RESEARCH ARTICLE **(Open Access)**

Trace element accumulation in the moss *Pseudoscleropodium purum* in south Albania

MAJLINDA TERPO[1*], MAJLINDA VASJARI[2], ROMEO MANO[1], MARSELA ÇOMO[1], MARIE AGOLLI[1]

[1] Biochemistry Department, Faculty of Natural Sciences, University "Eqrem Çabej", Gjirokastra, Albania

[2] Chemistry Department, Faculty of Natural Sciences, University of Tirana, Albania.

[3]Department of Mathematics & Computer sciences, Faculty of Natural Sciences, University "Eqrem Çabej", Gjirokastra, Albania

*Coresponding author e-mail: mterpo@yahoo.com

Abstract

For the first time the moss biomonitoring technique has been applied to air pollution monitoring in south Albania. The most important environmental features of mosses as a suitable tool of biomonitoring are: rootless, large surface, wide - spread population, a habit to grow in groups, long life – cycle, survival in a high – polluted environment, an ability to obtain nutrients from wet and dry deposition. The moss *Pseudoscleropodium purum* was used as a bioindicator and biomonitor of metal pollution. In this work the bioaccumulation of trace metals (Cd, Pb, Cu, Mn, Fe, Na, K and Zn) in moss samples collected from 9 sites of the southern part of Albania is presented. Moss samples were collected during the period September – October 2010 according to the guidelines of the UNECE ICP Vegetation. The concentrations of heavy metals in moss samples were determined using AAS technique equipped with flame and/or electro-thermal systems. AES method was used for Na and K determination. The variations of heavy metals concentrations with sampling sites are shown in heavy metal contamination diagrams. PCA and cluster analysis was used to identify the most polluted areas and characterize different pollution sources.

Key words: biomonitoring, *Pseudoscleropodium purum*, trace metals, atmospheric deposition

1. Introduction

Biomonitoring, in a general sense, may be defined as the use of bio-organisms/materials to obtain (quantitative) information on certain characteristics of the biosphere. The relevant information in biomonitoring (e.g. using plants) is commonly deduced from either changes in the behaviour of the monitor organism (impact: species composition and/or richness, physiological and/or ecological performance, morphology) or from the concentrations of specific substances in the monitor tissues. With proper selection of organisms, the general advantage of the biomonitoring approach is related primarily to the permanent and common occurrence of the organism in the field, even in remote areas, the ease of sampling, and the absence of any necessary expensive technical equipment [17].

Some plant species are sensitive to single pollutants or to mixtures of pollutants. Those species or cultivars are likely to be used in order to monitor the effects of air pollutants as bioindicator plants. They have a great advantage to show clearly the effects of phytotoxic compounds present in the ambient air. As such, they are ideal for demonstration purposes. However, they can also be used to monitor temporal and spatial distributions of pollution effects [16].

Mosses are good bioindicator of HM pollution in the atmosphere, after this successful discovery many European countries have used mosses in national and multinational surveys of atmospheric-metal deposition [6].

Biomonitoring with mosses is based on the fact that terrestrial carpet - forming species obtain most of their nutrients directly from wet and dry deposition, they clearly reflect the atmospheric deposition, especially well suited to heavy metals pollution on a larger time scale. Nutrient uptake from the atmosphere is promoted by their weakly developed cuticle, most bryophytes are small and the leaves of mosses are only one cell layer thick. Substantial properties of mosses as good indicator are: large surface to weight ratio, their slow growth rate and a habit of growing in groups. Air pollutants are deposited on mosses in aqueous solution, in gaseous form or attached to particles. The attachment of particles in mosses is affected e.g., by the size of the particles and the surface structure of the mosses. Ion exchange is a fast physiological-chemical process that is affected e.g., by the number and type of free cation exchange sites, the age of the cells and their reaction to desiccation, growing conditions, temperature, precipitation pH, composition of the pollutants and leaching. In the ion exchange process, cations and anions become attached to functional organic groups in the cell walls among other things through chelation [4, 6, 14].

The aim of this study was to investigate trace element accumulation in the moss *Pseudoscleropodium purum*, identifying the most polluted areas and defining different pollution sources.

2. Materials and Methods

2.1 Sampling procedure and sampling sites

Pseudoscleropodium purum moss was collected from 9 sites in South Albania during the period of September-October, 2010.

The sampling was carried out in accordance with the strategy of the European moss survey programme [13]. The moss was collected in open areas and forest gaps, avoiding areas close to trees, and always from the ground. The sampling sites were located at least 300 m from main roads, 100 m from local roads, and 200 m from villages. 5-10 subsamples from each site ($50x50m^2$) were taken on a random basis and finally mixed to make up a total sample. Sampling and sample handling was performed using polyethylene gloves and collected material was stored in paper bags.

2.2 Mosses treatment

In the laboratory foreign materials adhering to the surface of the samples such as tree bark, lichens, soil dust and detritus were removed carefully. For the analysis, only the green and greenish brown parts of the moss plants were used, as they generally are intended to represent a period of about 3years. Their metal content is generally considered to reflect the atmospheric deposition during that period [13]. The unwashed samples were dried at 40^0C and homogenized manually.

2.3 Samples digestion

An accurately weighted portion of each sample (about 0,5g DW) was placed in an open Teflon vessel. 15 ml of concentrated HNO_3 9:1 (Merc, pro analysi) was added to each vessel and the mixture was left at room temperature all night. The closed teflon vessels were heated for 3h at 80 - 90^0C and then the temperature was raised to 200^0C for 1h. Finally the vessels were cooled, carefully opened, and digests quantitatively transferred to calibrated flasks and were diluted with bi-distilled water to make 25 ml. These solutions were analysed for heavy metal concentrations.

2.4 Heavy metals determination

The contents of Zn, Fe, Mn were determined by flame absorption spectrophotometry (Varian, Spectra AA10 Plus). The contents of Cu, Cd, Pb were determined in an atomic absorption spectrophotometer with a graphite furnace (Analytic Jena, AA400). AES method with flame was used for Na and K determination (Varian, Spectra AA10Plus).

3. Results and Discussion

Concentrations of elements in *Pseudoscleropodium purum* from the sampled stations are shown in Table 1.

The accumulative ability of moss *Pseudoscleropodium purum* was evaluated through accumulation factor ($FA= C_{max}/C_{min}$). In Figure 1 are shown the maximum accumulation factors for each element.

Bryophytes could adsorb amounts of heavy metal ions due to the leafy multi-branches and numerous cation exchange sites on the surface. The stability of metal organic complexes, chelates, and the high cation exchange capacity of the tissues are primary conditions for the sorption of heavy metals by mosses [14]. Consequently, they can indicate the presence of the elements and their concentration gradients.

The uptake of metals depends very strongly on microenvironmental conditions wich can even cause leaching of metals from moss [5].

The intensity of metal content based on the mean values in moss samples follows the trend K > Fe > Na > Mn > Zn > Cu > Pb > Cd.

Data from Table 1 show that the level that each element determined in the samples was related to its toxicity. Elements that are well tolerated by these plants, either because they occur commonly (e.g. Fe) or they are metabolically important (e.g. Mn), were present at the highest concentrations. In contrast, highly toxic elements such as Cd were present at the lowest concentrations.

.

Table 1. Concentrations (µg/g) of elements in the moss species *Pseudoscleropodium purum*

Site/Element	*Zn*	*Fe*	*Mn*	*Cu*	*Cd*	*Pb*	*K*	*Na*
1.Krongj	38.3	448.22	15.71	2.07	0.05	0.39	2907.46	184.36
2.Memaliaj	33.82	426.68	54.64	2.66	0.02	0.31	2863.17	176.2
3.Luzat	12.73	492.1	27.43	1.65	0.03	0.34	1633.04	47.05
4.Peshtan	29.24	284.83	42.41	1.93	0.02	0.32	3883.21	155.4
5.Terihat	25.17	314.7	27.11	1.8	0.03	0.39	3169.09	186.69
6.Kakavi	37.93	235.64	58.35	1.88	0.06	0.25	3960.02	162.73
7.Permet	32.21	443.26	54.55	2.88	0.06	0.35	2985.38	208.69
8.Kelcyre	29.28	228.18	34.75	1.42	0.05	0.24	3067.36	131.99
9.Dracove	42.21	474.13	57.12	1.45	0.02	0.24	3850.32	95.63
Mediana	32.21	426.68	42.41	1.88	0.03	0.32	3067.36	162.73
Min	12.73	228.18	15.71	1.42	0.02	0.24	1633.04	47.05
Max	42.21	492.1	58.35	2.88	0.06	0.39	3960.02	208.69

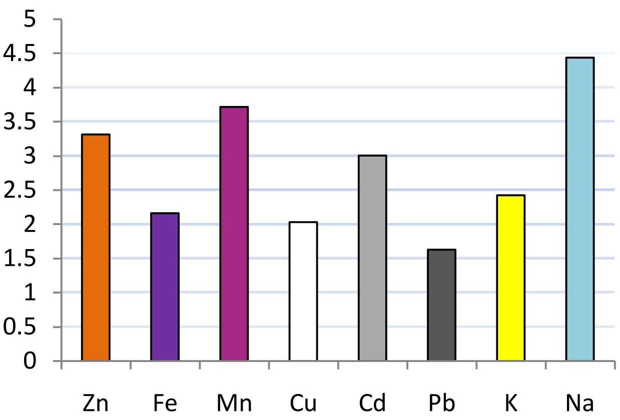

Figure 1. The maximum accumulation factors for each element in samples of moss *Pseudoscleropodium purum.*

The highest values for K (1633-3960 µg/g) are connected with active biological processes in moss [15]. Cell distribution of K is used as a measure of membrane integrity, and vitality of moss samples. Damage of the cell membrane due to the impact of air pollutants may imply a leakage of K from the cell compartments [3]. Fe concentration was higher (228-492 µg/g), which was coincident with the previous results that Fe might be the most accumulated and tolerated heavy metal in mosses [2.8]. Mn (16-58 µg/g) is most probably associated with the interaction of the moss with higher vegetation [15]. Zn (13-42 µg/g) and Cu (1.42-2.88 µg/g) are essential micronutrients and are able to pass through the cell membrane more readily, whereas Pb (0.24-0.39 µg/g) which is not essential for metabolic activity are mostly retained between cell wall and cell membrane [7]. Cd (0.02-0.06 µg/g) was the least abundant element; the reason might be that Cd is a toxic trace element

Cluster Analysis

To distinguish lithogenic and/or anthropogenic origin of the elements, cluster analysis was carried out. The results from the cluster analysis of variables (Zn, Fe, Mn, Cu, Cd, Pb, K, Na) for south-Albania sites are presented in Figure 2.

As shown in Figure 2, elements in our study were classified into three groups:

Cluster 1: K, Zn dhe Mn. Mn mainly comes from soil and is associated with the interaction of the moss with higher vegetation [1, 15]. K is connected with active biological processes in moss [15]. Contribution to anthropogenic zinc emissions was made by the “road transportation”. The road transport emission is almost entirely due to tyre wear, the zinc content of the tyre rubber is around 2% ZnO by weight [10].

Cluster 2: Pb, Cd, Cu, Na: includes soil dust (Na is a main element in the Earth’s crust) mixed with traffic related particles more than direct exhaust emission. For Pb, the industrial exhaust gas produced by coal burning was an important source. Pb acts as the marker element for motor vehicle emissions [11]. Recently, Hulskotte *et al*. [12] suggested that brake wear from road traffic vehicles is an important source of diffuse atmospheric (particulate) copper emission. The main source of Cd could be local sources like incineration of refuse (cadmium pigments and stabilizers in plastics, nickel-cadmium batteries). Elevated cadmium concentration could be due to polythenes, domestic waste, sewage sludge, plastic pipe, automobile tires and exhaust [9]. Phosphate fertilisers in agricultural areas and electricity and heat production are sources of Cd.

Cluster 3: Fe. Iron is a major element in bedrock and soil, and may come from wind-blowing soil dust and frictional work from construction sites which increases the atmospheric loading of dust particles in environment.

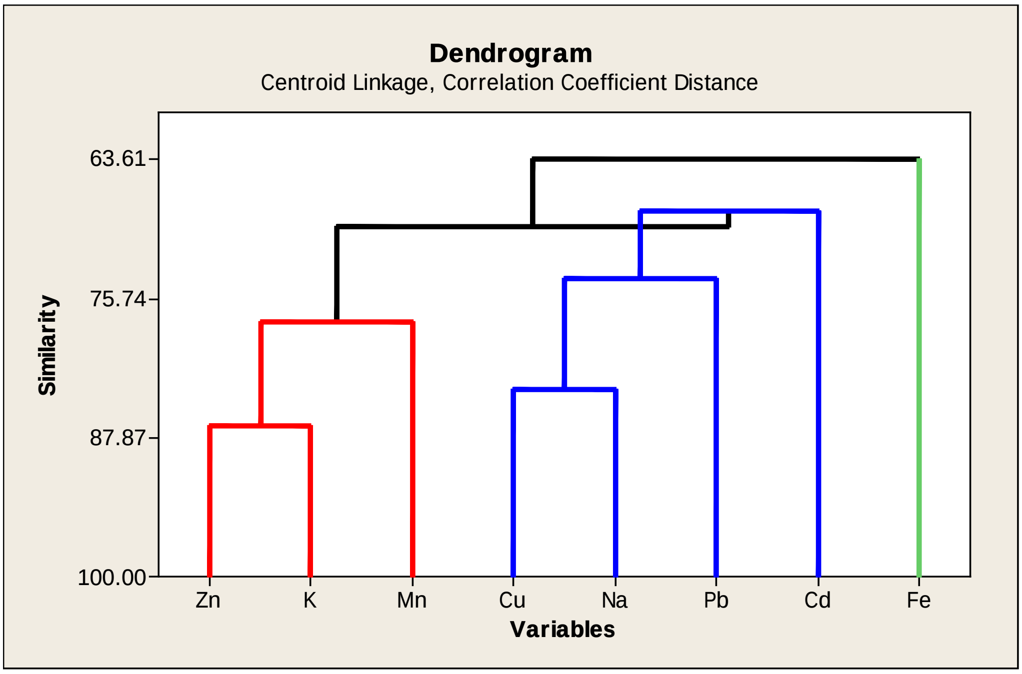

Figure 2. Classification into groups according to similarity between elements

4. Conclusion

From this present study, it can be said that the moss *Pseudoscleropodium purum* studied was useful bioindicator of heavy metals. Environmental conditions may alter the equilibrium between moss and deposition, and the effect may differ among locations where the moss grows. Also, biological processes in the moss may be affected by characteristics of the environment where the moss grows.

The investigated sites resulted with low concentration of heavy metals, wich show a slight level of contamination.

5. References

1. Bargagli R, Monaci F, Agnorelli C: **Oak leaves as accumulators of airborne elements in an area with geochemical and geothermal anomalies.** *Environ. Pollut.* 2003, 124, 321–329.
2. Berg T, Steinnes E: **Recent trends in atmospheric deposition of trace elements in Norway as evident from the 1995 moss survey.** *Science of the Total Environment* 1997, *208*, 197–206.
3. Brown DH, Brumelis G: **A biomonitoring method using the cellular distribution of metals in moss.** *Sci. Total Environ* 1996, 187:153–161.
4. Čeburnis D, Šakalys J, Armolaitis K, Valiulis D, Kvietkus K: **In – stack emissions of heavy metals estimated by moss biomonitoring method and snow – pack analysis.** *Atmospheric Environment* 2002, 36: 1465 – 1474.
5. Čeburnis D, Valiulis D: **Investigation of absolute metal uptake efficiency from precipitation in moss.** *Sci. Total Environ* 1999, 226, 247–253.
6. Chakraborty Sh, Paraktar GT: **Biomonitoring of trace element air pollution using mosses.** *Aerosol and Air Quality Research* 2006, 6 (3): 247-258.
7. Chettri MK, Sawidis T, Weryszko-Chmieleska E: **Localization and effects of heavy metals in lichen Cladonia.** *Biosphere* 2000, 5: 61 – 75.

8. Genoni P, Parco V, Santagostino A: **Metal biomonitoring with mosses in the surroundings of an oil fired power plant in Italy.** *Chemosphere* 2000, *41*: 729–733.

9. Grodzinska K, Szarek-Lukaszewska G: **Response of mosses to the heavy metal deposition in Poland – an overview.** *Environ. Pollut.* 2001, 114: 443-451

10. Harmens H, Norris D. and the participants of the moss survey: **Spatial and temporal trends in heavy metal accumulation in mosses in Europe (1990-2005).** Programme Coordination Centre for the ICP Vegetation, Centre for Ecology and Hydrology, Bangor, UK; 2008. http://icpvegetation.ceh.ac.uk

11. Huang X, Olmez I, Aras NK, Gordan GE: **Emmisions of trace elements from motor vehicles: potential marker elements and source composition profile.** *Atm. Environ* 1994, 28 (8), 1385-1391.

12. Hulskotte JHJ, Schaap M, Visschedijk AJH: **Brake wear from vehicles as an important source of diffuse copper pollution.** *Paper presented at 10th International Specialized Conference on Diffuse Pollution and Sustainable Basin Management, 18-22 September 2006, Istanbul, Turkey.*

13. Rühling A, Steinnes E: **Atmospheric heavy metal deposition in Europe 1995-1996.** *Nordic Council of Ministers, NORD* 1998, 15, 66 pp.

14. Shakya K, Chettri MK, Sawidis T: **Impact of Heavy Metals (Copper, Zinc, and Lead) on the Chlorophyll Content of Some Mosses.** *Arch Environ Contam Toxicol* 2008, 54: 412–421.

15. Steinnes E: **A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals.** *Sci. Total Environ* 1995, 161: 243-249.

16. Temmerman deL, Nigel J, Bell B, Garrec JP, Klumpp A, Krause GHM, Tonneijck AEG: **Biomonitoring of Air Pollutants with Plants.** *International society of environmental Botanists* 2005, 11(2): Available form: http://isebindia.com/05_08/05-04-1.html

17. Wolterbeek HTh: **Biomonitoring of trace element air pollution: principles, possibilities and perspectives**. *Environ. Pollut* 2002, 120: 11–21