EVALUATION OF MULTI-ELEMENT CONTENT AND BIOAVAILABILITY RECORDS FOR VARIOUS PLANT FOOD DUE TO THE HISTORICAL AND MODERN METAL POLLUTION EXPOSURE

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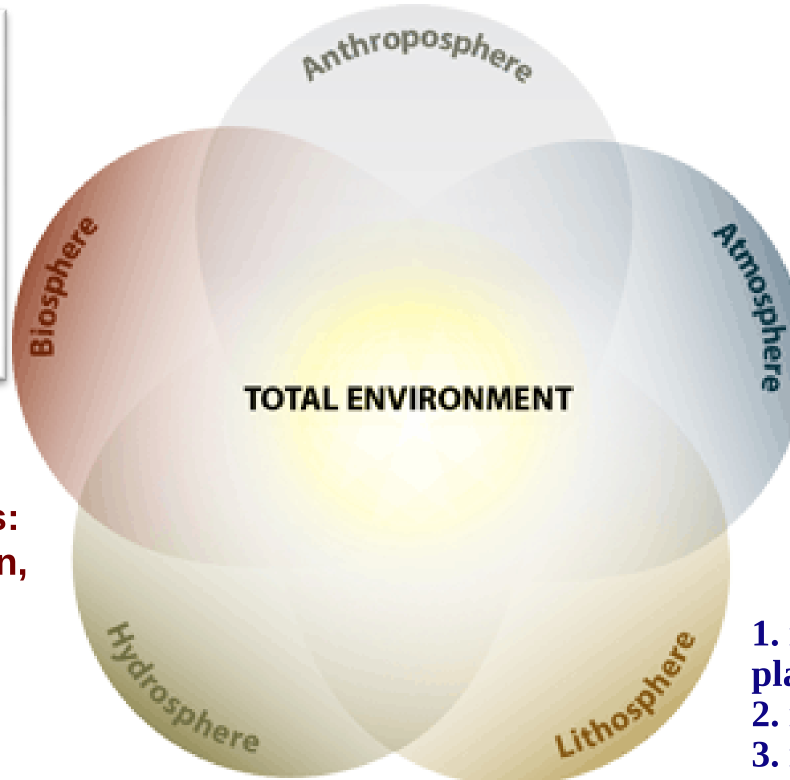
18th CEEPUS International Symposium and Summer School on Bioanalysis, June 25-30, 2018, Komárno, Slovakia

CHEMICAL ELEMENTS IN ENVIRONMENT

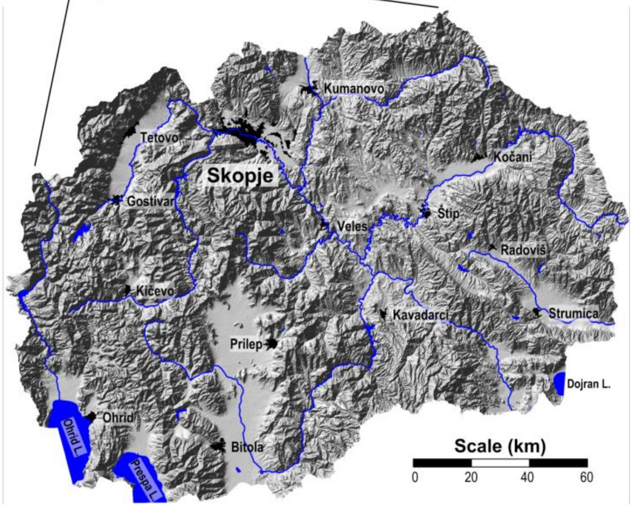


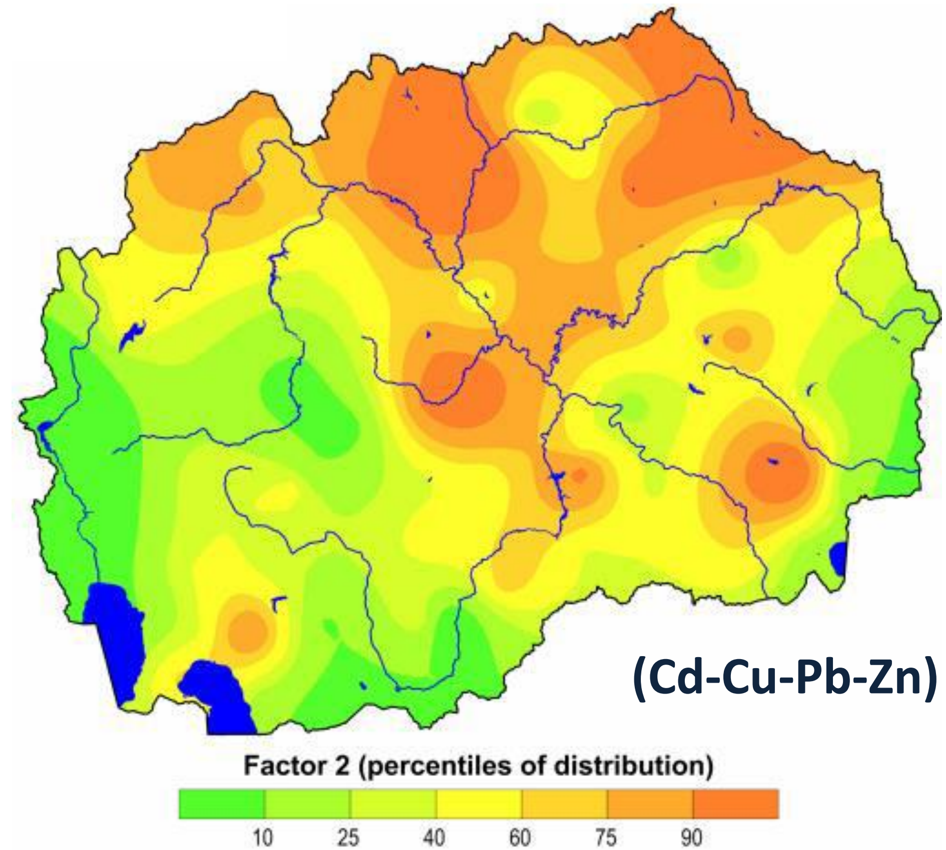
Biologically effective elements:
Na, Mg, Si, P, S, Cl, Ca, Ti, V, Mn, Fe, Co, Mo

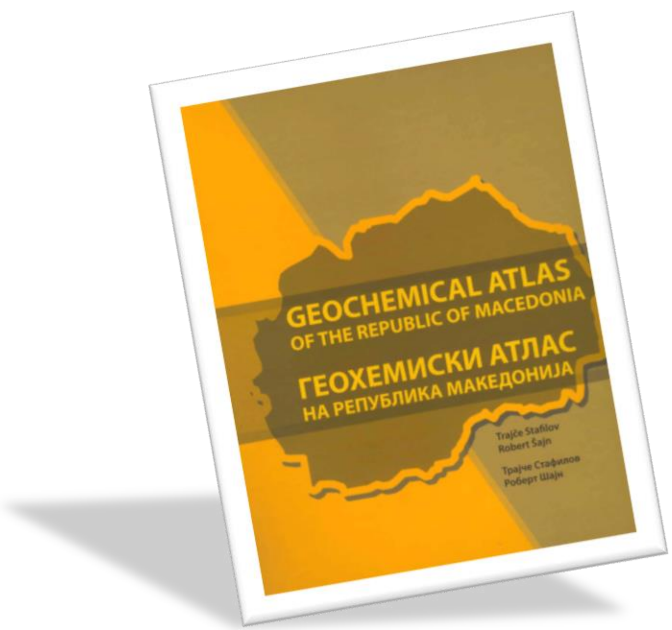
1. **municipal wastewater-treatment plants**
2. **manufacturing industries,**
3. **mining,**
4. **transportation**
5. **agricultural cultivation & fertilization…….**

Biologically hazardous elements:
Bi, Be, Al, Cr, Ni, As, Nb, Ag, Cd, Sb, Ba, Hg, Pb, Zn

MULTI-ELEMENT DISTRIBUTION IN SOIL REPUBLIC OF MACEDONIA

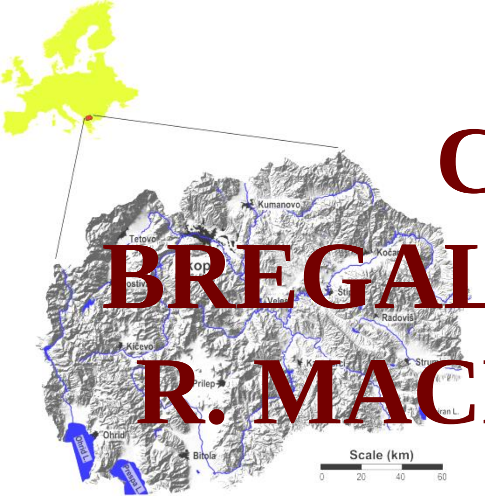




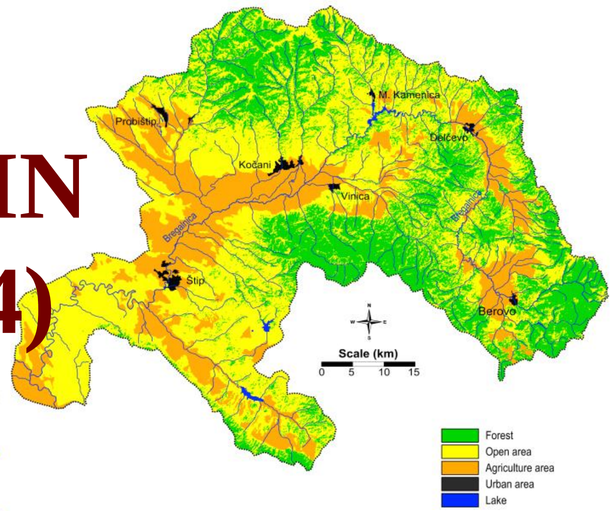


Dominant geochemical association In areas with anthropogenic introducing of heavy metals

Stafilov T., Sajn R. (2016) *Geochemical atlas of the Republic of Macedonia.* Faculty of Natural Sciences and Mathematics – Skopje.

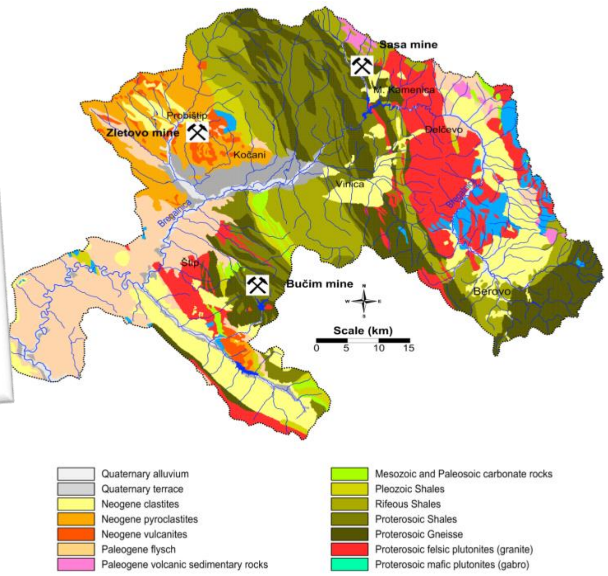


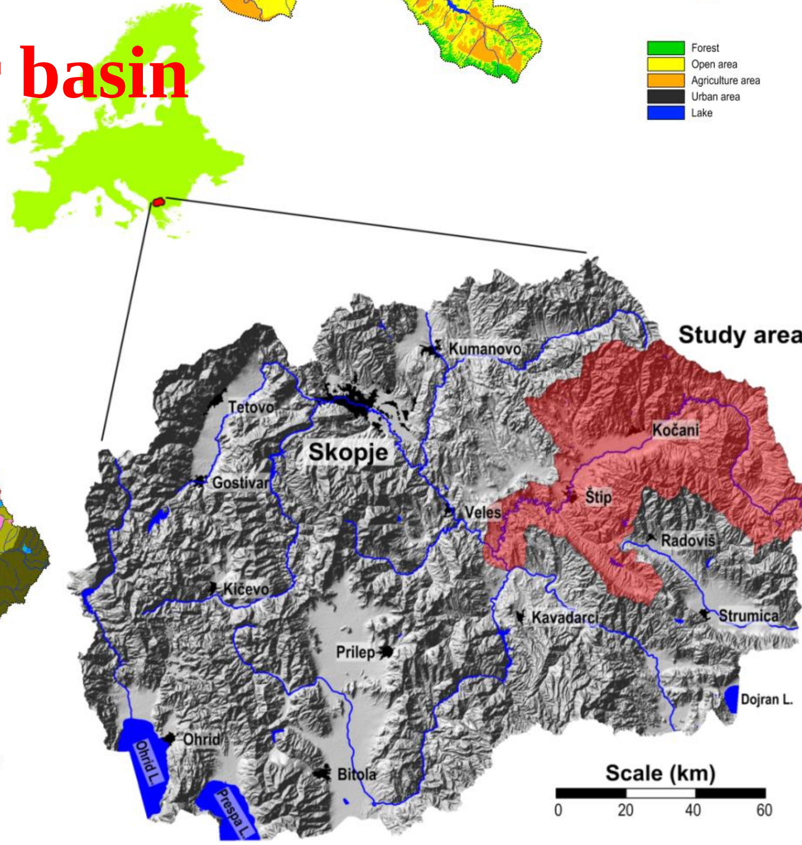
CASE STUDY:
BREGALNICA RIVER BASIN
R. MACEDONIA (2012-2014)



Bregalnica River basin

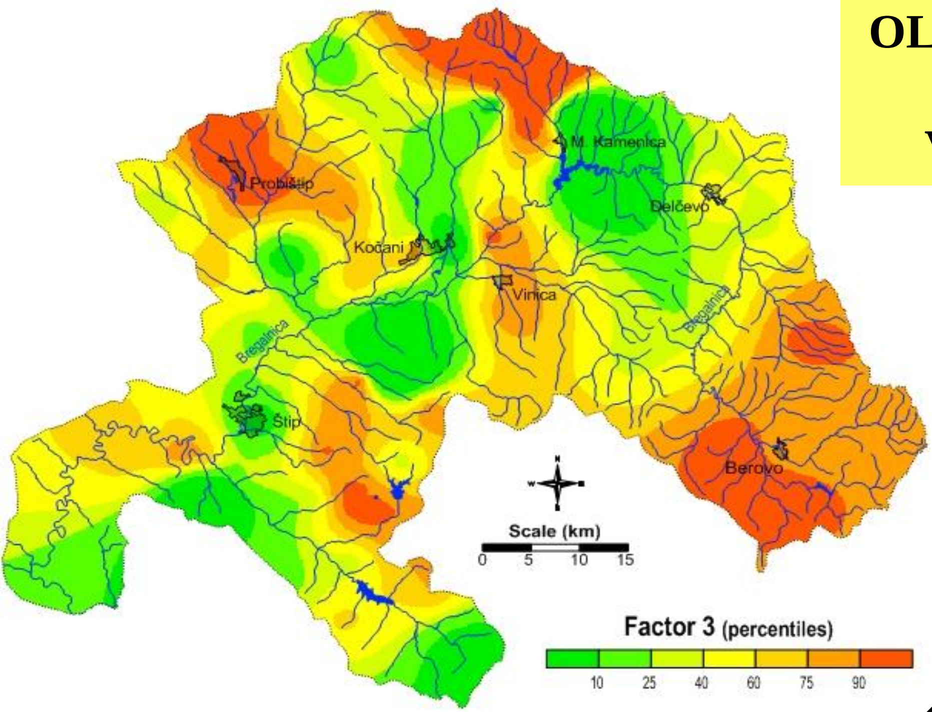
N: 41°27'-42°09'
E: 22°55'-23°01'





Stafilov T., Balabanova B., Sajn R. (2014) *Geochemical atlas of the region of the Bregalnica river basin.* Faculty of Natural Sciences and Mathematics – Skopje.

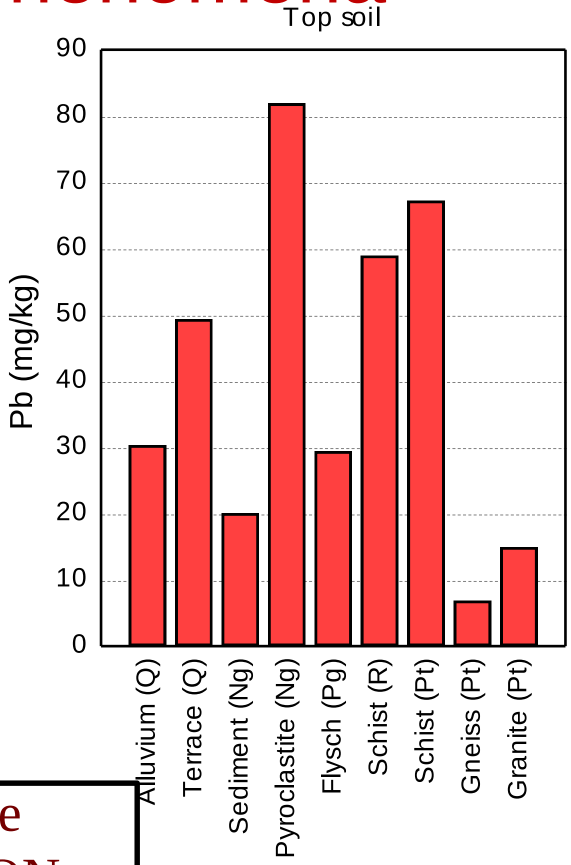
Lithogenic *vs.* Anthropogenic phenomena



(Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn)

OLIGOCENE AND NEOGENE VOLCANISM

Occurrence in area with dominance of



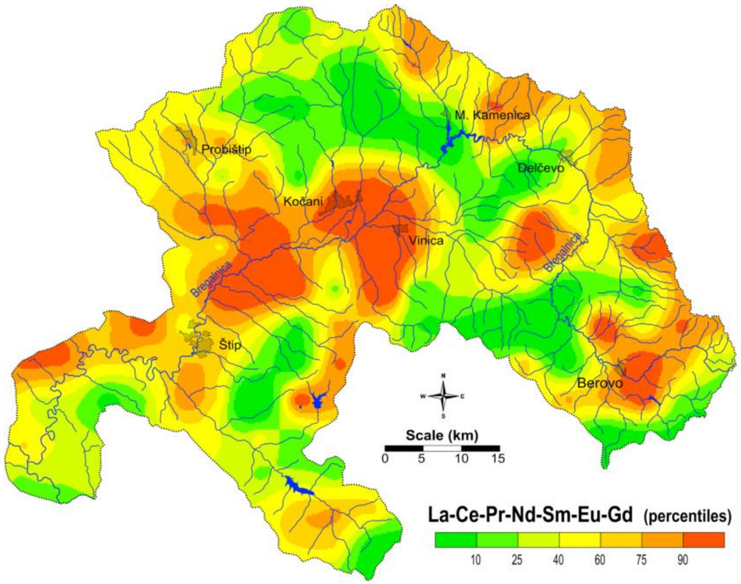
Multivariate EXTRACTION

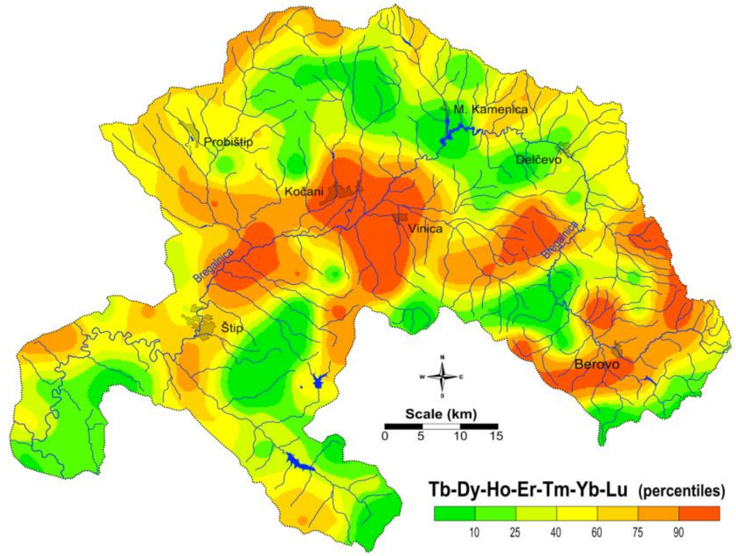
ANTHROPOGENIC ANOMALIES!!!

Total 69 elements: Ag, As, Al, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In,Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P,Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Ti, Th, Tl, Tm, V, W, Y, Yb, Zn and Zr

Balabanova et al. (2017) Archives of Environmental Contamination and Toxicology.
Balabanovaet al. (2017) Journal of Environmental Science and Health, Part A.
Balabanova et al. (2016) Environmental Science and Pollution Research.
Balabanova et al. (2016) Macedonian Journal of Chemistry and Chemical Engineering.
Balabanova et al. (2016) Journal of Environmental Science and Health, Part A.
Balabanova et al. (2015) Journal of Environmental Health Science & Engineering.
Balabanova et al. (2015) Macedonian Journal of Chemistry and Chemical Engineering.

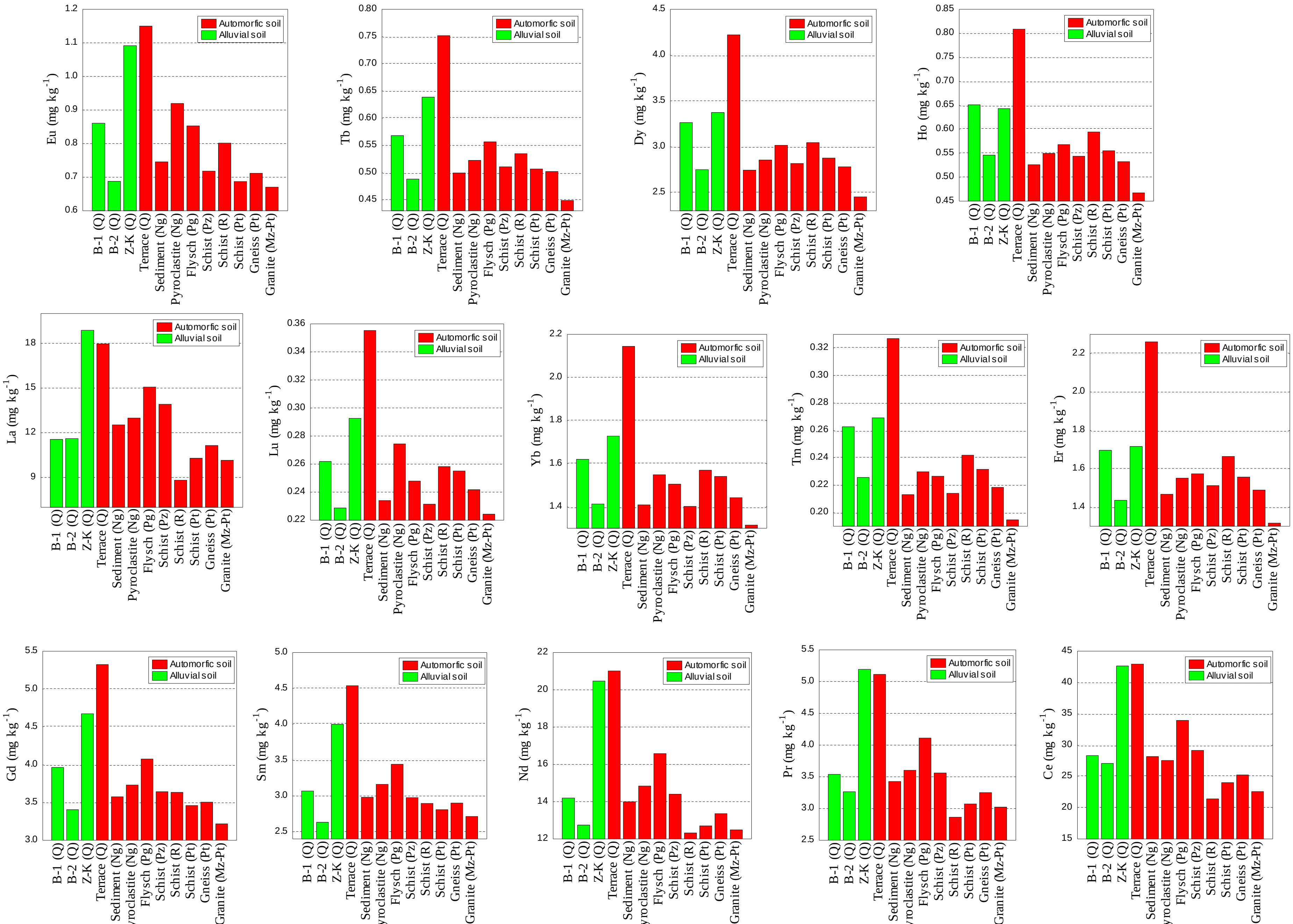
Lithogenic distribution of REEs

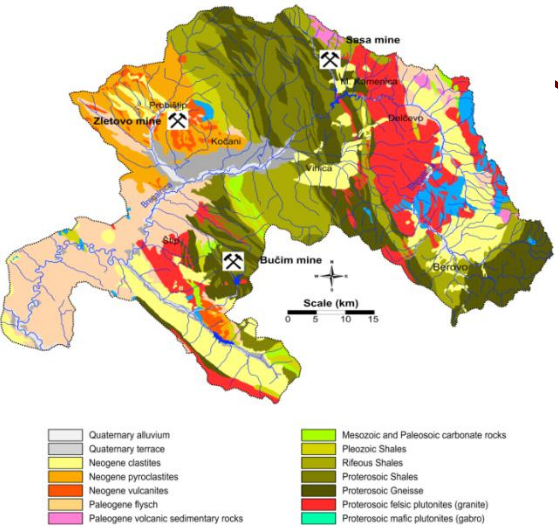


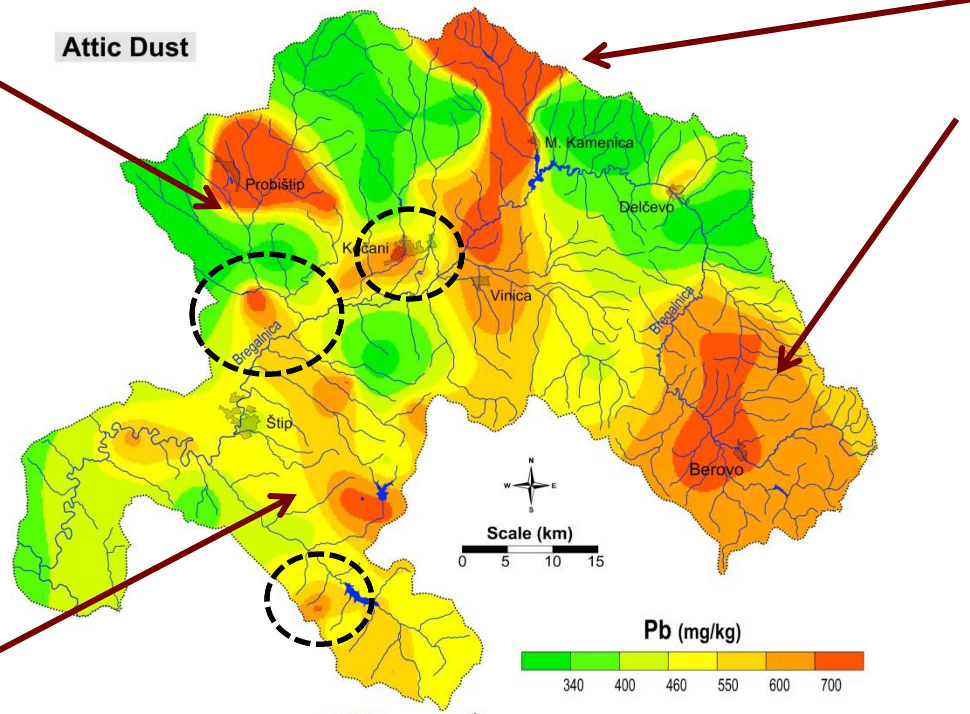


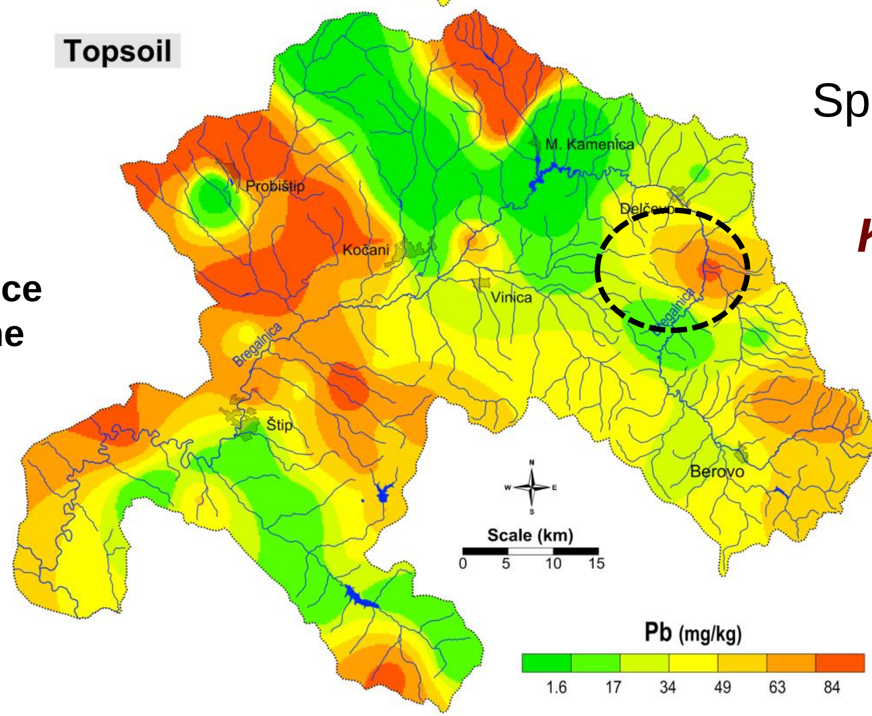
Ce$	1.00													
Dy	0.77	1.00												
Er	0.70	0.99	1.00											
Eu	0.84	0.92	0.89	1.00										
Gd	0.87	0.97	0.94	0.96	1.00									
Ho	0.72	1.00	1.00	0.90	0.95	1.00								
La	0.96	0.72	0.65	0.79	0.84	0.67	1.00							
Lu	0.70	0.94	0.96	0.87	0.90	0.95	0.65	1.00						
Nd	0.96	0.88	0.83	0.93	0.96	0.85	0.93	0.83	1.00					
Pr	0.97	0.84	0.79	0.90	0.93	0.81	0.95	0.79	1.00	1.00				
Sm	0.91	0.94	0.89	0.96	0.99	0.91	0.88	0.88	0.99	0.97	1.00			
Tb	0.82	0.99	0.97	0.95	0.99	0.98	0.78	0.93	0.93	0.89	0.97	1.00		
Tm	0.69	0.98	1.00	0.87	0.92	0.99	0.64	0.97	0.82	0.78	0.88	0.96	1.00	
Yb	0.69	0.97	0.99	0.87	0.92	0.98	0.65	0.99	0.82	0.79	0.89	0.95	1.00	1.00
	Ce	Dy	Er	Eu	Gd	Ho	La	Lu	Nd	Pr	Sm	Tb	Tm	Yb

Balabanova et al. (2016) Macedonian Journal of Chemistry and Chemical Engineering.


Automorfic soil
Alluvial soil
Eu (mg kg-1)
Tb (mg kg-1)
Dy (mg kg-1)
Ho (mg kg-1)
La (mg kg-1)
Lu (mg kg-1)
Yb (mg kg-1)
Tm (mg kg-1)
Er (mg kg-1)
Gd (mg kg-1)
Sm (mg kg-1)
Nd (mg kg-1)
Pr (mg kg-1)
Ce (mg kg-1)
B-1 (Q)
B-2 (Q)
Z-K (Q)
Terrace (Q)
Sediment (Ng)
Pyroclastite (Ng)
Flysch (Pg)
Schist (Pz)
Schist (R)
Schist (Pt)
Gneiss (Pt)
Granite (Mz-Pt)



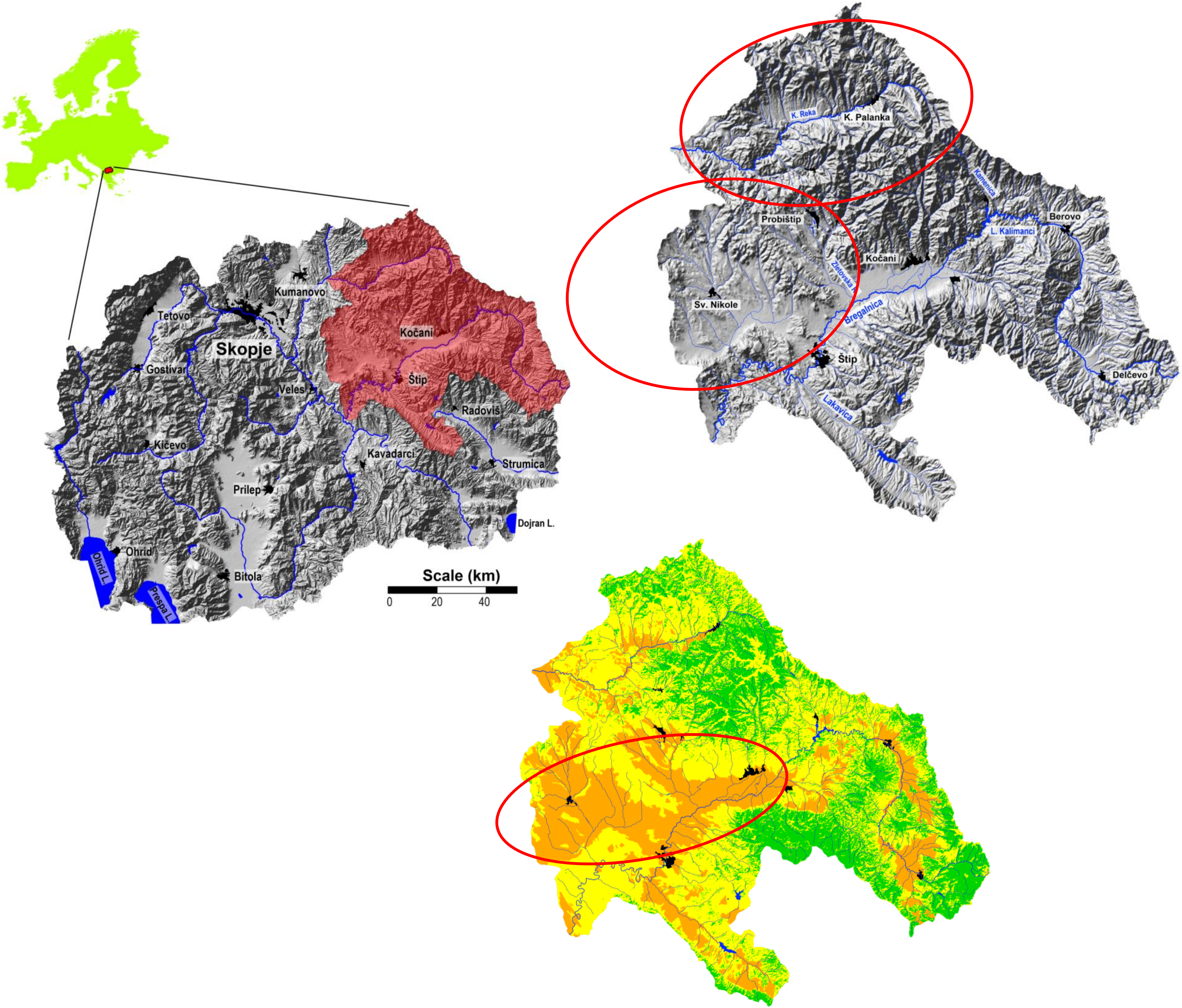




Spotting effect!!!!

***Kriging* anomaly?**

Areas with dominantly presence of the Oligocene and Neogene volcanism

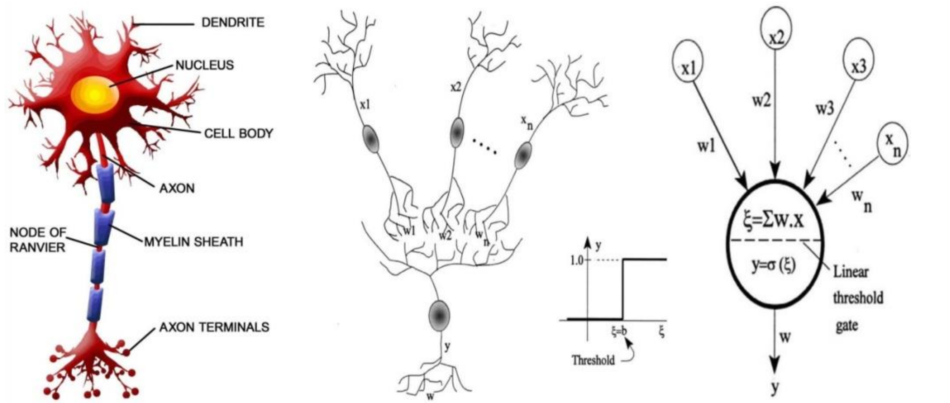


Tetovo
Kumanovo
Skopje
Gostivar
Veles
Kočani
Štip
Radoviš
Kičevo
Kavadarci
Strumica
Prilep
Dojran L.
Ohrid
Ohrid L.
Bitola
Prespa L.
Scale (km)
0
20
40
K. Reka
K. Palanka
Kamenica
Probištip
Berovo
L. Kalimanci
Kočani
Zletovska
Sv. Nikole
Bregalnica
Štip
Delčevo
Lakavica

Artificial neural networks

Artificial Neural Network - computer simulation of human neurons

SYSTEM THAT CAN HANDLE A LARGE NUMBER OF INPUT AND OUTPUT PARAMETERS

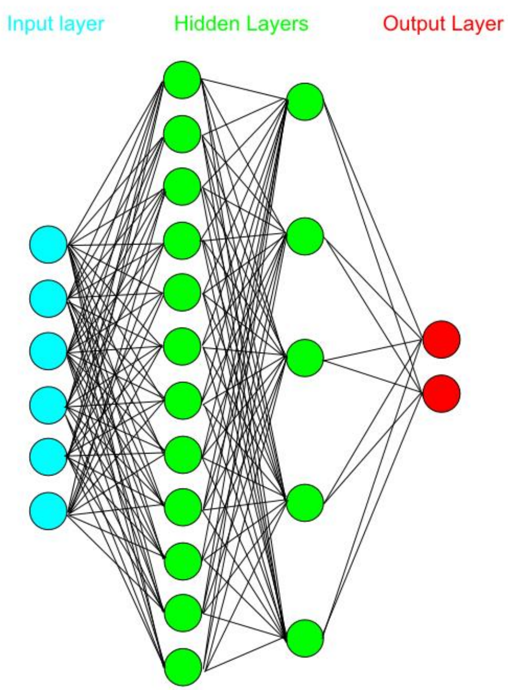


Biological neuron and mathematical model of McCulloch and Pitts neuron

REASONS FOR APPLICATION

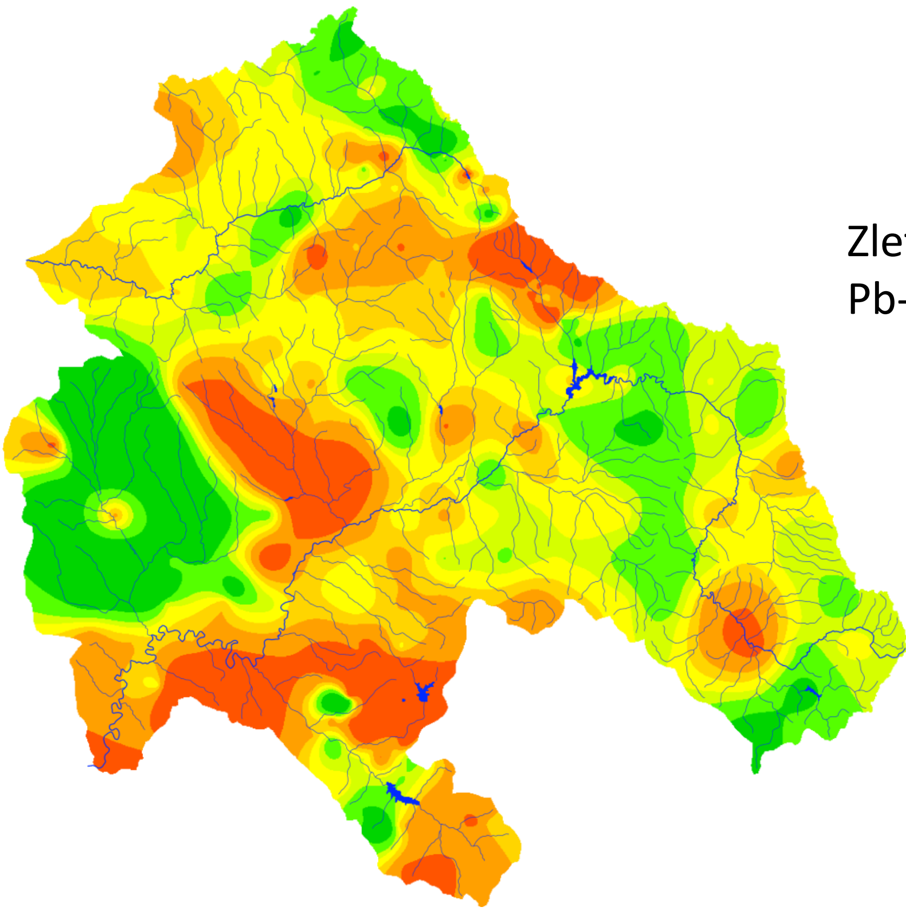
- They can model extremely complex systems, which cannot be modeled by methods based on linear algebra
- No problems with the dimensionality
- Due to well developed learning algorithms they are easy to use

Multilayer perceptron architecture

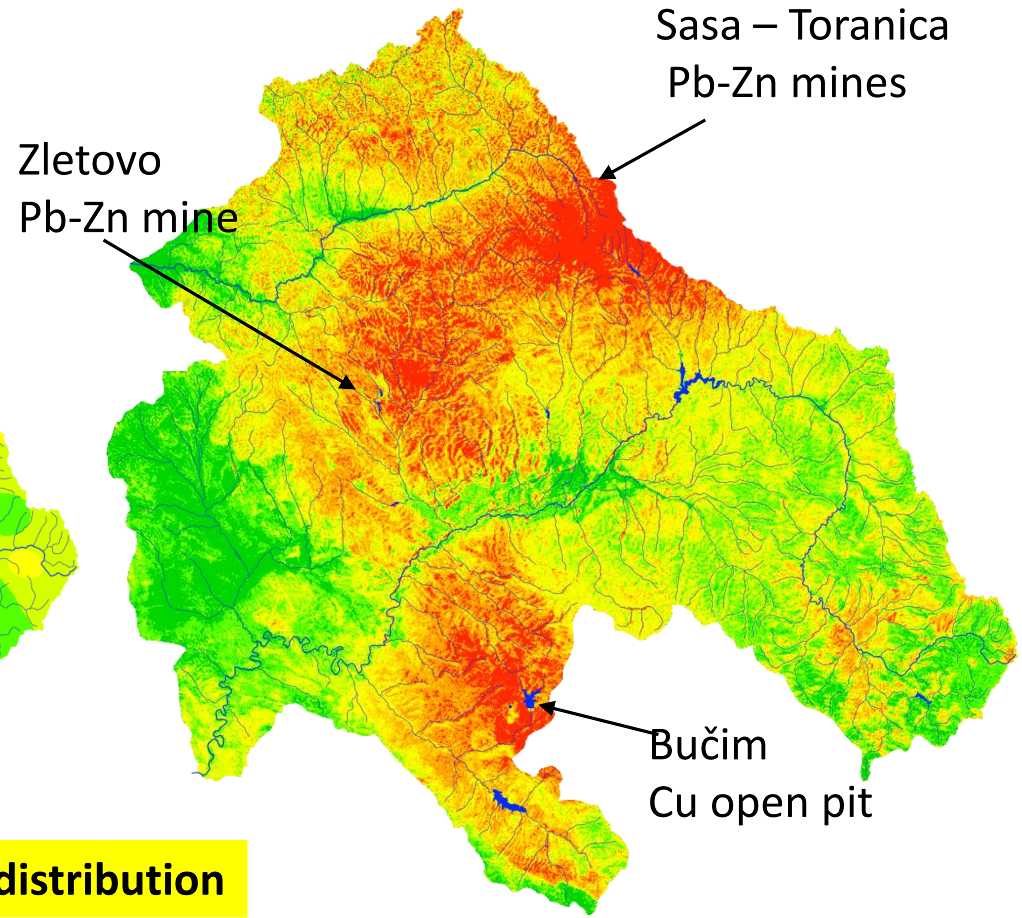


Multilayer perceptron

Universal Kriging



(ANN-MLP)



Copper distribution

(Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn)

PERSPECTIVES…..

MULTI-DISCIPLINARY APPROACH

TRACE AND RARE-EARTH ELEMENT ANALYSIS

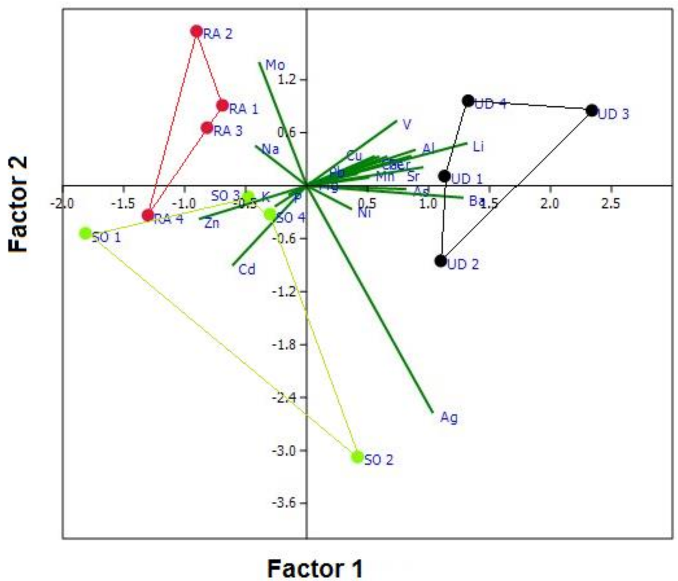
MULTI-ISOTOPE RATIO

METAL BINDING SCAN ANALYSIS

CHEMOMETRIC TOOLS:
Principal Component Analysis (PCA)
Cluster Analysis (CA)
Linear Discriminant Analysis (LDA)
Canonical Discriminant Analysis (CDA)
Artificial Neural Networks (ANN)

MULTI-ELEMENT CHARACTERIZATION OF PLANT FOOD

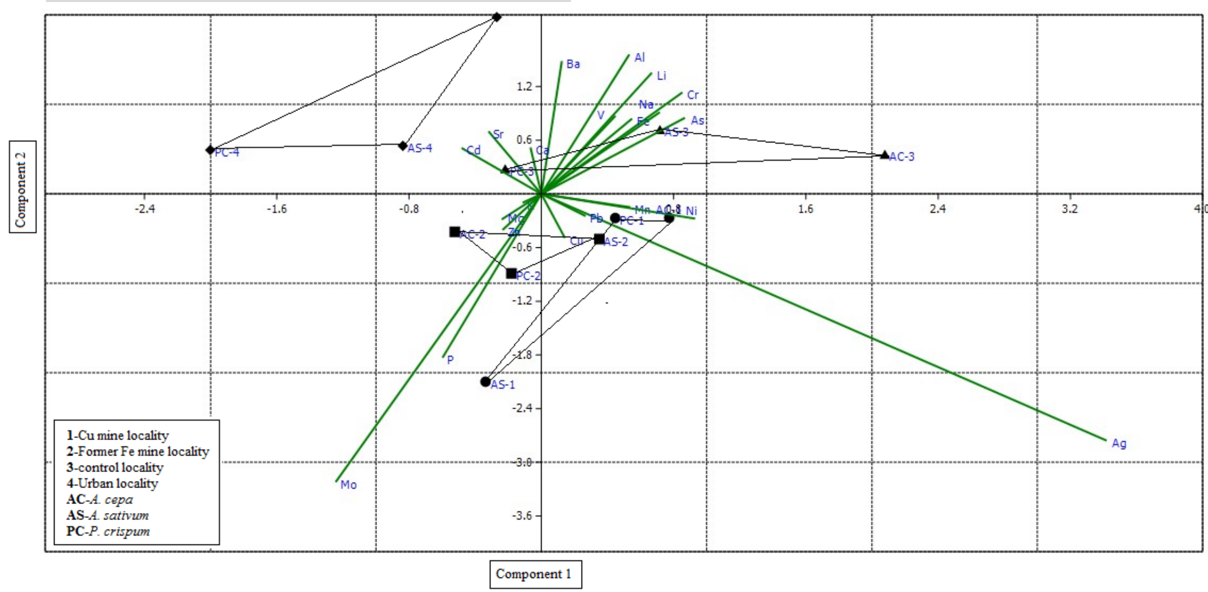
Spinach (*S. oleracea* - SO)
Sorrel (*R. acetosa* - RA)
Common nettle (*U. dioica* - UD)



1-Cu mine locality
2-Former Fe mine locality
3-control locality
4-Urban locality

- None of the species was specified as a hyper-accumulator
- species show potential for PHYTOSTABILIZATION of **Cd**, **Cu**, **Pb** and **Zn**

Garlic (*A. sativum - AS*)
Onion (*A. cepa- AC*)
Parsley (*P. hortense - PC*)



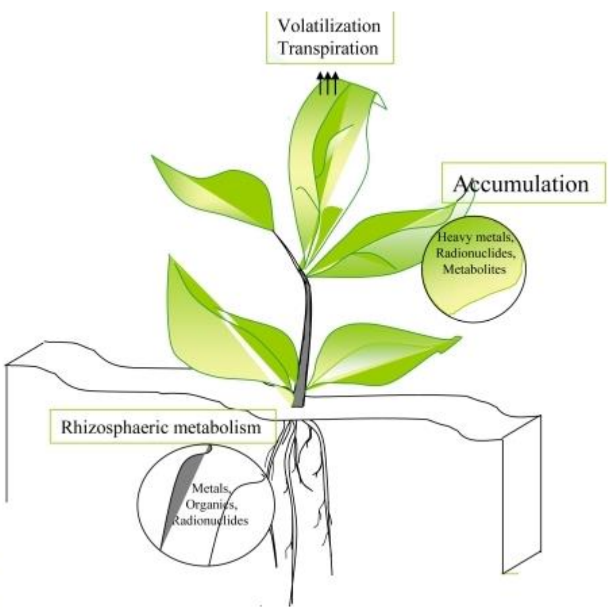
Balabanova B., Stafilov T., Bačeva K., (2015) Bioavailability and bioaccumulation characterization of essential and heavy metals contents in R. acetosa, S. oleracea and U. dioica from copper polluted and referent areas Journal of Environmental Health Science and Engineering

Isotopic measurements

Good to know………

• Small Pb abundance variations occurs in nature

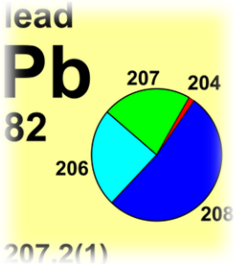
• The isotopic composition of lead in the environment is dependent on the local pollutant source



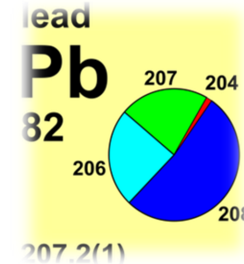
subsequent isotope ratio studies might provide unique means of differentiating between different plant source of origin

•Small Sr abundance variations

•Large atomic mass $^{87}Sr/^{86}Sr$ ratios change little as they pass from weathered rocks through soils to the food chain



Lead isotopes



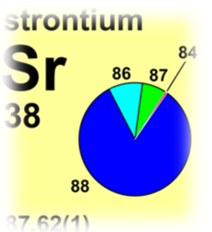
Four stable isotopes of Pb with the following approximate abundances:

- **^{208}Pb (52.4%)**
- **^{207}Pb (24.1%)**
- **^{206}Pb (22.1%)**
- **^{204}Pb (1.4%)**

^{208}Pb, ^{207}Pb and ^{206}Pb are formed by the radioactive decay of:

- ^{232}Th (half-life = 14 billion years),
- ^{235}U (half-life = 0.7 billion years),
- ^{238}U (halflife = 4.5 billion years), respectively.

Strontium isotopes



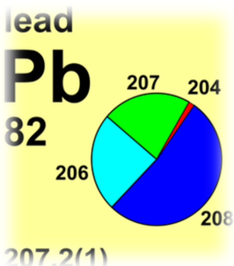
Strontium is a trace element that is found in most igneous, metamorphic and sedimentary rock

Four stable isotopes of Sr with the following approximate abundances:

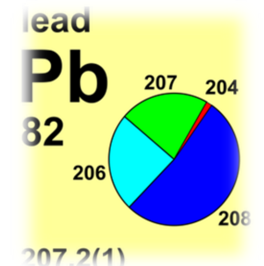
- **^{88}Sr (82.5%)**
- **^{87}Sr (7.04%)**
- **^{86}Sr (9.87%)**
- **^{84}Sr (0.56%)**

^{87}Sr is radiogenic formed by the radioactive decay of:

- ^{87}Rb (half-life = 4.88 x 10^{10} years)

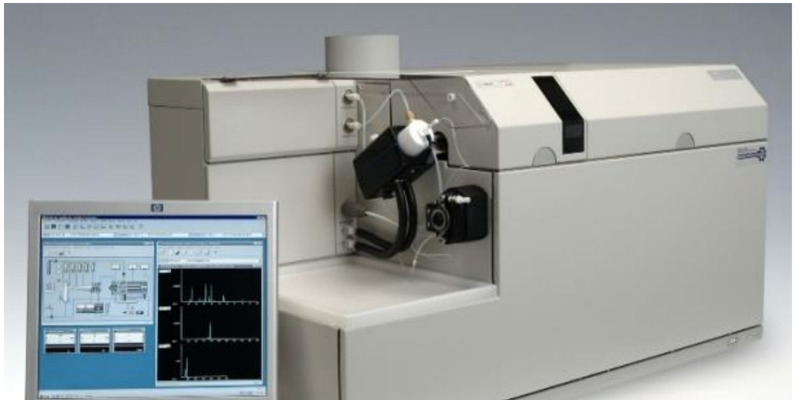


Isotopes measurements

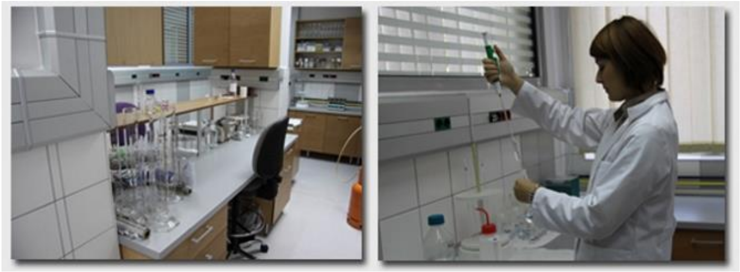


DETERMINATION OF Pb ISOTOPES

QUADROPOLE INDUCTIVELY COUPLED PLASMA WITH MASS SPECTROMETRY (Q-ICP-MS)



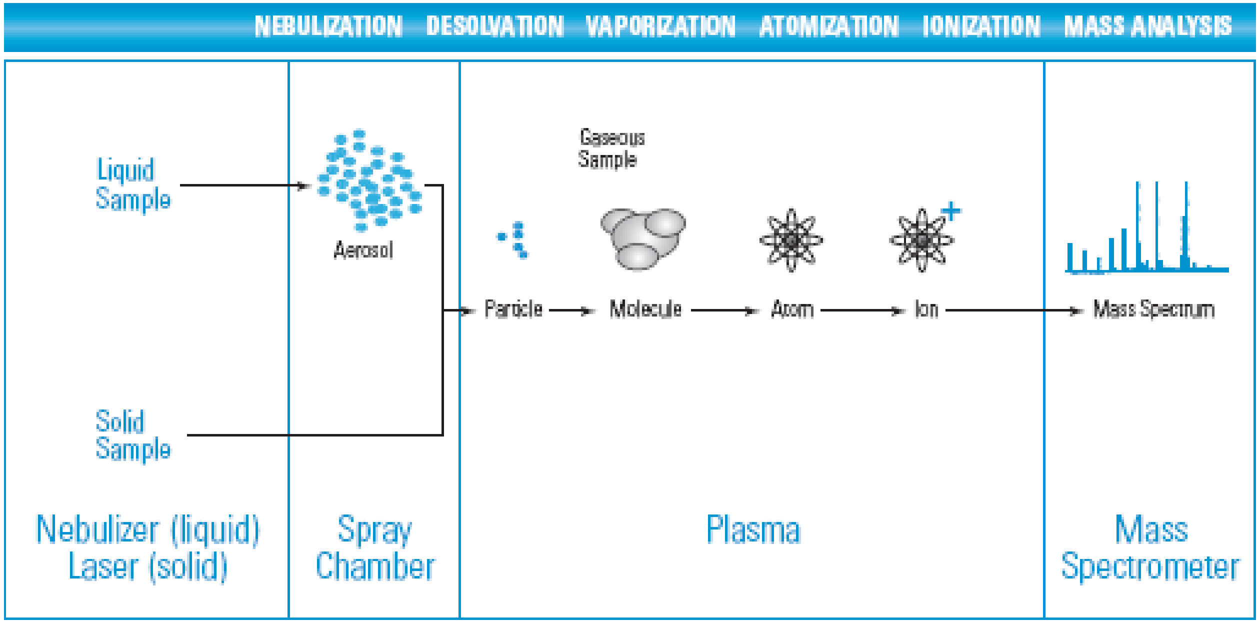
Model 7500 cx Agilent, USA

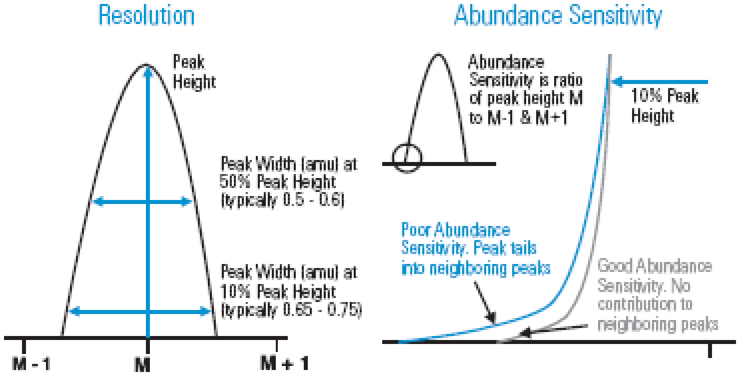


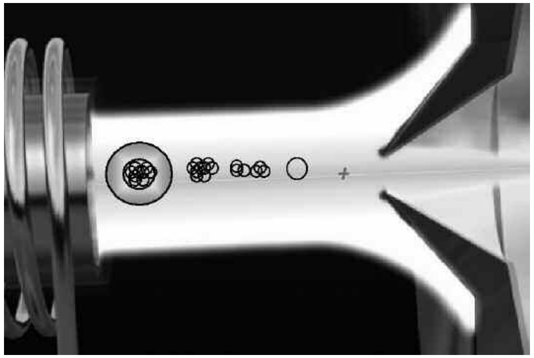
UNILAB

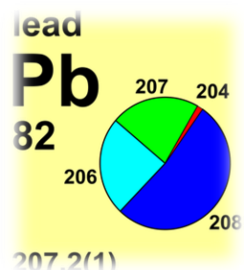
Faculty of Agriculture, GOCE DELCEV UNIVERSITY

ICP-MS measurements

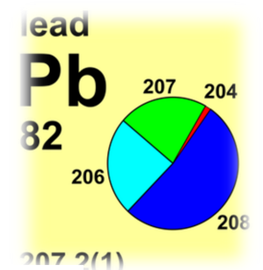


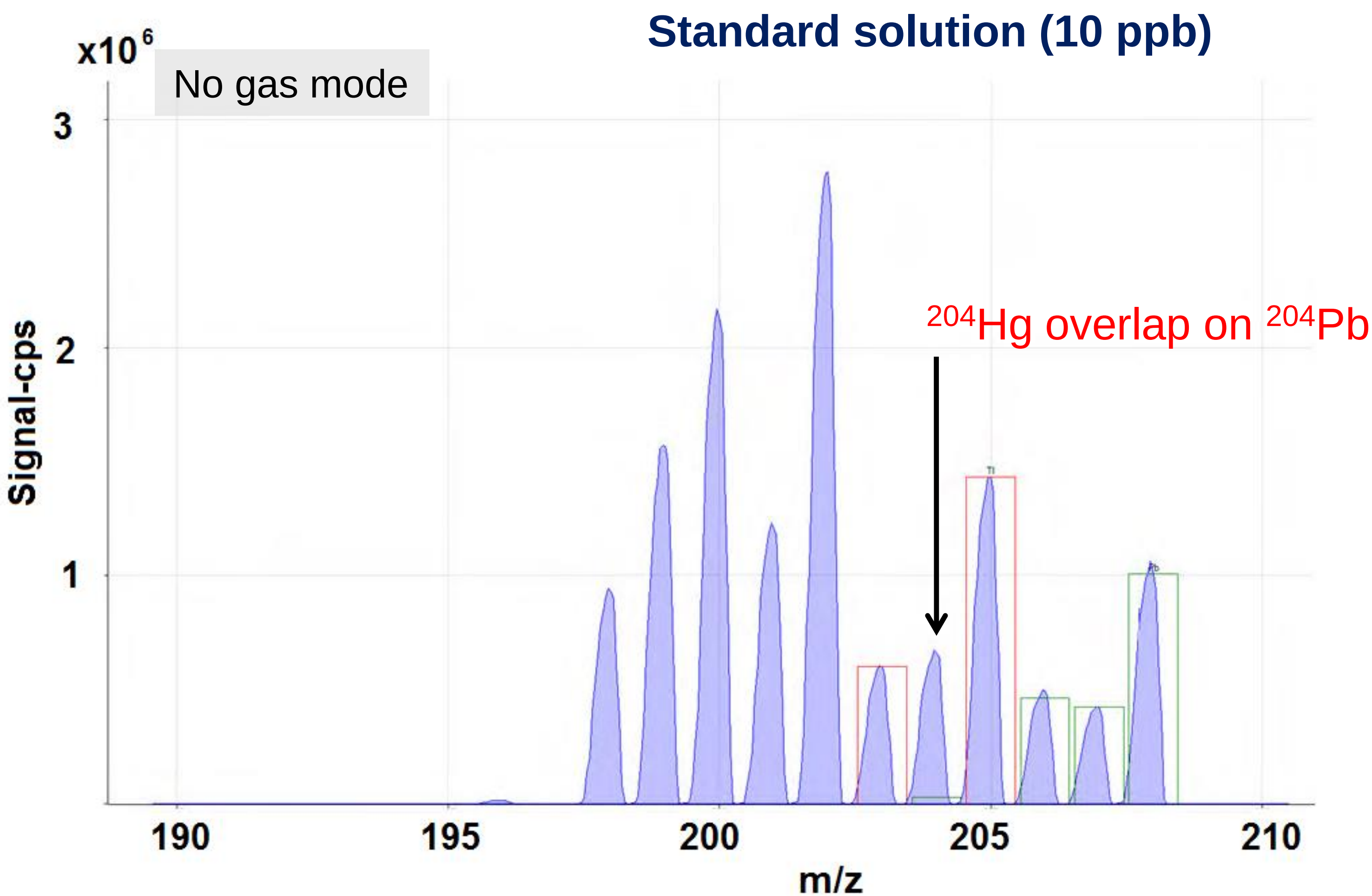




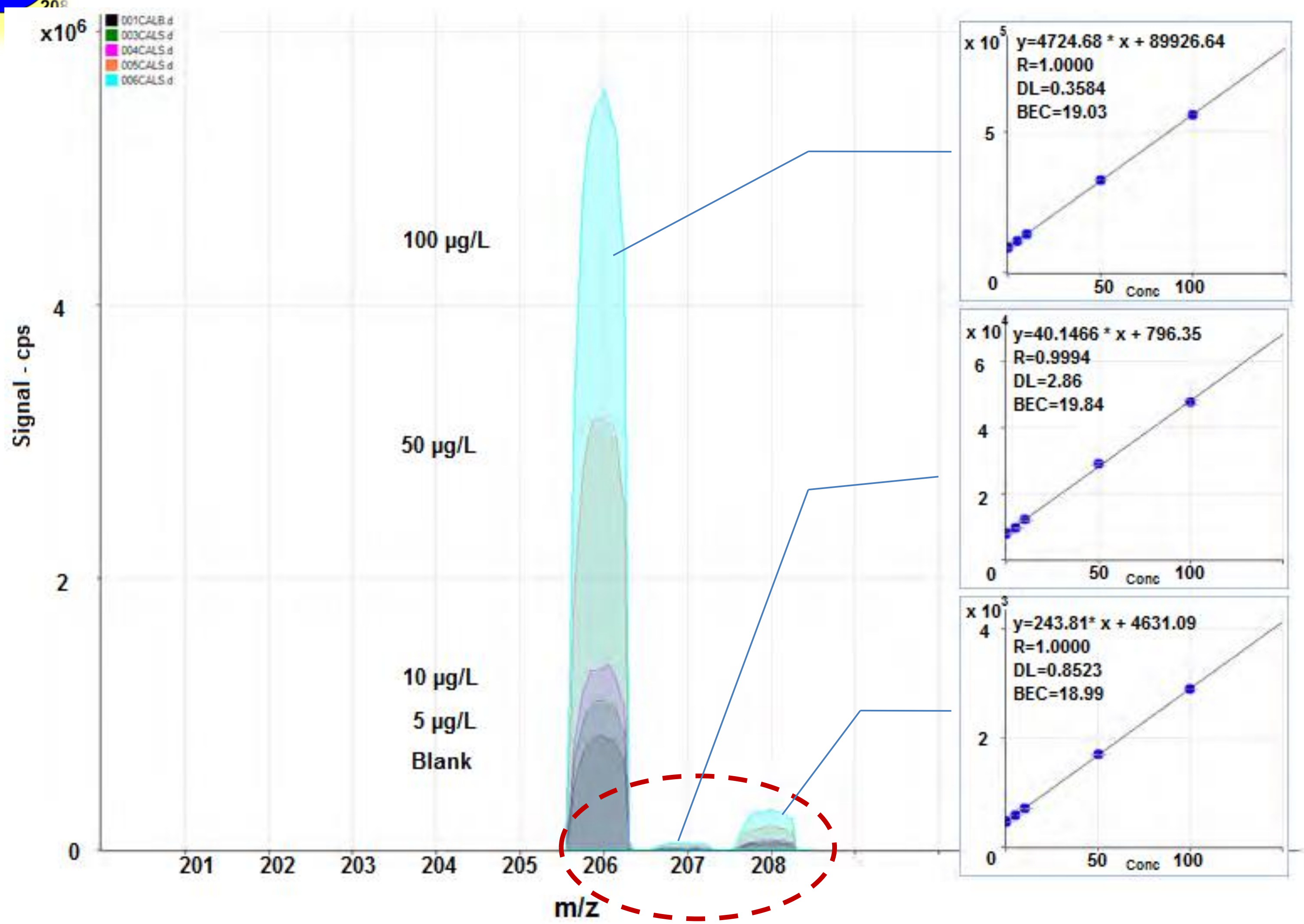


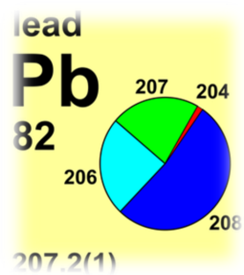
Lead isotopes measurements



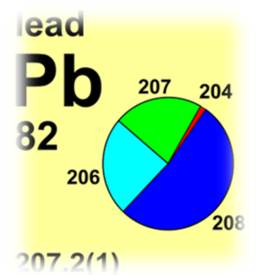


Lead isotopes measurements



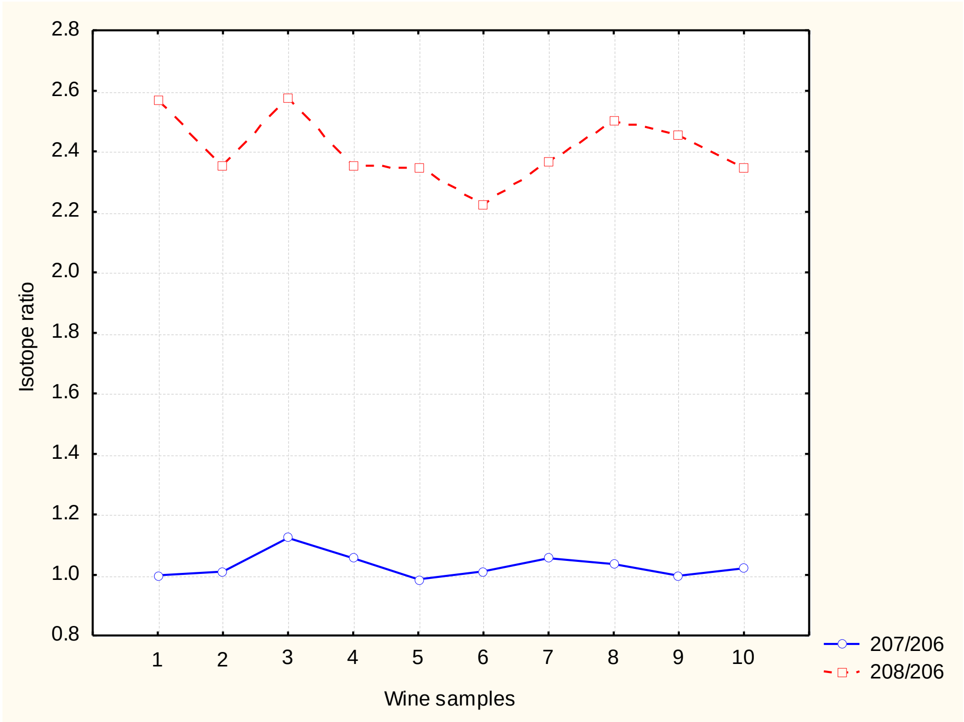


Lead isotopes measurements for wine samples



Vranec wines - samples from the same geographical region Tikveš - R. Macedonia

Wine code	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	Pb (μg/L)*
1	0.998	2.569	6.35
2	1.011	2.356	8.79
3	1.122	2.578	3.74
4	1.055	2.356	3.81
5	0.985	2.345	9.75
6	1.012	2.221	11.2
7	1.055	2.365	10.2
8	1.036	2.998	16.3
9	0.997	2.457	9.58
10	1.022	2.345	10.4



MULTI-ELEMENT CHARACTERIZATION

VRANEC WINES fermented with different yeast strains, autochthonous and commercial

7Li, 9Be, 11B, 23Na, 24 Mg, 27Al, 28Si, 31P, 34S, 43Ca, 48Ti, 51 V, 53Cr, 55Mn, 56Fe/57Fe, 59Co, 60Ni, 63Cu, 66Zn, 69Ga, 72Ge, 75As, 77Se, 85Rb, 88Sr, 95Mo, 107Ag, 114Cd, 115In, 120Sn, 121Sb, 125Te, 137Ba, 205Tl, 206Pb/207Pb/208Pb, and 209 Bi.

Autochthonous yeast, Vinalco

Four commercial yeasts: Clos, RC212, D254, BDX, from Lallemand

Total content		N	Diff.	Std. Dv. Diff	t	df	p
Vinalco yeast	613 mg/L	38	0.49	20.5	1.491	37	0.1444
Lallemand yeast	423 mg/L						

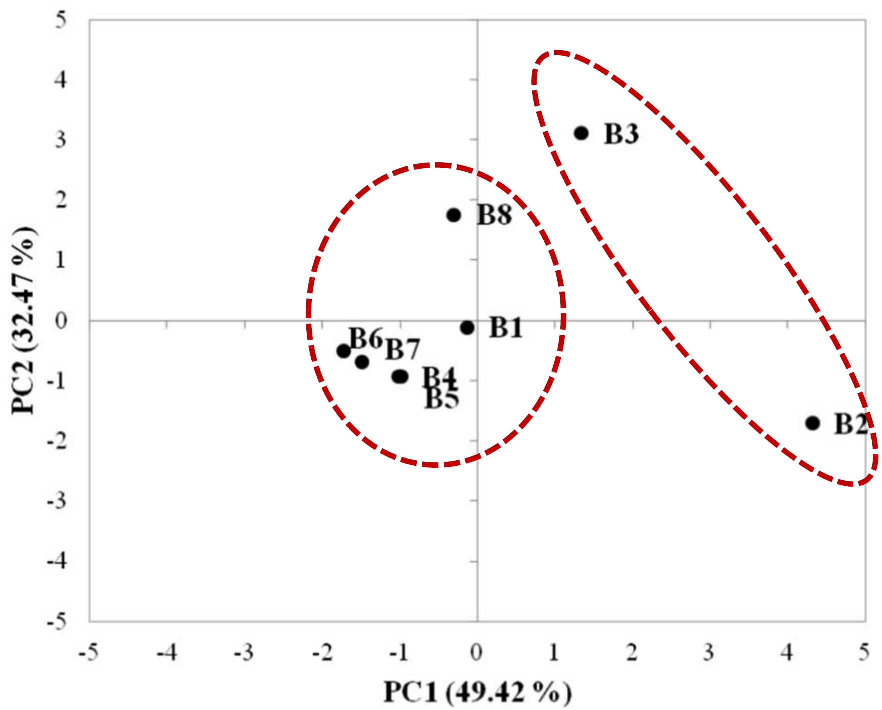
NO SIGNIFICANT DIFFERENCES !!!

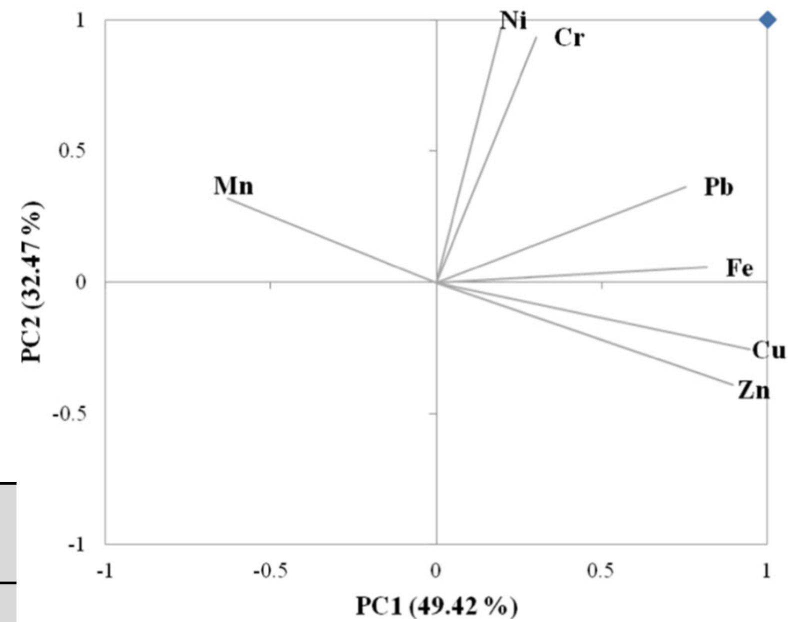
V. Ivanova-Petropulos, B. Balabanova et al., (2016) *Optimization and Validation of a Microwave Digestion Method for Multi-element Characterization of Vranec Wines.* Food Analytical Methods, 9 (1). pp. 48-60.

MULTI-ELEMENT CHARACTERIZATION

“Rakija” (grape brandy)

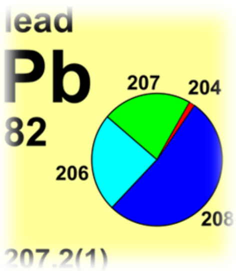
Brandy	Production	Alcohol (%, *v/v*)
B1	Domestic distillation, aged in **inox** tank	48
B2	Domestic distillation, aged **inox** tank	56
B3	Domestic distillation, aged **inox** tank	47
B4	Industrial distillation, aged in **barrel**	62
B5	Industrial distillation, aged in **barrel**	62
B6	Industrial distillation, aged with **light oak chips**	56
B7	Industrial distillation, aged with **medium oak chips**	56
B8	Industrial distillation, aged with **dark oak chips**	56





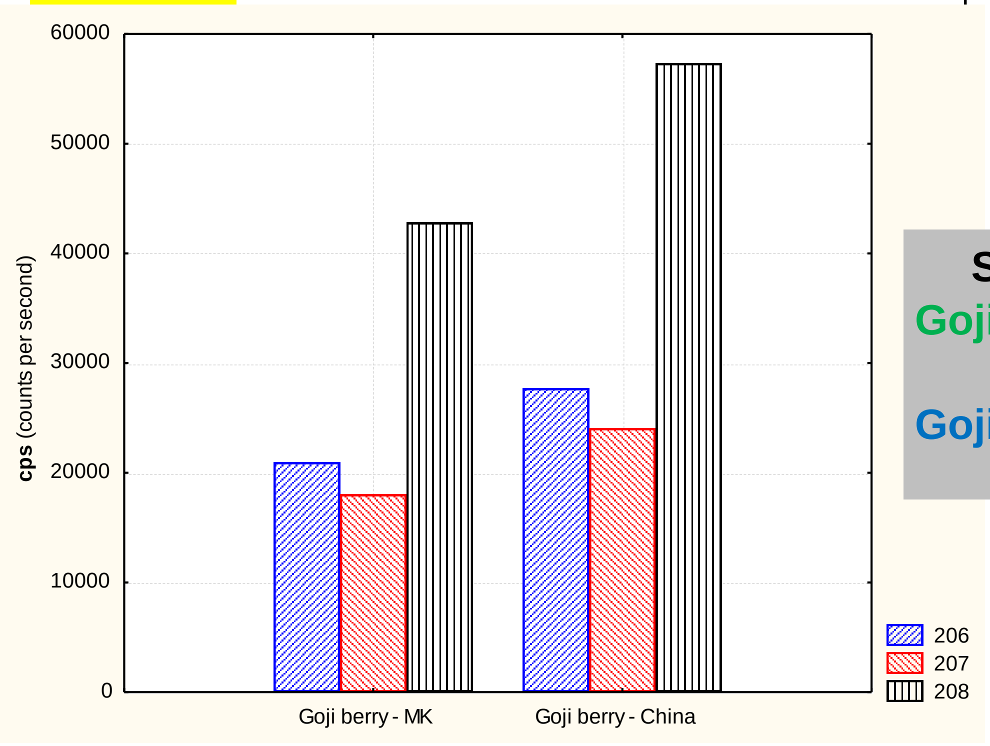
	Mn	Fe	Cu	Zn	Cd	Pb	Cr	Ni
(µg/L)	ICP-OES				GF-AAS			
B1	29	30	6120	23	< 0.3	8	< 0.7	2
B2	< 4	841	71200	3160	< 0.3	9	2	< 0.8
B3	49	241	17300	175	< 0.3	12	21	7
B4	38	62	2010	33	< 0.3	< 1.2	<0.7	< 0.8
B5	36	74	2250	27	< 0.3	< 1.2	<0.7	< 0.8
B6	118	37	3450	18	< 0.3	< 1.2	<0.7	< 0.8
B7	87	11	4360	< 5	< 0.3	< 1.2	<0.7	< 0.8
B8	110	594	5400	48	< 0.3	< 1.2	12	5

(2017) Rapid Determination of Trace Elements in Macedonian Grape Brandies for Their Characterization and Safety Evaluation. Food Analytical Methods, 10 (2). pp. 459-468.



Lead isotopes measurements in Goji berries

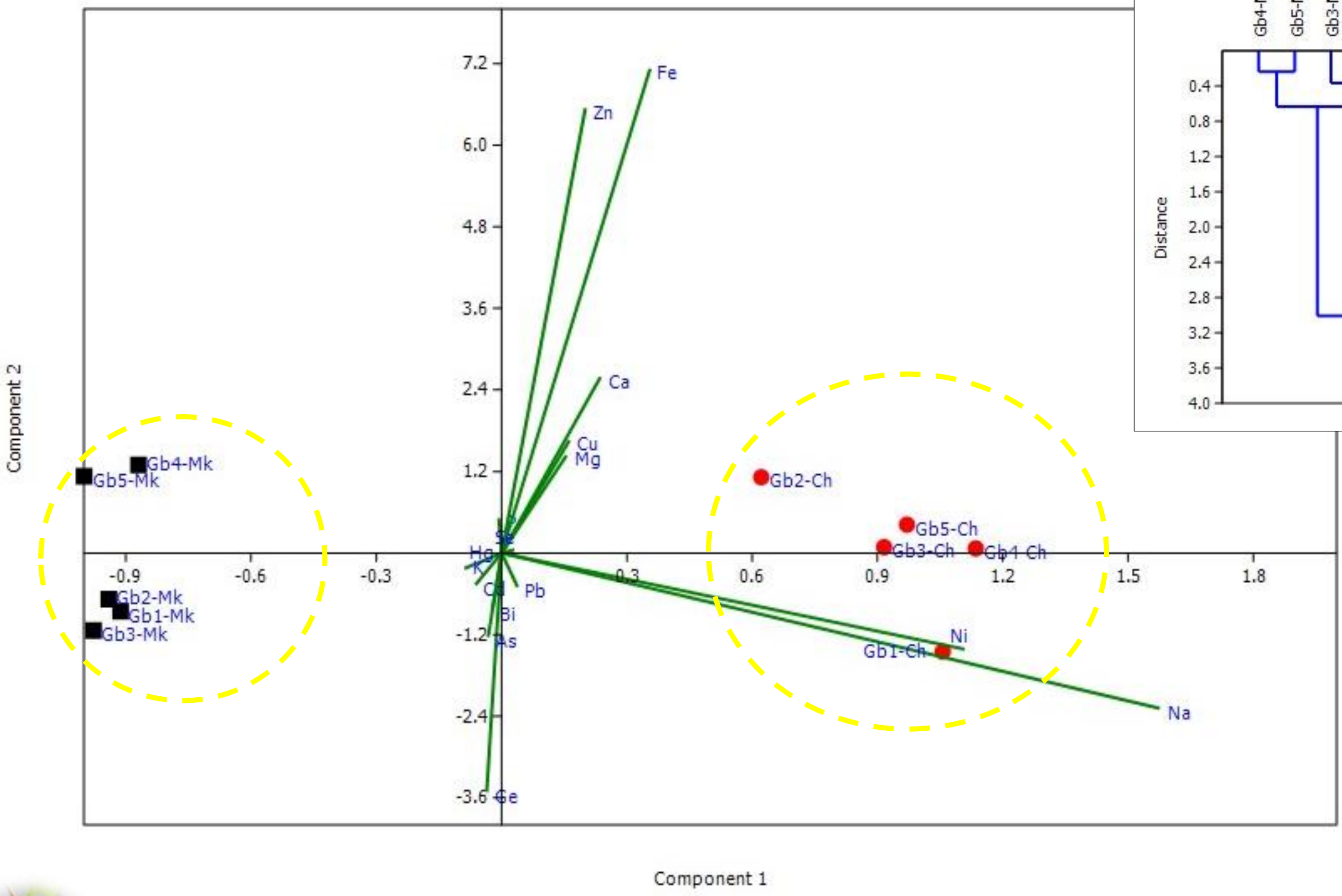
Total*	Varieties from R. China (in mg/kg)				Varieties from R. Macedonia (in mg/kg)				t	p
	min	max	Mean	SD	min	max	Mean	SD		
Pb	0.015	0.096	0.054	0.028	0.008	0.028	0.022	0.01	3.08	0.03

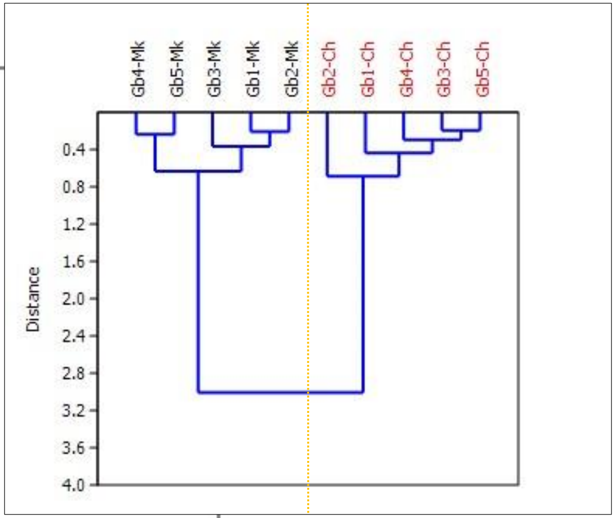


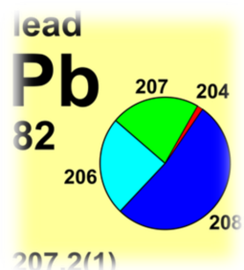
Sample	N	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
Goji berries - MK	10	0.859 ± 0.15	2.041 ± 0.09
Goji berries - Ch	10	0.868 ± 0.10	2.070 ± 0.08

NO SIGNIFICANT DIFFERENCES !!!

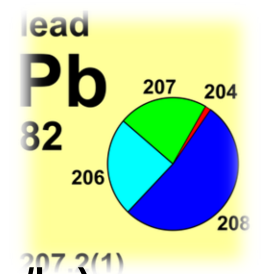
Multi-element measurements in Goji berries



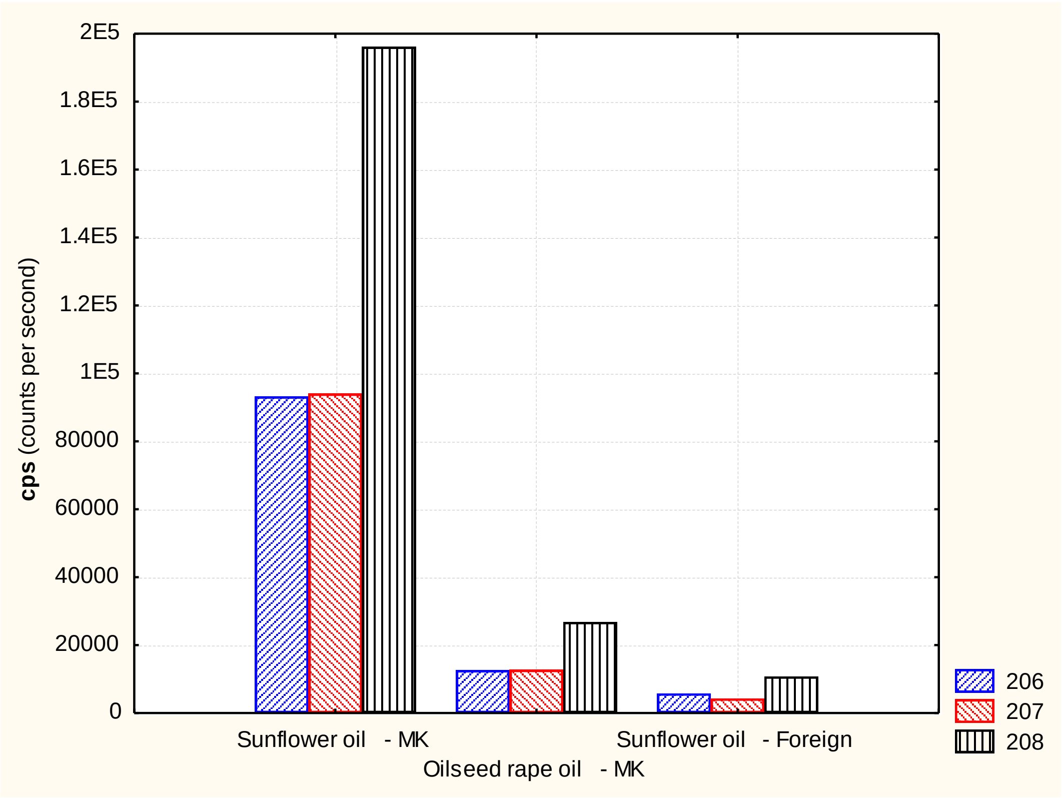




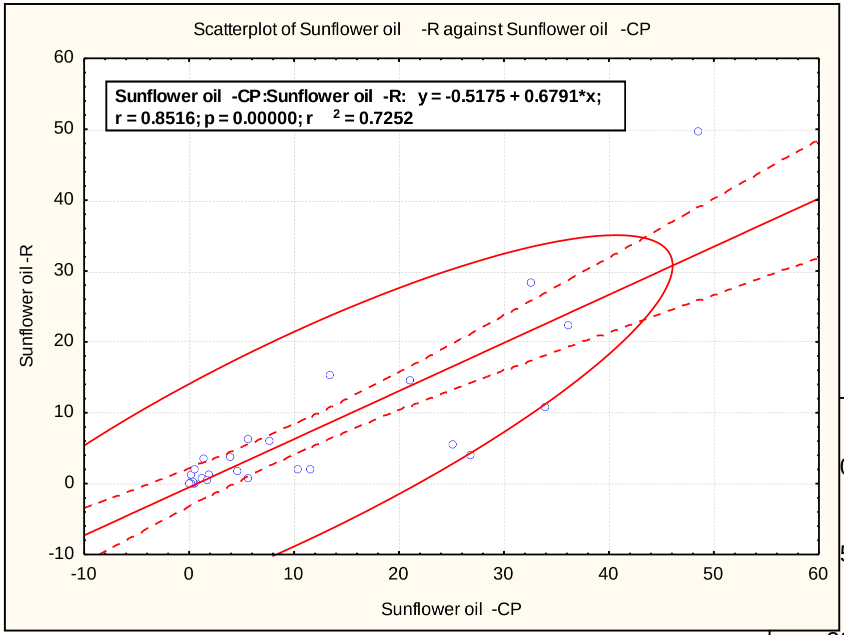
Lead isotopes measurements for edible oil samples

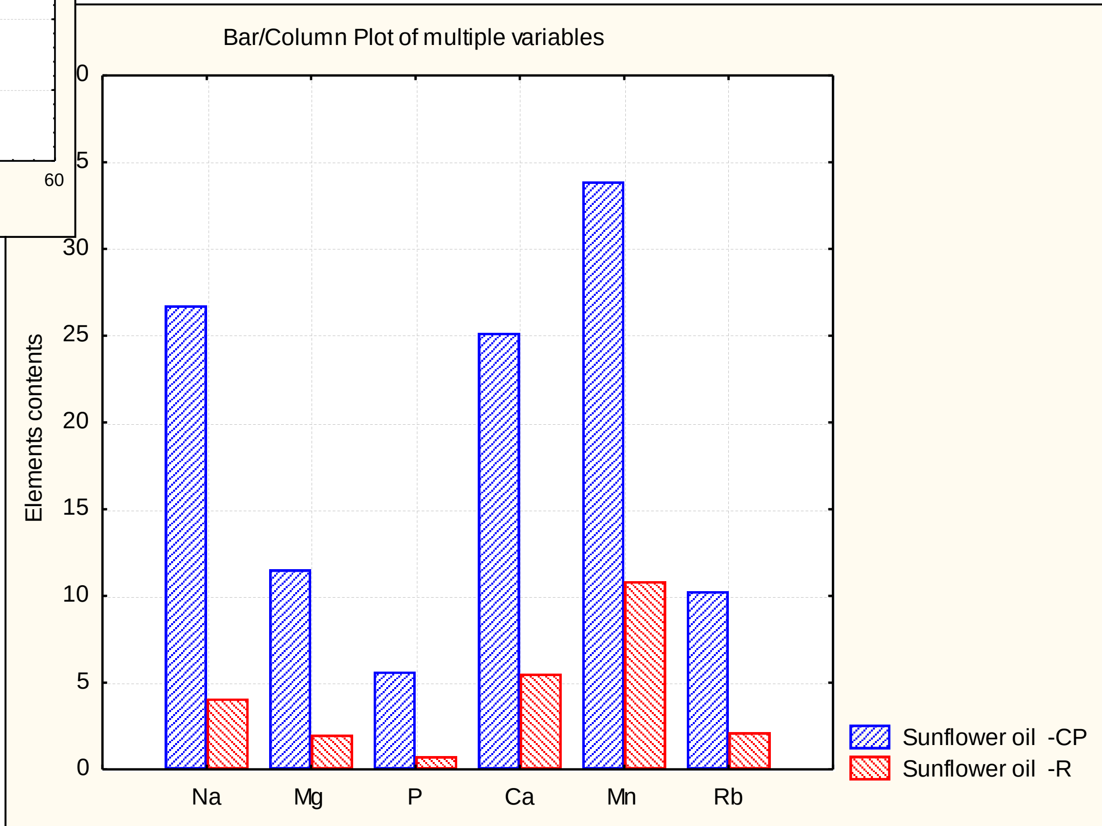


Sample	Origin	N	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	Pb-total (µg/kg) Range*
Sunflower oil	R. Macedonia	22	1.078 ± 0.30	2.769 ± 0.11	18.3-29.6
Sunflower oil	**Foreign**	10	**0.859 ± 0.18**	**2.044 ± 0.28**	6.25-15.4
Oilseed rape oil	R. Macedonia	6	1.09 ± 0.25	2.596 ± 0.08	11.5 -33.6

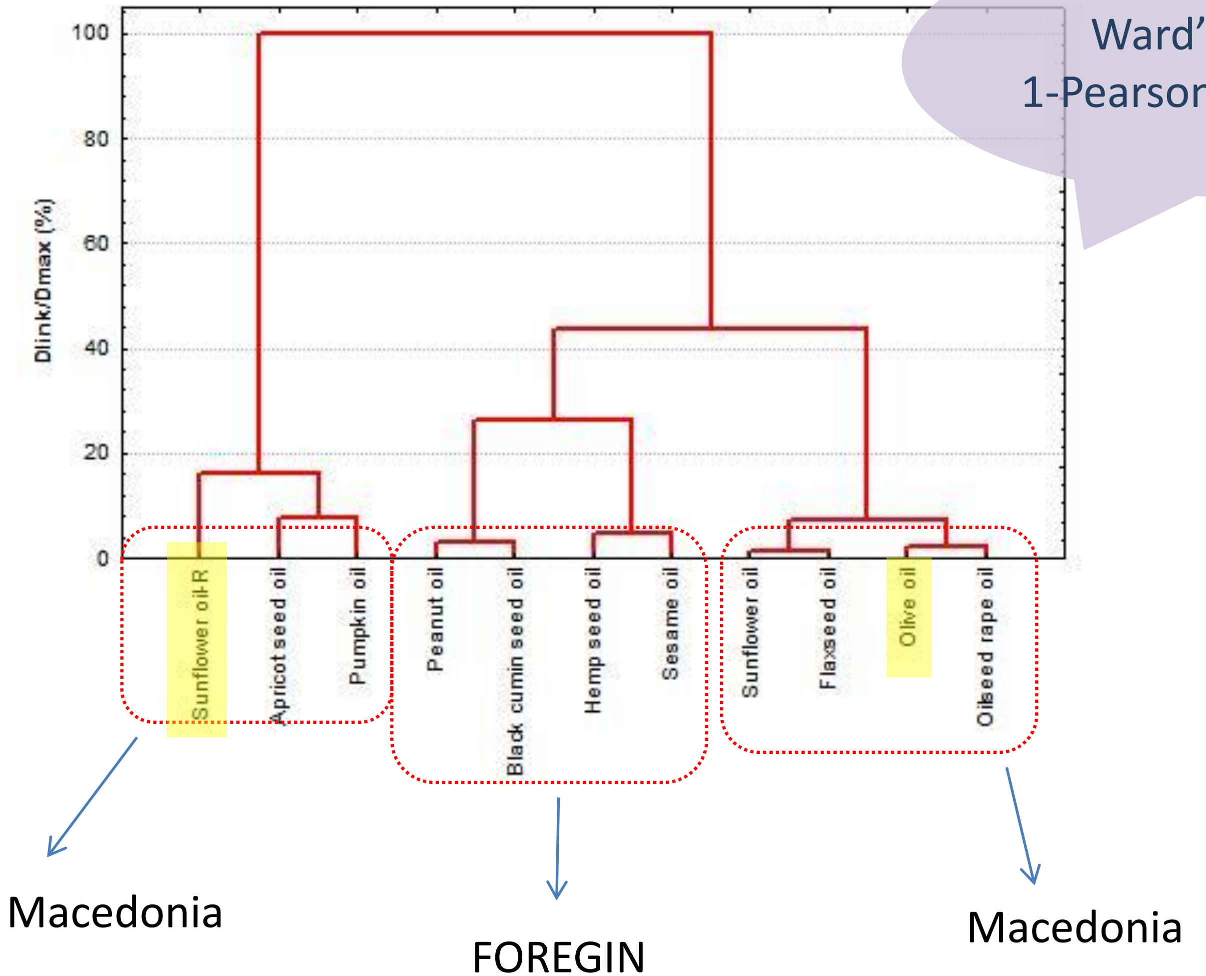


Multi-element measurements in edible oils





Multi-element measurements in edible oils



Distance measuring:
Ward's method
1-Pearson correlations

CONCLUSIONS

- **Q-ICP-MS** – sensitive method for simultaneous ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{88}Sr, measurements using single tune mode
- **$^{207}Pb/^{206}Pb$** and **$^{208}Pb/^{207}Pb$** ratios can be very useful for improving isotopic characterization of ENVIRONMENTAL ISOTOPE STUDIES.
- **Isotopic data often do not provide a *SIMPLE TRACER* to identify and distinguish source emissions.**
- **Multi-element characterization has much more expression in identification of geographical origin of the plant food**

Thank you for your attention!