The survey of atmospheric deposition of heavy metal in Albania by using moss biomonitoring, ICP-AES and NAA

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Albania, Mediterranean country on the Balkan Peninsula, South of Europe.
Geography
Location: Southeastern Europe
Geogr. Coord.: 41 00 N, 20 00 E
Climate: mild temperate; cool, wet winter; dry summer
ALBANIA
Surface 28 748 km²
AUTRICHE
HONGRIE
SLOVENIE
Ljubljana
Zagreb
Budapest
UKRAINE
Chişinău
MOLDAVIE
ROUMANIE
Belgrade
BOSNIE-HERZÉGOVINE
CROATIE
Sarajevo
SERBIE
MONTENEGRO
Podgorica
Pristina
KOSOVO
Skopje
MACEDOINE
Tirana
ITALIE
ALBANIE
GRÈCE
TURQUIE
BULGARIE
Bucarest
Mer Noire
Mer Adriatique
Mer Égée
Mer Ionienne
Athènes
RHODOPES
3000
2000
1500
750
250
100
0
m
km
0
50
100

Stationary Sources (power plants, factories) NO_2, SO_2, PM

Mobile Sources (vehicles) VOCs, NO_2, PM

Area Sources (waste incineration, gas stations) VOCs, NO2, SO2, PM

Natural Sources (forest fires) PM

Cr-Fe Metallurgycal plant

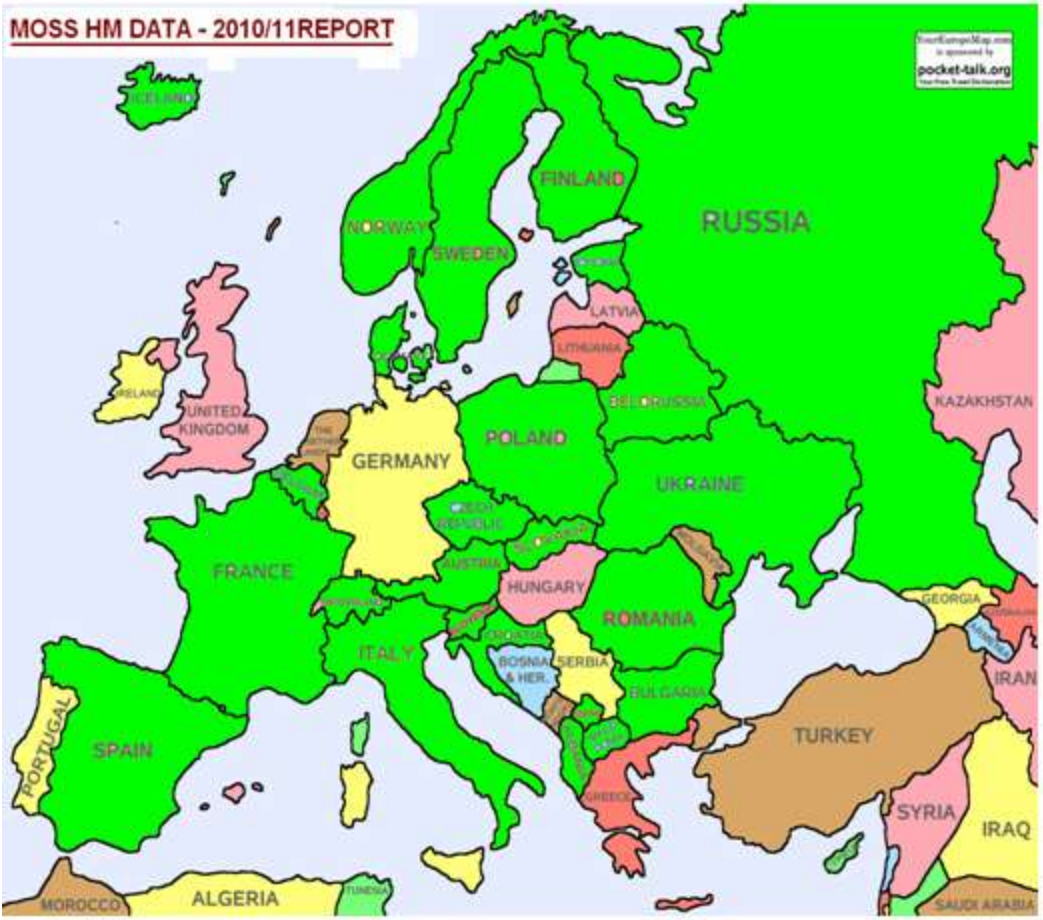
Traffic emission

Waste incineration

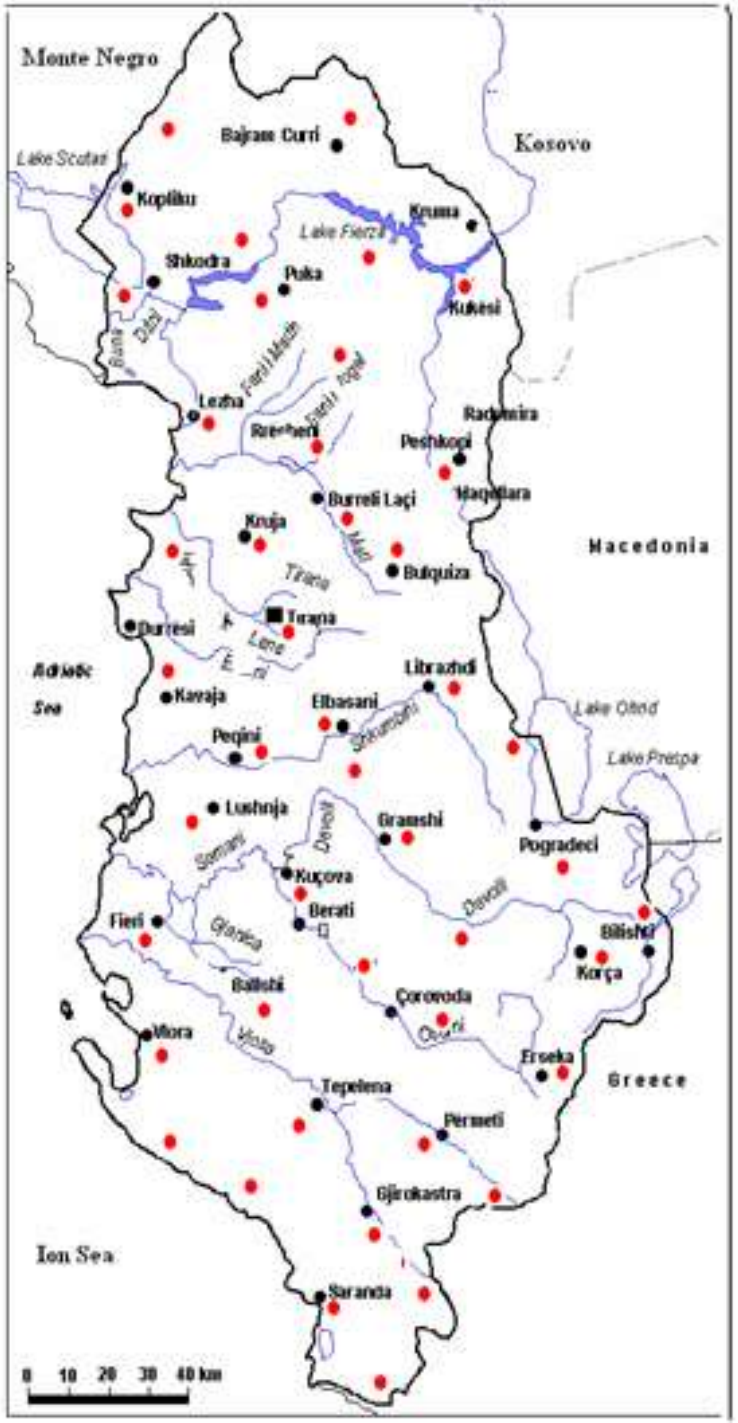
Forest fires in summer

Main Sources of Air Pollution in Albania

The first study of atmospheric deposition of metals in Albania (2010/2014)



- 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).
- In 2010 survey Albania joined ICP Vegetation Programe for the first time.
- 2005–26 Europe countries
- 2010 – 41 countries (32 European countries)



- **<u>44 moss samples</u> were collected during the period September – October 2010 and June-July 2011 in Albania. The University of Tirana, FNS, Dept. of Chemistry, Anal. Chem. Section was involved in sampling campaigns and the analysis of Hg via CVAAS method.**

The ICP/AES analysis of 19 elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb-US, Sr, V and Zn) was performed by the Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Republic of Macedonia.

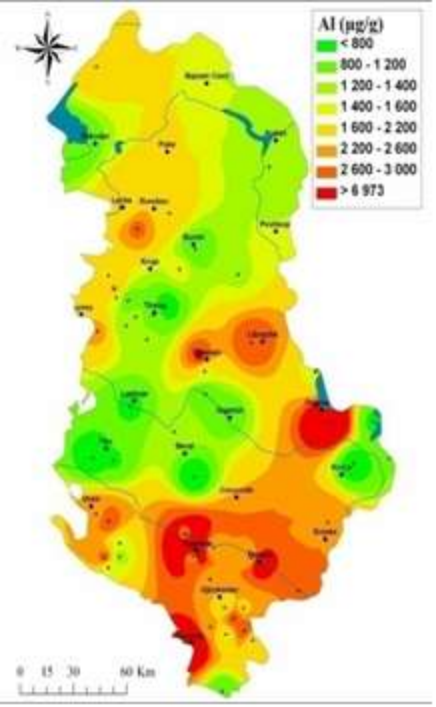
- 65 elements (including the elements like: As, Au, Br, Ce, Cl, Co, Cs, Dy, Eu, Hf, I, In, La, Lu, Nd, Rb, Sb, S, Sc, Se, Sm, Ta, Tb, Ti, Th, W and Yb), are performed by Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research Dubna, Russian Federation.

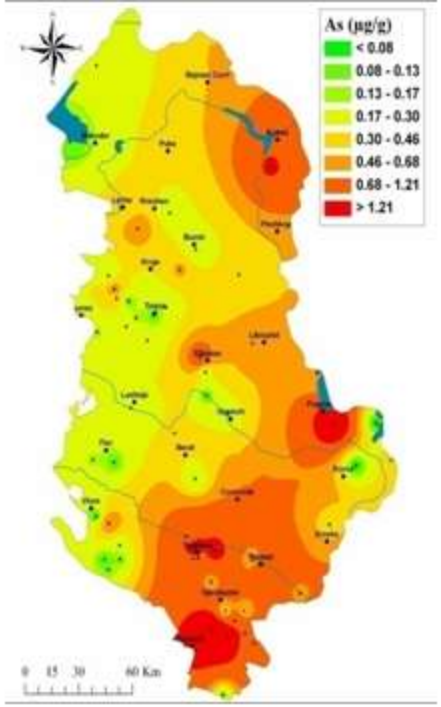
Data processing and statistical analyses

Various statistical analysis techniques can be used in spatial distribution measurements to reveal the underlying deterministic behaviors, and thus help clarify the cause and the effects of relationships of contaminants in environmental problems

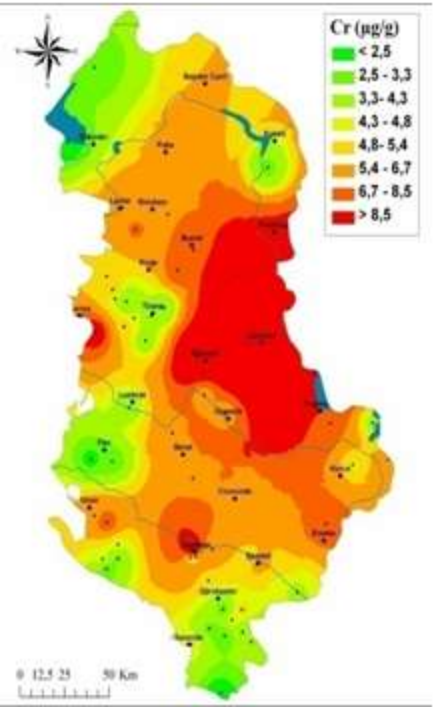
Descriptive Statistics method was applied to the elemental concentration data set to explain variations in the data.

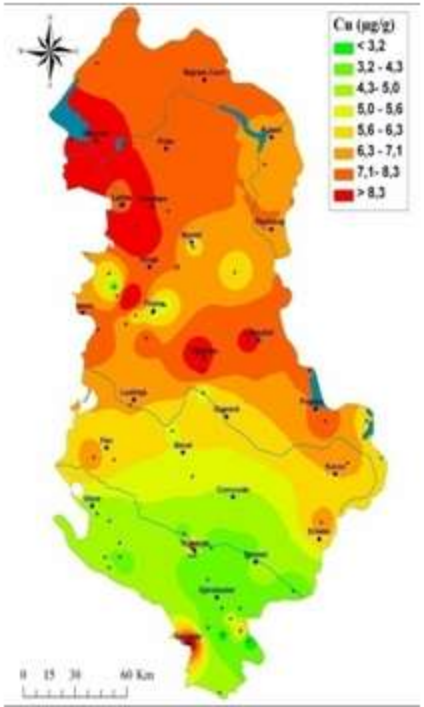
- The analytical data of all observations were entered into a ***data matrix*** and ***EWMA chart*** and ***multivariate analysis*** was used to interpret the spatial series data of this study.
- Univariate control chart was used to investigate moving range of two successive observations and to estimate variability of data. The data represented spatial distribution of Al, Cr, Fe, Ni, V and Zn elements, and were characterized by an irregular distribution of nonparametric data, median values were used instead of average data.
- The upper and lower control limits (UCL and LCL) were computed for median moving range, by applying pooled standard deviation and the proper values of λ (the weight of EWMA, $\lambda = 0$ to 1).
- The value of λ was carefully chosen to balance the robustness to non-normality and the detection ability to various shift magnitudes.
- Median values of Europe (2010) are used as elements reference line
- Multivariate data analysis (CA) and (FA) is used to the data set of Albania mosses to identify sources of metals content and to quantify their contribution to the variation of these parameters. The number of the groups and the most important factors were determined and discussed. MINTAB 15 software package was applied for data processing and statistical analyses.

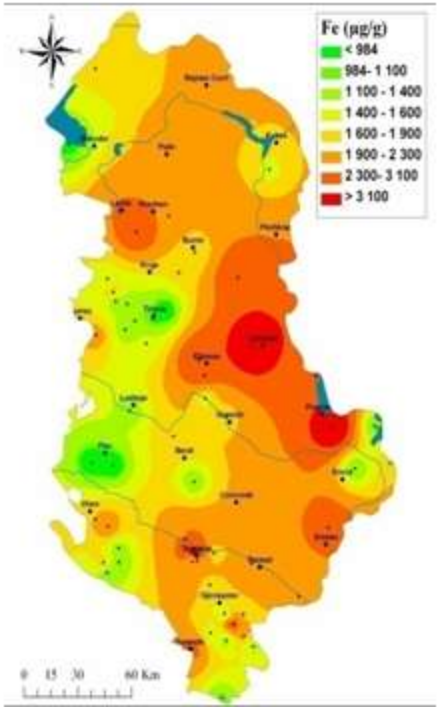


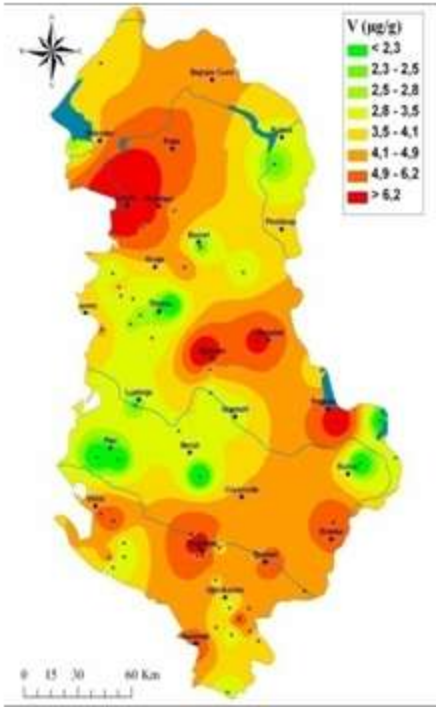


The oncentration of HM in moss samples allowed us to establish the extend of polluted areas and most important polluted sources.



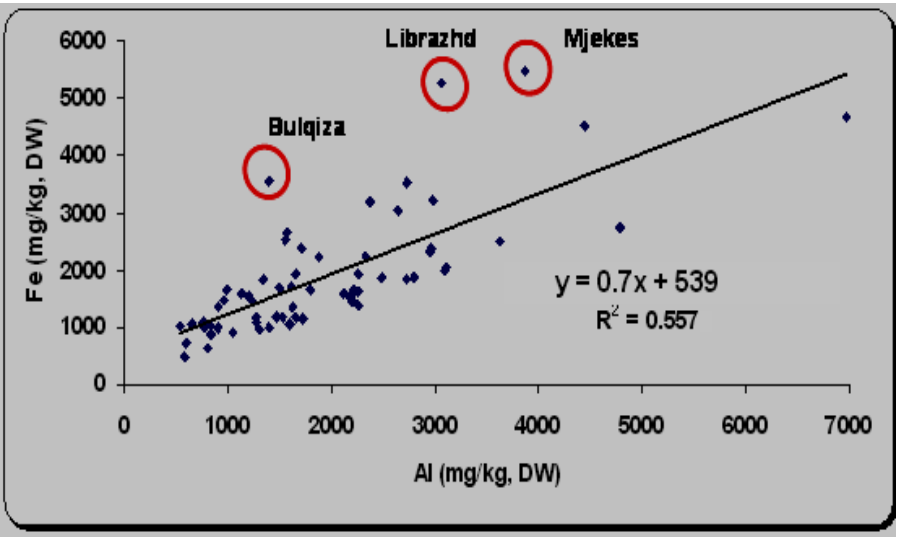




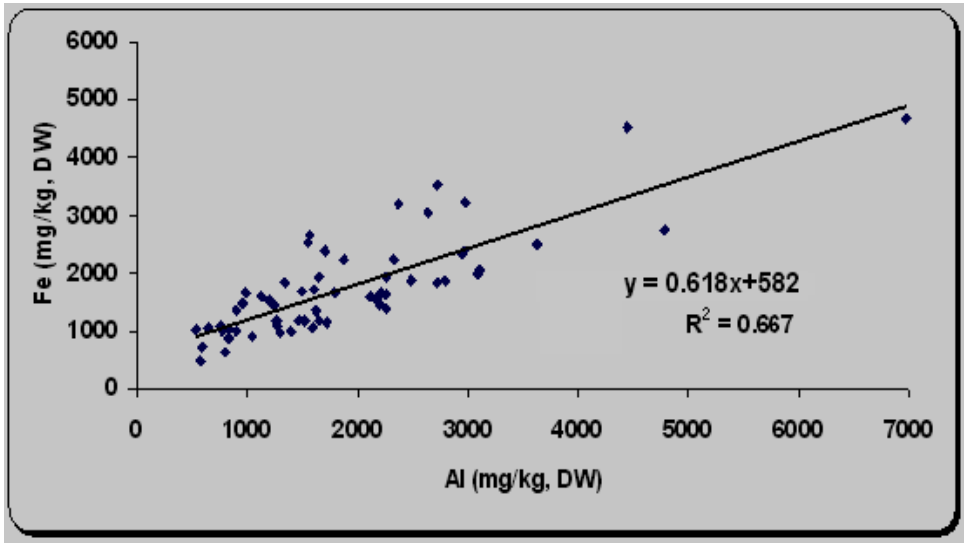


- The data of the elements Cd, Ni, Pb and Zn do not follow the normal or lognormal distribution ($P<0.05$).
- Cd, Ni, Pb and Zn – large ranges of variation; CV>75% - high disparity in their concentrations in moss samples. The order of CV values was: Ni (170%)>As (118%)>Pb (98%)>Cd (97%)>Cr (85%)>Zn (82%).
- Their mean > medians; are strongly positively skewed that is typical with elements abundance and distribution of mineral resources in the Earth's crust (Clarke&Washington 1924; Vinogradov 1962; Rudnick&Gao 2003) and are influenced by complicated factors (Wang et al 2010). The highest values of these elements were measured near the industrial centers positioned mainly in central part of the country.

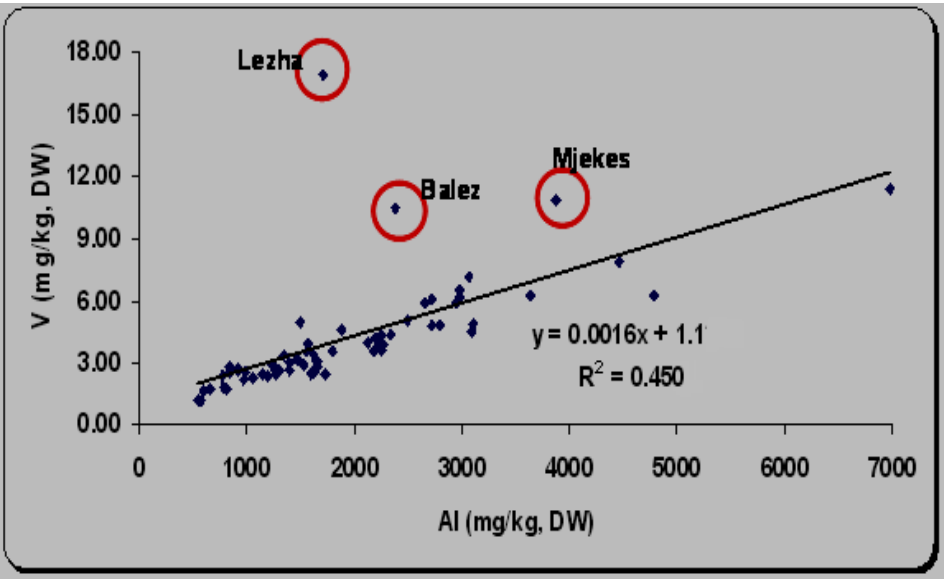
Linear Regression

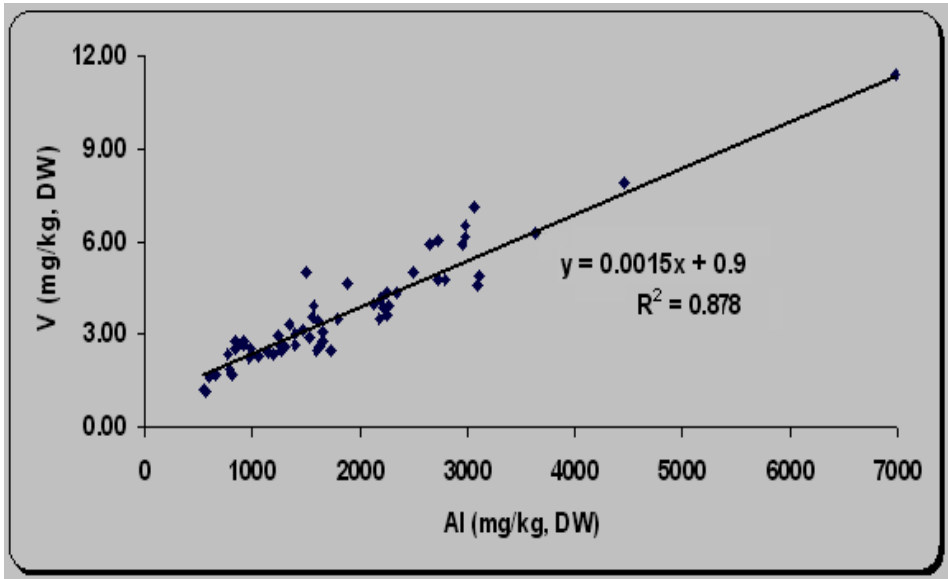


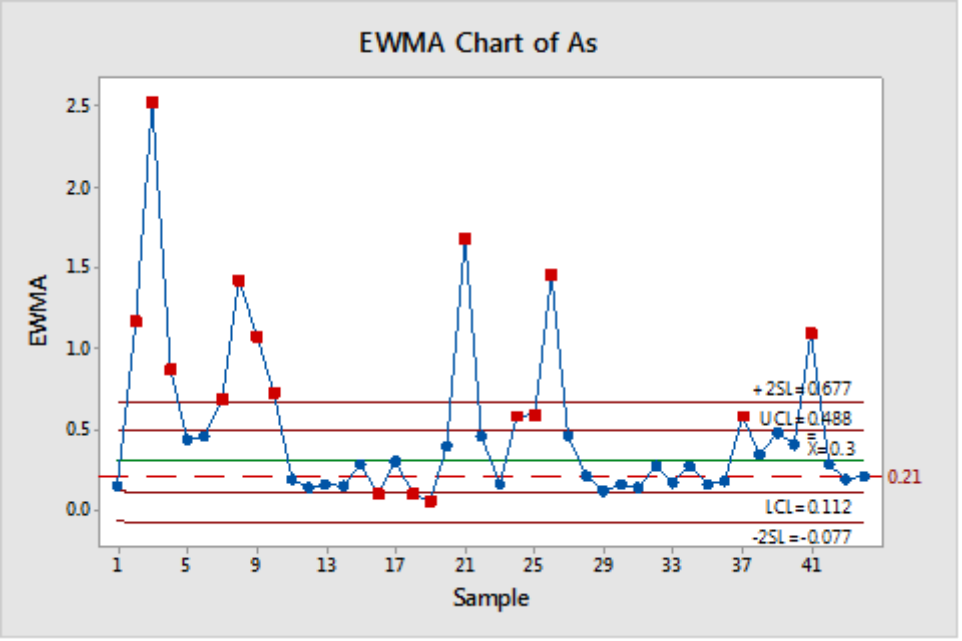
a. Original data

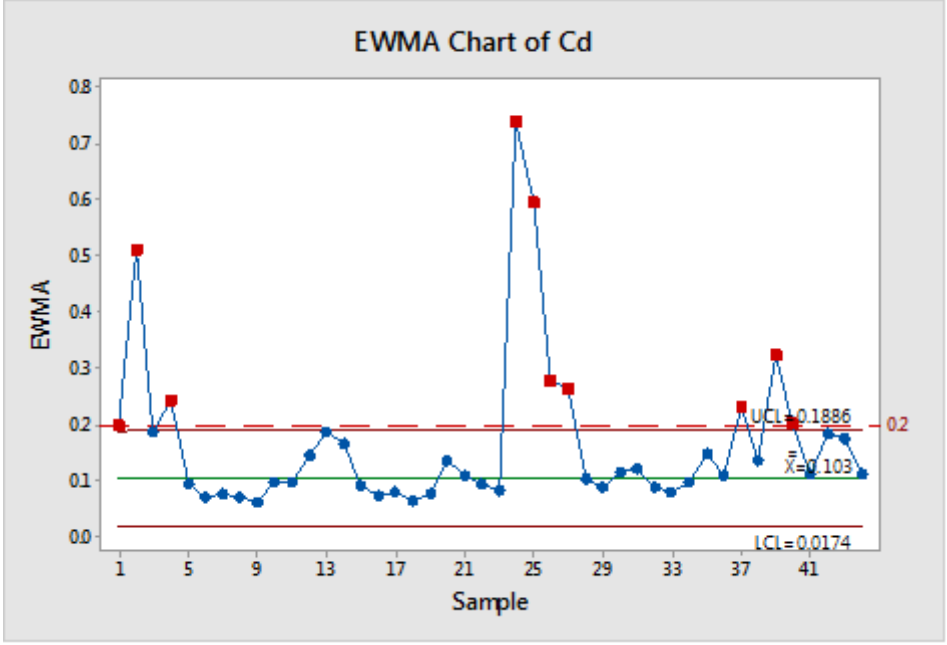


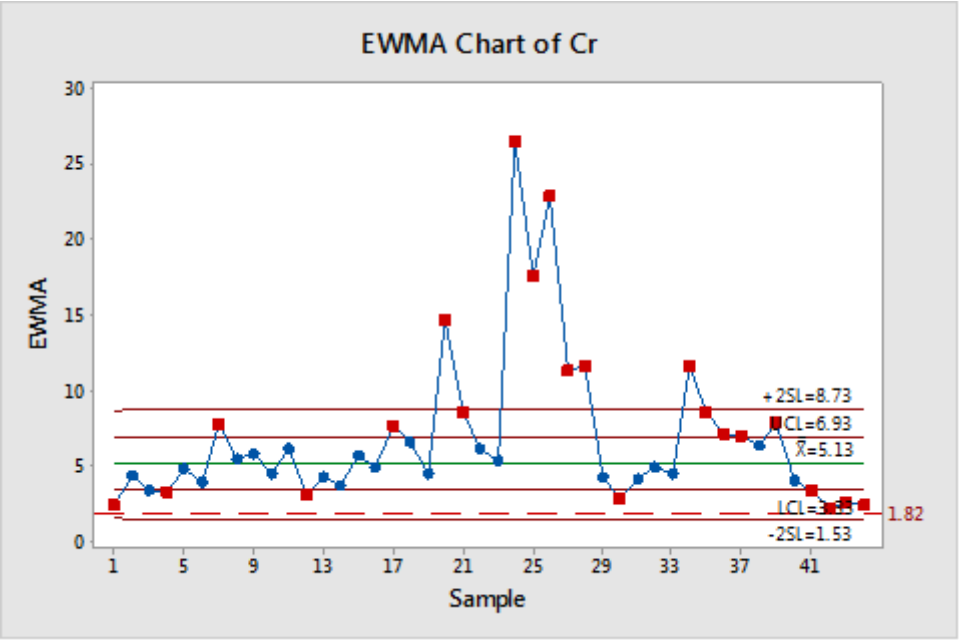
b. After exluding outliers

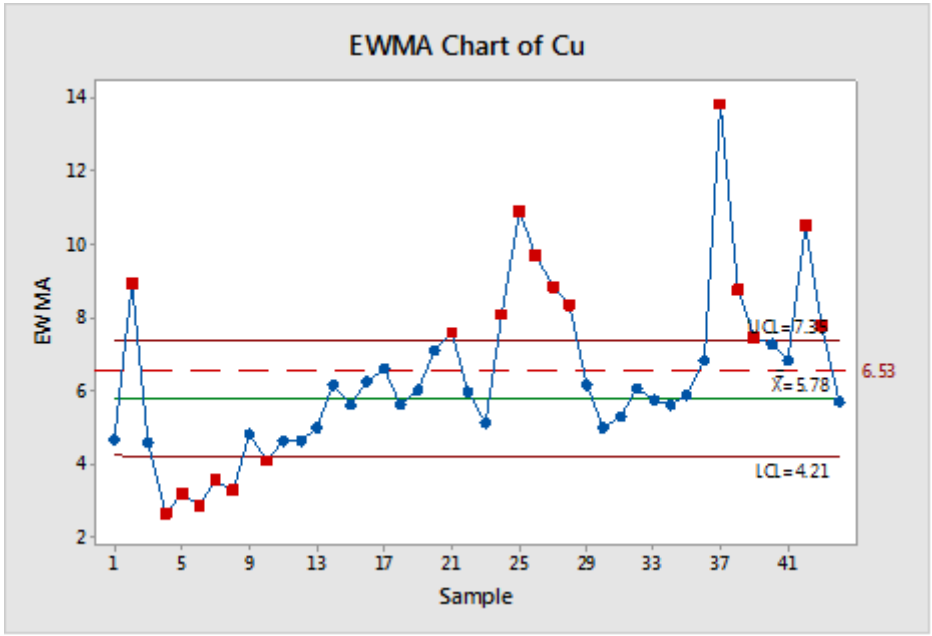


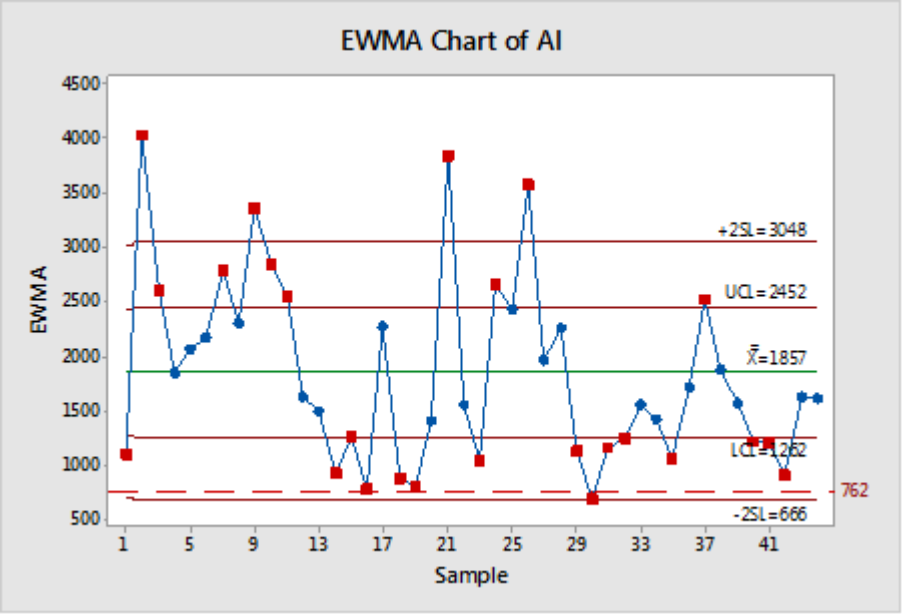


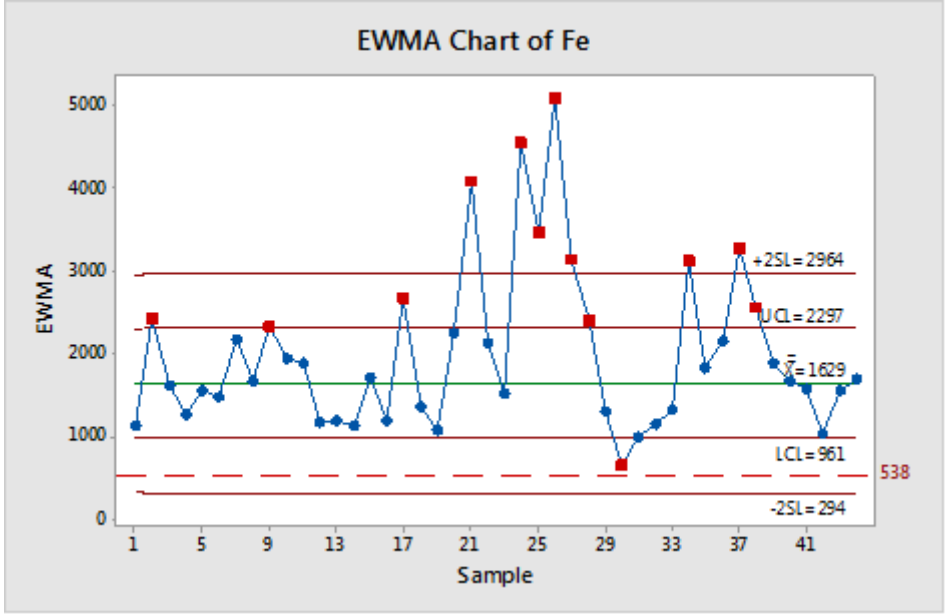

EWMA Chart of As
EWMA
Sample
+2SL=0.677
UCL=0.488
X̿=0.3
0.21
LCL=0.112
-2SL=-0.077

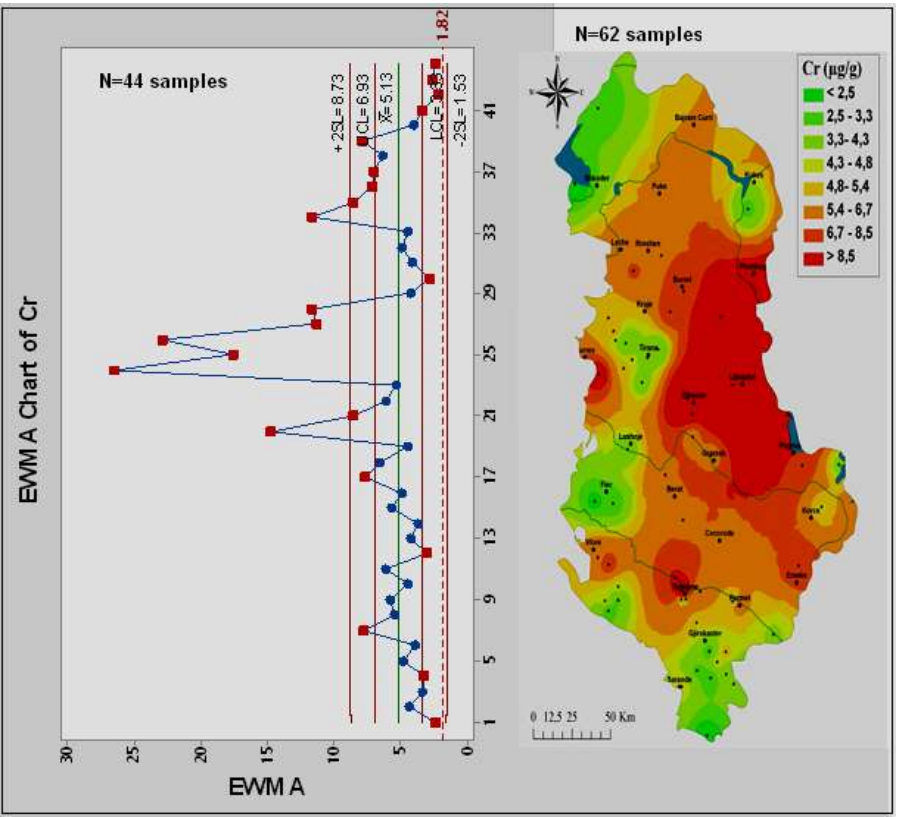

EWMA Chart of Cd
EWMA
Sample
UCL=0.1886
X̿=0.103
0.2
LCL=0.0174

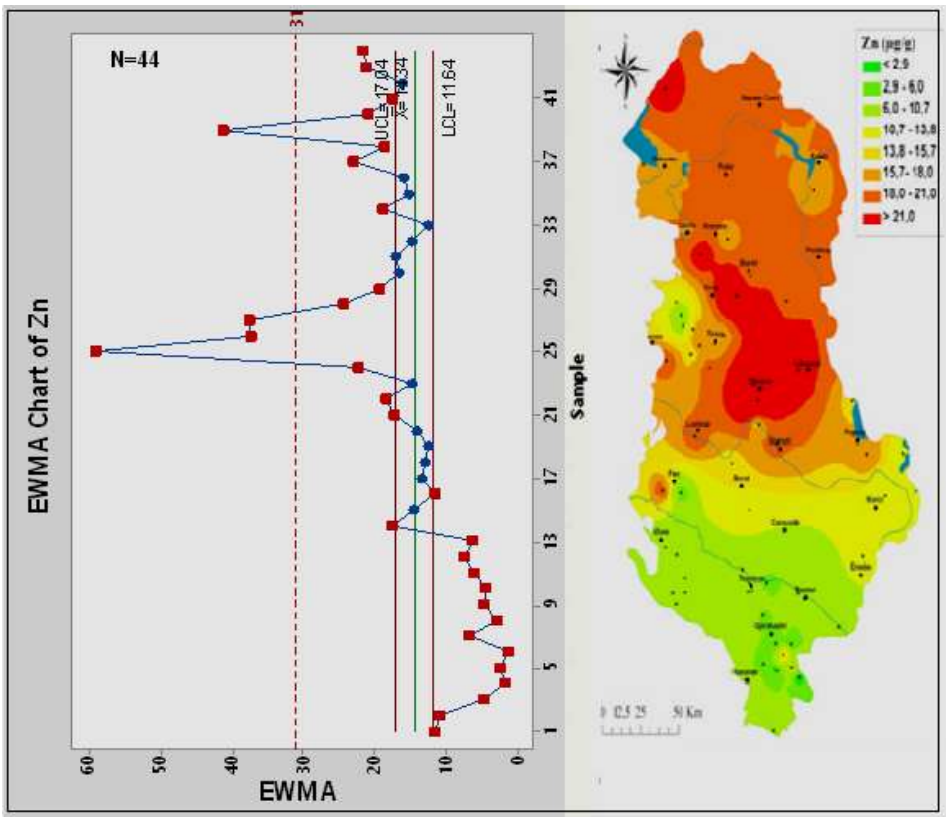

EWMA Chart of Cr
EWMA
Sample
+2SL=8.73
UCL=6.93
X̿=5.13
1.82
-2SL=1.53


EWMA Chart of Cu
EWMA
Sample
UCL=7.38
X̿=5.78
6.53
LCL=4.21


EWMA Chart of Al
EWMA
Sample
+2SL = 3048
UCL = 2452
X̄ = 1857
LCL = 1262
762
-2SL = 666


EWMA Chart of Fe
EWMA
Sample
+2SL = 2964
UCL = 2297
X̄ = 1629
LCL = 961
538
-2SL = 294


N=44 samples
EWMA Chart of Cr
EWMA
+2SL = 8.73
UCL = 6.93
X̄ = 5.13
-2SL = 1.53
N=62 samples
Cr (µg/g)
< 2,5
2,5 - 3,3
3,3- 4,3
4,3 - 4,8
4,8- 5,4
5,4 - 6,7
6,7 - 8,5
> 8,5


N=44
EWMA Chart of Zn
EWMA
UCL = 17.04
LCL = 11.64
Sample
Zn (µg/g)
< 2,9
2,9 - 6,0
6,0 - 10,7
10,7 - 13,8
13,8 - 15,7
15,7- 18,0
18,0 - 21,0
> 21,0

Multivariate analysis

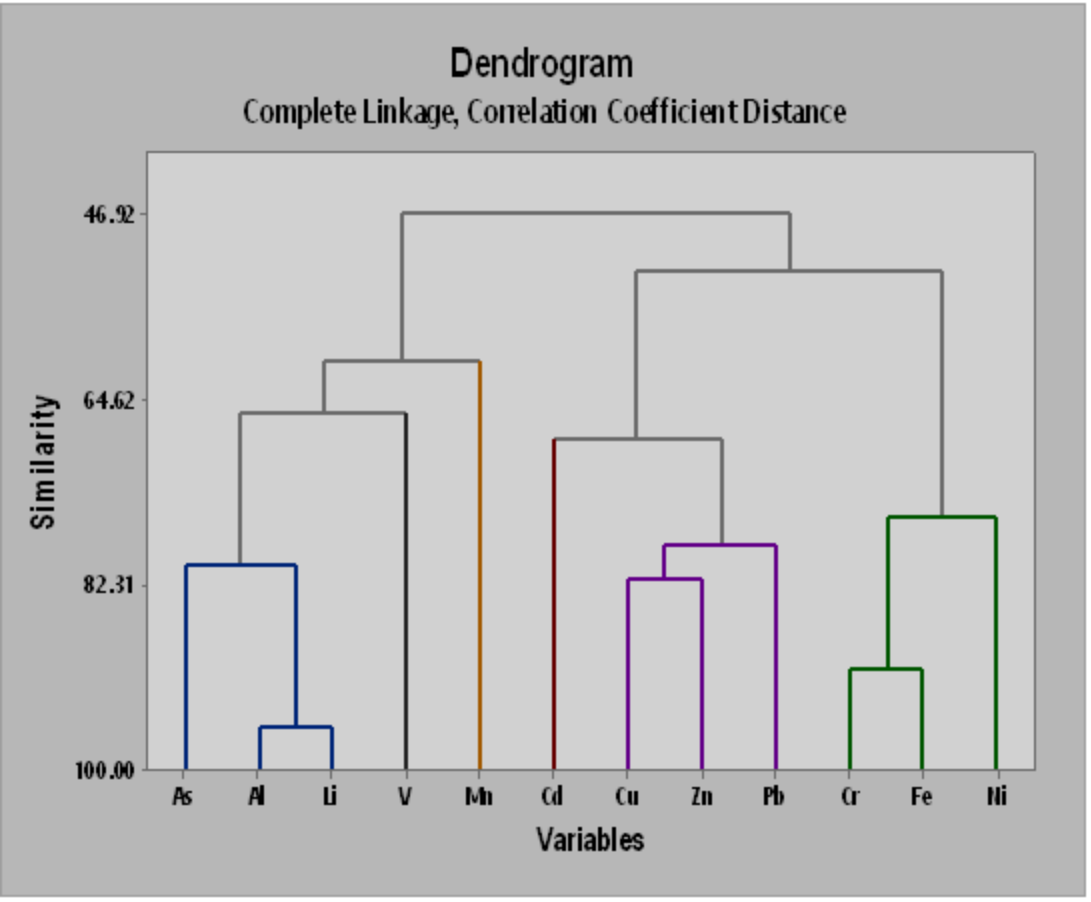
- **Multivariate data analysis is a tool to investigate complex data sets containing numerous measured parameters by revealing trends and relationships of these parameters.**

Pearson Correlation of the elements

	As	Cd	Cr	Cu	Ni	Pb	V	Zn	Mn	Al	Fe
Cd	0.13										
Cr	0.18	**0.57[1]**									
Cu	0.04	**0.48[1]**	**0.37[3]**								
Ni	-0.01	0.25	**0.62[1]**	0.12							
Pb	0.04	0.37	0.27	**0.59[1]**	0.05						
V	0.32	0.31	**0.45[2]**	0.38	0.08	0.3					
Zn	-0.06	**0.48[1]**	**0.43[2]**	**0.63[1]**	0.17	**0.56[1]**	0.36				
Mn	0.22	0.30	0.17	**0.41[3]**	0.04	0.01	0.28	0.10			
Al	**0.64[1]**	0.34	**0.40[3]**	0.26	0.05	0.10	**0.59[1]**	0.02	**0.54[1]**		
Fe	**0.43[2]**	**0.47[2]**	**0.81[1]**	**0.51[1]**	**0.51[1]**	0.27	**0.65[1]**	**0.40[3]**	**0.43[3]**	**0.73[1]**	
Li	**0.61[1]**	0.35	**0.41[3]**	**0.43[2]**	0.05	0.20	**0.69[1]**	0.19	**0.53[1]**	**0.92[1]**	**0.78[1]**

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

Cluster Analysis



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 done.

Factor Analysis

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

Conclusion

- The present survey confirms that the moss biomonitoring combined with statistical data treatments are important tools for the evaluation of atmospheric input of metals in the environment.
- It is clearly demonstrated that *Hypnum cupressiforme* pasively absorb metals from atmospheric deposition through the moss dense carpet.

- **The method is suitable for detecting spatial trends in metals deposition.**
- **EWMA univariate control chart was successfully used to investigate the spatial distribution of the elements and to estimate the variability of the data. It represents similar results with GIS technique in elements distribution.**

- The most polluted location with Al, Cr, Fe, Ni, V and Zn was found in the central part of the country, caused mainly by iron-chromium metallurgical plant and miner industry.

- Fe, Cr, Ni and V pollution maybe associated with Fe-Cr metallurgy, oil refinery, cement industry and mining industry in the polluted areas.

- High contents of aluminum found in the south-east direction of the country, is strongly reflecting the wind influence in this area.

- The effects of the major pollution sources of Al, Cr, Fe, Ni, V and Zn, located mainly in industrial zones, were readily detected by moss analysis.

- **Elbasani Metallurgical Combine and mining industry are the main contributors of Cr, Fe, Ni and V in Albania. The central part of the country is the most polluted area.**





Thank you for your attention!