SPATIAL DISTRIBIUTION OF Sc, LANTHANIDES, U, Th, Zr, Hf, Ta, AND Fe IN THE SURVEY OF ATMOSPHERIC DEPOSITION OF HEAVY METALS IN ALBANIA BY USING MOSS BIOMONITORING

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Abstract

The present work is a continuation of atmospheric deposition study of trace elements in Albania which was conducted in the framework of UNECE ICP Vegetation Program in order to provide a reliable assessment of air quality throughout Albania. A total of 45 elements were determination by epithermal neutron activation analysis (ENAA) at IBR-2 fast pulsed reactor in Dubna in carpet-forming-moss species (*Hypnum cupressiforme*) collected over the whole territory of the country at 44 sampling sites. This paper is focused mostly on rare elements like Zr, Hf, Ta, Sc, lanthanides and actinides as these elements were never previously determined in the air deposition of Albania. Fe as typical crustal element is also included in this study. Descriptive and multivariate statistics were used for the concentration data treatment using MINTAB 17 and STATISTICA 8 software package. The median values for elements under investigation were compared to those in the neighboring countries such as Bulgaria, Macedonia, Romania and Serbia, and Norway that is selected as a clean area. It was revealed that the accumulation of metals in mosses is associated with the wind blowing metal-enriched soils that are pointed out as the main emitting factor.

Key words: moss biomonitoring, atmospheric deposition, trace elements, NAA analysis.

Introduction

Air pollution is responsible for climate change due to the enhanced greenhouse effect, acid rain, and the depletion of the ozone layer that constitute important global environmental problems. It is caused by human activities and natural mechanisms [1]. Atmospheric deposition constitutes a major contribution of numerous heavy metals, which are of potential toxicity for ecosystems. Among these trace metals, the knowledge of the rare earth elements (REE) behaviors at the atmosphere–soil interface is of importance [2], because REE have similar and conservative behaviors and a relatively lack of human sources. REE group of elements comprises 17 elements; the 15 elements from lanthanides from La (Z = 57) to Lu (Z = 71), yttrium and scandium [3]. They present similar chemical properties [4]. A general classification divides lanthanides into two groups: light lanthanides (La–Eu) and heavy lanthanides (Gd–Lu). This classification is done based on the electron configuration of each element, which determines how they interact with other elements and compounds [3]. It is also based in the solubility of inorganic salts of lanthanides. Light lanthanides are considered more soluble than heavy ones [5], but there is no worldwide accepted definition for which lanthanide belongs to each group, because the solubility of REEs is low, due to the complex-formation. Total REE concentration in soil surface is up to 100–200 mg kg−1 [6,7]. Higher concentrations are caused by human activity, low mobility of REEs and their high adsorption to soils [8,4]. The use of the REE-rich phosphates fertilizers [9-11] is an important factor that causes the enrichment of REE's in soil.

Moss biomonitoring provides a complementary method evaluating the elemental deposition from the atmosphere to terrestrial systems. It is an easier and cheaper method

compared with the conventional precipitation analysis that ensures a high sampling density in the monitoring area. Mosses had been reported as well-known good bioaccumulators of trace metal [12-17]. The application of moss biomonitoring is an important tool of the research into the evaluation of the fallout of trace metal in European countries since 1987 [18-26].

Bryophyte mosses have not roots system, and take up nutrients and heavy metals from atmosphere. It is the reason that made them a suitable tool for spatial and temporal of atmosphere monitoring [17]. The moss survey is valuable for the identification of the sources of airborne pollution and identifies the regional differences and time trends in trace metal deposition [24]. Mineral particles, mainly from windblown dust, particularly from local soil in sparse vegetation and high erosion areas, can be absorbed by moss.

From the previous publications, it was identified that fine particulate matters present in air and caused from windblown soil dust were the main pollution source of trace elements in fallout of the moss samples of Albania [27-29]. The objective of the present study was to investigate the spatial distribution of the typical elements connected with dust (airborne) particles in atmospheric deposition, such as lanthanides, Zr, Hf, Ta, U, Th and Fe. This study provides to provide a reliable assessment of air quality throughout Albania. It should be available to produce information needed for better identification of the contamination sources and to improve the potential for assessing the environmental and health risks in Albania. The atmospheric deposition of Sc, lanthanides, U, Th, Zr, Hf, Ta and Fe in the whole territory of Albania by using moss biomonitoring and NAA analysis.

For the first time the moss biomonitoring technique was used to assess the environment pollution from lanthanides and actinides in the territory of Albania. Neutron Activation Analysis (NAA) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples from almost every conceivable field of scientific or technical interest [30]. In general, NAA is the most suitable technique for materials, which are difficult to convert into a solution for analysis [30]. INAA needs to be associated to other analytical techniques such as atomic absorption spectroscopy (AAS) that determine environmentally important elements that may not be analyzed by activation (a typical example: Pb) and/or are not easily analyzed because of a reduced sensitivity (such as Cd, and Ni, Cu and Hg) [31-33].

Methods and Materials

Study Area

The Republic of Albania (aprox. 28,000 km^2) is located in the south-eastern part of Europe and in the western part of the Balkan Peninsula. The first study of atmospheric deposition in Albania was performed under the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops (UNECE ICP Vegetation) by using moss biomonitoring and ICP/AES analysis for 20 elements.

The bryophyte family moss, *Hypnum cupressiforme* species were used in this study. Moss sampling was done according to the guidelines set out in the experimental protocol of the 2010/11 survey [34]. The criteria regarding the sampling points were respected during sampling campaign (3 to10 m away from the nearest projected tree; at least 300 m from main roads, villages and industries and at least 100 m away from smaller roads and houses). The samples were collected within an area of about 50 m x 50 m. About a liter of fresh moss composite samples was prepared for each sampling point, consisting of five sub-samples of only one moss species. The moss samples were collected from the ground (soil) or on the surface of decaying stumps. The smoking was forbidden during the sampling. The disposable

plastic and non-talcum gloves were used during the sampling and sample pretreatment for analysis. The green or greenish-brown parts representing 3–5 years of growth of the plant were used for further analysis without washing or other treatments. The coarse contamination of moss samples like litter, soil or animals were carefully removed. The samples were placed side by side in large paper bags, tightly closed to prevent contamination during the transportation.

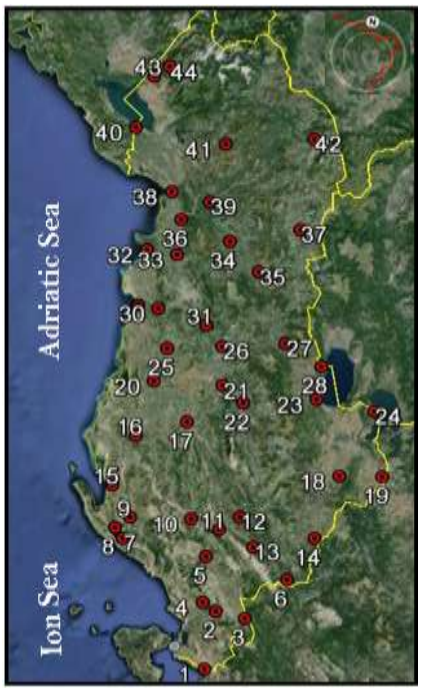

Figure 1 The map of sampling sites of the Albania (Centred at the Latitude: 41º00´ North of the Equator, Longitude: 20º 00´East of Greenwich)

2.2. Analysis

Sample preparation

In the laboratory the unwashed samples were air-dried to constant weight at 40˚C for 48 h, and extraneous plant material was removed.

Samples were sorted so that only the green living part of the moss, approximately corresponding to a three-year growth, was subjected to analysis. For neutron activation analysis samples were pelleted using simple presses.

Chemical analysis

The content of elements in the moss samples was determined by instrumental neutron activation analysis. The Neutron activation analysis was performed in the radioanalytical laboratory at the pulsed fast reactor IBR-2 at the Frank Laboratory of Neutron Physics (FLNP), JINR, Dubna, Russia.

Characteristics of neutron flux density in the two irradiation channels equipped with the pneumatic system and registration of gamma spectra can be found elsewhere [35]. The gamma-spectra of the induced activity were analysed using software developed in the FLNP, JINR. To determine elements in question samples with masses of around 0.3 g were packed in aluminum cups for long time irradiation. For these isotopes: Na, Sc, Cr, Fe, Co, Ni, Zn, As,

Se, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Hf, Ta, W, Th, and U, cadmium screened irradiation channel 1 with neutron flux density Φepi = 10^{12} n/(cm2 × s) was used. Samples were irradiated for about 100 hours than containers are cooled during 4 days than repacked and measured, using high purity germanium detectors, twice, the first time direct after repacked and the second time after 20 days the end of irradiation. Measurement time was 0.5 and 1.5 h, respectively. Element contents were determined on the basis of certified reference materials and flux comparators [35].

Quality Control

However, recently no reference sample of moss was commonly available. The accuracy of the analysis of mosses has been routinely checked using various references samples with similar nature available from suppliers such as National Institute of Standards And Technology and International Atomic Energy Agency [33].

Three certified reference materials were used to conduct quality control: SRM 2710 Montana Soil, NIST (National Institute of Standards and Technology), SRM-1632b (Trance elements in Coal) from the US , NIST, and Estuarine Sediment (BCR-667) from Sigma Aldrich in Belgium, in Institute for Reference Materials and Measurements (IRMM).The reference materials were packed together with the samples.

Data processing and statistical analyses

The concentration data onto selected elements (Sc, lanthanides, U, Th, Zr, Hf, Ta and Fe) in moss samples from 44 sampling sites was entered into a data matrix, and the descriptive statistics were used to interpret the results and to explain the data variations. The results of the descriptive statistics analysis of the elemental concentrations determined in the Albanian moss samples (min, max and median, see Table 1) were compared with those of others Balkan countries and Northern Norway (Table 2). The Pearson product-moment correlation coefficient is used to determine the significance of the relationship or association of two variables that may indicate that the variables do indeed affect each other, but it does not indicate what relationship it is.

Results and Discussion

The concentration data of Sc, lanthanides, U, Th, Zr, Hf, Ta and Fe were entered in a data matrix and was statistically treated by using Descriptive statistics. The statistical parameters of lanthanides and actinides in moss samples are shown in Table 1.

The order of the elements according to their abundance is Fe > Zr > Ce > La > Nd > Sc > Th > Dy > Sm > Hf > Gd > Yb > U > Eu > Ta > Tb > Tm. Most of elements under investigation show moderate variation (25< CV%< 75) and follow the lognormal distribution (P>0.05) that is typical for mineral particles [36,37] mainly windblown soil dusts [14], once this is confirmed also from values of skewness and kurtosis that are not very higher.

CV value is the highest for Gd (93%), followed by Eu (91%) and Tm (86%); and do not follow the lognormal distribution (P<0.05). Gd, Eu and Tm are characterized by high values of skewness and kurtosis; probably indicating that their distribution is influenced by complicated factors [38].

The concentration level of Sc, lanthanides, U, Th, Zr, Hf, Ta and Fe in moss samples of Albania were comparable with those of neighboring countries [39-42], but higher than the Norway [43] that is considered as a pristine area.

It should be pointed out that the Albanian data refers to 2010/2011 sampling period and the data from the other Balkan countries belong to 2000/2001 moss survey. The

concentrations of most elements in the soils tend to vary with time, while the rare earth elements are known to be stable in their geo-chemical environments [44].

Correlation of the elements

The correlation analysis was carried out to distinguish the elements of similar behaviour in the atmosphere before falling down by dry and/or wet deposition and the similar anthropogenic sources of the origin. The results of the correlation analysis are shown in Table 3.

Significant correlations were found between the concentration data of the elements onto moss samples. Among the 136 correlations, 68 are significant and strongly positive correlated ($R^2 \geq 0.7$, $p < 0.005$) and 46 are significant and moderate positive correlated ($0.4 \leq R^2 \leq 0.7$, $p < 0.005$) (Table 3). Only Eu does not correlate ($R^2 \leq 0.3$, $p > 0.05$) with the elements under investigation.

Conclusion

Moss biomonitoring and NAA analysis combined with statistical analysis are strong tools for multielement assessment in atmospheric deposition. The total distribution of lanthanides was found in moss samples. The concentration of the light lanthanides is higher than the concentration of heavy lanthanides showing that their origin is from natural sources associated with mineral particles and windblown soil dusts. Eu does not correlate ($R^2 \leq 0.3$, $p > 0.05$) with the elements under investigation while Gd, Dy and Tm appear moderate positive correlation ($0.4 \leq R^2 \leq 0.7$, $p < 0.005$). It is probably indicating that the distribution of these elements is affected by different factors (natural and anthropogenic factors) or the concentration data of these elements are affected from the sensitivity of the analytical method. The concentration of Gd, Eu, Dy, Tm in moss sample are compatible with the detection limit of the method and the standard deviation of reference materials during the determination of these element is up to 30%.

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Table 1 Descriptive statistics of the Sc, lanthanides, U, Th, Zr, Hf, Ta and Fe concentration data in moss samples (n= 44)

Parameters	Sc	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Tm	Yb	Zr	Hf	Ta	Th	U	Fe
Mean	0.923	2.151	4.096	2.154	0.322	0.102	0.247	0.050	0.427	0.045	0.179	8.527	0.249	0.058	0.524	0.166	2595
Standard Error	0.097	0.169	0.340	0.228	0.028	0.014	0.035	0.004	0.036	0.006	0.017	0.726	0.021	0.005	0.042	0.016	251
Median	0.717	1.855	3.585	1.630	0.269	0.079	0.155	0.044	0.354	0.032	0.140	7.290	0.207	0.048	0.460	0.134	1950
Standard Deviation	0.640	1.122	2.257	1.514	0.187	0.093	0.231	0.028	0.237	0.038	0.111	4.816	0.139	0.031	0.276	0.103	1666
Sample Variance	0.410	1.259	5.094	2.292	0.035	0.009	0.053	0.001	0.056	0.001	0.012	23.192	0.019	0.001	0.076	0.011	2776852
CV%	69	52	55	70	58	**91**	**93**	56	55	**86**	62	56	56	54	53	62	64
Kurtosis	3.742	0.268	0.493	0.717	1.383	18.251	4.617	0.453	1.763	8.354	2.035	1.961	0.717	0.511	0.191	2.370	2.79
Skewness	1.900	0.930	1.005	1.267	1.282	3.713	1.995	1.047	1.444	2.512	1.453	1.259	1.021	1.034	0.906	1.508	1.66
Range	2.897	4.327	9.035	6.012	0.855	0.573	1.104	0.108	1.044	0.204	0.500	22.620	0.600	0.126	1.078	0.441	7381
Minimum	0.193	0.623	0.845	0.488	0.034	0.022	0.026	0.014	0.156	0.009	0.045	2.480	0.070	0.013	0.132	0.045	539
Maximum	3.090	4.950	9.880	6.500	0.889	0.595	1.130	0.122	1.200	0.213	0.545	25.100	0.670	0.139	1.210	0.486	7920
Count	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44
Confidence Level (95%)	0.195	0.341	0.686	0.460	0.057	0.028	0.070	0.009	0.072	0.012	0.034	1.464	0.042	0.009	0.084	0.031	507

Table 2 The comparison of concentration data of Sc, lanthanides, U, Th, Zr, Hf, Ta and Fe [mg/kg] with neighboring countries and Norway

	Albania [Present work]		**Bulgaria [39]**		**Macedonia [40]**		**Romania [41]**		**Northern Serbia [42]**		**Northern Norway [43]**	
Samples	**44**		**99**		**73**		**70**		**92**		**100**	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Sc	0.717	0.193÷3.090	0.92	0.21÷7.20	0.81	0.12÷6.79	0.94	0.21÷6.13	1.31	0.27÷4.13	0.052	0.009÷0.220
Fe	1950	539÷7920	3000	689÷19400	2460	424÷17380	3290	815÷21340	3110	720÷9230	209	77÷1370
La	1.86	0.62÷6.49	3.3	1÷61.79	2.32	0.50÷22	2.4	0.4÷15.2	4.66	41518	0.189	0.045÷2.56
Ce	3.59	0.85÷10.6	6.8	1.75÷143	5.6	0.83÷42	6.1	0.9÷42.5	9.2	1.84÷28	0.342	0.095÷4.61
Nd	1.63	0.56÷5.75	3.15	0.01÷47	–	–	–	–	–	–	–	–
Sm	0.28	0.08÷0.89	0.6	0.19÷8.30	–	–	–	–	–	–	–	–
Tb	0.044	0.014÷0.172	0.076	0.02÷0.98	0.06	0.01÷0.56	0.07	0.01÷0.42	0.11	0.02÷0.36	0.003	0.002÷0.030
Dy	0.354	0.156÷1.2	0.43	0.01÷4.40	–	–	–	–	–	–	–	–
Tm	0.031	0.011÷0.238	0.057	0.02÷0.67	–	–	–	–	–	–	–	–
Yb	0.14	0.054÷0.545	0.22	0.05÷3.32	–	–	–	–	–	–	–	–
Hf	0.21	0.07÷0.67	0.45	0.11÷12.1	0.26	0.05÷3.8	0.56	0.12÷4.66	0.78	0.15÷2.6	–	–
Ta	0.05	0.01÷0.14	0.127	0.03÷1.52	0.09	0.013÷0.79	0.1	0.01÷0.66	0.11	0.024÷0.29	–	–
Th	0.47	0.14÷1.33	0.86	0.27÷23	0.67	0.12÷7.6	0.81	0.21÷4.16	0.82	0.18÷2.4	0.033	0.004÷0.24
U	0.14	0.05÷0.49	0.3	0.09÷6.28	0.21	0.03÷1.45	0.28	0.04÷1.36	0.32	0.08÷1.03	0.015	0.001÷0.138
Eu	0.079	0.022÷0.59										
Gd	0.155	0.026÷1.13										
Zr	7.29	2.48÷25.10										

Table 3 The correlation between the elements

	Sc	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Tm	Yb	Zr	Hf	Ta	Th	U
La	0.84															
Ce	0.84	0.97														
Nd	0.71	0.69	0.66													
Sm	0.82	0.90	0.85	0.63												
Eu	0.27	0.28	0.31	0.25	*0.31*											
Gd	0.51	0.58	0.60	*0.36*	0.50	0.14										
Tb	0.92	0.97	0.96	0.72	0.90	0.29	0.57									
Dy	0.69	0.53	0.54	0.43	0.58	0.06	0.24	0.63								
Tm	0.69	0.53	0.53	0.67	0.50	0.17	0.60	0.60	0.44							
Yb	0.88	0.83	0.84	0.73	0.75	0.21	0.48	0.86	0.55	0.64						
Zr	0.73	0.82	0.83	0.44	0.78	*0.31*	0.46	0.82	0.42	0.39	0.71					
Hf	0.77	0.90	0.91	0.54	0.82	0.24	0.58	0.89	0.48	0.48	0.78	0.94				
Ta	0.89	0.97	0.95	0.70	0.89	0.28	0.59	0.97	0.54	0.59	0.86	0.84	0.91			
Th	0.84	0.97	0.95	0.61	0.88	0.24	0.59	0.95	0.51	0.46	0.83	0.84	0.91	0.97		
U	0.79	0.86	0.88	0.48	0.82	0.24	0.51	0.86	0.44	0.37	0.74	0.82	0.85	0.85	0.86	
Fe	0.98	0.80	0.82	0.68	0.80	0.25	0.47	0.89	0.67	0.65	0.84	0.73	0.74	0.87	0.81	0.78

Cell contents: Pearson correlation, P-Value: [1] < 0.05

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