GREDIT2018

LONGTIME GEOCHEMICAL EVALUATION OF ANTHROPOGENIC ELEMENT'S DISTRIBUTION IN THE AIR USING DEPOSITED ATTIC DUST

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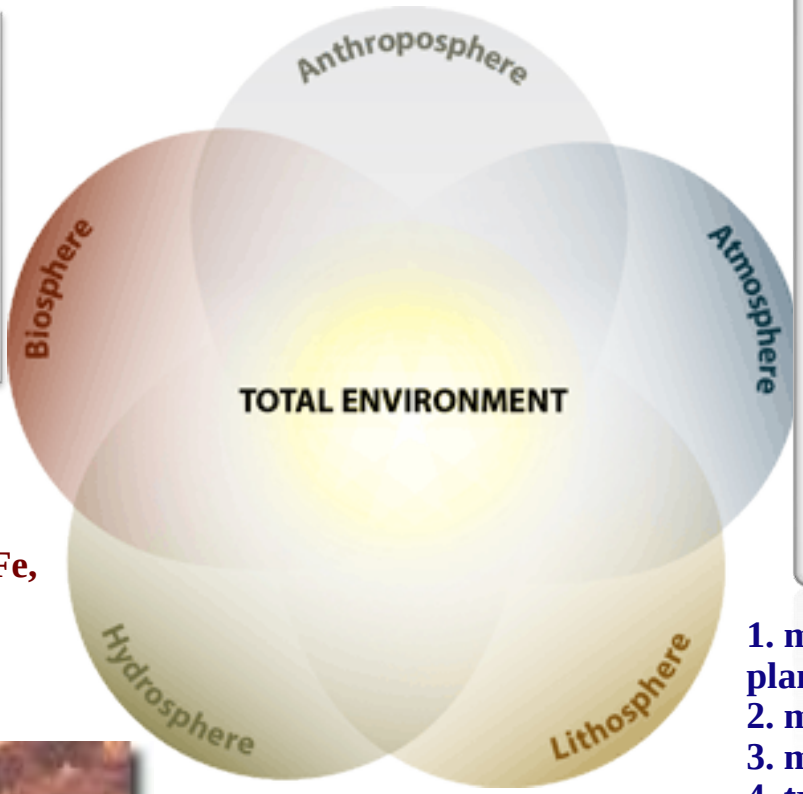
CHEMICAL ELEMENTS IN ENVIRONMENT

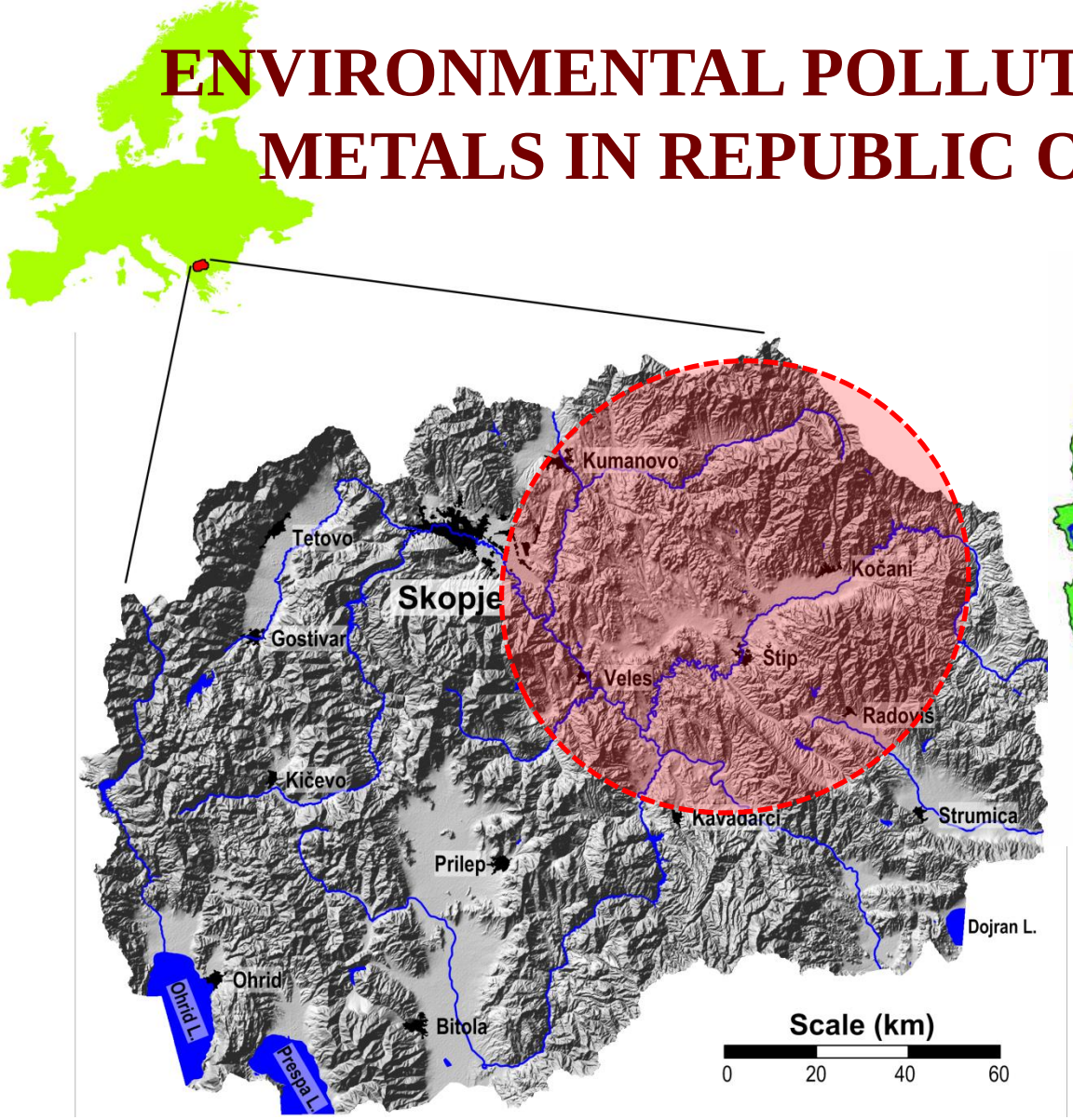


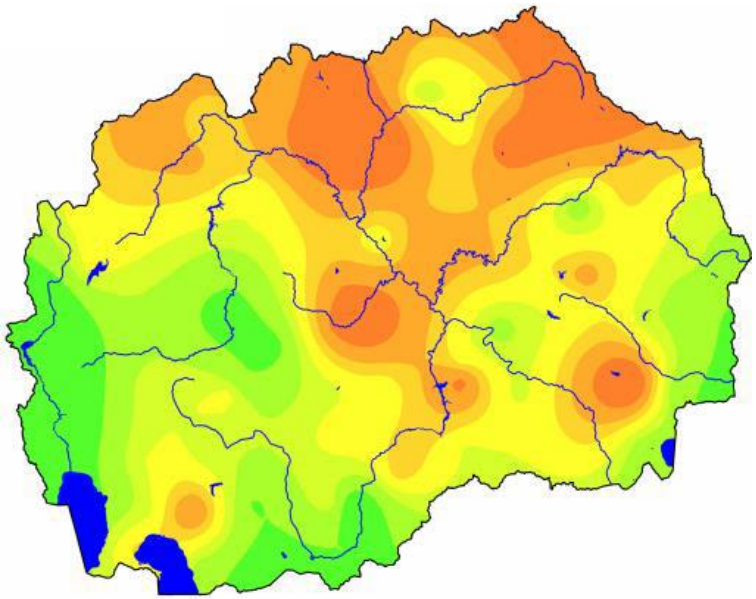
Biologically effective elements:
Na, Mg, Si, P, S, Cl, Ca, Ti, V, Mn, Fe, Co, Mo

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

ENVIRONMENTAL POLLUTION WITH HEAVY METALS IN REPUBLIC OF MACEDONIA



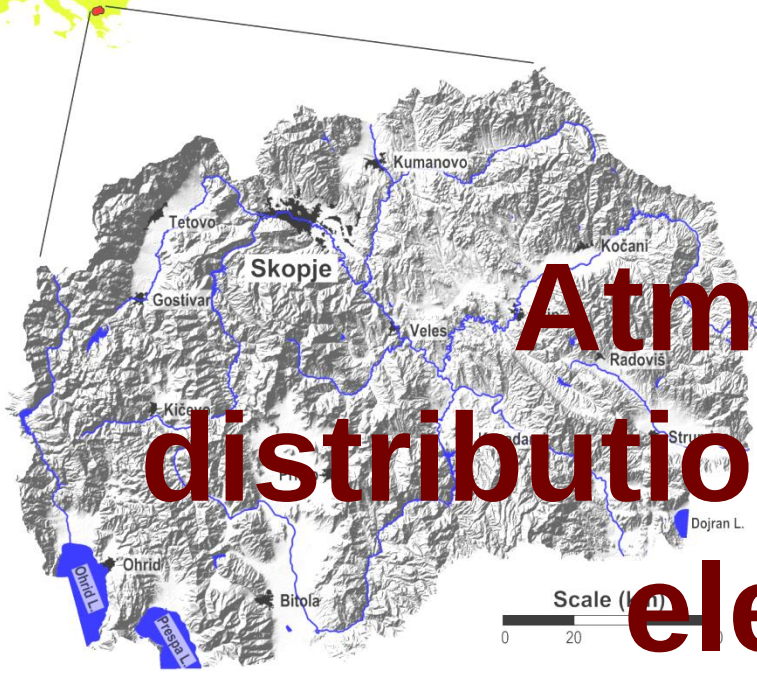


(Cd-Cu-Pb-Zn)

Dominant geochemical association In areas with anthropogenic introducing of heavy metals

Stafilov T. (2014). Environmental pollution with heavy metals in the Republic of Macedonia. *Contributions, Sect. Nat. Math. Biotech. Sci.*, MASA, **35**, 81–119.

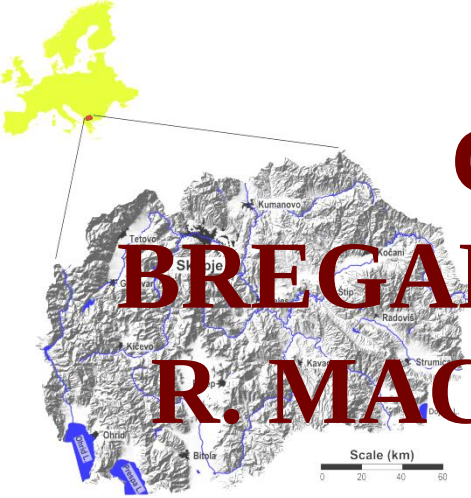
Barandovski L., Frontasyeva M.V., Stafilov T., Šajn R., Ostrovnaya T. (2015). Atmospheric deposition of trace elements in Macedonia studied by the moss biomonitoring technique. *Environ. Sci. Pollut. Res*. **22**, 16077-16097.



Atmospheric distribution/deposition of elements

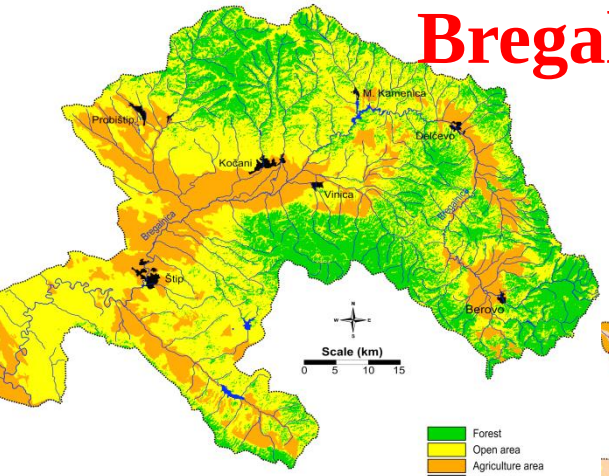
Case studies (2010-2012)

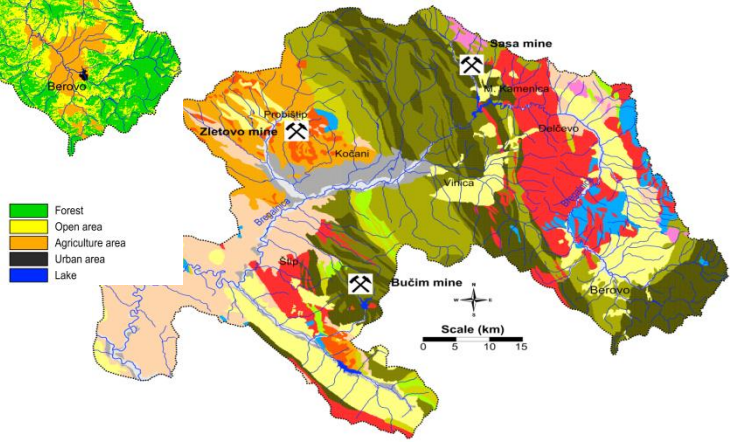
CASE STUDY:
BREGALNICA RIVER BASIN
R. MACEDONIA (2012-2014)



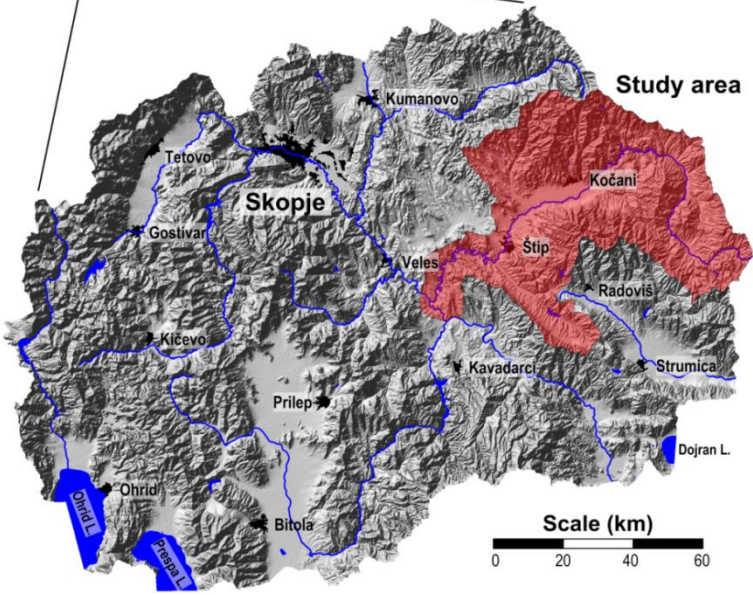
Bregalnica River basin

N: 41°27'-42°09'
E: 22°55'-23°01'





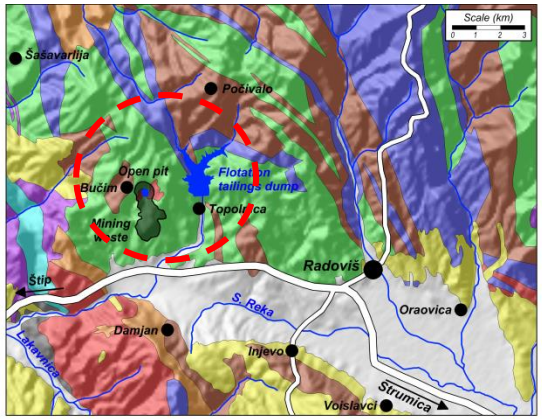
Forest
Open area
Agriculture area
Urban area
Lake



Quaternary alluvium
Quaternary terrace
Neogene clastites
Neogene pyroclastites
Neogene vulcanites
Paleogene flysch
Paleogene volcanic sedimentary rocks
Mesozoic and Paleosoic carbonate rocks
Pleozoic Shales
Rifeous Shales
Proterosoic Shales
Proterosoic Gneisse
Proterosoic felsic plutonites (granite)
Proterosoic mafic plutonites (gabro)

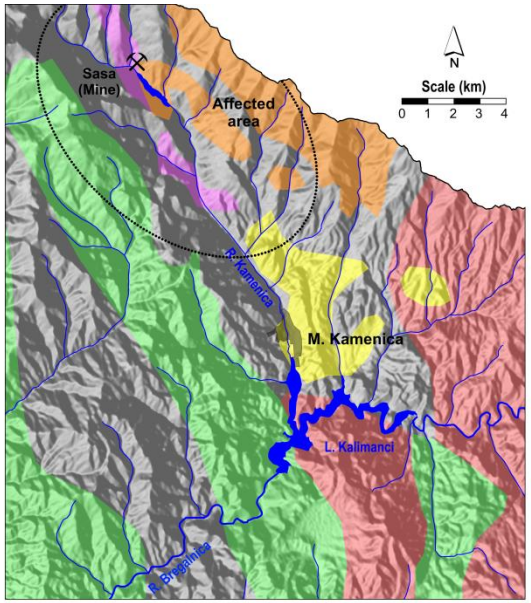
Potentially emission sources

Copper mine “Bučim”



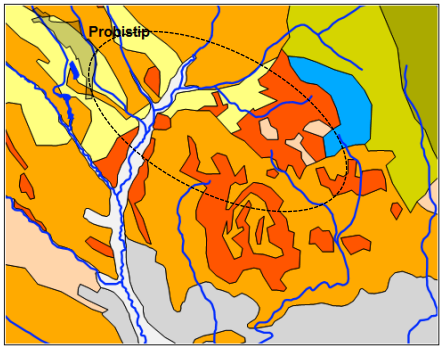
Плеистоценски седименти
Плиоценски седименти
Еоценски флиш
Еоценски андезити и пирокластити
Кредни песочници, лапорци и шкрилци
Јурски гранити
Прекамбријски и Палеозојски шкрилци
Прекамбријски микашист
Прекамбријски гнајсеви
Метаморфни карпи

Pb-Zn mine “Sasa”

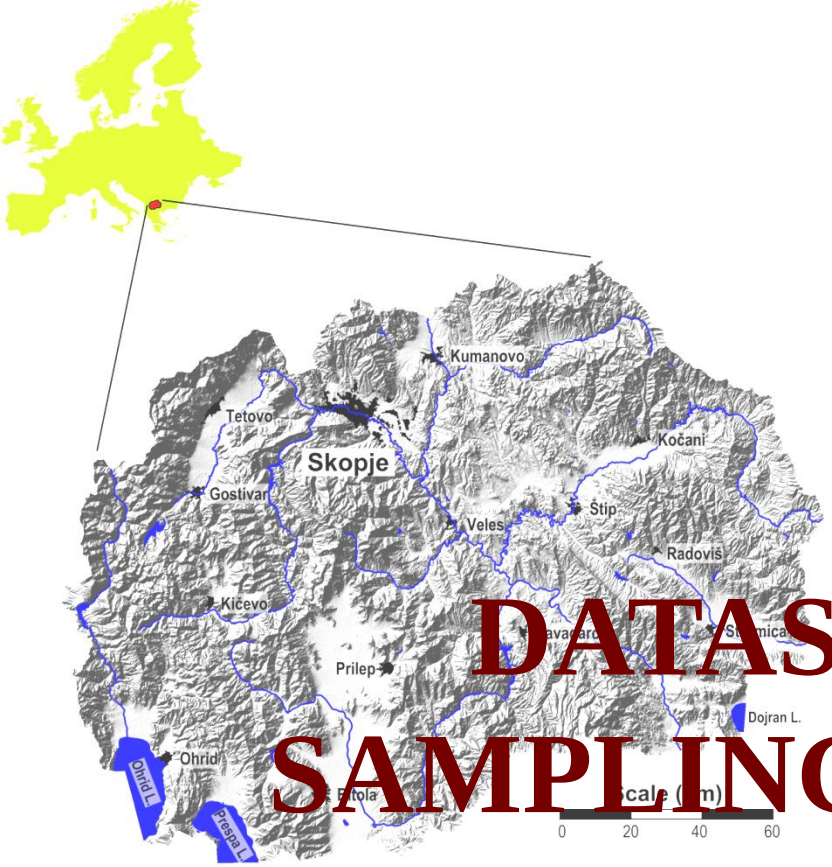


Неогени седименти
Неогени вулканити
Палеозојски плутонити
Рифејски шкрилци
Протерозојски шкрилци
Протерозојски гнајсеви

Pb-Zn mine “Zletovo”

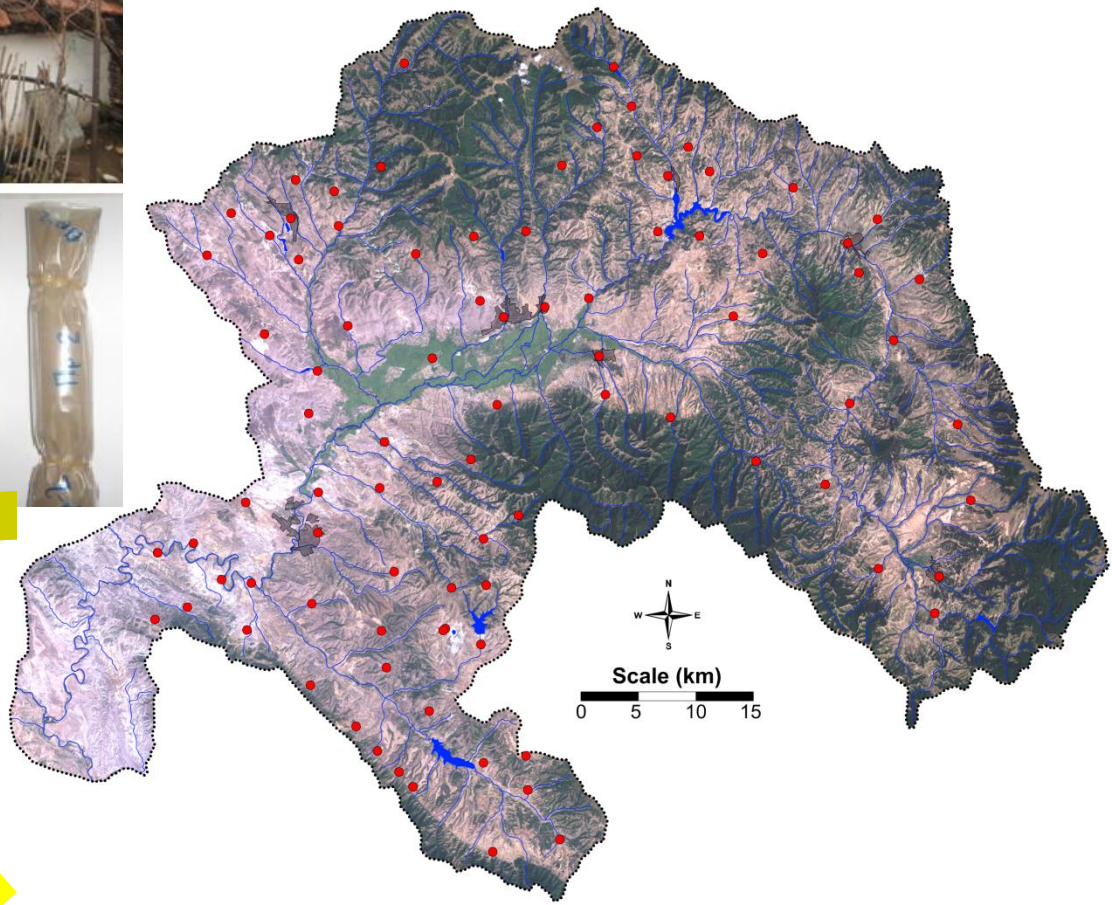


Квартерен алувиум
Квартерни тераси
Неогени кластити
Неогени пирокластити
Неогени вулканити
Палеогенски флиш
Мезозојски и Палеозојски карбонатни карпи
Плеозојски шкрилци
Рифејски шкрилци
Протерозојски шкрилци
Протерозојски гнајсеви
Протерозојски гранити



DATASET BUILDING
SAMPLING STRATEGY AND
ANALYTICAL METHODS

LONG-TIME DEPOSITION



ICP-MS SCIEX Perkin Elmer Elan DRC II (Canada)

INCDO-INOE 2000 Research Institute for Analytical Instrumentation (ICIA), Cluj-Napoca, Romania

Chemical preparation of samples according to **ISO 14869-1:2001**

ATTIC DUST

DATA PROCESSING

FIRST STEP……DATA NORMALISATION!!!!

BOX-COX TRANSFORMATION

$$y = \frac{x^{\lambda}-1}{\lambda}; \quad \lambda \neq 0$$

$$y = ln(\lambda); \; \lambda = 0$$

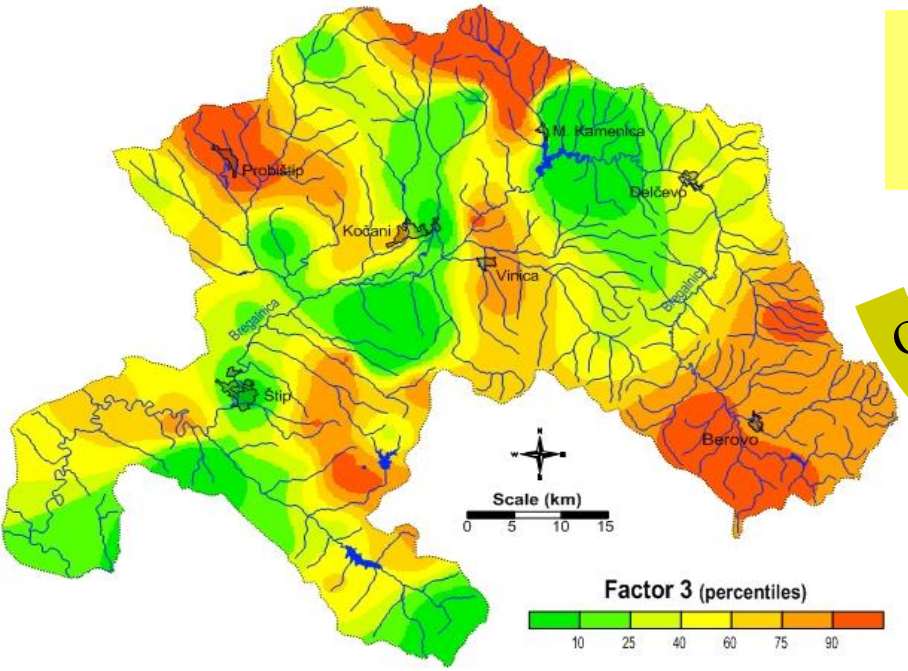
For a data set (x_1, x_2 … x_n), the parameter λ is estimated based on the assumption that the transformed values (y_1, y_2 … y_n) are normally distributed

MULTIVARIATE STATISTICS METHODS (CLUSTER AND R-MODE FACTOR ANALYSES)

Balabanova, B., Stafilov, T., Sajn, R., Tănăselia, C. (2016). Multivariate factor assessment for lithogenic and anthropogenic distribution of macro and trace elements in surface water. Case study: basin of the Bregalnica river, Republic of Macedonia. Maced. J. Chem. Chem. Eng., **35**, 1-16.

Balabanova, B., Stafilov, T., Sajn, R., Tănăselia, C. (2016). Multivariate extraction of dominant geochemical markers for deposition of 69 elements in the Bregalnica River basin, Republic of Macedonia (moss biomonitoring). Environ. Sci. Pollut. Res., **23**, 22852-22870.

ATTIC DUST - can reveal the longtime depositions of emitted dust?



OLIGOCENE AND NEOGENE VOLCANISM

Occurrence in area with dominance of

Multivariate EXTRACTION

Factor 3 (Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn)

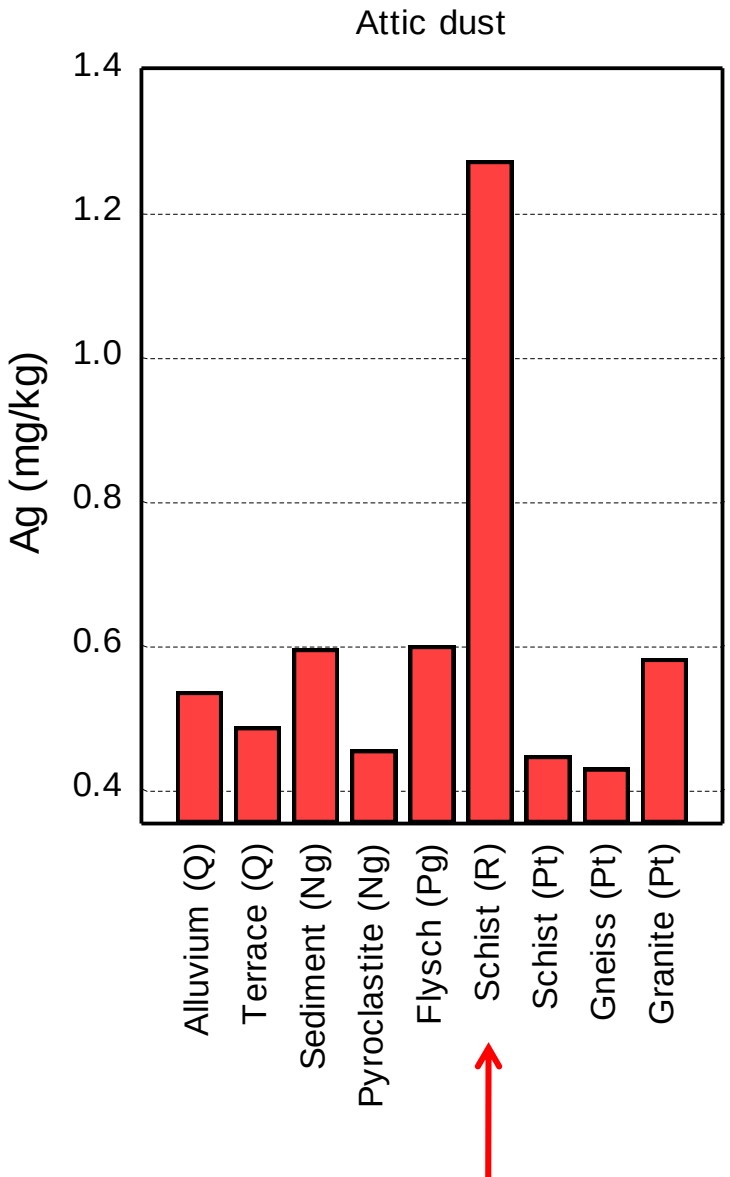
ANTHROPOGENIC ANOMALIES!!!

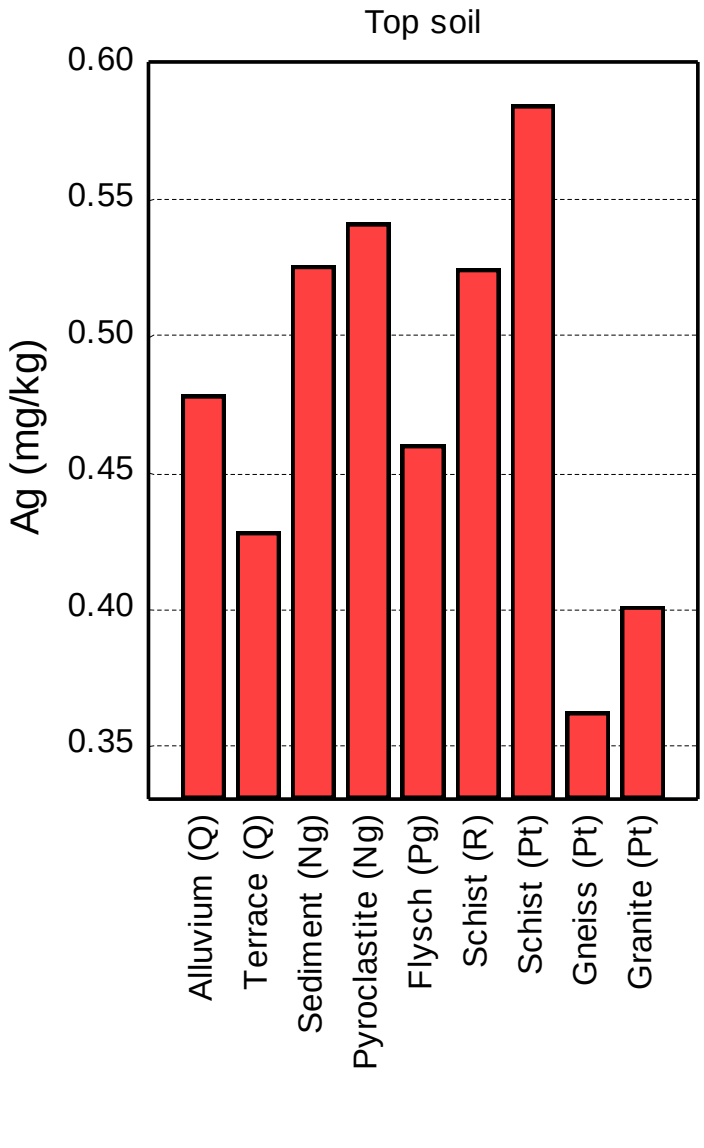
Total 69 elements: Ag, As, Al, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Ti, Th, Tl, Tm, V, W, Y, Yb, Zn and Zr

Balabanova, B., Stafilov, T., Šajn, R., Tanaselia C. (2017). Long-term geochemical evolution of lithogenic *vs.* anthropogenic distribution of macro and trace elements in household attic dust, *Arch. Environ. Contam. Toxicol*. **72**, 88.

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

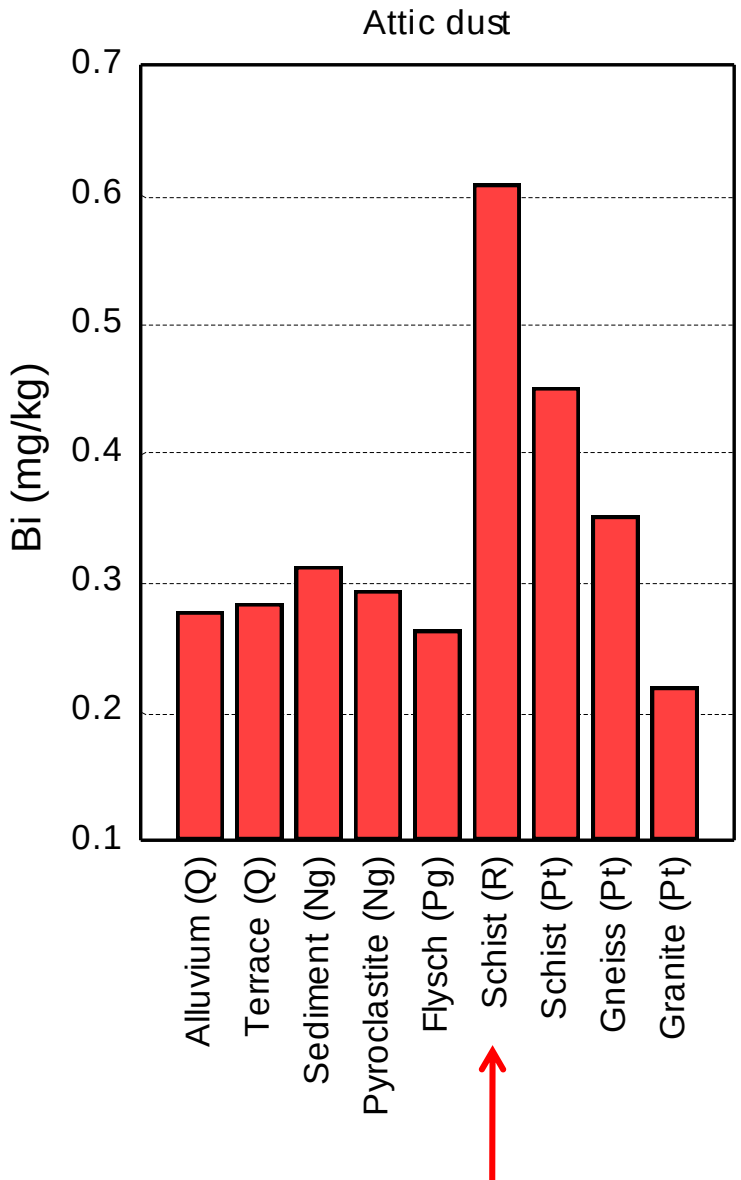
lithogenic *vs.* anthropogenic phenomena

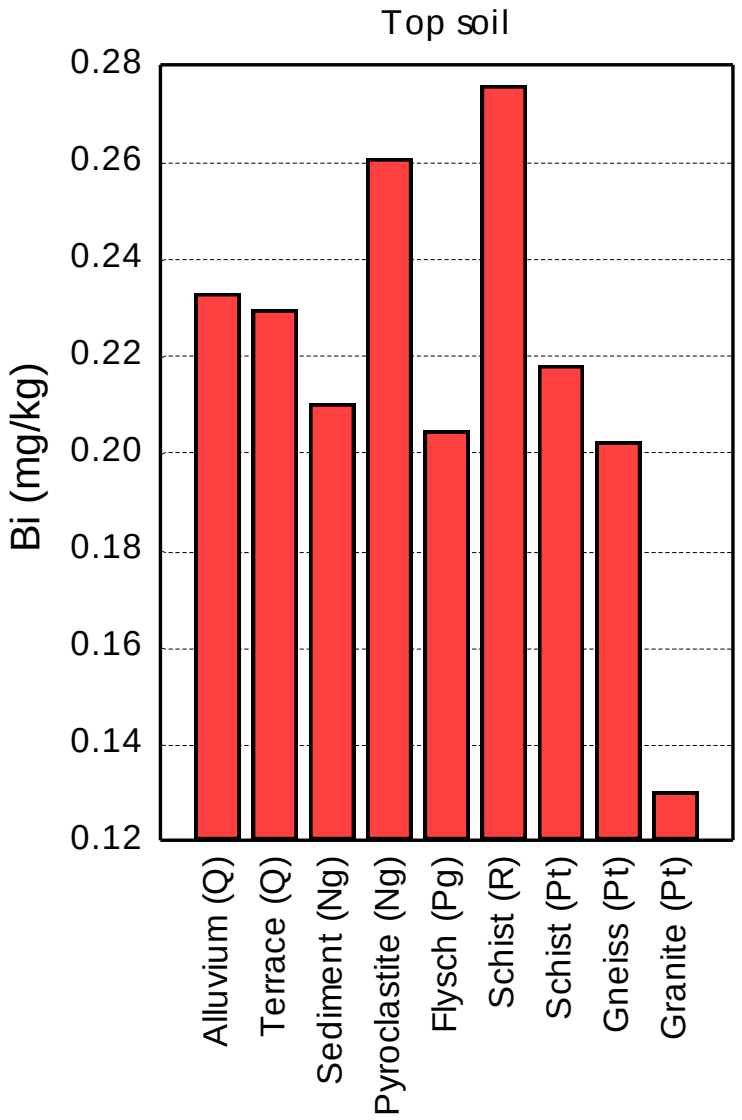




Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

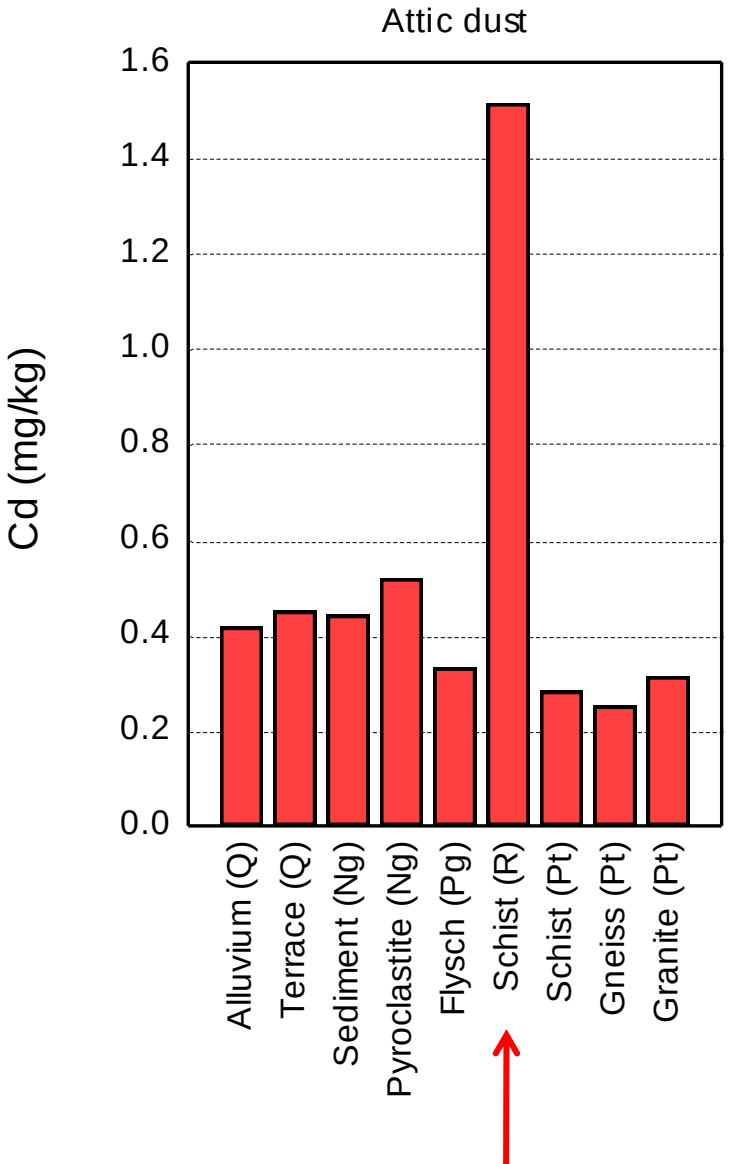
lithogenic *vs.* anthropogenic phenomena

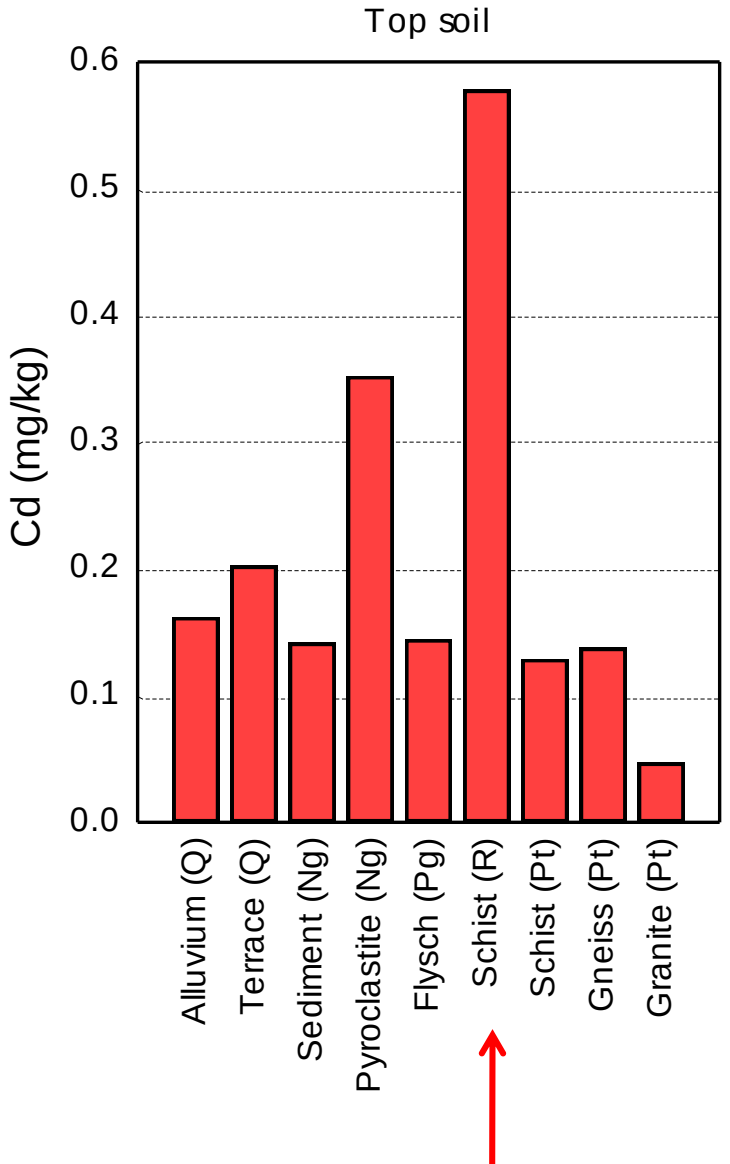




Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

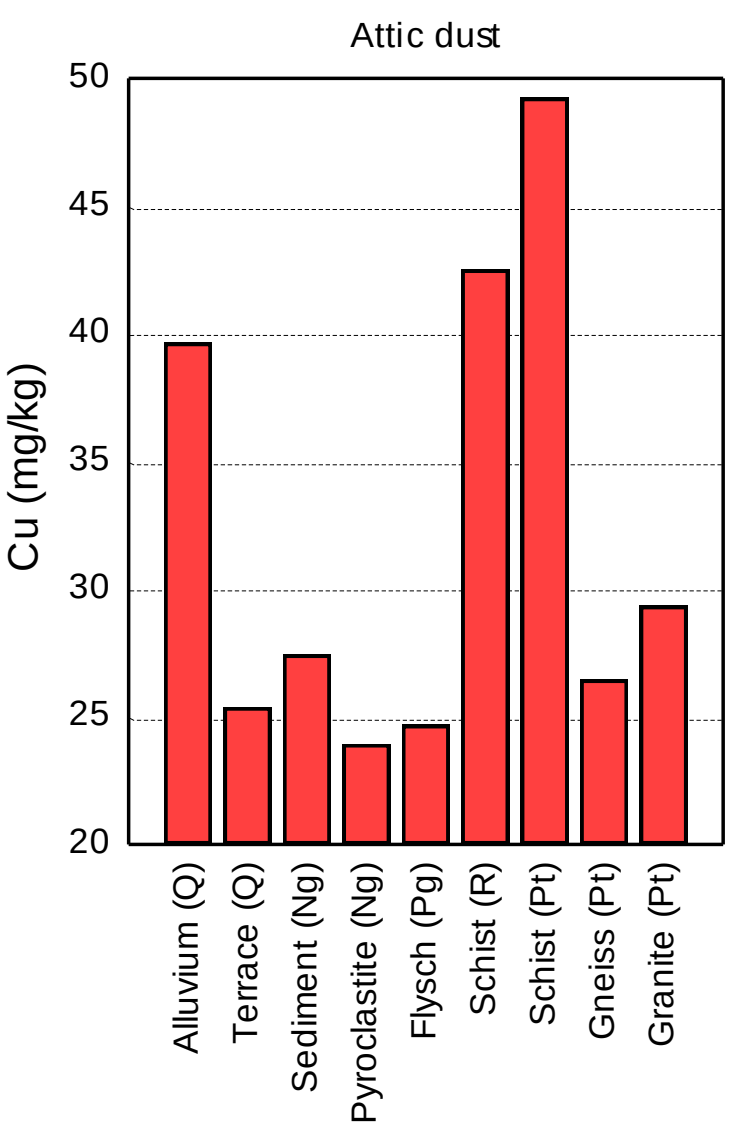
lithogenic *vs.* anthropogenic phenomena

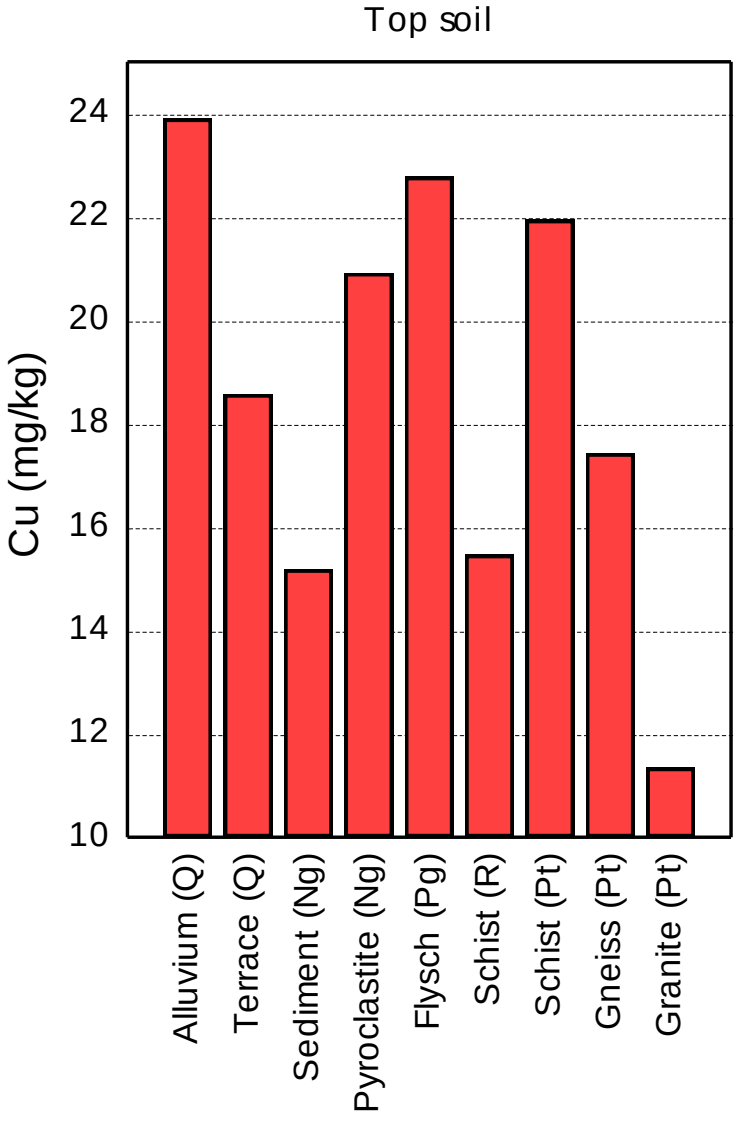




Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

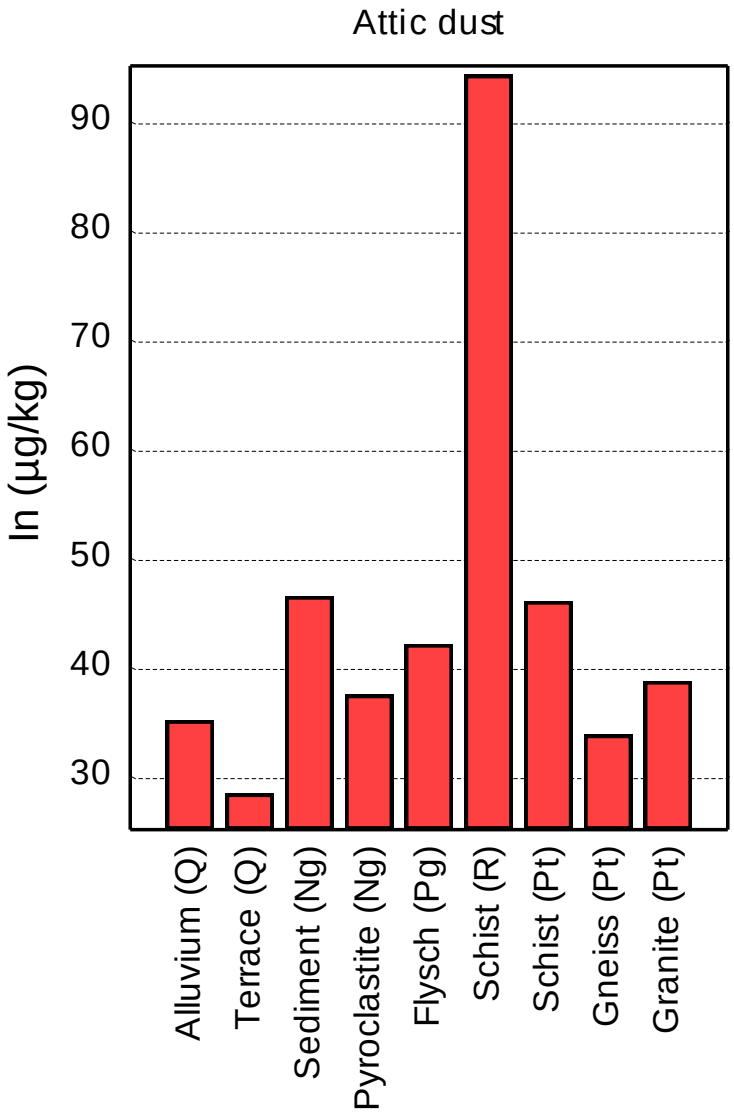
lithogenic *vs.* anthropogenic phenomena

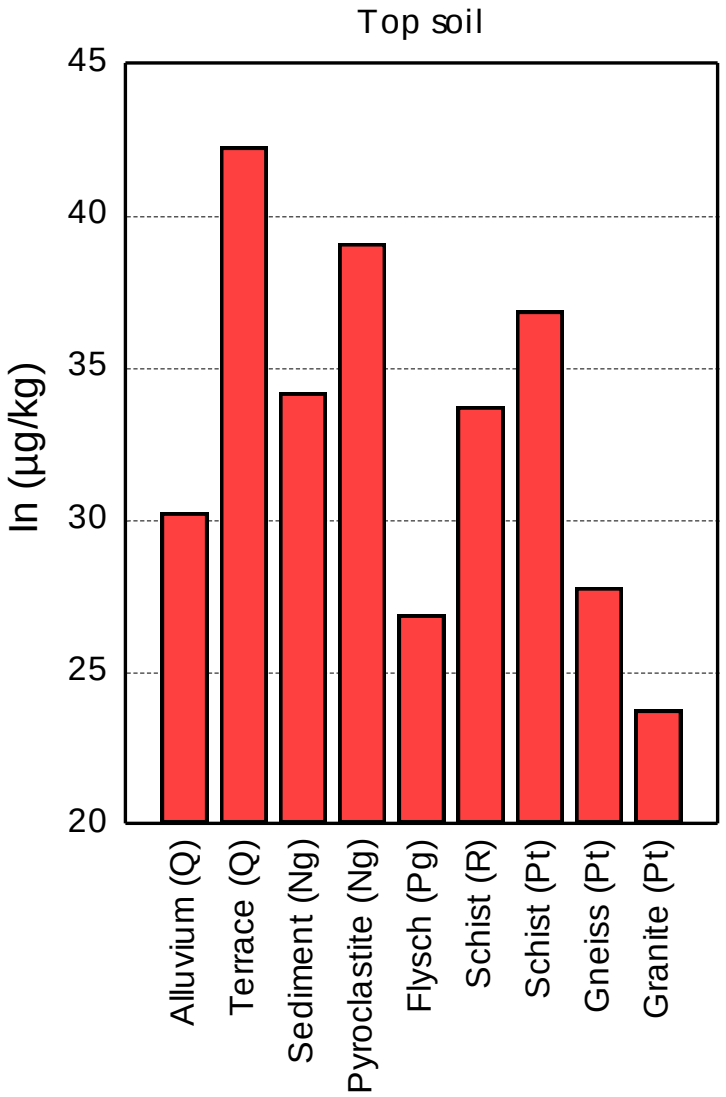




Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

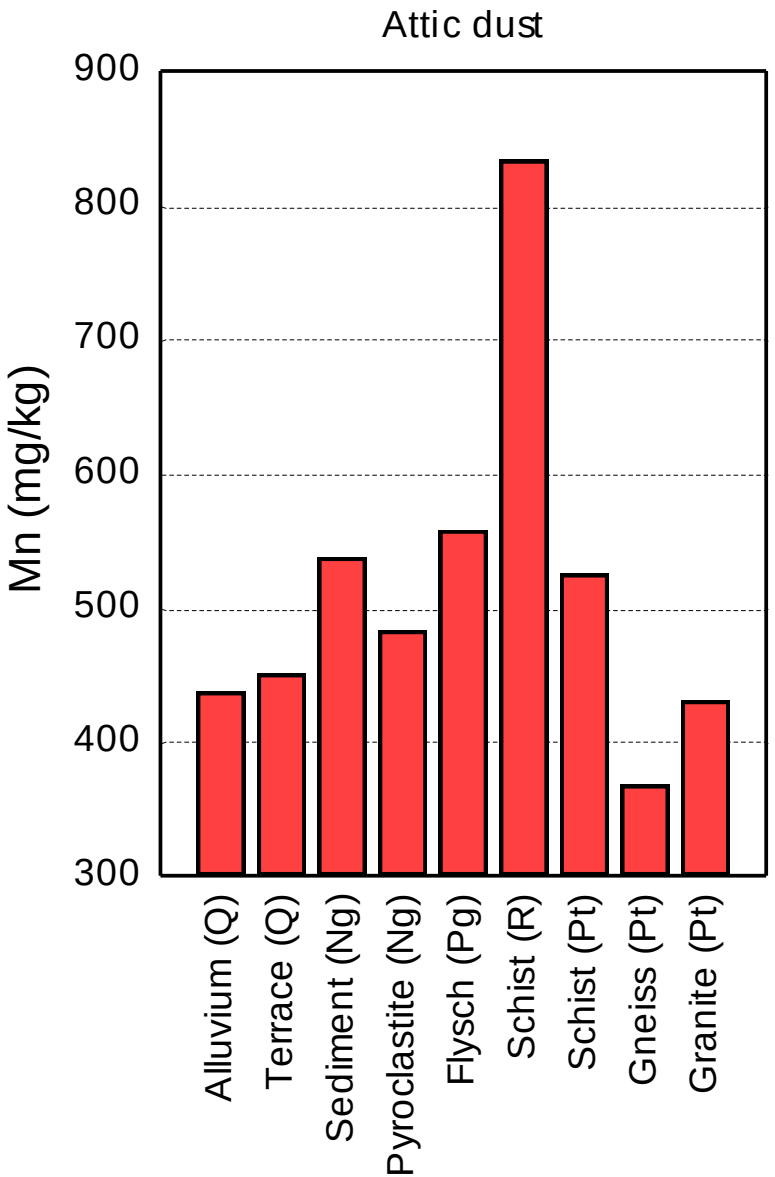
lithogenic *vs.* anthropogenic phenomena

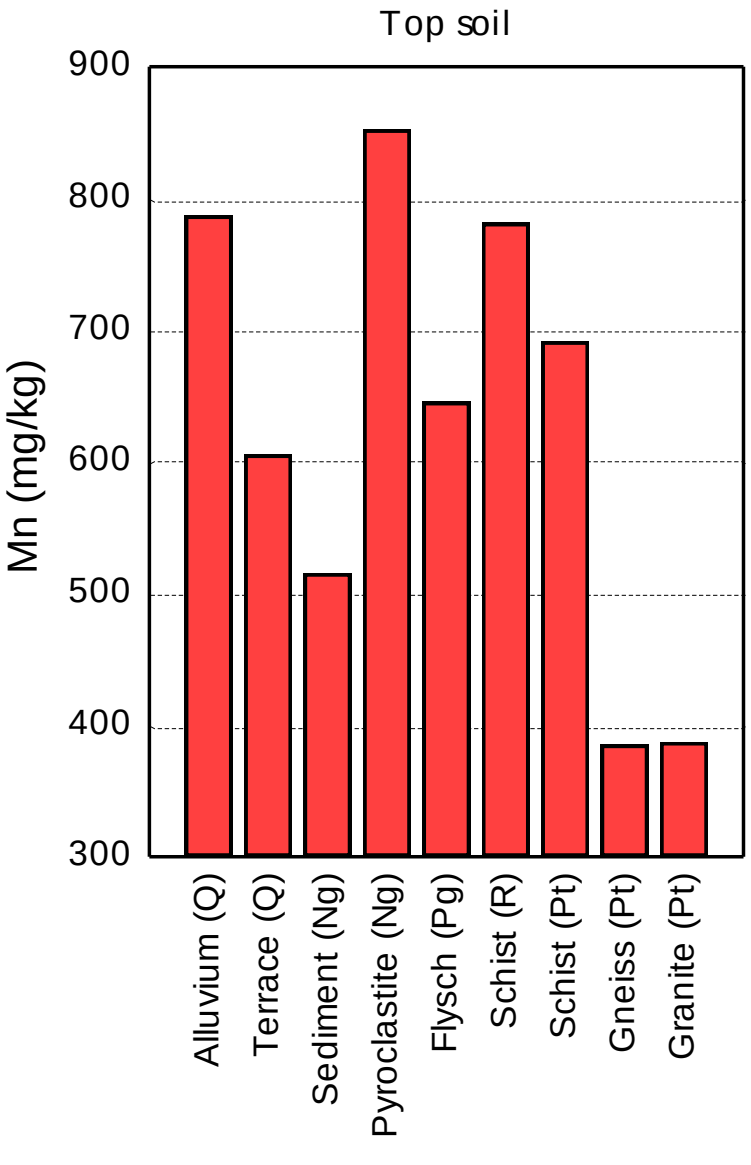




Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

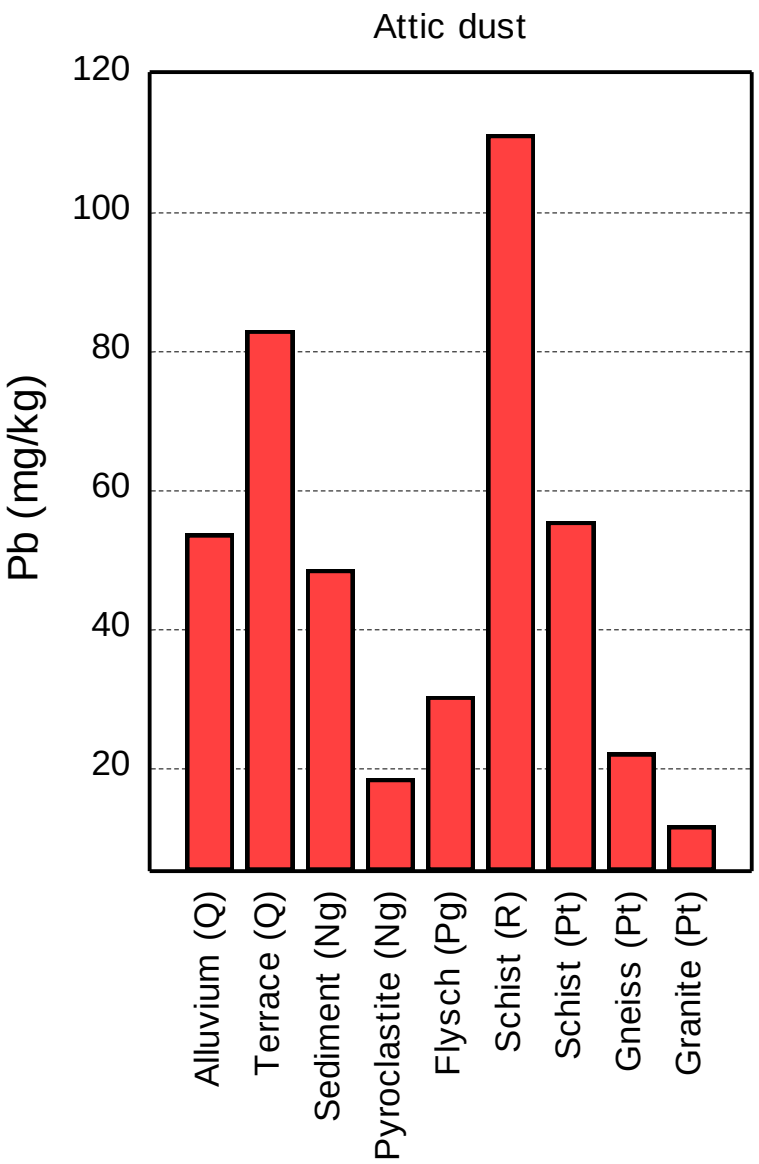
lithogenic *vs.* anthropogenic phenomena

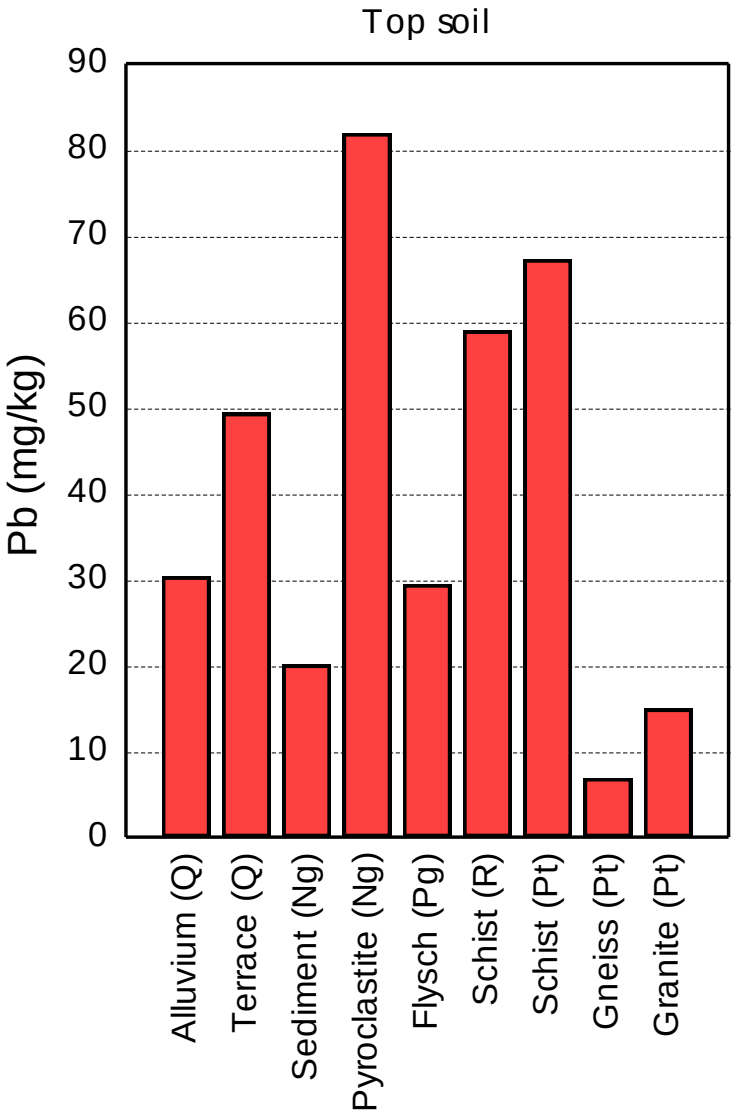




Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

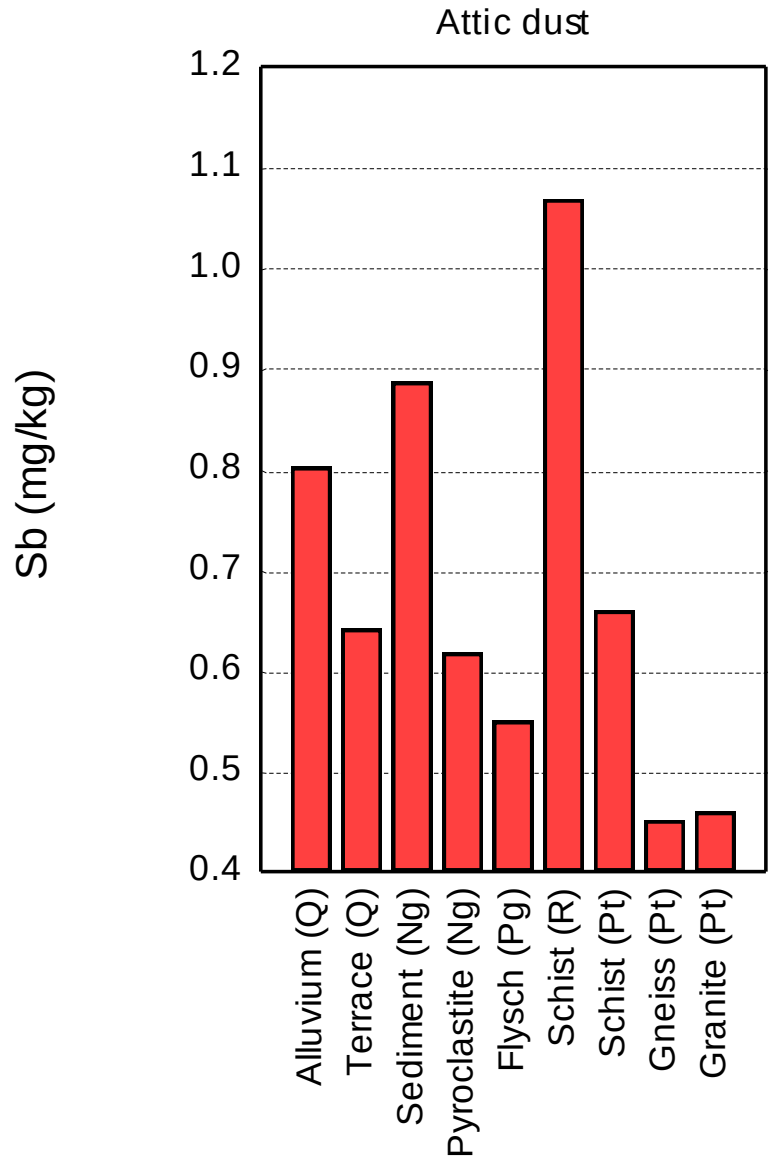
lithogenic *vs.* anthropogenic phenomena

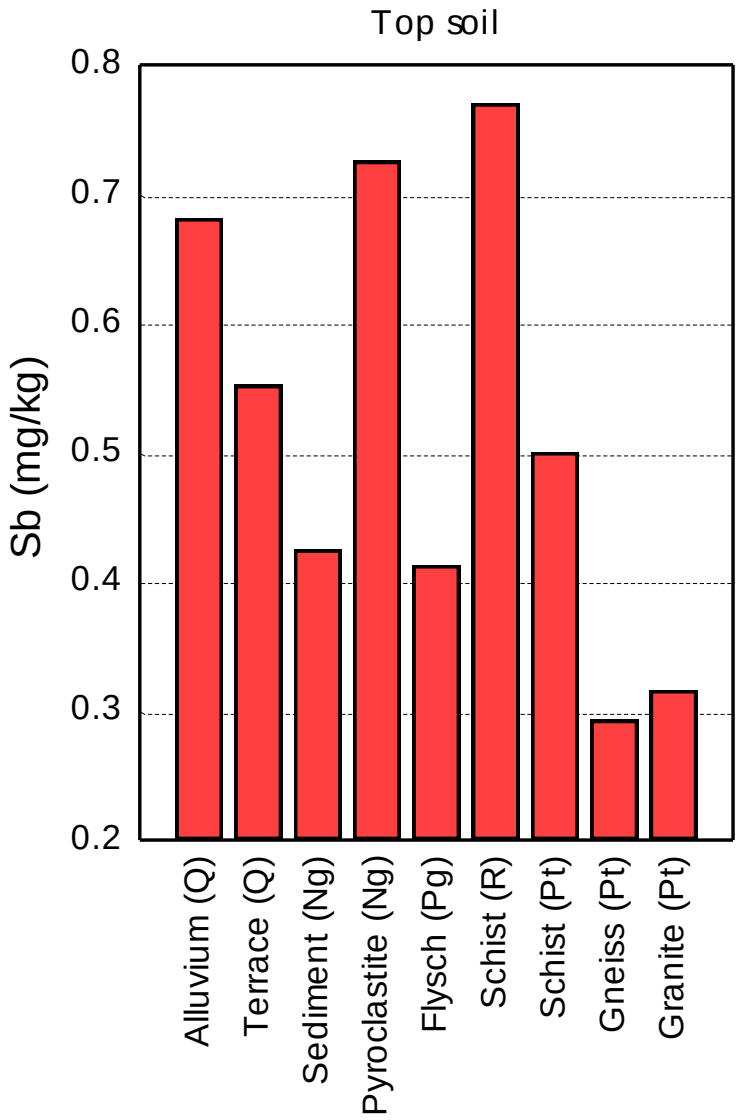




Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

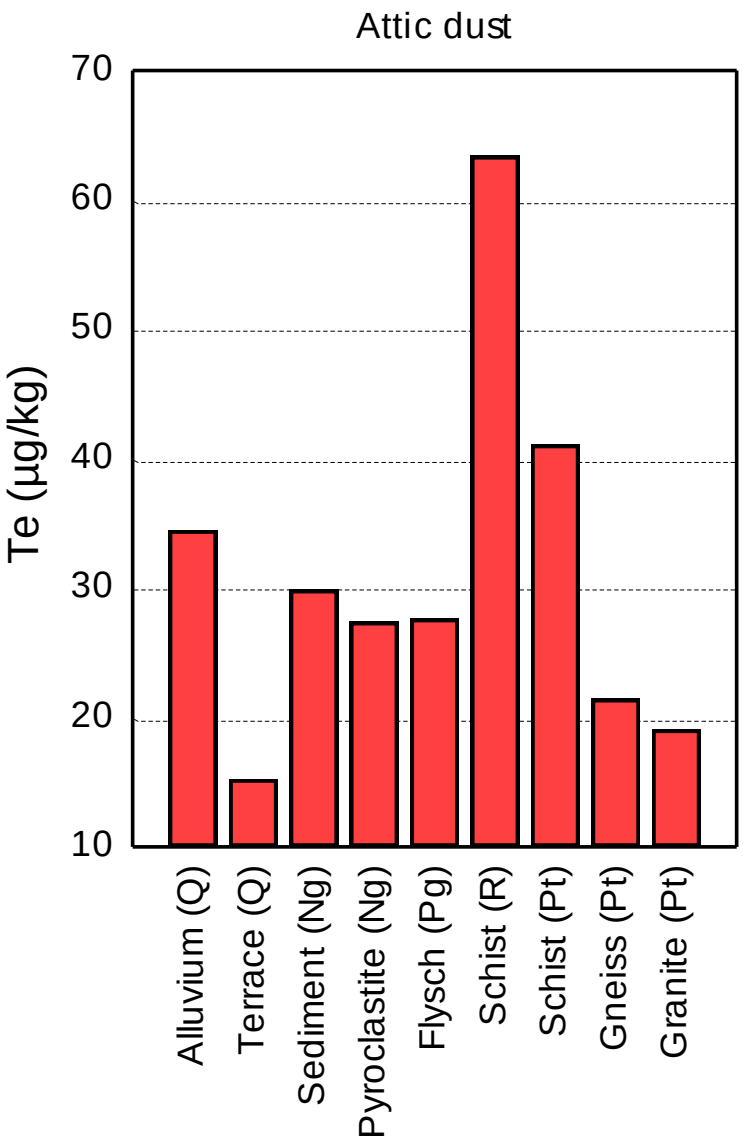
lithogenic *vs.* anthropogenic phenomena

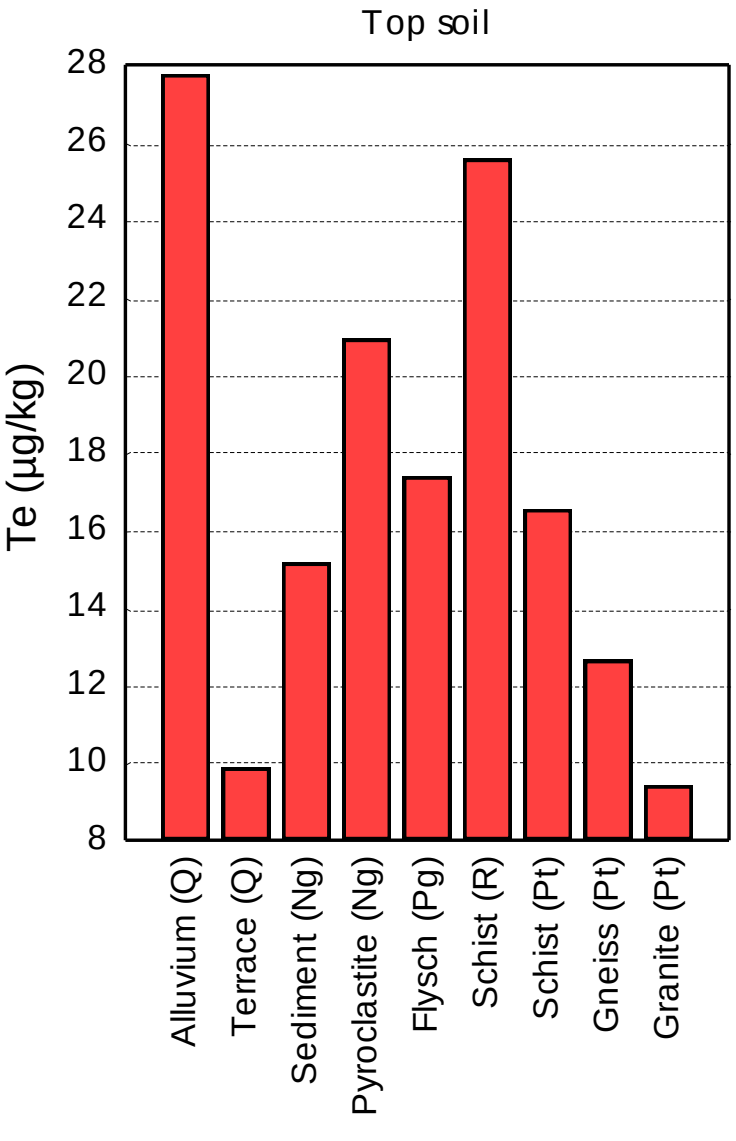




Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

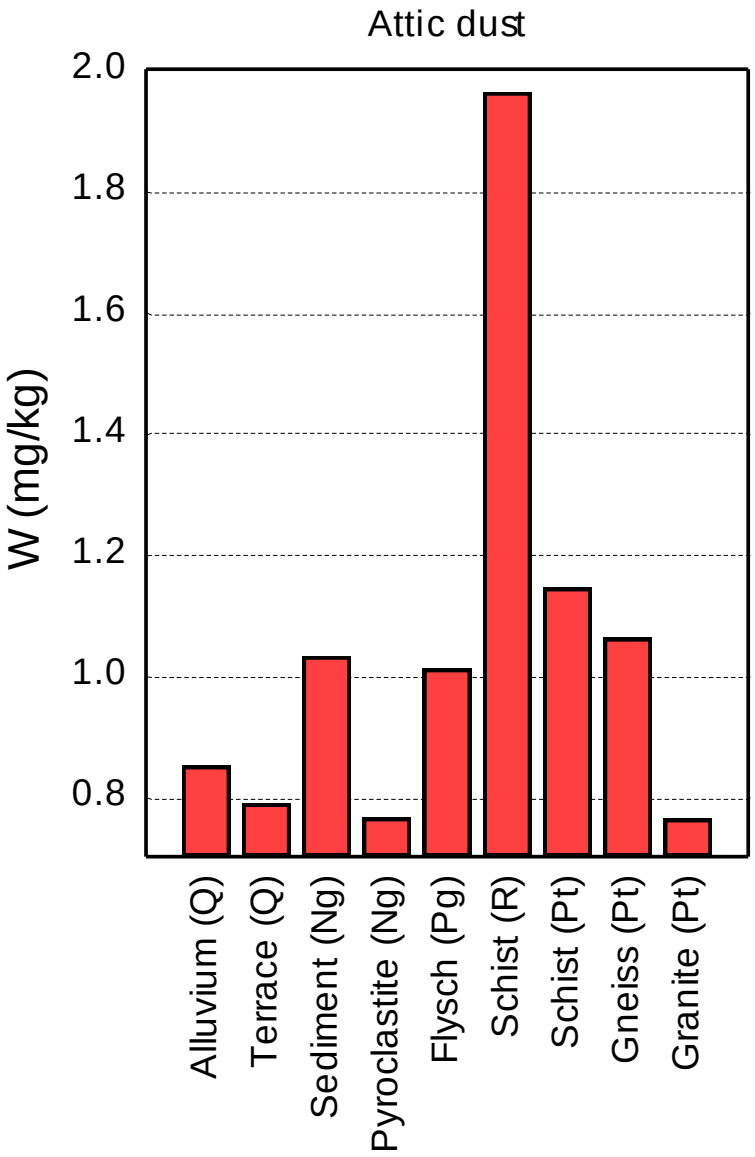
lithogenic *vs.* anthropogenic phenomena

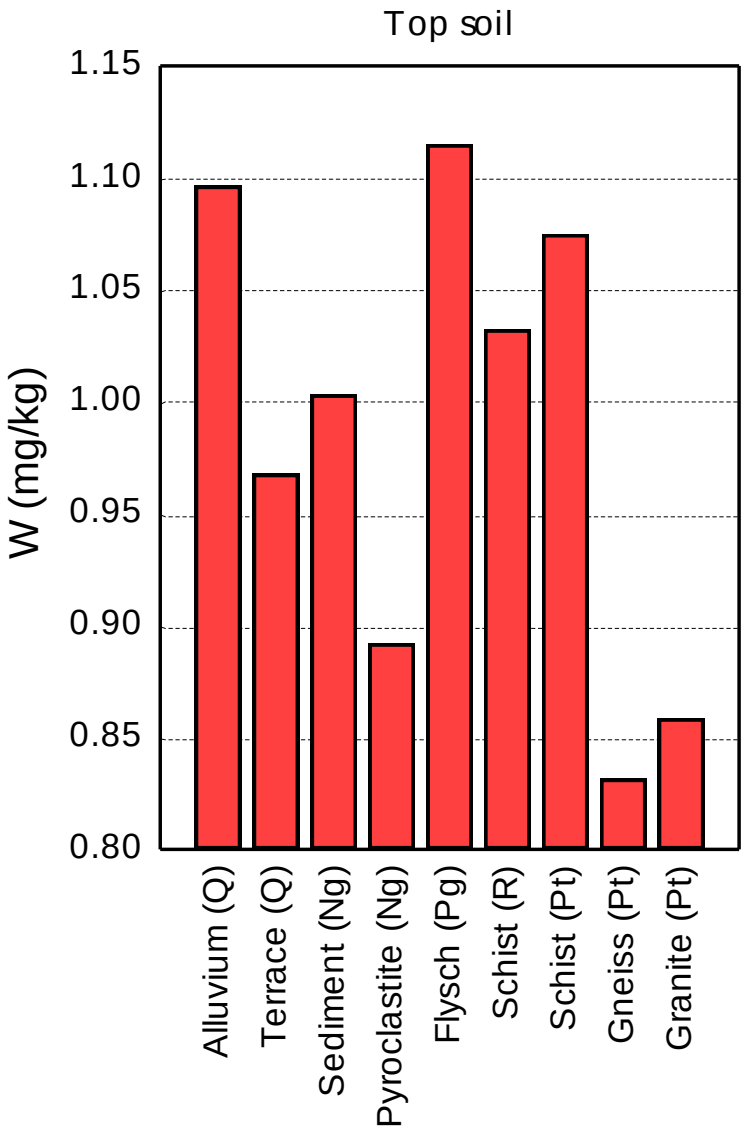




Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

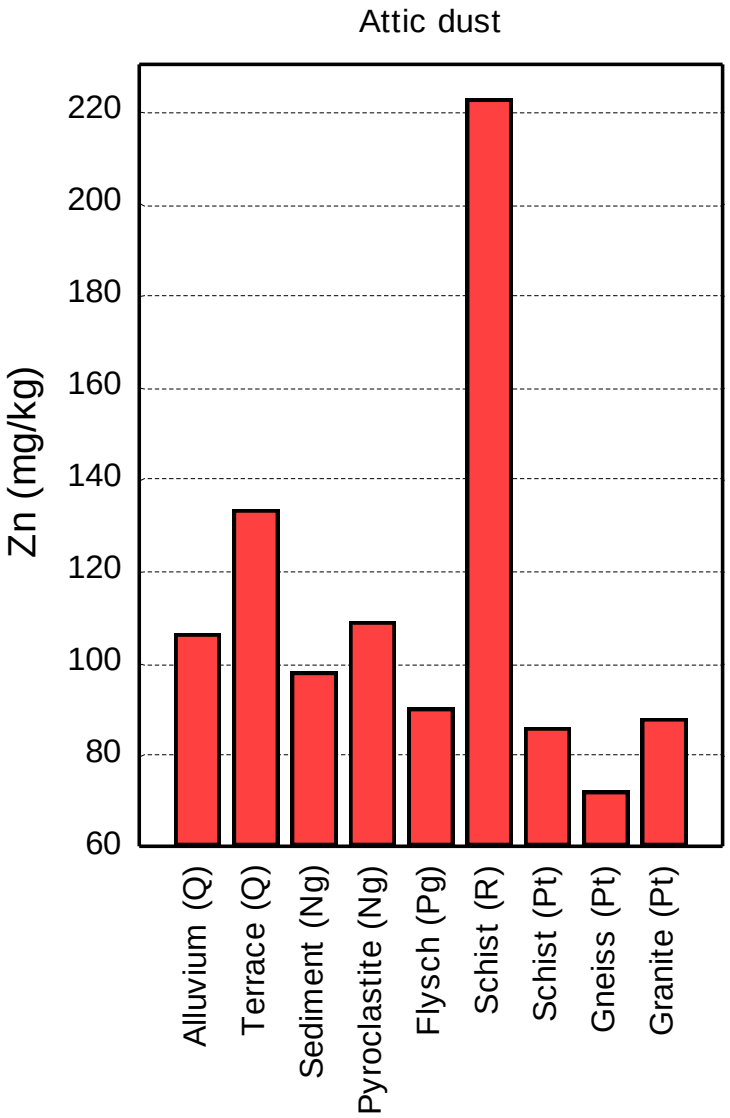
lithogenic *vs.* anthropogenic phenomena

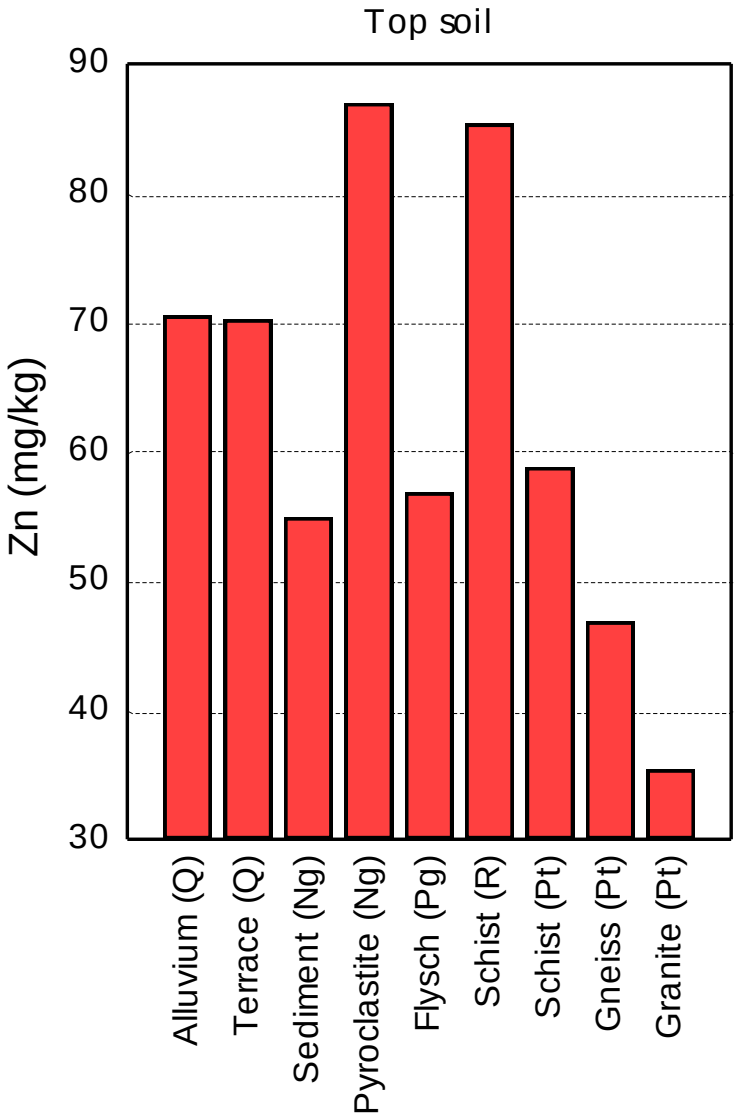


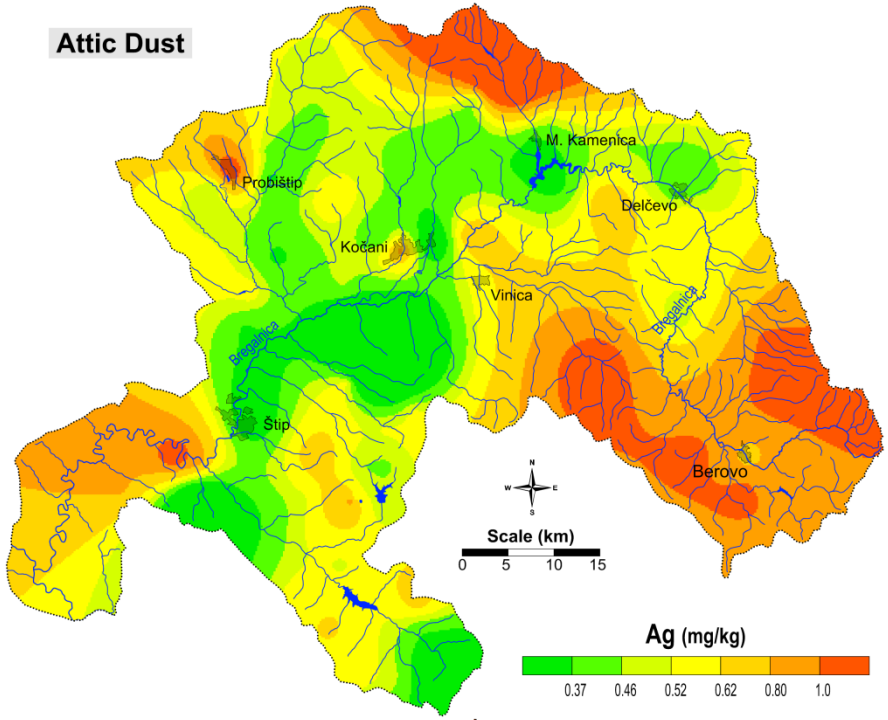


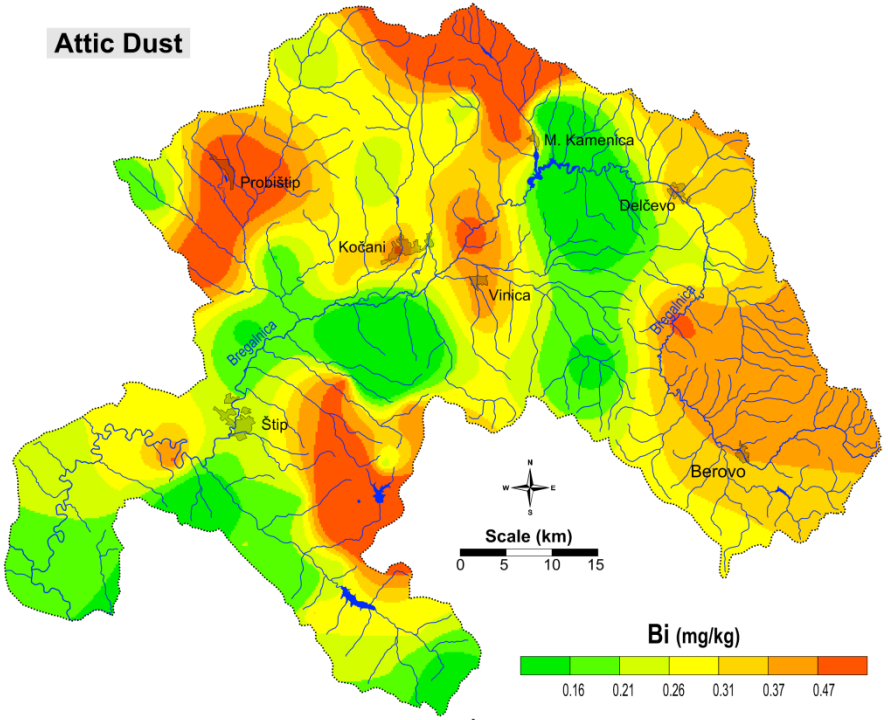
Ag-Bi-Cd-Cu-In-Mn-Pb-Sb-Te-W-Zn

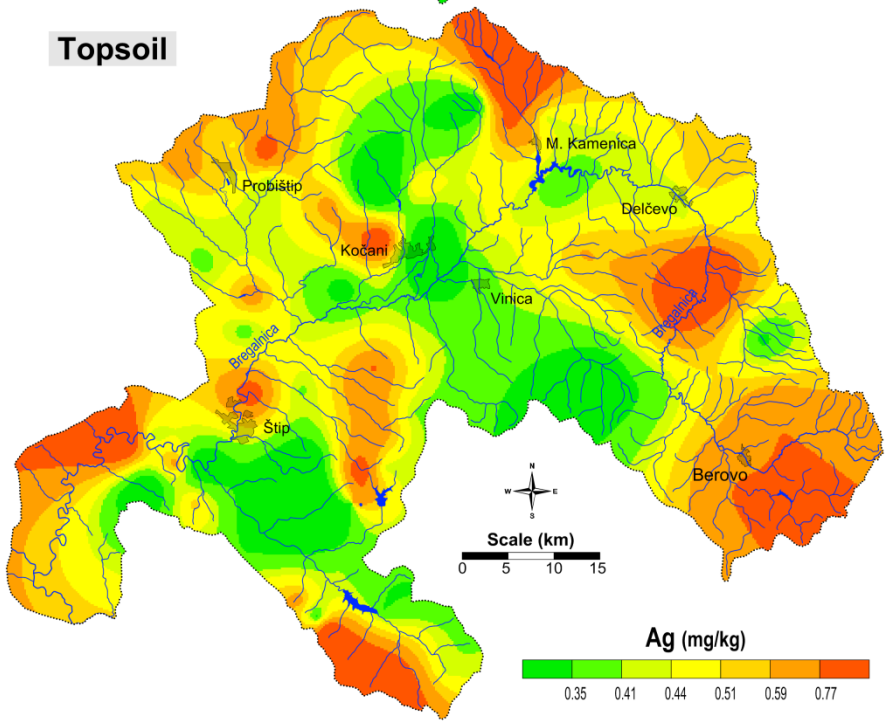
lithogenic *vs.* anthropogenic phenomena

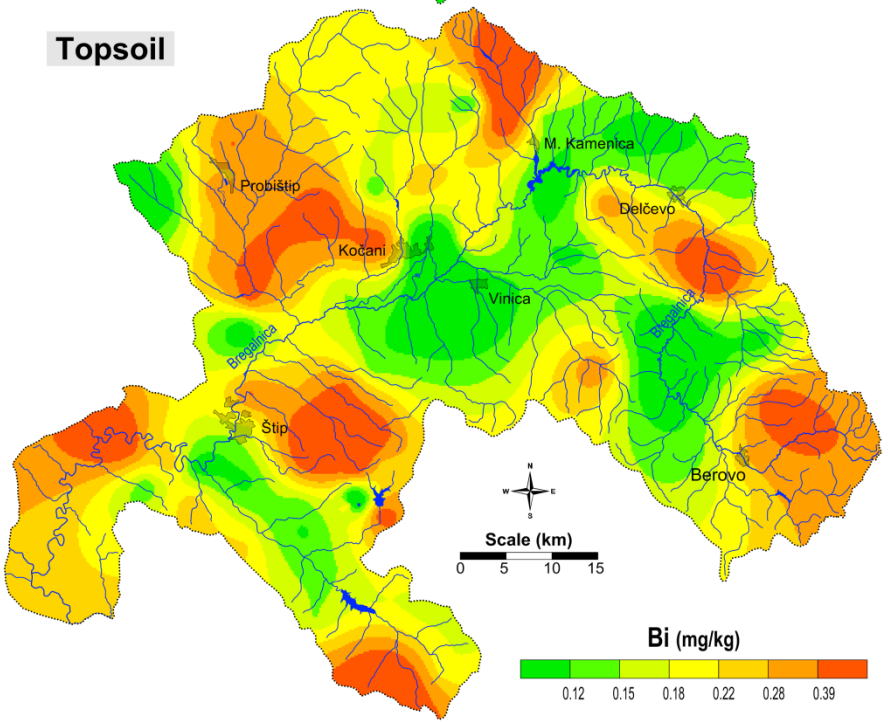





Attic Dust
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Bregalnica
Štip
Berovo
N
W
E
S
Scale (km)
0 5 10 15
Ag (mg/kg)
0.37 0.46 0.52 0.62 0.80 1.0


Attic Dust
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Bregalnica
Štip
Berovo
N
W
E
S
Scale (km)
0 5 10 15
Bi (mg/kg)
0.16 0.21 0.26 0.31 0.37 0.47


Topsoil
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Bregalnica
Štip
Berovo
N
W
E
S
Scale (km)
0 5 10 15
Ag (mg/kg)
0.35 0.41 0.44 0.51 0.59 0.77


Topsoil
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Bregalnica
Štip
Berovo
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Scale (km)
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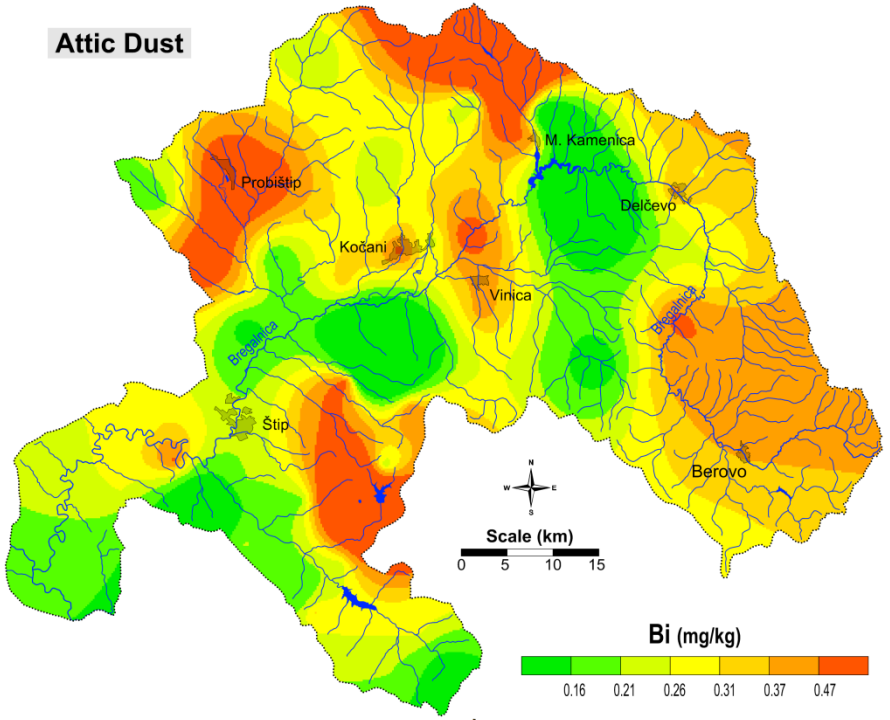
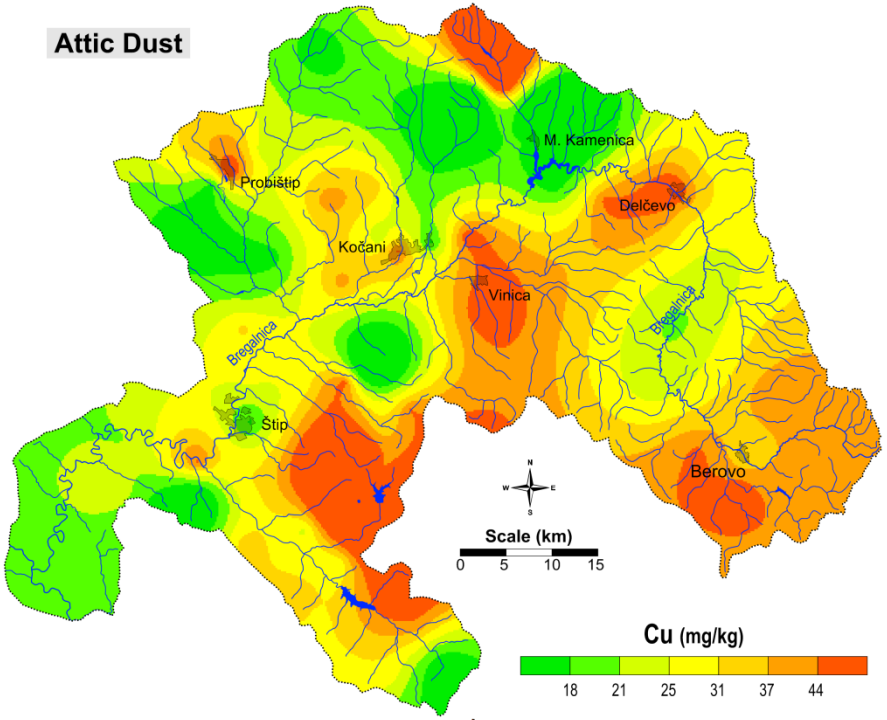
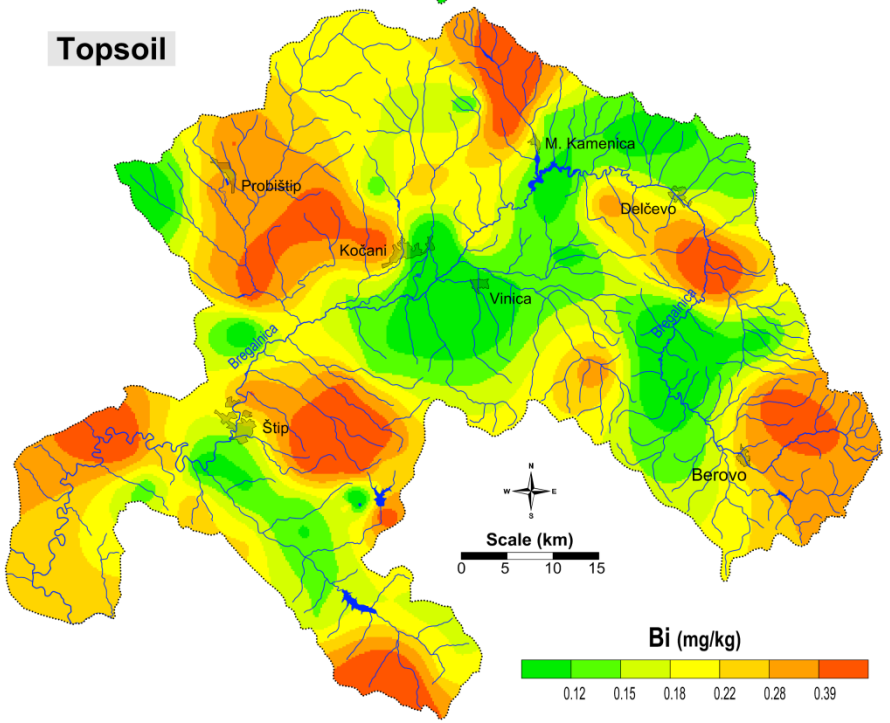
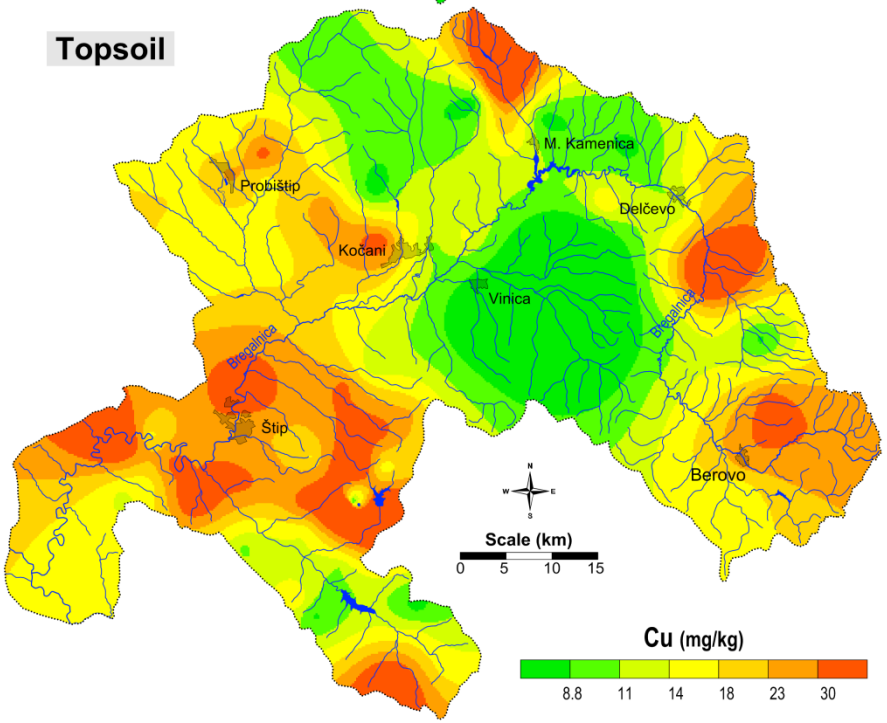
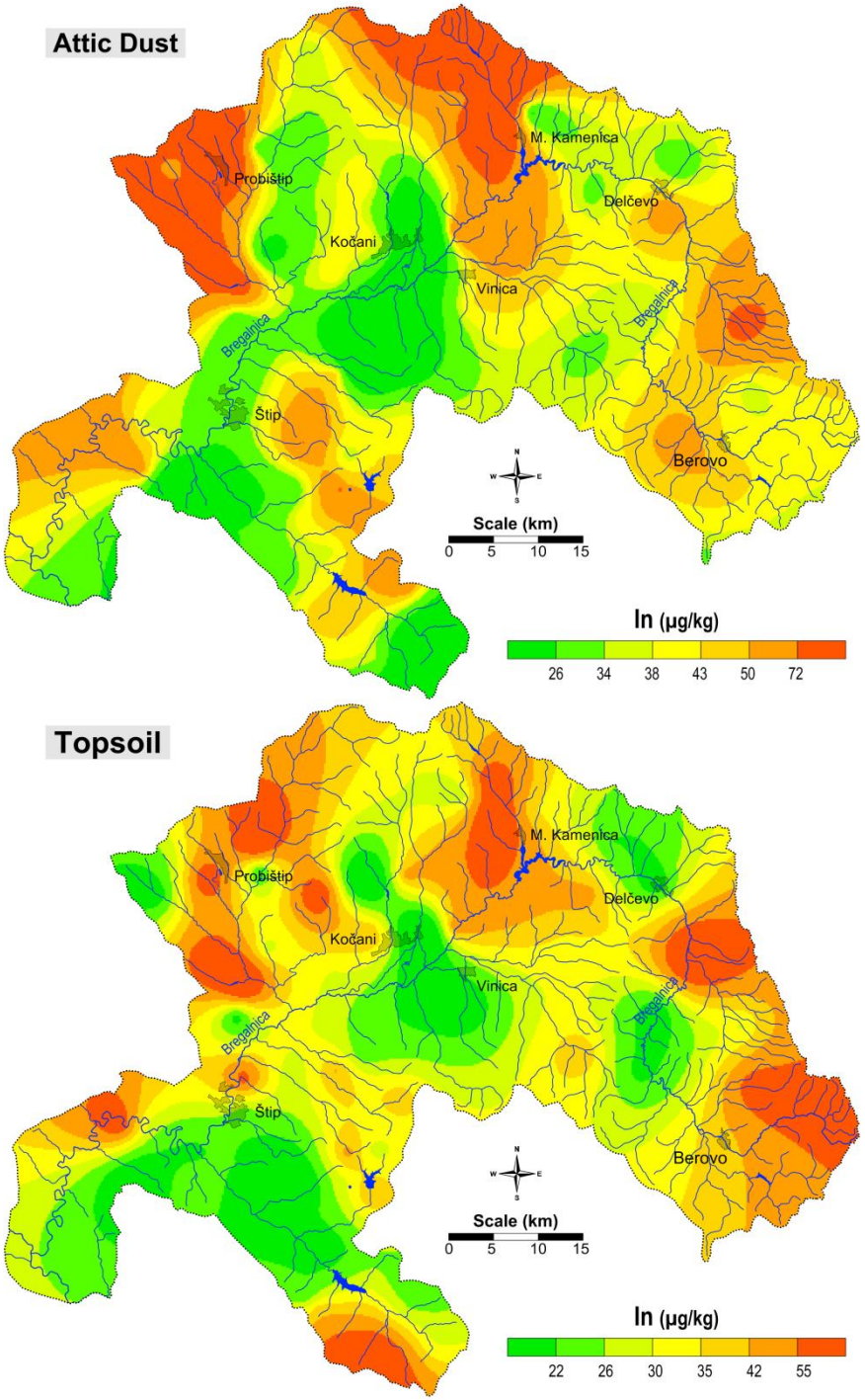
Bi (mg/kg)
0.12 0.15 0.18 0.22 0.28 0.39

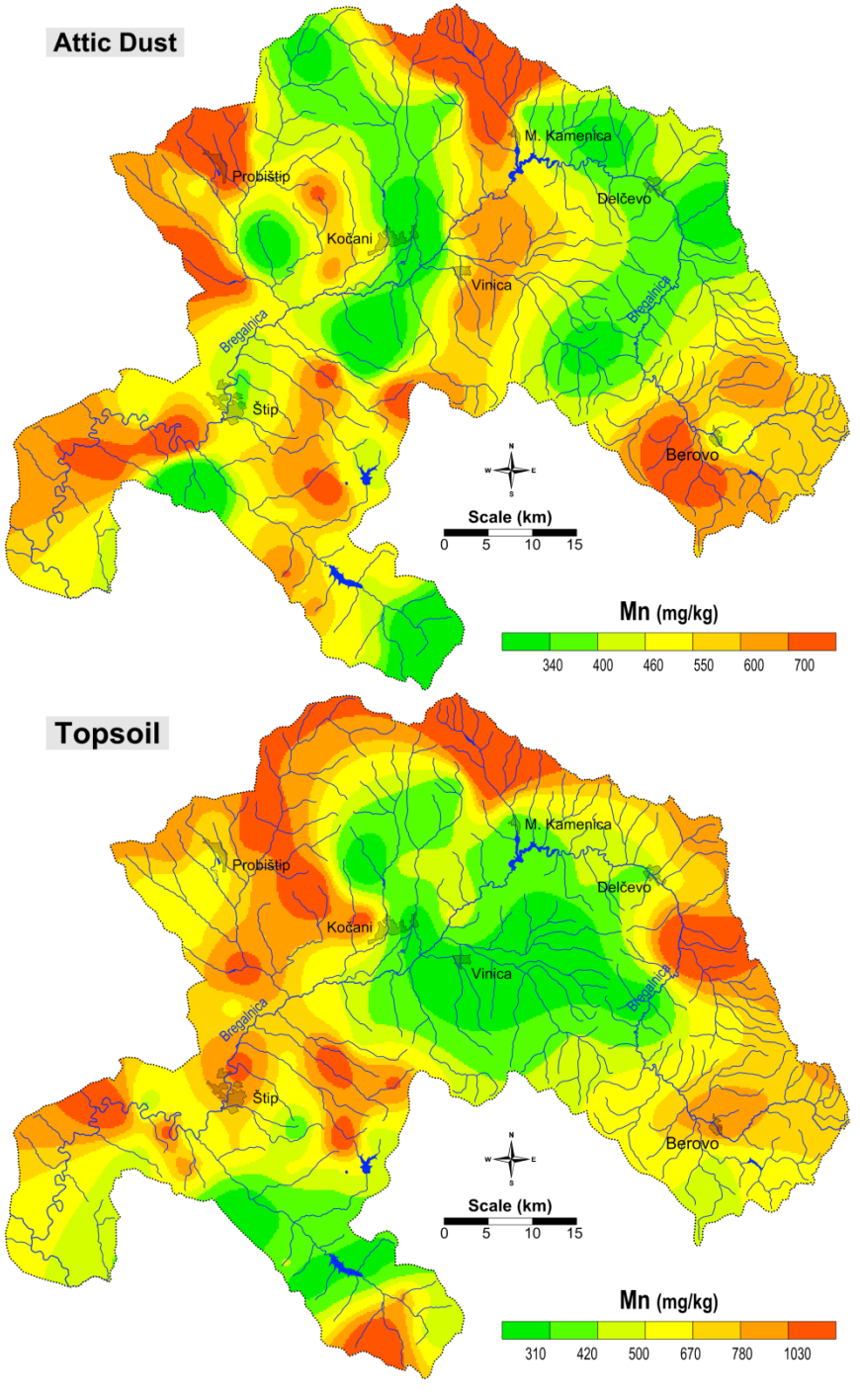

Attic Dust
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Bi (mg/kg)
0.16 0.21 0.26 0.31 0.37 0.47

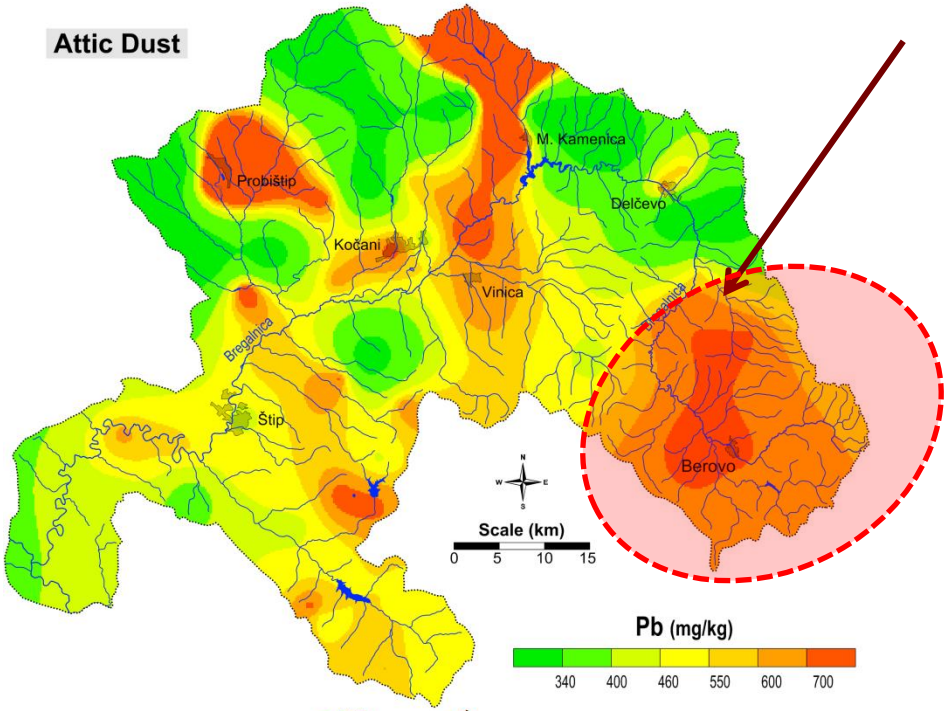

Attic Dust
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Cu (mg/kg)
18 21 25 31 37 44

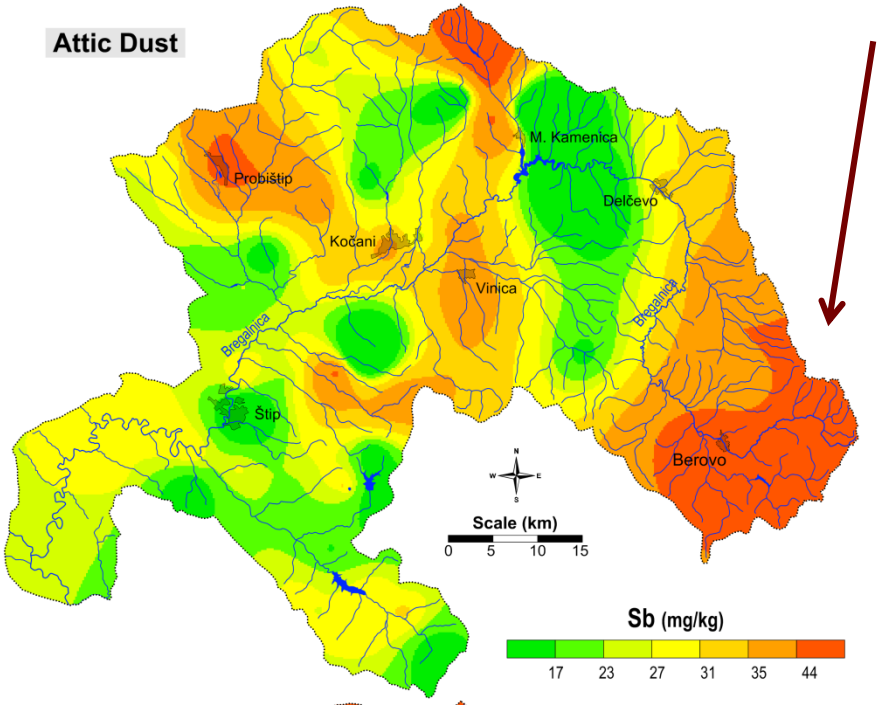

Topsoil
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Bi (mg/kg)
0.12 0.15 0.18 0.22 0.28 0.39

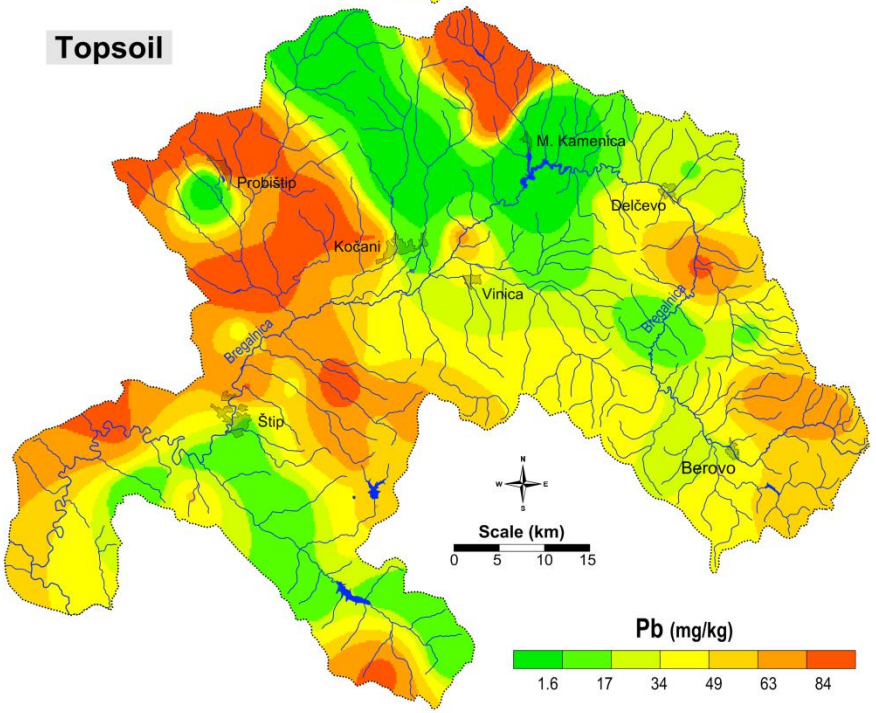

Topsoil
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Cu (mg/kg)
8.8 11 14 18 23 30

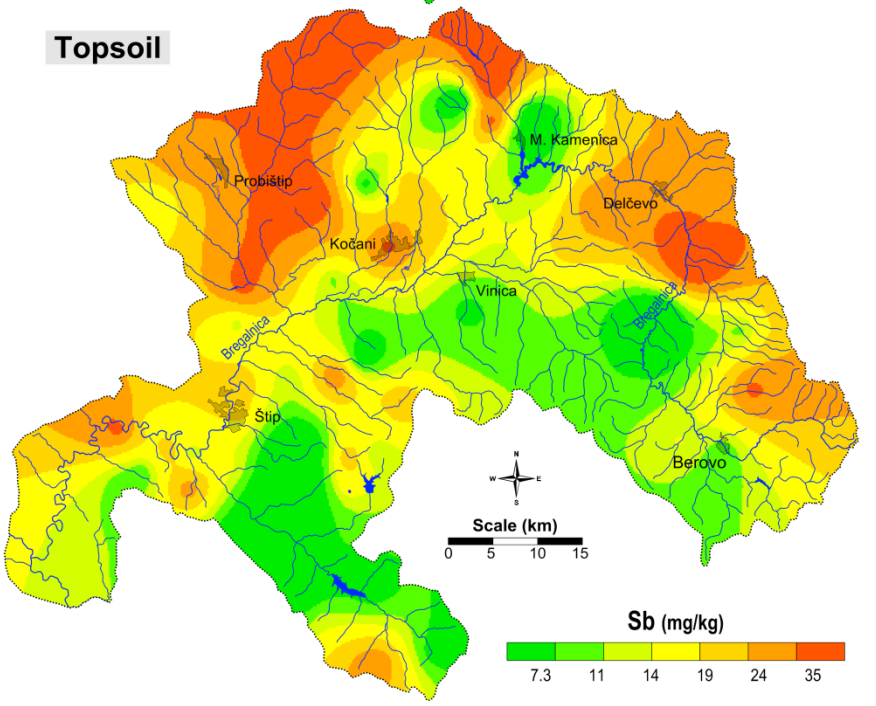

Attic Dust
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
In (µg/kg)
26 34 38 43 50 72
Topsoil
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
In (µg/kg)
22 26 30 35 42 55

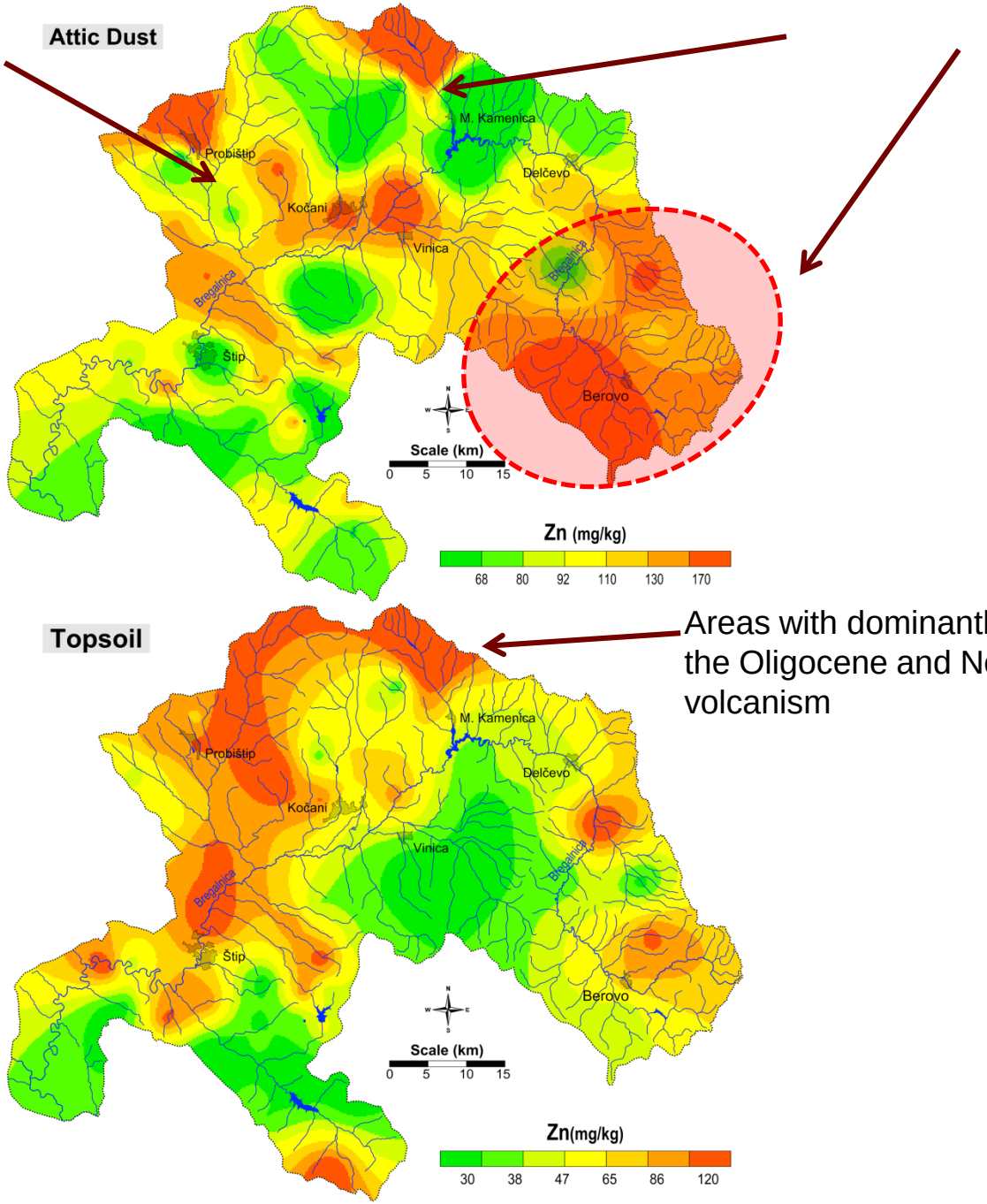

Attic Dust
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Mn (mg/kg)
340 400 460 550 600 700
Topsoil
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Mn (mg/kg)
310 420 500 670 780 1030


Attic Dust
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Pb (mg/kg)
340 400 460 550 600 700

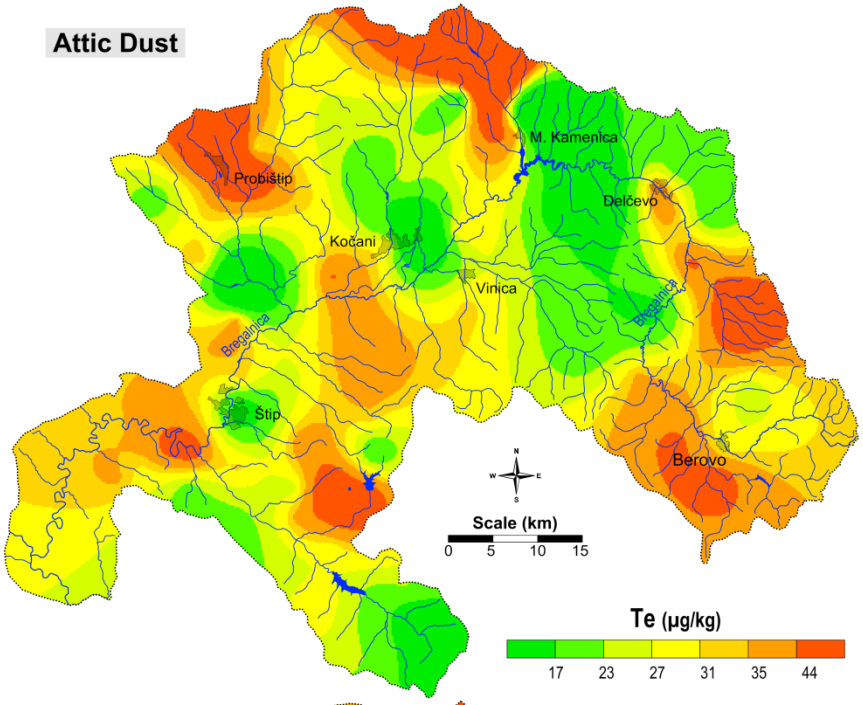

Attic Dust
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Sb (mg/kg)
17 23 27 31 35 44

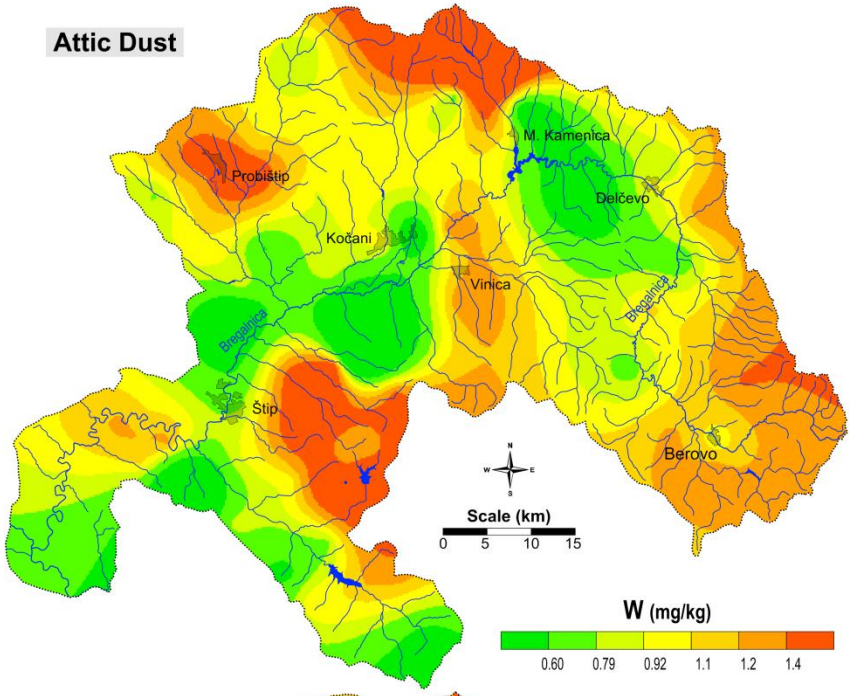

Topsoil
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Pb (mg/kg)
1.6 17 34 49 63 84

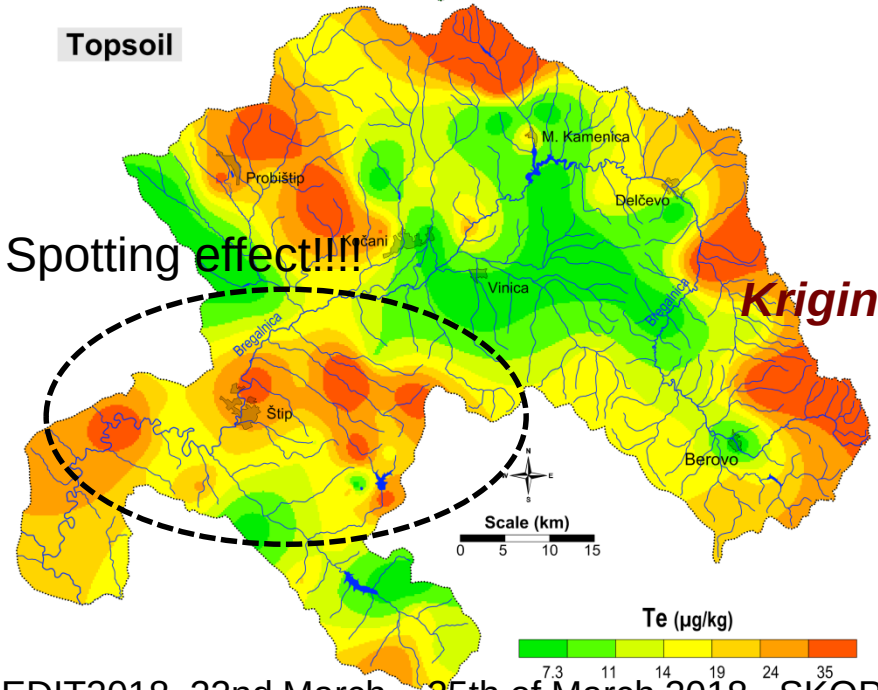

Topsoil
M. Kamenica
Probištip
Delčevo
Kočani
Vinica
Bregalnica
Štip
Berovo
Scale (km)
0 5 10 15
Sb (mg/kg)
7.3 11 14 19 24 35



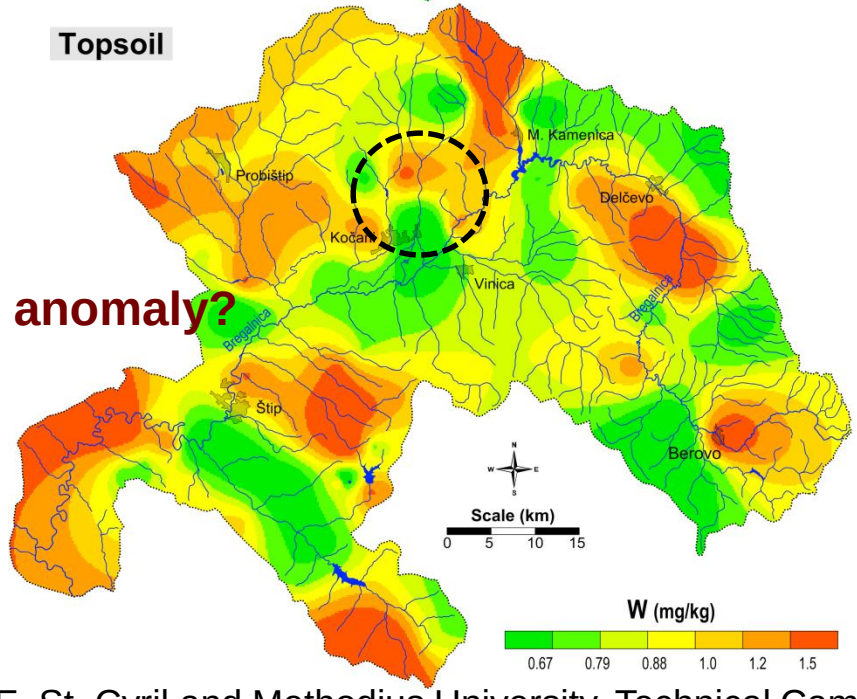
Areas with dominantly presence of the Oligocene and Neogene volcanism



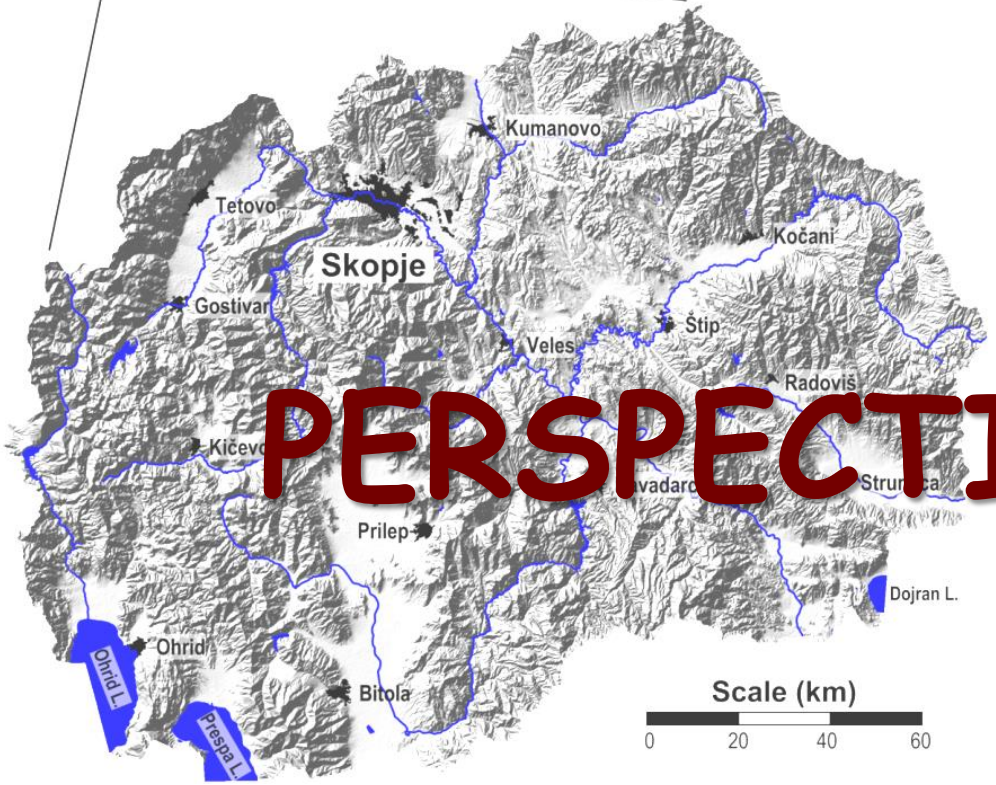




Spotting effect!!!!



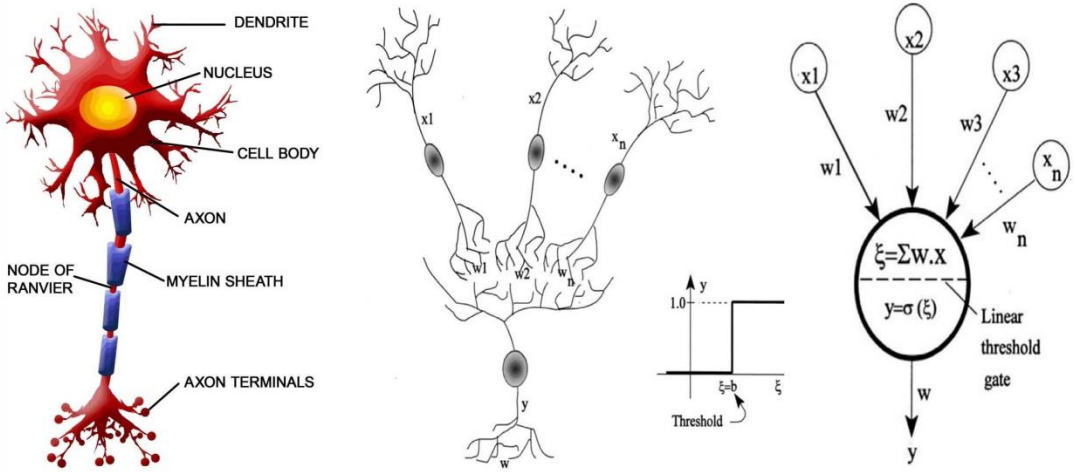
***Kriging* anomaly?**



PERSPECTIVES…..

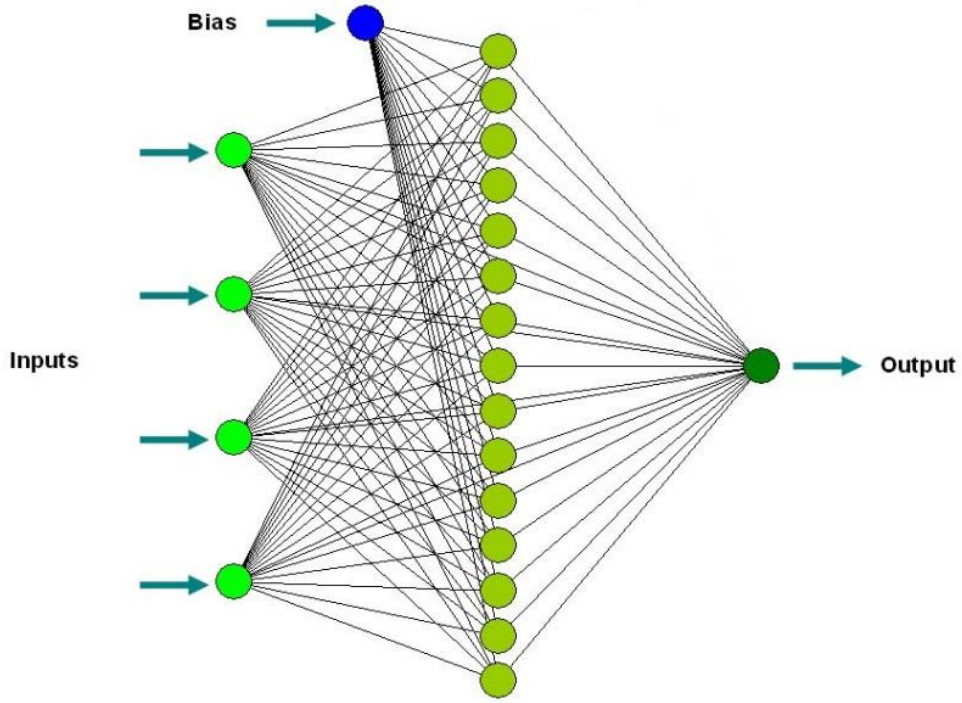
Artificial neural networks

Artificial Neural Network - A computer simulation of human neurons. A system (implemented in software or hardware) that is intended to emulate the computing structure of neurons in the human brain-MODELLING SYSTEM THAT CAN HANDLE A LARGE NUMBER OF INPUT AND OUTPUT PARAMETERS.



Biological neuron and mathematical model of McCulloch and Pitts neuron

MULTILAYER PERCEPTRON



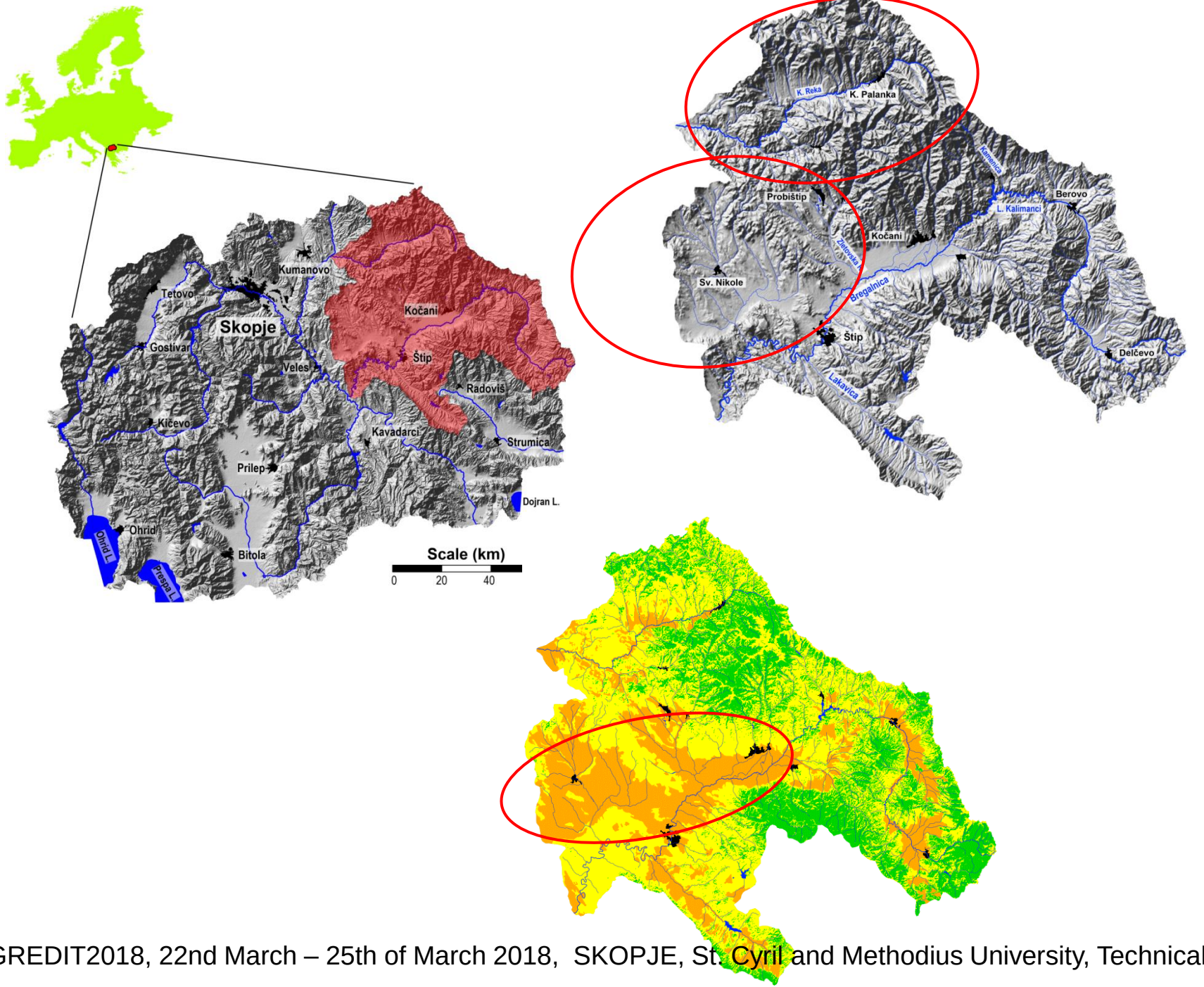
Multilayer perceptron architecture

REASONS FOR APPLICATION

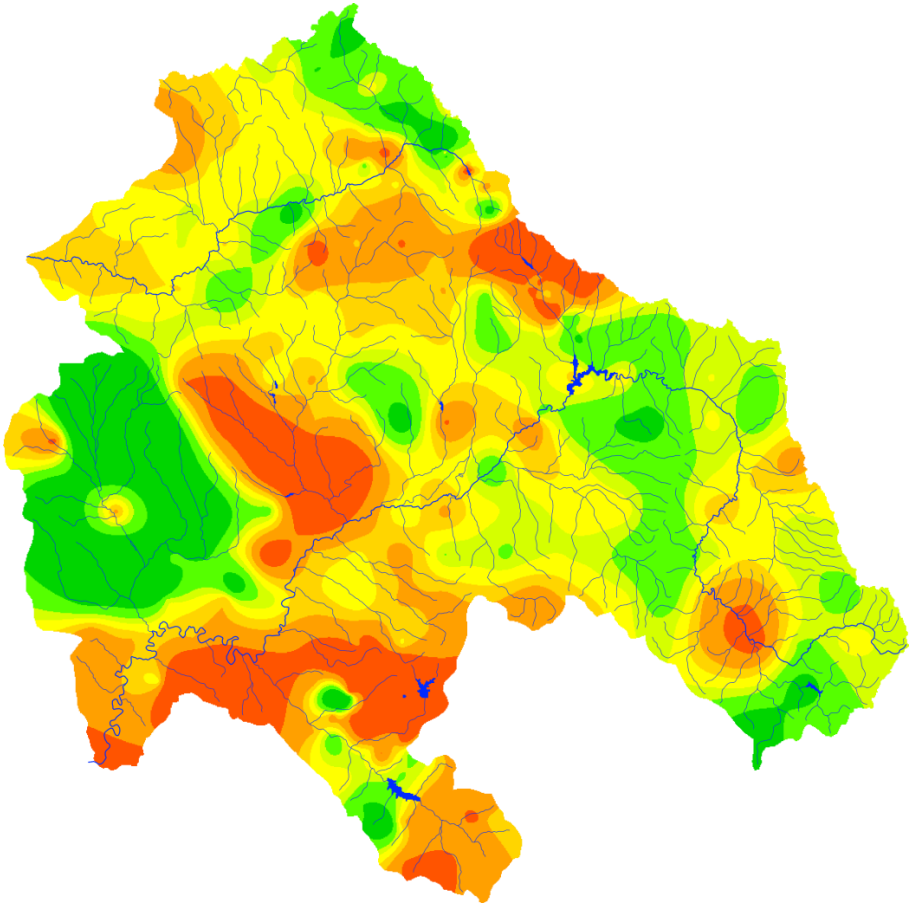
They can model extremely complex systems, which cannot be modeled by methods based on linear algebra.

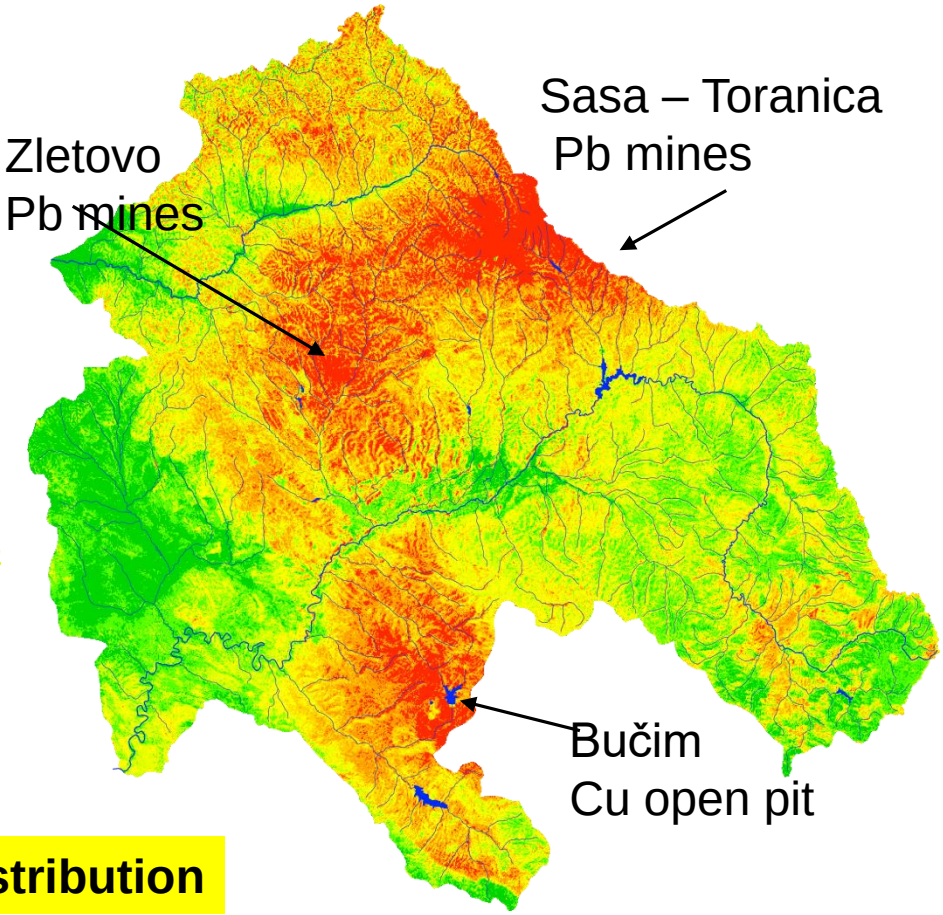
No problems with the dimensionality - it can be arbitrary.

Due to well developed learning algorithms they are easy to use.


Kumanovo
Tetovo
Skopje
Kočani
Gostivar
Štip
Veles
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

Universal Kriging (ANN-MLP)



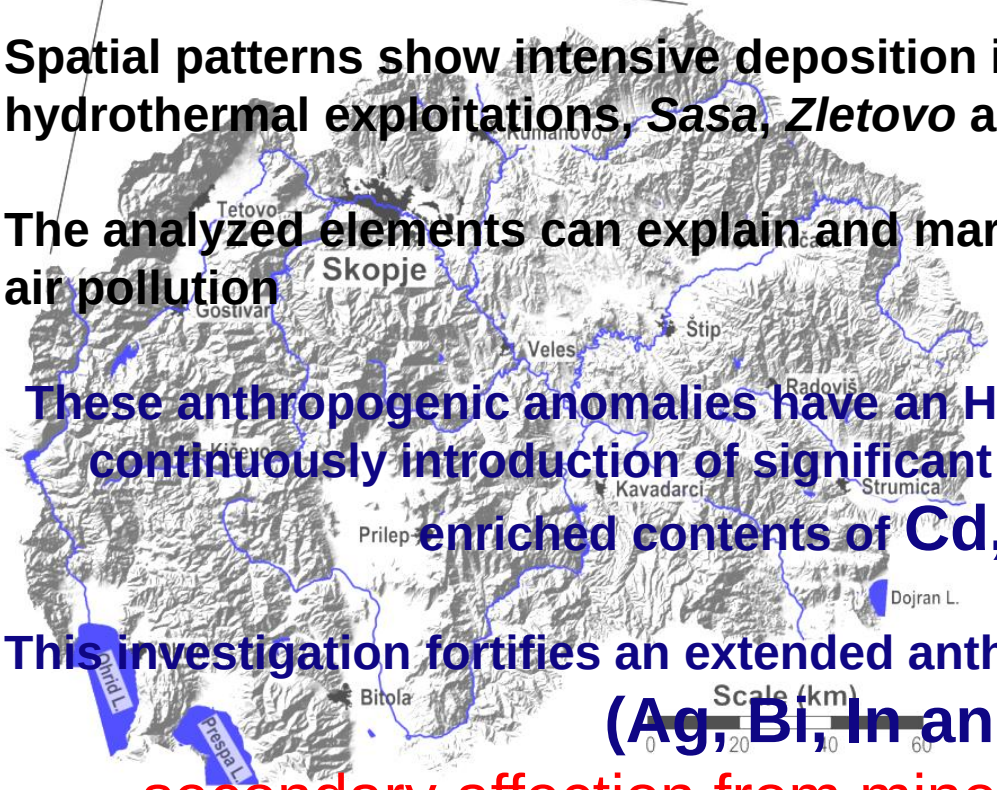


Copper distribution

CONLUSIONS

Spatial patterns show intensive deposition in the area of poly-metallic hydrothermal exploitations, *Sasa*, *Zletovo* and *Bučim*

The analyzed elements can explain and mark the anthropogenic affects on air pollution



These anthropogenic anomalies have an HISTORICAL RECORD for decades continuously introduction of significant emission of dust particle with enriched contents of Cd, Pb and Zn.

This investigation fortifies an extended anthropogenic association (Ag, Bi, In and Mn)

secondary affection from mine poly-metallic pollution

agricultural activities (use of urban sludge, manure and phosphate fertilizers)


GREEDIT2018
THANK YOU FOR YOUR ATTENTION!