The content of heavy metals in lichens was studied in some species [8-11], but no information were found in the consulted literature about *Everniadivaricata* species. So our results come to enlarge the knowledge about this species of arboreal lichens and its heavy metals content in correlation with altitude.

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2. MATERIALS AND METHODS

Lichens thallus and substrate (tree bark) samples, collected from four stations corresponding to four altitudes on Furnica Mountains: 900 m, 1200 m, 1500 m and 1800 m, were analysed by Energy Dispersive X-Ray Fluorescence spectrometry using an Elva-X spectrometer with an X-ray tube with Rh anode [12-14] from Valahia University of Targoviste.

The samples were excited for 300 s and the characteristic X-rays were detected by a multichannel spectrometer based on a solid state Si-pin diode X-ray detector with a 140 mm Be window and an energy resolution of 200 eV at 5.9 KeV. The Elva-X software was used to interpret the EDXRF spectra. The accuracy and precision of results were evaluated by measuring a certified reference sample (NIST SRM 1571- Orchard leaves samples). The concentrations of Ti, Cr, Mn, Fe, Zn and Pb were determined, in this paper the results are reported as a mean of heavy metals concentrations from n=5 samples from each altitude.

3. RESULTS AND DISCUSSION

Fig. 1 shows that iron content in *Everniadivaricata* thallus is very high for the samples harvested at 1500 m and 1800 m altitude when compared to the samples from 900 m and 1200 m altitude. Maximum of concentration was registered at 1500 m, about 1823.94 ppm, followed by the concentration registered at 1800 m, about 1308.01 ppm.

The quantities of iron foundunder 1500 m altitude were significant lower, between 526.232 ppm and 590.841 ppm.

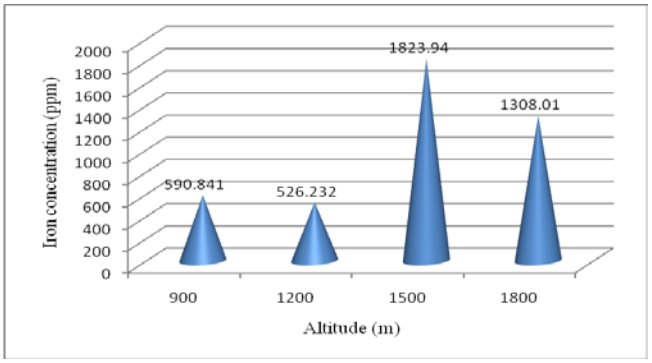

Fig. 1. Iron content in *Everniadivaricata* growing at different altitudes.

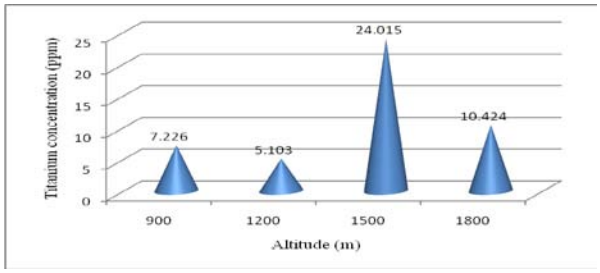

Fig. 2. Titanium content in *Everniadivaricata* growing at different altitudes.

Titanium content was at maximum concentration, of 24.015 ppm,in *Everniadivaricata* thallus sampled at 1500 m (Fig. 2). Minimum titanium content of 5.103 ppm was obtained at 1200 m altitude. By comparison, the content of titanium in lichens sampled at 1800 m was two times higher (of 10.424 ppm), but two times lower than the content foundin samples at

1500 m altitude. Titanium as well as iron was found in maximum concentration at 1500 m altitude.

Nickel content is significant higher in lichens sampled under 1800 m altitude (Fig. 3). Minimum of nickel concentration in lichens thallus was registered at 1800 m. Maximum of nickel content was in lichens samples harvested at 1200 m. Unlike iron and titanium, nickel is concentrated in lichens sampled under 1500 m altitude (Fig. 3).

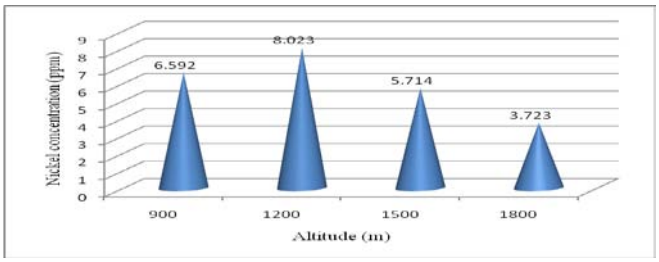

Fig. 3. Nickel content in *Everniadivaricata* growing at different altitudes.

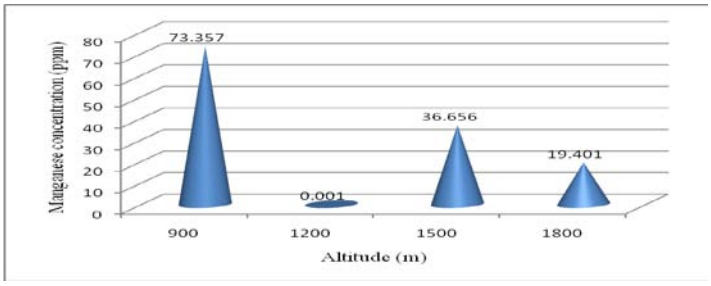

Fig. 4. Manganese content in *Everniadivaricata* growing at different altitudes.

The concentration of manganese was maximum in *Everniadivaricata*thallus sampled from 900 m altitude, of 73.357 ppm (Fig. 4). Minimum of manganese concentration was registered at 1200 m altitude, about 0.001 ppm. Manganese content had a significant increasing in lichens sampled from 1500 m altitude (36.656 ppm), reaching the half of value obtained at 900 m. At 1800 m altitude, the concentrations of manganese, 19.401 ppm, represent half of the concentration obtained in thallus collected from 1500 m.

Maximum content of chromium was determined at 1500 m altitude and was 6.287 ppm (Fig. 5). At the others three altitudesinvestigated, the concentrations of chromium in lichens were significantly reduced. Chromium content was between a minimum of 2.274 ppm and a maximum of 6.287 ppm. Chromium content in lichens was similar for the lichens samples collected 900 and 1200 m altitude.

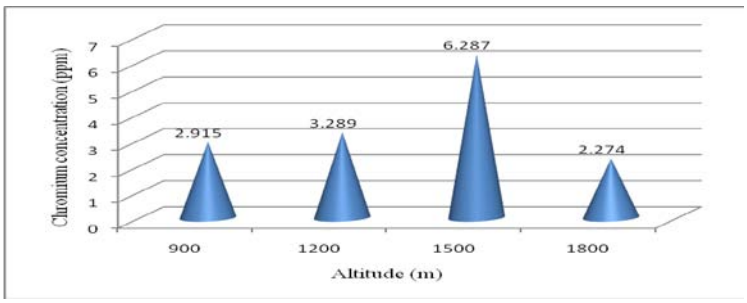

Fig. 5. Chromium content in *Everniadivaricata* growing at different altitudes.

The aspect of graph for zinc content (Fig. 6) is similar with the graph for nickel (Fig. 3), only the values differ significantly. So, maximum of zinc content was obtained at 1200 m altitude and it was 19.362 ppm. Minimum content of zinc was in lichens samples collected from 1800 m altitude and was 8.994 ppm. The medium quantities of chromium were found in lichens samples collected at 1500 and 1800 m altitude.

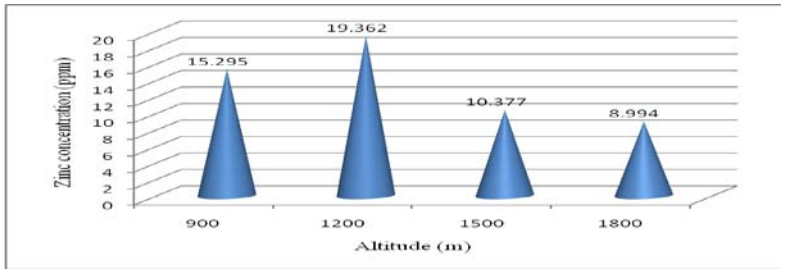

Fig. 6. Zinc content in *Everniadivaricata* growing at different altitudes.

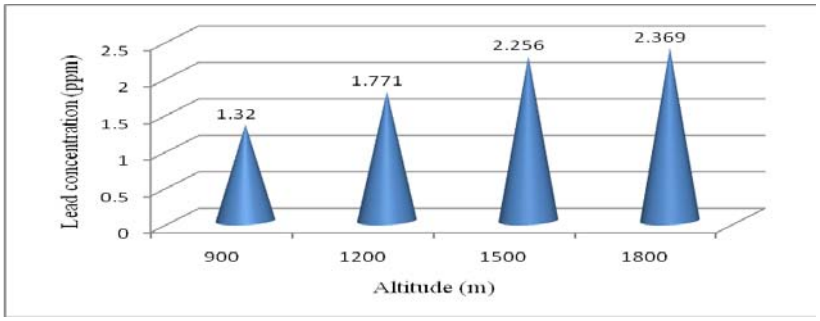

Fig. 7. Lead content in *Everniadivaricata* growing at different altitudes.

The aspect of Fig. 7, very different comparing to the others, shows that lead concentration was increasing very slightly from 900 m to 1800 m altitude. The values of lead were between 1.32 ppm, the minimum registered at 900 m, and the maximum of 2.369 ppm found in samples collected at 1800 m altitude. All concentrations determined were very low, lower than 3 ppm. The highest quantities of metal found were for iron in lichens samples collected from all four altitudes, between 526.232 ppm and 1823.94 ppm (Fig. 1). So, because the differences between iron content and the other heavy metal content wassignificant, the iron content cannot be presented in the diagram for comparison between metals. At 900m altitude (Fig. 8) manganese was found in the highest concentration (73.357 ppm) afteriron. The lowest concentrations were for chromium (2.915 ppm) and lead (1.32 ppm).

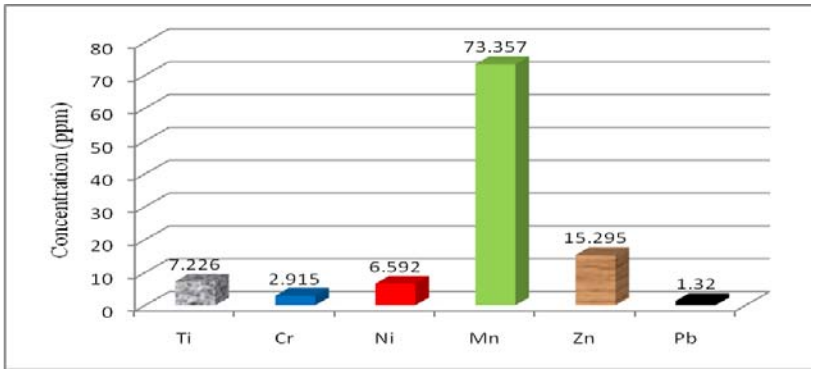

Fig. 8. Heavy metals content in *Everniadivaricata* growing at 900 m.

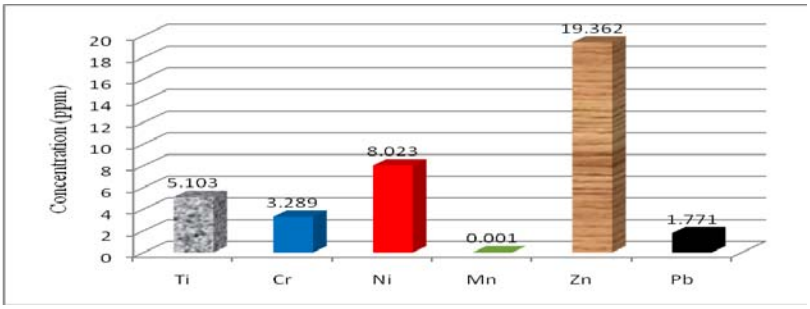

Fig. 9. Heavy metals content in *Everniadivaricata* growing at 1200 m.

Nickel and titanium contents were 6.592 ppm and respectively 7.226 ppm. The third place as value belongs to zinc which was obtained in medium concentration of 15.295 ppm. At 1200 m altitude the situation is quite different. Manganese was found in the lowest quantity (0.001 ppm) and zinc was on second place after iron (Fig. 1), about 19.362 ppm insamples of *Everniadivaricata* (Fig. 9). A medium concentration had nickel (8.023 ppm), followed by titanium (5.103 ppm). Significant lower concentrations had chromium (3.289 ppm) and lead (1.771 ppm).

In the lichens samples collected from 1500 m altitude values of manganese (Fig. 10) are on second place after iron (Fig. 1) with 36.656 ppm, followed by titanium with 24.015 ppm.

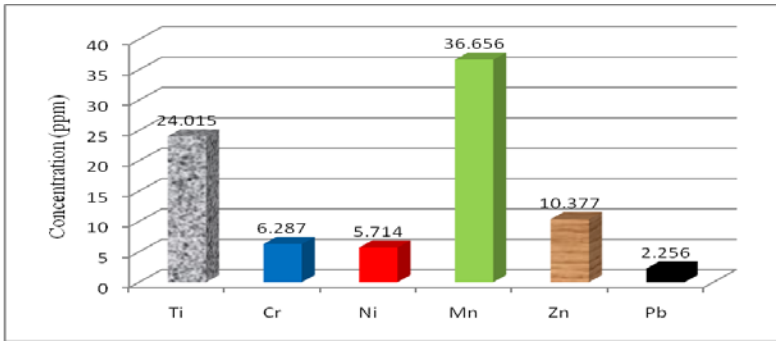

Fig. 10. Heavy metals content in *Everniadivaricata* growing at 1500 m.

The lowest concentration was registered for lead follow by nickel and chromium. Important concentrations were found for zinc (10.377 ppm). Can be seen important differences between Figs. 9 and 10 concerning the values of heavy metals content.

The aspect of Fig. 11 (about heavy metals content in lichens sampled at 1800 m altitude) is approximately the same with Fig. 10, only the values are different. So, manganese concentration is again on the second place as value after iron concentration (Fig. 1). Only the lowest concentration belongs to chromium not to lead, but they are similar as value.

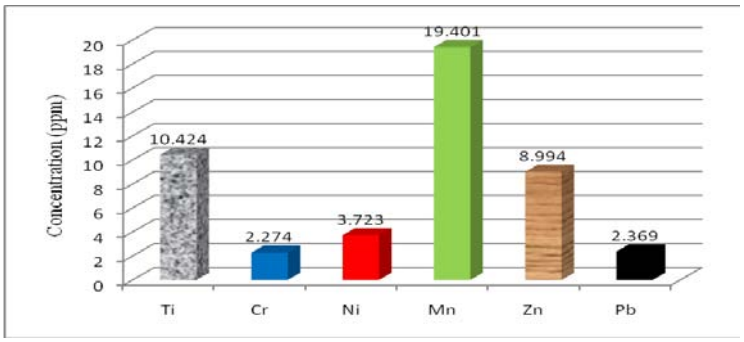

Fig. 11. Heavy metals content in *Everniadivaricata* growing at 1800 m.

4. CONCLUSIONS

Knowing that the lichens are bioindicator for heavy metals pollution of air, this study is a preliminar study regarding the heavy metals content of *Everniadivaricata* lichen species at different growing altitude. The concentrations of iron found in *Everniadivaricata* samples were the highest at all altitude when compare to the others heavy metals studied; maximum level of concentration was registered at 1500 m. Also the content of chromium was highest at 1500 m altitude as well as iron, but the values were very different. Maximum content of

nickel and zinc was registered in lichens samples collected from 1200 m altitude. Manganese was in the highest concentrations in lichens sampled at 900 m altitude. The lowest content of lead was obtained in all samples no matter the altitude, with very slight differences of values. Manganese is on the second place as content, after iron, in lichens samples at 900 m, 1500 m and 1800 m altitude, but had very low concentrations at 1200 m. At 1200 m altitude the second place after iron belongs to zinc content in lichens samples.

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