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Origin and spatial distribution of metals in moss samples in Albania: a hotspot of heavy metal contamination in Europe.

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Highlights:

- The origin of trace metals in moss samples is assessed through different methods.
- Mosses are able to reflect the spatial variability of trace elements air pollution.
- Mineral dust particles is the main source of trace elements in present moss samples.
- Geochemical interpretation of current moss data show high local dust emission.
- EF is used to distinguish contributions from atmospheric deposition or substrate soil.

Abbreviations:

AAS – Atomic absorption spectroscopy

C_i – Concentration of element i

CVAAS - cold vapor atomic absorption spectrometry

EF – Enrichment Factor

ENAA – epithermal neutron activation analysis

ETAAS - electrothermal atomic absorption spectrometry

FA – Factor analysis

GIS - Geographic Information System

HM – heavy metal

ICP-AES - inductively coupled plasma atomic emission spectrometry

INAA – Instrumental neutron activation analysis

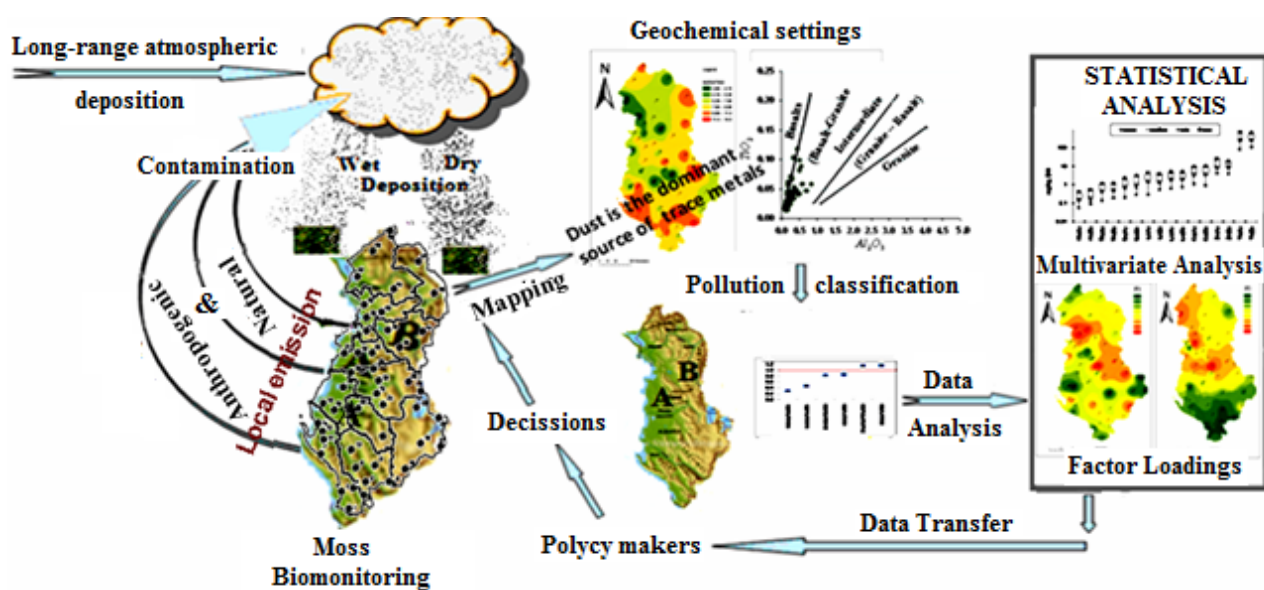
L_i - individual loads of element i

NAA - neutron activation analysis

PM – Particulate matter

RLE – Ratios of lithophile elements

Graphical Abstract



Origin and spatial distribution of metals in moss samples in Albania: A hotspot of heavy metal contamination in Europe

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Abstract

This study presents the spatial distribution of 37 elements in 48 moss samples collected over the whole territory of Albania and provides information on sources and factors controlling the concentrations of elements in the moss. High variations of trace metals indicate that the concentrations of elements are affected by different factors. Relations between the elements in moss, geochemical interpretation of the data, and secondary effects such as redox conditions generated from local soil and/or long distance atmospheric transport of the pollutants are discussed. Zr normalized data, and the ratios of different elements are calculated to assess the origin of elements present in the current moss samples with respect to different geogenic and anthropogenic inputs. Factor analysis (FA) is used to identify the most probable sources of the elements. Four dominant factors are identified, *i.e.* natural contamination;

dust emission from local mining operations; atmospheric transport of contaminants from local and long distance sources; and contributions from air borne marine salts.

Mineral particle dust from local emission sources is classified as the most important factor affecting the atmospheric deposition of elements accumulated in the current moss samples. The open slag dumps of mining operation in Albania is probably the main factor contributing to high contents of Cr, Ni, Fe, Ti and Al in the moss. Enrichment factors (EF) were calculated to clarify whether the elements in the present moss samples mainly originate from atmospheric deposition and/or local substrate materials.

Keywords: Atmospheric deposition, Moss biomonitoring, Trace metals, Geochemical interpretation, Anthropogenic sources.

1. Introduction

Air pollution is a global problem and has negative effects on human, animal and plant health (Kanawade et al., 2010). Pollutants emitted into the atmosphere are deposited at the Earth's surface where they accumulate in soil, sediment, and biota of terrestrial and aquatic ecosystems (Schröder et al., 2016). In general, the main emission sources of trace metals in the air are ore and metal processing, and manufacturing, as well as combustion processes (Duffus, 2002). There is increasing interest in the atmospheric transport of mineral dust that is believed to play an important role in several marine biogeochemical processes (Prospero et al., 2002), geochemical and geophysical processes, and in negative effects on human health (Prospero, 1999).

Soil dust is a major constituent of airborne particles transported over long distances in the global atmosphere (Prospero, 1999). In general, mineral dust particles may be emitted during mobilization and fragmentation of original un-dispersed soil subject to wind erosion (Perlwitz et al., 2015). Windblown dust and aerosol mineral composition depends upon the composition of the parent soil and its size fractionation during mobilization, and in principle, the elements observed in moss samples may therefore originate from geological, biological, and anthropogenic sources.

To improve the understanding and monitoring the effects of air pollutants on ecosystems and to scientifically assess the effectiveness of air pollution control strategies, ecological indicators are needed. Since the 1970s, Scandinavian countries have used mosses as biomonitors of trace metal atmospheric deposition, and since the 1990s, mosses are

generally used in Europe as a complementary monitoring tool for atmospheric deposition of trace metals. The use of native terrestrial mosses as biomonitors is now a well-recognized technique in studies of atmospheric deposition (Steinnes et al., 1997a; 1997b; 2011; Fernandez and Carballeira, 2002; Harmens et al., 2010a; 2011; 2013, 2015). It is a convenient and cheap way of determining the spatial and temporal trends of trace elements in atmospheric deposition (Steinnes et al., 1997a; 1997b; 2011; Harmens et al., 2015). The specific features of bryophytes such as a weakly developed cuticle (taking nutrients and water directly from the atmospheric deposition, large surface to mass ratio, and their habit of growing in groups) are strong reasons for making them suitable indicators of heavy metal atmospheric deposition (Steinnes et al., 1997a; 1997b; 2011; Markert et al., 1999; Onianwa, 2001; Schröder et al., 2010). In contrast to measurements with technical deposition samplers, moss surveys allow covering a broad range of spatial scales with the same method at a high spatial density after selecting the proper moss species as biomonitors (Schröder et al., 2016).

Albania is a small country (28000 km²) positioned in western Balkan in the south-east of Europe. It is characterized by a complex geographic relief and climate, high diversity of geologic setting, and is influenced by different contamination inputs. Activities in ex-industrial sites of copper, chromium, iron-nickel and oil industries have produced several million tons of industrial waste impacting the surrounding environment and has adversely effected natural resources, followed by a potential health risk for people who are continuously exposed to this pollution (UNDP–Albania, 2010). The lack of a national network on air quality monitoring as well as data on morbidity caused by air pollution, makes the assessment of the health impact of air pollution in Albania impossible (UNDP–Albania, 2010).

Moss biomonitoring in Albania started in 2010/2011 when researchers from Albania joined the European Moss Survey conducted within the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops, ICP Vegetation (Harmens et al., 2013). Heavy metal concentrations (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V) in 2010/2011 moss samples of Albania have been reported in several publications (Qarri et al., 2013; 2014a; 2014b; Bektashi et al., 2015; Allajbeu et al., 2016a; 2016b). The present paper reports on concentrations of 37 elements, their spatial distributions in 2010/2011 moss samples, and possible contributions from different sources and processes.

The European moss survey has demonstrated that the median of heavy metal concentrations in mosses between 1990 and 2010 have declined between 21 % and 77 % for As, V, Cd, Cr, Zn, Ni, Fe, and Pb, whilst some “hotspots” remained in 2010, particularly in Eastern Europe and Balkan countries (Harmens et al., 2015). The lowest

concentrations of heavy metals were generally found in northern Europe and the highest levels in eastern and south-eastern Europe, resulting in a north-west to south-east gradient for many metals in 2010 (Harmens et al., 2015). For Al, Fe, V and Cr, the highest median concentrations in mosses were generally found in Romania, Macedonia, Albania, Ukraine, and Bulgaria. Reported Ni concentrations were generally high in parts of south-eastern European countries and Iceland. The highest levels of Hg were observed in Albania and Macedonia, followed by Italy (Bolzano region), Poland, and France.

The main objective of this work is to identify factors leading to the high levels of some trace metals (Cr, Ni, V, Fe, Al) in 2010/2011 moss samples of Albania and to extend the study to their associations and relationships with other elements. The concentration data for 37 elements in moss samples are used to evaluate the possible relationships between elements, their most important sources of origin, geochemical interpretation of the data, and secondary effects yielding differences in their contents and distribution patterns. Differences in redox conditions of the area from where the dust originate, may generate differences in the properties of mineral dust particles that may help to distinguish their origin from local and/or long-distance migration of the contaminants.

2. Materials and methods

2.1. Geology and main ore mineralization of Albania

The morphology of Albanian soils is strongly related to geology of the area. About 75 % of Albanian territory is built by hilly and mountain morphological units, located in the northern, eastern and southern parts of the country. The relief is cut from east to west by seven river valleys. The traverse valleys make up the connection between coastal lowland and eastern highland areas.

Different geological formations in Albania have conditioned different distributions of mineralization and ore deposits. The Internal tectonic zones (in the east) contain primarily metallogenic mineral deposits. Ophiolite (iron sulfide mineral) formations are widespread. They are extended as a belt from the north to the south-east of Albania, and are distinguished by a high potential of Cr, Ni, Fe and Cu minerals. The next zone, the External tectonic zone, positioned within the coastal area between the Adriatic and the Ionian Sea (in the west) contain fossil fuels deposits. Rocks of carbonate composition are found in the south-western, central, and northern parts of Albania.

2.2. Sampling procedure

Carpet forming moss species *Hypnum cupressiforme* (Hedw) and *Pseudoscleropodium purum* (Hedw.) M. Fleisch (the latter only at two sampling sites) were collected in 2010/2011 from 48 sampling sites evenly distributed over Albania. A systematic sampling scheme was used (Qarri et al., 2014b). The moss sampling procedure and the preparation of the material for elemental analysis was done according to the guidelines described in the protocol for the 2010 European moss survey (Harmens et al., 2010b). Each sampling site was situated at least 300 m far from main roads, 100 m from local roads, and 200 m from villages or single houses. Most sites were located at small forest clearings to reduce any through-fall effects. Composite samples of ten sub-samples collected within an area of 50 m × 50 m were used for analysis (Harmens et al., 2010b). Disposable polyethylene gloves were used during the sampling and sample preparation to prevent potential contamination. Based on different mineralogical settings in the western and eastern parts, Albania was divided into two different zones (zone A and B) (see Fig. 1b) and moss samples are grouped and discussed based on their geographical positions shown in Fig. 1a.

a. b.

Fig. 1. Localization of sampling sites (a) and sketch map of zone A (Internal tectonic zone) and zone B (External tectonic zones) (b)

2.3. Chemical analysis

Microwave digestion (MARS, CEM, USA) was applied for total digestion of moss samples according to the method presented by Barandovski et al. (2008). All the reagents used in this study were of analytical grade: nitric acid, trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and bi-distilled water. Sixteen elements (Cu, Fe, Ni, Pb, V, Zn, Mn, Al, Li, Mg, P, K, Na, Ca, Sr and Ba) were determined in the moss samples by atomic emission spectrometry by inductively coupled plasma, ICP-AES (Varian 715-ES, ICP optical emission). As and Cd were determined by electrothermal atomic absorption spectrometry (ETAAS) (Varian, SpectrAA 640Z). Hg was determined using cold vapor atomic absorption spectrometry (CVAAS) (Varian 10+) and home made cold vapor equipment (Lazo and Cullaj, 2002; Lazo and Kucuku, 2012).

Wet digestion of homogeneous sub-sample (0.5 g sample and 10 ml nitric acid 9:1 v/v in half pressure Teflon tubes) was applied for Hg determination. The tightly closed tubes were left at room temperature for 48 hours, and then heated for 3 hours at 80-90 °C to convert all forms of Hg present in moss sample to divalent inorganic mercury, Hg^{2+}

(Lazo and Cullaj, 2002; Lazo and Kucuku, 2012). The complete digestion was performed at 200° C for 30 min. Then the tubes were opened and the acid was evaporated to a small volume. After cooling, the samples were transferred to 25 ml volumetric flasks subsequently filled to the mark with Osmosis treated water (Elga, PURELAB Option equipment). Three replicates per moss sample were digested and three replicate measurements per digest were done during ICP-AES analysis (Qarri et al., 2013). The ICP-AES and AAS analyses were done at the Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia, CVAAS analysis was done at the Department of Chemistry, Faculty of Natural Sciences, University of Tirana.

The elements Co, Cr, Ti, Se, Sb, Zr, Hf, Ta, Mo, W, Sc, La, Ce, Yb, Th, U, Rb, and Cs were determined by epithermal neutron activation analysis (ENAA) at the IBR-2 pulsed fast reactor FLNP JINR Dubna, Russia (Frontasyeva, 2011). Samples for ENAA, about 0.3 g, were pelletized in simple press forms and heat sealed in polyethylene foil for analysis based on short-lived radionuclides, while for elements with more long-lived radionuclides the samples were packed in aluminum cups. For short-lived radionuclides (only Ti in the current work) the samples were irradiated for 3 minutes in the second channel (Ch2) of the reactor, and to determine elements associated with long-lived radionuclides the samples were irradiated for 100 hours in the cadmium screened channel Ch1. After irradiation, gamma-ray spectra were recorded twice for each irradiation using a high-purity Ge detector (Frontasyeva and Pavlov, 2002).

The optimal operating instrumental parameters for each method are given in previous papers (Frontasyeva, 2011; Qarri et al., 2013; Maxhuni et al., 2015; Allajbeu et al., 2016a). The detection limits, calculated as 3 SD of the lowest instrumental measurements of the blanks (ICP-AES) and the lowest instrumental measurements of the signal (ENAA), are given in previous publications (Qarri et al., 2013; Allajbeu et al., 2016a). The quantification limits of the elements calculated from the GEINE 2000 software for the concentrations range of each element in the current moss samples are shown in Table 1.

Table 1 Limits of quantification (LOQ) of the elements (mg kg⁻¹)

2.4. Quality control

The quality of ICP-AES results was checked by multiple analyses of the examined samples and by simultaneous analysis of the international moss reference materials M2 and M3 (Steinnes et al., 1997a). The determined values for M2 and M3 were in good agreement with the recommended values and are reported in an earlier publication (Qarri et al., 2013). In addition, blank values were measured in parallel to the decomposition and the analysis of the samples. Quality control of the CVAAS results was ensured by multiple analysis of the IAEA-140/TM reference sample (Fucus homogenate). The mean content of Hg (0.036 ± 0.012 mg kg⁻¹, DW) is in good agreement with the certified value, 0.038 mg kg⁻¹, DW).

The quality control of ENAA results was performed by simultaneous analysis of the reference materials SRM- 2710 (Montana Soil, NIST- National Institute of Standards and Technology), 1632b (Trace elements in Coal, US, NIST), BCR-667 (Estuarine Sediment, IRMM Institute for Reference Materials and Measurements), SRM-1633b (Constituent elements in coal fly ash, US NIST-National Institute of Standards and Technology). Because nuclear reactions and decay processes are virtually unaffected by the chemical and physical structure of the material during and after irradiation, the composition of the matrix has little influence on the induced activity, and the major advantages of NAA, particularly INAA, are the relative freedom from matrix effects and interferences, high accuracy, and very low or zero blank contributions. The absence of matrix effects thus allows the use of standards that have different composition (and even physical state) from that of the sample (Frontasyeva, 2011; Filby, 1995).

The reference materials and 10–12 moss samples were packed together in each transport container. The certified and experimental values (mean \pm standard deviation) for elements with known certified values (mg kg⁻¹) used for quality control of the analysis and for calculating the concentrations of the elements, are shown in Table 2. From the data in Table 2 it appears that the mean contents of the elements under investigation are in good agreement with the certified data.

Table 2 Certified and experimental values (mean \pm standard deviation) for elements with known certified values (mg kg⁻¹) used for quality control of the analysis and for calculating the concentrations of the elements

Note: The subscription of each element refer to the certified material used to calculate the concentration of the elements (¹ BCR-667; ² SRM 2710; ³ SRM 1632b; ⁴ SRM 1633b)

2.5. Data processing and statistical analyses

The contents of trace metals in moss samples were calculated on a dry matter basis. Statistical methods were applied to interpret data sets and to define any anomalies. As a first step, the frequency distribution of the data was examined through frequency plots of each element that can help identifying the type of distribution of the data and possible outliers.

The relationships between elements were tested using Spearman's correlation confirmed by the statistical significance levels at $P < 0.001$, $P < 0.005$ and $P < 0.01$. To assess the relationships between the elements content in moss and to determine potentially influencing environmental factors, factor analysis (FA) was applied as an extension of the correlation analysis to explore hidden multivariate structures in the data (Reimann et al., 2002) and to clarify links between elements that tend to have similar origins or to subsequently develop similar associations in the moss matrix. The most important factors are discussed in the following. The statistical analyses were conducted using the MINITAB 17 software package.

Considerable information may be acquired by plotting the geographic distribution of the elements applying Geographic Information System (GIS). GIS maps are plotted to explain the spatial distribution of $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio that reflect different metallogenic settings of local emission. Arc-GIS 10.2 was used in combination with local deterministic methods and the inverse distance weighting for mapping the spatial distribution of the factor loadings (FL_{site}) and for spatial interpolation. FL_{site} is calculated as percentile of the sum of the product of individual loads of each element and respective site concentration (Barandovski et al. 2008, Allajbeu et al. 2016b):

$$FL_{\text{site}} = \text{average}(100 \frac{\sum(C_i)_{\text{site}}}{\sum(C_i)_{\text{max}}} L_i)$$

where C_i is the concentration of the i^{th} element and L_i is the factor loading of the same element.

Enrichment factor (EF) is used to distinguish between the soil and/or airborne origin of trace elements in current moss. EF was calculated by using Al as a marker of soil substrate contamination of the moss samples (Frontasyeva and Pavlov, 2002; Sardans and Peñuelas, 2005).

$$EF = \frac{(C_x/C_{Al})_{moss}}{(C_x/C_{Al})_{soil}}$$

where C_x represents the concentration of an individual element in current moss and its substrate soil. EF values higher than 1 represent anthropogenic origin, and values higher than 3 represent remarkable airborne enrichment of the elements in moss samples (Sardans and Peñuelas, 2005).

3. Results and discussion

3.1 Frequency distribution

The frequency distribution of the data was examined through frequency plots of each element. Current data represent different statistical distributions indicating the data to be affected by different factors. Most of the elements (except Zn, Cd, Pb, Ce, Na, K, Rb) follow a lognormal distribution ($P > 0.05$) that is characteristic for the lithogenic origin of the crustal elements (Vinogradov, 1962) and may be related to atmospheric deposition of windblown mineral dust particles. Zn and K data are highly skewed right with high differentiation from background level, while Na is skewed left mostly at background level.

3.2. Geochemical origin of elements in moss samples of Albania

Distribution patterns of trace elements using lichen and/or moss analysis may represent either bulk precipitation or local lithology (Aubert et al., 2006; Agnan et al., 2013; Allajbeu et al., 2016a). For a better interpretation of geochemical classification and to show the origin of elements present in current moss samples with respect to different types of rocks of local area, the Spearman correlation coefficient, the distribution of the elements and Zr normalized elements, and the ratios of the redox sensitive elements (Chiarenzelli et al., 2001) were used.

3.2.1 Major elements (Al, Ca, Fe, K, Mg)

The results of descriptive statistic analysis of elemental concentrations in moss samples of each zone are shown in the Box-plot diagram of statistical parameters (Fig. 2).

Fig. 2. Box-plot diagram of statistical parameters of the concentrations of major elements in mosses samples of zone A and zone B.

The order of the median concentrations of the elements in moss samples of zone A were $Al \approx Fe < Mg < K < Ca$, and of zone B were $Al < Fe < K < Mg < Ca$. Differences between concentrations of major elements of both zones probably have been influenced by the differences in lithology and grain size differences in the parent dust of emission sources (Hofer et al., 2013; Armstrong-Altrin et al., 2016). High Ca content is found in current moss, higher than the content of crustal elements such as Al, Fe, Mg, K and Ti, which may indicate the presence of calcium carbonate fractions in the area.

The range of the variation of Al content in moss samples is moderate ($< 75\%$). Al is mostly associated with feldspar and clay minerals (Dinelli et al., 2005). Grain-size variation in sedimentary setting is the most common cause of Al variations, with high Al content in clays and low Al content in silicate sands (Huisman et al., 2000). Any mineral particles present in atmospheric deposition are related to fine PM particles in the atmosphere. For this reason, the role of grain-size variations is not a determinant factor of Al variation in atmospheric deposition. This variation is probably affected by the differences in sedimentary settings of the area from where the PMs originate. The uniformity in dust composition reflects the fact that the mobilized fraction of the soil is a highly-weathered product that has been derived from number of sources in the region.

To interpret the geochemical origin of major elements, Al vs. Ti plots is used as provenance indicator for sedimentary terrains (McLennan et al., 1979) that distinguish the sources of three rock categories: basalt, intermediate and granite provenances. Al vs. Ti bivariate plots of the current moss predominantly belongs to *basalt and less to basalt - granite (felsic) intermediate* source (Fig. 3). Fine-grained soils, particularly clay, have higher Ti contents than coarse material, and the Ti contents will be positively correlated with Al (Huisman et al., 2000). High correlation between Al and Ti were found in current moss samples ($r^2 = 0.630$, $p = 0.000$) indicating the presence of *clay minerals (montmorillonite and illite)* in the area under investigation. The Al/Ti ratios range from 2.65 to 9.71 for mafic rocks, 9.71 to 18.54 for intermediate rocks and 18.54 to 61.8 for felsic rocks (Hayashi et al., 1997). The Al/Ti ratios of the current moss range from 2.7 to 12.8, with a median value of 6.6 (mean 6.7) indicating that the origin of these elements is mostly from mafic magnetite rocks and less from intermediate (mafic magnetite – felsic) rocks. These findings are clearly indicating the origin of these elements from local mineral dust particles associated

with different geochemical origin. The origin of these elements from different bedrock formations is in the same line with the Albanian geological settings (Hoeck et al., 2005; Xiong et al., 2015; Bortolotti et al., 2015).

Fig. 3. Al vs. Ti bivariate plots (Sari and Koca, 2012)

K and Ca contents in moss samples are higher in zone A than zone B, indicating the alkaline origin of sand fractions of zone A. It is supported from carbonate setting of most part of zone A (NAMR, 2010). The K/Al ratios of clay minerals range from 0 to 0.47; from 0.47 to 1.41 for feldspar rocks (Cox et al., 1995), and > 15.7 for per-alkali rocks. K/Al ratio of current moss vary from 0.53 to 15.12 (the median value is 2.2 and the mean value is 2.9). Two outlier points were found at zone A with K/Al values of 10.5 and 16.2 indicating that the origin of K in current moss is mainly from the feldspar and K-feldspar sources (Armstrong-Altrin et al., 2016). It suggest that the minerals responsible for the increased of K/Al ratios should be present in silt and/or sand fractions (Huisman et al., 2000). On other hand, K is an essential nutrient for plant growth and is classified as a macronutrient due to large quantities of K being taken up by plants during their life cycle. For this reason, the K/Al ratio could not be the best significant parameter indicating their source in moss. The Al/Ti and K/Al distribution patterns in current moss samples are shown in GIS maps of Fig. 4.

a. b.

Fig. 4. Al/Ti (a) and K/Al (b) distribution patterns

3.2.2. Trace elements

Trace elements (As, Ba, Cd, Ce, Co, Cr, Cs, Cu, Hf, Hg, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Se, Sr, Ta, Th, Ti, U, V, W, Yb, Zn and Zr) are important prevalence tools for rock derived origin of elements in soil and dust samples. The results of descriptive statistic analysis of concentration data of the elements in the moss samples of each zone are shown in the Box-plot diagram of statistical parameters (Fig. 5).

a.b. c.

Fig. 5. Box-plot diagram of statistical parameters of concentration data for trace elements present in current moss samples: *a. Litophile elements; b. Biophile elements; c. Calcophile elements*

For better interpretation, the elements are separated and discussed on the basis of their geochemical classification as given by Goldschmidt (1937).

3.2.2.1. *Lithophile elements (Ce, La, Li, Sc, Th, Ti, Yb, Zr)*

The concentrations of lithophile trace elements in moss samples of both zones follow the same order of median concentrations, i.e. $Yb < Th < Sc < Li < La < Ce < Zr < Ti$, which is the same as their order of concentrations in the upper continental crust (UCC) (Rudnick and Gao, 2004) thus indicating their natural origin. The range of the variation of Sc, La, Ce and Yb in moss samples of zone B are lower than zone A, while their respective median values of zone B are higher than in zone A (Fig. 5), indicating the presence of different geochemical abundances. La, Ce and Yb are mainly concentrated in carbonatite and felsic rocks (Nagarajan et al., 2007), and Sc can occur in higher concentrations, generally in alkaline rocks, where it can form separate Sc minerals (Iain and Chassè, 2016).

The median concentrations of Ti, Zr, La, Ce, Th and Sc are generally found higher in moss samples from zone B compared to zone A. Since these findings are probably demonstrating the differences in mineralogy settings between zones A and B, the localized mineralogical composition of both zones may cause the differences to the spatial distribution of these elements in current moss samples. Possible differences in the relative abundance of lithophile elements were investigated by calculating Th/Sc, Ti/Sc and Zr/Sc ratios that reflect their geochemical normalized data of the elements after Sc normalization process (Fig. 6). Sc has been widely used as a conservative, lithophile reference element in studies of atmospheric aerosols to define the crustal aerosol (Shotyk et al., 2016). From Sc normalized data, it is shown that Zr/Sc and Ti/Sc ratios do not differ significantly between the zones and from UCC values given by different authors. This may reflect the lithogenic origin of Zr and Ti, and the variations in each zone may reflect the origin of different mineralogical settings. The Th/Sc ratio is smaller than the corresponding UCC value. High values of Th/Sc in zone A are affected by the lower level of Sc that is mainly enriched in zone B.

Fig. 6. Box-plot diagrams of statistical parameters of Th/Sc, Ti/Sc and Zr/Sc ratios (normalized data)

For better explaining of geochemical classification and origin of the elements present in moss samples, the ratios of lithophile elements (RLE) such as La/Sc, La/Co, Th/Sc, Th/Co, and Cr/Th were calculated (Table 3). Th/Sc, Th/Co

and La/Sc ratios in zone A (0.47-0.80, 0.15-0.62, and 1.78-3.86 respectively) are quite stable and close to corresponding UCC values (0.75, 0.61, and 2.21 respectively) by indicating the lithogenic origin of Th, La and Sc in moss samples of zone A. The RLEs values of zone B are higher than of zone A (except Pb/Sc) by indicating the derivation of these elements of zone B mostly from dense minerals source (Shotyk et al., 2016).

Table 3 The range of the ratios between different lithophile elements

3.2.2.2. Biophile micro elements (typical micro elements Cu, Mo, and V)

The order of distribution of median concentrations of biophile elements in moss samples of zones A and B were Mo<V<Cu. The concentration range of Mo and V in moss samples of zone A is higher than of zone B. This is probably due to V and Mo enrichment from oil, gas and coal minerals present in zone A, oil and gas industry, as well as shipping activity in coastal areas of the Adriatic and Ionian Seas. The median concentration of Cu in moss samples of zone B is higher than of zone A. This is probably due to the enrichment of Cu in zone B that is rich with sulfide mineralization (Lazo et al. 2007).

3.2.2.3. Chalcophile elements (typical elements As, Cd, Cu, Hg, Ni, Pb and Zn)

The order of the distribution of the median concentrations in moss samples of both zones were Cd<Hg<As<Pb<Cu<Zn<Ni. Zone B is characterized by various mineral deposits such as Cr, Cu, Ni and Fe minerals. Zone A is characterized by carbonate rocks and sediments of Adriatic and Ionian Seas (NAMR, 2010). The median values of most elements in Zone B were higher than in zone A (Fig. 5c), which is probably linked with long range atmospheric transport of pollutants from other parts of Europe (Harmens et al., 2015), fuel combustion, and most importantly with wind blown dust from industrial waste deposits and sulfide mineral dumps. The statistical data of Ni (mean, median, minimum and maximum values) differ significantly for both zones. The range of the variation of Ni of zone B (4.1 – 131 mg/kg, DW) is higher than the respective range of Ni in zone A (1.56 – 34.0 mg/kg, DW). Higher Ni concentration in moss samples of zone B compared to zone A is mainly due to Ni enrichment from Ni, Fe – Ni and Ni – silicate mineralization followed by ultrabasic settings present in zone B. To explain the variations on the concentrations of calcophile elements in moss samples of each zone, the Sc normalized values of the elements were investigated. Lower Pb/Sc ratio of zone A (1.32 – 23.58, median = 3.18) compared to

zone B (1.18 – 9.17, median = 4.3) support the anthropogenic origin of Pb in moss samples of zone B. Pb/Sc ratio of the mosses from zone A (average 5.21, median 3.18) is higher than respective ratio of Upper Continental Crust (2.4, Pb 17 mg/kg to Sc 7 mg/kg), and close to the value of soil average Pb/Sc ratio (= 5) (Bowen, 1979), indicating lithogenic origin of Pb in zone A. The maximum value of Pb/Sc ratios (23.6) is found in Station 43 (Zogaj) that is affected from the transboundary pollution from metals (Al and Fe) processing industry in Montenegro (Peck, 2004).

3.2.2.4. Elements sensitive to redox conditions (Cr, Co, Mo, U, V, Ni and Zn)

Aiming to distinguish the redox properties of regional conditions that affect the composition of mineral dust particles, the elements sensitive to redox condition, such as Ni and Zn, redox-sensitive trace elements, such as U, V, Mo, Co, Cr, and the ratios of elements such as Ti/V, V/Ni, V/Cr, V/(V+Ni), Cr/Ni, Cu/Zn, (Cu+Mo)/Zn were calculated (Table 4).

Table 4 Cr, Ni, Mo, V, U and Zn median ratios between zone A and zone B

Ni, Cr, U and Zn are mainly concentrated in zone B, indicating the presence of oxidizing conditions in this zone that is rich in Fe, Ni and Cr minerals. Mo content of zone A does not differ significantly from zone B ($\text{Mo(A)}/\text{Mo(B)} = 0.97 \pm 1$), indicating the presence of this element in both zones. V is concentrated mainly under reducing conditions (oil, gas, coal and carbonate areas), and/or affected by aerosols emissions from shipping activity or burning of fossil fuels (Viana et al., 2014), and that may explain the higher V concentration in zone A than in zone B. It is a typical carbonate area rich in oil, gas and coal minerals, and is under the effect of shipping emission by providing good conditions for V enrichment.

The order of the ratios of median values of Cr, Ni, Mo, V, U and Zn of zone A to zone B (in both zones), was $(\text{Ni(A)}/\text{Ni(B)} < \text{Cr(A)}/\text{Cr(B)} < \text{U(A)}/\text{U(B)} < \text{Zn(A)}/\text{Zn(B)} < 1 < (\text{Mo(A)}/\text{Mo(B)} \approx 1 < (\text{V(A)}/\text{V(B)} > 1)$ (Table 4). In general, MORB and continental flood basalts have Ti/V ratios of about 20-50 (Shervais 1982). The range of Ti/V ratios in current moss samples is 35-163 (Zone A) and 35-152 (Zone B) (Table 5). Most of the moss samples of zones A and B resulted with Ti/V ratios > 48, indicating the origin of mineral dust particles from alkaline rocks (Shervais 1982). Six moss samples of zone A (St. 11, 14, 19, 28, 46 and 48) and two moss samples of zone B resulted with Ti/V

ratios within the range of 35 – 48, indicating the origin of mineral dust particles from MORB and basalt provenance (Shervais 1982).

Table 5 Range of the ratios between elements sensitive to redox conditions

In general, zone A shows higher V/Ni, V/Cr, V/(V+Ni), Cu/Zn and (Cu+Mo)/V ratios compared to zone B, indicating the predominance of reducing conditions in zone A that are mainly derived from carbonates, black shists (Peltola, 1968), and organic matter (Galarraga et al., 2008) present in this zone. Zone B shows lower values these parameters by indicating it is characterized by strong oxidizing conditions (Nagarajan et al., 2007). In addition, the values of Zr-normalized redox-sensitive elements were investigated in both zones (see Table 6). Zone A had higher V/Zr, Mo/Zr, and lower Ni/Zr, Cr/Zr and Co/Zr ratios compared to zone B, indicating stronger reducing conditions in zone A and stronger oxidizing conditions in zone B.

Table 6 Zr-normalized values of different elements

The P/Ce ratio ranges from 55 - 5160 in zone A, which is significantly different from the P/Ce ratio (range 69 - 972) in zone B. The presence of higher P contents in moss samples of zone A compared to zone B, is linked with the presence of phosphorite minerals present in the south, which indicates some contribution of monazite regional mineral dust particles of zone A. Phosphorite deposits are located mainly in the carbonate rocks of the Ionian tectonic zone, in the Tepelena, Gjirokastra and Saranda regions of zone A (NAMR, 2010).

3.3. Multivariate analysis

Spearman correlation analysis of the concentration matrix data was carried out to distinguish between lithogenic and anthropogenic origin of the elements in moss samples. Differences between the mineralogical settings of zones A and B are clearly reflected by the Spearman correlations between most lithophile elements. Significant and strong positive correlations ($p \leq 0.005$) were found between Al and the elements Li, V, Ti, Fe, As, Hf, Zr, Sc, La, Ce, Yb, Th, U, Cs, Ba, Sr, Ta and W. Fe has strong positive correlations ($p \leq 0.005$) with Li, Ni, Cr, Co, As, Hf, Zr, Ta, Mo,

W, Sc, La, Ce, Yb, Th, U, Ba and Sr. Ti has strong positive correlations ($p \leq 0.005$) with Li, Cr, Fe, Ni, Co, Zr, Hf, Ta, W, Sc, La, Ce, Yb, Th, U, Cs, Ba, Sr, Sb, Mo and Rb. All these significant correlations are probably related to lithogenic and crustal origin of these elements.

Ti show positive correlation ($r^2 = 0.56$, $p = 0.000$) with Al (proxy for clay minerals), suggesting the illite fractions as the primary source of titanium. Ti and Zr are also positively correlated ($r^2 = 0.60$, $p = 0.000$), indicating heavy minerals as their potential sources (Hofer et al., 2013). High Ti – Zr correlations indicate the presence of heavy minerals in the area. High correlations of Al, Fe, and Ti with La and Th are probably associated with the enrichment of these elements in felsic rocks. High correlations between Ti and Sc, Cr, Co, Rb, and Cs are probably associated with the enrichment of Ti in alkaline rocks. All these findings indicate that the local dust fraction is a predominant source of several elements in the current moss samples. K has strong positive correlation with P, while Ca does not correlate with elements under investigation. It is probably indicating high uptake of these elements as essential nutrients to the moss.

For a further interpretation of results, Factor analysis (FA) was applied to the data matrix of 37 elements from 48 sampling sites. The factors extracted from the results of FA were interpreted as source categories contributing to elements concentrations at the sampling sites. The identification of the source categories was undertaken by examination of the profiles of the factors, i.e. loadings of the elements and other variables. In general, the main criteria in selecting the number of optimal factors and models of major source identification, is that for Eigen values larger than 1. The results of FA are shown in Table 7 and Fig. 7.

Table 7 Results of Factor analysis (Rotated Factor Loadings and Communalities, Varimax Rotation)

Values in bold, show high positive (> 0.4) or high negative (< -0.4) loads

Fig. 7. GIS maps of factor loadings: a. F1 – Al, Mn, V, Ti, Fe, Co, Se, Hf, Zr, Ta, W, Sc, La, Ce, Yb, Th, U, Rb, Cs, Ba, Sr and Li, b. F2 – Cu, Pb, Zn, Hg, Sb, Mo, Rb and Ca, c. F3 – Cr, Ni, Co, Zn, Mg and P, F4 - Al, Na, K and P

Four factors representing 72.8 % of the total variance were extracted as main factors that are important to explain the distribution of elements, including trace metals, and distinguishing their sources of origin. Additional two factors

were characterized by a very low variance (3.7 and 2.8 %) and were excluded from further calculations. The association of the elements with each factor is analyzed as follows:

Factor 1 is the strongest factor representing 34.3 % of the total variance and high positive loads (> 0.5) for Al, Mn, V, Ti, Fe, Co, Se, Zr, Ta, Hf, W, Sc, La, Ce, Yb, Th, U, Rb, Cs, Ba, Sr and Li. This factor can be explained by elements associated with crustal elements (Harmens et al., 2015) either from local dust emission or possibly from soil particles adhering to the moss samples.

Factor 2 is the second strongest factor, representing 11.7 % of the total variance. It accounts for high loads (> 0.5) of Cu, Pb, Zn, Hg, Sb, Mo (*chalcophile elements*), Rb and Ca. High loadings of these elements in the same factor show that they are probably derived from similar sources and/or affected from similar factors.

Factor 2 can be explained by elements associated with long range atmospheric transport of pollutants from other parts of Europe (Harmens et al., 2015), and probably also from local anthropogenic factors such as high temperature metal processing, traffic emission, and particles, windblown dust from industrial waste deposits. The concentration level of Hg in European moss samples is quite stable for a long period of time (respectively since 2005 and 1990) (Harmens et al., 2015), and the high variation in Albanian moss samples may be associated with local emissions. The influence of sulfide minerals and the open slag dumps of ex-copper industry in Albania are probably main contributors to Factor 2. Cd, Hg and Pb concentrations are also strongly affected by fuel combustion.

Factor (F3) represents 11.2 % of the total variance and is associated with high loads of Ni, Cr, Fe, Co, Zn and Mg, and negative loads of K and P. This association is probably related to metal industry (Metallurgical Plant and Iron-Nickel Metallurgy of Elbasan plants) and the geogenic contribution to Cr and Fe-Ni mineralization derived mainly from ferromagnetite rocks (Guo et al., 2013). High Mg values are probably related to the presence of ophiolitic masses and/or to the ultramafic fraction of geological formations, which affect the distribution of Ni and Cr (Dinelli et al., 2005). Albania is well known for higher abundance of chromium minerals compared to other Mediterranean countries.

Factor (F4) represents 9.1 % of the total variance and is characterised by high loads of Al, V, Sr and Li, and negative loads of K, Na and P. This is probably related to the association of K with phosphorite minerals and salt rocks (the latter containing 78 to 82 % NaCl) located in the south of zone A (NAMR, 2010). Elements such as Na and Mg may also be derived from airborne marine aerosols, while the presence of Al, V, Sr and Li is probably

linked with clay minerals and bauxites positioned in the western part of the country. The negative loadings of K, Na and P and positive loadings of Al, V, Sr and Li indicate their inverse distributions inside the same areas.

3.4. Enrichment factors

One key question related to the present moss samples is whether the elements mainly originate from atmospheric deposition or from the soil and/or substrate. In general, the chemistry of hosting soils and substrate has been shown to have a significant effect on the elemental concentrations in plants. Mosses are rootless plants that take nutrients from atmospheric deposition. No correlations were found between the concentration data of the same elements in moss and corresponding soil data from the Geochemical Atlas of Albania (Zajmi et al., 1997) representative of the present moss sampling sites. The lack of correlation between element concentrations in moss and their concentration in the hosting soils indicate that trace metal concentrations in moss are mostly originating from atmospheric deposition and less from the substrate soil that moss lives on. With the aim to distinguish the soil and airborne origin of trace elements in current moss, enrichment factors (EF) were calculated using Al as a marker of substrate pollution (Sardans and Peñuelas, 2005; Achotegui-Castells et al., 2013).

The concentration data of elements in surface soil (collected at a depth of 5 cm and a grid of 10x10 km²) from the Geochemical Atlas of Albania were also used for calculation of EF values. The order of EFs values based on their respective medians are Cr < Ni < Fe < Ti < Pb < Ca < Cu < Zn. The EF values vary from 1.9 (Fe) to 8.7 (Zn), by indicating that their enrichment in moss is affected by factors other than substrate soil (Sardans and Peñuelas, 2005). Ti, Pb, Ca, Cu and Zn have EF values higher than 3, indicating considerable airborne enrichment of these elements in moss samples in Albania. Lower EF values for Cr, Ni and Fe in current moss are related to their high concentrations in the corresponding soil. The concentrations of Cr and Ni in the surface soil layer of Albania are very high, indicating the existence of mechanisms of geochemical properties of the area and/or atmospheric deposition in the soil. Soil samples at various serpentine and industrial sites in Albania contain high levels of Ni, Cr and Co (Shallari et al., 1998; Peck et al., 2008). In addition, high levels of Ni and Cr (> 200 mg/kg) in soils of West Albania represent their local emission or historical accumulation in soil. High concentrations of these elements are also present in carbonate soils in South-West part of Albania, indicating their anthropogenic origin mainly as atmospheric deposition from local sources. In this case, Cr and Ni emissions from the petrol refinery of Ballsh, and

possibly also from mineral dumps positioned in different parts of the country, and mining operations, may play an important role in the generation of contaminated atmospheric dust and aerosol (Csavina et al., 2012).

4. Conclusions

The following conclusions can be drawn:

- Moss sampling can be used as a complementary method for investigating the presence of trace metals as contaminants in the atmosphere. Their spatial variability and distribution pattern may allow better understanding their natural and/or anthropogenic origin. The presence of typical crustal elements is apparently mainly associated with local and long-term wind blown mineral dust particles, which is considered to be a main emitting source of trace metals in atmospheric deposition in Albania.
- Spatial distributions of elements and relationships between them, the geochemical interpretation of the current data and the secondary effects, such as redox conditions show local and long-distance migration of these pollutants and their sources of origin. Spearman correlation coefficients, Zr normalized data and the ratio of the redox sensitive elements may interpret the geochemical classification and may show the origin of elements present in the current moss samples considered with respect to different types of local rocks and anthropogenic input.
- Factor analysis is a useful tool to identify the most significant associations of the elements and their probable sources of origin. Four dominant factors are identified, *i.e.* natural contamination linked with lithogenic elements ; dust from local mining operations; atmospheric transport of pollutants from local and distant sources; and contributions from air borne marine salts. The negative loadings of K, Na and P and positive loadings of Al, V, Sr and Li indicate their inverse distribution inside the same area.
- The association of observed distribution patterns of elements in moss samples with local geochemistry of the area under investigation appears to be a useful tool in determining the origin of the elements that are linked strongly with the presence of mineral dust particles in aerosols.
- Albania is exposed to high levels of heavy metal pollution particularly for elements linked with mining operations and mineral dumps. Generally, areas in western part of Albania remain exposed to high levels of heavy metal pollution linked mostly with oil and gas industry and shipping traffic, whereas areas in eastern part of Albania

remain exposed to high levels of heavy metal pollution linked mostly with mineral operations, mineral dumps and mineral processing industry.

- The EF values of the elements in current moss indicate their substantially enrichment by airborne pollution with significant emissions from local sources. Stronger implementation of air pollution abatement policies in Albania are recommended for reducing heavy metal concentrations in its territory.

- It is highly recommended to continue the spatial distribution monitoring of trace elements in the future.

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References:

- Achotegui-Castells, A., Sardans, J., Ribas, A., Peñuelas, J., 2013. Identifying the origin of atmospheric inputs of trace elements in the Prades Mountains (Catalonia) with bryophytes, lichens, and soil monitoring. *Environ. Monit. Assess.* 185, 615–629, doi: 10.1007/s10661-012-2579-z.
- Agan, Y., Sejalón-Delmas, N., Probst, A., 2013. Comparing early twentieth century and present-day atmospheric pollution in SW France: a story of lichens. *Environ. Pollut.* 172, 139–148.

- Allajbeu, Sh., Yushin, N.S., Lazo, P., Qarri, F., Duliu, O.G., Frontasyeva, M.V., 2016a. Atmospheric Deposition of Rare Earth Elements in Albania Studied by the Moss Biomonitoring Technique, Neutron Activation Analysis and Gis Technology. *Environ. Sci. Pollut. Res.* 23,14087–14101.
- Allajbeu, Sh., Qarri, F., Marku, E., Bekteshi, L., Ibro, V., Frontasyeva, M.V., Stafilov, T., Lazo, P., 2016b. Contamination scale of atmospheric deposition for assessing air quality in Albania evaluated from most toxic heavy metal and moss biomonitoring. *Air Qual. Atmos. Health.* 10, 587–599.
- Armstrong-Altrin, S.J., Lee, L.I., Kasper-Zubillaga, J.J., Trejo-Ramírez, E., 2016. Mineralogy and geochemistry of sands along the Manzanillo and El Carrizal beach areas, Southern Mexico: implications for palaeoweathering, provenance and tectonic setting. *Geol. J.* 52 (4), 559–582.
- Aubert, D., LeRoux, G., Krachler, M., Cheburkin, A., Kober, B., Shotyk, W., Stille, P., 2006. Origin and fluxes of atmospheric REE entering an ombrotrophic peat bog in Black Forest (SW Germany): evidence from snow lichens and mosses. *Geochim. Cosmochim. Acta.* 70, 2815–2826.
- Barandovski, L., Cekova, M., Frontasyeva, M.V., Pavlov, S.S., Stafilov, T., Steinnes, E., Urumov, V., 2008. Atmospheric deposition of trace element pollutants in Macedonia studied by the moss biomonitoring technique. *Environ. Monit. Assess.* 138,107–118.
- Bekteshi, L., Lazo, P., Qarri, F., Stafilov, T., 2015. Application of normalization process in the survey of atmospheric deposition of heavy metals in Albania by using moss biomonitoring. *Ecol. Indic.* 56,48–59.
- Bortolotti, V., Chiari, M., Marroni, M., Pandolfi, L., Principi, G., Saccani, E., 2015. Geodynamic evolution of ophiolites from Albania and Greece (Dinaric-Hellenic belt), one, two or more oceanic basins. *Int. J. Earth. Sci. (GeolRundsch).* 102, 783–811.
- Bowen, H.J.M., 1979. *Environmental Chemistry of the Elements*. Academic Press, London, UK, pp 333.
- Csavina, J., Field, J., Taylor, M.P., Gao, S., Landázuri, A., Betterton, E.A., Sáez, A.E., 2012. A Review on the Importance of Metals and Metalloids in Atmospheric Dust and Aerosol from Mining Operations. *Sci. Total Environ.* 433C, 58–73.
- Chiarenzelli, J., Aspler, L., Dunn, C., Cousens, B., Ozarko, D., Powis, K., 2001. Multi-element and rare earth element composition of lichens, mosses and vascular plants from the Central Barrenlands Nunavut Canada. *Appl. Geochem.* 16, 245–70.

- Cox, R., Lowe, D.R., Cullers, R.L., 1995. The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the Southwestern United States. *Geochim. Cosmochim. Acta.* 59, 2919-2940.
- Dinelli, E., Cortecchi, G., Lucchini, F., Zantedeschi, E., 2005. Sources of major and trace elements in the stream sediments of the Arno river catchment (Northern Tuscany, Italy). *Geochem. J.* 39,531-545.
- Duffus, J.H., 2002. Heavy Metals—A meaningless term. *Pure and Appl. Chem.* 74, 793-807.
- Fernandez, J.A., Carballeira, A., 2002. Biomonitoring metal deposition in Galicia (NW Spain) with mosses: factors affecting bioconcentration. *Chemosphere.* 46, 535-542.
- Filby, R.H., 1995. Isotopic and nuclear analytical techniques in biological systems: a critical study. *Pure & Appl. Chem.* 67, 1929–1941.
- Frontasyeva, M.V., 2011. Neutron activation analysis for the Life Sciences. *Phys. Part Nuclei.* 42, 332-378. <http://www.springerlink.com/content/f836723234434m27/>
- Frontasyeva, M.V., Pavlov, S.S., 2000. Analytical investigation at the IBR-2 Reactor in Dubna. Preprint JINR E14-2000-177, Dubna, p. 5–32.
- Galarraga, F., Reategui, K., Martínez, A., Martínez, M., Llamas, F.J., Márquez, G., 2008. V/Ni ratio as a parameter in palaeoenvironmental characterisation of nonmature medium-crude oils from several Latin American basins. *J. Pet. Sci. Technol.* 61, 9–14.
- Goldschmidt, V., 1937. The principles of distribution of chemical elements in minerals and rocks. *J. Chem. Soc.* 655–673.
- Guo, H., Du, Y., Zhou, L., Yang, J., Guong, H., 2013. Trace and rare earth elemental geochemistry of carbonate succession in the Middle Gaoyuz Guong Formation, Pingquan Section: Implications for Early Mesoproterozoic ocean redox conditions. *J. of Palaeogeogr.* 2, 209-221.
- Harmens, H., Norris, D.A., Sharps, K., Mills, G., Alber, R., Aleksiyenak, Y., Blum, O., Cucu-Man, S.M., Dam, M., De Temmerman, L., Ene, A., Fernández, J.A., Martinez-Abaigar, J., Frontasyeva, M., Godzik, B., Jeran, Z., Lazo, P., Leblond, S., Liiv, S., Magnússon, S.H., Maňková, B., Pihl Karlsson, G., Piispanen, J., Poikolainen, J., Santamaria, J.M., Skudnik, M., Spiric, Z., Stafilov, T., Steinnes, E., Stihl, C., Suchara, I., Thöni, L., Todoran, R., Yurukova, L., Zechmeister, H.G., 2015. Heavy metal and nitrogen concentrations

- in mosses are declining across Europe whilst some “hotspots” remain in 2010. *Environ. Pollut.* 200, 93-104.
- Harmens, H., Norris, D.A., Mills, G. and the participants of the moss survey, 2013. Heavy metals and nitrogen in mosses. spatial patterns in 2010/2011 and long-term temporal trends in Europe, ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK.
- Harmens, H., Norris, D.A., Cooper, D.M., Mills, G., Steinnes, E., Kubin, E., Thöni, L., Aboal, J.R., Alber, R., Carballera, A., Coskum, M., de Temmerman, L., Frolova, M., González-Miqueo, L., Jeran, Z., Leblond, S., Liiv, S., Maňkovská, B., Pesch, R., Poikalainen, J.R., Rühling, Å., Santamaria, J.M., Simone, P., Schröder, W., Suchara, I., Yurukova, L., Zechmeister, H.G., 2011. Nitrogen concentrations in mosses indicate the spatial distribution of atmospheric nitrogen deposition in Europe. *Environ. Pollut.* 159, 2852-2860.
- Harmens, H., Norris, D.A., Steinnes, E., Kubin, E., Piispanen, J., Alber, R., Aleksiyenak, Y., Blum, O., Coşkun, M., Dam, M., De Temmerman, L., Fernández, J.A., Frolova, M., Frontasyeva, M., González-Miqueo, L., Grodzińska K., Jeran Z., Korzekwa S., Krmar M., Kvietkus K., Leblond S., Liiv, S., Magnússon, S.H., Maňkovská, B., Pesch, R., Rühling, Å., Santamaria, J.M., Schröder, W., Spiric, Z., Suchara, I., Thöni, L., Urumov, V., Yurukova, L., Zechmeister, H.G., 2010a. Mosses as biomonitors of atmospheric heavy metal deposition: spatial and temporal trends in Europe. *Environ. Pollut.* 158, 3144- 3156.
- Harmens, H., Mills, G., Hayes, F., Norris, D. and the participants of the ICP Vegetation, 2010b. Monitoring of atmospheric deposition of heavy metals, nitrogen and POP's in Europe using bryophytes. Monitoring manual 2010 survey. ICP Vegetation Programme Coordination Centre, CEH Bangor, UK. <http://icpvegetation.ceh.ac.uk>
- Hayashi, K., Fujisawa, H., Holland, H.D., Ohmoto, H., 1997. Geochemistry of approximately 1.9 Ga sedimentary rocks from northeastern Labrador, Canada. *Geochim. Cosmochim. Acta.* 61, 4115-4137.
- Hofer, G., Wagreich, M., Neuhuber, S., 2013. Geochemistry of fine-grained sediments of the upper Cretaceous to Paleogene Gosau Group (Austria, Slovakia): Implications for paleoenvironmental and provenance studies. *Geosc. Frontiers.* 4, 449-468.
- Hoeck, V., Koller, F., Mesel, T., Onuzi, K., Kneringer, K., 2005. The Jurassic South Albanian ophiolites, MOR- vs.SSZ-type ophiolites. *Lithos.* 65, 143-164.

- Huisman, J.D., Klaver, T.G., Veldkamp, A., van Os, H.J.B., 2000. Geochemical compositional changes at the Pliocene-Pleistocene transition in fluviodeltaic deposits in the Tegelen-Reuver area (southeastern Netherlands). *Int. J. Earth Sci.* 89, 154-169.
- Iain S., Chassè M., 2016. Scandium. William M. White. *Encyclopedia of Geochemistry*, Springer International Publishing Switzerland, pp.1-4.
- Kanawade, M.S., Hamigi, D.A., Gaikwad, W.R., 2010. Ecological Effect of Pollution. *Int. J. Chem. Eng. and Appl.* 1, 332-335.
- Lazo, P., Kucuku, M., 2012. Analysis of Mercurial Preservatives in Different Vaccines by Cold Vapor Atomic Absorption Spectrophotometry. *J. Anal. Sci. Technol.* 3, 121-127.
- Lazo, P., Cullaj, A., Deda, T., 2007. Arsenic in soil environment in Albania. In: Battacharia P, Mukherjee AB, Bundschuh J, Zevenhoven JR, Loeppert RH. (Ed.), *Arsenic in Soils and Groundwater Environment. Trace Metals and other Contaminants in the Environment.* 9, 237-256.
- Lazo, P., Cullaj, A., 2002. Determination of the different states of mercury in seawater near the Vlora and Durres Bays. *Anal. Bioanal. Chem.* 374, 1034-1038.
- Markert, B., Wappelhorst, O., Weckert, V., Herpin, U., Siewers, U., Friese, K., Breulmann, G., 1999. The use of bioindicators for monitoring the heavy-metal status of the environment. *J. Radioanal. Nucl. Chem.* 240, 425-429.
- Maxhuni, A., Lazo, P., Kane, S., Qarri, F., Marku, E., Harmens, H., 2015. First survey of atmospheric heavy metal deposition in Kosovo using mossbiomonitoring. *Environ. Sci. Poll. Res.* 23, 744-755.
- McLennan, S.M., Fryer, B.J., Young, G.M., 1979. The geochemistry of the carbonate rich Espanola Formation (Huronian) with emphasis on the rare-earth elements. *Canadian Jour. Earth Sci.* 16, 230-239.
- Nagarajan, R., Madhavaraju, J., Nagendra, R., Armstrong-Altrin, S.J., Moutte, J., 2007. Geochemistry of Neoproterozoic shales of the Rabanpalli Formation, Bhima Basin, Northern Karnataka, Southern India: implications for provenance and paleoredox conditions. *Revista Mexicana de Ciencias Geológicas.* 2, 150-160.
- NAMR (National Agency of Natural Resources), 2010. Mineral Resources in Albania. <http://www.akbn.gov.al/images/pdf/publikime/Minierat.pdf>

- Onianwa, P.C., 2001. Monitoring Atmospheric Metal Pollution: A Review of the Use of Mosses as Indicators. *Environ. Monit. Assess.* 71, 13-48.
- Peck, P.,Stuhlberger, C., Tremblay, G., Davé, N., 2008. Albanian mining-related risks: Identification and verification of “mining environmental hot spots”, UNEP Programme coordinated ADA project and the Environment & Security Initiative: “Improving regional cooperation for risk management from pollution hotspots as well as transboundary management of shared natural resources”, Lund/Geneva/Ottawa.
- Peck P., 2004. Reducing Environment and Security Risks from Mining i n South Eastern Europe. EXECUTIVE SUMMARY. http://www.grid.unep.ch/envsec/mining/draft_report.php
- Peltola, E., 1968. On some geochemical features in the black schists of the Outokumpu area, Finland. *Bull. Geol. Soc. Finland*, 40, 39-50.
- Perlwitz, J.P., García-Pando, C.P., Miller, R.L., 2015. Predicting the mineral composition of dust aerosols – Part 1.Representing key processes. *Atmos. Chem. Phys.* 15, 11593–11627.
- Prospero, M.J., Ginoux, P., Torres, O., Nicholson, E.S., Gill, E.T., 2002. Environmental characterization of global sources of atmospheric soil dust identified with the nimbus 7 total ozone mapping spectrometer (TOMS) absorbing aerosol product. *Rev. Geophys.* 40, (1), doi:10.1029/2000RG000095.
- Prospero, J.M., 1999. Long-range transport of mineral dust in the global atmosphere. Impact of African dust on the environment of the southeastern United States. *Proc. Natl. Acad. Sci. USA.* 96, 3396–3403.
- Qarri, F., Lazo, P., Stafilov, T., Bekteshi, L., Baceva, K., Marka, J., 2014a. The survey of atmospheric deposition of Al, Cr, Fe, Ni, V and Zn in Albania by using moss biomonitoring and ICP-AES. *Air Qual. Atmos. Health.* 7, 297-307.
- Qarri, F., Lazo, P., Bekteshi, L., Stafilov, T.,Frontasyeva, M., Harmens, H., 2014b. The effect of sampling scheme in the survey of atmospheric deposition of heavy metals in Albania by using moss biomonitoring. *Environ. Sci. Pollut. Res.* 22, 2258-2271.
- Qarri, F., Lazo, P., Stafilov, T., Frontasyeva, M., Harmens, H., Bekteshi, L., Baceva, K., Goryainova, Z., 2013. Multi-elements atmospheric deposition study in Albania. *Environ. Sci. Pollut. Res.* 21, 2486-2518.
- Reimann, C., Filzmoser, P., Garrett, R.G., 2002. Factor analysis applied to regional geochemical data: Problems and possibilities. *Appl. Geochem.* 17, 185–206.
- Rudnick, R.L., Gao, S., 2004. Composition of the continental crust. *Treatise on Geochem.* 3, 1–64.

- Sardans, J., Peñuelas, J., 2005. Trace element accumulation in the moss *Hypnum cupressiforme* Hedw. and the trees *Quercus ilex* L and *Pinus halepensis* Mill. in Catalonia. *Chemosphere*. 60, 1293–1307.
- Sari, A., Koca, D., 2012. An Approach to Provenance, Tectonic and Redox Conditions of Jurassic-Cretaceous Akkuyu Formation, Central Taurids, Turkey. *Mineral. Res. Expl. Bull.* 144, 51-74.
- Schröder, W., Nickel, S., Schönrock, S., Meyer, M., Wosniok, W., Harmens, H., Frontasyeva, M.V., Alber, R., Aleksiyenak, J., Barandovski, L., Carballeira, A., Danielsson, H., de Temmermann, L., Godzik, B., Jeran, Z., Karlsson, G. P., Lazo, P., Leblond, S., Lindroos, J.A., Liiv, S., Magnússon, S.H., Mankovska, B., Martínez-Abaigar, J., Piispanen, J., Poikolainen, J., Popescu, I.V., Qarri, F., Santamaria, J.M., Skudnik, M., Špirić, Z., Stafilov, T., Steinnes, E., Stihl, C., Thöni, L., Uggerud, H.T., Zechmeister, H.G., 2016. Spatially valid data of atmospheric deposition of heavy metals and nitrogen derived by moss surveys for pollution risk assessments of ecosystems. *Environ. Sci. Pollut. Res.* 23, 10457-10476
- Schröder, W., Holy, M., Pesch, R., Harmens, H., Ilyin, I., Steinnes, E., Alber, R., Aleksiyenak, Y., Blum, O., Coşkun, M., Dam, M., De Temmerman, L., Frolova, M., Frontasyeva, M., González-Miqueo, L., Grodzińska, K., Jeran, Z., Korzekwa, S., Krmar, M., Kubin, E., Kvietskus, K., Leblond, S., Liiv, S., Magnússon, S., Maňková, B., Piispanen, J., Rühling, L., Santamaria, J., Spiric, Z., Suchara, I., Thöni, L., Urumov, V., Yurukova, L., Zechmeister, H.G. 2010. Are cadmium, lead and mercury concentrations in mosses across Europe primarily determined by atmospheric deposition of these metals? *J. Soils Sediments*. 10, 1572-1584
- Shallari, S., Schwartz, C., Hasko, A., Morel, J.L., 1998. Heavy Metals in Soils and Plants of Serpentine and Industrial Sites of Albania. *Sci. Tot. Environ.* 209, 133-142.
- Shervais, J.W., 1982. Ti-V plots and the petrogenesis of modern and ophiolitic lavas. *Earth Planet. Sci. Letters*. 59: 101-18
- Shotyk, W., Bicalho, B., Cuss, C.W., John, M., Duke, M., Noernberg, T., Pelletier, R., Steinnes, E., Zacccone, C., 2016. Dust is the dominant source of “heavy metals” to peat moss (*Sphagnum fuscum*) in the bogs of the Athabasca Bituminous Sands region of northern Alberta. *Environ. Int.* 92-93, 494-506.
- Steinnes, E., Berg, T., Uggerud, H.T., 2011. Three decades of atmospheric metal deposition in Norway as evident from analysis of moss samples. *Sci. Total Environ.* 412-413, 351–358.

- Steinnes, E., Rühling, Å., Lippo, H., Mäkinen, A., 1997a. Reference materials for large-scale metal deposition surveys. *Accred. Qual. Assur.* 2, 243-249.
- Steinnes, E., Allen, R.O., Petersen, H.M., Rambaek, J.P., Varskog, P., 1997b. Evidence of large scale heavy- metal contamination of natural surface soils in Norway from long-range atmospheric transport. *Sci. Total Environ.* 205, 255-266.
- UNDP–Albania, 2010. Ferrochrome Smelter in Elbasan; Fwienv Contract n° 1-BH-0381. Consultancy Services to conduct Environmental Impact Assessment of ten High Priority Environmental Hotspots to form the basis for a major Remediation Programme, for the project: “Identification and Prioritization of Environmental Hot Spots in Albania” Eia Report Final
- Viana, M., Hammingh, P., Colette, A., Querol, X., Degraeuwe, B., Vlieger, I., Aardenne, J. 2014. Impact of maritime transport emissions on coastal air quality in Europe. *Atmos. Environ.* 90, 96-105. doi:10.1016/j.atmosenv.2014.03.046
- Vinogradov, A.P., 1962. Average contents of chemical elements in the principal type of igneous rocks of the Earth’s crust. *Geokhimiya.* 7, 641-664.
- Xiong, T., Yang, J., Robinson, P.T., Dilek, Y., Milushi, I., Xu, X., Chen, Y., Zhou, W., Lai, S., Tian, Y., Huang, Z., 2015. Petrology and geochemistry of high Cr podiform chromitites of Bulqiza, Eastern Mirdita Ophiolite EMO, Albania. *Ore Geol. Rev.* 70, 188–207.
- Zajmi, A., Tashko, A., Zharra, A., Mazreku, A., Jaupi, P., 1997. *Geochemical Atlas of Albania*. CGGE (ed.). Centre of Geophysical and Geochemical Research, Tirana, Albania.



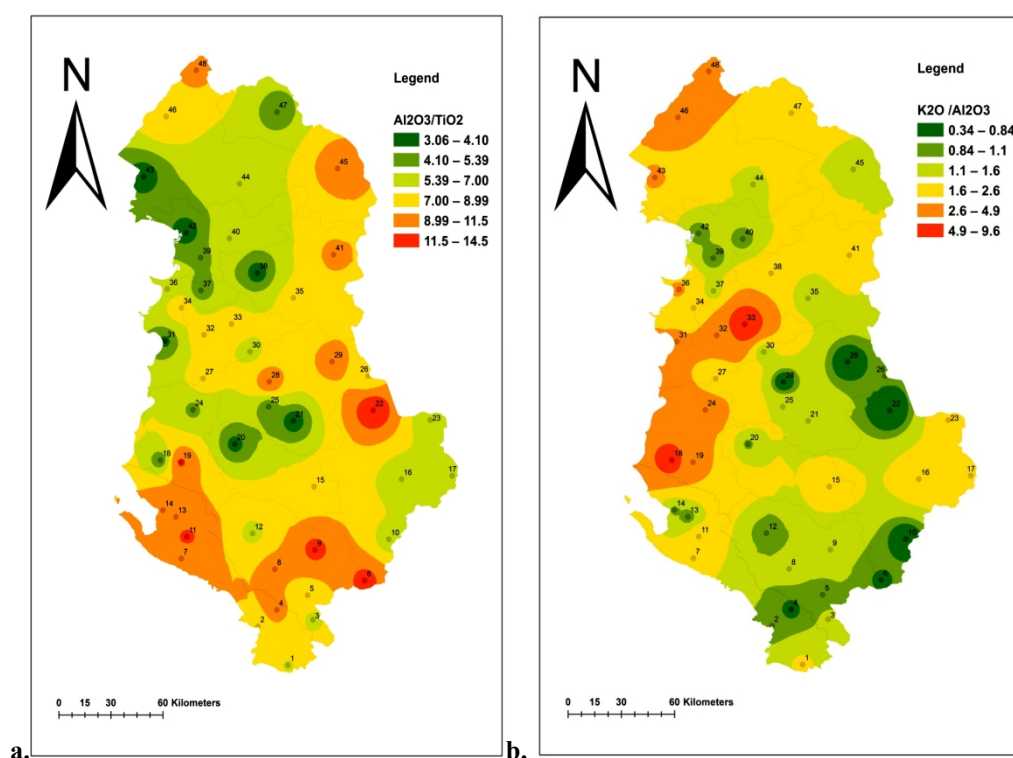


Fig. 4.

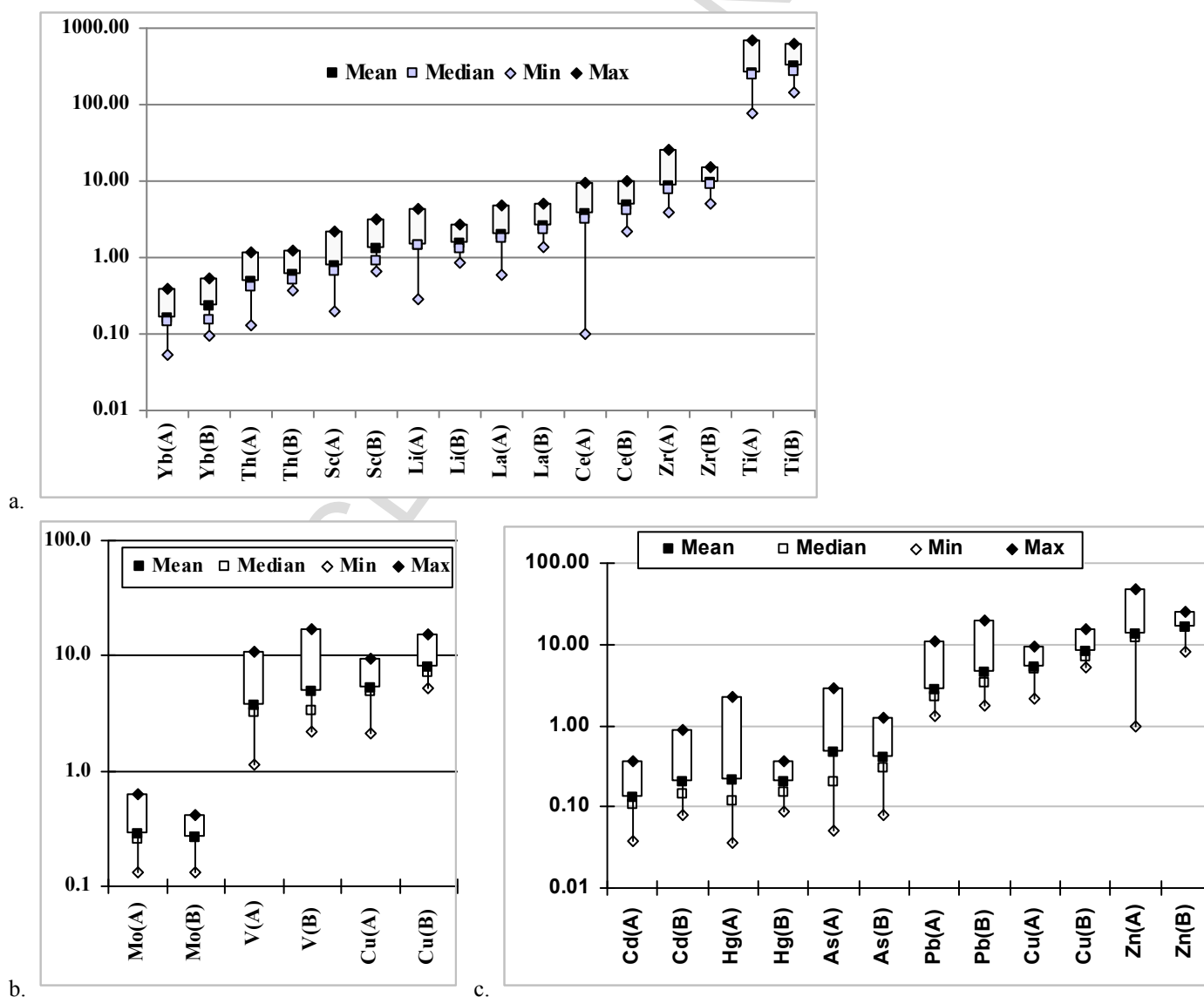


Fig. 5.

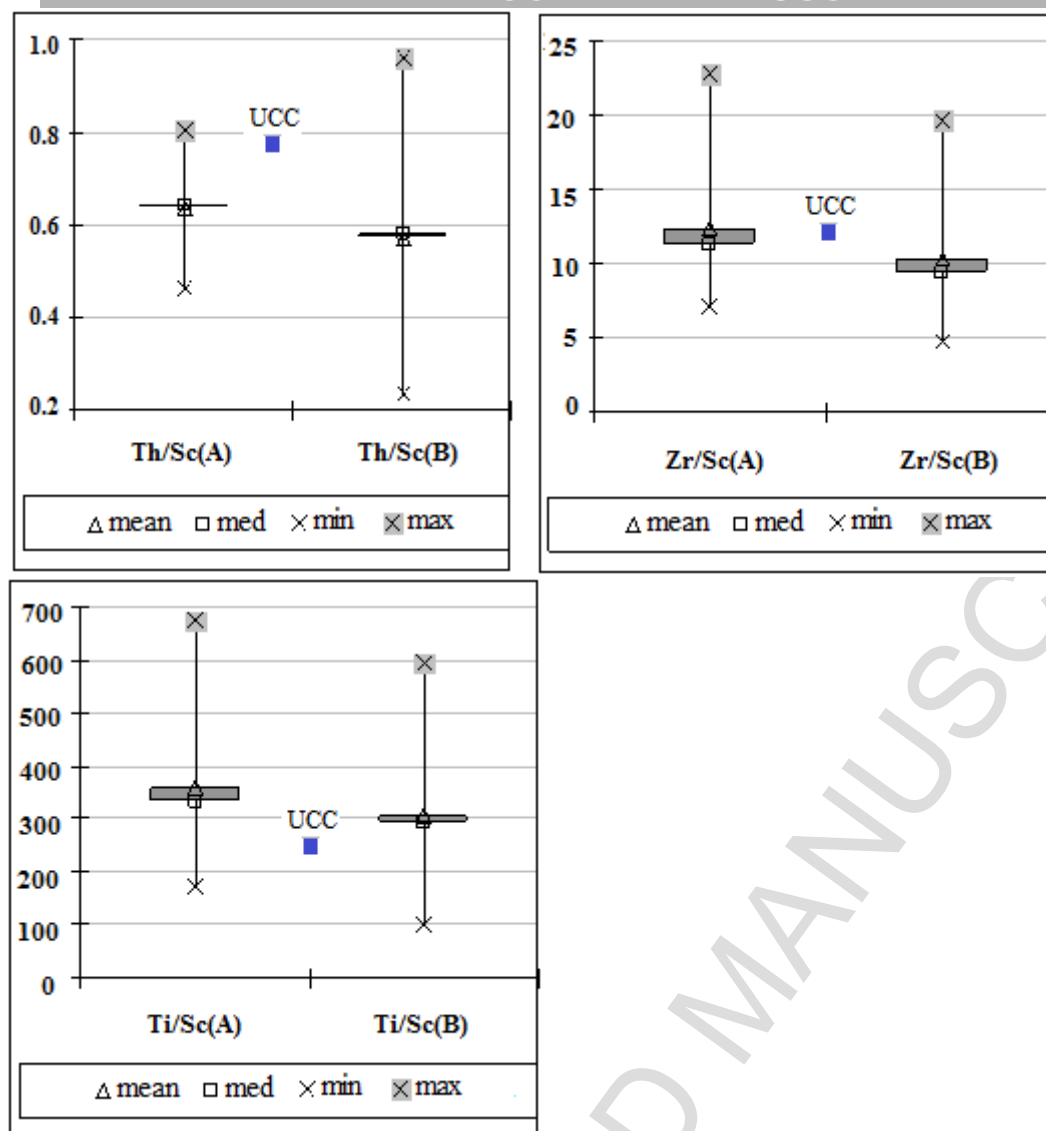
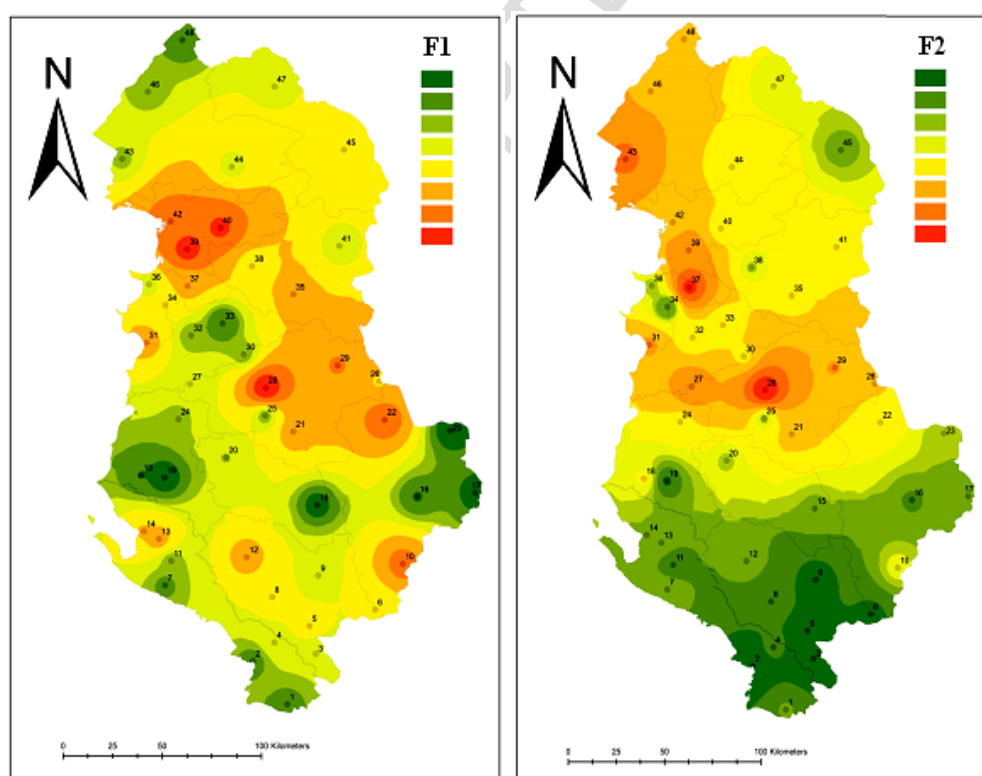


Fig. 6.



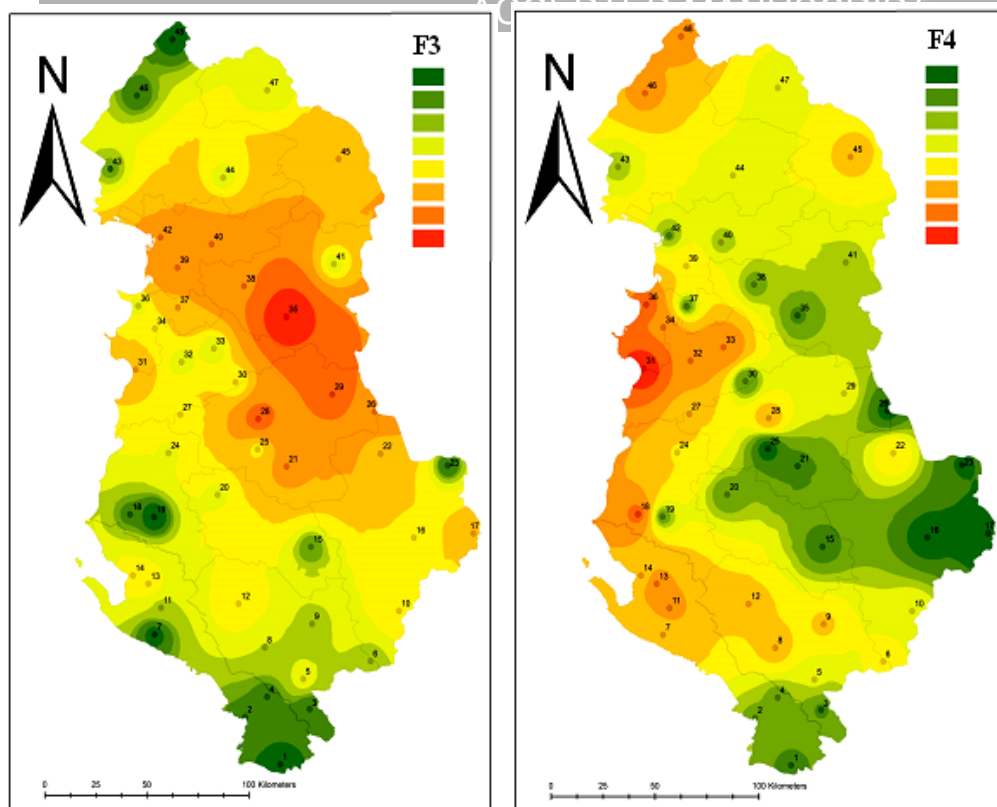


Fig. 7

Table 1 Limits of quantification (LOQ) of the elements (mg kg⁻¹)

Elements	LOQ	Elements	LOQ	Elements	LOQ
Ti	63	Zr	2.79	Yb	0.035
Cr	1.21	Mo	0.032	Hf	0.021
Co	0.024	Sb	0.005	Ta	0.002
Se	0.071	Cs	0.0065	W	0.019
Rb	0.123	La	0.02	Th	0.005
Sc	0.01	Ce	0.456	U	0.0026

Table 2 Certified and experimental values (mean \pm standard deviation) for elements with known certified values (mg kg⁻¹) used for quality control of the analysis and to calculate the concentration of the elements

Elements	Certified value	Determined value	Elements	Certified value	Determined value
Ti ⁴	7 910 \pm 142	7 896 \pm 184	Nd ¹	25.00 \pm 1.40	25.0 \pm 8.2
Sc ¹	13.70 \pm 0.69	13.7 \pm 0.7	Sm ¹	4.66 \pm 0.20	4.65 \pm 0.23
Cr ¹	178 \pm 16	178 \pm 17	Eu ¹	1.00 \pm 0.01	0.99 \pm 0.19
Fe ¹	44 800 \pm 986	44 819 \pm 2106	Gd ¹	4.410 \pm 0.119	4.42 \pm 0.28
Co ¹	23.00 \pm 1.29	23.0 \pm 1.3	Tb ¹	0.682 \pm 0.017	0.681 \pm 0.024
Se ³	1.290 \pm 0.109	1.29 \pm 0.17	Tm ¹	0.326 \pm 0.025	0.325 \pm 0.070
Rb ³	5.05 \pm 0.11	5.06 \pm 0.90	Yb ¹	2.20 \pm 0.09	2.19 \pm 0.24
Zr ²	230 \pm 69.0	230 \pm 70	Hf ²	7.30 \pm 2.19	7.29 \pm 2.19
Mo ²	1.60 \pm 0.48	1.60 \pm 0.51	Ta ¹	0.8760 \pm 0.0175	0.876 \pm 0.027
Sb ²	19.4 \pm 1.8	19.4 \pm 1.8	W ²	3 \pm 0.9	3.00 \pm 0.92
Cs ¹	7.80 \pm 0.70	7.81 \pm 0.71	Th ³	1.342 \pm 0.036	1.34 \pm 0.04
La ¹	27.80 \pm 1.00	27.83 \pm 1.11	U ¹	2.26 \pm 0.15	2.26 \pm 0.15
Ce ¹	56.70 \pm 2.49	56.6 \pm 3.4			

Note: The subscription of each element refer to the certified material used to calculate the concentration of the elements (¹ BCR-667; ² SRM 2710; ³ SRM 1632b; ⁴ SRM 1633b)

Table 3 The range of the ratios between different lithophile elements

Parameters	Th/Co(A)	Th/Sc(A)	La/Co(A)	La/Sc(A)	Cr/Th(A)	Th/Co(B)	Th/Sc(B)	La/Co(B)	La/Sc(B)	Cr/Th(B)	Pb/Sc (A)	Pb/Sc (B)
Min.	0.15	0.47	0.53	1.78	3.60	0.06	0.23	0.20	0.82	4.8	1.32	1.18
Max.	0.62	0.80	2.92	3.86	25.10	0.72	0.96	2.67	4.26	60.5	23.58	9.17

Table 4. Cr, Ni, Mo, V, U and Zn median ratios between zone A and zone B

Parameters	Ni(A)/Ni(B)	Cr(A)/Cr(B)	U(A)/U(B)	Zn(A)/Zn(B)	Mo(A)/Mo(B)	V(A)/V(B)
Ratios	0.42	0.48	0.65	0.81	1.00	1.17

Table 5 The range of the ratios between elements sensitive to redox conditions

Parameters	Ti/V(A)	Ti/V(B)	V/Ni(A)	V/Ni(B)	V/Cr(A)	V/Cr(B)	V/(V+Ni)(A)	V/(V+Ni)(B)	Cr/Ni(A)	Cr/Ni(B)	Cu/Zn(A)	Cu/Zn(B)	(Cu+Mo)/Zn(A)	(Cu+Mo)/Zn(B)	(Ni/Co)(A)	(Ni/Co)(B)
Min.	35	35	0.32	0.02	0.37	0.01	0.24	0.02	0.6	0.26	0.15	0.27	0.16	0.29	0.5	1.8
Max.	163	152	1.77	0.76	1.7	1.12	0.64	0.43	2.28	8.04	2.69	0.71	2.75	0.73	2.9	31

Table 6 Zr-normalized values of different elements

Parameters	U/Zr (A)	U/Zr (B)	V/Zr (A)	V/Zr (B)	Mo/Zr (A)	Mo/Zr (B)	Cr/ Zr (A)	Cr/ Zr (B)	Co/Zr (A)	Co/Zr (B)	Ni/Zr (A)	Ni/Zr (B)	Hf/Zr (A)	Hf/Zr (B)
Min.	0.007	0.012	0.18	0.19	0.012	0.012	0.021	0.39	0.062	0.07	0.29	0.32	0.013	0.02
Max.	0.038	0.027	0.82	0.75	0.089	0.067	0.432	0.41	0.280	1.06	1.43	21	0.043	0.03

Table 7 Results of **Factor analysis** (Rotated Factor Loadings and Communalities Varimax Rotation)

Variable	Factor1	Factor2	Factor3	Factor4	Communality
Al	0.707	0.119	-0.108	0.519	0.794
Mn	0.688	-0.192	0.232	-0.260	0.631
V	0.754	0.366	0.062	0.404	0.869
Ti	0.779	0.139	0.039	0.044	0.630
Cr	0.183	0.083	0.784	0.092	0.662
Fe	0.585	0.317	0.434	0.392	0.785
Ni	0.023	0.011	0.793	0.222	0.680
Co	0.528	-0.014	0.726	-0.038	0.807
Cu	0.352	0.511	0.393	-0.366	0.673
Pb	0.052	0.627	0.102	-0.067	0.411
Zn	0.145	0.659	0.432	-0.278	0.718
As	0.252	0.115	-0.173	0.636	0.511
Cd	0.013	0.396	0.344	0.037	0.277
Hg	0.313	0.687	0.191	0.213	0.652
Se	0.402	0.052	0.062	-0.007	0.168
Sb	0.361	0.678	0.281	0.060	0.673
Hf	0.878	0.229	0.044	0.161	0.852
Zr	0.812	0.245	0.098	0.126	0.744
Ta	0.420	0.167	0.138	0.138	0.243
Mo	0.377	0.633	-0.093	-0.012	0.551
W	0.738	0.353	0.195	0.188	0.743
Sc	0.867	0.094	0.320	-0.072	0.869
La	0.899	0.279	0.088	0.155	0.917
Ce	0.915	0.253	0.102	0.095	0.920
Yb	0.865	0.001	0.141	-0.089	0.775
Th	0.918	0.248	0.072	0.149	0.932
U	0.824	0.215	0.200	0.181	0.799
Na	-0.119	0.125	-0.054	-0.602	0.396

K	-0.008	0.033	-0.481	-0.576	0.583
Rb	0.592	0.510	-0.182	-0.299	0.733
Cs	0.855	0.269	0.157	-0.017	0.828
Ba	0.599	-0.037	-0.165	0.197	0.427
Mg	0.104	0.310	0.827	-0.144	0.811
Ca	0.101	0.563	-0.213	0.146	0.394
Sr	0.526	0.151	-0.049	0.484	0.556
P	0.043	0.021	-0.408	-0.678	0.629
Li	0.746	0.337	-0.003	0.443	0.867

Values in bold show high positive (> 0.4) or high negative (< -0.4) **loadings**