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THE STUDY OF ATMOSPHERIC DEPOSITION OF HEAVY METALS IN TIRANA AND VLORA CITIES, ALBANIA, BY ACTIVE MOSS BIOMONITORING TECHNIQUE

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ABSTRACT

Active biomonitoring of air quality was performed using the moss *Hypnum cupressiforme* in Tirana and Vlora urban areas, Albania. Moss bags were exposed with irrigation for 6 months at 7 sites of Tirana city and 9 sites of Vlora city along the main streets. Heavy metals (Cu, Pb, Zn, Mn, Fe and Cd) were determined by atomic absorption spectrometry by using flame/and or electro thermal system. CVAAS was used for mercury determination, and atomic emission spectrometry for K and Na determination. The target elements in this study are Cd, Hg, Cu, Pb, Zn and Mn. For better interpretation of data, the elements Fe, K and Na were also included. The cities are being moderately polluted due to the high vehicular emissions, and use of adulterated fuel in vehicles. Therefore, we have been tried to categorize different places in the city, on the basis of the mentioned metal concentrations in the mosses and data statistical treatment. Mercury shows most sounding results (13.39 µg/g, DW), near Vlora hot spot site, polluted by metallic mercury. The comparison with unexposed moss allowed us assessing the enrichments factors in exposed moss samples for all determined elements. To distinguish different geochemical mobility of elements and geochemically bound elements, correlation analysis was carried out. Two groups of elements were found: the first one (Zn, Fe, Cu, K and Na) does not display high accumulation factors ($AF_{mean}<3$), whereas Pb and Cd in Tirana sites, or Hg and Mn in Vlora sites, display moderate accumulation factors ($AF_{mean} >3$).

KEYWORDS: active biomonitoring, urban area, heavy metals, accumulation factor, multivariate analysis, moderately polluted

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1 INTRODUCTION

Heavy metals pollution became a significant problem of environmental toxicology in recent years. These metals, even if deposited constantly in small rates over long periods of time, accumulate in the environment and will probably pose an increasing major environmental and human health hazard in future [1]. Thus, it seems very important to develop and improve a long-term active/and or passive monitoring technique to assess the type and level of heavy metal pollution of any particular area. In general, the main emission sources of heavy metals in air are ore and metal processing and manufacturing, as well as combustion processes, because heavy metals are minor constituents of fuels (coal, gasoline) [2].

The bio-monitoring techniques appear to be especially useful in highly polluted areas (industrial and/or urban) to examine deposition patterns and to recognize point sources. In particular, mosses are bio-organisms that accumulate large amounts of trace metals, making them good bioaccumulators to estimate metal pollution [3].

Mosses accumulate passively and retain the elements that reach them via atmospheric dry and wet deposition. The idea of using autochthonous 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 [4], while the use of transplants or moss bags was introduced later [5, 6]. Their high cation exchange capacity and high surface to volume ratio favour the accumulation of the large concentrations of heavy metals across the moss cell wall for a long period [7-9].

The use of native terrestrial mosses as bio-monitors is now a well-recognized technique in atmospheric contamination studies [11], and is applied as a practical mode in establishing and characterizing deposition sources. Although the bio-monitoring technique is widely known, it was never used before for investigating trace elements in Albania.

The report of Tirana area quality for the year 2008 gives some data about the pollution level of the air in the city [10]. The range of some important parameters regarding air quality valuation is as follows: Lead 0.028-0.66 μg/m^3 (Albania standard: max permitted level: 1 μg/m^3) [13], PM10/PM2.5 - 13-354 μg/m^3 or 1.5 times higher than maximum permitted level for Albania (PM10) Annual (arithmetic mean) 250 μg/m^3), or 7 times higher than maximum permitted level of European countries (PM10 50 μg/m^3 for 24 h; 40 μg/m^3 for 1 year) [12].

Therefore, the goal of this study was to perform the active bio-monitoring of the air quality using the moss *Hypnum cupressiforme* within and around Tirana and Vlora urban areas, Albania. Moss bags were exposed with irrigation for 6 months, respectively, at 7 sites of Tirana city, and 9 sites of Vlora city, along the main streets.

2 MATERIALS AND METHODS

2.1 Study areas

The carpet moss samples (*Hypnum cupressiforme* species) were collected in a clean rural area (Llogora, N: 40^o 12' 31.1"; E: 19^o 35' 06.7"). Extraneous material was removed from the moss and it was cleaned of soil particles in laboratory, and then prepared for exposure. The moss bags were transferred to 7 sites in Tirana and 9 sites of the Vlora areas (Fig. 1). Moss samples are hanged on the ceilings of the first floor balcony, 2 m above ground level. The exposure period was from October 2010 to the end of March 2011.

Moss bags were exposed with irrigation at all sampling sites. Irrigation of moss bags was achieved by placing them on the top of a cellulose (100%) sponge packed in a polyethylene box (150x110x80 mm) with the bottom immersed in distilled water. Distilled water was added to the boxes at the intervals of 15 to 20 days depending on meteorological conditions (precipitation and temperature). To check for a possible contamination, the elemental composition of the sponge was determined after acid digestion, and concentrations for all elements were below the detection limits. The polyethylene boxes were decontaminated before use by soaking in 5% nitric acid for 48 h and washed with double-distilled water.

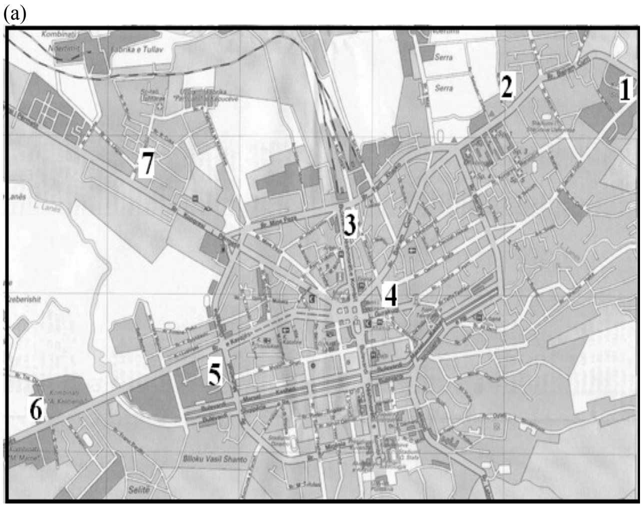
2.2 Method of analysis

Wet digestion of a homogeneous sub-sample was applied. About 0.5 g moss sample was transferred to the half pressure Teflon tubes and 10 ml nitric acid (9:1) was added. The closed tubes were put at room temperature for 48 h, and then digested for 3 h at 80-90 ºC. The temperature was increased to 200 ºC and kept for 1 h, for further digestion. The tubes were opened and the acid was evaporated till a very small volume. After cooling, the mass was transferred to 25-ml volumetric flasks which were filled till the mark with osmosis-treated water. Heavy metals, such as Cu, Cd, Pb, and Mn, were determined by AAS equipped with electro-thermal system by using a novA400 instrument (Analytik Jena). Flame-AAS was used for Zn and Fe determination; a cold vapor atomic absorption spectrometer (CVAAS) was used for mercury determination, and AES method for K and Na by using a Varian SpectrAA 10+ instrument.

2.3 Quality control of the analysis

The quality control was performed by comparing the metal contents of background sample (*Hypnum cupressiforme* species, collected in a clean rural area, Llogora, N: 40^o 12' 31.1"; E: 19^o 35' 06.7"), and analyzed by different techniques: AAS and ICP-AES. The results of ICP method provided and performed by the Institute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University, are in good agreement with our results (AAS). The certified M2 and M3 moss samples were used for quality control of ICP-AES analysis. The results of the analyses are listed in Table 1.

(a)



(b)

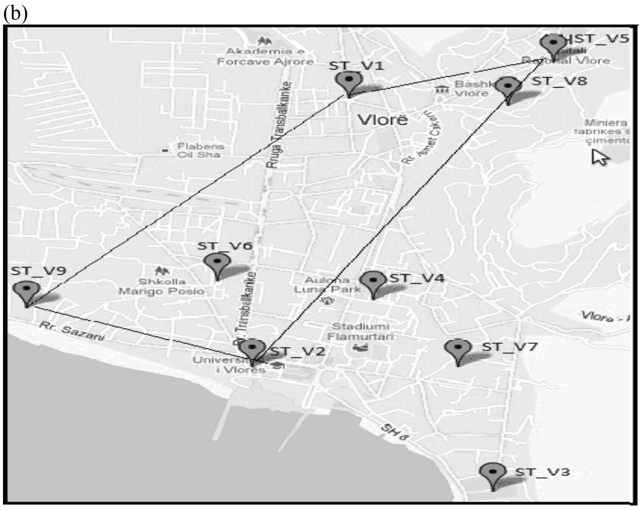


FIGURE 1 - Map of exposure sites in Tirana (a) and Vlora (b) ((a): 1 - Dajti Cable Car Str.; 2 - Tirana Hospital; 3 - Railway Str.; 4 - Tirana Center; 5 - 21-Dec Str.; 6 – Combine; 7 – Lapraka; (b): ST_V1: New Road; ST_2: Vlora Universities; ST_3: Cold Water; ST_4: Luna Park; ST_5: "Partizan" Square; ST_6: Road May 24th; ST_7: Electric Power Station; ST_8: Road 4 Heroes; ST_9: Vlora Old Beach).

TABLE 1 - Metal concentrations (mg/kg, DW) in moss background sample.

INDEX	Zn	Fe	Mn	Cu	Cd	Pb	K	Na
LLOGORA (ALB19) (AAS)	8.33	954	46.1	3.22	0.15	2.93	3675	194
LLOGORA (ALB19) (ICP-AES)	7.84	985	41.7	4.62	0.15	2.98	3697	191

3 RESULTS AND DISCUSSION

Concentrations of seven heavy metals and two major elements, K and Na, determined in moss exposed at different sites are listed in Tables 2 and 3. The box plot of the elements ranked in increasing order (black line means unexposed moss bags) of exposed moss bag concentrations for both Tirana and Vlora areas are presented on Fig. 2.

The intensity of metal content, based on the mean values of moss bags exposed in Tirana and Vlora sites, follows the trend: K > Fe > Na > Mn > Zn > Pb > Cu > Cd > Hg. The range of variation of Pb, Cd and Fe in moss samples exposed at Tirana is larger than that of Vlora. The main sources of lead, cadmium and iron include the emission from engines of old cars, the use of leaded petrol, waste incineration and industry. Intensive traffic in Tirana could be the main factor of high Pb content in about 47% of the analyzed moss samples. Proximity to the road, and wear and tear of the automobile parts, could be also the reason [14], especially of Cd contamination.

The range of variation of Hg, Zn and Mn in moss samples exposed at Vlora sites is larger than of Tirana. The main sources of mercury in Vlora are its ex-hot spot site contaminated by metallic mercury from an ex-chlorine alkaline plant [15, 16], while Mn and Zn elements can be classified as anthropogenic and lithogenic in origin. Mn is associated with traffic-related sources, such as corrosion of metallic parts, concrete materials, re-entrained dust from roads, tear and/or wear of tires, and

TABLE 2 - Heavy metal concentrations (in mg/kg, DW) in moss samples of Tirana area.

Station	**Zn**	**Fe**	**Mn**	**Cu**	**Cd**	**Pb**	**Hg**	**K**	**Na**
T1	7.1	876	46	3.0	0.22	4.2	0.057	2899	221
T2	7.2	973	35	1.3	0.33	12.2	**0.135**	3781	249
T3	8.8	1193	46	2.6	0.14	5.8	0.092	2684	183
T4	9.3	1944	82	1.8	0.22	17.6	**0.112**	3442	330
T5	7.5	1274	46	2.8	0.27	11.6	0.084	3333	213
T6	6.3	557	35	1.3	**0.49**	2.6	**0.376**	3678	214
T7	7.9	716	46	3.6	0.21	6.5	**0.432**	3227	225

TABLE 3 - Heavy metal concentrations (in mg/kg, DW) in moss samples of Vlora area.

Station	**Zn**	**Fe**	**Mn**	**Cu**	**Cd**	**Pb**	**Hg**	**K**	**Na**
ST_V1	**13.6**	885	46.0	2.5	0.12	1.6	**0.234**	3080	174.3
ST_V2	**13.2**	802	**82.0**	1.8	0.07	3.9	**0.234**	3327	226
ST_V3	**19.8**	949	**104.0**	**3.6**	0.06	**6.0**	0.052	2749	151.3
ST_V4	1.6	**1309**	**93.0**	2.1	0.06	**5.2**	0.052	2839	197.2
ST_V5	3.7	771	**104.0**	0.9	0.05	1.2	**0.130**	1433	67.0
ST_V6	5.2	**1003**	**197.0**	1.7	**0.20**	2.1	**0.313**	**4687**	323.6
ST_V7	6.3	985	**151.0**	1.8	0.17	3.3	0.052	3329	360.0
ST_V8	3.1	975	**151.0**	1.2	0.13	1.6	**0.130**	1698	229.8
ST_V9	4.2	986	**127.0**	1.5	0.10	1.9	**0.964**	**4042**	344.7

Descriptive statistics was applied to the results obtained. Minimal. maximal and mean values for both cities are given in Table 4.

TABLE 4 - Statistical data of monitoring areas.

Station	**Site**	**Hg**	**Cd**	**Cu**	**Pb**	**Zn**	**Mn**	**Na**	**Fe**	**K**
Background	**Llogora**	0.072	0.15	4.60	3.53	7.84	41.70	191.5	985	3697
Min.	**Tirana**	0.057	0.14	1.30	2.60	6.30	35.00	183	557	2684
	Vlora	0.052	0.05	0.90	1.20	1.60	46.00	67	771	1433
Mean	**Tirana**	0.180	0.27	2.34	8.64	7.73	48.00	233	1076	3292
	Vlora	0.223	0.11	2.17	3.03	7.85	109.67	230	965	3020
Max.	**Tirana**	**0.432**	**0.49**	3.60	**17.60**	9.30	**82.00**	**330**	**1944**	**3781**
	Vlora	**0.964**	0.20	3.60	**6.00**	**19.80**	**197.00**	**360**	**1309**	**4687**

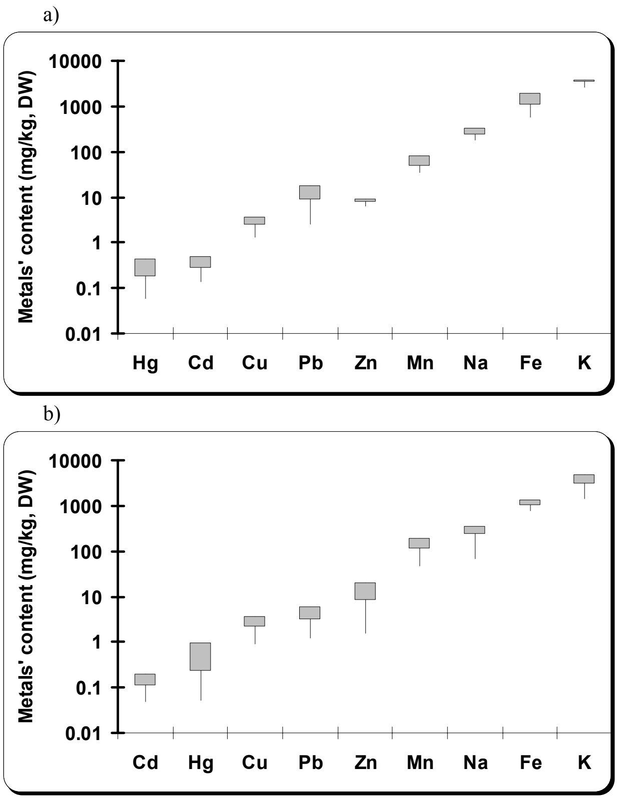


FIGURE 2 - Box plot of exposed moss bag concentrations (expressed as µg /g, DW): a) Tirana area, b) Vlora area (the elements are ranked in increasing order).

contribution of vehicular Mn emissions arising from petrol additives [17].

The loss of Cu and Zn in most of moss samples of Tirana sites could be caused by washing out and leaching process; in similar way, this was described for Mn by Couto et al. [18], while in Vlora sites only the loss of Cu was evident in all moss samples.

The loss of potassium in our moss bag samples after 6-months exposure, compared to non-exposed control was smaller than literature data [19]. Due to the maintenance of moss humidity during the exposure, the loss of K from the moss tissue is less pronounced for wet moss bags than for dry ones [19]. The results indicate that sandy dust of Vlora beach and suspended road dust (PM10) are the most significant sources of the analyzed potassium at Vlora sites.

To evaluate the accumulation degree, we used the *Accumulation Factor* (AF) defined as the concentration ratio between the exposed and the blank moss bags, and (AF = $C_{exp} / C_{background}$) was calculated (Tables 5 and 6).

The AF results reflect the different geochemical mobility of elements [20]. The elements given in Tables 4 and 5 can be divided into two groups. The first group of elements (Zn, Fe, Cu, K and Na) does not display high accumulation factors (mean AF < 3), while Pb and Cd in Tirana sites, as well as Hg and Mn in Vlora sites, display moderate accumulation factors (mean 3<AF<10). The site ST_V9 of Vlora results to be highly mercury-polluted (AF>10). As is mentioned before, the main sources of mercury in Vlora are its ex-hot spot site contaminated by metallic mercury from an ex-chlorine alkali plant [15, 16].

The accumulation of these elements (Mn and Hg) in Vlora sites suggests that non-crustal sources are relevant for these elements but also a variety of pollution emissions may contribute to their loading in ambient air.

On the contrary, Na, K and Fe have rather high concentrations but low accumulation factors (*<3*), which suggests negligible contribution of anthropogenic sources and main origin from air-borne dust.

TABLE 5 - Accumulation factors for determined elements in Tirana area.

Station	Zn	Fe	Mn	Cu	Cd	Pb	Hg	K	Na
T1	0.91	0.89	**1.10**	0.65	**1.47**	**1.19**	0.79	0.78	**1.15**
T2	0.92	0.99	0.84	0.28	**2.20**	**3.46**	**1.88**	1.02	**1.30**
T3	**1.12**	**1.21**	**1.10**	0.57	0.93	**1.64**	**1.28**	0.73	0.96
T4	**1.19**	**1.97**	**1.97**	0.39	**1.47**	**4.99**	**1.56**	0.93	**1.72**
T5	0.96	**1.29**	**1.10**	0.61	**1.80**	**3.29**	**1.17**	0.90	**1.11**
T6	0.80	0.57	0.84	0.28	**3.27**	0.74	**5.22**	0.99	**1.12**
T7	1.01	0.73	**1.10**	0.78	**1.40**	**1.84**	**6.00**	0.87	**1.17**

TABLE 6 - Accumulation factors for determined elements in Vlora area.

Station	Zn	Fe	Mn	Cu	Cd	Pb	Hg	K	Na
V1	**1.73**	0.90	1.10	0.54	0.80	0.45	**3.25**	0.83	0.91
V2	**1.68**	0.81	1.97	0.39	0.47	**1.10**	**3.25**	0.90	1.18
V3	**2.53**	0.96	**2.49**	0.78	0.40	**1.70**	0.72	0.74	0.79
V4	0.20	**1.33**	**2.23**	0.46	0.40	**1.47**	0.72	0.77	1.03
V5	0.47	0.78	**2.49**	0.20	0.33	0.34	**1.81**	0.39	0.35
V6	0.66	1.02	**4.72**	0.37	**1.33**	0.59	**4.35**	**1.27**	**1.69**
V7	0.80	1.00	**3.62**	0.39	**1.13**	0.93	0.72	0.90	**1.88**
V8	0.40	0.99	**3.62**	0.26	0.87	0.45	**1.81**	0.46	**1.20**
V9	0.54	1.00	**3.05**	0.33	0.67	0.54	**13.39**	1.09	**1.80**

3.1 Correlation and multivariate analysis of the data

To distinguish lithogenic/and or anthropogenic origin of the elements, correlation and cluster analysis were carried out. The results of correlation analysis are listed in Tables 7 and 8. The results from the cluster analysis of variables (Zn, Fe, Mn, Cu, Cd, Pb, Hg, K, Na) for Tirana sites are presented in Table 9, and those for Vlora site in Table 10.

TABLE 7 – The results of correlation analysis for Tirana area.

Element	**Zn**	**Fe**	**Mn**	**Cu**	**Cd**	**Pb**	**Hg**	**K**	**Na**
Zn	1.00								
Fe	**0.81**	1.00							
Mn	**0.79**	**0.87**	1.00						
Cu	0.21	-0.12	0.04	1.00					
Cd	**-0.77**	-0.47	-0.45	**-0.67**	1.00				
Pb	**0.59**	**0.85**	**0.69**	-0.25	-0.23	1.00			
Hg	-0.33	**-0.60**	-0.29	0.06	0.44	-0.40	1.00		
K	-0.41	-0.08	-0.11	**-0.70**	**0.78**	0.35	0.34	1.00	
Na	0.44	**0.68**	**0.79**	-0.36	-0.02	**0.80**	-0.12	0.45	1.00

TABLE 8 - The results of correlation analysis for Vlora area.

Element	**Zn**	**Fe**	**Mn**	**Cu**	**Cd**	**Pb**	**Hg**	**K**	**Na**
Zn	1.00								
Fe	-0.41	1.00							
Mn	-0.46	0.18	1.00						
Cu	**0.81**	0.18	-0.35	1.00					
Cd	-0.22	0.08	**0.69**	-0.18	1.00				
Pb	0.45	0.45	-0.20	**0.73**	-0.39	1.00			
Hg	-0.19	-0.07	0.12	-0.25	0.09	-0.39	1.00		
K	0.08	0.22	0.33	0.19	**0.55**	0.08	**0.51**	1.00	
Na	-0.26	0.29	0.61	-0.14	**0.73**	-0.08	**0.47**	**0.75**	1.00

TABLE 9 - Cluster Analysis of Variables: Zn, Fe, Mn, Cu, Cd, Pb, Hg, K, Na (Tirana sites).

Amalgamation Steps							
Step	Number of clusters	Similarity level	Distance level	Clusters joined		New cluster	Number of obs. in new cluster
1	8	93.7315	0.125370	2	3	2	2
2	7	92.5591	0.148818	2	6	2	3
3	6	90.5880	0.188240	1	2	1	4
4	5	89.8923	0.202154	1	9	1	5
5	4	88.7723	0.224554	5	8	5	2
6	3	72.4293	0.551414	1	5	1	7
7	2	72.1979	0.556042	1	7	1	8
8	1	60.5127	0.789746	1	4	1	9
Final Partition - Cluster 1: Zn, Fe, Mn, Pb, Na; **Cluster 2:** Cu; **Cluster 3:** Cd, K; **Cluster 4:** Hg; obs. = observations							

TABLE 10 - Cluster Analysis of variables: Zn, Fe, Mn, Cu, Cd, Pb, Hg, K, Na (Vlora sites).

Correlation Coefficient Distance, Single Linkage Amalgamation Steps							
Step	Number of clusters	Similarity level	Distance level	Clusters joined		New cluster	Number of observations in new cluster
1	8	90.3881	0.192239	1	4	1	2
2	7	87.3180	0.253641	8	9	8	2
3	6	86.4878	0.270244	1	6	1	3
4	5	86.4626	0.270747	5	8	5	3
5	4	84.7309	0.305382	3	5	3	4
6	3	75.6362	0.487276	3	7	3	5
7	2	72.3700	0.552599	1	2	1	4
8	1	64.6418	0.707165	1	3	1	9
Final Partition - Cluster 1: Zn, Cu, Pb; **Cluster 2:** Fe; **Cluster 3:** Mn, Cd, K, Na; **Cluster 4:** Hg							

The highest correlation coefficients among heavy metals in moss samples of Tirana area are observed for Zn, Fe, Mn, Pb and Na; that is probably due to emission from traffic, and to suspension or re-suspension of road and city dust, which includes soil dust mixed with traffic-related particles more than direct exhaust emission and city dust.

Cu and Cd, K, as well as Zn and Cd in air were significantly negatively correlated between them, suggesting that Cu and Cd as well as Zn and Cd are mostly from different origin.

The main source of Cd could be locally like cigarette smoking [21], incineration of refuse materials (cadmium pigments and stabilizers in plastics, nickel-cadmium batteries). Elevated Cd concentration could be due to polythenes, domestic waste, sewage sludge, plastic pipes, automobile tires and exhaust [22]. The most probable source of Cd and K may be related to organic urban waste incineration, and the origin of Hg is uncertain.

The level of fine dust particles known as PM10, the highly unmanaged urbanization, and high density of the population inside city areas are also causal factors for the high correlation between Mn and Na in most of moss bag samples. Similar problems were evident also in other countries [23, 24].

Iron was most-correlated to Mn, Pb and Na. Fe, Mn and Na are the main elements in the Earth's crust, and they may come from wind-blowing soil dust and frictional work from construction sites in the ambient environment which increases the atmospheric loading of dust particles, while Pb acts as marker element for motor vehicle emissions [23].

The high correlation coefficients between Zn, Cu and Pb in Vlora site support the recent finding that Cu is one of the metals most closely related to vehicle circulation in urban areas. The most probable source of Zn, Cu and Pb accumulation are vehicle-related particles; the source of Pb and Cu is probably from vehicular exhaust. Higher concentration of Zn, with regard to control samples, in urban areas could be associated with dry deposition of metal spewed out from automobiles, motor oil, and wear and tear of vehicular parts, and abrasion of tires [26]. The present finding is an agreement with Makhol and Mladenoff [25], who also described high concentration of Zn along the road, and they attributed that fuel is the main factor of Zn pollution.

Mn was most correlated to Cd, which could have originated from city dust caused by paving and non-paving roads, as well as by building industry dusts. The dust origin of Cd is supported by the good correlation between Cd and Na, as well as that of K and Na, typical constituents of Earth crust.

3.2 Multivariate analysis

The results of principal component factor analysis of the correlation matrix for elements in moss bags are presented in Tables 11 and 12.

Table 11 presents three extracted factors explaining more than 83% of the total variance for Tirana area. The first factor, explaining most of the variance (45.5%), has high loadings for Pb, Fe, Mn, Zn and Na (mostly associated with city dust, traffic exhaust, soil and re-suspended road dust). The second factor, with 28.6% of the total variance, shows high loading for Cu pointing to the contribution of cation exchange processes in moss. Factor 3 accounts for 9.5%, and has high loadings for Hg which is unknown for Tirana site.

Table 12 presents four extracted factors explaining more than 82% of the total variance for Vlora site. The first factor, explaining most of the variance (34.9%), has high loadings for Na, Mn, Cd and Hg, which may come from wind-blowing soil dust and frictional work from construction sites in ambient environment increasing the atmospheric loading of dust particles which are mostly associated with city dust. The second factor, with 24% of the total variance, shows high loading for Pb, Zn, Fe and K pointing to the contribution from traffic sources. Factor 3 accounts for about 15% of the total variance (Cu element), associated with dust mixed with traffic exhaust. Factor 4 accounts for about 11% of the total variance (Fe, Mn and Hg), associated with dust particles (Fe and Mn), as well as wind flow (metallic Hg present at V9 station).

The high correlation coefficients between Zn, Fe, Pb and Na in Vlora site support the recent finding that these metals are most closely related to vehicle-related particles; the source of Pb and Cu is probably from vehicular exhaust. Higher concentration of Zn, with regard to the control samples, in urban area could be associated with dry

TABLE 11 - Principal Component Analysis (PCA): Zn, Fe, Mn, Cu, Cd, Pb, Hg, K, Na (Tirana site).

Eigenvalue	**4.4478**	**2.8514**	**0.9510**	**0.3639**	0.2697	0.1162	0.0000	-0.0000
Proportion	**0.494**	**0.317**	**0.106**	**0.040**	0.030	0.013	0.000	-0.000
Cumulative	0.494	0.811	0.917	0.957	0.987	1.000	1.000	1.000

TABLE 12 - Principal Component Analysis (PCA): Zn, Fe, Mn, Cu, Cd, Pb, Hg, K, Na (Vlora site).

Eigenvalue	**3.4861**	**2.2587**	**1.4544**	1.0296	0.3819	0.2193	0.1628	0.0072
Proportion	**0.387**	**0.251**	**0.162**	0.114	0.042	0.024	0.018	0.001
Cumulative	0.387	0.638	0.800	0.914	0.957	0.981	0.999	1.000

deposition of metal spewed out from automobiles, motor oil, wear and tear of vehicular parts, and abrasion of tires [27]. The present finding is an agreement with Makhol and Mladenoff [26], who also described high concentration of Zn along the road, and they attributed that fuel is the main factor of Zn pollution.

The second factor related to Fe loading may be of lithogenic origin, as main element of earth`s crust.

The third factor related to Cd and K negative loading may originate from ion leaching caused by high humidity in Vlora coastal area.

The fourth factor related to Hg loading may originate from mercury pollution of V9 station (500 m far from the shore), easily distributed in the air by coastal wind.

Similar results were found in another Balkan area [27], providing that active moss bio-monitoring with different moss species could be used for screening and monitoring of atmospheric trace element pollution in urban areas.

4 CONCLUSION

Most of the analyzed heavy metals were significantly accumulated in *Hypnum cupressiforme* wet moss bags exposed for 6 months at 16 sites of two urban areas in Albania, Tirana city and Vlora city. The range of variation of Hg, Zn and Mn in moss samples exposed in Vlora area is bigger than that of Tirana. The main source of mercury in Vora is the ex-hot spot site contaminated by metallic mercury from an ex-chlorine alkaline plant. By the study of accumulation factors, the elements can be divided into two groups. The first group of elements (Zn, Fe, Cu, K and Na) showed low accumulation factors (mean AF<3), while Pb and Cd in Tirana area, as well as Hg and Mn in Vlora area, showed moderate accumulation factors (mean AF>3).

The highest correlation coefficients among Zn, Fe, Mn, Pb and Na in moss samples of Tirana and Vlora areas were probably due to emission from traffic, and to suspension or re-suspension of road dust and city dust, which include soil dust mixed with traffic-related particles.

Iron was most correlated to Mn, Pb and Na, and may originate from wind-blowing soil dust and frictional work from construction sites in ambient environment increasing the atmospheric loading of dust particles, while Pb acts as the marker element for motor vehicle emissions.

PCA analysis evidenced the presence of 3 extracted factors explaining more than 83% of the total variance for Tirana area. Dust (formed by city dust, soil and re-suspended road dust) and traffic exhaust are pointed out as the factors causing different loadings of the elements. Factor 3 accounts for 9.5%, has high loadings for Hg but is unknown for Tirana site.

Four extracted factors were explaining more than 82% of the total variance for Vlora site. Wind-blowing soil dust, city dust, traffic sources, traffic exhaust and coastal influence are pointed out as the factors causing different loadings of the elements.

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REFERENCES

[1] Walkenhorst, A., Hagemeyer, J., Beckle, S. H. (1993) Passive monitoring of airborne pollutants, particularly trace metals, with tree bark. In: Markert, B. (ed.) Plants as Biomonitors. Wiley **VCH.** 523-538.

[2] Lammel, G., Ghim, Y. S., Broekaert, J. A. C., Gao, H. W. (2006) Heavy metals in air of an Eastern China coastal urban area and the Yellow Sea, Fresenius Environmental Bulletin **15** (12a)., 1539–1548

[3] Steinnes, E. (1995) A critical evaluation of the use of naturally growing moss to monitor the deposition of atmospheric metals. Sci. Total Environ., **160/161**: 243-249.

[4] Rühling, Å., Tyler, G. (1968) An ecological approach to the lead problem. Bot. Notiser, **121**, 321-342

[5] Goodman, G.T., Roberts, T.M., Plants and soils as indicators of metals in the air. Nature, **231,** 287–292

[6] Little, P. and Martin, M.H. (1971) Biological monitoring of heavy metal pollution. Environ. Pollut., **6,** 1-19

[7] Markert, B., Wappelhorst, O., Weckert, V., Herpin, U., Siewers, U., Friese, K., Breulmann, G. (1999) The use of bio-indicators for monitoring the heavy-metal status of the environment. Journal of Radioanalytical and Nuclear Chemistry, **240**, (2), 425-429.

[8] Gerdol, R, Bragazza, L., Marchesini, R., Alber, B., Bonetti, L., Lorenzoni, G., Achilli, M., Buffoni, A., De Marco, Goodman, G.T., Roberts, T.M. (1971) Plants and soils as indicators of metals in the air. Nature, **231,** 287–292

[9] Fernandez, J. A., Ederra, A., Nunez, E., Martinez- Abaigar, J., Infante, M., Heras, P., Elias, M. J., Mazimpaka, V., Carballeira, A. (2002) Bio monitoring of metal deposition in northern Spain by moss analysis. The Sci. Tot. Environ., **300**, 115-127

[10] Tirana Air Quality Report (Ecat) (2008) Env. Centre for Administration & Technology, Tirana

[11] Fernandez, J., Carballeira, A. (2001) Evaluation of contamination, by different elements, in terrestrial mosses. Archives of Environ. Contamin. Toxicol. **40,** 461-468

[12] European Air Quality Standards, http://ec.europa.eu/environment/air/quality/standards.htm.

[13] Albanian air quality standards for some pollutants Criteria pollutant Averaging time Primary Standards Secondary standards, State of Environment 2005 – 2007b, Agency of Environment Publication

[14] Pearson, J., Wells, D.M., Seller, K.J., Bennett, A., Soares, A., Woodall, J., Ingroyille, M.J. (2000) Traffic exposure increase natural 15 N and heavy metal concentrations in mosses. New Phytology, **147**, 317-326

[15] Lazo, P., Cullaj, A., Baraj, B. (2003) An evaluation of Hg, Cr and Heavy Metals pollution in seawater and sediments of Durres Bay Adriatic Sea – Albania, J. Phys. IV France, **107**, 715-720

[16] Lazo, P., Cullaj, A., Baraj, B. (2003) Some consideration of Hg level in environment of Vlora Bay, Adriatic Sea, Journal of Environmental Protection and Ecology, **Special Issue**, 320-324

[17] Forbes, P.B.C., Thanjekwayo, M., Okonkwo, J. O., Sekhula, M., Zvinowanda, C. (2009) Lichens As Bio monitors For Manganese And Lead In Pretoria, South Africa, Fresenius Environmental Bulletin, Vol.18 (5), 609-614

[18] Couto, J. A. Fernandez, J., Aboal, R., Carballeira, A. (2004) Active biomonitoring of element uptake with terrestrial mosses: a comparison of bulk and dry depositions. Science of the Total Environment, **324**, 211-222

[19] Aničić, M., Tasić, M., Frontasyeva, M. V. , Tomašević, M., Rajšić, S. , Strelkova, L. P., Popović, A., Steinnes, E. (2008) Environmental Chemistry Letters, **7,** 55-60

[20] Calabrese, S., D'Alessandro. W., Parello, F., Bellomo. S., Brusca, L., Application of the moss bag bio monitoring technique in an active volcanic environment (Mt. Etna, Italy), available on http://www.earth-prints.org/bitstream/2122/7053/1/ICOBTE_Calabrese%26al.pdf.

[21] Kotzias, D., Geiss, O., Leva, P., Bellintani, A., Arvanitis, A., Kephalopoulos, S. (2004) Impact of various air exchange rates on the levels of environmental tobacco smoke (ETS) components, Fresenius Environmental Bulletin, **13** (12b), 1536-1549

[22] Grodzinska, K., Szarek-Lukaszewska, G. (2001) Response of mosses to the heavy metal deposition in Poland - An overview. Environ. Pollut., **114**, 443-451.

[23] Huang, X. Olmez, I., Aras, N. K., Gordan, G. E. (1994) Emissions of trace elements from motor vehicles: potential marker elements and source composition profile. Atm. Environ. **28 (8),** 1385-1391

[24] Monaci, F., Moni, F., Lanciotti, E., Grechi, D., Bargagli, R. (2000) Bio monitoring of airborne metals in urban environments: new tracers of vehicle emission, in place of lead. Environmental Pollution, **107**, 321-327

[25] Makhol, M.M., Mladenoff, D.J. (2005) Efficacy of biomonitoring (moss bag) technique for determining element deposition trends on mid range (375 Km) scale. Environ. Monit. Asses., **104**, 8-88

[26] Imperato, M., Admo, P., Naimo, D., Arienzo, M., Stanzione, D., Violant, P. (2003) Spatial distribution of heavy metals in urban soils of Naples city Italy. Environ. Pollut., 124, 247-256

[27] Aničić, M., Tasić, M., Frontasyeva, M. V. , Tomašević, M., Rajšić, S. , Mijić, Z. and Popović, A. (2009) Active moss bio monitoring of trace elements with Sphagnum girgensohnii moss bags in relation to atmospheric bulk deposition in Belgrade, Serbia, Environmental Pollution, **157**, 673–679

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