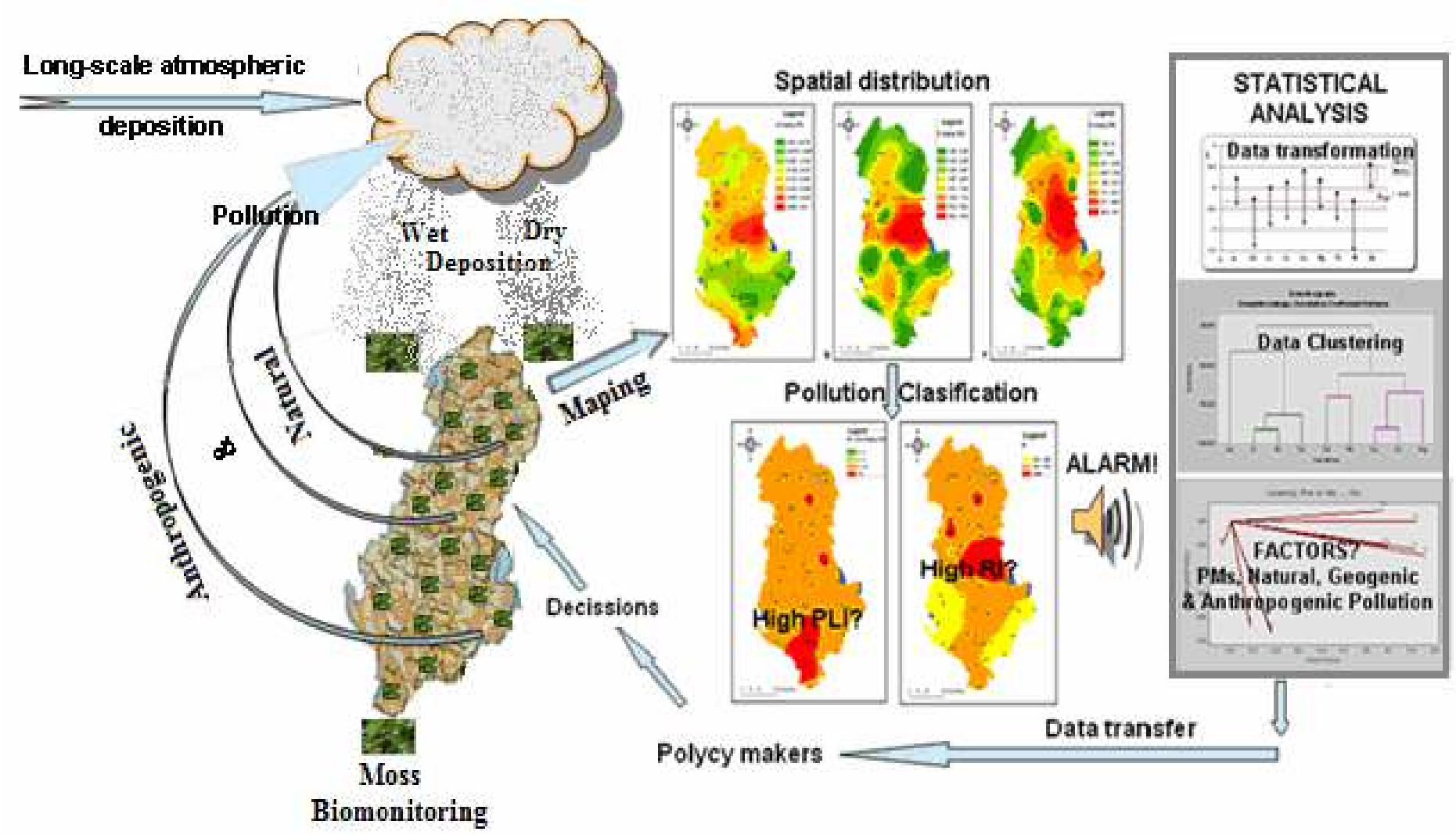
First Albanian moss biomonitoring survey and some future considerations

P. Lazo, F. Qarri,L. Bekteshi,S. Allajbeu, M. V. Frontasyeva, T. Stafilov
Department of Chemistry, FSN, University of Tirana, Albania
b Department of Chemistry, University of Vlora, Albania
Department of Chemistry, University of Elbasan, Albania
Frank Laboratory of Neutron Physics, JINR, Dubna, Russia
Institute of Chemistry, FS, Sts. Cyril and Methodius University, Skopje, Macedonia

2010-2014: First Albanian moss biomonitoring survey



Sample analysis

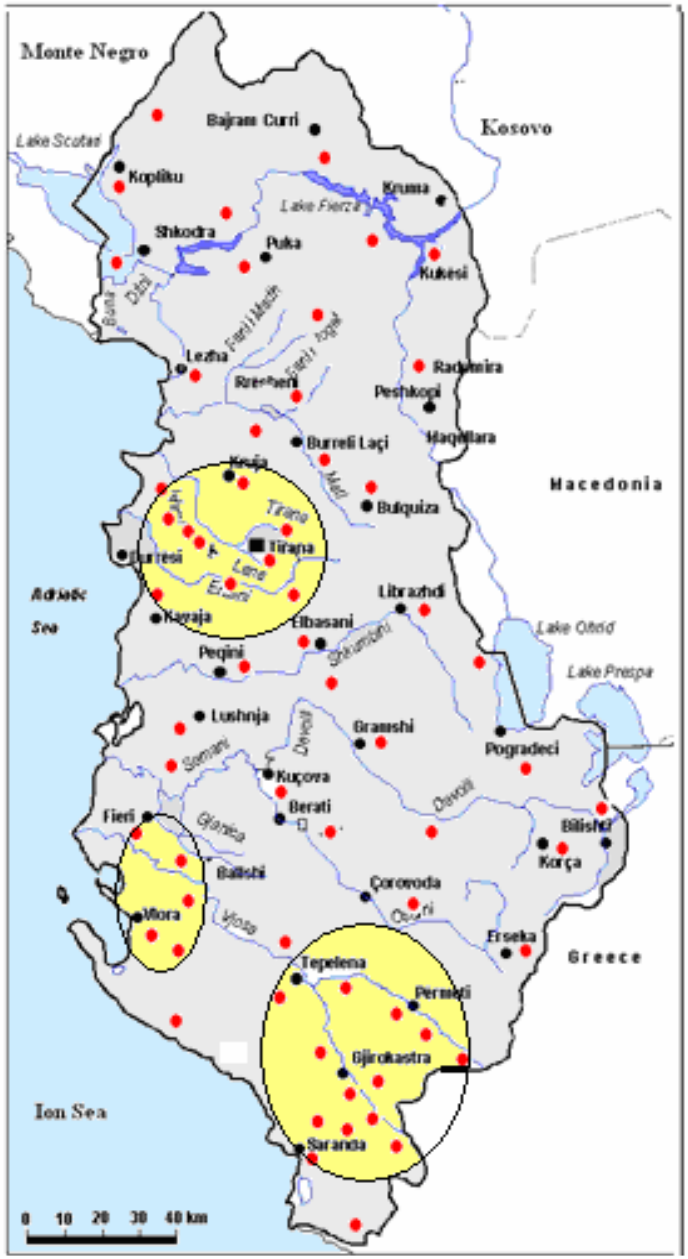
- 62 moss samples (Hypnum cupressiforme) were collected over the whole territory of Albania (28 700 sq. meters)
- The ICP/AES analysis of 19 elements (Al, B, Ba, Ca, Cd Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb-US, Sr, V and Zn) was performed by the Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University, Skopje, Republic of Macedonia.
- 46 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.

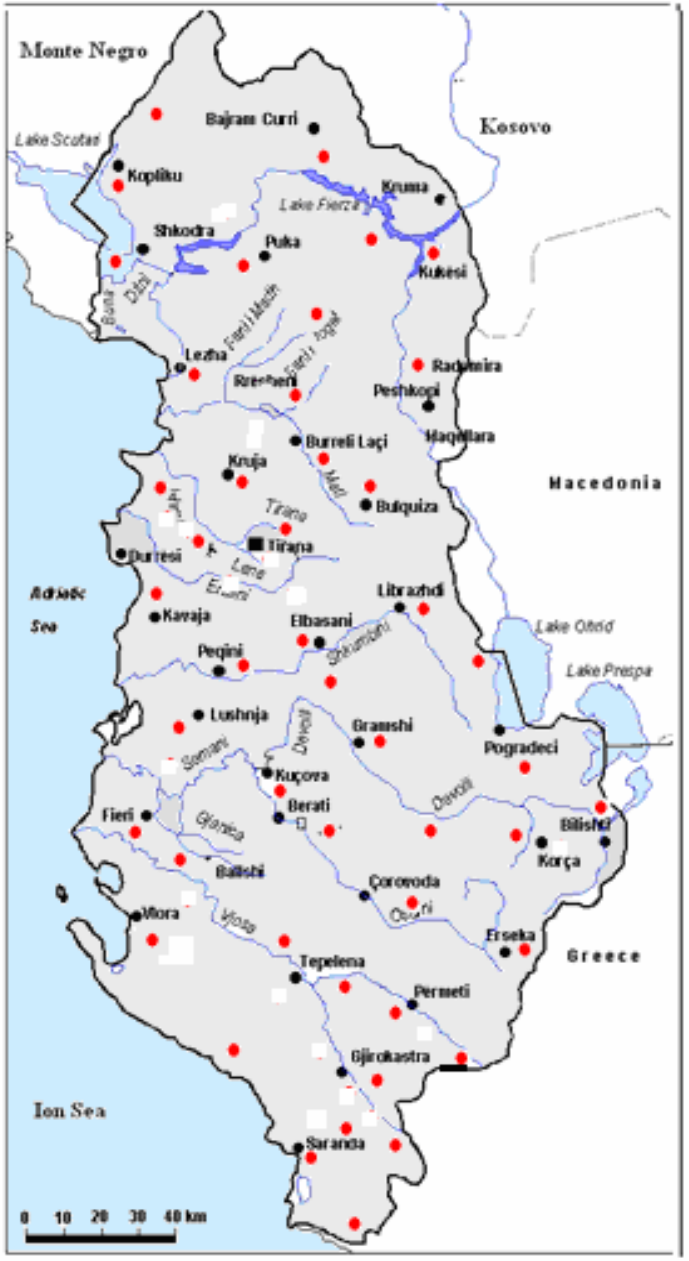
F. Qarri, P. Lazo, T. Stafilov, M. Frontasyeva, H. Harmens, L. Bekteshi, K. Baceva, Z. Goryainova , Multi-elements atmospheric deposition study in Albania. Env. Sc. and Poll. Res. 2013, DOI:10.1007/s11356-013-2091-1

THE EFFECT OF SAMPLING SCHEME

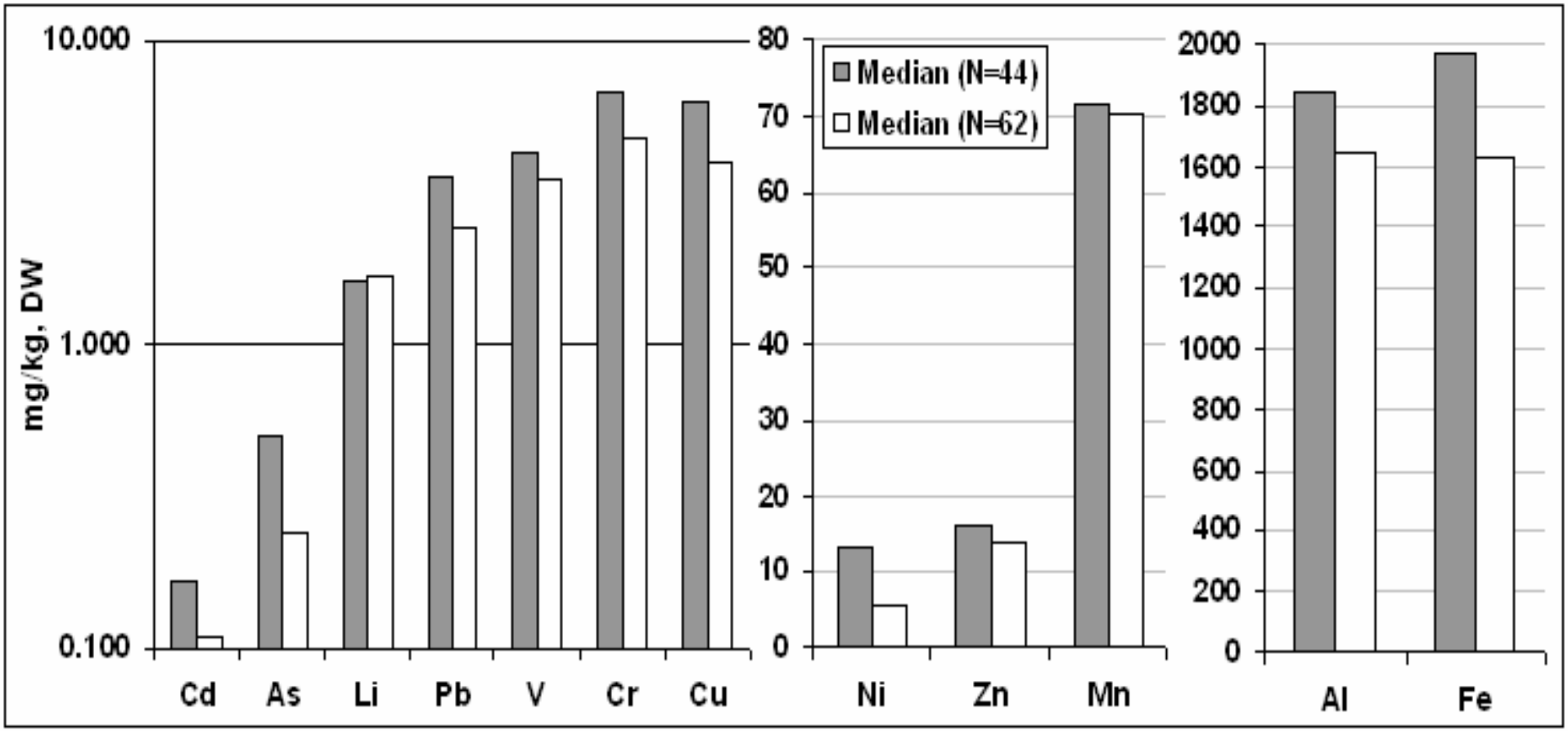
Due to high variation of the data the effect of sampling scheme is studies

64 sampling sites (random sampling scheme)



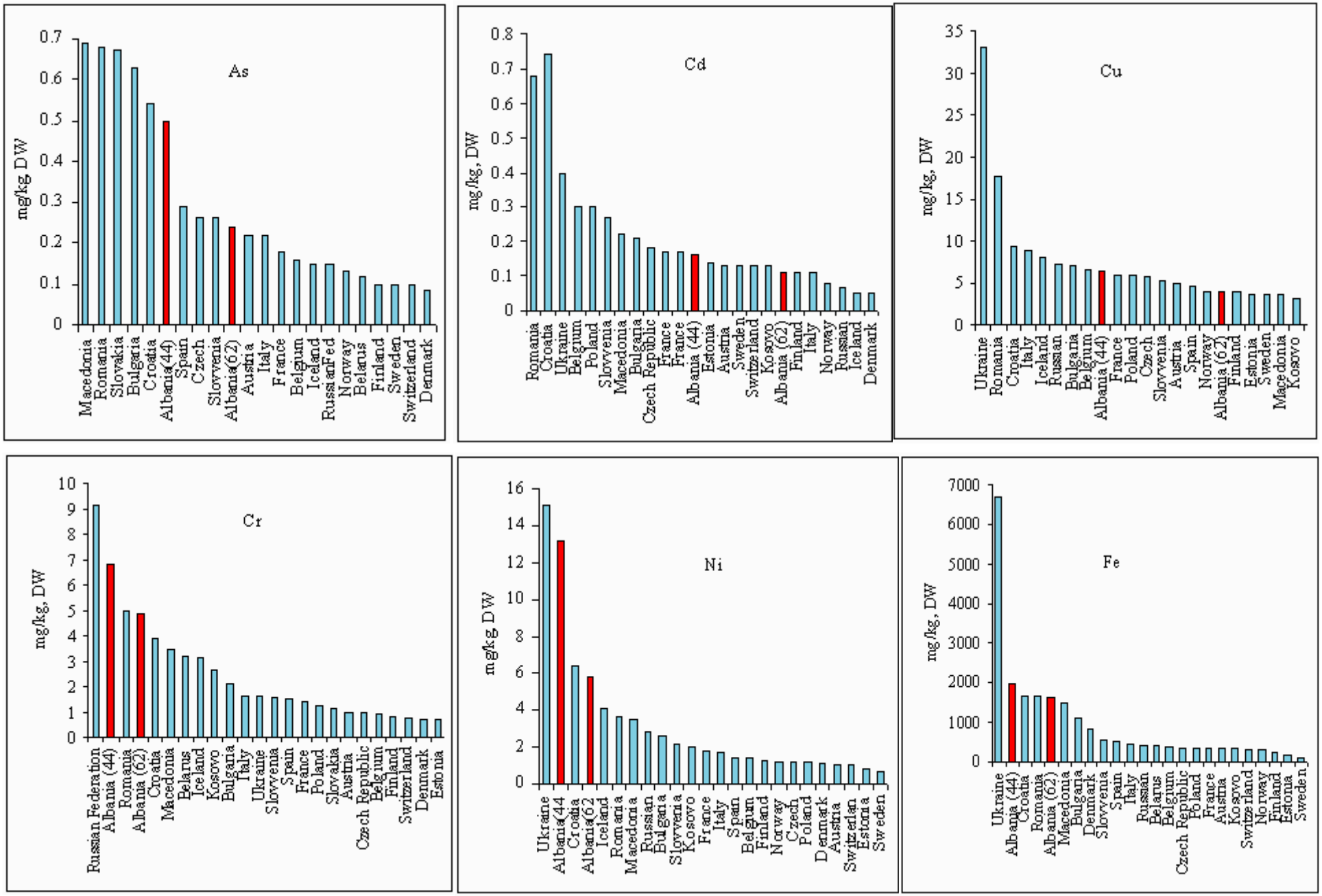


44 sampling sites (approximately systematic sampling scheme)

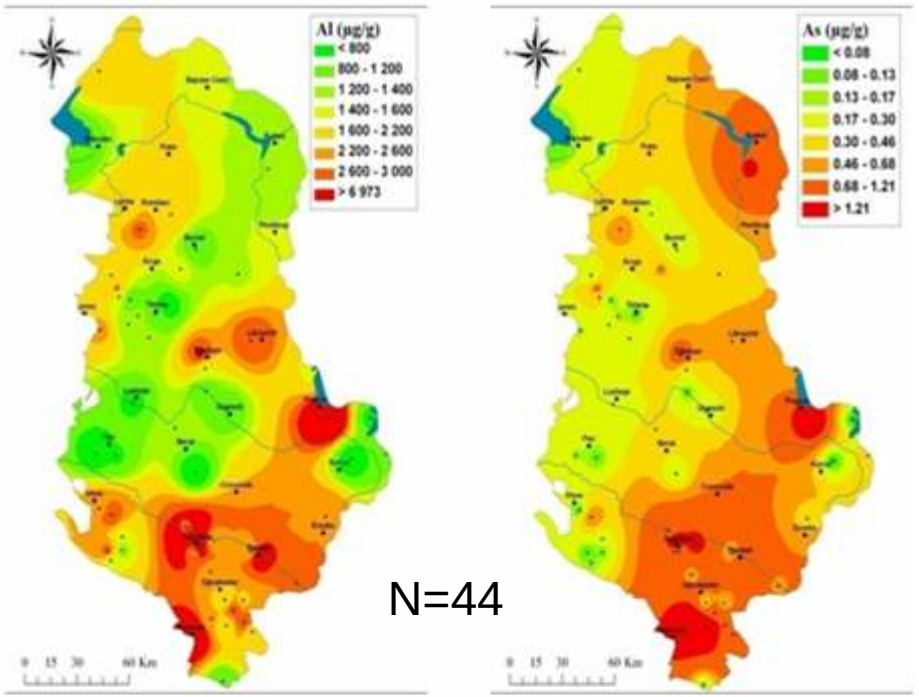


Data comparison between two sampling schemes

F. Qarri, P. Lazo, L. Bekteshi, T. Stafilov, M. Frontasyeva, H. Harmens, The effect of sampling scheme in the survey of atmospheric deposition of heavy metals in Albania by using moss biomonitoring, Env. Sci. and Poll. Res. 2014, DOI: 10.1007/s11356-014-3417-3



Data comparison between two sampling schemes

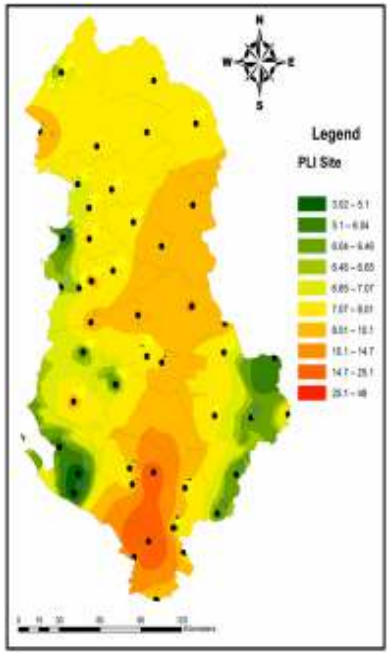


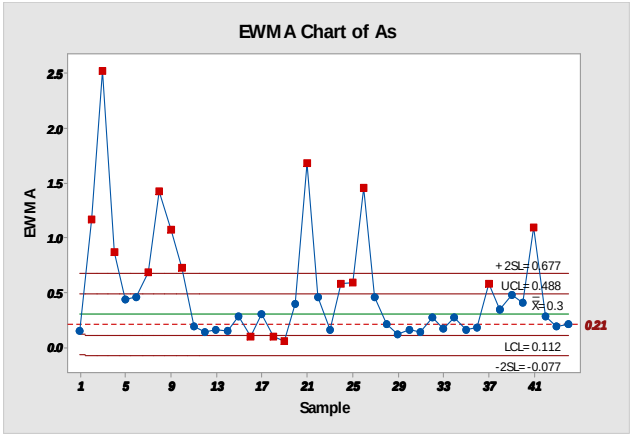
N=44

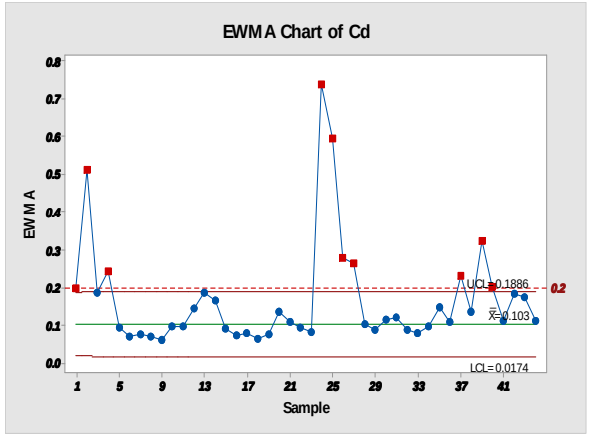
The conc. of HM in moss allowed to distinguish the spatial distribution and the polluted zones.

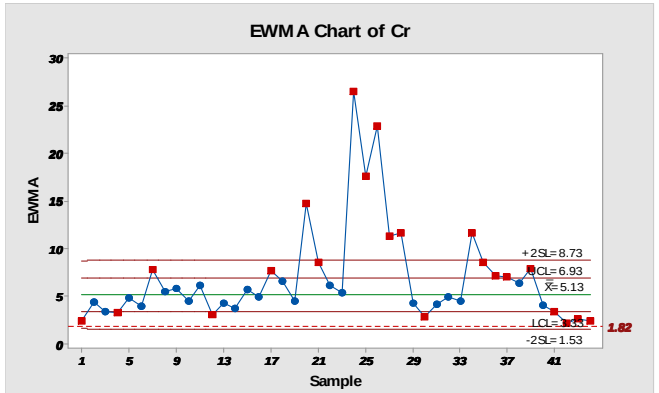
East: most polluted area - geogenic

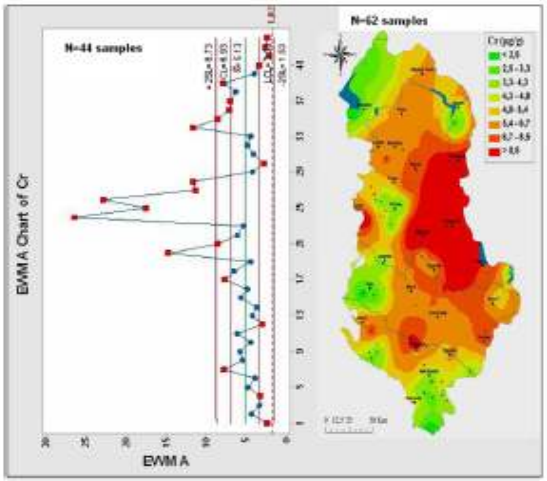
West: (coastal area) - low pollution level - effect of sea salt

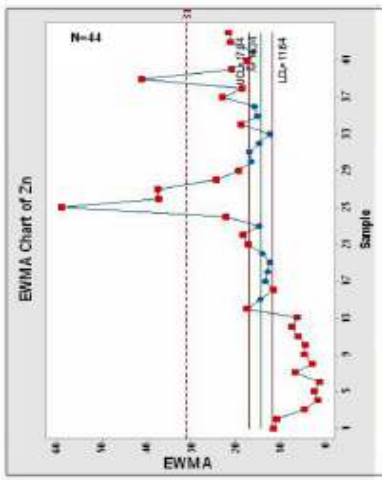


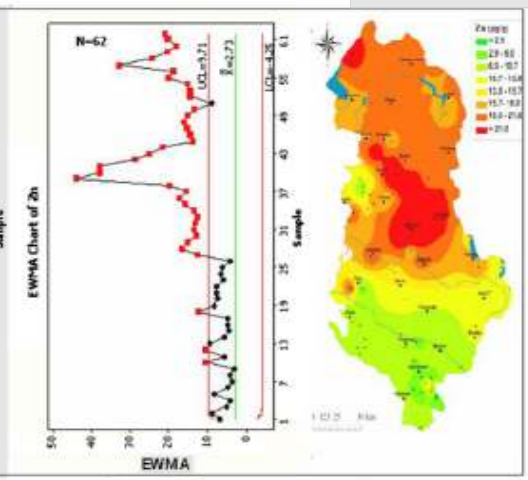












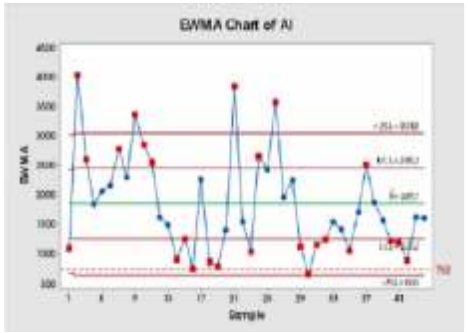
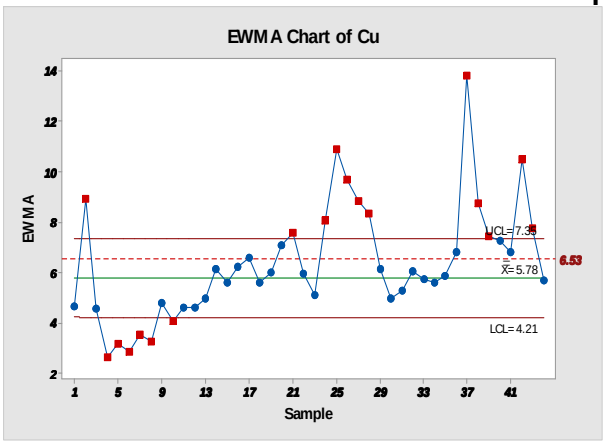
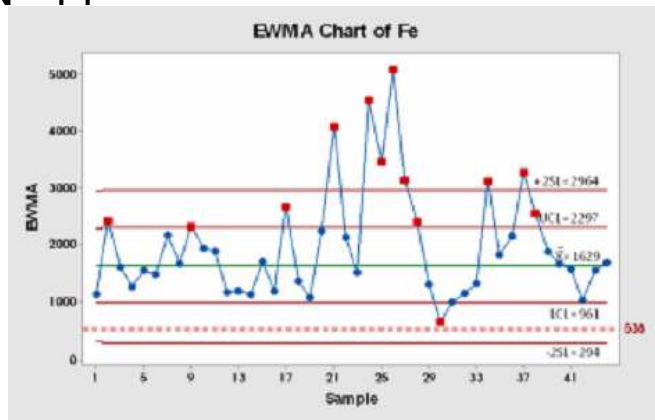


Fig. 3. Cr and Zn spatial distributions in Albania based on EWMA univariate control chart and GIS technique

N=44





The spatial distribution, bacground level and most contaminated sites were investigated through EWMA charts. Data normalization (Li as reference element) is applied to distinguish anthropogenic level from the natural pollution level.

L. Bekteshi, P. Lazo, F. Qarri, T. Stafilov (2015) Application of normalization process in the survey of atmospheric deposition of heavy metals in Albania by using moss biomonitoring, Ecological Indicators (ECOLIND), 03/2015; DOI: 10.1016/j.ecolind.2015.03.001

The CF, PLI_{site} and RI values are calculated for the pollution characterization:

$$CF = \frac{C_i}{BC_i}$$

$$PLI_{site} = \sqrt[n]{CF_1 \times CF_2 \times .... \times CF_n}$$

$$RI = \Sigma(T_i \frac{C_i}{BC_i})$$

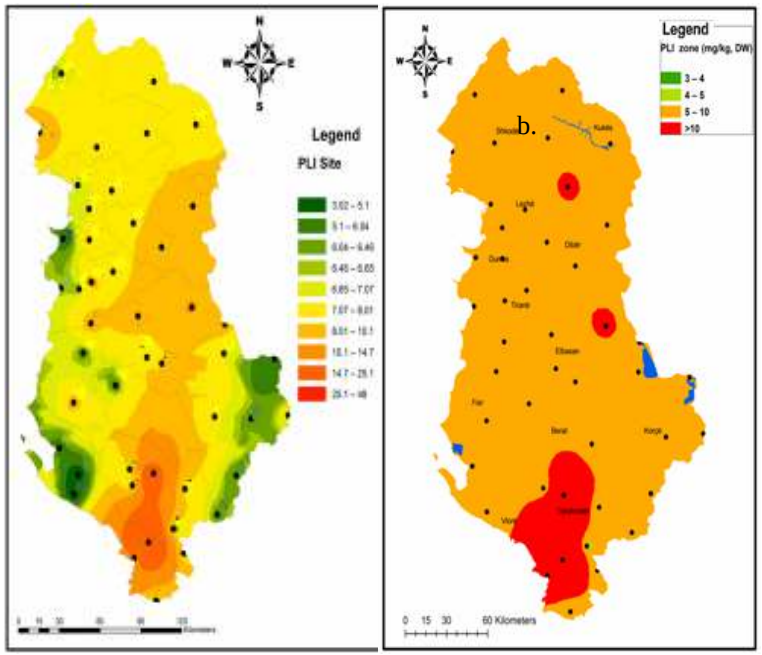
CF[1]	PLI[2]	RI[3]	$T_{i\ of\ the\ elements}$[3]
0-1 (C1) No cont.	0 background level	≤ 150 low pollution	1 – Zn
1-2 (C2) Suspected Cont.	0 - 1 unpolluted	150 - 300 moderate pollution	2 - Cr
2-3.5 (C3) Slight Cont.	1-2 moderately to unpolluted	300 - 600 considerable pollution	5 - Cu, Ni, Pb
3.5-8 (C4) Moderate Cont.	2 - 3 moderately polluted	> 600 highly pollution	10 - As
8-27 (C5) Severe Cont.	3-4 moderately to highly polluted		30 - Cd
> 27 (C6) Extreme Cont.	4 - 5 highly polluted		40 - Hg
	> 5 extremely polluted		

[1] Fernandez&Carballeira (2001); [2] Zhang et al. 2011; [3] Hakanson 1980

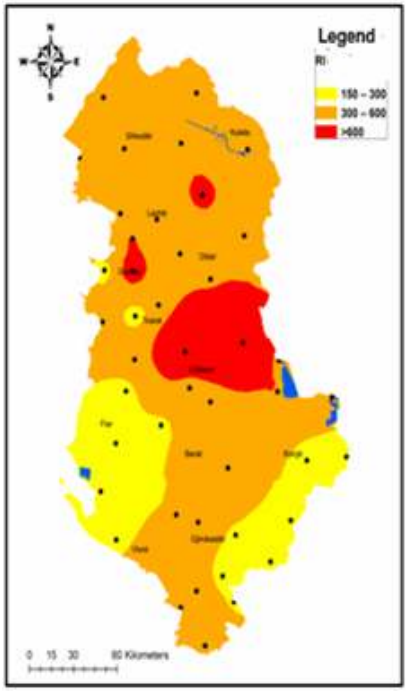
a.

The classification of the contamination

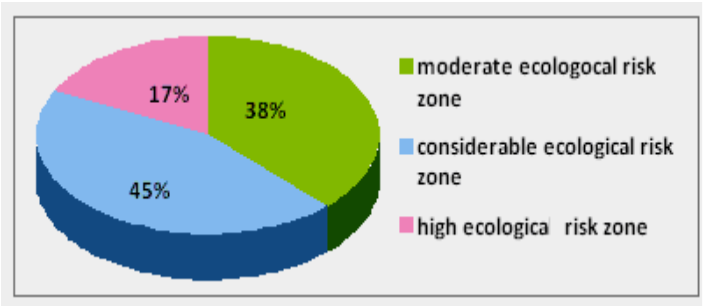
Parameters	As	Cd	Cr	Cu	Ni	Pb	Zn	Hg	Co
CF	8.3	2.8	3.0	2.2	6.3	2.1	8.5	4.8	4.7
Classification	(C5)	(C3)	(C3)	(C3)	(C4)	(C3)	(C5)	(C4)	(C4)
Poll. Level	Highly	Slightly	Slightly	Slightly	Moder.	Slightly	Highly	Moder.	Moder.



GIS maps of PLI spatial distribution (a) and PLI level (b)



GIS maps of RI (Hg, Cd, As)



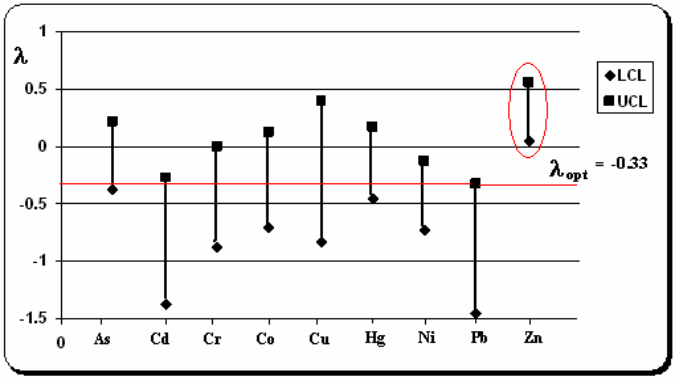
The surface of crop field area (% of total) for each atmospheric deposition RI classification based on 2010/2011 moss survey.

EFFECT OF THE STATISTICAL DISTRIBUTION OF THE DATA

Pearson correlation of Box-Cox transformated data

Elements	As	Cd	Cr	Cu	Ni	Pb	Zn	Hg	Co
As	1								
Cd	0.236	1							
Cr	0.310[3]	0.131	1						
Cu	-0.01	0.434[2]	0.347[3]	1					
Ni	0.069	0.044	0.850[1]	0.403[2]	1				
Pb	0.149	0.545[1]	0.179	0.663[1]	0.403[2]	1			
Zn	-0.182	0.303[3]	0.264	0.839[1]	0.384[3]	0.507[1]	1		
Hg	-0.027	0.399[2]	0.354[3]	0.477[1]	0.267	0.463[1]	0.502[1]	1	
Co	0.214	0.053	0.709[1]	0.302[3]	0.705[1]	0.154	0.178	0.195	1

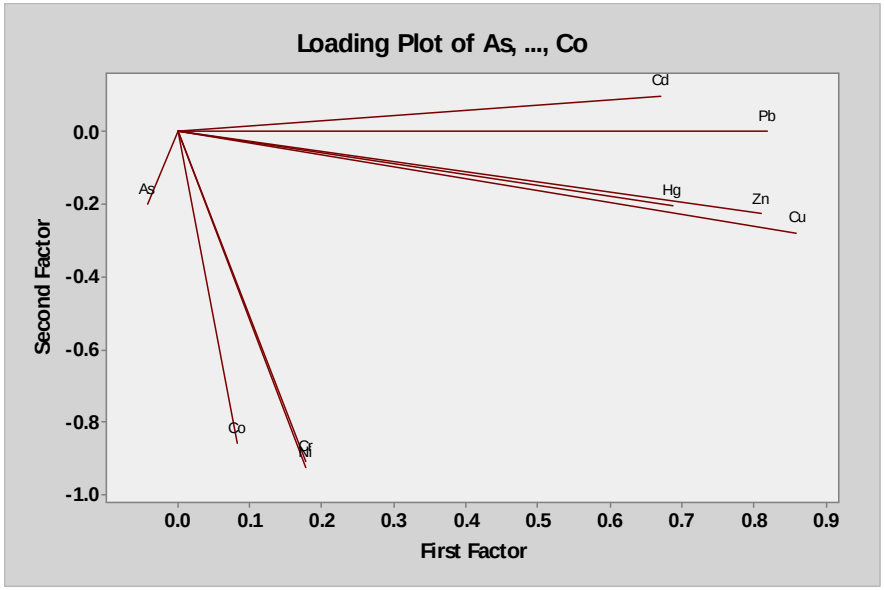
Cell Contents: Pearson correlation, P-Value: [1] < 0.005; [2] < 0.01; [3] < 0.05



The concentration data are not normally distributed and to avoid the robustness the data are transformed by using Box-Cox transormation by applying the same Transformation factor: λopt = -0.33

The optimal range of Box-Cox transformation factor (λ) of each element

FA Analysis



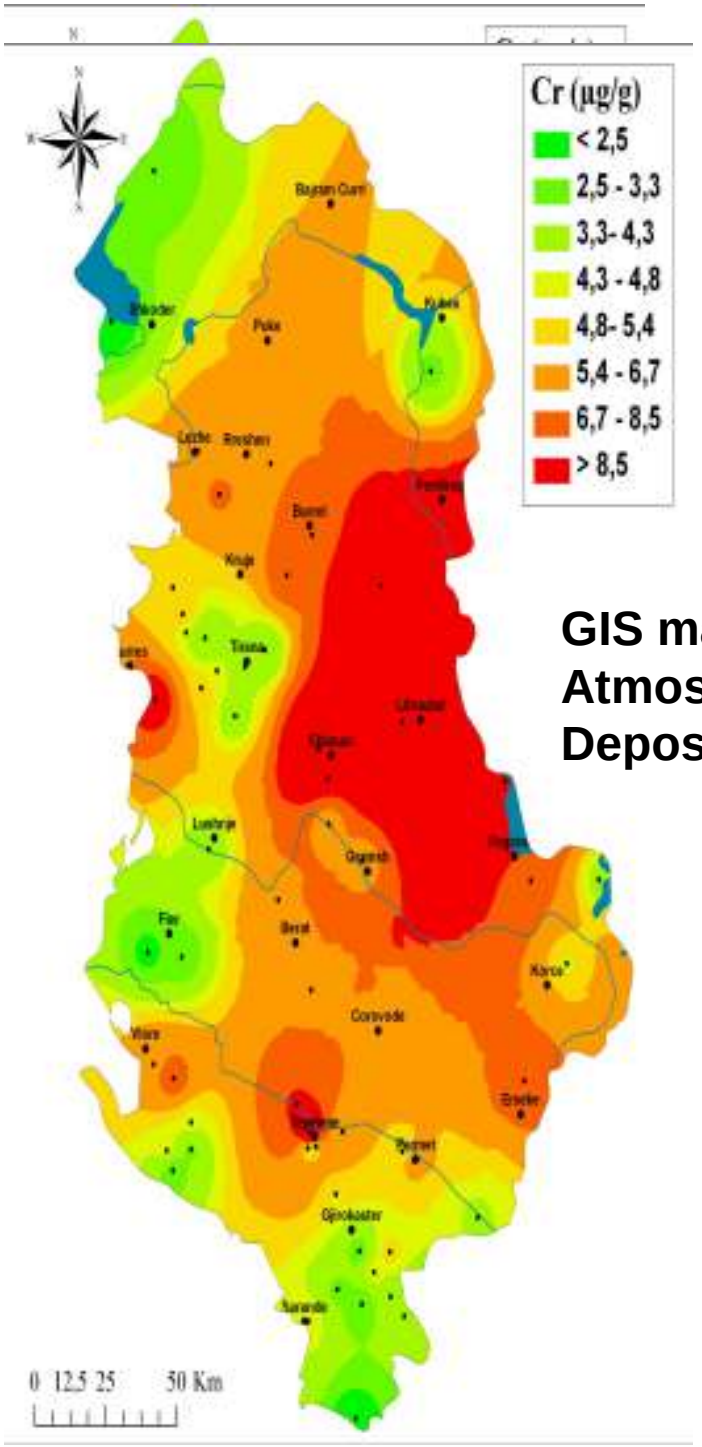
	F1	F2	F3	Comulative
As	-0.044	-0.198	*0.893*	0.839
Cd	*0.670*	0.099	*0.487*	0.696
Cr	0.178	*-0.907*	0.183	0.887
Cu	*0.860*	-0.278	-0.114	0.829
Ni	0.176	*-0.923*	-0.104	0.893
Pb	*0.818*	0.003	0.246	0.729
Zn	*0.809*	-0.227	*-0.352*	0.830
Hg	*0.687*	-0.205	-0.018	0.514
Co	0.083	*-0.858*	0.126	0.758
Variance	3.056	2.629	1.292	6.977
% Var	0.340	0.292	0.144	0.775

Three main factors were extracted (Eigen values>1)

F1: Cd, Cu, Pb, Zn, Hg – geogenic factor of sulfide minerals particles caused from windblowing soil dust

F2: Cr, Ni, Co – anthropogenic factor: metal processing (Cr-Ni-Fe metallurgy in Elbasan area) and geogenic factor of Cr-Ni, Ni and Fe minarals

F3: As – with high values in the south of the country related to anthropogenic origin from agriculture activity and the use of pesticides and herbicides



GIS map of Cr Atmospheric Deposition

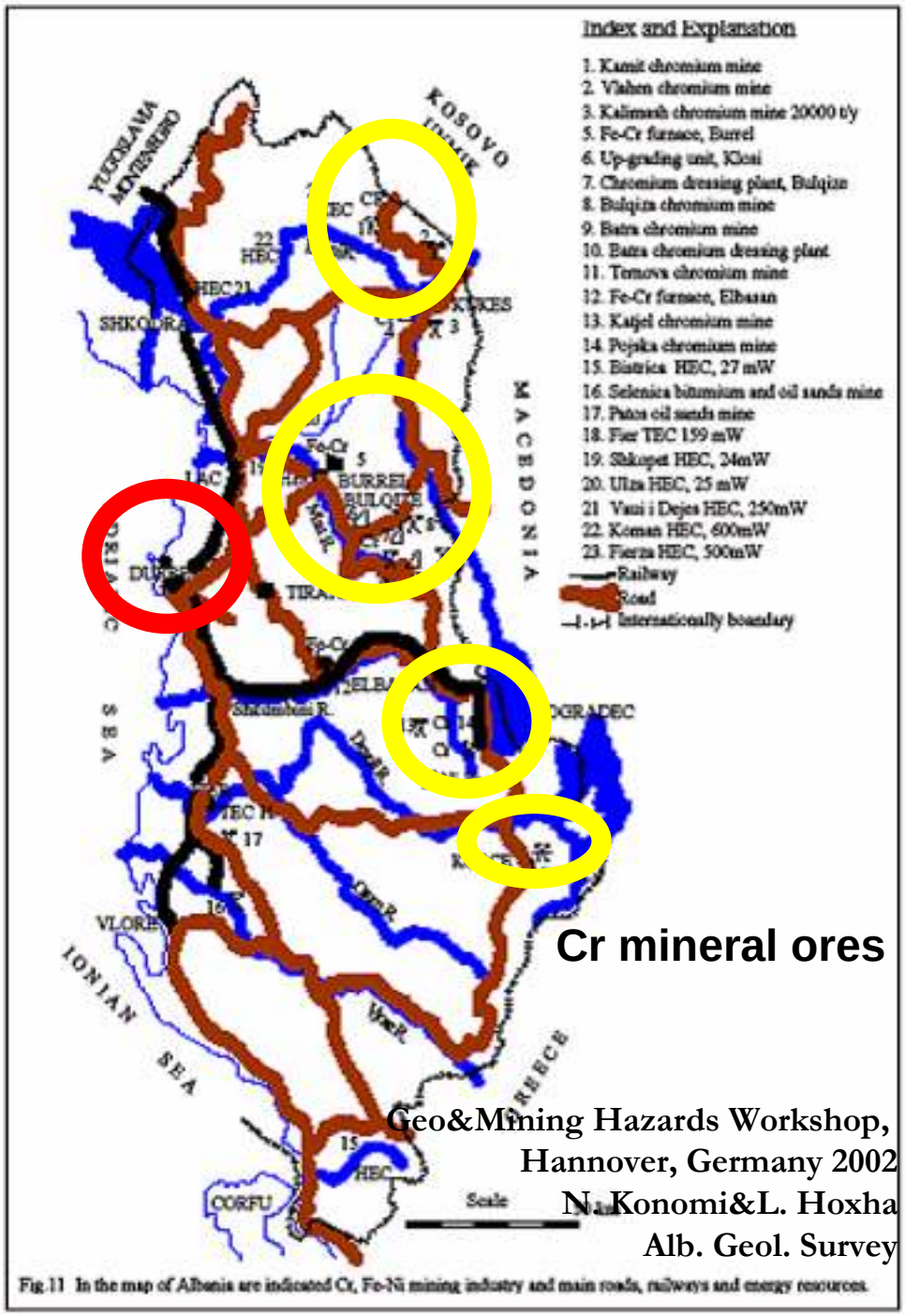
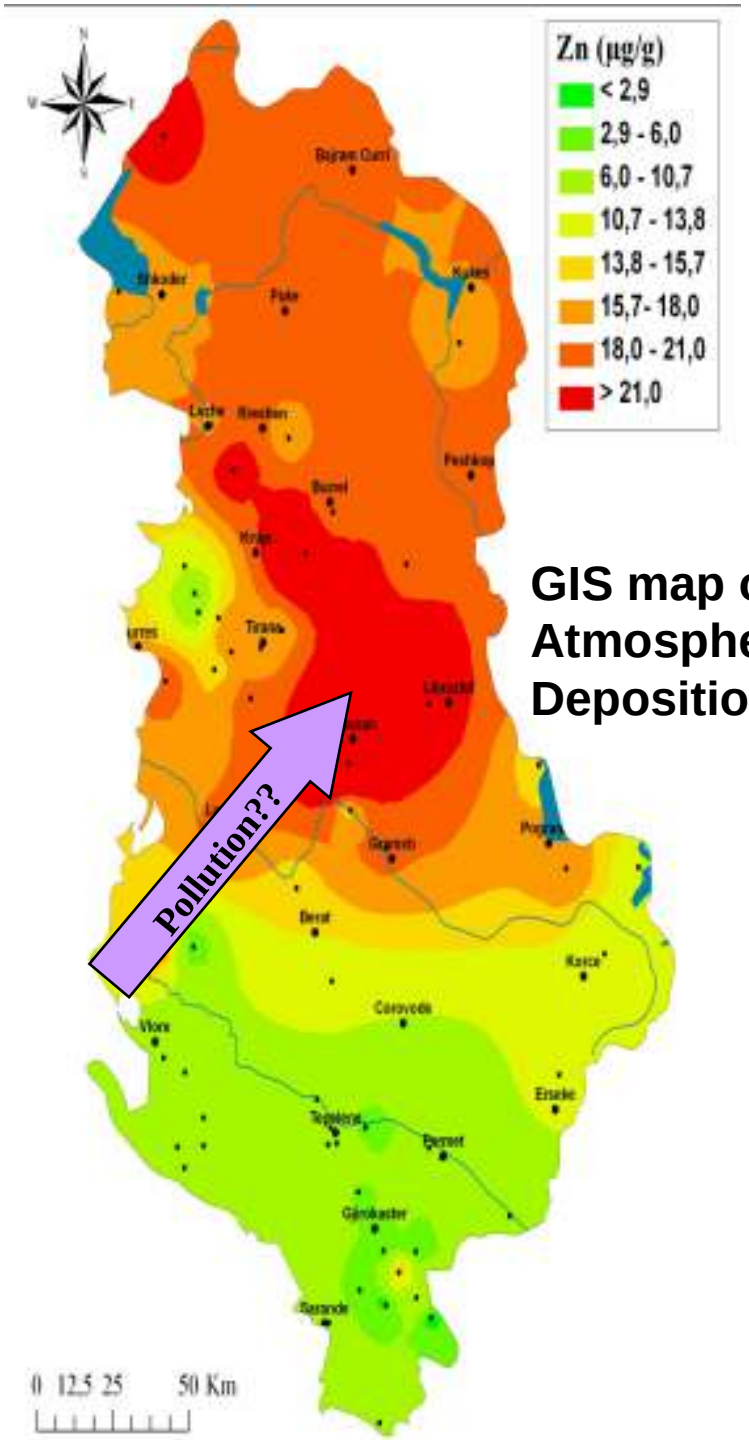


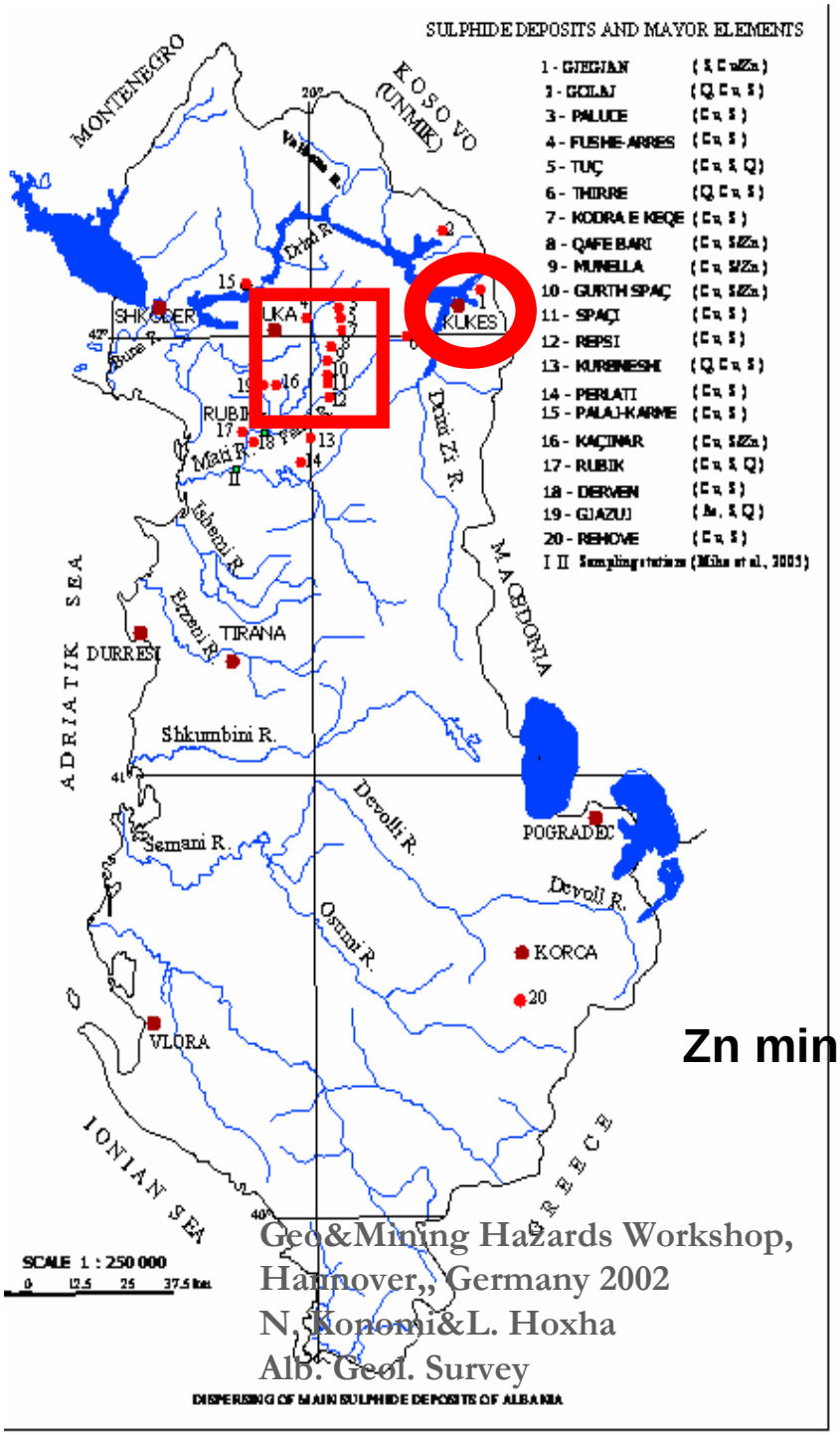
Fig.11 In the map of Albania are indicated Cr, Fe-Ni mining industry and main roads, railways and energy resources.

Cr mineral ores

Geo&Mining Hazards Workshop,
Hannover, Germany 2002
N. Konomi&L. Hoxha
Alb. Geol. Survey



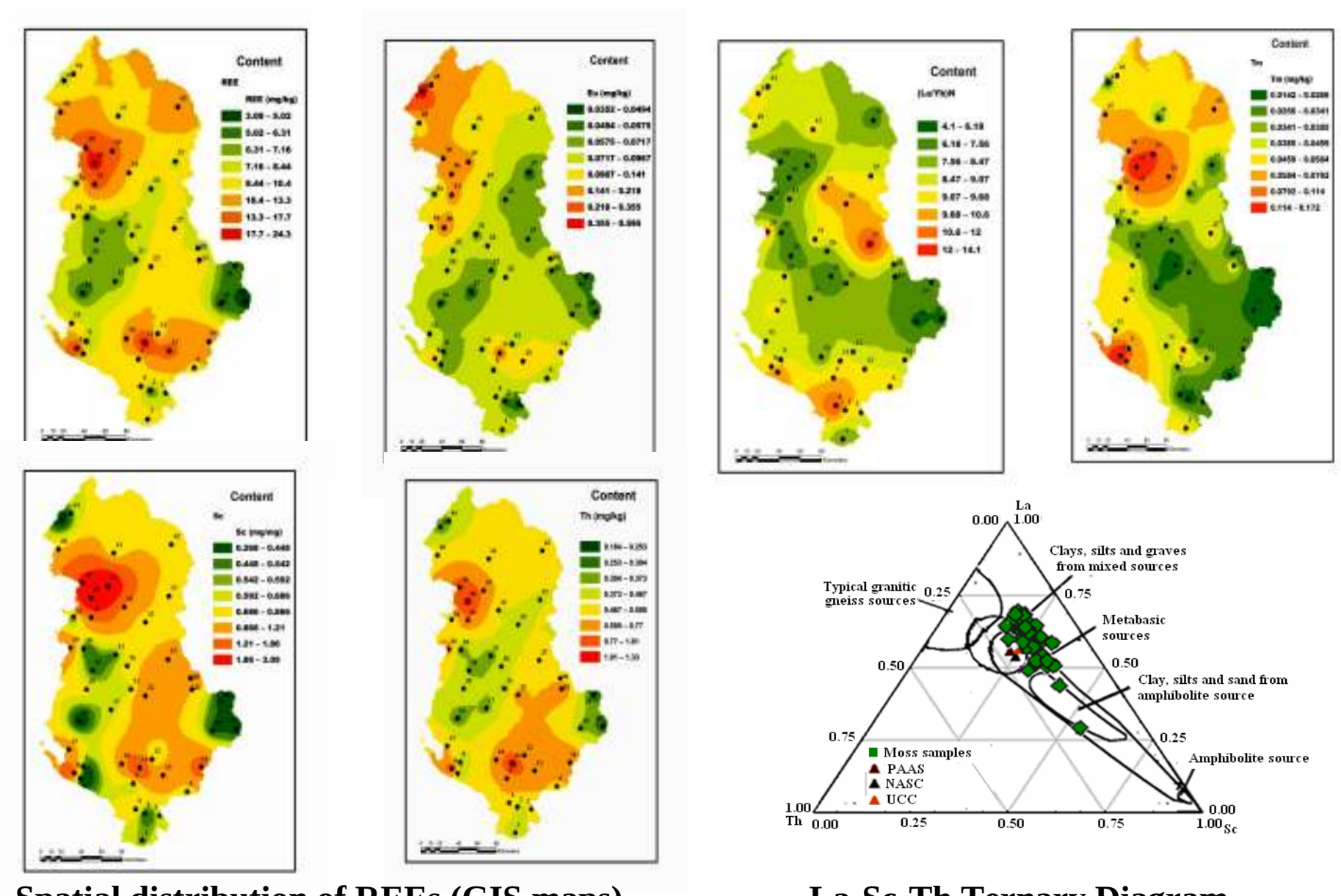
GIS map of Zn Atmospheric Deposition



Zn mineral ores

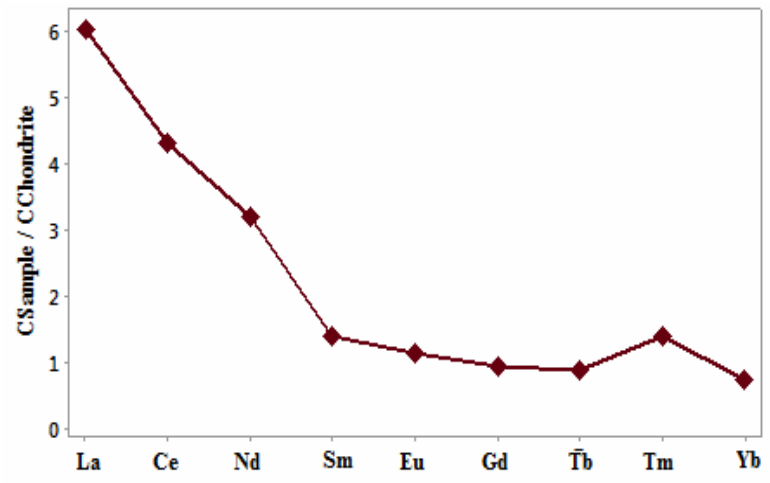
Geo&Mining Hazards Workshop,
Hannover,, Germany 2002
N, Konomi&L. Hoxha
Alb. Geol. Survey

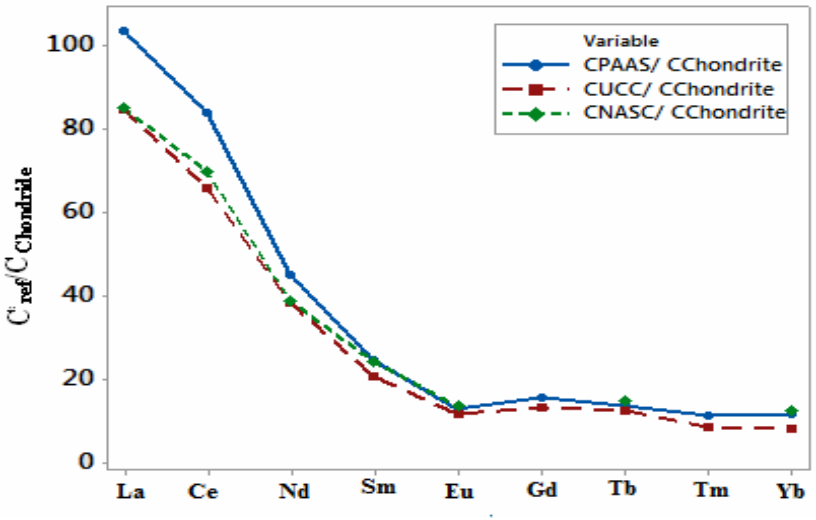
NAA analysis REE elements



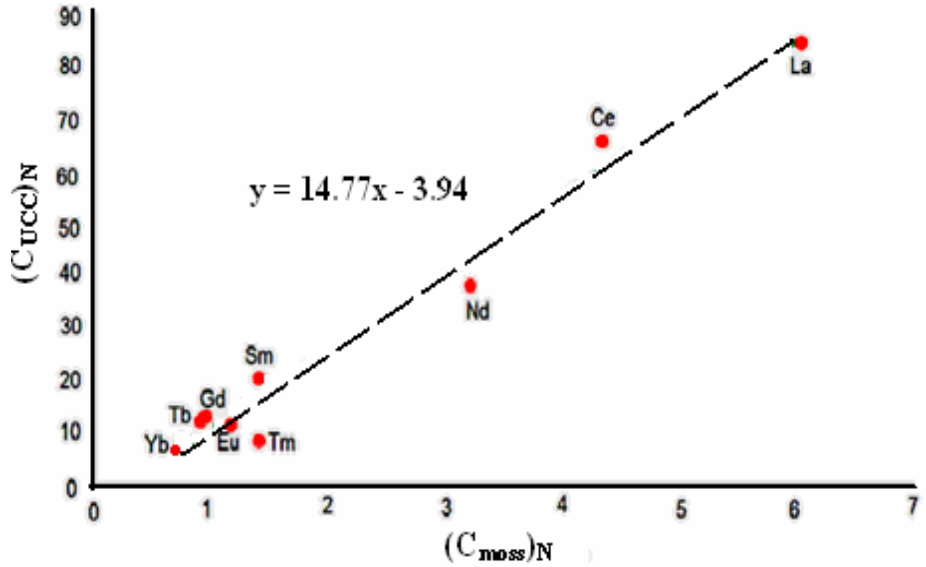
Spatial distribution of REEs (GIS maps)

La-Sc-Th Ternary Diagram





Spider Diagrams of (REEs)N in moss samples and Upper Continental Crust (UCC) (Rudnick and Gao 2003), North American Shale Composite (NASC) (Gromet et al. 1984), Average Post-Archaean Australian Shale PAAS (Taylor and McLennan 1985). Chondrite values are taken from (Taylor and McLennan 1985)



Linear regression of $C_{(moss)N}$ vs. $C_{(UCC)N}$

Mixed origin from slites, cly minerals, graves and metabasic sources of REEs were evident from terary diagram

UCC origin of REEs was tested from the chondrite normalized data and Spider Diagrams; and linear regression of C(moss)N vs. C(UCC)N

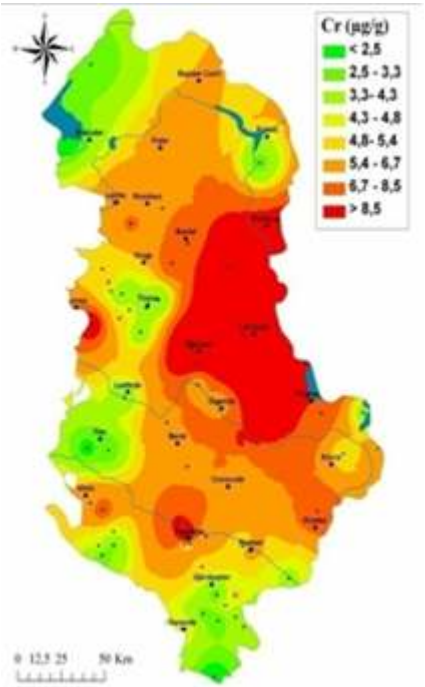
Sh. Allajbeu, N.S. Yushin, F. Qarri, O.G. Duliu, P. Lazo, M. V. Frontasyeva – Atmospheric Deposition of REEs in Albania Studied by the Moss Biomonitoring Technique, NAA analysis and Gis Technology. Env. Sc. and Poll. Res.

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.**
- **Local emitters and the sources of the elements were identified.**
- **The median values of Al, Hg, Cr, Ni, Fe and As onto moss samples of Albania are among the highest values of European moss**

- **CF values indicate small to high contamination level of HM in Albanian atmospheric deposition; PLIzone = 7.2 > 5 indicate moderate to high polution loads, and RI>150 indicate moderate to high ecological risk.**

- **Elbasan-Librazhd area (central part of the country) is the most polluted.**



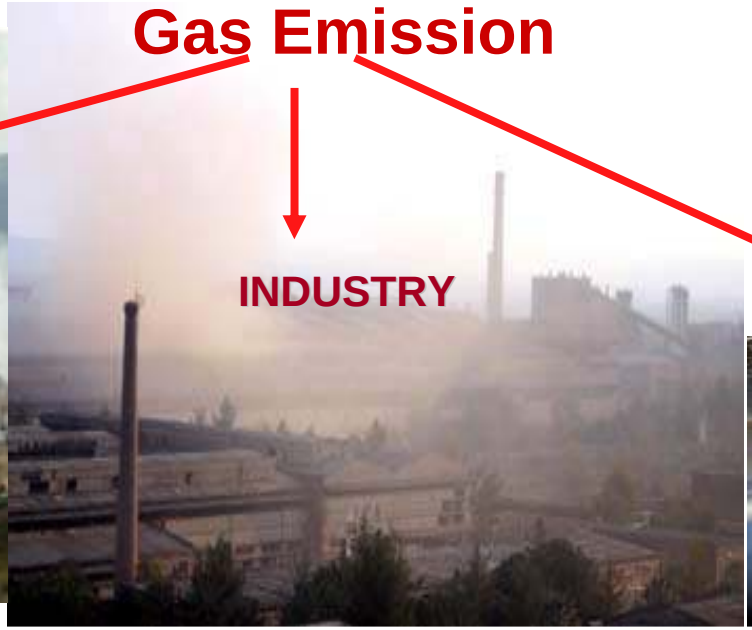
P. Lazo, T. Stafilov. F. Qarri, L. Bekteshi, S. Kane, Sh. Allajbeu, M. Frontasyeva, H. Harmens Characterization of Heavy Metals Atmospheric Deposition for Evalueting Air Quality by Using Moss Bioindicatoring, ICP/AES and ENAA Analysis

Main pollution soureces.

Repsi – Cu mineral dumps

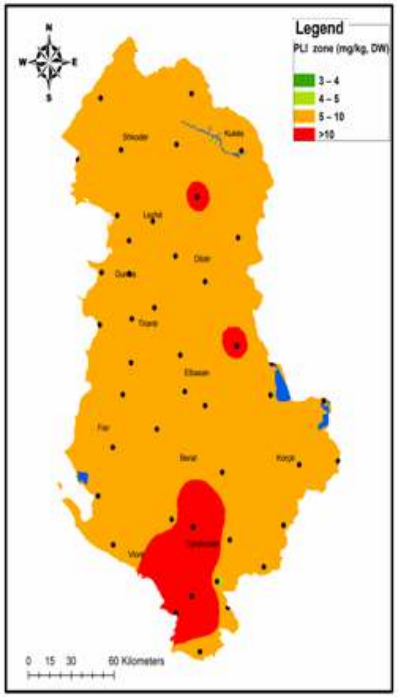
Rubik: ex-Cu metalurgy

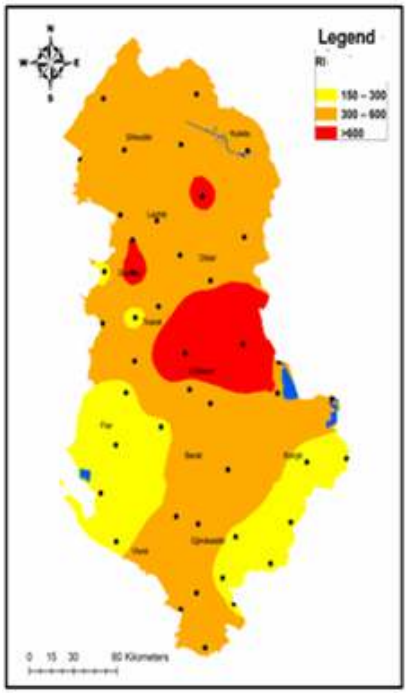
Gas Emission



FUTURE CONSIDERATIONS

1. Sampling: MSS





Total: 57 sampling sites (H. cupr. 43 samples; Scl. Purum. 30 samples)
At 15 sampling sites were sampled both species (H. cpr. and Scl. Purum)

2. Analysis

Analyzed for 18 elements (ICP/AES)
Will be analyzed for As, Cd, Pb, Hg

3. Pollution characterization:

Need to establish the critical levels of HMs

4. Sampling frequency; once/5 years

- green part of moss – represent 3 years growth

5. Homogenity of the samples

– use a plastic mortar

Thank You for Your Attention!