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LEAD, COPPER AND ZINC CONTENT IN NATIVE LICHENS AND MOSSES COLLECTED FROM BAIA MARE SMELTER AREA

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Abstract: This paper presents results concerning the atmospheric pollutants deposition over the industrial area of Baia Mare. Such studies are in general difficult to achieve, mainly due to the lack of suitable, sensitive and inexpensive techniques (such as using bioindicators) that allow simultaneous measurements at a large number of sampling sites. The aim of this study was to test the Pb, Cu and Zn concentrations monitoring procedure by using lichens and mosses in the vicinity of industrial sources, in the absence of any information concerning emission, meteorological parameters and biogeochemistry. The Pb, Cu and Zn concentrations were determined in native lichen and moss samples collected from Baia Mare areas. For lichens and mosses the results were compared with the same level of elements determined in a control sample, collected from an unpolluted area. In order to assess the pollution degree in this region the same elements were determined in soil samples, too. The ratios of these three elements were calculated versus the normal, alert and intervention levels in soils accepted for Romania and published in "Monitorul Oficial" [9].

Introduction

Airborne contaminants are usually measured with specialized instruments but, during the last three decades, lichens and mosses have increasingly been used as indicators of metal contaminants. Most works on the accumulation of heavy metals by lichens and mosses has focused on pollution from smelters, power plants, busy roads, urban sites and rural areas. According to literature over five hundred papers have been published on this topic [2,3,5].

The pollution level in the Baia Mare area is one of the highest in Romania, due to the emissions from S.C. Allied Deals Phoenix S.A. and S.C. Romplumb S. A. At the east end of the town there is a large copper smelter (Phoenix Company) using copper and mixed ores from many different sources. Here, the main pollutants are SO_2 and airborne particulate matter containing Cu, Pb, Zn, As, etc., practically all the elements contained in the mine products. Two km north of this point, in a valley, the second pollutant source in Baia Mare is located, which is a plant for manufacturing and recycling metallic Pb (Romplumb Company). This plant is the main polluter with Pb and Zn.

Bartók (1989), Ştefănescu and Bartók, (1998), performed previous studies concerning lichenological mapping of the air pollution intensity in the industrial basin of Baia Mare. These results proved the correlation between the presence of certain species of lichens and the level of atmospheric pollution in the investigated area.

This paper presents the results concerning the atmospheric pollutants deposition over the industrial area of Baia Mare. Such studies are in general difficult to achieve, mainly due to the lack of suitable, sensitive and inexpensive techniques (such as using bioindicators) that allow simultaneous measurements at a large number of sampling sites. The aim of this study was to test the Pb, Cu and Zn concentrations monitoring procedure by using lichens and mosses in the vicinity of industrial sources, in the absence of any information concerning pollutants emission, meteorological parameters and biogeochemistry. The Pb, Cu and Zn concentration were measured in native lichen and moss samples collected from Baia Mare area. The results were

compared with the level of the same elements determined in a control samples, collected from an unpolluted area. In order to assess the pollution degree in this region the same elements were determined in soil samples, too. The ratios of these three elements were calculated versus the normal, alert and intervention levels in soils accepted for Romania and published in "Monitorul Oficial" [9].

Sampling and sample digestion procedures

Lichen, moss and soil samples were collected from 11 sites located at various distances from the Phoenix and Romplumb Companies. The sampling sites are marked in Fig. 1.

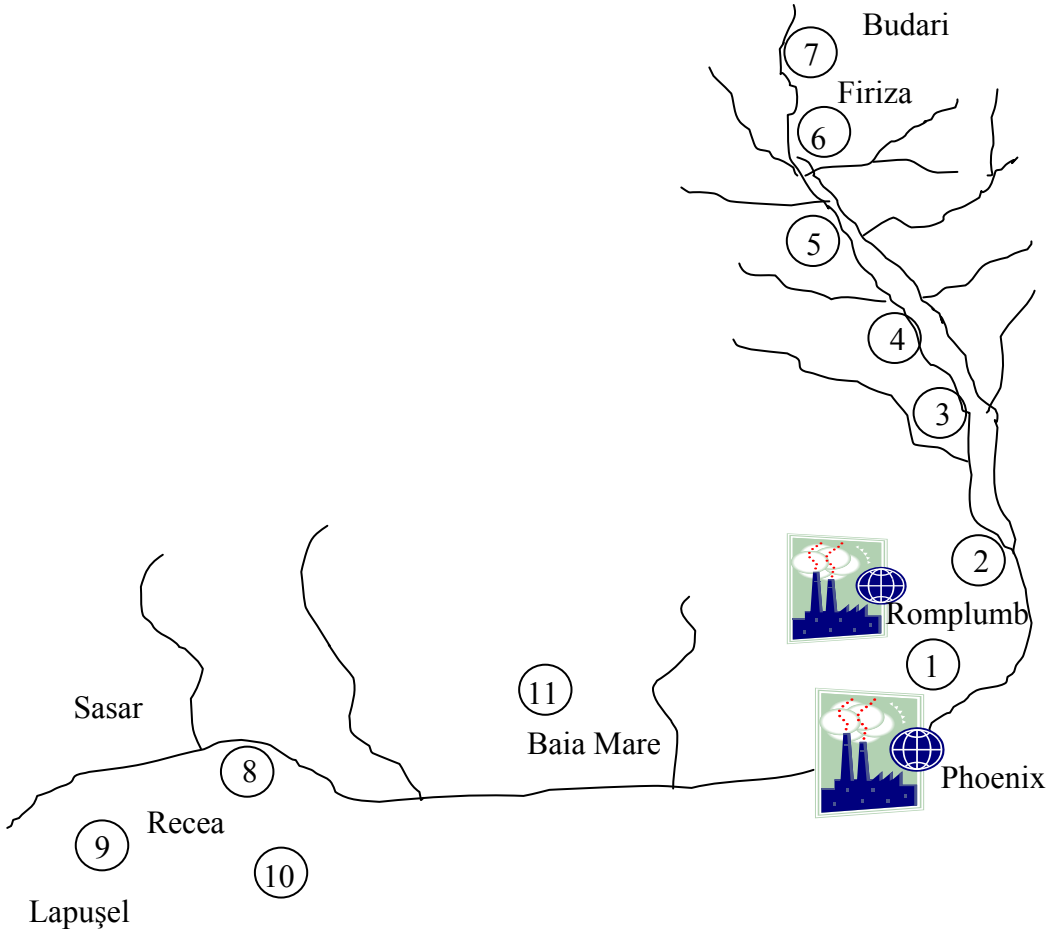


Fig. 1: Sketch map of the Baia Mare area and the location of the sampled sites.

There have been collected five lichen species (*Cladonia coniocraea, Cladonia caespiticia, Cladonia cornuto-radiata, Cladonia furcata, Cladonia fimbriata*) from sites 1-6 and 11, and 11 species of mosses (*Ceratodon purpureus, Amblystegium varium, Pohlia annotina, Brachythecium velutinum, Amblystegium varium, Weissia microstoma, Bryum argenteum, Bryum flaccidum, Brachythecium populeum, Bryum klinggraeffii, Pohlia wahlenbergii)* from sites 1, 2, and 4-9.

The bryophytes and lichens communities have their structural characteristics related to environmental factors. Mosses and lichens are components of the same vegetation stratum and almost all have the common feature of being poikilohydric. However, there are major ecological differences between these two groups.

The relative increase of mosses (and corresponding decrease of lichens) as compared to the total number of bryophyte and lichen species is highly correlated with increasing pH, moisture and with finer soil textures [4,6]. Accordingly, in Baia Mare industrial areas more moss species than lichens have been found.

The lichen and moss samples were carefully removed manually from their substrate and covered in tissue paper. They were subsequently stored in plastic bags prior to drying and cleaning. Soil samples were also collected beneath the location of every lichen and moss sample, which were bagged in self-sealing paper envelopes and left to dry at room temperature.

An amount of 0.5 g of (each lichen and moss) samples was digested with HNO_3/H_2O_2 mixture and diluted to 50 ml with distillated water to the final analysis volume.

In each case, an amount of 0.25 g of finely ground soil sample was digested with Lunge reagent (3:1 HNO_3:HCl v/v). The resulting samples were cooled and bulked to 100 ml.

Pb, Cu and Zn contents in all the samples were analyzed by flame atomic absorption spectrometry using a Perkin-Elmer Model 3030B atomic absorption spectrometer with air-acetylene flame.

Results and Discussions

This study demonstrates that there are different accumulation levels of contaminant in the sampling sites. It also shows that there are two main point sources of pollution in the Baia Mare area and the concentration of all measured elements, both in native lichens and mosses, are higher than in the control areas.

In lichens, Pb ranges from 103mg/kg (d.w., dry weight) in slightly polluted areas, up to 9513 mg/kg d.w. next to the main pollutant source (Romplumb Company). Copper ranges from 97 mg/kg up to 383 mg/kg, while Zn ranges from 69 mg/kg up to 290 mg/kg. The samples collected in the unpolluted area (Băişoara Mountain) exibited 40 mg/kg of Pb, Cu and Zn 9 mg/kg and 60 mg/kg, respectively.

Figure 2 presents the ratio of Pb, Cu and Zn concentrations in native lichens collected from Baia Mare area versus the concentration of the same element determined in lichens collected from an unpolluted area. Among the investigated elements, Pb shows the strongest accumulation in lichens, exceeding 238 times the control value in the vicinity of Romplumb Company. This result was expected, because this Company is the main source of Pb pollution. In the lichens collected between Romplumb and Phoenix the Pb level was 90 times higher than in the control samples.

Cu-containing particles are released in large amounts in the smelter area, fact reflected in the pollution degree of lichens. Therefore, at 10 km distance from the Phoenix plant pollution is still 11 times higher than in the background samples, the maximum value of contamination (43 times) being recorded at 6.25 km distance from the Phoenix Company.

For Zn, the concentrations showed relatively similar values in all samples, the pollution degree ranging between 1.2- 4.8 times more than in the unpolluted area. The general trend is less clear than that of Cu and Pb. The same behaviour of Zn was observed in the neighborhood of Zlatna smelter [7].

In native mosses, Pb ranges from 40 mg/kg up to 1677 mg/kg, the maximum value being also measured in the vicinity of the Romplumb plant. Copper ranges from 95 mg/kg up to 782 mg/kg, while Zn ranges from 159 mg/kg up to 1183 mg/kg.

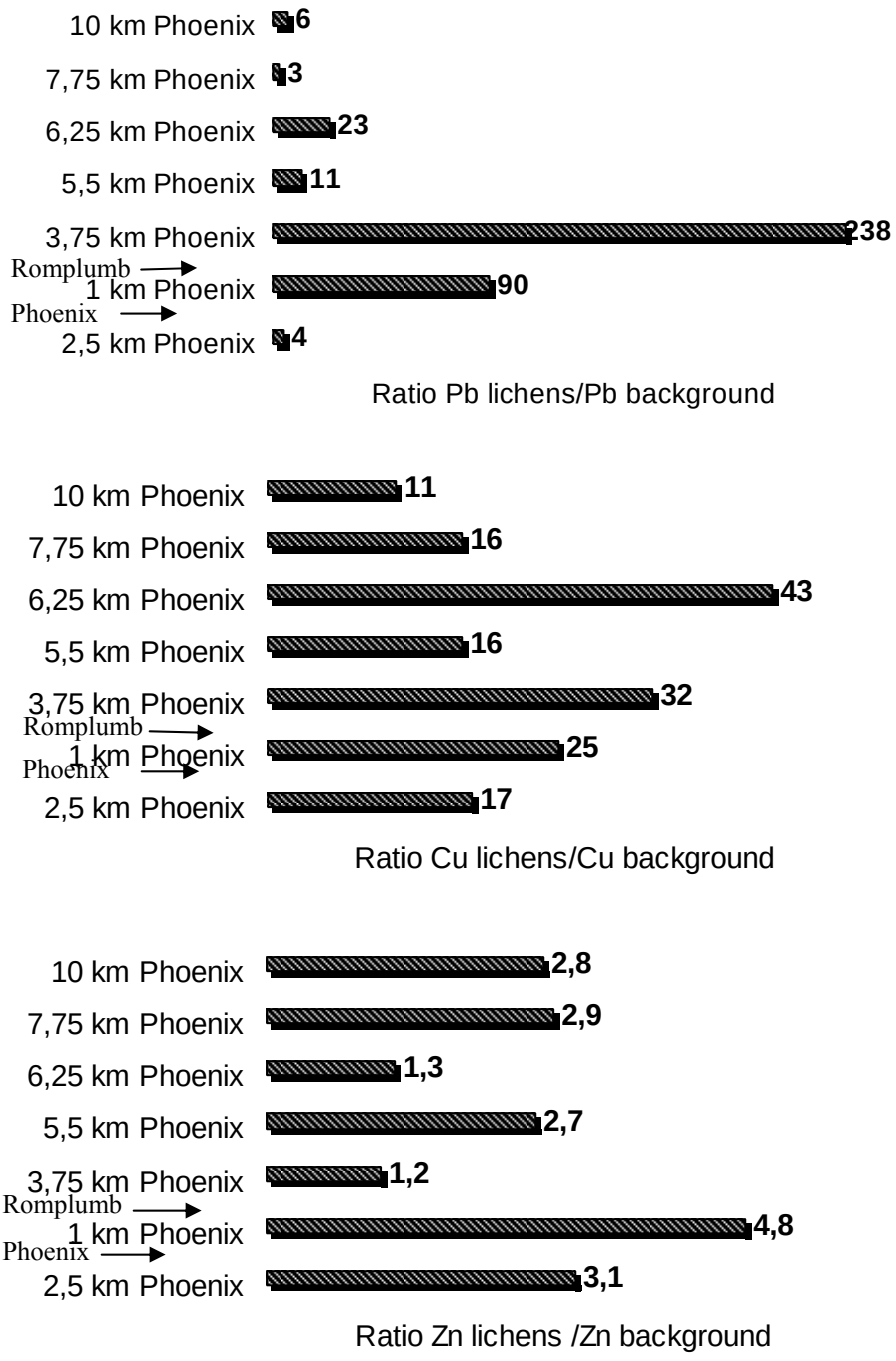


Fig. 2: The ratio of Pb, Cu and Zn concentration in native lichens collected from Baia Mare area *versus* those determined in lichens collected from an unpolluted area.

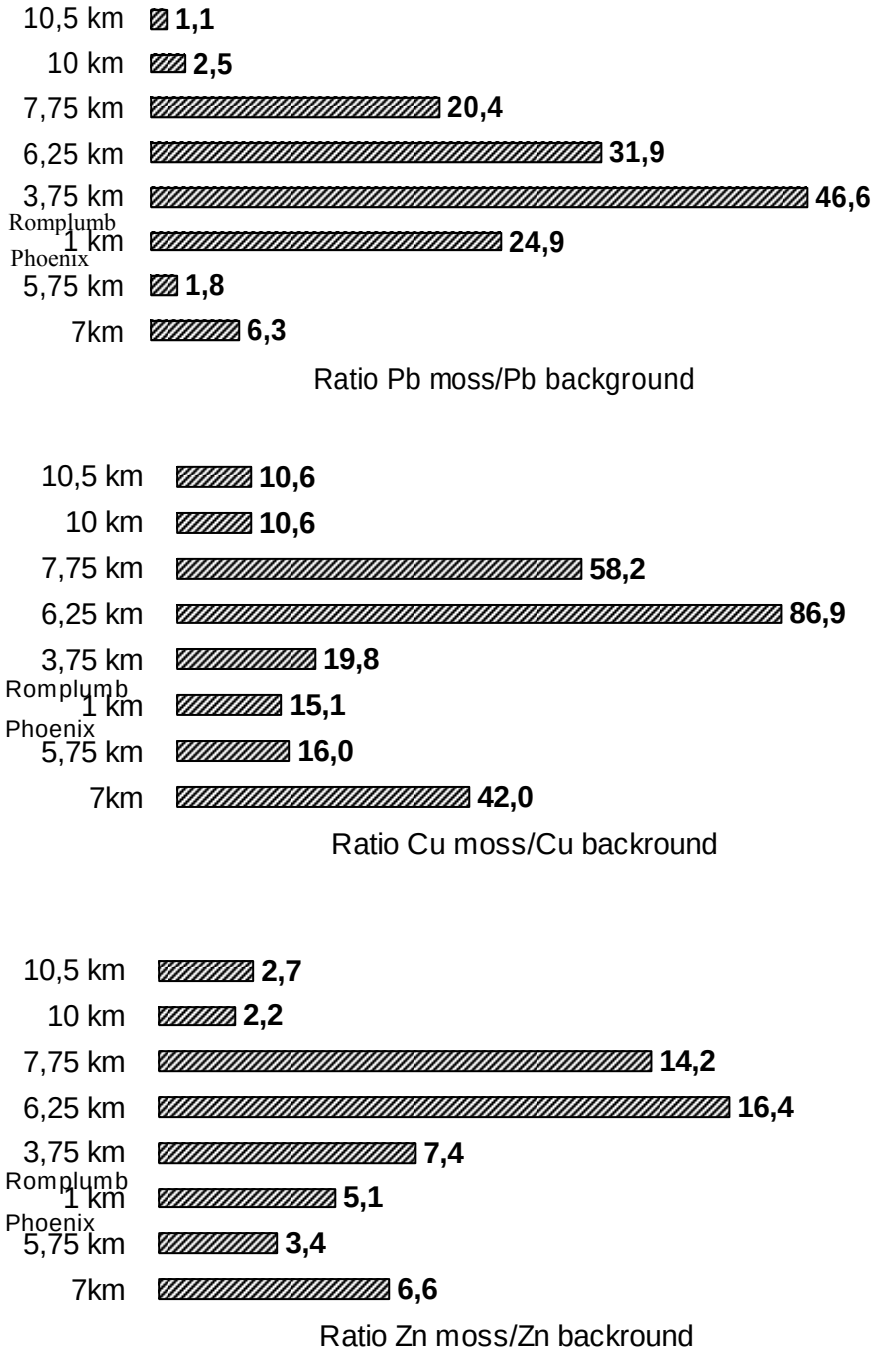
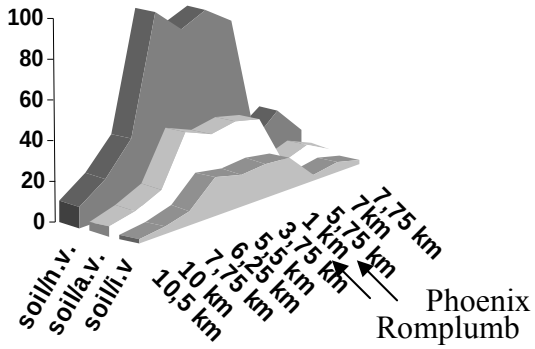
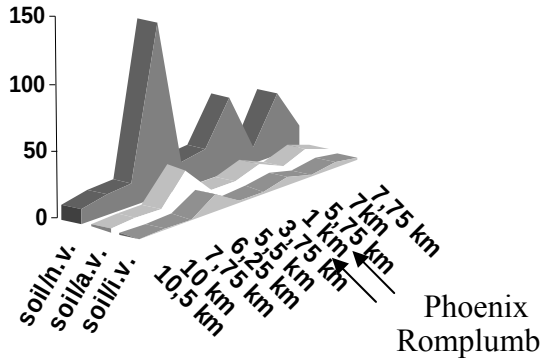


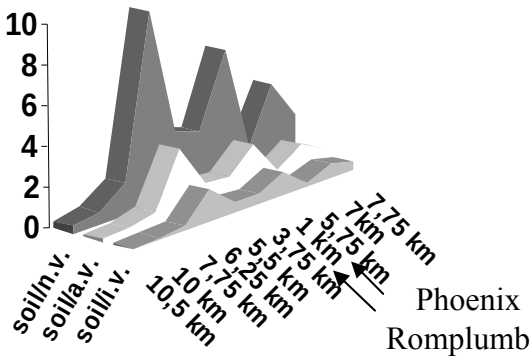
Fig. 3: Ratio Pb, Cu and Zn concentrations in native mosses collected from Baia Mare area *versus* the same element concentrations in mosses collected from unpolluted area.



Pb



Cu



Zn

Fig. 4: Ratio of Pb, Cu and Zn concentrations *versus* normal (n.v. 20, 20, 100 mg/kg), alert values (a.v. 50, 100, 300 mg/kg) and intervention values (100, 200, 600 mg/kg) of the same elements in soil samples collected from Baia Mare area.

The Pb, Cu and Zn concentrations determined in the moss sample collected from an unpolluted area were 36 mg/kg, 9 mg/kg and 72 mg/kg, respectively.

Figure 3 exhibits the ratio of Pb, Cu and Zn concentrations in native mosses collected from Baia Mare area versus the same elements in the control moss samples. The degree of Cu

accumulation in mosses is higher than that in lichens. The highest concentration of Cu, measured at 6.25-km distance from Phoenix Company, is 87 times higher than that determined in the control sample.

In the same sampling sites, the maximum Pb values for both lichens and mosses were determined. The general trend between the sites is less obvious, but the decrease of Pb concentration away from the sources is evident.

The Zn accumulation in mosses reached the lowest levels among the three investigated elements. The behaviour of Zn is similar with that of Cu.

In order to assess the pollution degree in the studied area Pb, Cu and Zn concentrations in soil samples were determined, too. The ratio of Pb, Cu and Zn concentrations in soils versus the normal, alert and intervention level of the same elements in soils [9] are represented in Fig. 4. The Pb contamination is above 1500 mg/kg in four sampling sites in the vicinity of both plants to a distance of 6.25 km; to the same distance, Cu and Zn concentrations were found the highest (2646 mg/kg and 972 mg/kg, respectively). In all the studied sites Pb, Cu and Zn levels exceeded the intervention level. The intervention levels were surpassed in the case of Pb by 19 times, in the case of Cu 13.2 times, while Zn 1.6 times. The Pb content of the soil is positively correlated to the Pb content of the mosses (Fig. 5); no other correlation among the other measured elements, or between soil-lichen or soil-moss concentrations was found.

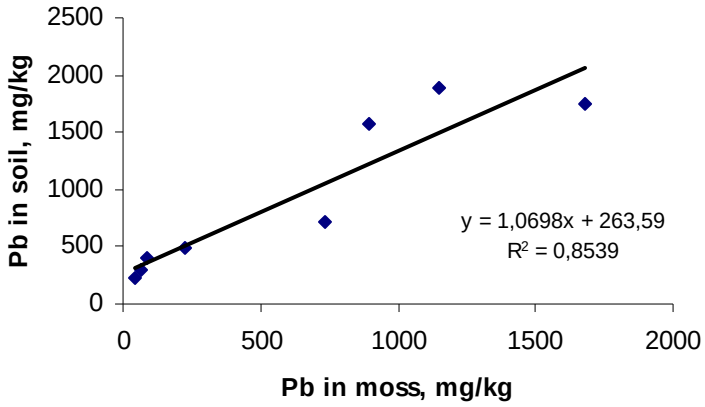


Fig. 5: Relations between Pb concentration in soil samples and in mosses collected from Baia Mare smelter areas

Conclusions

The concentrations of pollutant elements measured in the sites of Baia Mare indicated high levels of pollution in the area around the smelters. The accumulation degrees of Pb, Cu and Zn are different in lichens and mosses. The mean values for the three analyzed elements from all sites in the industrial areas were calculated. According to these data, the following successions of mean concentrations (mg/kg) could be recorded for each element:

Pb: lichens (2140) > soil (918) > moss (610)
Cu: soil (708) > moss (292) > lichens (206)
Zn: moss (527) > soil (328) > lichens (161)

Based on these results it is evident that the studied industrial region is most strongly polluted with Pb and Cu.

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CONŢINUTUL DE PLUMB, CUPRU ŞI ZINC ÎN LICHENII ŞI MUŞCHII NATIVI DIN ZONA INDUSTRIALĂ BAIA MARE.

(Rezumat)

Pentru determinarea gradului de poluare cu Pb, Cu şi Zn în zona industrială Baia Mare şi zonele limitrofe s-au utilizat lichenii şi muşchii nativi ca bioindicatori, datorită proprietăţilor acestor plante de a reţine şi acumula pulberile şi suspensiile emanate de combinatele S.C. Phoenix S.A. şi S.C. Romplumb S.A. În această zonă flora lichenologică este mult redusă, atât ca diversitate, cât şi ca abundenţă. Din această cauză, numai lichenii aparţinând genului *Cladonia* cu o toxisensibilitate mai redusă, respectiv 11 specii de muşchi care aparţin la 5 genuri, s-au utilizat pentru monitorizarea gradului de poluare. Concentraţiile de Pb, Cu şi Zn determinate în lichenii şi muşchii nativi au fost comparate cu concentraţiile aceloraşi elemente măsurate în probe martor colectate dintr-o zonă nepoluată (Băişoara). De asemenea, pentru evaluarea gradului de poluare a zonei investigate, s-au analizat cele trei elemente şi din probe de sol. Rezultatele obţinute au fost comparate cu valorile normale, pragurile de alertă şi de intervenţie prevăzute în Monitorul Oficial al României [9].