

HEALTH RISKS OF HEAVY METALS FROM AIR POLLUTION IN ALBANIA

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Abstract

The most toxic heavy metals, cadmium, lead and mercury in air are mainly emitted as a result of various industrial activities, traffic emission and waste incineration. Even in low concentration, heavy metals accumulate in the soil and enter the food chain of certain animals by causing different disorders. On other hand, heavy metals are persistent in the environment and are subject to bioaccumulation in food-chains. Because of the persistence and potential of heavy metals for global atmospheric transfer, atmospheric emissions affect even at the most remote regions. This study is focused on the sources, chemical properties and spatial distribution of environmental pollution with cadmium, lead and mercury caused by different emission sources in Albania and evaluates the health in the most polluted areas.

The atmospheric deposition of Cd, Pb and As in Albania was investigated by using carpet-forming moss species (*Hypnum cupressiforme*) as bioindicators. This research is a part of the international program (International Co-operative Programme (ICP) Vegetation, UNECE) carried out in most European countries since 1987, investigating the impacts of air pollutants on crops and natural vegetation. Sampling was carried out during the dry seasons of autumn 2010 and summer 2011 at 44 sites distributed all over Albania.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis made it possible to determine concentrations of 19 elements including key toxic metals such as Pb, Cd, As, and Cu. Data were processed by using the MINTAB 15 software package.

The median values of the elements in moss samples of Albania were high for Al, Cr, Ni, Fe, and V and low for Cd, Cu, and Zn compared to other European countries, but generally were of a similar level as some of the neighboring countries.

This study was conducted in order to produce information needed for better identification of contamination sources and improving the potential for assessing environmental and health risks in Albania, associated with toxic metals. The Elbasan Metallurgical Combine and mining industry are the main contributors of iron, chromium, nickel, and vanadium in Albania. The pollution emitted from the Elbasan Metallurgical Combinat has caused serious pollution on the Shkumbini River, many problems to the microenvironment, and adverse effects on the human health, especially in pregnant and lactating mothers. The prevalence and severity of respiratory allergic diseases such as bronchial asthma have been increased in recent years among the people of this area.

Key words: Heavy metals, Air pollution, Bioindicator, Mosses.

1. Introduction

Heavy metal contamination of the environment has attracted the attention of the scientists all over the world (Pelgrom *et al.* [1]; Wang and Stuanes [2]; Nadal *et al.* [3]; Wang *et al.* [4]; Harmens and Noris [5]; Harmens *et al.* [6]). The increase of heavy metal concentrations in the environment may have a potential hazard to humans caused by the accumulation in our food chain after a long time of exposure. The distribution of heavy metals in the environment depends strongly to weather and local conditions (Nali and Lorenzini [7]). The aerosols with small falling velocity are easily transported by the wind, and if deposited constantly even in small rate for a long time period, the environmental accumulation will probably pose an increase of environmental and health hazards. The plants are greatly affected by chemical and physical conditions of the environment

and may reflect the changes of environmental conditions (Decoteau [8]). In general, the biomonitoring provide the data of integrated exposure over a certain period of time and provide the spatial distribution over a large scale of monitoring by using many sites simultaneously (Chakraborty and Paratkar [9]). The mosses are recommended as good bioindicators of metal pollution in the atmosphere since 1960 (Rühling and Tyler [10]). The process of the accumulation of pollutants in mosses occurs through different mechanisms like the layers of particles, entrapment on the surface of the cells, through the incorporation into the outer wall of cells, the ion exchange processes, and metabolically controlled passage into the cells (Markert *et al.*, [11]; Fernandez *et al.*, [12]; Brown & Bates, [13]).

Albania is a small country (28,000 km²) with a complex geographic relief and geologic setting, and characterized by high anthropogenic influence. The atmospheric deposition of metals in Albania was performed under the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops with heavy metals in Europe (UNECE ICP Vegetation). Twelve elements, such as conservative elements (Al and Fe) and trace elements, such as: As, Cd, Cr, Cu, Ni, Pb, V, and Zn, were measured in moss samples collected in whole territory of Albania during the moss survey in the dry autumn and summer period of 2010 and 2011 (Qarri *et al.* [14]). The distribution of the elements in each sampling site identified the sites of the country with higher levels of these elements, and the main anthropogenic and geological sources. The main anthropogenic sources of heavy metals are various industrial processes, mining, foundries, smelters, combustion of fossil fuel and gasoline, and waste incinerators. The major heavy metals of concern to the European Monitoring and Evaluation Programme (EMEP) are Hg, Cd, and Pb, because they are the most toxic and have known serious effects on human health. Environmental exposure to high concentrations of heavy metals has been linked with various cancers and kidney damage. Numerous studies worldwide have confirmed that both long-term and short-term exposure to air pollutants are associated with increases in mortality and morbidity (Venner *et al.*, [15]; Dockery *et al.*, [16]). An increasing number of studies have indicated that different transition metals may act as possible mediators of particle-induced injury and inflammation (Dreher *et al.*, [17]; Schaumann *et al.*, [18]; Chen and Lippmann [19]). The focus has often been on transition metals such as: iron (Fe), vanadium (V), nickel (Ni), chromium (Cr), copper (Cu), and zinc (Zn) on the basis of their ability to generate reactive oxygen species (ROS) in biological tissues (Schwarze *et al.*, [20]). Using single-component regression analysis, Gurgueira *et al.* [21] described that the content of Fe, Mn, Cu and Zn was strongly associated with the oxidative stress generated in the lung, whereas Fe, Al, Si

and Ti was associated with the effects observed in the heart. The spatial and temporal variation in the risk of PM is partially explained by chemical composition (Bell [22]). Associations between particles and health outcomes in epidemiological studies may be the result of multiple components acting on different physiological mechanisms. Some epidemiological data have shown positive correlations between the vanadium content of urban air and mortality from bronchitis, pneumonia, nephritis and cancer (Duffus [23]). According to The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Priority List of Hazardous substances by ATSDR (Agency for Toxic Substances & Disease Registry) 2007 several heavy metals are prioritized based on a combination of their frequency, toxicity, and potential for human exposure and possible adverse impact to human health. In this list are present: arsenic, lead, mercury, cadmium, cobalt, nickel, zinc, chromium, manganese, copper.

2. Materials and Methods

2.1 Materials

Sampling was performed in a relatively dry season in September - October 2010 and June - July 2011 to a total of 62 sampling stations. Sampling stations were not evenly distributed due to geographical problems. Sampling was performed according to the guidelines of the Convention on Long-range Transboundary Air Pollution (LRTAP Convention) - ICP Vegetation protocol and sampling strategy of the European Programme on Biomonitoring of Heavy Metal Atmospheric Deposition (Harmens, [24]). The recommended moss species, *Hypnum cupressiforme*, were widespread in whole Albanian territory. The sampling point locations were situated at least 300 meter away from main roads or buildings, and 100 m from small roads and single houses. Most of the samples were collected in open areas. Samples were stored in paper bags and transferred to the analytical laboratories. Samples were cleaned from extraneous material (litter and dead leaves). The distribution of the sampling sites is shown in Figure 1.

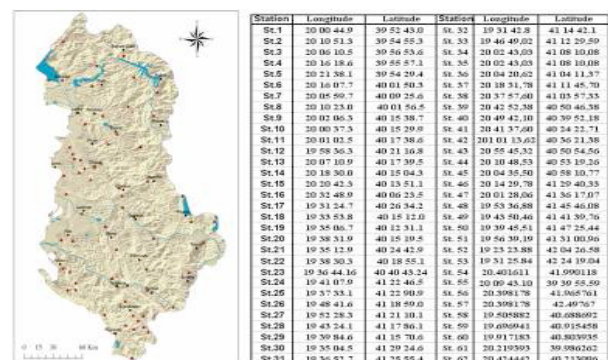


Figure 1. The map of sampling sites and their geographic coordinates

2.2 Methods

The content of 19 elements in the moss samples were determined by inductively coupled plasma - atomic emission spectrometric (ICP-AES) method (Varian, 715ES) performed at the Institute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University, Skopje, Macedonia. Moss samples were digested by Microwave digestion system (Marsx, CEM, USA). All of the reagents used for this study were with analytical grade: nitric acid trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and re-distilled water.

The total digestion of moss samples is done according to the method presented by Barandovski *et al.*, [25]. The quality control of ICP-AES results was checked by multiple analyses of samples and the certified moss reference materials M2 and M3 (Steinnes *et al.*, [26]; Harmens *et al.*, [27]).

The descriptive statistics method was applied to the elemental concentration data set to interpret results and variations in the data.

3. Results and Discussions

3.1 Concentration of 19 elements

The data on the concentration of 19 elements in 62 moss samples from Albania are summarized in a data

matrix. Aiming to valuate contamination level and elements distribution, the analytical results were statistically treated by using descriptive statistics (Table 1). The order of the elements according to their abundance is: Cd < As < Li < Pb < V < Cu < Ni < Cr < Zn < Ba < Sr < Mn < Na < P < Mg < Fe < Al < K < Ca.

High disparity exists in the concentrations of most elements in the moss samples. Coefficients of variation (CV) for most elements are moderate (25 - 75%; Table 2). CV value is the highest for Ni (170%) followed by: As (118%), Pb (98%), Cd (97%), Cr (85%) and Zn (82%). Only Ca has relatively weak variability, with CVs below 25%. Coefficients of skewness are greater than 2 for most elements, and only Ba, Ca and Mg have a coefficient lower than 2, indicating that the frequency distribution of most moss elements in the study area are strongly positively skewed. All the coefficients of kurtosis of moss elements exceed 0, suggesting that most values are still concentrated around the central tendencies. The great variation, positively skewed distribution, and high kurtosis suggest that the trace element concentrations were affected by complicated factors (Wang *et al.* [28]). For better interpretation of the results, the contamination factors (CF) scales were used. The data of the contamination factors (CF) are shown in Table 3.

Table 1. Descriptive statistics of mosses elements in Albania (N = 59) (mg/kg, DW)

Element	Minimum	Mean	Median	Maximum	ST.DEV	CV (%)	Kurtosis	Skewness
As	0.05	0.541	0.305	2.86	0.64	118	3.51	1.97
Cd	0.04	0.170	0.107	0.9	0.16	97	8.57	2.81
Li	0.28	1.644	1.425	5.58	1.01	61	4.01	1.78
Sr	10.80	22.19	21.71	47.17	6.27	28	3.52	1.24
V	1.15	4.23	3.51	16.94	2.79	66	7.50	2.40
Zn	1.00	14.06	13.77	68.15	11.59	82	8.10	2.26
Ba	6.00	21.87	21.21	42.80	8.34	38	-0.40	0.21
Ni	1.56	11.36	5.85	130.74	19.30	170	27.07	4.83
Pb	1.34	3.28	2.41	19.73	3.21	98	17.28	4.05
Cr	1.62	6.38	4.75	31.76	5.39	85	9.65	2.84
Cu	2.14	6.07	5.58	15.66	2.80	46	3.13	1.49
Mn	22.19	70.45	56.34	284	50.72	72	6.57	2.40
Na	27.90	94.54	87.13	338	50.79	54	8.89	2.39
Al	535.06	1958	1638	6974	1178	60	4.89	1.76
Ca	4424.00	7094	6734	12433	1715	24	0.38	0.84
Fe	468.72	1892	1618	5488	1105	58	2.66	1.64
K	1831.37	3736	3414	10043	1706	46	2.94	1.62
Mg	1139.62	2576	2347	5152	1033	40	-0.58	0.54
P	407.38	792	756	1839	286	36	3.09	1.53

Table 2. Descriptive statistics of concentration of Hg element in *Hypnum Cupressiforme*

Variable	Mean	SD	Variance	CV	Min	Max	Median
Hg	0,2	0,2872	0,0825	119,61	0,04	2.23	0,1300

Table 3. The data of the contamination factors (CF) and contamination classification

Parameter	Al	As	Ba	Ca	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sr	V	Zn
CF	8.25	3.33	1.25	2.43	1.88	8.78	1.55	7.80	1.42	0.22	5.10	2.07	1.36	3.83	0.52
Classification	C5	C3	C2	C3	C2	C5	C2	C4	C2	C1	C4	C3	C2	C4	C1
Contamination	Severe	Slight	Suspected	Slight	Suspected	Severe	Suspected	Moderate	Suspected	No Contaminant	Moderate	Slight	Suspected	Moderate	No Contaminant

By examining the CFs data of each element as shown in Table 3, there are a few observations can be made. The CFs results indicate that the elements: Mn, Zn, Ba, Cd, Cu, Mg and Sr may be the factors which caused the contamination of the first two categories of scale, C1 and C2, which are described as uncontaminated area (a CF of 2 can easily obtained from natural variation), depended on the metal considered. As and Ca may be the factors which caused the contamination of the third category of scale, C3 and are described as slightly polluted area. The As, Ca origin belongs mainly to sulfide minerals (Lazo *et al.*, [29]) and calcium carbonates formation in some areas of Albania. From all of the 19 elements, there are a few metals that may be the factors which caused the contamination of moderately or severely polluted scale of classification, like Fe, Ni, V (CF = 4) and Al, Cr (CF = 5).

The highest values of these elements were measured near the industrial centers (the central part of the country). Hg was found to be higher at station positioned near ex mercury Hot Spot site Vlore. Due to high content of metallic mercury in the area of ex-chemical pant Plazhi i Vjeter (Lazo *et al.*, [29]), the highest value of mercury concentration was found in Vlora city.

High disparity exists in the concentrations of: Al, Cr, Fe, Ni, V, and Zn in the moss samples. The present median values of the elements: Al, Fe, V, Cr, Ni, and Zn, typically associated with air pollution are generally comparable with those presented from Macedonia and other neighboring countries (Qarri *et al.*, [14], Balabanova *et al.*, [30]; Barandovski *et al.*, [31], [32]; Spiric *et al.*, [33]; Thöni *et al.*, [34]), but substantially higher than the corresponding values from most European countries (except Zn) (Harmens *et al.*, [24], [26]).

3.2 Aluminum, Chromium, Iron, Nickel and Vanadium

Aluminum is a good indicator of mineral particles. The background level of Al in Albanian moss samples is higher than the European 2010 moss biomonitoring survey. The highest Al concentration was found in the south and in central part of Albania. The main contribution of Cr, Fe, Ni and V elements is coming from the

Elbasan ferrochromium metallurgical plant (Lazo *et al.*, [35]) and mine industry in Albania. The high level on wind-blow dust in the south and high level (for most metals) of industrial activity is focused in the mid-east of Albania. The association Cr and Fe is also related to air pollution (Lazo *et al.*, [35]). The high concentration of iron were found in vicinity of Pogradec iron-nickel mine and in Bulqiza chromium mines area. Albania is known as a country with a high chrome potential, as compared to the other Mediterranean countries. The main deposits of this mineral are situated in the Ophiolites of the Eastern Belt area, along the direction Tropoja-Kukes-Bulqiza-Shebenik-Pogradec (eae-al.org, [36]). Contamination by chromium was similar to the pattern of Fe deposition because of the same emission sources.

Higher levels of chromium were found in Elbasan-Librazhd-Pogradec area and in Bulqiza area. It might be associated with iron-chromium industry in Elbasan (Lazo *et al.*, [34]) and chromium mining industry of these areas (eae-al.org, [36]). Albania is known as a country with a high chrome potential, compared to the other Mediterranean countries. The main deposits of this mineral are situated in the Ophiolites of the Eastern Belt area, along the direction Tropoja-Kukes-Bulqiza-Shebenik-Pogradec [36]. Higher levels of nickel might be associated with iron-chromium industry in Elbasan (Lazo *et al.*, [35]) and nickel mining industry in these areas (eae-al.org, [36]). Iron-nickel and nickel-silicate are mainly located in Devoll, Pogradec, Librazhd and Kukes areas. The deposits are composed by Nickel-silicate ore, Iron-nickel ores and re-deposited or secondary crust nickel-silicate ores [36]. Also nickel has been linked to geogenic source and emissions from vehicles, oil combustion, road dust, and iron metallurgy industry.

Contamination by vanadium was very similar to the pattern of Fe deposition. Generally, concentrations of nickel or vanadium were significantly associated with fine particles (PM10 and PM2.5) mortality (Bell *et al.*, [37]). Studies have linked various particle components to human physiological responses, such as nickel changes in heart rate variability (Cavallari *et al.*, [38]) and vanadium in oxidative DNA damage (Sørensen *et*

al., [39]). The high concentration values were found in vicinity of Elbasani Metallurgical Combine, Lezha area mentioned for titan-magnetite mineralization and at ex-coal mining industry area.

Elbasan Metallurgical Combine and mining industry are the main contributors of iron, chromium, nickel and vanadium in central part of Albania. Generally, the area was classified to be highly and/or moderately polluted by heavy metals (Lazo *et al.*, [35]). The pollution emitted from Elbasan Metallurgical Combine has caused serious pollution in soils of this area and on Shkumbini River (the main watershed in this region). The presence of emitted toxic gases, vapors and dust, has caused many problems to the microenvironment and adverse effects in the human health, especially pregnant and lactating mothers (Kristo *et al.*, [40]). The prevalence and severity of respiratory allergic diseases such as bronchial asthma have been increased in recent years among the people of this area. The level percentage of pulmonary disease in Elbasan city (hospital cases) for chronic bronchitis and bronchial asthma is increased respectively around 10 times for chronic bronchitis and 1.6 times for bronchial asthma during the period 2002 - 2007 (Lika *et al.*, [41]).

3.3 Arsenic, Cadmium, Copper and Zinc

Arsenic concentrations in mosses were generally low in western part of Albania and higher in east part of Albania, but lower than neighboring countries (Harmens *et al.*, [27]). Cu, Cd and Zn concentrations were generally low in mosses sampled in Albania compared to many other European countries (Harmens *et al.*, [27]). Road transport may have a considerable effect on the distribution of these elements in air pollution in Albania. The effects associated with the cadmium level include kidney and bone damage and cancer. The kidney is the critical organ with regard to long-term occupational and environmental exposure to cadmium, and all health-based recommendations relate to the early disturbance of renal function. Cadmium can affect calcium and phosphorus metabolism generally, both in industrial workers and in people exposed in the general environment. Painful bone disorders, including osteomalacia, osteoporosis and spontaneous bone fracture, have been observed in humans chronically exposed to cadmium in food. Osteomalacia most often affects women with several risk factors such as poor nutrition and multiparity (WHO/IPCS, 1992). In its latest evaluation of the carcinogenic risk from cadmium exposure, IARC (1993) concluded that there was sufficient evidence to classify cadmium and cadmium compounds as human carcinogens.

3.4 Lead

Lead is by far the most well-studied toxic metal, and a wide range of biological effects dependent upon the

level and duration of the exposure are known (The Agency for Toxic Substances and Disease Registry (ATSDR, 2005 [42]).

Adults who were poisoned by lead during childhood have increased blood pressure, which is a significant risk factor for cardiovascular diseases and mortality. Non-fatal mechanisms include renal effects; anemia owing to the inhibition of several enzymes involved in haem synthesis; acceleration of skeletal maturation; alteration of hormone levels and immunity parameters; and encephalopathy (at high exposure) and various other diseases of the nervous system. Impairment of neurodevelopment in children is the most critical lead effect. The relative contributions of different lead sources differ depending on local conditions.

The present median value of Pb in Albania, associated with air pollution is comparable with those observed in Croatia, Kosovo, Macedonia (Harmens *et al.*, [6] and [27], Barandovski *et al.*, [25], Balabanova *et al.*, [30]), but substantially higher than the corresponding values from other European countries (Harmens *et al.*, [6] and [27]). CV value is higher for Pb (98 %). By examining the CFs data of lead as shown in Table 3, we can see that CFs results indicate that the element Pb is associated with the contamination of the third category of scale, C3, described as slightly polluted areas. Lead levels in ambient air have decreased during the last decades.

3.5 Merkury

Mercury can damage the brain, nerves, kidneys and lungs. Methylmercury is a potent neurotoxin. It is difficult to distinguish mercury toxicity symptoms from those of some other common ailments. The symptoms include tremors, muscular weakness, depression, personality changes and short-term memory loss in adults, and skin rashes, particularly redness and peeling of the hands and feet, in children.

The highest concentration of Hg was found at the station situated in the front of an ex-chlorine alkali Plant of Vlora area, mentioned as main mercury "Hot Spot" pollution site in Albania. The area of approximately 11 ha had been contaminated by elemental mercury. Since 2011, the mercury polluted soils were encapsulated, but the emitted metallic mercury emitted in Vlora Bay for a long period (for about 20 years) due to soil erosion process, is still present in sediments of the Bay. As it expected, the lowest concentration of Hg was found in distance from the coastal line.

4. Conclusions

- This study was conducted to evaluate how heavy metals deposition affect the health of people and it confirms that the moss biomonitoring is a valuable tool for the evaluation of atmospheric input of metals

in the environment. The method is suitable for detecting spatial trends in heavy metal deposition.

- Only a few metals that belong to the group of elements which caused moderately or severely contamination, like Fe, Ni, V (CF = 4) and Al, Cr (CF = 5) were identified. One of the most polluted location with high concentrations of Al, Cr, Fe, Ni, V and Zn was in central part of the country, caused mainly from iron-chromium metallurgical plant and miner industry. The prevalence and severity of respiratory allergic diseases such as bronchial asthma have been increased in recent years among the people of this area. The level percentage of pulmonary disease in Elbasan city (hospital cases) for chronic bronchitis and bronchial asthma is increased respectively around 10 times for chronic bronchitis and 1.6 times for bronchial asthma during the period 2002 - 2007. Fe, Cr, Ni and V pollution might be associated with iron-chromium metallurgy, oil refinery, cement industry, mining industry and heavy traffic in the polluted areas.

- The effect of traffic compared to the influence of industry is much milder as the sampling points were not close to the roads and was clear demonstrated in Zn distribution.

- High contents of aluminum was found in the south-east direction of the country.

- The presence of emitted toxic gases, vapors and dust, has caused many problems to the microenvironment and adverse effects in the human health, especially pregnant and lactating mothers. The prevalence and severity of respiratory allergic diseases such as bronchial asthma have been increased in recent years among the people of this area.

- Effects of the major pollution sources located in industrial zones could be readily detected on the basis of moss analysis. However, the elements Al, Fe, Cr, Ni and V appear the highest median values among European countries and these exceeds may result in plants' effects due to the accumulative nature of heavy metals in soils.

- Soil dust, industry emissions, waste incineration and road traffic were pointed as main factors causing air pollutions from heavy metals in Albania.

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