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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

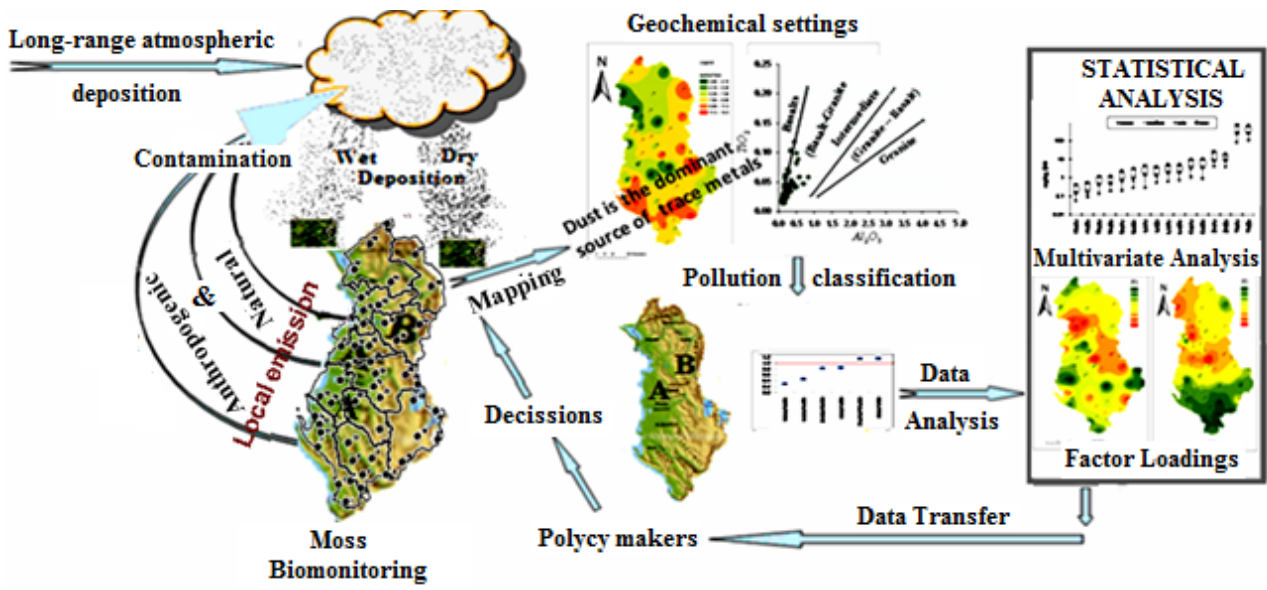
$L_i$  - individual loads of element i

NAA - neutron activation analysis

PM – Particulate matter

RLE – Ratios of lithophile elements

## Graphical Abstract



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

3

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18

19 **Abstract**

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

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

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

35

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

38

### 39 1. Introduction

40 Air pollution is a global problem and has negative effects on human, animal and plant health (Kanawade et al.,  
41 2010). Pollutants emitted into the atmosphere are deposited at the Earth's surface where they accumulate in soil,  
42 sediment, and biota of terrestrial and aquatic ecosystems (Schröder et al., 2016). In general, the main emission  
43 sources of trace metals in the air are ore and metal processing, and manufacturing, as well as combustion processes  
44 (Duffus, 2002). There is increasing interest in the atmospheric transport of mineral dust that is believed to play an  
45 important role in several marine biogeochemical processes (Prospero et al., 2002), geochemical and geophysical  
46 processes, and in negative effects on human health (Prospero, 1999).

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

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

56 generally used in Europe as a complementary monitoring tool for atmospheric deposition of trace metals. The use of  
57 native terrestrial mosses as biomonitors is now a well-recognized technique in studies of atmospheric deposition  
58 (Steinnes et al., 1997a; 1997b; 2011; Fernandez and Carballeira, 2002; Harmens et al., 2010a; 2011; 2013, 2015). It  
59 is a convenient and cheap way of determining the spatial and temporal trends of trace elements in atmospheric  
60 deposition (Steinnes et al., 1997a; 1997b; 2011; Harmens et al., 2015). The specific features of bryophytes such as a  
61 weakly developed cuticle (taking nutrients and water directly from the atmospheric deposition, large surface to mass  
62 ratio, and their habit of growing in groups) are strong reasons for making them suitable indicators of heavy metal  
63 atmospheric deposition (Steinnes et al., 1997a; 1997b; 2011; Markert et al., 1999; Onianwa, 2001; Schröder et al.,  
64 2010). In contrast to measurements with technical deposition samplers, moss surveys allow covering a broad range  
65 of spatial scales with the same method at a high spatial density after selecting the proper moss species as  
66 biomonitors (Schröder et al., 2016).

67 Albania is a small country (28000 km<sup>2</sup>) positioned in western Balkan in the south-east of Europe. It is characterized  
68 by a complex geographic relief and climate, high diversity of geologic setting, and is influenced by different contamination  
69 inputs. Activities in ex-industrial sites of copper, chromium, iron-nickel and oil industries have produced several  
70 million tons of industrial waste impacting the surrounding environment and has adversely effected natural resources,  
71 followed by a potential health risk for people who are continuously exposed to this pollution (UNDP–Albania,  
72 2010). The lack of a national network on air quality monitoring as well as data on morbidity caused by air pollution,  
73 makes the assessment of the health impact of air pollution in Albania impossible (UNDP–Albania, 2010).

74 Moss biomonitoring in Albania started in 2010/2011 when researchers from Albania joined the European Moss  
75 Survey conducted within the framework of the International Cooperative Programme on Effects of Air Pollution on  
76 Natural Vegetation and Crops, ICP Vegetation (Harmens et al., 2013). Heavy metal concentrations (As, Cd, Cr, Cu,  
77 Fe, Hg, Ni, Pb, V) in 2010/2011 moss samples of Albania have been reported in several publications (Qarri et al.,  
78 2013; 2014a; 2014b; Bektashi et al., 2015; Allajbeu et al., 2016a; 2016b). The present paper reports on  
79 concentrations of 37 elements, their spatial distributions in 2010/2011 moss samples, and possible contributions  
80 from different sources and processes.

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

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

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

97

## 98 **2. Materials and methods**

### 99 *2.1. Geology and main ore mineralization of Albania*

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

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

110

### 111 *2.2. Sampling procedure*

112 Carpet forming moss species *Hypnum cupressiforme* (Hedw) and *Pseudoscleropodium purum* (Hedw.) M. Fleisch  
113 (the latter only at two sampling sites) were collected in 2010/2011 from 48 sampling sites evenly distributed over  
114 Albania. A systematic sampling scheme was used (Qarri et al., 2014b). The moss sampling procedure and the  
115 preparation of the material for elemental analysis was done according to the guidelines described in the protocol for  
116 the 2010 European moss survey (Harmens et al., 2010b). Each sampling site was situated at least 300 m far from  
117 main roads, 100 m from local roads, and 200 m from villages or single houses. Most sites were located at small  
118 forest clearings to reduce any through-fall effects. Composite samples of ten sub-samples collected within an area of  
119 50 m × 50 m were used for analysis (Harmens et al., 2010b). Disposable polyethylene gloves were used during the  
120 sampling and sample preparation to prevent potential contamination. Based on different mineralogical settings in the  
121 western and eastern parts, Albania was divided into two different zones (zone A and B) (see Fig. 1b) and moss  
122 samples are grouped and discussed based on their geographical positions shown in Fig. 1a.

123

124 a. b.

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

127

### 128 2.3. Chemical analysis

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

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



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

147  
148 The elements Co, Cr, Ti, Se, Sb, Zr, Hf, Ta, Mo, W, Sc, La, Ce, Yb, Th, U, Rb, and Cs were determined by  
149 epithermal neutron activation analysis (ENAA) at the IBR-2 pulsed fast reactor FLNP JINR Dubna, Russia  
150 (Frontasyeva, 2011). Samples for ENAA, about 0.3 g, were pelletized in simple press forms and heat sealed in  
151 polyethylene foil for analysis based on short-lived radionuclides, while for elements with more long-lived  
152 radionuclides the samples were packed in aluminum cups. For short-lived radionuclides (only Ti in the current  
153 work) the samples were irradiated for 3 minutes in the second channel (Ch2) of the reactor, and to determine  
154 elements associated with long-lived radionuclides the samples were irradiated for 100 hours in the cadmium  
155 screened channel Ch1. After irradiation, gamma-ray spectra were recorded twice for each irradiation using a high-  
156 purity Ge detector (Frontasyeva and Pavlov, 2002).

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

163

164 **Table 1** Limits of quantification (LOQ) of the elements (mg kg<sup>-1</sup>)

165

166 *2.4. Quality control*

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

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

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

188  
189 **Table 2** Certified and experimental values (mean  $\pm$  standard deviation) for elements with known certified values  
190 (mg kg<sup>-1</sup>) used for quality control of the analysis and for calculating the concentrations of the elements

191  
192 Note: The subscription of each element refer to the certified material used to calculate the concentration of the  
193 elements (<sup>1</sup> BCR-667; <sup>2</sup> SRM 2710; <sup>3</sup> SRM 1632b; <sup>4</sup> SRM 1633b)

194

195 *2.5. Data processing and statistical analyses*

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

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

207 Considerable information may be acquired by plotting the geographic distribution of the elements applying  
208 Geographic Information System (GIS). GIS maps are plotted to explain the spatial distribution of  $Al_2O_3/TiO_2$  ratio  
209 that reflect different metallogenic settings of local emission. Arc-GIS 10.2 was used in combination with local  
210 deterministic methods and the inverse distance weighting for mapping the spatial distribution of the factor loadings  
211 ( $FL_{site}$ ) and for spatial interpolation.  $FL_{site}$  is calculated as percentile of the sum of the product of individual loads of  
212 each element and respective site concentration (Barandovski et al. 2008, Allajbeu et al. 2016b):

$$214 \quad FL_{site} = average(100 \frac{\sum(C_i)_{site} L_i}{\sum(C_i)_{max}})$$

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

216  
217 Enrichment factor (EF) is used to distinguish between the soil and/or airborne origin of trace elements in current  
218 moss. EF was calculated by using Al as a marker of soil substrate contamination of the moss samples (Frontasyeva  
219 and Pavlov, 2002; Sardans and Peñuelas, 2005).

220

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

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).

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

249  
250 The order of the median concentrations of the elements in moss samples of zone A were  $Al \cong Fe < Mg < K < Ca$ , and of  
251 zone B were  $Al < Fe < K < Mg < Ca$ . Differences between concentrations of major elements of both zones probably  
252 have been influenced by the differences in lithology and grain size differences in the parent dust of emission sources  
253 (Hofer et al., 2013; Armstrong-Altrin et al., 2016). High Ca content is found in current moss, higher than the content  
254 of crustal elements such as Al, Fe, Mg, K and Ti, which may indicate the presence of calcium carbonate fractions in  
255 the area.

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

264 To interpret the geochemical origin of major elements, Al vs. Ti plots is used as provenance indicator for  
265 sedimentary terrains (McLennan et al., 1979) that distinguish the sources of three rock categories: basalt,  
266 intermediate and granite provenances. Al vs. Ti bivariate plots of the current moss predominantly belongs to *basalt*  
267 *and less to basalt - granite (felsic) intermediate* source (Fig. 3). Fine-grained soils, particularly clay, have higher Ti  
268 contents than coarse material, and the Ti contents will be positively correlated with Al (Huisman et al., 2000). High  
269 correlation between Al and Ti were found in current moss samples ( $r^2 = 0.630$ ,  $p = 0.000$ ) indicating the presence of  
270 *clay minerals (montmorillonite and illite)* in the area under investigation. The Al/Ti ratios range from 2.65 to 9.71  
271 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  
272 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  
273 origin of these elements is mostly from mafic magnetite rocks and less from intermediate (mafic magnetite – felsic)  
274 rocks. These findings are clearly indicating the origin of these elements from local mineral dust particles associated

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

277

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

279

280 K and Ca contents in moss samples are higher in zone A than zone B, indicating the alkaline origin of sand fractions  
281 of zone A. It is supported from carbonate setting of most part of zone A (NAMR, 2010). The K/Al ratios of clay  
282 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  
283 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  
284 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  
285 is mainly from the feldspar and K-feldspar sources (Armstrong-Altrin et al., 2016). It suggest that the minerals  
286 responsible for the increased of K/Al ratios should be present in silt and/or sand fractions (Huisman et al., 2000). On  
287 other hand, K is an essential nutrient for plant growth and is classified as a macronutrient due to large quantities of  
288 K being taken up by plants during their life cycle. For this reason, the K/Al ratio could not be the best significant  
289 parameter indicating their source in moss. The Al/Ti and K/Al distribution patterns in current moss samples are  
290 shown in GIS maps of Fig. 4.

291 **a. b.**

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

293

### 294 3.2.2. Trace elements

295 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,  
296 V, W, Yb, Zn and Zr) are important prevalence tools for rock derived origin of elements in soil and dust samples.  
297 The results of descriptive statistic analysis of concentration data of the elements in the moss samples of each zone  
298 are shown in the Box-plot diagram of statistical parameters (Fig. 5).

299

300 a.b. c.

301 **Fig. 5.** Box-plot diagram of statistical parameters of concentration data for trace elements present in current moss

302 samples: a. *Litophile elements*; b. *Biophile elements*; c. *Calcophile elements*

303

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

306

### 307 3.2.2.1. *Lithophile elements (Ce, La, Li, Sc, Th, Ti, Yb, Zr)*

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

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

326

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

328

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

331 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  
332 corresponding UCC values (0.75, 0.61, and 2.21 respectively) by indicating the lithogenic origin of Th, La and Sc in  
333 moss samples of zone A. The RLEs values of zone B are higher than of zone A (except Pb/Sc) by indicating the  
334 derivation of these elements of zone B mostly from dense minerals source (Shotyk et al., 2016).

335

336 **Table 3** The range of the ratios between different lithophile elements

337

338 *3.2.2.2. Biophile micro elements (typical micro elements Cu, Mo, and V)*

339 The order of distribution of median concentrations of biophile elements in moss samples of zones A and B were  
340 Mo<V<Cu. The concentration range of Mo and V in moss samples of zone A is higher than of zone B. This is  
341 probably due to V and Mo enrichment from oil, gas and coal minerals present in zone A, oil and gas industry, as  
342 well as shipping activity in coastal areas of the Adriatic and Ionian Seas. The median concentration of Cu in moss  
343 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  
344 sulfide mineralization (Lazo et al. 2007).

345

346 *3.2.2.3. Chalcophile elements (typical elements As, Cd, Cu, Hg, Ni, Pb and Zn)*

347 The order of the distribution of the median concentrations in moss samples of both zones were  
348 Cd<Hg<As<Pb<Cu<Zn<Ni. Zone B is characterized by various mineral deposits such as Cr, Cu, Ni and Fe  
349 minerals. Zone A is characterized by carbonate rocks and sediments of Adriatic and Ionian Seas (NAMR, 2010).  
350 The median values of most elements in Zone B were higher than in zone A (Fig. 5c), which is probably linked with  
351 long range atmospheric transport of pollutants from other parts of Europe (Harmens et al., 2015), fuel combustion,  
352 and most importantly with wind blown dust from industrial waste deposits and sulfide mineral dumps. The statistical  
353 data of Ni (mean, median, minimum and maximum values) differ significantly for both zones. The range of the  
354 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  
355 mg/kg, DW). Higher Ni concentration in moss samples of zone B compared to zone A is mainly due to Ni  
356 enrichment from Ni, Fe – Ni and Ni – silicate mineralization followed by ultrabasic settings present in zone B. To  
357 explain the variations on the concentrations of calcophile elements in moss samples of each zone, the Sc normalized  
358 values of the elements were investigated. Lower Pb/Sc ratio of zone A (1.32 – 23.58, median = 3.18) compared to



359 zone B (1.18 – 9.17, median = 4.3) support the anthropogenic origin of Pb in moss samples of zone B. Pb/Sc ratio  
 360 of the mosses from zone A (average 5.21, median 3.18) is higher than respective ratio of Upper Continental Crust  
 361 (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  
 362 lithogenic origin of Pb in zone A. The maximum value of Pb/Sc ratios (23.6) is found in Station 43 (Zogaj) that is  
 363 affected from the transboundary pollution from metals (Al and Fe) processing industry in Montenegro (Peck, 2004).

364

365 *3.2.2.4. Elements sensitive to redox conditions (Cr, Co, Mo, U, V, Ni and Zn)*

366 Aiming to distinguish the redox properties of regional conditions that affect the composition of mineral dust  
 367 particles, the elements sensitive to redox condition, such as Ni and Zn, redox-sensitive trace elements, such as U, V,  
 368 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  
 369 calculated (Table 4).

370

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

372

373 Ni, Cr, U and Zn are mainly concentrated in zone B, indicating the presence of oxidizing conditions in this zone that  
 374 is rich in Fe, Ni and Cr minerals. Mo content of zone A does not differ significantly from zone B ( $Mo(A)/Mo(B) =$   
 375  $0.97 \cong 1$ ), indicating the presence of this element in both zones. V is concentrated mainly under reducing conditions  
 376 (oil, gas, coal and carbonate areas), and/or affected by aerosols emissions from shipping activity or burning of fossil  
 377 fuels (Viana et al., 2014), and that may explain the higher V concentration in zone A than in zone B. It is a typical  
 378 carbonate area rich in oil, gas and coal minerals, and is under the effect of shipping emission by providing good  
 379 conditions for V enrichment.

380 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  
 381  $(Ni(A)/Ni(B) < Cr(A)/Cr(B) < U(A)/U(B) < Zn(A)/Zn(B) \ll 1 < (Mo(A)/Mo(B) \cong 1 < (V(A)/V(B) > 1)$  (Table 4). In general,  
 382 MORB and continental flood basalts have Ti/V ratios of about 20-50 (Shervais 1982). The range of Ti/V ratios in  
 383 current moss samples is 35-163 (Zone A) and 35-152 (Zone B) (Table 5). Most of the moss samples of zones A and  
 384 B resulted with Ti/V ratios  $> 48$ , indicating the origin of mineral dust particles from alkaline rocks (Shervais 1982).  
 385 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

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

388

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

390

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

398

399 **Table 6** Zr-normalized values of different elements

400

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

406

### 407 3.3. Multivariate analysis

408 Spearman correlation analysis of the concentration matrix data was carried out to distinguish between lithogenic and  
409 anthropogenic origin of the elements in moss samples. Differences between the mineralogical settings of zones A and  
410 B are clearly reflected by the Spearman correlations between most lithophile elements. Significant and strong  
411 positive correlations ( $p \leq 0.005$ ) were found between Al and the elements Li, V, Ti, Fe, As, Hf, Zr, Sc, La, Ce, Yb,  
412 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,

413 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,  
 414 Ta, W, Sc, La, Ce, Yb, Th, U, Cs, Ba, Sr, Sb, Mo and Rb. All these significant correlations are probably related to  
 415 lithogenic and crustal origin of these elements.

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

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

431

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

433

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

435

436 **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,  
 437 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

438

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

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

443 *Factor 1* is the strongest factor representing 34.3 % of the total variance and high positive loads (> 0.5) for Al, Mn,  
444 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  
445 elements associated with crustal elements (Harmens et al., 2015) either from local dust emission or possibly from  
446 soil particles adhering to the moss samples.

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

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

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

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

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

470

#### 471 *3.4. Enrichment factors*

472 One key question related to the present moss samples is whether the elements mainly originate from atmospheric  
473 deposition or from the soil and/or substrate. In general, the chemistry of hosting soils and substrate has been shown  
474 to have a significant effect on the elemental concentrations in plants. Mosses are rootless plants that take nutrients  
475 from atmospheric deposition. No correlations were found between the concentration data of the same elements in  
476 moss and corresponding soil data from the Geochemical Atlas of Albania (Zajmi et al., 1997) representative of the  
477 present moss sampling sites. The lack of correlation between element concentrations in moss and their concentration in the  
478 hosting soils indicate that trace metal concentrations in moss are mostly originating from atmospheric deposition and less from  
479 the substrate soil that moss lives on. With the aim to distinguish the soil and airborne origin of trace elements in current  
480 moss, enrichment factors (EF) were calculated using Al as a marker of substrate pollution (Sardans and Peñuelas,  
481 2005; Achotegui-Castells et al., 2013).

482 The concentration data of elements in surface soil (collected at a depth of 5 cm and a grid of 10x10 km<sup>2</sup>) from the  
483 Geochemical Atlas of Albania were also used for calculation of EF values. The order of EFs values based on their  
484 respective medians are Cr < Ni < Fe < Ti < Pb < Ca < Cu < Zn. The EF values vary from 1.9 (Fe) to 8.7 (Zn), by  
485 indicating that their enrichment in moss is affected by factors other than substrate soil (Sardans and Peñuelas, 2005).  
486 Ti, Pb, Ca, Cu and Zn have EF values higher than 3, indicating considerable airborne enrichment of these elements  
487 in moss samples in Albania. Lower EF values for Cr, Ni and Fe in current moss are related to their high  
488 concentrations in the corresponding soil. The concentrations of Cr and Ni in the surface soil layer of Albania are  
489 very high, indicating the existence of mechanisms of geochemical properties of the area and/or atmospheric  
490 deposition in the soil. Soil samples at various serpentine and industrial sites in Albania contain high levels of Ni, Cr  
491 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  
492 Albania represent their local emission or historical accumulation in soil. High concentrations of these elements are  
493 also present in carbonate soils in South-West part of Albania, indicating their anthropogenic origin mainly as  
494 atmospheric deposition from local sources. In this case, Cr and Ni emissions from the petrol refinery of Ballsh, and

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

497

#### 498 4. Conclusions

499

500 The following conclusions can be drawn:

501

502 • Moss sampling can be used as a complementary method for investigating the presence of trace metals as  
503 contaminants in the atmosphere. Their spatial variability and distribution pattern may allow better understanding  
504 their natural and/or anthropogenic origin. The presence of typical crustal elements is apparently mainly associated  
505 with local and long-term wind blown mineral dust particles, which is considered to be a main emitting source of  
506 trace metals in atmospheric deposition in Albania.

507 • Spatial distributions of elements and relationships between them, the geochemical interpretation of the current  
508 data and the secondary effects, such as redox conditions show local and long-distance migration of these pollutants  
509 and their sources of origin. Spearman correlation coefficients, Zr normalized data and the ratio of the redox sensitive  
510 elements may interpret the geochemical classification and may show the origin of elements present in the current  
511 moss samples considered with respect to different types of local rocks and anthropogenic input.

512 • Factor analysis is a useful tool to identify the most significant associations of the elements and their probable  
513 sources of origin. Four dominant factors are identified, *i.e.* natural contamination linked with lithogenic elements ;  
514 dust from local mining operations; atmospheric transport of pollutants from local and distant sources; and  
515 contributions from air borne marine salts. The negative loadings of K, Na and P and positive loadings of Al, V, Sr  
516 and Li indicate their inverse distribution inside the same area.

517 • The association of observed distribution patterns of elements in moss samples with local geochemistry of the area  
518 under investigation appears to be a useful tool in determining the origin of the elements that are linked strongly with  
519 the presence of mineral dust particles in aerosols.

520 • Albania is exposed to high levels of heavy metal pollution particularly for elements linked with mining operations  
521 and mineral dumps. Generally, areas in western part of Albania remain exposed to high levels of heavy metal  
522 pollution linked mostly with oil and gas industry and shipping traffic, whereas areas in eastern part of Albania

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

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

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

529

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542

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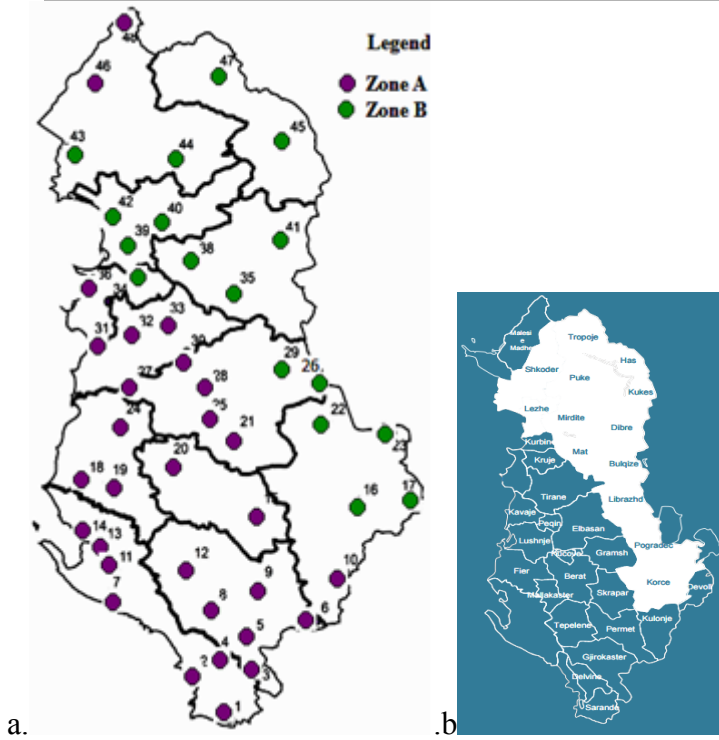
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a.  
Fig. 1.

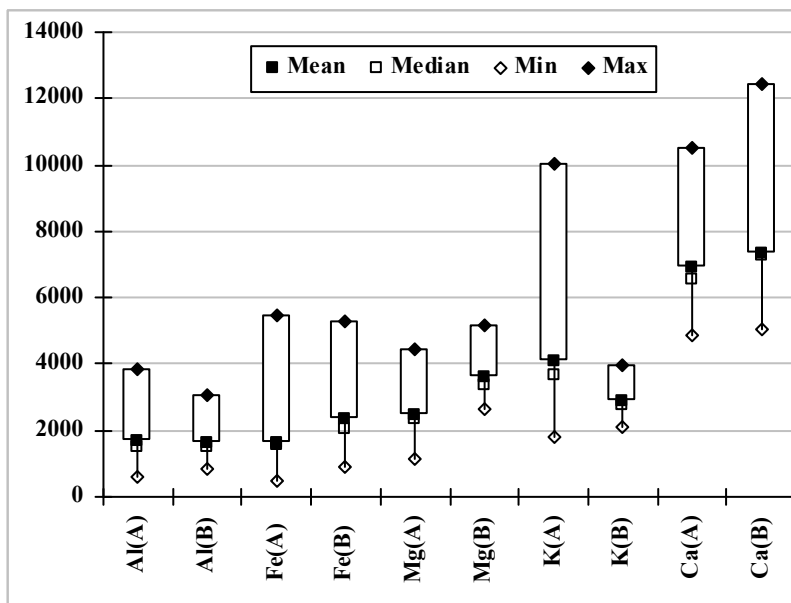


Fig. 2

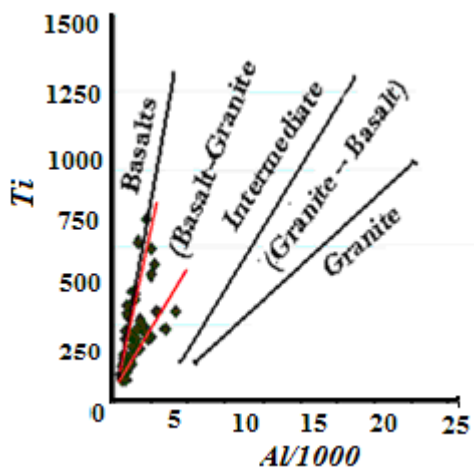


Fig. 3.

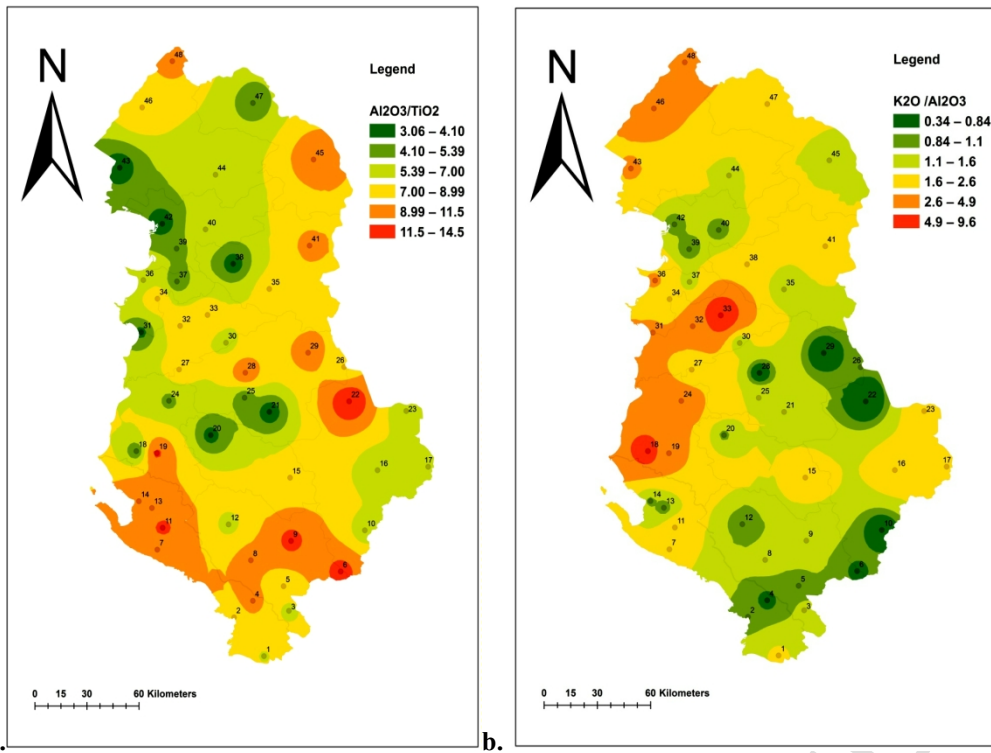


Fig. 4.

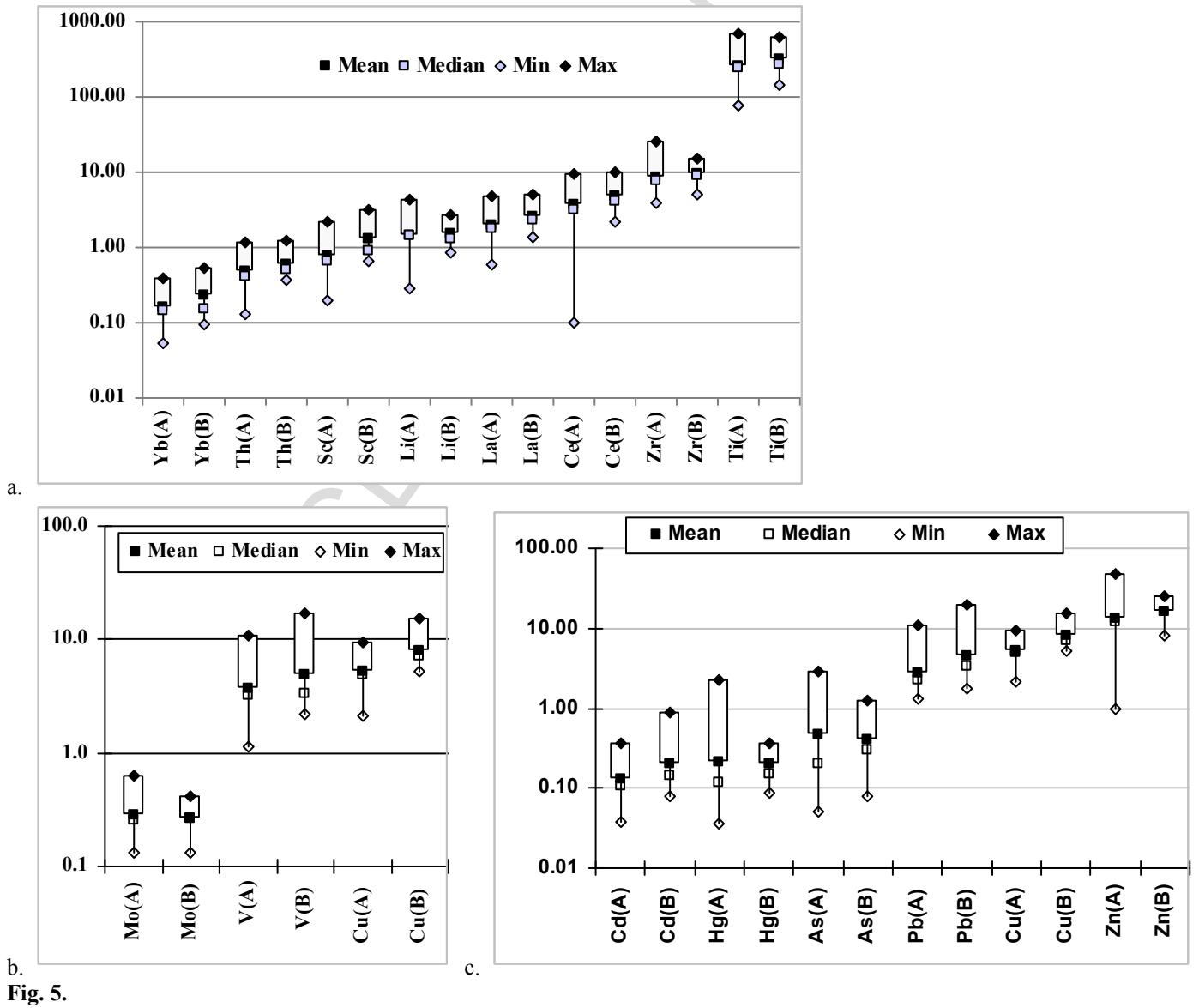


Fig. 5.



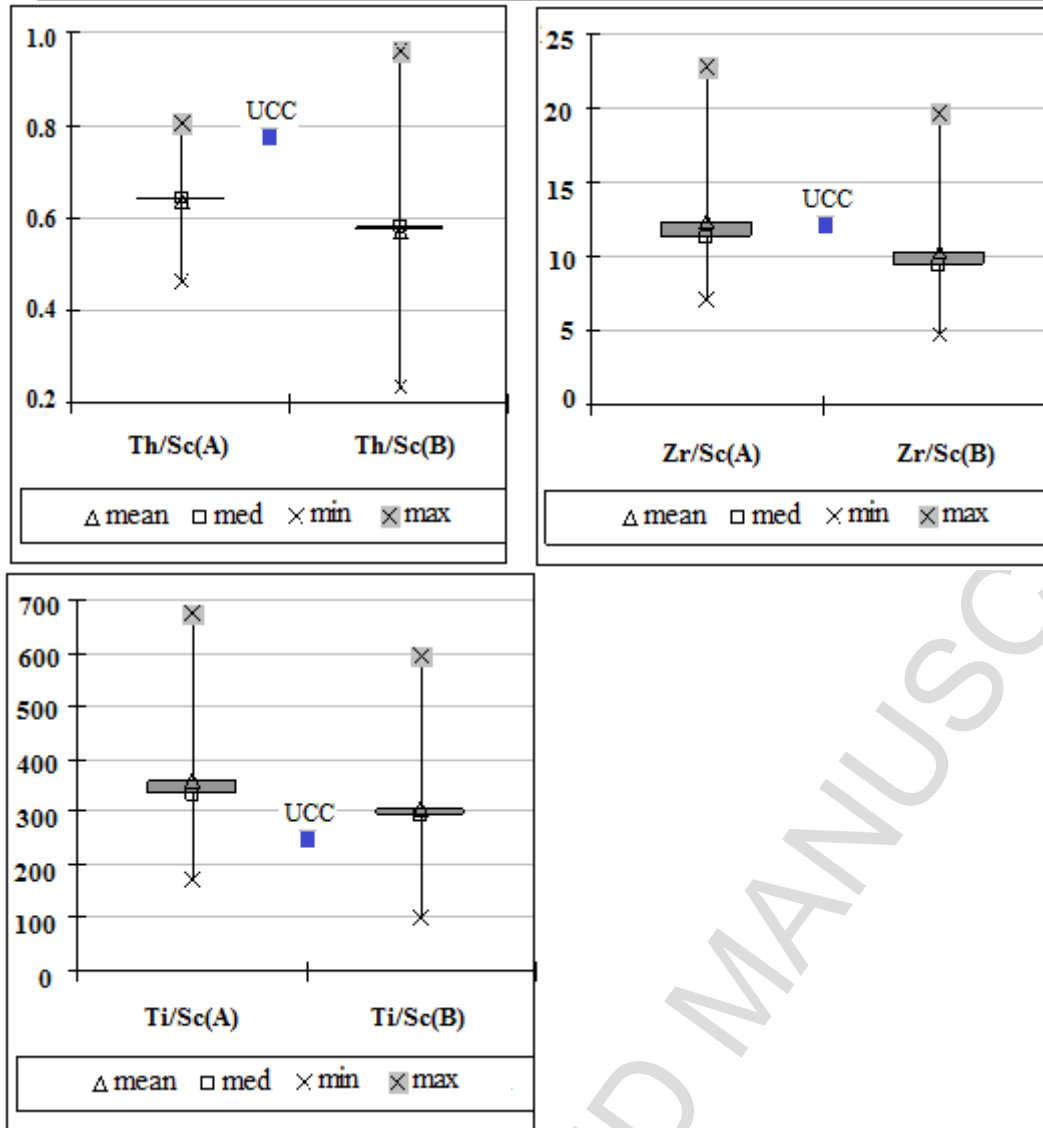
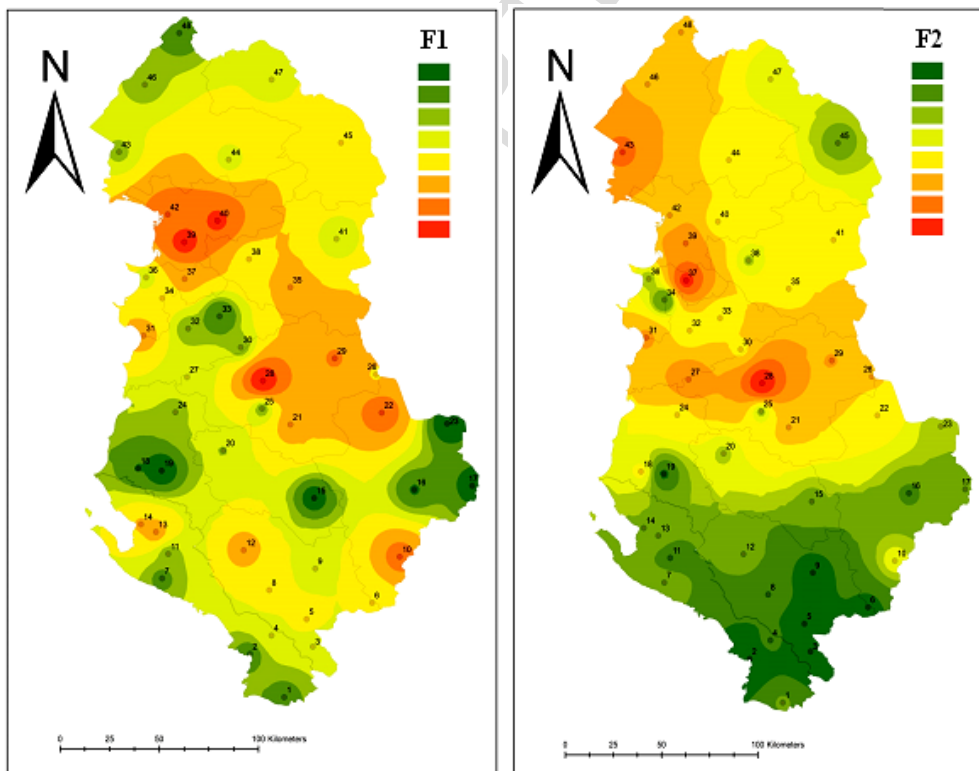


Fig. 6.



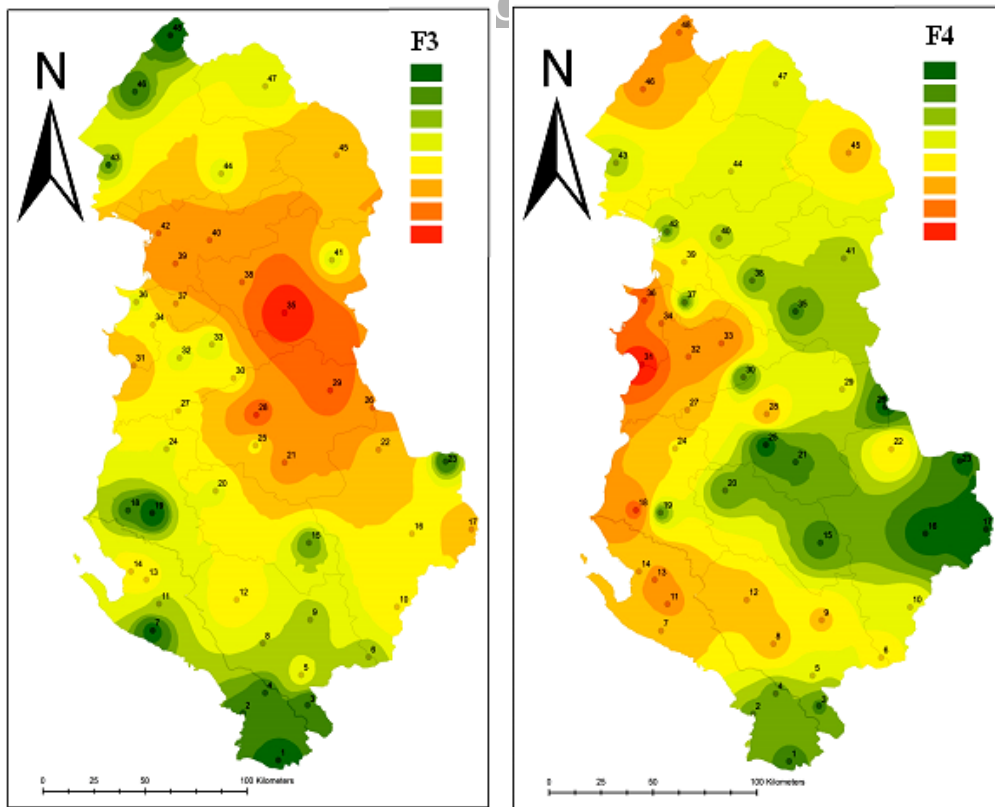


Fig. 7

**Table 1** Limits of quantification (LOQ) of the elements (mg kg<sup>-1</sup>)

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<sup>-1</sup>) 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 <sup>4</sup>	7 910 $\pm$ 142	7 896 $\pm$ 184	Nd <sup>1</sup>	25.00 $\pm$ 1.40	25.0 $\pm$ 8.2
Sc <sup>1</sup>	13.70 $\pm$ 0.69	13.7 $\pm$ 0.7	Sm <sup>1</sup>	4.66 $\pm$ 0.20	4.65 $\pm$ 0.23
Cr <sup>1</sup>	178 $\pm$ 16	178 $\pm$ 17	Eu <sup>1</sup>	1.00 $\pm$ 0.01	0.99 $\pm$ 0.19
Fe <sup>1</sup>	44 800 $\pm$ 986	44 819 $\pm$ 2106	Gd <sup>1</sup>	4.410 $\pm$ 0.119	4.42 $\pm$ 0.28
Co <sup>1</sup>	23.00 $\pm$ 1.29	23.0 $\pm$ 1.3	Tb <sup>1</sup>	0.682 $\pm$ 0.017	0.681 $\pm$ 0.024
Se <sup>3</sup>	1.290 $\pm$ 0.109	1.29 $\pm$ 0.17	Tm <sup>1</sup>	0.326 $\pm$ 0.025	0.325 $\pm$ 0.070
Rb <sup>3</sup>	5.05 $\pm$ 0.11	5.06 $\pm$ 0.90	Yb <sup>1</sup>	2.20 $\pm$ 0.09	2.19 $\pm$ 0.24
Zr <sup>2</sup>	230 $\pm$ 69.0	230 $\pm$ 70	Hf <sup>2</sup>	7.30 $\pm$ 2.19	7.29 $\pm$ 2.19
Mo <sup>2</sup>	1.60 $\pm$ 0.48	1.60 $\pm$ 0.51	Ta <sup>1</sup>	0.8760 $\pm$ 0.0175	0.876 $\pm$ 0.027
Sb <sup>2</sup>	19.4 $\pm$ 1.8	19.4 $\pm$ 1.8	W <sup>2</sup>	3 $\pm$ 0.9	3.00 $\pm$ 0.92
Cs <sup>1</sup>	7.80 $\pm$ 0.70	7.81 $\pm$ 0.71	Th <sup>3</sup>	1.342 $\pm$ 0.036	1.34 $\pm$ 0.04
La <sup>1</sup>	27.80 $\pm$ 1.00	27.83 $\pm$ 1.11	U <sup>1</sup>	2.26 $\pm$ 0.15	2.26 $\pm$ 0.15
Ce <sup>1</sup>	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 (<sup>1</sup> BCR-667; <sup>2</sup> SRM 2710; <sup>3</sup> SRM 1632b; <sup>4</sup> 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	<b>0.707</b>	0.119	-0.108	<b>0.519</b>	0.794
Mn	<b>0.688</b>	-0.192	0.232	-0.260	0.631
V	<b>0.754</b>	0.366	0.062	<b>0.404</b>	0.869
Ti	<b>0.779</b>	0.139	0.039	0.044	0.630
Cr	0.183	0.083	<b>0.784</b>	0.092	0.662
Fe	<b>0.585</b>	0.317	<b>0.434</b>	0.392	0.785
Ni	0.023	0.011	<b>0.793</b>	0.222	0.680
Co	<b>0.528</b>	-0.014	<b>0.726</b>	-0.038	0.807
Cu	0.352	<b>0.511</b>	0.393	-0.366	0.673
Pb	0.052	<b>0.627</b>	0.102	-0.067	0.411
Zn	0.145	<b>0.659</b>	<b>0.432</b>	-0.278	0.718
As	0.252	0.115	-0.173	<b>0.636</b>	0.511
Cd	0.013	0.396	0.344	0.037	0.277
Hg	0.313	<b>0.687</b>	0.191	0.213	0.652
Se	<b>0.402</b>	0.052	0.062	-0.007	0.168
Sb	0.361	<b>0.678</b>	0.281	0.060	0.673
Hf	<b>0.878</b>	0.229	0.044	0.161	0.852
Zr	<b>0.812</b>	0.245	0.098	0.126	0.744
Ta	<b>0.420</b>	0.167	0.138	0.138	0.243
Mo	0.377	<b>0.633</b>	-0.093	-0.012	0.551
W	<b>0.738</b>	0.353	0.195	0.188	0.743
Sc	<b>0.867</b>	0.094	0.320	-0.072	0.869
La	<b>0.899</b>	0.279	0.088	0.155	0.917
Ce	<b>0.915</b>	0.253	0.102	0.095	0.920
Yb	<b>0.865</b>	0.001	0.141	-0.089	0.775
Th	<b>0.918</b>	0.248	0.072	0.149	0.932
U	<b>0.824</b>	0.215	0.200	0.181	0.799
Na	-0.119	0.125	-0.054	<b>-0.602</b>	0.396

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

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