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Monitoring heavy metal pollution in Elbasan using passive and active moss

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Abstract

Environmental pollution is increasing day by day, posing a very serious problem for human health. A large number of pollutants, including heavy metals, are adversely affecting our environment. Heavy metals are emitted from solid fuel combustion, vehicular emission and in industrial processes. Mosses are widely used as bio-monitors. Since the mosses have not roots system, and their leaves have not protective layer, they absorb nutrients through their thin leaves, directly from the air. Accumulation of heavy metals in the leaves of the mosses, is attributed to the presence of negative charges that possess in leaves. The assessment of heavy metal pollution in the Elbasani area was carried out in this study, by using native mosses (passive method) and "moss bag" (active method of monitoring) bio-monitoring. *Hypnum cupressiforme* sp. was used in both monitoring methods. The "moss bags" were exposed for 6 months at various points in the area, while the native mosses were collected at two points in the study area. Heavy metals as Ni, Cr, Fe, Ca, Mg and Zn were analyzed in exposed and native mosses. Indigenous moss samples were analyzed with ICP / AES technique, while the exposed samples, "moss bags", were analyzed with FAAS technique (Fe, Zn, Ca, Mg) and with GFAAS technique (Cr, Ni). The data obtained was used for calculating the contamination factor (CF). The results of CF data show that the Elbasani area is polluted by heavy metals due to industrial activity.

Keywords: bio-monitor, moss-bag, heavy metals, ICP/AES, FAAS, GFAAS.

1. Intrduction

Pollutants include all chemical elements or compounds that are released into the atmosphere mainly by human activity and that cause environmental pollution and damage to living organisms. [9].

The majority of the heavy metals and sulphur or nitrogen compounds, that are considered pollutants, are released mainly from industrial activities that have material processing composed of heavy metals [11, 12].

Levels and the extent of spread of pollution in the air depends on the composition of the emissions, atmospheric and topographic conditions. The majority of the remain close to the source, but some can travel for thousands of kilometers. In general heavy metals occur in air in different phases, as solids, gases or adsorbed particles heaving aerodynamic sizes ranging from 0.01 to 100 μm and larger.

Heavy metals are quite stable pollutants because they do not degrade over time, so that they accumulate in the environment and will probably pose an increasing of human health hazard, even when they are in low concentrations [14].

Air quality can be monitored by measuring the pollutants directly in the air or in deposition, or by using biomonitors [7].

The term biomonitor is used to refer to an organism, or to part of it, that depicts the occurrence of pollutants on the basis of specific symptoms, reactions, morphological changes or concentration [8].

Mosses as useful indicators for biological monitoring of regional atmospheric depositions and heavy metal contamination of their environment were developed at the end of the 1960s. The use of native terrestrial mosses as biomonitor is now a well-recognized technique in studies of atmospheric contamination [4].

Mosses are low plant that thrive in a humid climate and posses many properties that make them suitable for monitoring air pollutants [10]. Nutrient uptake from the atmosphere is promoted by their weakly developed cuticle (so nutrients and water taken directly from the leaves), large surface to weight ratio and their habits of growing in groups. Thickness of moss leaves are unicellular, making exhibited in all directions to capture the nutrient.

The accumulation of pollutants in mosses occur through a number of different mechanisms: as layers of particles or entrapment on the surface of cells, incorporation into outer walls of cells through ion exchange processes and metabolically controlled passage into the cell [2]. The attachment of particles is affected by the size of the particles and surface structure of the mosses. Ion exchange is a fast physiological- chemical process that affected by the number and type of free cation exchange sites.

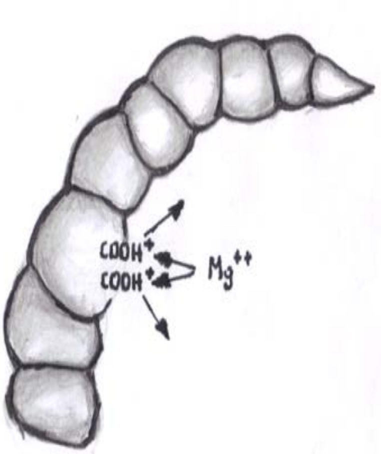

Figure 1. Entrapment of metals on surface of moss cell.

High ion-exchange capacity is connected to the high concentration of un-esterificated pectates of poliuronic acids mainly in cell walls of moss. In cell walls occurs the first capturing step of heavy metal cations [6].

The chemical composition of deposition has a large effect on the accumulation of pollutants, because the uptake of mosses for individual elements varies considerably [1]. The uptake efficiency of the most common heavy metal follow mostly the order BP > Co > Cr > Cu > Mo > Ni > V > Zn > As. [13, 14].

Air quality biomonitoring becomes by two methods:

1. passive method that uses mosses directly from the study area.
2. active method relates to transplant moss from another area in the area (this method is used mainly in urban or industrial areas).

Moss monitoring method is more efficient because the collection, processing and analysis of samples carried with low cost. Because the mosses are widespread in nature they are ideal for determining the trend of the spread of pollution in space and time, and to compare pollution levels in different area [5]. Mosses as *hypnum cupressiforme* for reasons that form dense carpet are quite convenient in such studies.

This study is focused on the evaluation of the air pollution level of Elbasani region, from the heavy metals, through the passive and active methods and based on the obtained results to determine the most polluted sites.

2.Matrial and methods

2-1. Study area

The study area is situated in Elbasani region as a most contaminated region in Albania. For analysis with passive method the *Hypnum cupressiforme* moss species was collected from 4 sites in region. The sampling was carried out in accordance with the strategy of the European Moss Survey Programme. 5-10 subsamples from each site (50mx50m) were taken on a random basis and finally mixed to make up a total sample. Extraneous material was removed and was cleaned of soil particles in laboratory and then was prepared for chemical analysis with ICP-AES technique.

Figure 2. The map of monitoring sites. (St.A active method, St.P passive method)

With active method, the carpet moss samples (*hypnum cupressiforme* species) were collected in a clean rural area (Llogara). From the collected moss was removed the extraneous material, than samples were cleaned from soil particles in laboratory and were prepared for the exposure. Moss samples were placed in plastic boxes (10x15 cm) hanged on appropriate open place (protected from rain falls), 2 m above the ground. Moss bag were transferred at 4 different sites of Elbasani region. The exposure period was 6 months. After six months of exposure, moss samples were placed to the laboratory, cleaned from extraneous material and air dried till constant weight (at 25-35ºC) for 3 days.

2-2. Chemical treatment of moss samples

We use the wet digestion of homogeneous subsamples for the decomposition of organic material. About 0.5 gr moss sample was transferred to the half pressure Teflon tubes and 10 ml nitric acid (9:1) was added. The closed tubes were put in room temperature for 48 hours and were digested for 3 hours at 80-90ºC. The temperature was increased at 200ºC and was kept for an hour for further digestion. After cooling the mass was transferred to 25 ml flasks with osmoses treated water. Heavy metals as Cr and Ni were determined by GF-AAS technique. Ca, Fe, Zn and Mg were determined by F-AAS technique.

The unexposed moss sample from Llogara site was used as background one. Determination of heavy metal levels in the background sample was carried out using two different technique such as AAS and ICP-AES. The results of ICP –AES technique provided by Institute of Chemistry University of Skopje, were in good agreement with our results, using AAS technique (table 1). The certified M2 and M3 moss sample used for quality control of the results by ICP-AES analysis.

Table 1. Metal concentration (μg/g, DW) in moss background sample

Element/Method	***Fe***	***Cr***	***Ni***	***Zn***	***Pb***	***Cu***
AAS	1013	2.47	2.25	8.07	3.13	4.48
ICP-AES	985	2.32	2.33	7.84	2.98	4.62

3. Results and Discussion

Concentration of six heavy metals determined in moss (passive method) at 4 sites are listed in table 2, whereas the concentration of heavy metals in exposed moss (moss bag) at 4 sites in study area are listed in table 3.

Table 2. Metal concentration (μg/g, DW) in native moss.(ICP-AES technique)

Element/station	***Fe***	***Cr***	***Ni***	***Zn***	***Pb***	***Cu***
St.P-1	1462	3.34	3.33	19.63	2.55	7.84
St.P-2	3288	15.36	13.65	68.15	16.97	11.58
St.P-3	5488	24.27	33.96	31.91	10.76	9.39
St.P-4	2643	8.42	10.36	37.67	5.87	8.59

Table 3. Metal concentration (μg/g, DW) in exposed moss (moss bag) (AAS technique)

Element/station	***Fe***	***Cr***	***Ni***	***Zn***	***Pb***	***Cu***
St.A-1	1630	2.45	3.78	12.78	6.13	15.87
St.A-2	2717	3.37	9.73	35.92	42.82	10.90
St.A-3	1358	2.44	10.54	196.12	14.22	7.27
St.A-4	1792	3.07	7.72	16.20	33.08	9.08

Metal concentration values in St.P-1 are minimal, compared with the values stations St.P-2, St.P -3 and St.P-4. Also concentrations of elements in the moss of this station are within the interval of metal concentrations of moss collected in Norway. The comparative results for some of the elements are given in Table 4.

By using as background concentrations in St.P-1, we compute the contamination factor (CF), as the ratio of the concentration of each element in the study area, with values of background concentrations.

Table 4. The values of concentration of elements in St.P-1 and in Norwegian moss.

Elements	***Fe***	***Cu***	***Cr***	***Ni***	***Pb***	***Zn***
St.P-1	1462	7.84	3.34	3.33	2.55	19.63
Norwegi moss	770-1370	2.1-9.2	0.1-4.2	0.12-6.6	0.64-6.12	7.9-173

Table 5. The values of contamination factor (CF)

Element/station	*Fe*	*Cr*	*Ni*	*Zn*	*Pb*	*Cu*
St.P-1	1.90	33.40	27.75	2.48	3.98	3.73
St.P-2	4.27	153.60	113.75	8.63	26.52	5.51
St.P-3	7.13	242.70	283.00	4.04	16.81	4.47
St.P-4	3.43	84.20	86.33	4.77	9.17	4.09

Table 6. Contamination level in stations of area, based on CF

CF	*>27*	*8-27*	*3.5-8*	*2-3.5*	*1-2*	*<1*
Contamination rate	Extreme	High	Average	Lighly	No contamin	Clean

Based on the data of Table 5, it is shown that the area under investigation is classified as extremely polluted by Cr and Ni, and moderately polluted by Cu. The stations St.P-2 and St.P-3 are highly polluted by Pb; St.-2 is highly polluted by Zn; whereas St.-3 and 4, as well as St.-2 and 3 are moderate polluted by Zn and Fe respectively.

The high concentrations values of Cr and Ni in this area are associated with by their emission from industrial activities positioned in this area. Steel smelter metallurgy, ferrochrome processing plant are the main polluters of these elements. High values of Pb and Zn are associated with the use of fuels such as diesel or coal in cement factory. The impact of higher traffic in the vicinity of these stations is also another factor for contamination by Pb and Zn.

To evaluate the accumulation degree of heavy metal in moss bag samples, the accumulation factor (AF) is used. The values of (AF) of each element in each station are given in Table 7. The accumulation factor is defined as the concentration ratio between exposed samples (c_{exp}) and the black moss bags ($c_{background}$). The results of AF reflect different geochemical mobility of elements [3].

Table 7. The values of Accumulation Factor (AF)

Element/station	*Fe*	*Cr*	*Ni*	*Zn*	*Pb*	*Cu*
St.A-1	1.65	1.59	1.68	1.68	2.05	3.54
St.A-2	2.75	3.95	4.32	4.58	14.36	2.43
St.A-3	1.37	4.31	4.68	25.01	4.77	1.62
St.A-4	1.82	1.98	3.43	2.06	11.10	2.03

Based on the values of accumulation factor (AF) the elements studied on the area divided into three groups. The first group of elements Zn and Pb display high accumulation factor (AF>10), the second group Cu, Ni, Cr display moderate accumulation factor (3<AF<10) and Fe which display low accumulation factor AF<3.As seen from the table, exposed mosses at stations 2 and 3 display high values of accumulation factor for some elements. Stations 2 and 3 show high levels of contamination with Zn and Pb (AF >10) as well as average levels of contamination by Cu, Ni, Cr (3<AF<10). This fact related with proximity of these stations with complex metallurgical and other industries like cement and building materials.

From the study with both, passive and active biomonitoring methods, we arrive at the conclusion that St.P-1, St.P-2 stations, and St.A -1, St.A-2 stations represent average or high levels of heavy metal contamination.

4. Conclusion

Active and passive moss biomonitoring are cheap and suitable tools for air monitory and assessment. based on passive and active moss biomonitoring techniques, the Elbasan area is classified as being moderately polluted. Both biomonitoring methods display that the area under investigation is classified as extremely polluted by Cr and Ni, and moderately polluted by Cu.

The stations St.P-2 and St.P-3 are highly polluted by Pb; St.-2 is highly polluted by Zn; whereas St.-3 and 4, as well as St.-2 and 3 are moderate polluted by Zn and Fe respectively.

The metal concentration in mosses, are influenced by many factors such as the type of metal emitted and the chemical and physical properties of the metal containing particles. The main source of pollution in this area are metal processing, fuel and fosile burning and cement industry with old technology that are positioned in this area. Some other source of emission, are the emission from automobile exhaust and wind soil dust of crustal material.

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