The Accumulation of Metals in Lichens

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Abstract
The capacity to accumulate metal in the lichen communities has been used to identify the level of air pollution due road traffic. Several analyses have been conducted in the study, on tissue from lichens collected from six areas: the park of a town, various sites on the town's freeway and on a county road segment with moderate traffic. The analyzed lichens were from the *Parmelia spp.* species which grow naturally on trees found in borderline lanes of motorways. Based on the degree of heavy metal accumulation such as Cd, Cr, Cu, Fe Mn, Pb, Ni and Zn in the *Parmelia spp.* lichens, a correlation has been made, with the road traffic. According to the metal bioaccumulation degree in lichens tissue, it has been established that the sources such as traffic from the outskirts of cities, from the perimeter of gas stations and of county roads continuously spread products which contain these elements, into the atmosphere. The fast information regarding the quality of the air in the environment allows the use of lichens as organism which can indicate environmental conditions and their modification by accumulating substances.

Keywords: lichen, metal bioaccumulation, *Parmelia spp.*, traffic.

1. Introduction

Lichens have a wide life span and they are found, naturally, on trees, stones, etc. Due to their lack of roots and the fact that they are situated in the atmospheric layer of the earth, the lichens have a greater exposure to atmospheric pollutants and lack access to nutrients in the soil. Their lives depend on the atmospheric deposits, on the water that runs on the surfaces on which they are attached, on the atmospheric gases and on other relatively diluted sources which ensure their food. Thus, the content of substances in the lichens reflects, mostly, the quality of the atmosphere, respectively, the content of nutritional substances and pollutants. Their accumulation properties, especially for metals, in their tissues make them useful for temporary and spatial studies of the environmental quality. Many species of lichens are present in large geographical areas, fact that permits various studies of pollution to be conducted on extended areas. They can be monitored under these conditions during any season of the year. The species of lichens which grow on trees, rocks or buildings are often the fittest organisms for the study of air quality. The effects of pollution on the lichen communities regard: the growth rate or physiological state of the organisms taken into study, the degree of bioaccumulation of pollutants and their distribution. The lichens have specific answer models for rise of atmospheric pollutants [1], varying from high resistance or sensibility to low sensibility [2]. The selectivity of lichens regarding the bioaccumulation of heavy metals in the tissue is very small [3-4]. Consequently the lichens accept the trans-membrane transfer of metals which they will later bio-accumulate [5-6]. According to studies, it has been remarked that the concentration of metals in the environment has had significant effects on the level of accumulation of Cd Cu, Cr Ni, Pb, Zn, etc., measured in the tissues of the lichens. The high concentrations of metals determined from the

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lichen tissue have corresponded to the metals Pb and Cu, fact which suggests that, probably, these metals have a greater affinity for the ion exchange sites found in the cellular wall of the lichens [7]. Other authors have determined high concentrations of Cr, Pb, Ni, Zn in the *Parmelia spp.* found in urban and suburban areas [8]. The acid deposits with a content of heavy metals can significantly reduce the survival of lichens in geographic areas affected by acid rain. In lichens from the *Bryoria fuscescens* species, exposed for 2 months at acid rains (simulated) that contain Cu^{++} ions and Ni^{++}ions at a pH=3, it has been noticed that the algae and the fungi have different behavior patterns. The alga component was strongly affected and the vanishing of the chlorophyll agents along with the blackening of the algae has been noticed. It has been remarked that metals, such as Cu, Pb and Zn significantly affect the physiology of the lichens. These metals are important constituents of vehicle emissions and have determined a positive correlation with the protein content of the lichens. Cd and Zn were linked due to the resemblance between their chemical structures. Urban pollution is caused by intense traffic [6]. The clearing of an urban center from heavy or medium traffic by building ring roads tangential to the city has led to a transfer of pollution from the central areas to the peripheral ones [9-12]. The bio-accumulation degree of the metals Cd Cu, Cr Fe, Mn, Ni, Pb, Zn in the tissue of the lichens belonging to *Parmelia spp.* from an urban centre with a population of 65.000 inhabitants and from the ring roads of the city have been addressed in the present study.

2. Materials and methods

For this study, lichens from the *Parmelia spp.* species have been selected. The lichens have been collected off species of trees found in the area of ring roads and county roads. The study sites have comprised a representative study of approximately 500 m in length, parallel to the axe of the road. The length of the path was determined by the presence of lichens on trees found on the edge of the road. Trees with a diameter of 10-40 cm, acacia, oak, linden tree or sycamore, avoiding young trees and the trees which were large in diameter. The inclination of the trees which provided support for the lichens was of max. 10%. The tree species which had no moss or important lesions on the bark were selected from the sampling areas. The sampling has been done in the height interval of the tree-100-150 cm, to avoid the influences of the soil from the base of the trees, or of the water from the precipitation that washes out the roads and is trans-located through vehicles onto the trees in their vicinity. The lichens have been collected during rainy months of autumn. The lichens have been separated from the woody cuticle and washed three times with distilled water. They were dried and milled in order to mix the material. The dry matter (105±5°C) was determined from the milled material. The dry lichen material (D.M) was calcinated at 550° C. The ashes were digested using a mixture of HCl and HNO_3 on a sand bath. The formed residuum was collected using 3 ml HCl 1:1. The resulted acid solution was filtered through Sartorius FT 2-206 filter papers. The calcination crucible was washed 3 times with 3 ml HCl 1:1. The solution for dissolving the residue and the washing solutions were put in volumetric flask of 25 ml. In the volumetric flask, the solution was brought to the limit using HCl 1:1. The metal determination has been done through analysis with a spectrophotometer AAS TYPE, Avanta. The certified reference material BCR 482 lichen (IRMM) Geel Belgium was used to validate the analytical determinations [13].

3. Results and discussion

In table 1, there are presented the areas from which the lichens *Parmelia spp.* taken into study were collected, namely a city called CS 1 with 65.000 inhabitants and 2 areas in the periphery of the city's ring roads as well as a gas station situated in a limitrophe area of the ring road. The specimens of compared lichens come from neighbouring areas of a county road and from an unpolluted area in a natural reserve. It can be deduced from Table no. 1 that the samples of lichens collected from the city's ring road have presented brownish spots which indicates a much lower alteration of the tissue. The lichens situated at 50 m from the gas station have also presented brownish spots. The comparative quantities of bio-accumulated metals Cu, Cr and Ni in lichens from the species *Parmelia spp.* are presented in Figure 1. It can be noticed in the figure that the quantity

of Cr accumulated in the lichens was very small. In the central area, Cr had the lowest value- 9.1 mg/kg. In the areas of intense traffic, the quantity of bio-accumulated Cr reached 27.3 mg/kg, which is 3 times higher than the ones in the city and in the park. The quantity of bio-accumulated Cu in the control sample was 5.7 mg/kg. In the other categories of lichens, the quantity of bio-accumulated Cu was 2.2-4.4 times the quantity bio-accumulated in the control areas.

Table 1. Prelevation areas for the *Parmelia spp.* Species

No	Pu Collection point	Aspect
1	CS 1- urban park.60,000 inhabitants	Gray greenish, rosettas 3-5cm high presence of lichens on tree trunks
2	C 2 ring road of CS 1	Gray, rosettes, 3-5cm low presence
3	C 3 ring road of CS 1	Gray brownish spots, rosettes 3-4cm low presence
4	C 4 gas station on the ring road of CS 1	Gray brown spots rosettes 2-4cm low presence
5	C 5 county road area	Gray,rosettes 1-5cm, low presence
6	control	Gray greenish, large rosettes, high presence on trunks

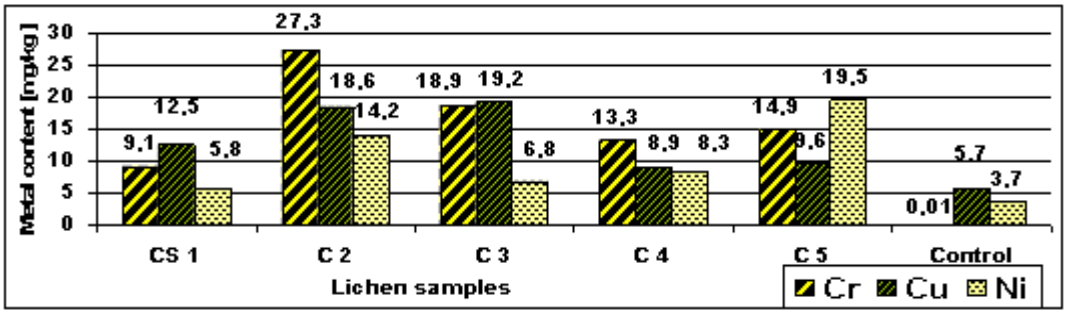

Figure 1. Comparative presentation of the quantities of Cr, Cu and Ni bio-accumulated in the tissues of the *Parmelia spp.* lichens

The quantity of Ni in the control area was 3.7 mg/kg. The quantity rose by 50% in the lichens analyzed from the central area while the quantity of Ni in the traffic areas was 5 times higher than the one in control areas.

In Figure 2 are presented the comparative quantities of Mn, Pb and Zn bio-accumulated in *Parmelia spp.* lichens are presented. It can be noticed from Figure 2 that the quantity of Mn accumulated in the lichens from the control sample was similar to the quantity bio-accumulated in the lichens from the central part of the city. The quantity of Mn from the lichens found in the vicinity of highways was 2.3-2.4 times higher than in the ones taken from the control area. The quantity of Pb and Zn bio-accumulated in the lichens from the control areas was 6 mg/kg. In the city center, the quantity of bio-accumulated Pb rises to 15 mg/kg and Zn rises to 22 mg/kg. In the areas of the ring roads, the quantity of Pb and Zn bio-accumulated in lichens is 7 times higher and the Zn may rise 4 times vs the quantities of Pb and Zn bio-accumulated in control lichens.

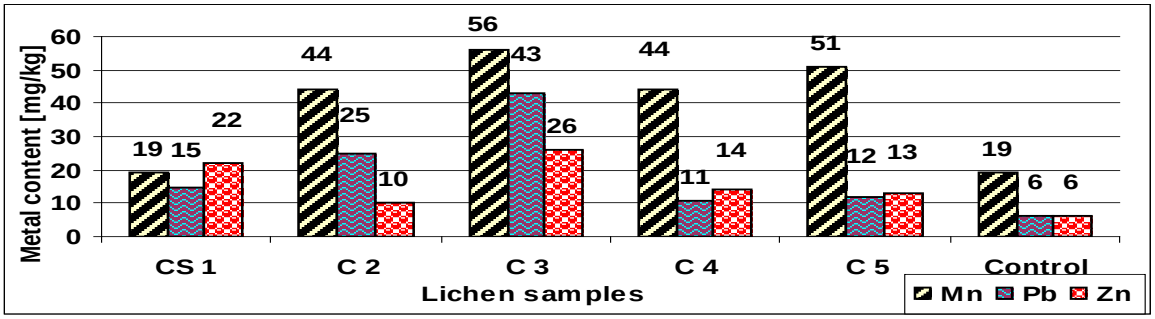

Figure 2. Comparative presentation of the metal quantities of Mn, Pb and Zn bio-accumulated in the tissue of the lichens from the *Parmelia spp.* species

In Figure 3 are presented the quantities of Cd and Fe bio-accumulated in the *Parmelia spp.* lichens are comparatively presented. It is noticed that in figure no. 3a as well as in the control sample Cd was not accumulated. In the central area, the quantity of Cd bio-accumulated in the lichens was low 0.4 mg/kg. In the areas of intense traffic the bio-accumulated quantity of Cd rises by 57 times *vs*. the quantity found in the lichens from the city park. In figure no. 3b it can be noticed that in the control sample, Fe bio-accumulated in the lichens rise by 2.4-4.2 times the quantity bio-accumulated by the lichens in the park. Lichens from the species *Parmelia spp.* have accumulated the lowest quantities of Cd. However, a quantity of 2.3 mg/kg of Cd bio-accumulated on certain segments of the highway indicated the dispersion of this metal in the atmosphere in high quantity. The bio-accumulated quantities of Fe in lichens were, in all cases, around hundreds of grams. The quantities of Mn and Pb bio-accumulated in the lichens collected from trees found in the neighborhood of traffic roads may reach 43-56 mg/kg. This report of bio-accumulation of metals in lichens has been recorded at high traffic pollution levels, low park pollution levels and lichens in conventionally clean areas such as a natural reserve. For example, the bio-accumulation of metals in areas which lack pollution or are low in pollution was in the following order: Cd~ Cr < Ni < Cu ≤ Pb~ Zn ≤ Mn <<<< Fe. In traffic, the order of bio-accumulation of the metals Cr, Ni, Cu, Pb, Zn and Mn has been slightly modified.

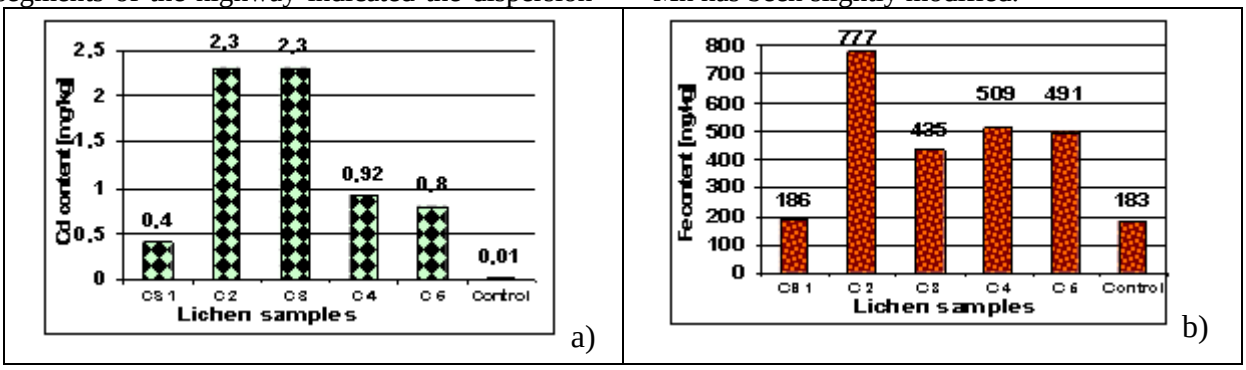

Figure 3. Comparative presentation between the quantities of metals bio-accumulated in the tissue of lichens belonging to the *Parmelia spp.* a) Cd b) Fe

4. Conclusions

To enhance the influence of the level of pollution inside traffic areas on the capacity to accumulate metals in the biosensor of the lichens, studies were conducted in 6 areas: the park of a city and different sites on the ring road as well as on a segment from a county road with moderate traffic. The study has been conducted on *Parmelia spp.* lichens which grow naturally on tree species found in the neighbourhood of the highways. The degree of accumulation for the following metals Cd, Cr, Cu, Fe, Mn, Ni and Zn in the *Parmelia spp.* has been correlated with the intensity of traffic. According to the degree of bio-accumulation of the following Cd, Cu, Ni, and Pb in lichens, it has been established that the sources such as traffic jams in limitrophal areas and near the perimeter of gas stations as well as from the county roads, continuously spread products which contain these elements into the atmosphere. The lichens can bring information which is fast, regarding the quality of the surrounding air.

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