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The effect of sampling scheme in the survey of atmospheric deposition of heavy metals in Albania by using moss biomonitoring

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Abstract

The atmospheric deposition of heavy metals in Albania was investigated by using a carpet-forming-moss species (*Hypnum cupressiforme*) as bioindicator. Sampling was done in the dry seasons of autumn 2010 and summer 2011. Two different sampling schemes are discussed in this paper: a random sampling scheme with 62 sampling sites distributed over whole territory of Albania and systematic sampling scheme with 44 sampling sites distributed over the same territory. Unwashed, dried samples were totally digested by using microwave digestion and the concentrations of metal elements were determined by ICP-AES and AAS (Cd and As). 12 elements, such as conservative and trace elements (Al, Fe and As, Cd, Cr, Cu, Ni, Mn, Pb, V, Zn, Li) were measured in moss samples. Li as typical lithogenic element is also included. The results reflect local emission points. The median concentrations and statistical parameters of elements were discussed by comparing two sampling schemes. The results of both sampling schemes are compared with the results of other European countries. Different levels of the contamination valuated by the respective contamination factor (CF) of each element are obtained for both sampling schemes, while the local emitters identified like, iron-chromium metallurgy and cement industry, oil refinery, mining industry, and transport have been the same for both sampling schemes. In addition, the natural sources, from the accumulation of these metals in mosses caused by metal-enriched soil, associated with wind blowing soils was pointed as another possibility of local emitting factors.

Keywords: air pollution; sampling scheme; metals; moss biomonitoring; ICP-AES; EWMA; multivariate analysis; Albania

Introduction

Heavy metal contamination of environment has attracted the attention of the scientists all over the world (Pelgrom et al. 1995; Mazon et al. 2002; Wang and Stuanes 2003; Nadal et al. 2005; Zeng et al. 2009; Wang et al. 2010; Harmens et al. 2008, 2010). The increase of heavy metal concentrations in the environment may have a potential hazard to humans caused by the accumulation in our food chain after a long time of exposure. The distribution of heavy metals in the environment is depended strongly to weather and local conditions (Nali and Lorenzini 2007), especially to wind speed and direction, and vertical and horizontal thermal gradients (Lee and Hieu 2011). The aerosols with small falling velocity are easily transported by the wind and if deposited constantly even in small rate for a long time period, the environmental accumulation will probably pose an increase of environmental and health hazard. The plants are greatly affected by chemical and physical conditions of the environment and may reflect the changes of environmental conditions (Decoteau 1998). In general, the biomonitors provide the data of integrated exposure over a certain period of time and also provide the spatial distribution over a large scale of monitoring by using many sites simultaneously (Chakrabortty S and Paratkar GT 2006). The mosses are recommended as good bioindicators of metal pollution in the atmosphere since 1960 (Rühling & Tyler 1968). *Hypnum cupressiforme, Scleropodium purum, Hylocomium splendens and Pleurozium schreberi* are the most referred species that are larger abundant in Europe (Onianwa 2000; Marka and Sabovljevic 2011). The deposition of air pollutants on mosses is mainly occurs in three forms: as aqueous solution, gaseous form and attached particles. The process of the accumulation of pollutants in mosses occurs through different mechanisms, like the layers of particles, entrapment on the surface of the cells, through the incorporation into the outer wall of cells, through the ion exchange processes and metabolically controlled passage into the cells (Brown and Bates, 1990).

Albania is a small country (28 000 km^2) with a complex geographic relief and geologic setting, and characterized by high anthropogenic influence. The first study of moss biomonitoring atmospheric deposition of metals in Albania was performed under the framework of the *International Cooperative Programme on Effects of Air Pollution on Natural Vegetation* and Crops with heavy metals in Europe (UNECE ICP Vegetation). 12 elements, such as conservative elements (Al, Fe), and trace elements, such as As, Cd, Cr, Cu, Ni, Pb, V and Zn, were measured in moss samples collected in whole territory of Albania during the moss survey in the dry autumn and summer period of 2010 and 2011 (Qarri et al. 2013). The results obtained in this study have been compared with those from the investigations obtained in similar studies in some neighbouring and European countries (Qarri et al. 2013). The distribution of the elements in each sampling site identified the sites of the country with higher levels of these elements and also the main anthropogenic and geological sources.

The purpose of this article is to examine and to interpret the effect of sampling design and density in long-scale environmental study. The sampling design is a fundamental part of data collection for scientifically based decision making (EPA QA/G-5S, 2002). There is no survey investigating how important the homogeneity assumptions are regarding to the practical applications of the reliability parameters (Lanner 2009). The design and density of sampling scheme can significantly influence the interpretation of the survey (Mathews 1996). Systematic sampling is often used in environmental applications because it is practical and convenient to implement in the field. It often provides better precision (i.e., smaller confidence intervals, smaller standard errors of population estimates) and more complete coverage of the target population than random sampling EPA QA/G-5S (2002). The effects of sampling scheme are widely discussed by Skøien and Blöschl (2006). The effects of sampling density variation are considered and related to the quality of data interpretation and environmental assessment. The results are compared with our previous study (Qarri et al. 2013) with a detailed description of spatial trends in heavy metal concentrations in mosses and changes in local emission sources at the national level done in 2010/11.

Materials and methods
Sampling procedure

The carpet-forming mosses *Hypnum cupressiforme* and *Pseudoscleropodium purum* species were selected for analysis. The distribution of the sampling sites throughout Albania is shown in Figure 1. Moss sampling was done according to the guidelines set out in the experimental protocol for the 2010/11 survey (ICP Vegetation 2010). Each sampling site was located at least 300 m from main roads and populated areas and at least 100 m from any road or single house and by excluding the forests or plantation areas, by moving in small open spaces. Sampling and sample handling were carried out using plastic gloves and bags. The composite samples of about five subsamples were used as representative samples of each sampling site. Dead materials and litter were removed from the samples and only the last two to three years' growth segments were used for the analyses. Samples were dried at room temperature and stored in paper bags under those conditions until chemical analysis.

Due to a high diversity of geographical and topographical features of the country, the sampling scheme used in the previous study presents irregular structures and clusters that may have a strong impact on the estimation of the statistics of the variable's data and may affect the analysis of the studied phenomenon. To increase the homogeneity of samples distribution all over the country by ensuring more or less homogeneously distributed with equal density of sampling sites, the number of the sampling sites is reduced from 62, as it reported in our previous research papers (Qarri et al. 2013, 2014), to 44 sampling sites (see Fig. 1). The detailed information regarding the description of sampling points are given in our previous publication (Qarri et al. 2013)

Figure 1 The map and the coordinates of sampling sites of Albania a) *irregular sampling scheme* (N=62 samples); b) close to *systematic sampling scheme* (N=44 samples)
(Latitude: 41°00´ North of the Equator, Longitude: 20° 00´East of Greenwich)

Chemical analysis

Acid-digestion for total digestion of moss samples according to the method presented by Barandovski et al. (2008) and Balabanova et al. (2010) of dried samples was performed in a microwave oven (MARS, CEM, USA). All of the reagents that we used in this study were with analytical grade: nitric acid, trace pure (Merck, Germany), hydrogen peroxide, p.a. (Merck, Germany), and bi-distilled water.

The metal concentrations were determined by using inductively coupled plasma spectrometry (Varian 715-ES, ICP optical emission). Optimal operating instrument parameters and the detection limits calculated as 3 SD of the lowest instrumental measurements of the blanks are given in the previous study (Balabanova et al. 2010; Qarri et al. 2014). Electrothermal atomic absorption spectrometry (ETAAS) was used for the determination of As and Cd (Varian, SpectrAA 640Z), performed at the Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Macedonia. All metal concentrations (including mercury) are expressed as mg kg^{-1} dry weight at 40°C. For further data processing, values below the quantification limit were set at the quantification limit.

Quality control

The quality control of ICP-AES results was checked by multiple analyses of the examined samples and the certified moss reference materials M2 and M3 (Steinnes et al. 1997; Harmens et al. 2013). The measured concentrations were in good agreement with the recommended values. The certified and the obtained data for the content of the analyzed elements in the certified reference moss samples M2 and M3 are reported in the previous study (Qarri et al. 2013). Besides, blanks run parallel to the decomposition and the analysis of the samples.

Data processing and statistical analyses

Various statistical analysis techniques can be used in spatial distribution measurements to reveal the underlying deterministic behaviours, and thus help clarify the cause and the effects of relationships in environmental problems (Qarri et al. 2013). The analytical data were entered into a 12x44 data matrix and Descriptive Statistics method was applied to the elemental concentration data set to interpret results and explain variations in the data.

The analysis of variance (ANOVA) is used to clarify the effect of sampling scheme, i.e. homogeneity and density of sampling scale, to statistical analysis of the data. The ANOVA compare the continuous measurements to determine if

the measurements are sampled from the same or different distributions. It is an analytical tool used to determine the significance of factors on measurements. Two-way ANOVA which tests the effects of two factors and their interaction on a response variable is used to compare the variances of the data obtained by two different sampling schemes. The two-way ANOVA tests for the null hypotheses of equal means for each factor are used. As we have only one observation per sampling site, two-way ANOVA without replicate is used. However, the F-statistic test for the null hypothesis of no sampling scheme effect (Ho) is highly significant ($p < 0.0001 \ll 0.05$) is applied. The *Mann-Whitney* test is applied to check the uncertainty of sampling scheme. The Mann-Whitney test compares two independent groups of random sampled data from two populations that have the same shape, the equal variances and the data have a scale that is continuous or ordinal if discrete. The Mann-Whitney test is used to calculate the statistic test of the following hypotheses:

Null hypothesis (H0): The two samples come from identical populations and the central tendency of the populations is equal ($\eta1 - \eta2=0$).

Alternative hypothesis (H1): The two samples come from different populations and the central tendency of the populations is not equal ($\eta1 - \eta2 \neq 0$).

The Pearson Product-Moment correlation coefficient is used to determine the significance of the relationship or association of two variables that may indicate that the variables do indeed affect to each other, but it does not indicate what relationship it is. Finally, the data were processed by cluster analysis (CA) and factor analysis (FA) with Varimax Rotation by using the MINTAB 17 software package. Cluster analysis, is an important tool in multivariate statistical analysis, and were used to identify and characterize the contamination sources. It is used to detect the groups of samples with similar patterns of element concentrations, and the numbers of the groups and the most important factors are discussed. Cluster analysis simply discovering the structures in data without explaining interpretation why they exist. Some basic knowledge about the studied system may help to explain and interpret the results of cluster analysis and the structure of the data.

FA is a powerful technique often used in ecology to reduce the amount of data and stabilize subsequent statistical analyses (Vaughan and Ormerod 2005). FA plot of loadings were used to shows correlations between the original variables and the first two factors.

The possibility to use Time series analysis of atmospheric pollution data is discussed (Salcedo et al. 1999; Lam et al. 1999), by finding good correlation among variables (Lam et al. 1999). EWMA chart was used to detect the linear trend of the variables (Bissell 1984; Aerne et al. 1991) in univariate mode. EWMA control scheme is also efficient in detecting potential shifts in location, scale, and shape parameters (Liu et al. 2013). In addition, nonparametric control charts in multivariate spatial rank-based have been discussed by Zou et al. (2012). The analytical data of all observations were entered into a data matrix and EWMA chart and multivariate analysis was used to interpret the spatial series data of this study. As is described by Qarri et al. (2013), the univariate control chart was used to investigate the moving range of two successive observations and to estimate variability of data by using median values were used instead of average data for spatial distribution characterized by an irregular distribution of nonparametric data set. The values of the European median of each element are used as a reference line. The upper and lower control limits (UCL and LCL) were computed for the median moving ranges, by applying pooled standard deviation, the proper values of λ (the weight of EWMA, that range from 0 to 1) and k- value . The value of λ was carefully chosen to balance the robustness to non-normality and the detection ability to various shift magnitudes (Stoumbos and Sullivan 2002). Based on the median concentration of each element, the proper k values (k=(1 to 3)StDev) is selected. For the elements with high values of standard deviation compare to their median values, a small k value is selected.

Results and Discussions
Spatial patterns in Albania
The 2010/2011 data on the concentrations of 12 elements in 44 moss samples from Albania are summarized in a data matrix. The analytical results were statistically treated by using Descriptive statistics. Statistical data of the concentrations of the trace metal in moss samples are shown in Table 1.

Table 1 Descriptive statistics of the concentrations data of Al, As, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn (mg/kg, DW) in moss samples (n=44)

The order of the distribution of the elements based on their median values is as follows: Fe>Al>Mn>Zn>Ni>Cr>Cu> V> Pb> Li>As>Cd. Most of the studied elements (except Cd, Pb and Zn) follow the lognormal distribution ($p > 0.05$). The elements Ni, As, Pb, Cd, Cr and Zn present high disparity in their concentrations in moss samples characterized by high coefficients of variation (CV>75%) and lower mean values against their high variances (see Table 1). The order of their CV values is as follows: Ni (164%)>As (120%) >Pb (101%)>Cd (98%)>Cr (86%)>Zn (76%). It means they are positively skewed, that is typical with elements abundance and distribution of mineral resources in the Earth's crust (Clarke and Washington 1924; Vinogradov 1962). On the other hand their high values of skewness and kurtosis indicate that their distribution is influenced by complicated factors Generally, the highest values of these elements were measured near the industrial centers (iron-chromium metallurgical plant, cement factory, oil refinery etc.) and heavy traffic positioned mainly in the central part of the country and mines and mineral dumps.

The present median values of the elements Al, Fe, V, Cr, Ni and Zn, typically associated with air pollution are generally comparable with those presented from other neighboring countries (Balabanova et al. 2012; Barandovski et al. 2012,

2013; Spiric et al. 2012; Thöni et al. 2011), but higher than the corresponding values from most European countries (Harmens et.al. 2010, 2013). These countries participate at ICP Vegetation Programme of 2010/2011 and have used the same methodology for the 2010/11 survey like moss species, field sampling and analytical methodology, and a quality control exercise was conducted for assessing the analytical performance of the participating laboratories. Moss reference material M2 and M3, first prepared for the 1995/6 European moss survey (Steinnes et al., 1997), are used for quality control (Harmens et al. 2013). The data set of 2010/2011 survey (Qarri et al. 2013) is characterized by the lognormal distribution (P>>0.05, except Cu and Pb) of most of heavy metal concentration in moss samples. The lognormal is a skewed distribution. Therefore the mean and median of lognormal distribution do not provide similar estimates for the location and there is no obvious answer to the question of which is the more meaningful measure of location.. In this case, all three measures are useful, while the data sets with high kurtosis tend to have a distinct peak near the mean that may be used as the typical value. After the reduction of the number of samples from 62 (Qarri et al. 2013, 2014) to 44, some statistical data and particularly the mean and the median values are increased, by indicating differences in the contamination levels among the sampling sites caused by the influence of sampling scheme. The excluded sampling points are characterized by low content of the studied elements (except Al), so the differences between the mean values of two sampling schemes are more significant than the differences between the median values of the elements.

The results are compared with our previous study (Qarri et al. 2013). Among 25 European countries that reported the concentration of trace metals in moss samples collected on 2010/2011 (Harmens et al. 2010), the order of median distribution of the elements of Albanian moss samples compared with other European countries have changed by moving between the countries with higher concentration of these elements. The pairs of the variances of the data set of 12 elements obtained for N=44 sampling scheme and for N=62 sampling scheme (see Table 2) are compared by using ANOVA analysis (Two Factors Without Replication). The results are shown in Table 3.

Table 2 The variances of the data set of 12 elements obtained for N=44 and for N=62 sampling scheme (Qarri et al.2013)

Table 3 The data of ANOVA analysis (Two-Factors Without Replication)

ANOVA

The results of a paired F-test of the raw data set that express the pairs of the variances of the same element for two sampling schemes, is higher than the value of F_{crit}. The F-statistic for the null hypothesis of no difference between two sampling schemes is significant (F=99.3>> F_{crit} =2.82, P<0.001). The F-statistic for the null hypotheses of no difference between two sampling schemes is not significant (p-value = 0.55> 0.05 for column data). Thus, we conclude that two sampling schemes are strongly affecting the environmental data of moss samples. The number of samples of the raw data of each column variable of each sampling scheme are not equal (N_1=44 and N_2 =62), so the *Mann-Whitney* test is also applied to check the uncertainty of sampling scheme. The results of the *Mann-Whitney* tests of η1 = η2 vs η1 ≠ η2 are significant at P>0.05, that accept the *Null hypothesis (H0) as true.* As the variances of two sampling scheme are not equal, the results of the *Mann-Whitney* test are doubtful and the results of F-statistic test are true.

For a better interpretation of the results, the *contamination factor scales* (CF) were calculated. Different approaches are used to evaluate the pollution status of heavy metals in sediments and soils (Geo-accumulation Index-I_{geo}, Enrichment Factor-EF, Pollution Load Index-PLI and Risk assessment Code-RAC) (Dung et al. 2013), while contamination factor (CF) is proposed to use for assessing heavy metal pollution of air by using mosses as bioindicator (Fernandes et al. 2000). The CFs are calculated as the ratio of the median value of each element for Albanian mosses and the median value of the respective element taken from a control area of Norwegian terrestrial mosses (Steiness 2011). A Norwegian place (Steiness 2011) with very low contaminated level and contamination sources is used as control area and the analytical data obtained from the moss survey of this area (Steiness 2011) are used for the calculation of CF values as is recommended by Fernandes et al. (2000). The CF scale allows the categorization of the sampling sites by taking into account the method of dispersion of each contaminant in the atmosphere. The scale is based on specific approach to terrestrial mosses, established by Fernandez et al. (2000). The results of CF values are shown in Table 4.

Table 4 The data of the contamination factors (CF) and contamination classification (Fernandez et al. 2000) for metal concentrations in mosses in Albania (N=44)
[1] Norway data (Steiness 2011); [2] No contaminated

The CFs results indicate that the elements Cu and Zn are associated with the first two categories of scale, C2 and C1, i.e., uncontaminated areas (a CF of 2 can easily be obtained from natural variation), while the Cd is associated with the third scale (C3) of contamination category and is described as slightly polluted areas. The elements As and V are associated with the moderately polluted scale of classification (CF=4) and Cr, Ni, Fe and Al (CF=5) are associated with the severe polluted scale of classification. The effect of sampling scheme is very significant regarding CF values of most of the elements are higher compare to our previous study given for N=62 sampling sites (Qarri et al. 2014).

The EWMA univariate charts (Qarri et al. 2013) were constructed to detect the variability of the data and local emission points (Figure 2). The results of EWMA Chart of the studied elements are shown in Table 5. The maps of the distributions of these elements are reported in our previous research paper (Qarri et al. 2014).

Table 5 The results of EWMA Chart of As, Cd, Cr, Cu, Ni, Pb, V, Zn, Mn, Al, Fe, Li regarding the most contaminated areas

Figure 2 The EWMA univariate charts of the studied elements spatial distribution in all sampling sites in Albania (X – the median value, "----" – the European median, UCL – the upper control limit, LCL – the low control limit).

The median values of As, Cr, Ni, Al and Fe of moss samples of Albania are higher than the corresponding median values of Europe, while the median values of Cd, Cu, Pb and Zn of moss samples of Albania are lower than the corresponding median values of Europe. The background level Cr, Ni, Al and Fe (the values lower than LCL) of moss samples of Albania are higher than the corresponding median values of Europe, by indicating the high pollution level of these elements in moss samples of Albania. Heavy metals are not biodegradable and they occur in environment and living organisms and it is difficult to distinguish their natural and anthropogenic concentrations. Most of the guidelines for environmental legislation are based on background values and toxicity levels (Carlon 2007).
We have applied the statistical method for the evaluation of the background level of heavy metal in moss samples that are used for air monitory of this study. The median values and the 2 maximum absolute standard deviation (MAD) (Matschullat et al. 2000, Reimann et al. 2005) are used to identify the outliers of each element. The values of [median + 2 SDEV] are referred as the upper limit of geochemical background variation and this was suggested as ''threshold level'' for clean up goal of environmental legislation (Reimann et al. 2005), while the values of [median - 2 SDEV] are referred as the background level. The most contaminated areas and their sampling sites are listed in Table 5.

The EWMA control charts of both sampling schemes (N=44 and N=62) and GIS mapping technique (Qarri et al. 2013, 2014) provided similar results, as is shown for Cr and Zn in Figure 3.

Figure 3 Cr and Zn spatial distributions in Albania based on EWMA univariate control chart and GIS technique

Arsenic
Arsenic concentrations in mosses were generally low in western part of Albania. High levels of arsenic were observed in the eastern part of Albania, but lower than Macedonia, Romania and Bulgaria (Qarri et al. 2013; Harmens et al. 2013). Arsenic occurs naturally in soil and minerals and may enter the air as windblown dust particles (WBK & Associates Inc. 2004).

Cadmium, Cupper and Zinc
Cu, Cd and Zn concentrations were generally low in mosses sampled in Albania compared to many other European countries (Harmens et al. 2013). These elements are typical elements which are consequences of air transport and they are not influenced by lithological background. Road transport may have a considerable effect on the high content of Pb in mosses, while Pb acts as the marker element for motor vehicle emissions (Huang et al. 1994). Zn and Cu are mostly associated with city dust, traffic exhaust, soil and re-suspended road dust. Zn is present near the heaviest traffic areas in the central part of Albania and in the north of the central part of the country with high mineralization of sulfides (Lazo et al. 2007).

Chromium, Iron, Nickel, Vanadium and Aluminium
The main contribution of Cr, Fe, Ni and V elements is coming from the Elbasan iron-chromium metallurgical plant (Lazo et al., 2013) and mining industry in Albania. The maps (Qarri et al. 2013) suggest a high level of wind blow dust in the south and high level (for most metals) of industrial activity focused on the central part of Albania. These associations may be attributed to their geogenic origin (Tume et al. 2010). The association Cr and Fe are also related to air pollution (Lazo et al. 2013). Their highest concentration (Fig. 2) is present near the iron-chromium metallurgy in Elbasan town and chromite deposition areas of Albania.
Aluminium is a good indicator of mineral particles, mainly from wind blown soil dust. The spatial pattern of aluminum concentrations in mosses may provide an indication of the contribution of wind re-suspension to the deposition of metals to mosses, reflecting to some extent historical deposition of heavy metals (Harmens et al. 2013).
The highest Al concentration was found in the south part of Albania caused by the wind influence is stronger in Southeast direction (aea-al.org, Albania/WERA_Ex%20Summary) and in the central part that is under the influence of metallurgical plant and cement industry in Elbasan area.

Multivariate analysis
Correlation of the elements
To distinguish between lithogenic and anthropogenic origin of the elements in moss samples, correlation analysis was carried out. The results of correlation analysis are shown in Table 6. Significant correlation (p<0.001) was found among the certain pairs of trace metals, especially Al/Li (r^2=0.92), Al/Fe (r^2=0.73), Cr/Fe (r^2=0.81), and Li/Fe (r^2=0.78) (Table 6). Al and Li are typical crustal elements (Clarke and Washington 1924; Vinogradov 1962) by suggesting their lithogenic origin in moss samples caused by wind blowing soil dust.

Table 6 Pearson Correlation Coefficient between element concentrations in mosses in Albania.

Cell Contents: P-Value: [1] P<0.001, [2] P<0.005, [3] P<0.01

Significant correlations were found between the moss trace and major elements. Among the 60 correlations, 31 correlations are significant and positive (Table 7). Linear regression is displayed for the significantly correlated elements ($r^2>0.5$, P <0.005) and the statistical parameters are calculated.

Table 7 Univariate linear regressions between selected elements in moss samples of Albania (N=44)

The linear regression for the most significantly correlated elements ($R^2>0.8$, P <0.005) indicate that the values of the slopes$\neq$0 and F> F_{crit} =1.8 (P<0.005) meaning that the linear relationship between two elements (x and y) is significant.

Multivariate analysis
To investigate the similarity of the distribution of the variables among moss samples, a cluster analysis was applied to the available data set.

Figure 4 The dendrogram of cluster analysis of 12 elements studied at 44 moss samples in Albania. (Correlation Coefficient Distance, Complete Linkage, Similarity Level 70%); Final Partition: Cluster 1: As, Al Li. Cluster 2: Cd; Cluster 3: Cr Ni Fe; Cluster 4: Cu Pb Zn; Cluster 5: V: Cluster 6: Mn

The dendrogram of cluster analysis based on Pearson correlation coefficients (see Fig. 3), shows that the deposited elements can be divided into two subgroups and six small groups (Single Linkage; Correlation Coefficients Distance; Similarity level 70 %). The first subgroup is associated with Al, Li, As, V and Mn that are typical elements of lithogenic and geogenic origin. The second subgroup is associated with Cd, Cu, Zn, Pb, Cr, Fe and Ni that are typical elements of geogenic and anthropogenic origin.
Cluster (1) is associated with Li, Al and As. The association of Li and Al (similarity level >90%) may be attributed to their lithogenic origin as typical elements of crustal soils (Clarke and Washington, 1924). The presence of these elements in moss samples reflects the dry and wet deposition of soil dust particles (PM10 and PM2.5). As is probably originate from lithogenic and geogenic origins that related to sulfide mineralization in the north part of Albania (Lazo et al. 2007);
Cluster (2) is associated with Cd. Phosphate fertilizers in agricultural areas are the most important emission source of Cd in moss samples (Harmens et al. 2010) caused by during dry and wet deposition. The association of Cluster (2) with Cluster (4) (Cu, Zn and Pb) in the same subgroup with 64.8% of similarity may be related to their anthropogenic origin caused by manufacturing industries, construction, road transport and waste incineration.
Cluster (3) is associated with Cr, Ni and Fe as typical elements of chromium ores positioned mainly in Bulqiza, Shebenik and Librazhdi areas, chromium mineral processing plants and industrial emission of Elbasani chromium-iron metallurgical plant.
Cluster (4) is associated with Pb, Cu and Zn. These are typical elements which are consequences of air transport and not influenced by lithological background. Road transport may have a considerable effect on the high content of Pb in mosses, while Pb acts as the marker element for motor vehicle emissions (Huang et al. 1994). Zn and Cu are mostly associated with city dust, traffic exhaust, soil, and re-suspended road dust. Zn is present near the heaviest traffic areas in the central part of Albania and in the north of the central part of the country with high mineralization of sulfides (Lazo et al. 2007).
The same result was obtained in our previous article (Qarri et al. 2014). The association of Clusters (2, 3 and 4) in the same subgroup explains that they have some common factors partly influenced (with similarity level only 46.9%) on their distribution in moss samples. The most probable factor is metal industry, manufacturing industry and road transport.
Cluster (5) is associated with V. This association may be attributed to the geogenic origin of titanium-magnetite ores of Lezha area, and anthropogenic origin caused by petroleum reefing industry in the south part of the country.
Cluster (6) is associated only with Mn. This association may be attributed to wind soil dust and anthropogenic origin of industrial emissions, particularly iron alloy production, iron and steel foundries. The combustion of fossil fuels, and re-entrainment of manganese-containing soils are another way of anthropogenic emission of manganese release in the air (Lioy, 1983).
This kind of classification clearly explains the lithogenic, geogenic and anthropogenic associations of these elements that are probably caused by wet and dry depositions of soil dust in moss samples, and traffic and industry emissions. For a better interpretation of factors influencing the association and distribution of the studied elements in moss samples, factor analysis with Varimax Rotation was used (Table 8). The results of Factor analysis, the factors with high variances and high factor loadings were interpreted as source categories contributing to elements distribution and their concentration level at the sampling sites. The main criteria in selecting the optimal models of source identification of major sources with physically reasonable Factors are those Eigen values or variances larger than 1 after Varimax Rotation.

Table 8 Maximum Likelihood Factor Analysis of the Correlation Matrix of As, Cd, Cr, Cu, Ni, Pb, V, Zn, Mn, Al, Fe, Li

Three main factors were extracted from factor analysis. These factors explain 65.5% of the variance using 12 variables of the data set (Table 8).

Factor 1 (F1) explains 29.3% of the total variance and is dominated by the elements Al, Li, Fe, As, V and Mn with high positive factor loadings (see Table 8). This group of elements is probably naturally distributed as typical soil elements (Rudnick 2003) and typical elements of crustal material (Clarke and Washington 1924; Vinogradov 1962). Most probably, this factor may reflect the contamination of moss samples by soil particles caused by wind soil dust. The presence of Al in this group is a confirmation of this assumption, since Al compounds are insoluble and most of the Al found in biological systems comes from dust contamination (Qarri et al. 2014).

Factor 2 (F2) explains 20.4% of the total variance and is dominated by Zn, Cu, Pb and Cd with high positive factor loadings. This factor is probably distinguished by the typical anthropogenic source related mainly to traffic emissions. The elements Cr, Fe and V appear weak positive factor loadings at F2, by explaining their dual form of distribution: geogenic (F1) and anthropogenic (F2) one.

Factor 3 (F3) explains another 15.8% of the total variance and is dominated by Cr, Ni and Fe with high positive factor loading (see Table 8). The association of these elements is distinguished by their geogenic origin (chromite mineralization and nickel-iron mineralization of Albania (aea-al.org) and anthropogenic origin of industrial emission from chromium-iron metallurgy positioned in Elbasan area (central part of Albania).

Factor 4 (F4) is the weakest one that explains another 11.6% of the total variance and is dominated only by Mn with high positive factor loading (see Table 8). The manganese presence in the air is caused by both natural and anthropogenic origin. Natural emission sources of manganese to the atmosphere are the result of erosion of soils and dusts.

Conclusions

The ranges and medians of the concentrations in mg/kg, DW of twelve metals in the moss samples of Albania reflect high pollution level. Our finding shows that the spatial distributions of these elements do not depend in sampling scheme. In both cases (N=44, more or less regular distribution of sampling sites, and N=62, or heterogeneously distributed sampling sites) the statistical parameters are object of high variability. After the reduction of the number of samples from 62 (Qarri et al. 2013, 2014) to 44, some statistical data and particularly the median values are increased, by mean that higher pollution level exists among the sampling sites. The median values of the studied elements (N=44) are higher than the median values of Europe 2010 study. It is proved that the sampling scheme regarding the homogeneity and density of sampling sites has a strong effect on the statistical results of the analytical data set and the level of the pollution in the studied area. It is proved that the systematic sampling scheme with an accepted sampling homogeneity and density level provided more reliable results.

Most of the elements (except Al) spatial patterns have a low concentration in the south area of the country, and high values in the East and NE part of the country. A local "hot spot" in the central part of Albania was distinguished that is caused mainly from metal alloy industry and mining industry. The Al spatial patterns show a low concentration in the north area of the country, and high values in the central part and SE part of the country. The modified EWMA univariate control chart (Qarri et al. 2014) was successfully used to investigate the spatial distribution of the elements and to estimate the variability of the data. The spatial distribution of the elements shows similar views for N=44 and N=62 sampling sites, by indicating a lower effect of sampling scheme in spatial distribution of the data.

The results obtained show again that the moss biomonitoring provides a cheap, complementary method to deposition analysis for the identification of areas at risk from high atmospheric deposition fluxes of heavy metals. The differences in metals concentration in mosses between different parts of the country and the location of emission sources were expressed clearly, that reflect local variation in heavy metal deposition.

Statistical analysis of the data is a powerful tool of data analysis that help us to distinguish reasonable conclusions regarding the spatial distribution of the elements, to reveal the underlying deterministic behavior, and thus help clarify the cause and the effects of relationships in environmental problems.

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Figure Captures

Figure 1 The map of Albania sampling sites: a) irregular sampling scheme (N=62 samples); b) close to systematic sampling scheme (N=44 samples)

(Latitude: 41º00´ North of the Equator, Longitude: 20º 00´East of Greenwich)

Figure 2 The EWMA univariate charts of the studied elements spatial distribution in all sampling sites in Albania (X – median value, "----" - European median, UCL – upper control limit, LCL – low control limit).

Figure 3 Cr and Zn spatial distributions in Albania based on EWMA univariate control chart and GIS technique

Figure 4 The dendrogram of cluster analysis of 12 elements studied at 44 moss samples in Albania.

(Correlation Coefficient Distance, Complete Linkage, Similarity Level 70%); Final Partition: Cluster 1: As, Al Li. Cluster 2: Cd; Cluster 3: Cr Ni Fe; Cluster 4: Cu Pb Zn; Cluster 5: V: Cluster 6: Mn
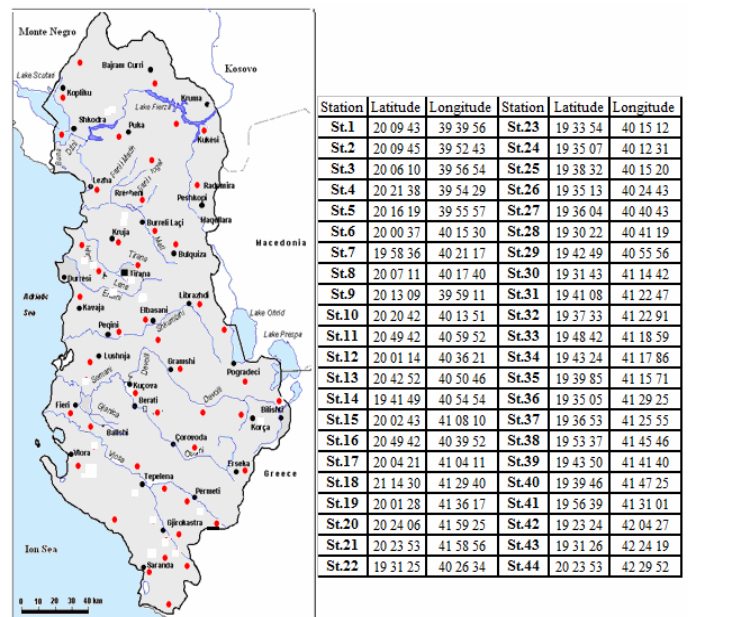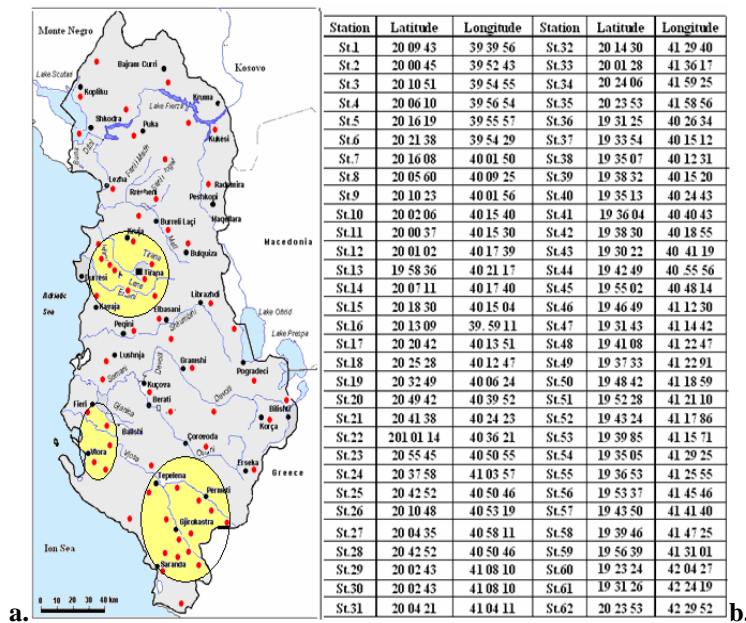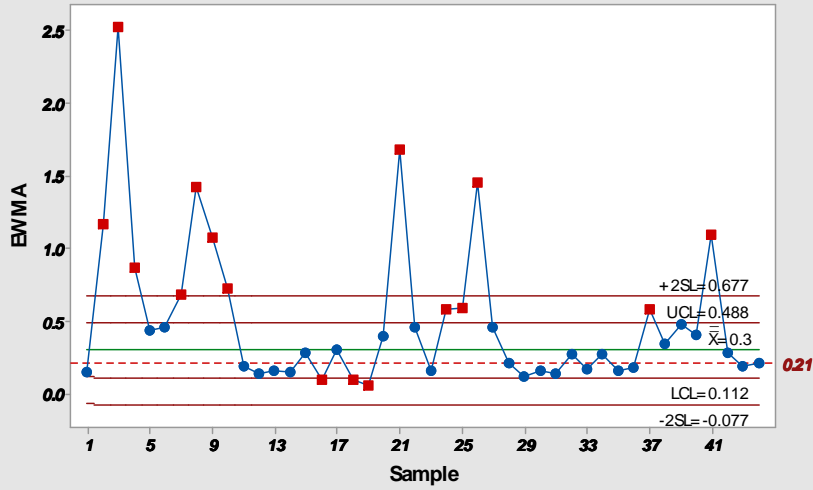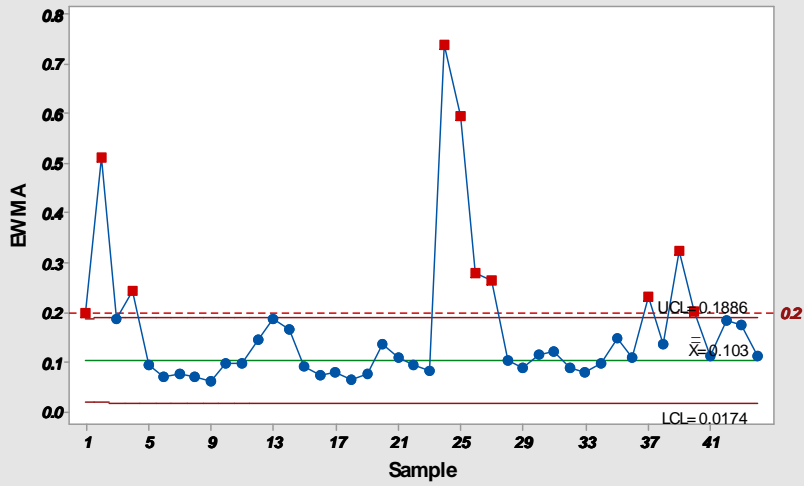

a.

Station	Latitude	Longitude	Station	Latitude	Longitude
St.1	20 09 43	39 39 56	St.32	20 14 30	41 29 40
St.2	20 00 45	39 52 43	St.33	20 01 28	41 36 17
St.3	20 10 51	39 54 55	St.34	20 24 06	41 59 25
St.4	20 06 10	39 56 54	St.35	20 23 53	41 58 56
St.5	20 16 19	39 55 57	St.36	19 31 25	40 26 34
St.6	20 21 38	39 54 29	St.37	19 33 54	40 15 12
St.7	20 16 08	40 01 50	St.38	19 35 07	40 12 31
St.8	20 05 60	40 09 25	St.39	19 38 32	40 15 20
St.9	20 10 23	40 01 56	St.40	19 35 13	40 24 43
St.10	20 02 06	40 15 40	St.41	19 36 04	40 40 43
St.11	20 00 37	40 15 30	St.42	19 38 30	40 18 55
St.12	20 01 02	40 17 39	St.43	19 30 22	40 41 19
St.13	19 58 36	40 21 17	St.44	19 42 49	40 55 56
St.14	20 07 11	40 17 40	St.45	19 55 02	40 48 14
St.15	20 18 30	40 15 04	St.46	19 46 49	41 12 30
St.16	20 13 09	39 . 59 11	St.47	19 31 43	41 14 42
St.17	20 20 42	40 13 51	St.48	19 41 08	41 22 47
St.18	20 25 28	40 12 47	St.49	19 37 33	41 22 91
St.19	20 32 49	40 06 24	St.50	19 48 42	41 18 59
St.20	20 49 42	40 39 52	St.51	19 52 28	41 21 10
St.21	20 41 38	40 24 23	St.52	19 43 24	41 17 86
St.22	201 01 14	40 36 21	St.53	19 39 85	41 15 71
St.23	20 55 45	40 50 55	St.54	19 35 05	41 29 25
St.24	20 37 58	41 03 57	St.55	19 36 53	41 25 55
St.25	20 42 52	40 50 46	St.56	19 53 37	41 45 46
St.26	20 10 48	40 53 19	St.57	19 43 50	41 41 40
St.27	20 04 35	40 58 11	St.58	19 39 46	41 47 25
St.28	20 42 52	40 50 46	St.59	19 56 39	41 31 01
St.29	20 02 43	41 08 10	St.60	19 23 24	42 04 27
St.30	20 02 43	41 08 10	St.61	19 31 26	42 24 19
St.31	20 04 21	41 04 11	St.62	20 23 53	42 29 52

b.

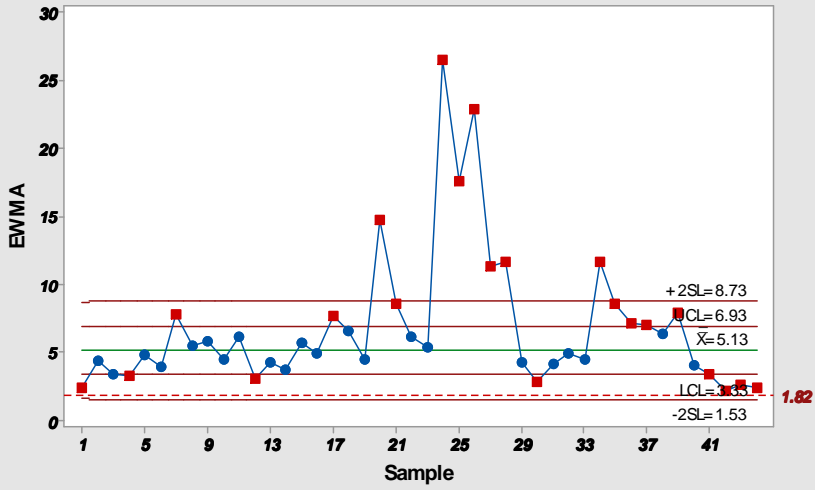| Station	Latitude	Longitude	Station	Latitude	Longitude
St.1	20 09 43	39 39 56	St.23	19 33 54	40 15 12
St.2	20 09 45	39 52 43	St.24	19 35 07	40 12 31
St.3	20 06 10	39 56 54	St.25	19 38 32	40 15 20
St.4	20 21 38	39 54 29	St.26	19 35 13	40 24 43
St.5	20 16 19	39 55 57	St.27	19 36 04	40 40 43
St.6	20 00 37	40 15 30	St.28	19 30 22	40 41 19
St.7	19 58 36	40 21 17	St.29	19 42 49	40 55 56
St.8	20 07 11	40 17 40	St.30	19 31 43	41 14 42
St.9	20 13 09	39 59 11	St.31	19 41 08	41 22 47
St.10	20 20 42	40 13 51	St.32	19 37 33	41 22 91
St.11	20 49 42	40 59 52	St.33	19 48 42	41 18 59
St.12	20 01 14	40 36 21	St.34	19 43 24	41 17 86
St.13	20 42 52	40 50 46	St.35	19 39 85	41 15 71
St.14	19 41 49	40 54 54	St.36	19 35 05	41 29 25
St.15	20 02 43	41 08 10	St.37	19 36 53	41 25 55
St.16	20 49 42	40 39 52	St.38	19 53 37	41 45 46
St.17	20 04 21	41 04 11	St.39	19 43 50	41 41 40
St.18	21 14 30	41 29 40	St.40	19 39 46	41 47 25
St.19	20 01 28	41 36 17	St.41	19 56 39	41 31 01
St.20	20 24 06	41 59 25	St.42	19 23 24	42 04 27
St.21	20 23 53	41 58 56	St.43	19 31 26	42 24 19
St.22	19 31 25	40 26 34	St.44	20 23 53	42 29 52

Fig. 1

EWMA Chart of As

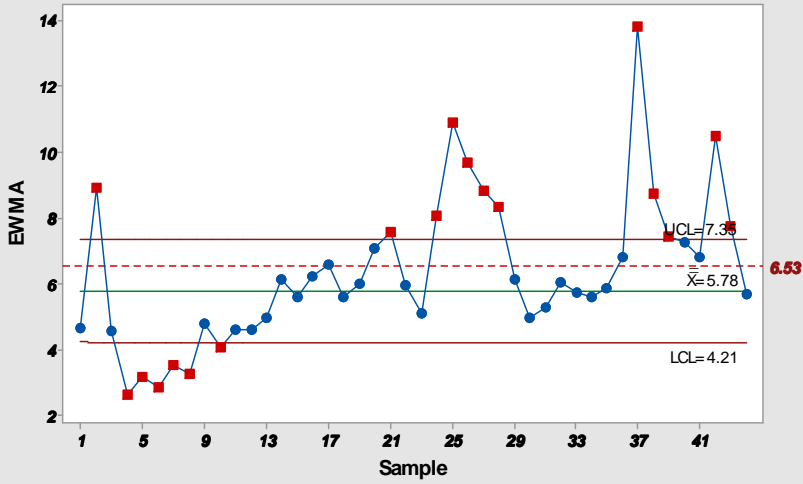EWMA Chart of Cd

EWMA Chart of Cr

EWMA Chart of Cu

EWMA Chart of Ni

EWMA Chart of Pb

EWMA Chart of V

+2SL=6.00
UCL=4.73
$\bar{\bar{X}}$=3.46
1.72
LCL=2.19
-2SL=0.92

EWMA Chart of Zn

31
UCL=17.04
$\bar{X}$=14.34
LCL=11.64

EWMA Chart of Al

+2SL=3048
UCL=2452
$\bar{\bar{X}}$=1857
LCL=1262
762
-2SL=666

EWMA Chart of Fe

+2SL=2964
UCL=2297
$\bar{\bar{X}}$=1629
LCL=961
538
-2SL=294
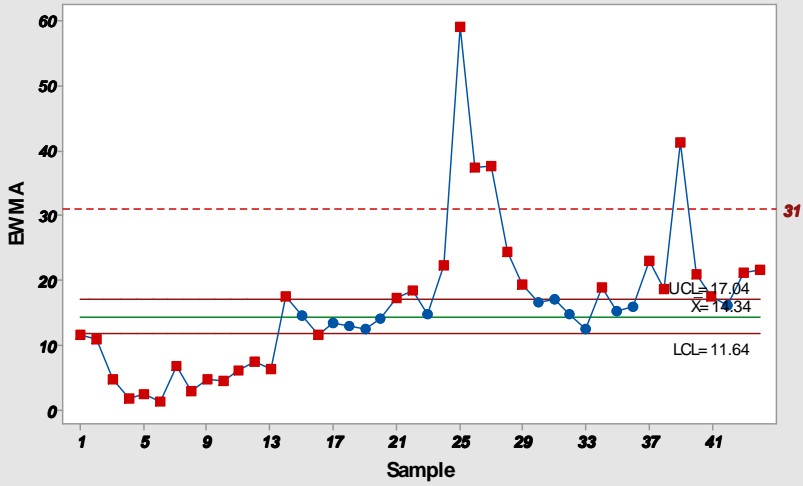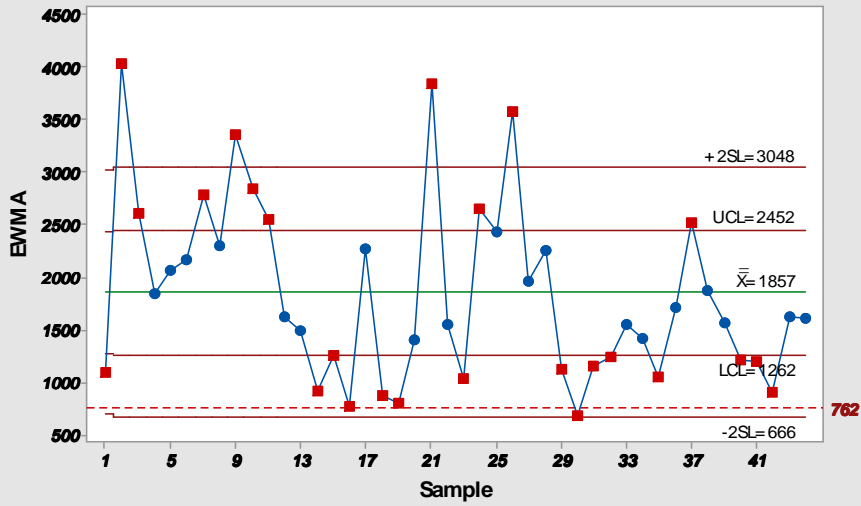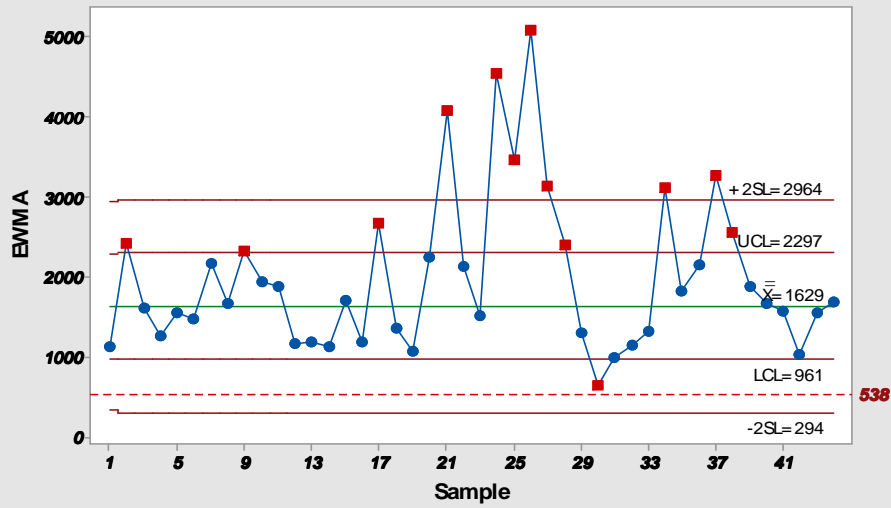
Fig. 2

Fig. 3

Fig. 4

Table 1 Descriptive statistics of the concentrations data of Al, As, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn (mg/kg, DW) in moss samples (n=44)

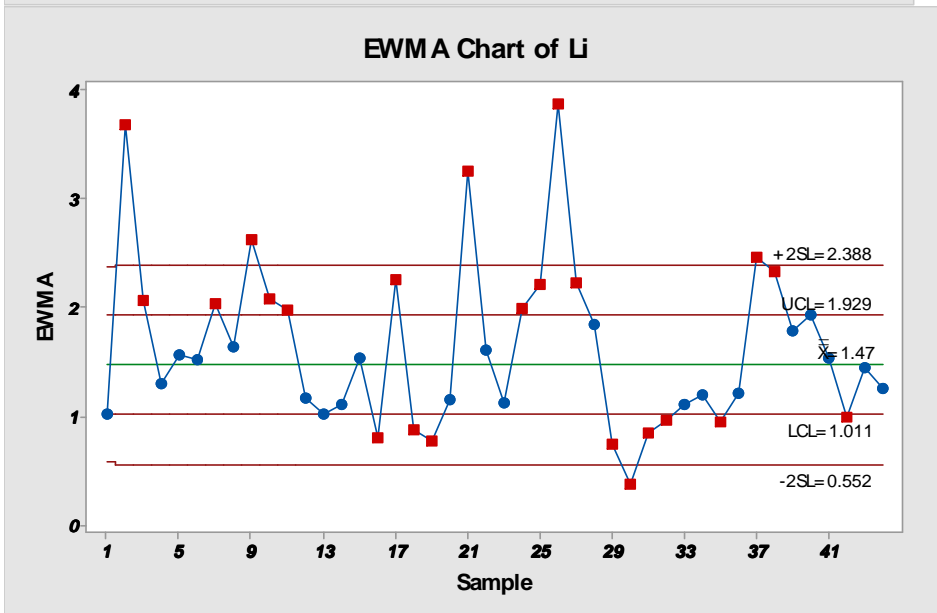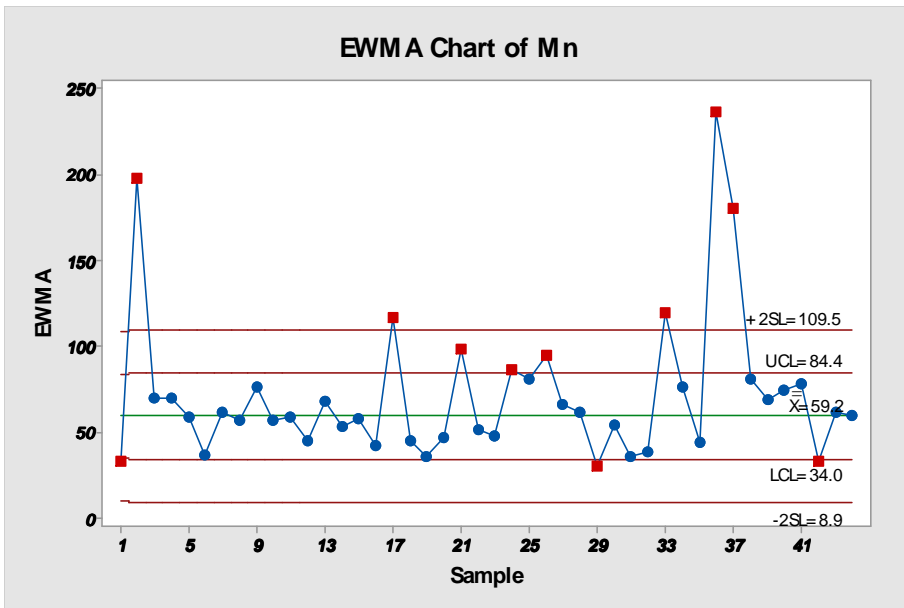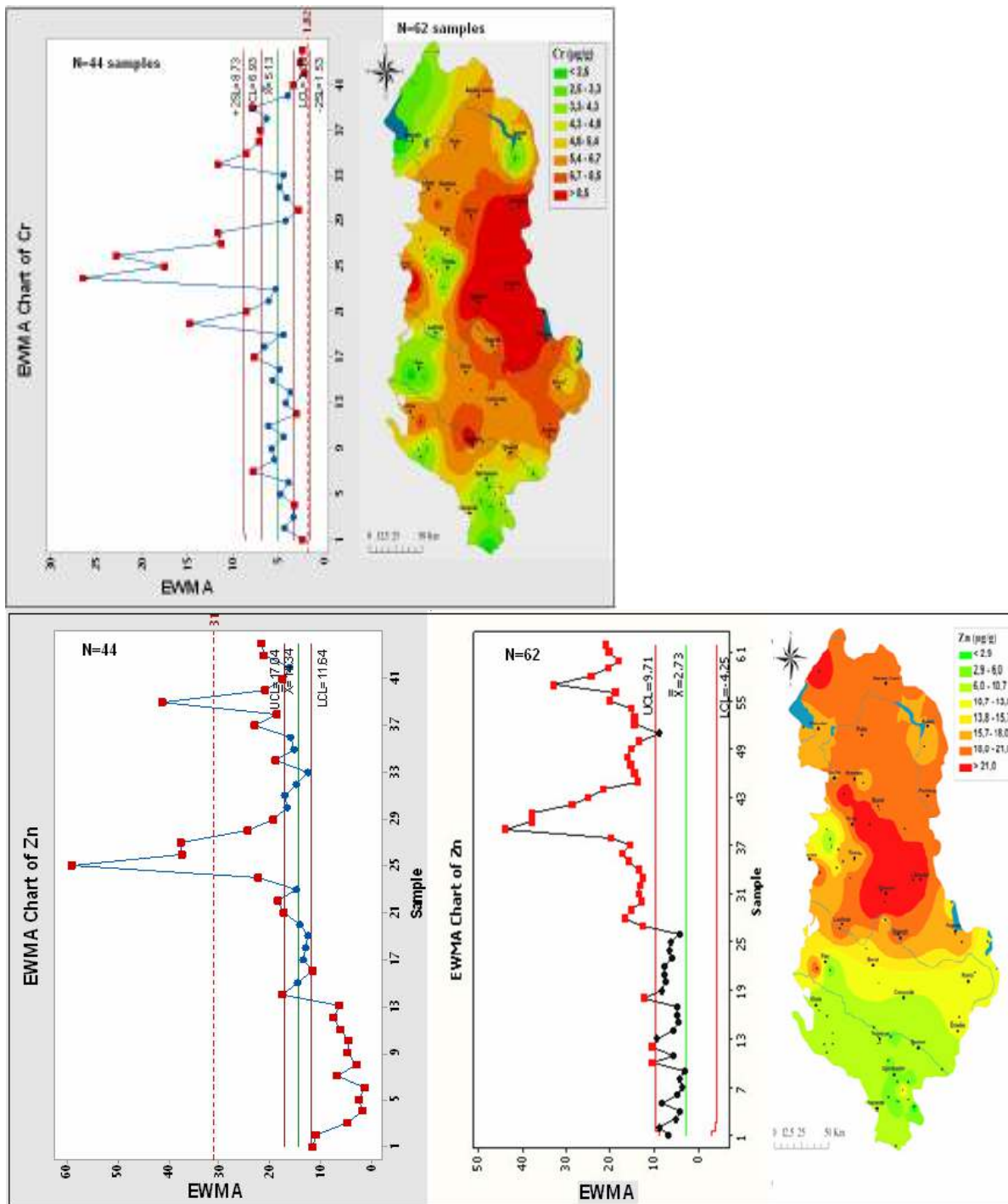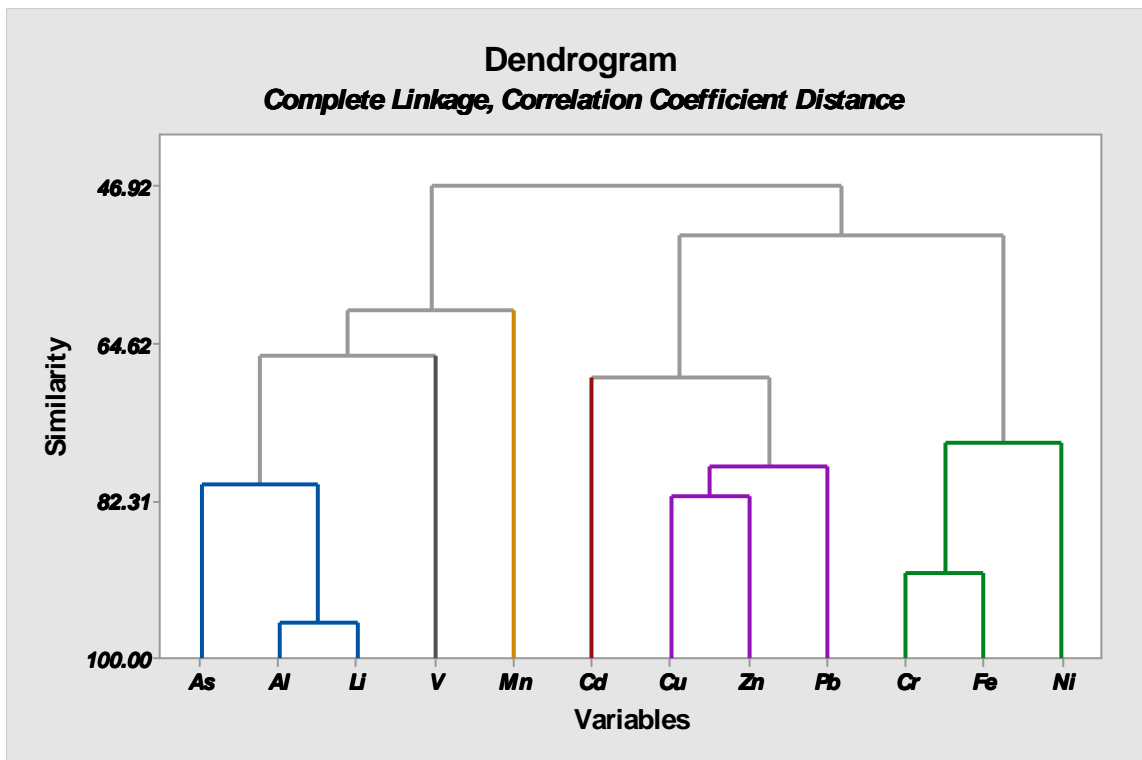| Stat. parameters	As	Cd	Cr	Cu	Li	Mn	Ni	Pb	V	Zn	Al	Fe
Mean	0.50	0.165	6.80	6.33	1.62	71.45	13.19	3.58	4.27	16.13	1,837	1,975
Standard Error	0.09	0.024	0.88	0.38	0.14	7.87	3.28	0.55	0.44	1.84	153	170
Median	0.30	0.103	5.13	5.78	1.47	59.32	6.67	2.42	3.46	14.34	1,587	1,629
Standard Deviation	0.60	0.162	5.85	2.54	0.92	52.23	21.73	3.62	2.90	12.21	1,013	1,127
Sample Variance	0.36	0.026	34.20	6.43	0.84	2728	472	13.08	8.41	149	1,027,025	1,269,512
CeffVar (%)	120	98	86	40	56	73	165	101	68	76	55	57
Kurtosis	**5.30**	**10.32**	**8.36**	3.16	2.16	**7.43**	**20.95**	**12.91**	**8.04**	**7.33**	1.10	2.53
Skewness	**2.23**	**3.018**	**2.69**	1.36	1.40	**2.54**	**4.28**	**3.55**	**2.48**	**2.20**	1.14	1.60
Range	2.81	0.842	30.14	13.42	4.06	261	129	18.34	15.80	67.15	4,246	5,019
Minimum	0.05	0.058	1.62	2.14	0.28	22.19	1.56	1.40	1.15	1.00	535	469
Maximum	2.86	0.9	31.76	15.55	4.34	284	131	19.73	16.94	68.15	4,781	5,488
Count	44	44	44	44	44	44	44	44	44	44	44	44
Confidence Level(95.0%)	0.18	0.049	1.78	0.77	0.28	15.88	6.61	1.10	0.88	3.71	308	343

Table 2 The variances of the data set of 12 elements obtained for N=44 and for N=62 sampling scheme

Elements	As	Cd	Cr	Cu	Ni	Pb	V	Zn	Mn	Al	Fe	Li
Var (N=62)	0.393	0.026	27.67	7.39	352	10.6	7.44	129	2406	1.33E+06	1.17 E+6	1.053
Var (N=44)	0.359	0.026	34.2	6.43	472	13.1	8.41	149	2728	1.03E+06	1.27 E+6	0.84

Table 3 The data of Anova analysis: Two-Factor Without Replication

SUMMARY	Count	Sum	Average	Variance
As	2	0.752	0.376	0.001
Cd	2	0.052	0.026	0.000
Cr	2	61.87	30.93	21.33
Cu	2	13.82	6.91	0.451

Ni	2	824	412	7,273
Pb	2	23.7	11.8	3.11
V	2	15.8	7.92	0.474
Zn	2	278	139	209
Mn	2	5,135	2,567	5,1842
Al	2	2,354,539	1,177,269	4.515E+10
Fe	2	2,441,047	1,220,524	4.8E+09
Li	2	1.893	0.947	0.023
Variance (N=44)	12	2,501,990	208,499	2.376E+11
Variance (N=62)	12	2,299,950	191,663	2.023E+11

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	4.79E+12	11	4.35E+11	99.3	2.281E-09	2.82
Columns	1,700,847,198	1	1.70E+09	0.39	0.55	4.84
Error	48,245,989,732	11	4.39E+09			
Total	4.84E+12	23				

Table 4 The data of the contamination factors (CF) and contamination classification (Fernandez et al. 2000) for metal concentrations in mosses in Albania (N=44)

Element	As	Cd	Cr	Cu	Ni	Pb	V	Zn	Fe	Al
Median	0.5	0.165	6.8	6.33	13.19	3.58	4.27	16.13	1,975	1,837
Median[1]	0.093	0.058	0.55	3.6	1.14	1.17	0.92	26.5	209	200
CF	5.38	2.84	12.36	1.76	11.57	3.06	4.64	0.61	9.45	9.19
Clasiffication	C4	C3	C5	C2	C5	C3	C4	C1	C5	C5
Contamination	Moderat	Slight	Severe	Suspected	Severe	Slight	Moderate	N.C.[2]	Severe	Severe

[1] Norway data (Steiness 2007); [2] No contaminated

Table 5 The results of EWMA Chart of As, Cd, Cr, Cu, Ni, Pb, V, Zn, Mn, Al, Fe, Li regarding the most contaminated areas

Element	Test Failed at stations:	Locations
As	2, 3, 4, 7, 8, 9, 10, 21, 24, 25, 26, 37, 41	Saranda and Permet area, Pogradec-Librazhd-Elbasan area, Milot and Peshkopi
Cd	1, 2, 4, 24, 25, 26, 27, 37, 39, 40	Konispol-Delvin, Pogradec-Librazhd-Elbasan area, Milot, Kruja, Kukes
Cr	7,17, 20, 21, 24, 25, 26, 27, 28, 34, 35, 36, 37, 39	Memaliaj, Ersek, Pogradec-Elbasan area, Bulqiz, Burrel, Reshen, Milot and Kruja
Cu	2, 21, 24, 25, 26, 27, 28, 37, 38, 39, 42, 43	Saranda, Pogradec-Librazhd-Elbasan area, Milot, Lezha, Kruja, Shkodra
Pb	24, 25, 26, 27, 40, 42, 43, 44	Pogradec-Librazhd-Elbasan area, Kukes, Shkodra
Ni	16, 18, 20, 21, 22, 24, 25, 26, 27, 28, 34, 35, 36, 37, 38	Korca-Pogradec-Librazhd-Elbasan area, Bulqiz, Burrel, Reshen, Milot, Lezha
V	2, 7, 9, 10, 11, 17, 21, 24, 25, 26, 27, 37, 38, 39	Saranda-Permet, Kanina, Ersek, Pogradec-Elbasan area, Milot, Lezha, Kruja
Zn	14, 21, 22, 24, 25,26, 27, 28, 29, 34, 37, 38, 39, 40, 41, 43, 44	Lushnja, Pogradec, Gramsh, Banja, Pogradec-Librazhd-Elbasan area, Berxull, Lezha, Bulqiza, Milot, Kokes, Peshkopi, Shkodra
Mn	2, 17, 21, 24, 26, 33, 36, 37,	Saranda, Memaliaj, Kanin, Pogradec-Elbasan, Shkafan, Reshen, Milot
Al	2, 3, 7, 9, 10, 11, 21, 24, 37	Saranda-Permet, Kanin, Pogradec, Librazhd, Milot
Fe	2, 9, 17, 21, 24, 25, 26, 27, 28, 34, 37, 38	Saranda, Permet, Ersek, Pogradec-Elbasan, Bulqiz, Milot, Lezha
Li	2, 3, 7, 9, 10, 11, 17, 21, 24, 25, 26, 27, 37, 38	Saranda-Permet, Kanin, Ersek, Pogradec-Librazhd-Elbasan, Milot, Lezha

Table 6 Pearson Correlation Coefficient between element concentrations in mosses in Albania.

	As	Cd	Cr	Cu	Ni	Pb	V	Zn	Mn	Al	Fe
Cd	0.13										
Cr	0.18	**0.57[1]**									

Cu	0.04	**0.48¹**	**0.37³**								
Ni	-0.01	0.25	**0.62¹**	0.12							
Pb	0.04	0.37	0.27	**0.59¹**	0.05						
V	0.32	0.31	**0.45²**	0.38	0.08	0.3					
Zn	-0.06	**0.48¹**	**0.43²**	**0.63¹**	0.17	**0.56¹**	0.36				
Mn	0.22	0.30	0.17	**0.41³**	0.04	0.01	0.28	0.10			
Al	**0.64¹**	0.34	**0.40³**	0.26	0.05	0.10	**0.59¹**	0.02	**0.54¹**		
Fe	**0.43²**	**0.47²**	**0.81¹**	**0.51¹**	**0.51¹**	0.27	**0.65¹**	**0.40³**	**0.43³**	**0.73¹**	
Li	**0.61¹**	0.35	**0.41³**	**0.43²**	0.05	0.20	**0.69¹**	0.19	**0.53¹**	**0.92¹**	**0.78¹**

Cell Contents: P-Value: [1] P<0.001, [2] P<0.005, [3] P<0.01

Table 7 Univariate linear regressions between selected elements in moss samples of Albania (N=44)

The regression equation	S	R^2	F	P	F_{crit}
Al = 194.3 + 1,016 Li	405	0.844	227.7	0.000	1.8
Fe = 489.4 + 0.809 Al	782	0.529	47.2	0.000	1.8
Fe = 426.3 + 957 Li	715	0.607	64.8	0.000	1.8
Fe = 913.9 + 156 Cr	668	0.656	80.2	0.000	1.8

Table 8 Maximum Likelihood Factor Analysis of the Correlation Matrix of As, Cd, Cr, Cu, Ni, Pb, V, Zn, Mn, Al, Fe, Li

Variable	Factor1	Factor2	Factor3	Communality
As	0.657	-0.097	0.036	0.442
Cd	0.225	0.478	0.279	0.358
Cr	0.277	0.323	0.796	0.814
Cu	0.246	0.792	0.110	0.700
Ni	-0.041	0.043	0.806	0.653
Pb	0.047	0.689	0.016	0.477
V	0.609	0.362	0.182	0.535
Zn	-0.018	0.818	0.204	0.711
Mn	0.521	0.168	0.032	0.301
Al	0.943	0.033	0.133	0.908
Fe	0.670	0.336	0.649	0.983
Li	0.953	0.234	0.095	0.973
Variance	3.513	2.443	1.899	7.855
% Var	0.293	0.204	0.158	0.655

Rotated Factor Loadings and Communalities (Varimax Rotation)