

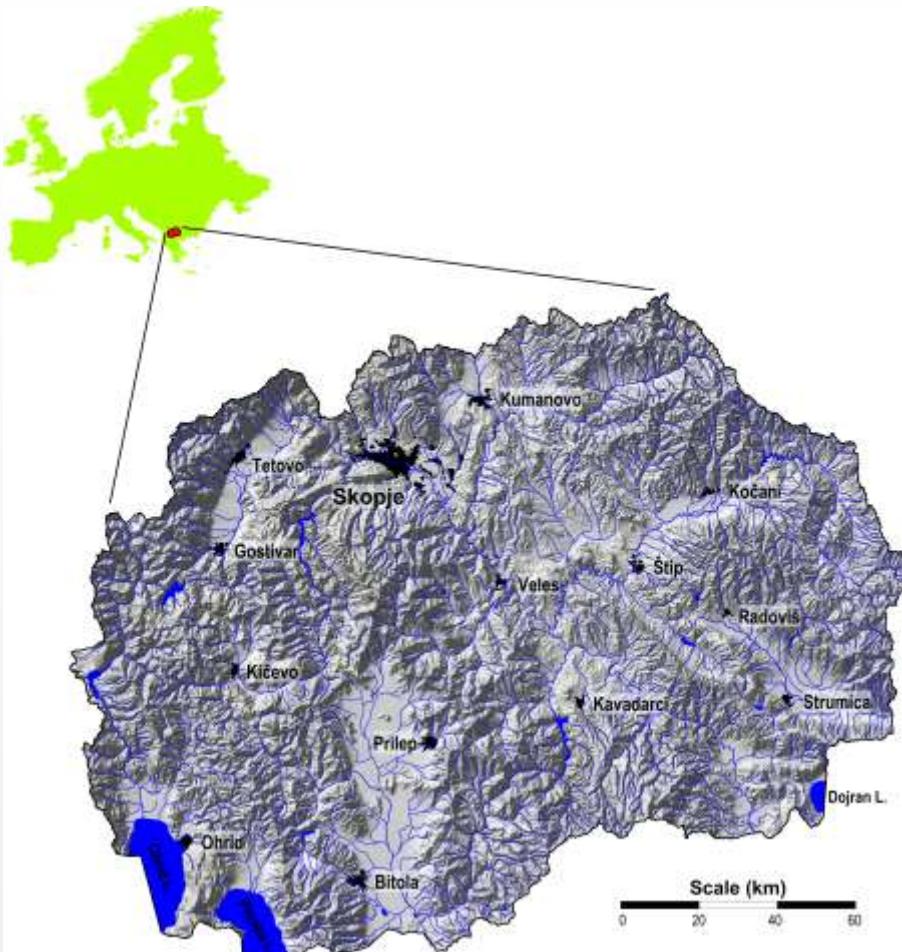
# **THE APPLICATION OF AAS, ICP-AES AND ICP-MS IN ENVIRONMENTAL POLLUTION STUDIES**

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**22<sup>nd</sup> International Seminar on Interaction of Neutrons with Nuclei:  
“Fundamental Interactions & Neutrons, Nuclear Structure, Ultracold Neutrons, Related Topics”,  
Dubna, May 27-30, 2014**

# MACEDONIA



## The Republic of Macedonia

- Located in the central part of the Balkan Peninsula (landlocked country).
- Area of 25,713 km<sup>2</sup> (50% of the territory in mountainous regions).
- The climate is continental in the north and with strong Mediterranean influence in the south.
- The population of the country is around 2 million people (about 60% live in urban areas).



# Ss Cyril and Methodius University, Skopje

## Универзитет “Свети Кирил и Методиј” - Скопје

The **Saints Cyril and Methodius University of Skopje** is the largest university in Macedonia. It was named after the Byzantine brothers Cyril and Methodius, also known as the 'Apostles to the Slavs', enlighteners who developed the precursors to **Cyrilic** script used today in most Slavic languages (IX century).

More than 50,000 students study at the Skopje University. Furthermore, the teaching and research staff number 2,400 people.

The University was established in 1949 and has 23 faculties and 9 research institutes.

# Faculty of Natural Sciences and Mathematics



- Institute of Chemistry
- Institute of Physics
- Institute of Biology
- Institute of Geography
- Institute of Mathematics

## Laboratory of Atomic Spectroscopy

# Atomic spectrometry

## - Atomic absorption spectrometry

- Flame AAS
- Electrothermal AAS (ETAAS)
- Hydride generation AAS (HG-AAS)
- Cold vapour AAS (CV-AAS)



## - Atomic emission spectrometry (AES)

- Inductively coupled plasma – AES (ICP-AES)



# Application of atomic spectroscopy

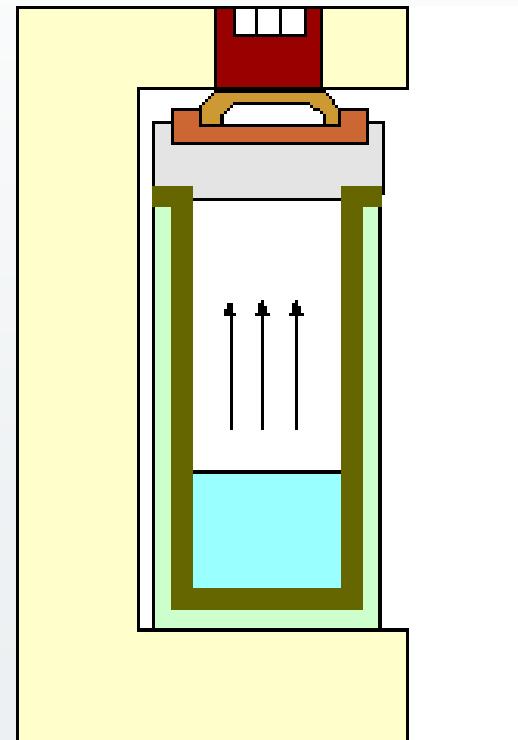
- Water analysis
- Food analysis
- Clinical analysis
- Environmental samples (soil, sediments, plants, etc.)
- Mining, metallurgy
- Petrochemistry
- Etc.

# Sample preparation

Microwave digestion:

- Milestone model ETHOS PLUS with MPR-100/10S
- CEM Microwave digestion system, Model MarsX

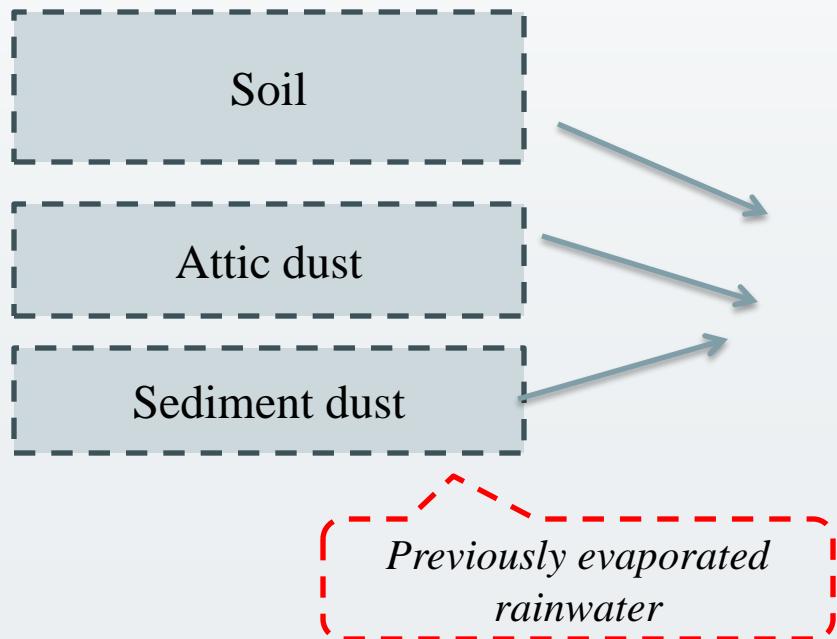
Digestion with  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$



# SAMPLE PREPARATION



Step	Temperature/°C	Time/min	Power/W	Pressure/bar
1	180	5	500	20
2	180	10	500	20



Total digestion with  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{HF}$ ,  $\text{HCl}$

# The major industries in Macedonia

- Mining (Pb, Zn, Cu, Ni, Cr)
- Metallurgy (Pb, Zn, Cd, Fe-Ni, Fe-Cr, Fe-Si, Fe, steel)
- Thermoelectric power plants (using coal)
- Chemical industry (pharmacy, refinery, plastics, ...)
- Metal processing
- Electronics
- etc.

# **1. AIR POLLUTION**

- Biomonitoring (moss, lichens)
- Dust (attic dust, deposited dust)

# **2. SOIL POLLUTION**

- Topsoil
- Subsoil
- Vertical distribution

# **3. WATER POLLUTION**

- Water
- Sediments
- Biota

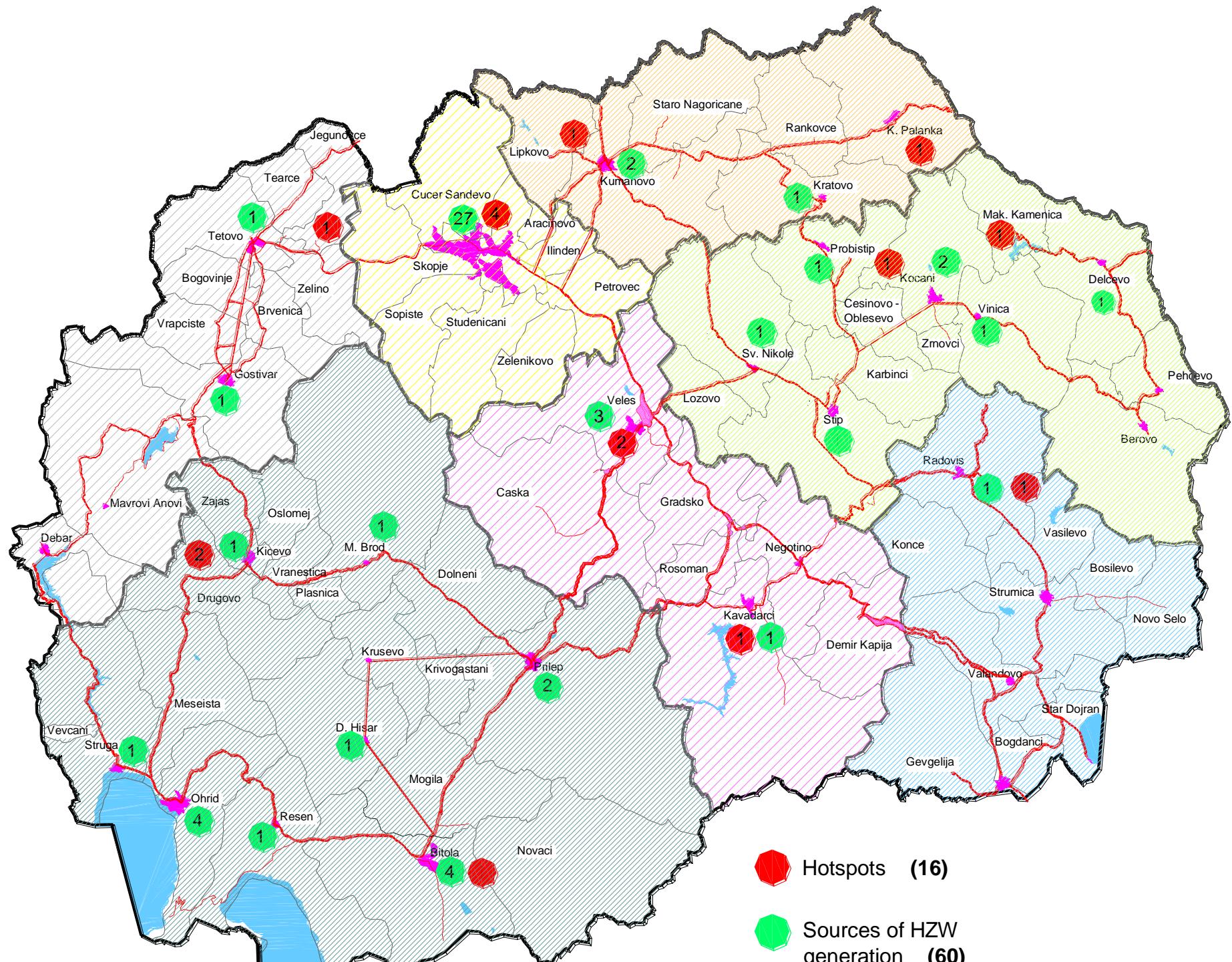
# National Solid Waste Management Plan and Feasibility Studies

## ***Special Studies “E”: Industrial Hazardous Waste***

To guide/assist in the gathering and the reviewing existing data, and to specify the methodology to identify the potentially most environmental dangerous industrial ‘hotspots’ in the R. Macedonia, including **sampling of the identified and selected industrial ‘hotspots’.**

### **Annual HZW generation**

Nr.	Waste stream	Generated total waste t/y	HZW	
			t/y	%
1	Waste from mining	17,246,000	4,546,000	26.4%
2	Wastes from thermal processes	2,090,726	75,347	3.6%
3	Waste from other process industries	108,877	2,047	1.9%
	Total	19,445,603	4,623,394	31.9%



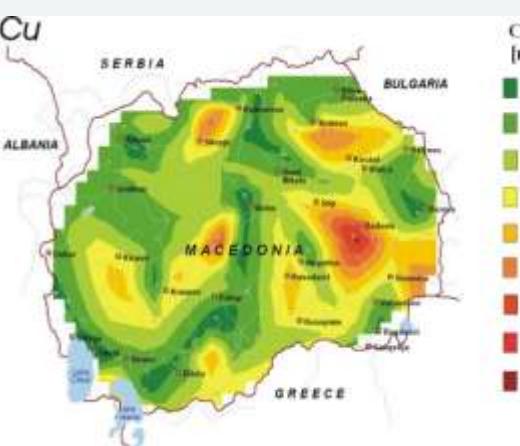
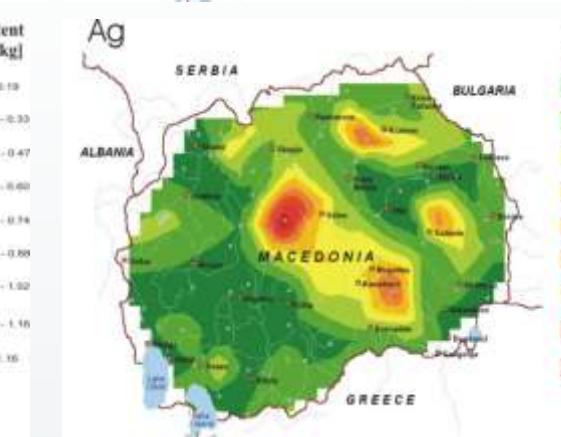
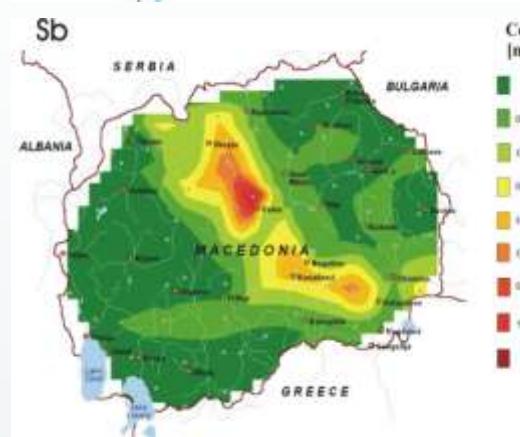
Hotspots (16)

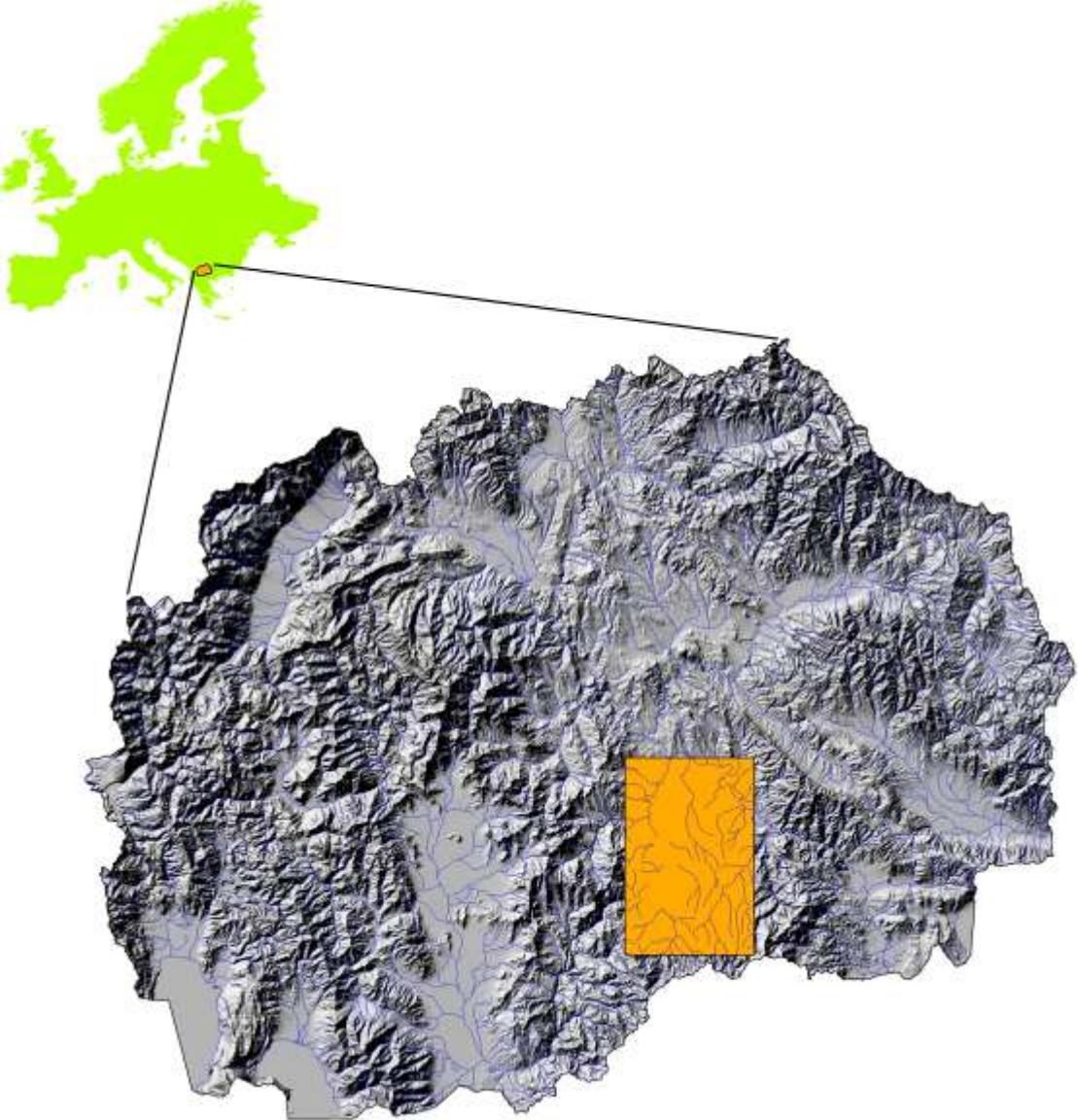
Sources of HZW generation (60)

# MACEDONIA

## LOCATIONS AND SAMPLING POINTS (73)



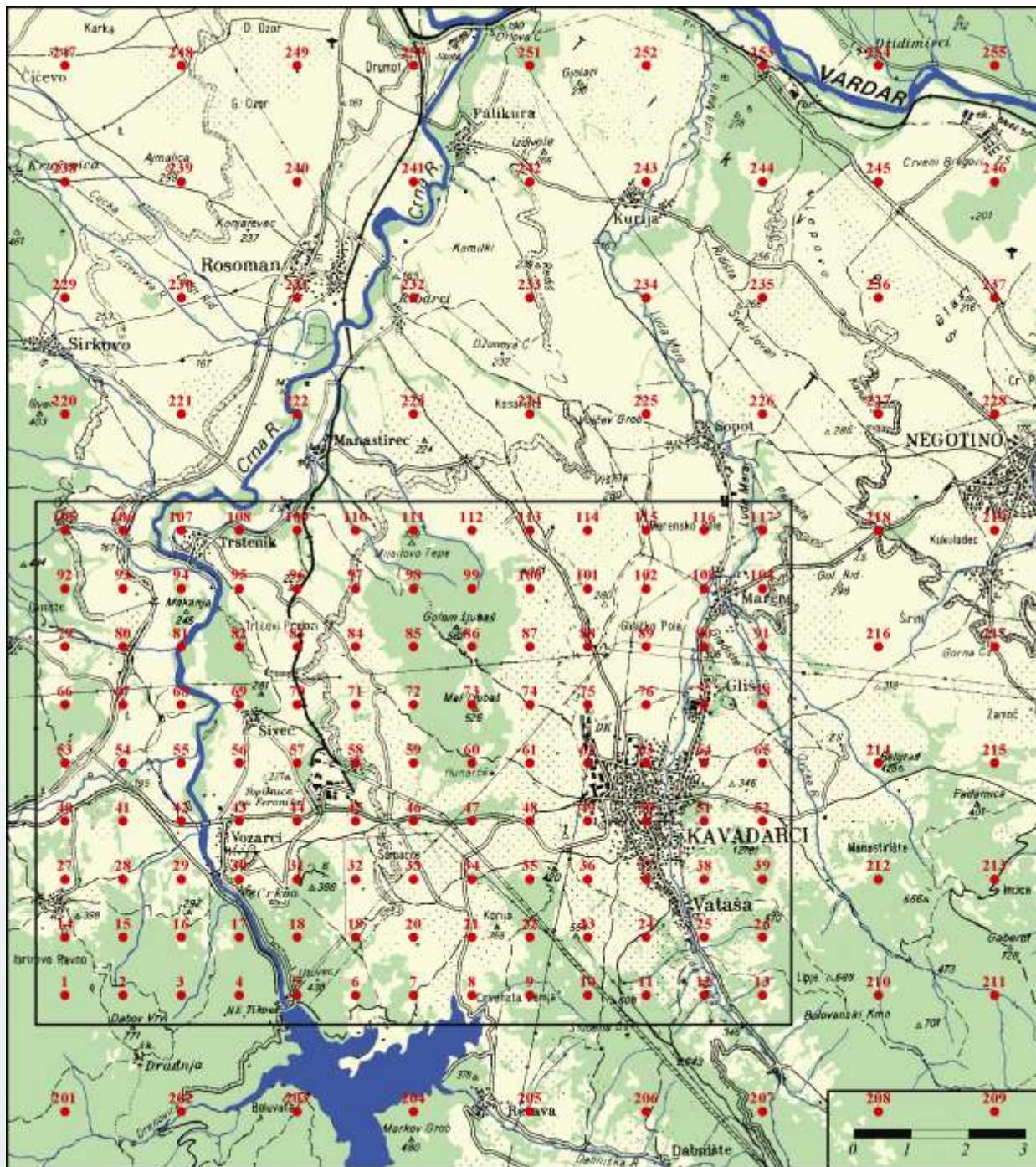




## Kavadarci region (ferronickel smelter)

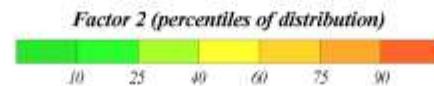
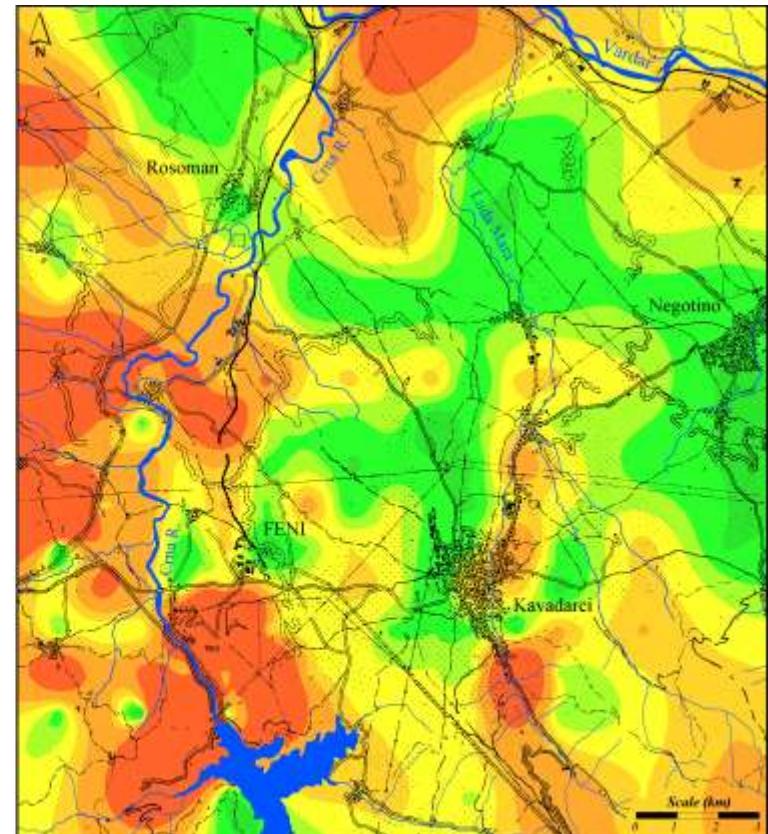
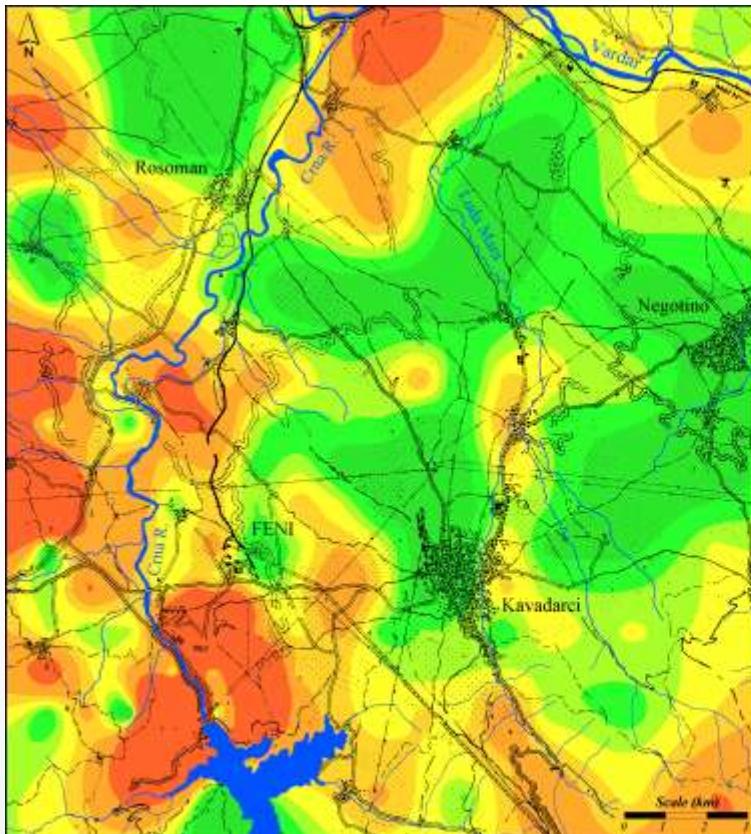
T. Stafilov, R. Šajn, B. Boev, J. Cvetković, D. Mukaetov, M. Andreevski, Geochemical atlas of Kavadarci and the environs, Faculty of Natural Sciences and Mathematics, Skopje, 2008.

T. Stafilov, R. Šajn, B. Boev, J. Cvetković, D. Mukaetov, M. Andreevski, S. Lepitkova, Distribution of some elements in surface soil over the Kavadarci region, Republic of Macedonia, *Environmental Earth Sciences*, **61**, 1515-1530 (2010).



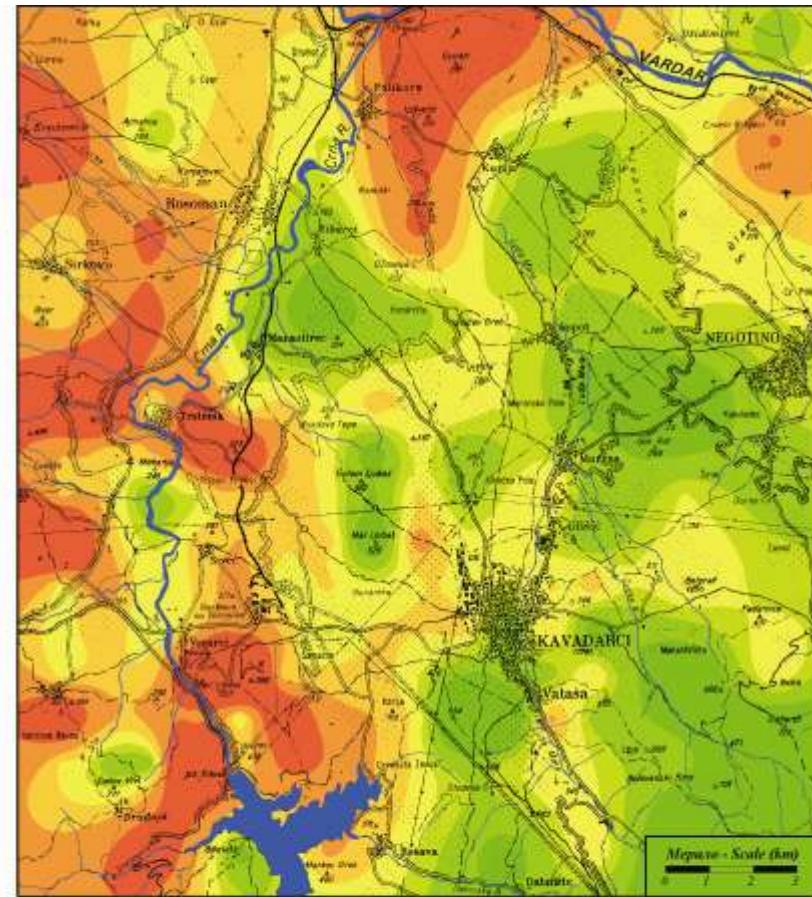
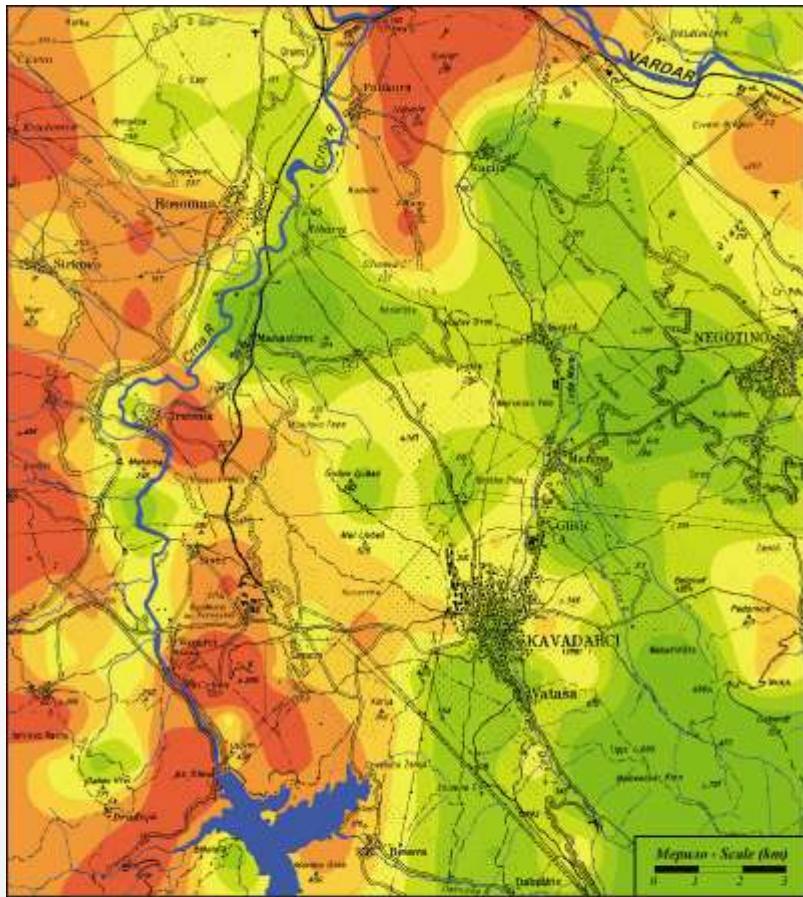
**172 locations  
topsoil (0-5 cm)  
subsoil (20-30 cm)  
Sampling grid, 2x2 km  
in urban zone, 1x1 km**

**45 samples for  
radiochemical analysis  
(4 x 4 km)**



Distribution of Factor 2 scores (Co, Cr, Mg and Ni) in topsoil (left) and subsoil (right)

This association is dependent on the lithogenesis. Their highest contents are in areas of Paleozoic and Mesozoic rocks and Eocene upper flysch zone and their lowest values in area of the Pleistocene tuff, Holocene deluvium and Holocene alluvium.

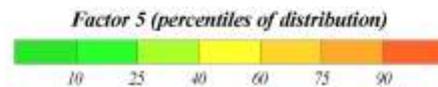
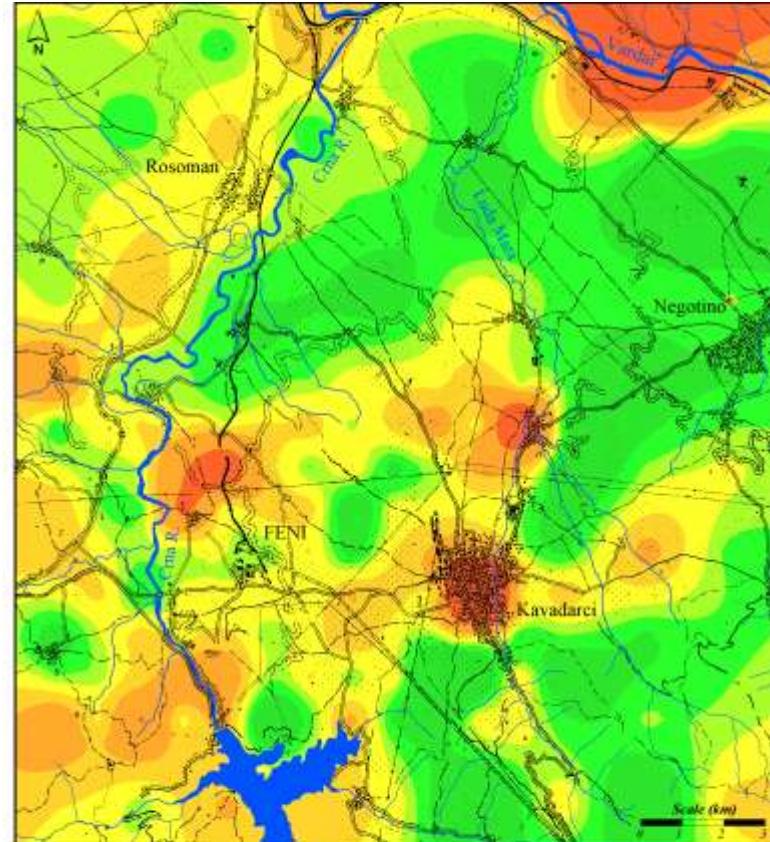
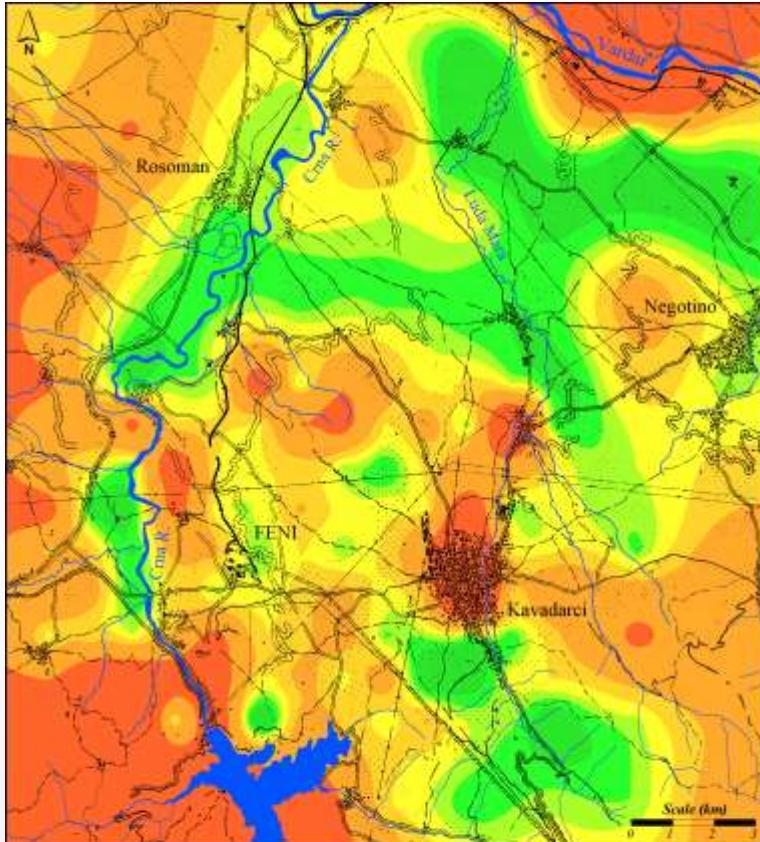


Ni (mg/kg)

41 53 62 76 94 131

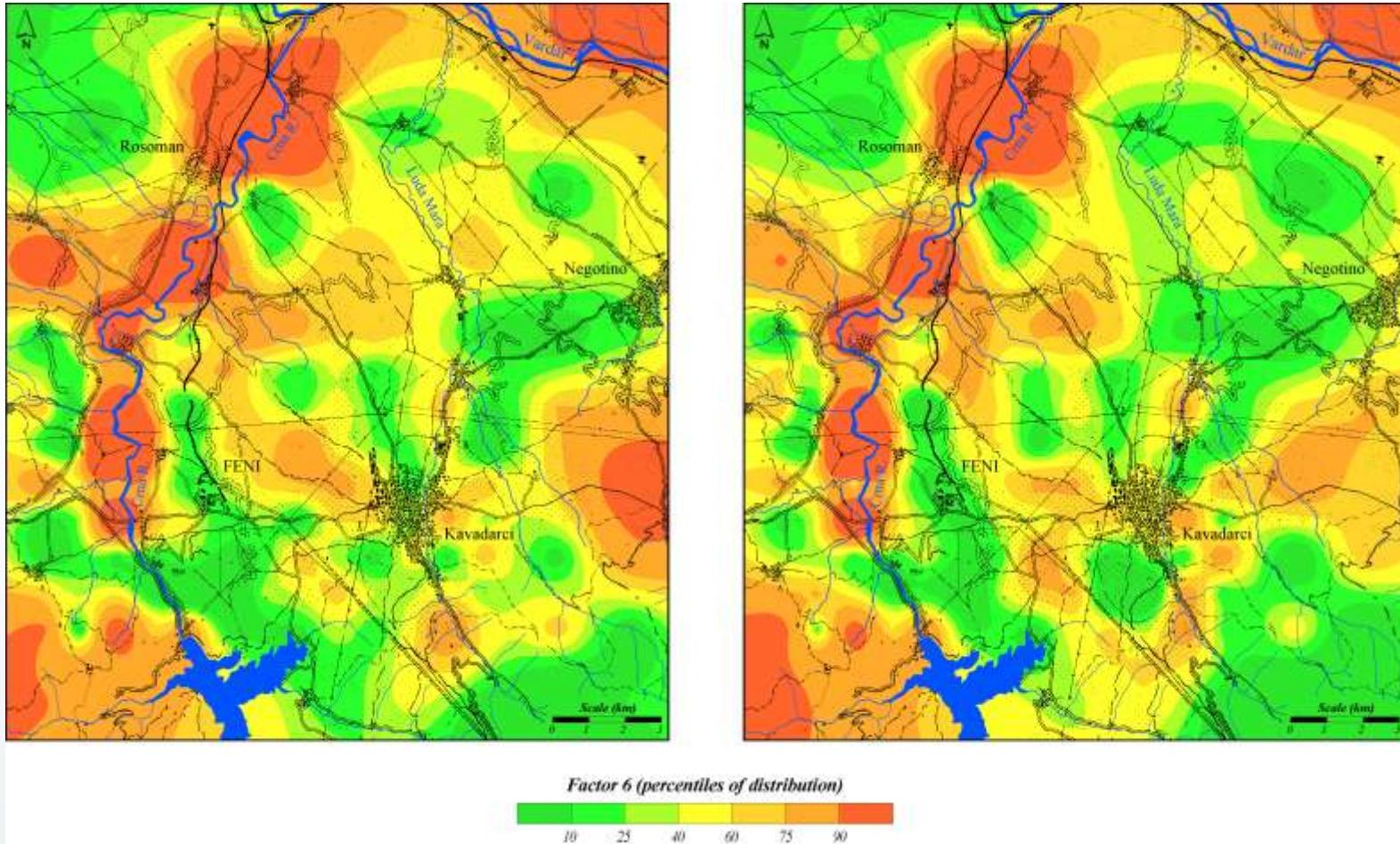
Distribution of Ni in topsoil (left) and subsoil (right)

The ferronickel smelter plant has not contributed significantly to the measured content of these elements, which occurs in high contents in the background.



Distribution of Factor 5 scores (Cd, Hg, Pb and Zn) in topsoil (left) and subsoil (right)

High contents and the enrichments of these elements are noticeable in the area of Paleozoic and Mesozoic rocks with a clear anomaly in the top soil. High contents of Cd, Hg, Pb and Zn found in areas with high content in organic material of topsoil or the long distance transports (alluvium of the river Vardar from the Pb-Zn smelter in Veles).



Distribution of Factor 6 scores (As, Sb and Tl) in topsoil (left) and subsoil (right)

Samples from Holocene alluvium of the Crna Reka show high contents of As, Sb and Tl. (average enrichment of 4 to 4.5 times). It is as a consequence of natural erosion from the mine deposits of Allchar on Kožuf Mountain, as well from mine activities in the past.

# Moss biomonitoring (31 moss samples) near the ferronickel smelter plant

47 elements analyzed by ICP-MS, ICP-AES and AAS

## Geogenic geochemical association – F1

Elements	N	Dis.	X	Md	Min	Max
Al, %	35	Log	0,20	0,18	0,052	1,3
Ca, %	35	Log	1,1	1,1	0,63	5,9
K, %	35	Log	0,56	0,55	0,26	1,2
Na, %	35	Log	0,029	0,032	0,005	0,10
P, %	35	Log	0,28	0,29	0,099	0,56
Ti, %	35	Log	0,015	0,015	0,004	0,083
Ag, mg kg <sup>-1</sup>	35	Log	0,13	0,12	0,030	8,1
As, mg kg <sup>-1</sup>	35	Log	0,94	1,0	0,040	6,2
Au, mg kg <sup>-1</sup>	35	Log	0,026	0,034	0,005	0,96
Ba, mg kg <sup>-1</sup>	35	Log	46	46	19	360
Ga, mg kg <sup>-1</sup>	35	Log	1,1	0,92	0,28	7,1
Hg, mg kg <sup>-1</sup>	35	Log	0,054	0,060	0,005	0,17
La, mg kg <sup>-1</sup>	35	Log	2,3	1,8	0,77	44
Mn, mg kg <sup>-1</sup>	35	Log	130	130	27	560
Mo, mg kg <sup>-1</sup>	35	Log	0,55	0,88	0,025	10
Sb, mg kg <sup>-1</sup>	35	Log	0,17	0,090	0,020	1,6
Sr, mg kg <sup>-1</sup>	35	Log	39	40	11	130
Th, mg kg <sup>-1</sup>	35	Log	0,81	0,66	0,21	18
U, mg kg <sup>-1</sup>	35	Log	0,22	0,19	0,070	2,1
V, mg kg <sup>-1</sup>	35	Log	8,4	7,6	2,5	43

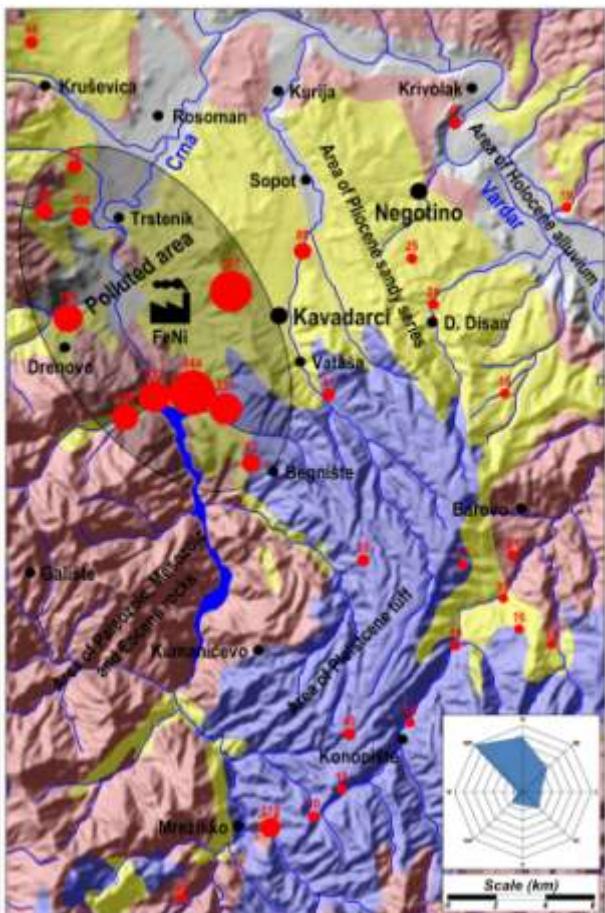
## Anthropogenic geochemical association - F2

Elements	N	Dis.	X	Md	Min	Max
Co, mg kg <sup>-1</sup>	35	Log	2.8	2.1	0.69	15
Cr, mg kg <sup>-1</sup>	35	Log	18	13	4.7	120
Cu, mg kg <sup>-1</sup>	35	Log	8.0	7.8	3.8	15
Fe, %	35	Log	0.27	0.24	0.065	0.87
Mg, %	35	Log	0.33	0.33	0.11	1.2
Ni, mg kg <sup>-1</sup>	35	Log	44	31	14	340

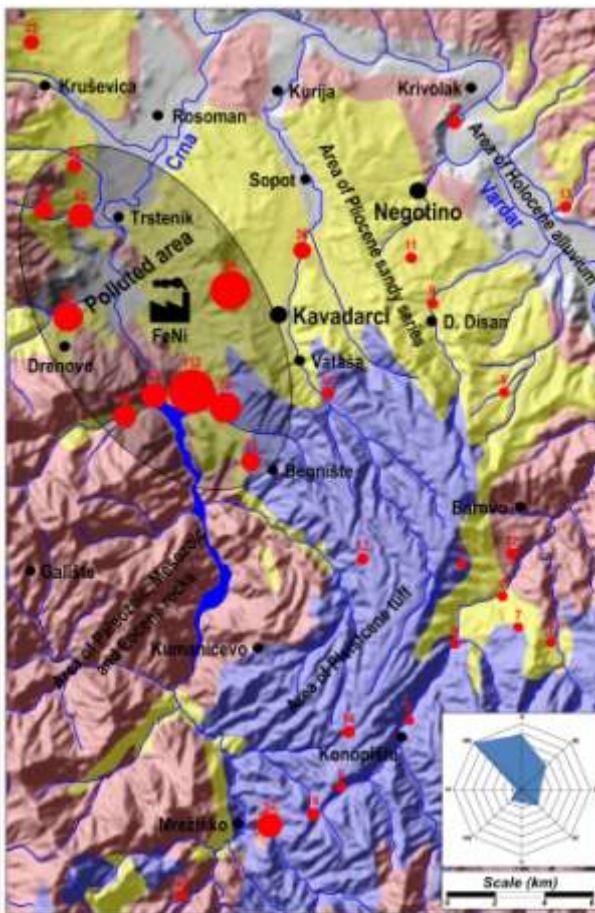
## Geogenic geochemical association – F3

Elements	N	Dis.	X	Md	Min	Max
As, mg kg <sup>-1</sup>	35	Log	0,94	1,0	0,040	6,2
Cd, mg kg <sup>-1</sup>	35	Log	0,19	0,19	0,040	0,71
Cu, mg kg <sup>-1</sup>	35	Log	8,0	7,8	3,8	15
Hg, mg kg <sup>-1</sup>	35	Log	0,054	0,060	0,0050	0,17
I, mg kg <sup>-1</sup>	35	Log	0,41	0,40	0,12	0,99
Pb, mg kg <sup>-1</sup>	35	Log	9,8	8,8	5,4	31
Zn, mg kg <sup>-1</sup>	35	Log	68	56	30	350

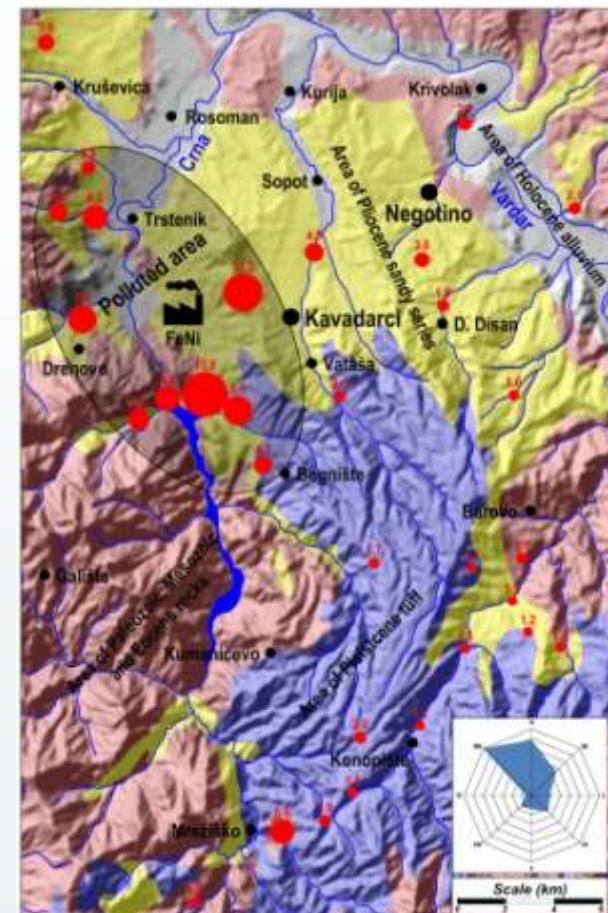
# Anthropogenic influence from FENI smelter



Distribution of Ni ( $\text{mg kg}^{-1}$ )



Distribution of Cr ( $\text{mg kg}^{-1}$ )



Distribution of Co ( $\text{mg kg}^{-1}$ )

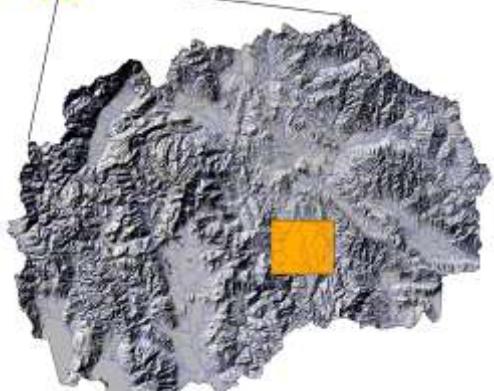
Element	Europe moss survey 2005/2006 (n = 6049)		Macedonia, moss survey 2002 (n = 73)		Macedonia moss survey 2005 (n = 72)		Macedonia moss survey 2010 (n = 72)		Kavadarci moss survey, 2008 (n = 31)	
	Median	min-max	Median	min-max	Median	min-max	Median	min-max	Median	min-max
Cd	0.20	0.07-1.26	0.16	0.02-2.95	0.29	0.06-3.01	0.22	0.07-2.24	0.19	0.040-0.51
Co	-	-	1.09	0.24-13.6	1.13	0.42-5.29	-	-	2.1	1.1-14
Cr	2.32	0.72-29.3	7.47	2.33-122	6.79	2.09-82	3.48	1.03-39.7	15	5.8-110
Cu	6.80	3.07-91	22	3-83	6.65	0.68-21.4	5.00	2.78-14.9	7.7	4.9-15
Fe	799	233-6147	2458	424-17380	2239	999-8130	1490	513-6348	2300	1300-8700
Mg	-	-	2377	674-7421	1307	656-3994	1894	609-4855	3300	1300-7000
Ni	2.26	0.71-63.4	2.4	0.09-24	5.82	1.80-43.1	4.45	1.25-52	31	14-340
Pb	4.91	1.76-46.9	6.0	1.5-37.2	7.62	0.1-46.6	4.61	1.87-22	8.4	5.4-19
Zn	33.6	15.2-177	39	14-203	35.6	16.4-91.3	19.9	1.0-365	55	30-190

Element	FeNi (n=10)		Rest (n=21)		ER
	Average	SD	Average	SD	
Cd	0.30	0.10	0.17	0.10	1.78
Co	7.0	3.5	2.2	1.3	3.14
Cr	57	29	14	10	3.99
Fe	4700	2100	2500	1400	1.92
Mg	4500	1300	3200	1000	1.42
Ni	180	99	34	25	5.20
Pb	13	3.6	8.1	2.0	1.64
Zn	110	47	56	33	2.03



# ATTIC DUST

**Atmospheric dust collected from wooden part  
under the roof of 30 old houses**



**Sampling of attic dust**



K. Bačeva, T. Stafilov, R. Šajn, C. Tănăselia, S. Ilić Popov, Distribution of chemical elements in attic dust in the vicinity of ferronickel smelter plant, *Fresenius Environmental Bulletin*, **20**(9), 2306-2314 (2011).

# ATTIC DUST

Element	N	Dis.	X	Md	Min	Max
Al, %	31	Log	2.5	2.6	0.58	7.5
Ca, %	31	N	2.9	3.0	1.2	3.8
Fe, %	31	N	3.7	3.5	0.53	6.5
K, %	31	Log	1.3	1.3	0.83	2.0
Mg, %	31	N	0.44	0.45	0.10	0.83
Na, %	31	N	0.84	0.84	0.20	1.9
Ti, %	31	N	0.38	0.38	0.02	0.58
Ag, mg kg <sup>-1</sup>	31	Log	2.7	2.3	1.1	9.0
As, mg kg <sup>-1</sup>	31	Log	18	16	4.7	190
Ba, mg kg <sup>-1</sup>	31	Log	320	350	36	1800
Ga, mg kg <sup>-1</sup>	31	N	15	15	0.69	32
Hg, mg kg <sup>-1</sup>	31	Log	0.09	0.18	0.005	4.6
La, mg kg <sup>-1</sup>	31	N	17	17	0.90	49
Sb, mg kg <sup>-1</sup>	31	Log	2.4	2.3	1.0	5.2
Sr, mg kg <sup>-1</sup>	31	N	170	160	51	231
Th, mg kg <sup>-1</sup>	31	Log	5.3	7.0	0.26	25
U, mg kg <sup>-1</sup>	31	Log	3.4	3.4	0.54	12
V, mg kg <sup>-1</sup>	31	N	110	100	9.8	200

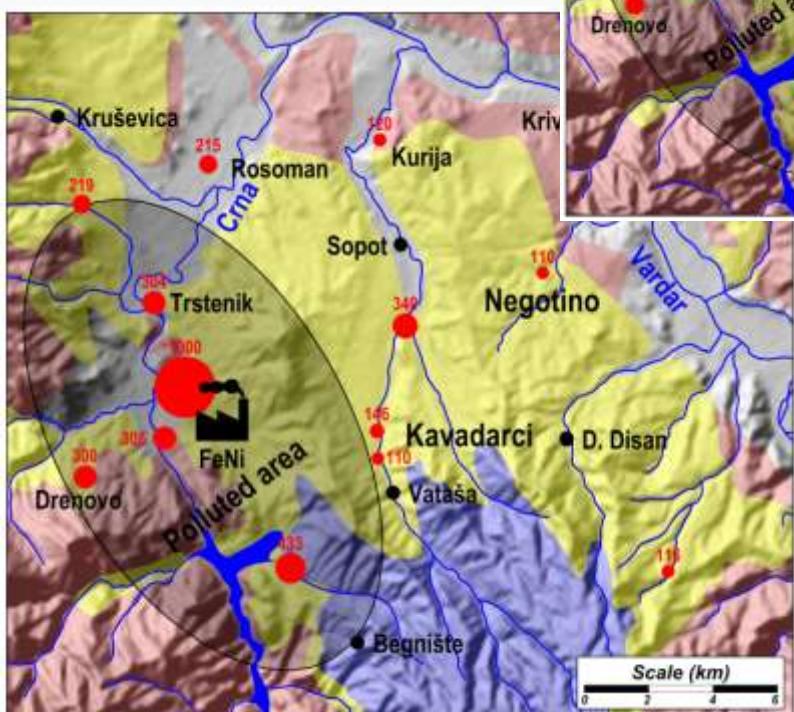
Geochemical association - anthropogenetic group

Element	N	Dis.	X	Md	Min	Max
Co, mg kg <sup>-1</sup>	31	Log	18	17	10	52
Cr, mg kg <sup>-1</sup>	31	Log	140	140	72	510
Mn, mg kg <sup>-1</sup>	31	N	510	500	410	680
Mo, mg kg <sup>-1</sup>	31	Log	3.0	4.0	0.23	21
Ni, mg kg <sup>-1</sup>	31	Log	230	220	89	1200

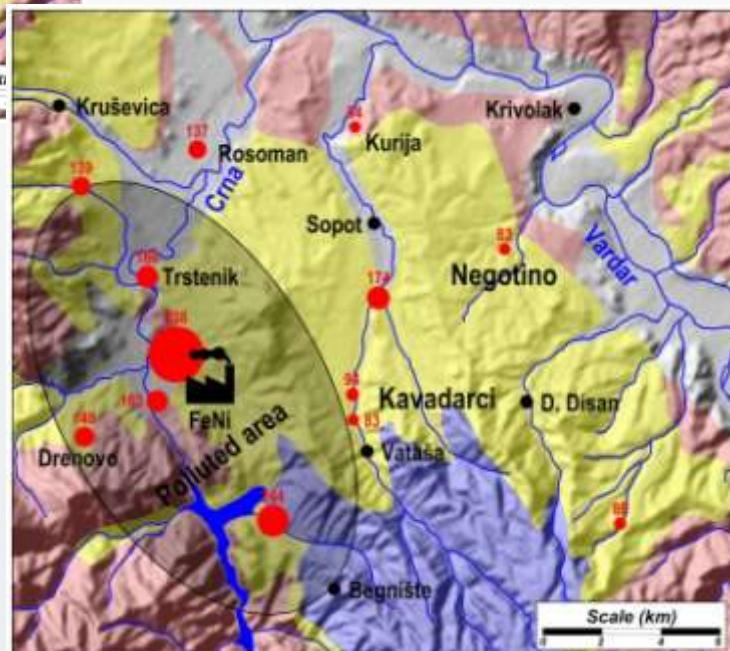
Geochemical association – geogenic group

Element	N	Dis.	X	Md	Min	Max
Cd, mg kg <sup>-1</sup>	31	Log	8,6	8,2	3,8	16
Cu, mg kg <sup>-1</sup>	31	N	50	52	32	66
I, mg kg <sup>-1</sup>	31	N	0,47	0,40	0,02	1,2
Pb, mg kg <sup>-1</sup>	31	Log	180	180	66	390
Zn, mg kg <sup>-1</sup>	31	Log	350	350	230	600

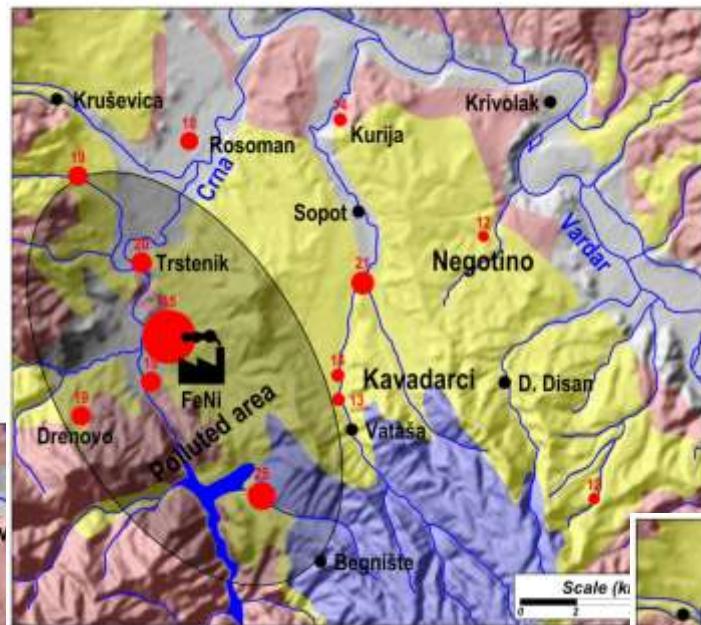
# Anthropogenetic influence from FeNi smelter



Ni (mg kg<sup>-1</sup>)



Co (mg kg<sup>-1</sup>)



Cr (mg kg<sup>-1</sup>)

# CONTAMINATION OF TOPSOIL IN VELES REGION, MACEDONIA



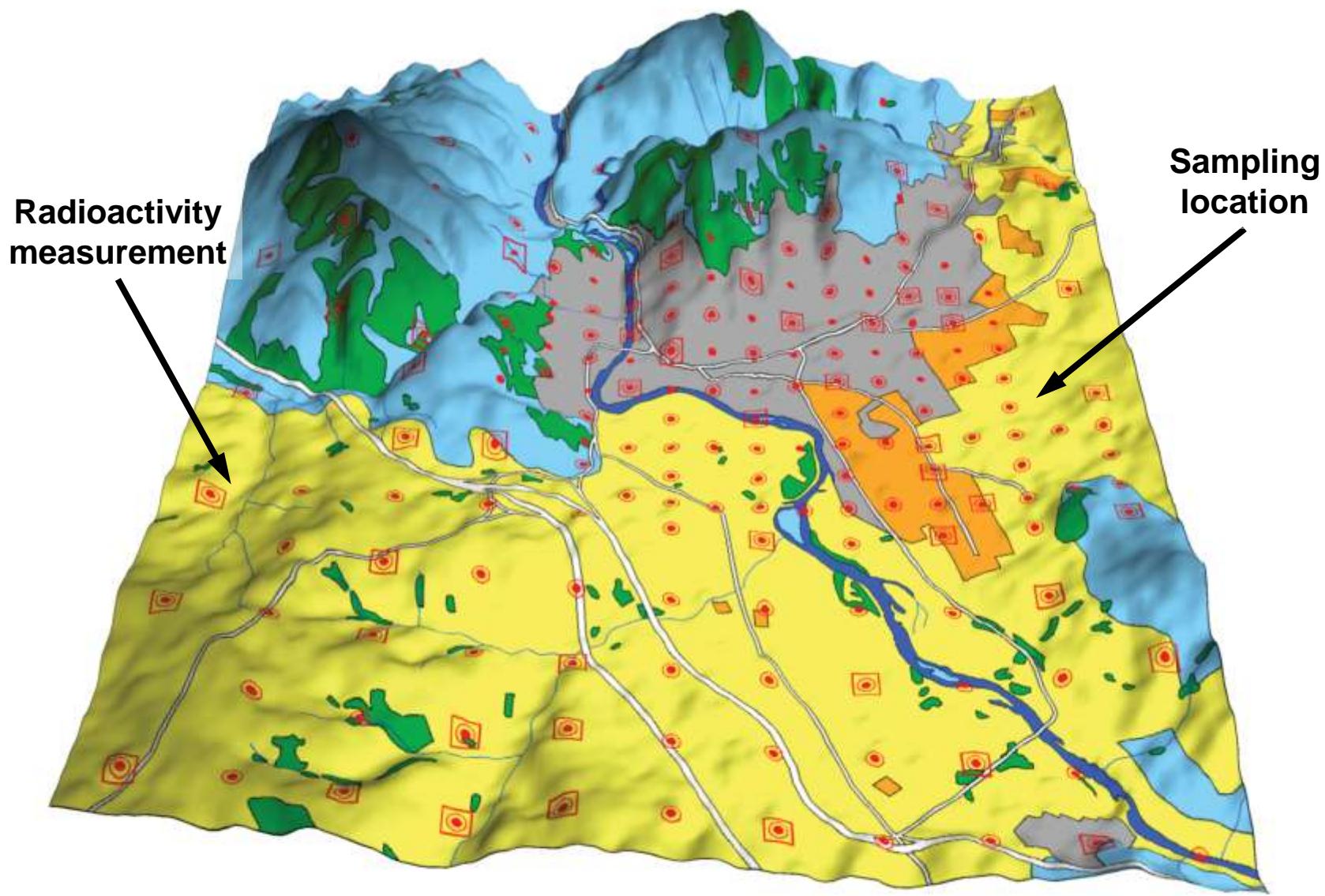
**Slag deposit: 1,500,000 t**

**1.0 % Pb  
8.7 % Zn  
0.0013 % Cd  
0.78 % Cu**



T. Stafilov, R. Šajn, Z. Pančevski, B. Boev, M. V. Frontasyeva, L. P. Strelkova, Heavy metal contamination of surface soils around a lead and zinc smelter in the Republic of Macedonia, *Journal of Hazardous Materials*, **175**, 896-914 (2010).

# Sampling design (201 soil samples)

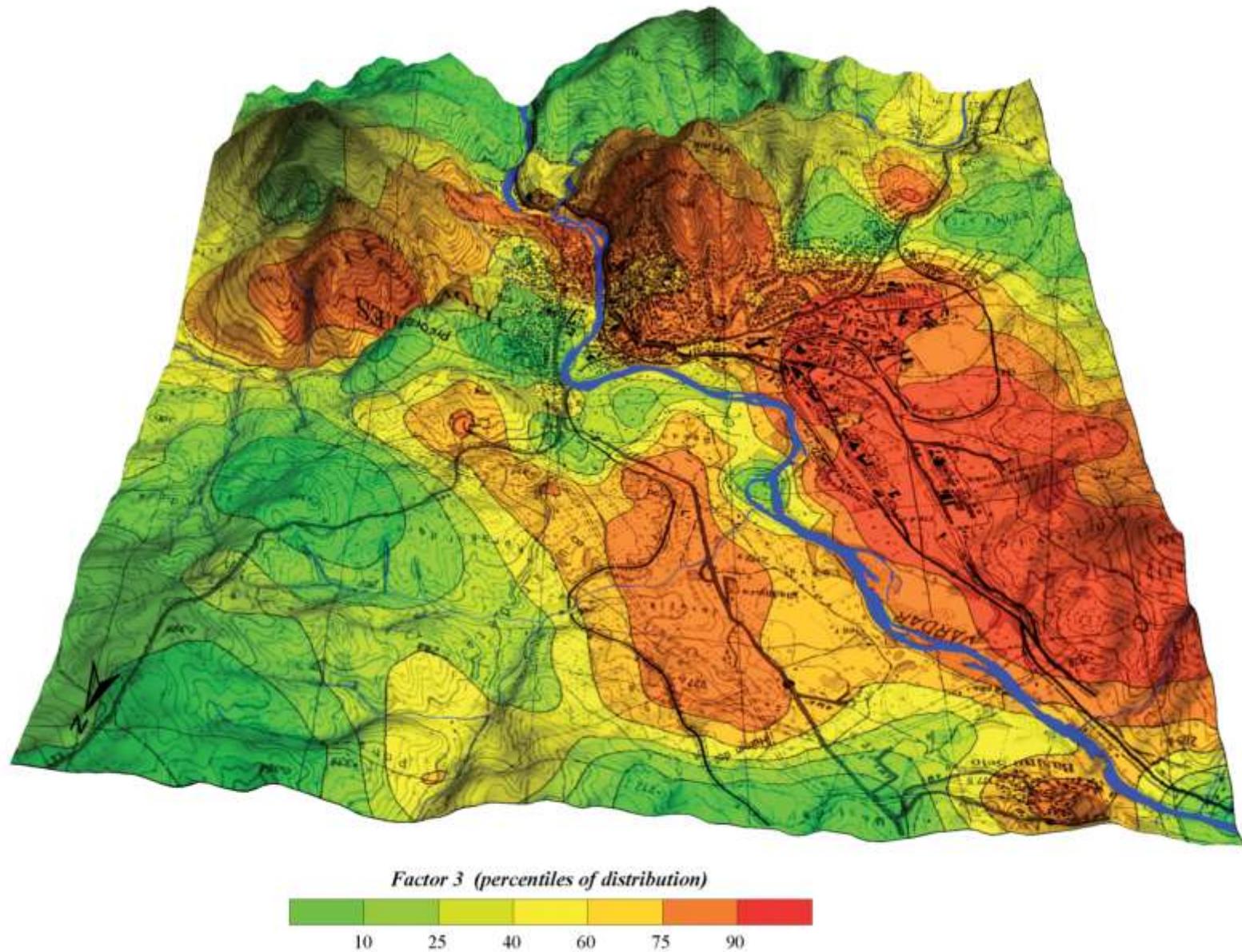


44 elements (NAA+AAS)

Al, As, Au, Ba, Br, Ca, Co, Cr, Cs, Cu, Dy, Fe, Hf, Hg, In, La, K, Mg, Mn, Mo, Na, Nd, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Tl, Tm, U, V, W, Yb and Zn

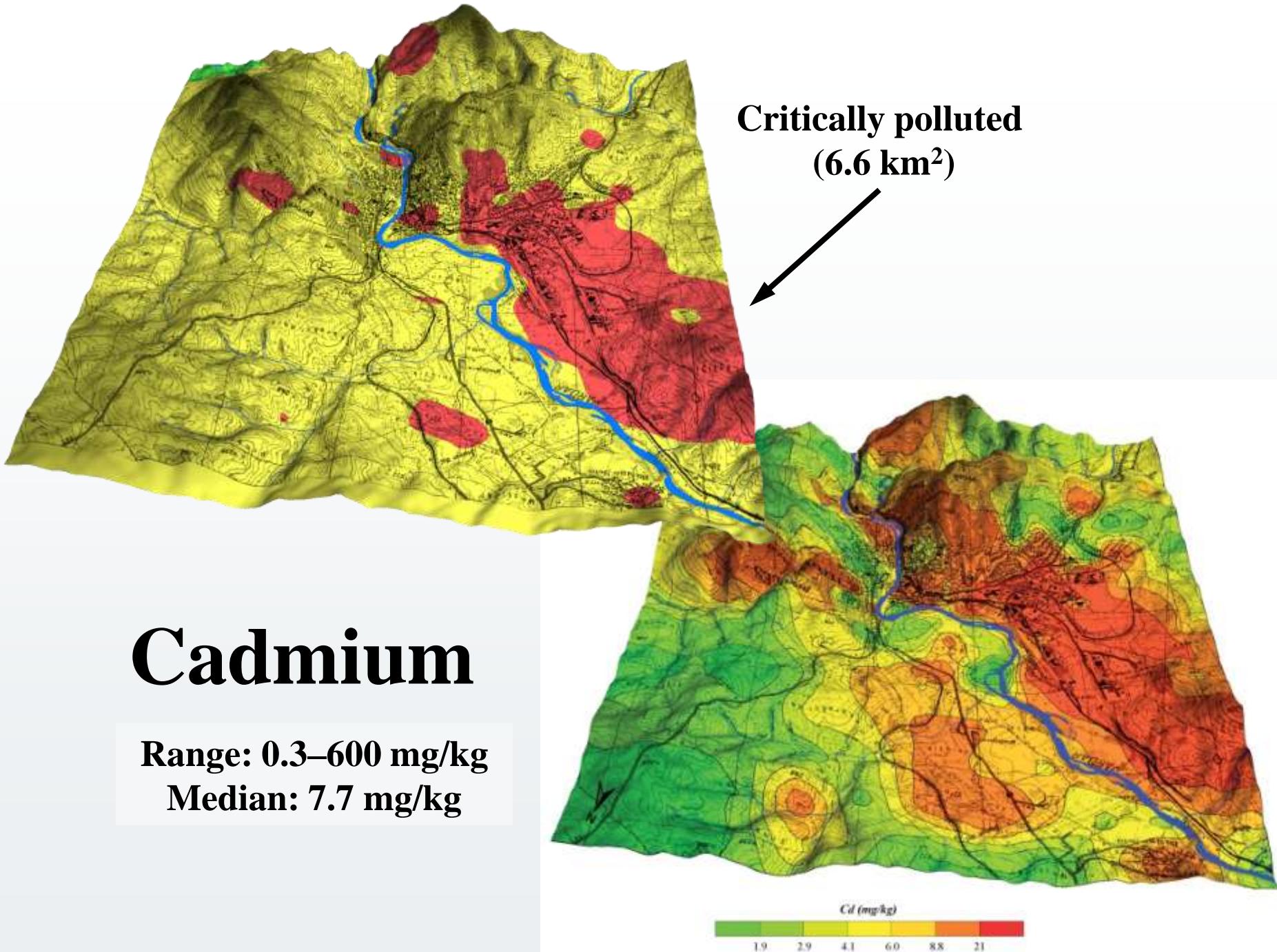
# Distribution of Factor 3

(Zn, Cd, Pb, Sb, In, Cu, Hg, As)



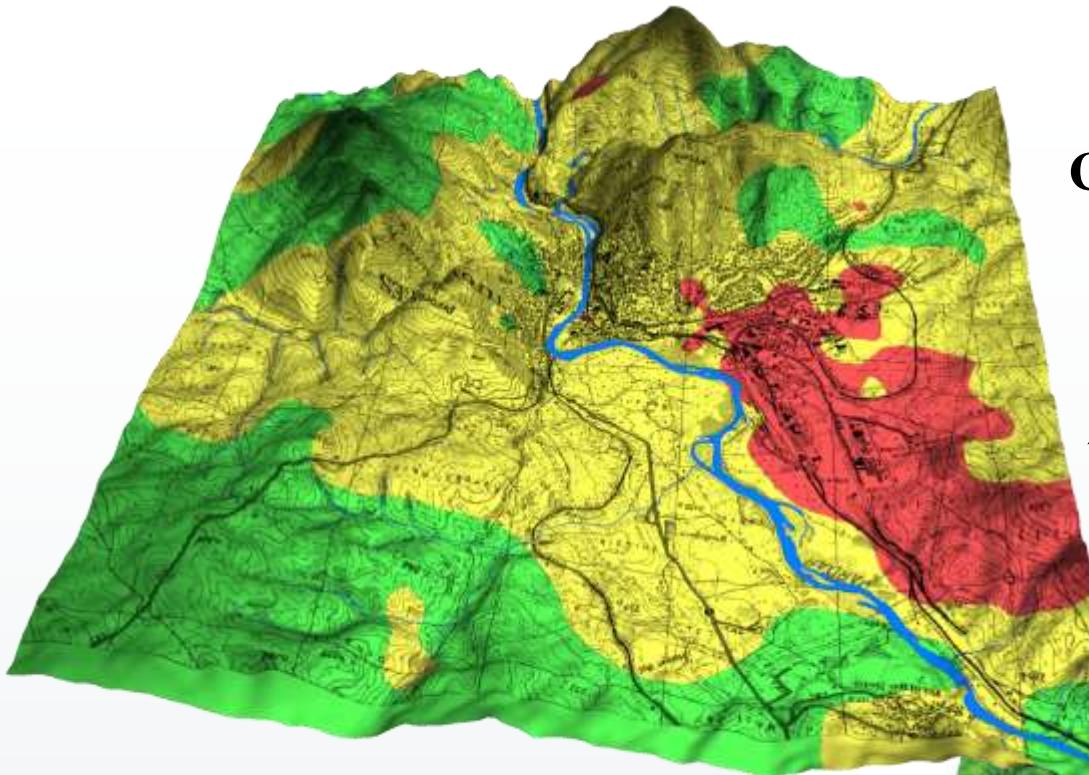
# Cadmium

Range: 0.3–600 mg/kg  
Median: 7.7 mg/kg

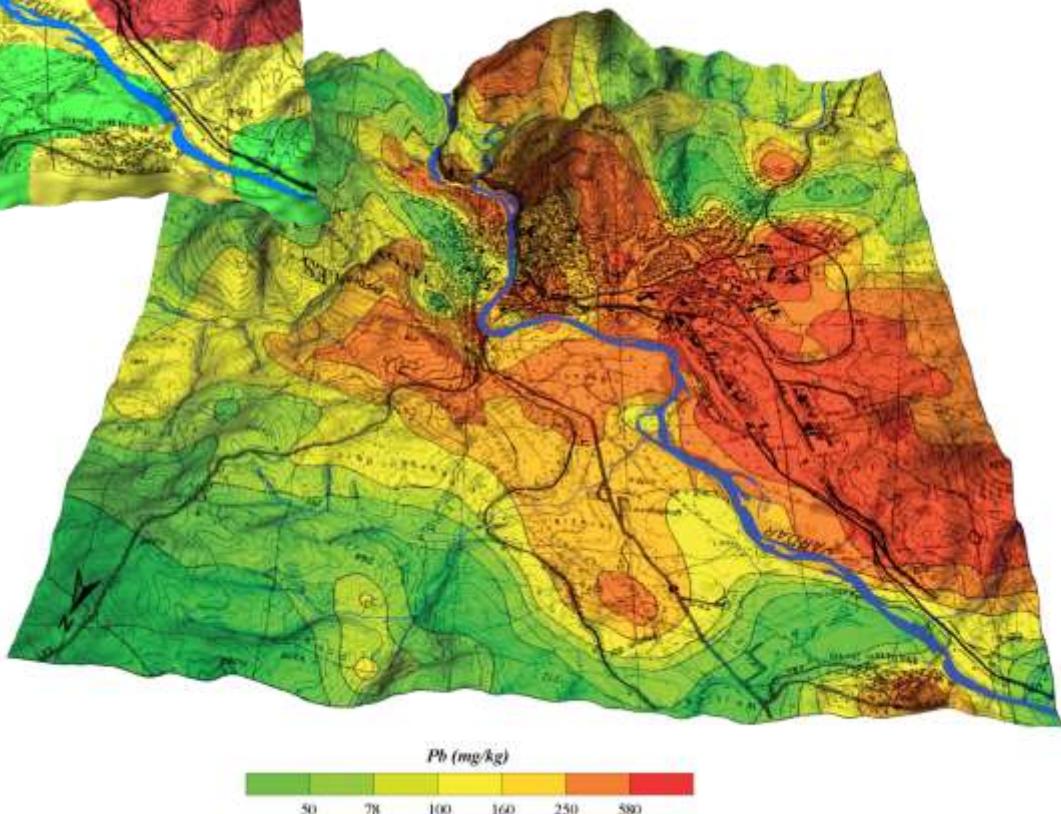


# Lead

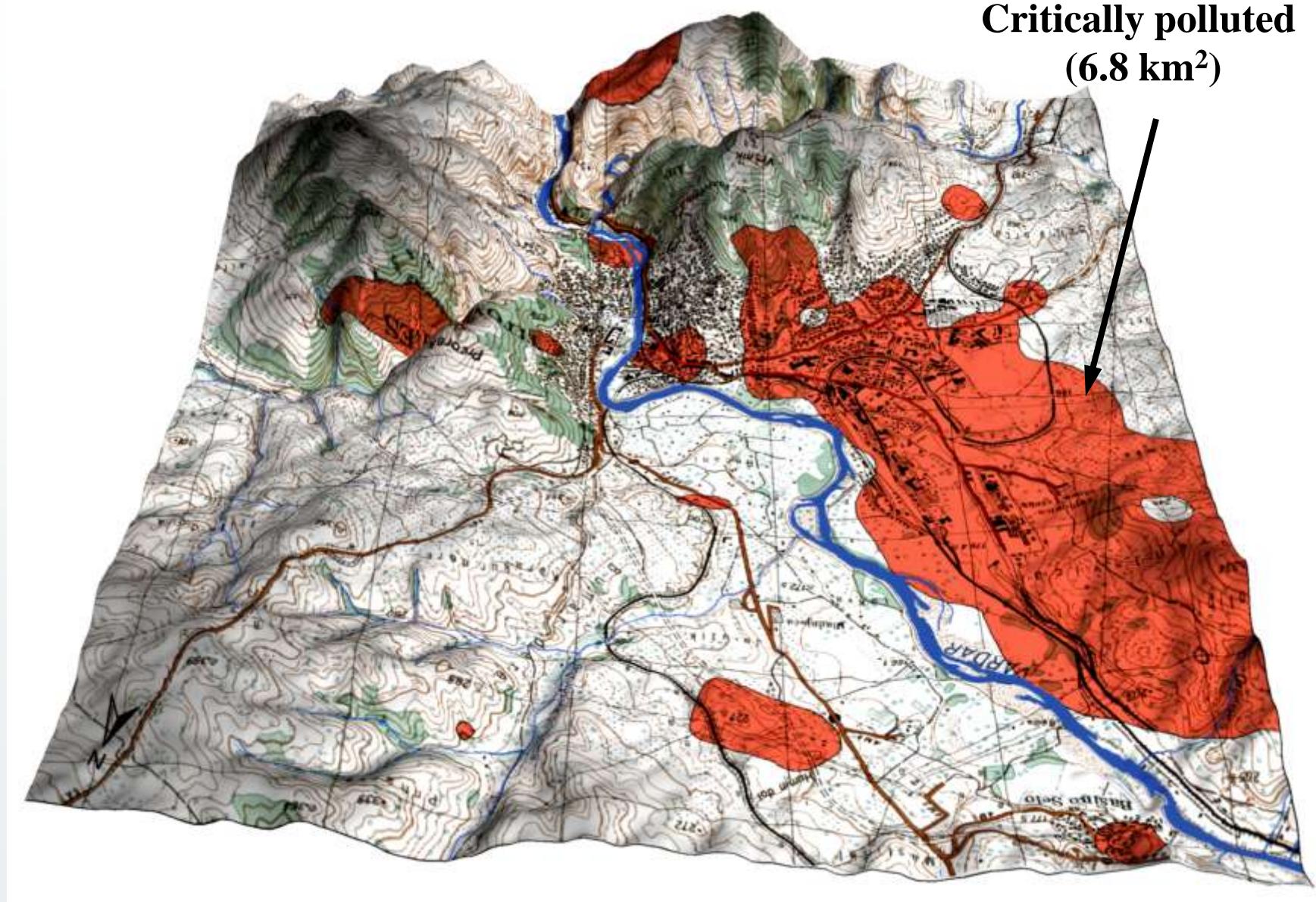
Range: 13–15000 mg/kg  
Median: 210 mg/kg



Critically polluted  
(4.2 km<sup>2</sup>)



# Critically polluted area



## Groundwaters in Veles and Veles Region

No	Sampling point	Pb, µg/L	Zn, µg/L	Cd, µg/L	Hg, µg/L	As, µg/L	Cu, µg/L
1	Vardar, Buss Station	6.03	280	0.24	0.12	11.8	51.0
2	Vardar, most Bašino Selo	7.92	264	0.22	0.09	11.3	54.4
3	Drnjevica	0.97	821	<0.01	0.11	3.91	<2.0
4	Šorka-Sirmes	2.38	344	0.046	0.09	3.64	21.7
5	Grad - Branko	0.76	1395	0.029	0.09	2.16	<2.0
6	Internat	2.22	269	0.015	0.09	4.32	<2.0
7	Kiro Ćučuk	2.27	528	0.093	0.10	4.05	19.9
8	Puzevo češmiče	2.92	<10	0.030	0.09	1.03	17.9
MPL for drinking water		10	3000	3	1	10	2000
MPL for surface and groundwaters, I class		10	100	1	0.2	30	10
MPL for surface and groundwaters, II class		10	100	0.1	0.2	30	10
MPL for surface and groundwaters, III class		30	200	10	1	50	50
MPL for surface and groundwaters, IV class		30	200	10	1	50	50

## Slag content, in mg/kg

Pb	Zn	Cd	Cu	Sb	As	Sn
11500	78928	11.4	7028	1.8	0.44	<0.8

## Leaching test of the slag

pH = 7

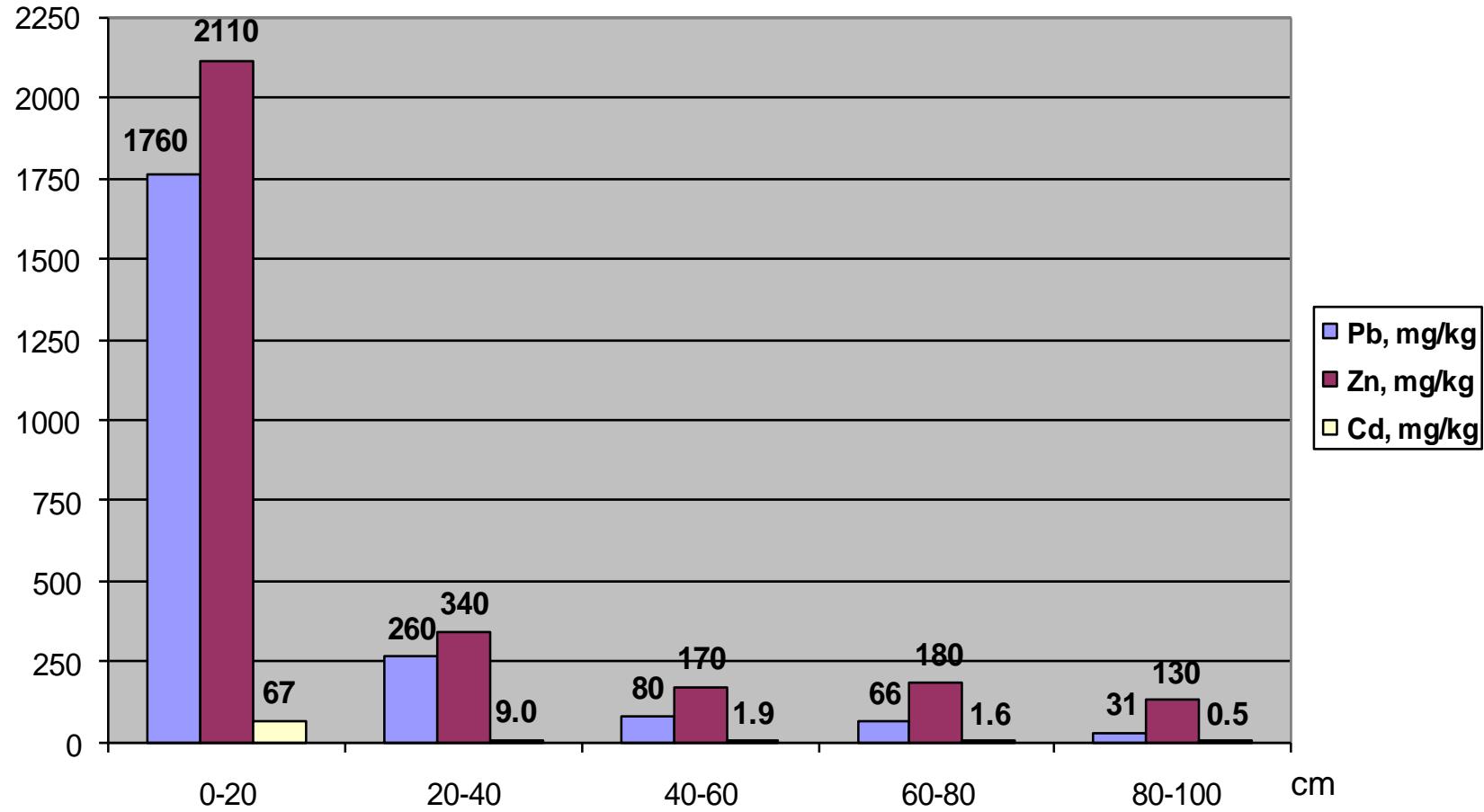
Parameter	µg/L	mg/kg
Pb	1.21	0.024
Zn	2122	42.4
Cd	4.15	0.08
Cu	18.2	0.36
Sb	-	-
As	-	-
Sn	<2	<0.04

pH = 4

Parameter	mg/L	mg/kg
Pb	84.0	1680
Zn	70.0	1400
Cd	0.07	1.49
Cu	11.4	227
Sb	0.0025	0.05
As	0.021	0.41
Sn	<0.002	<0.04

# Soil profiles (I)

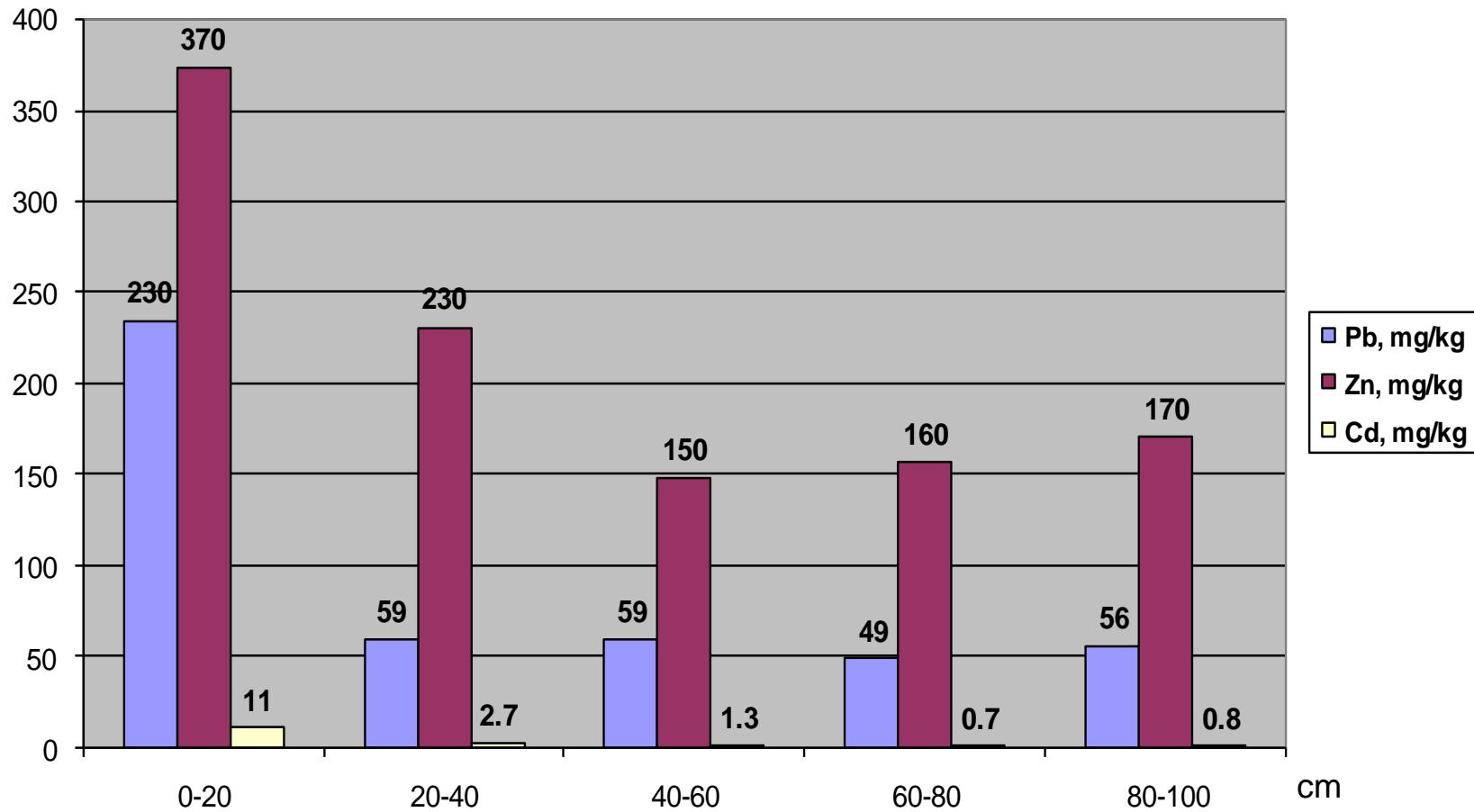
## Close to Smelter Plant



	Pb, mg/kg	Zn, mg/kg	Cd, mg/kg	As, mg/kg
Referent value	85	140	0.8	29
Intervention value	530	720	12	55

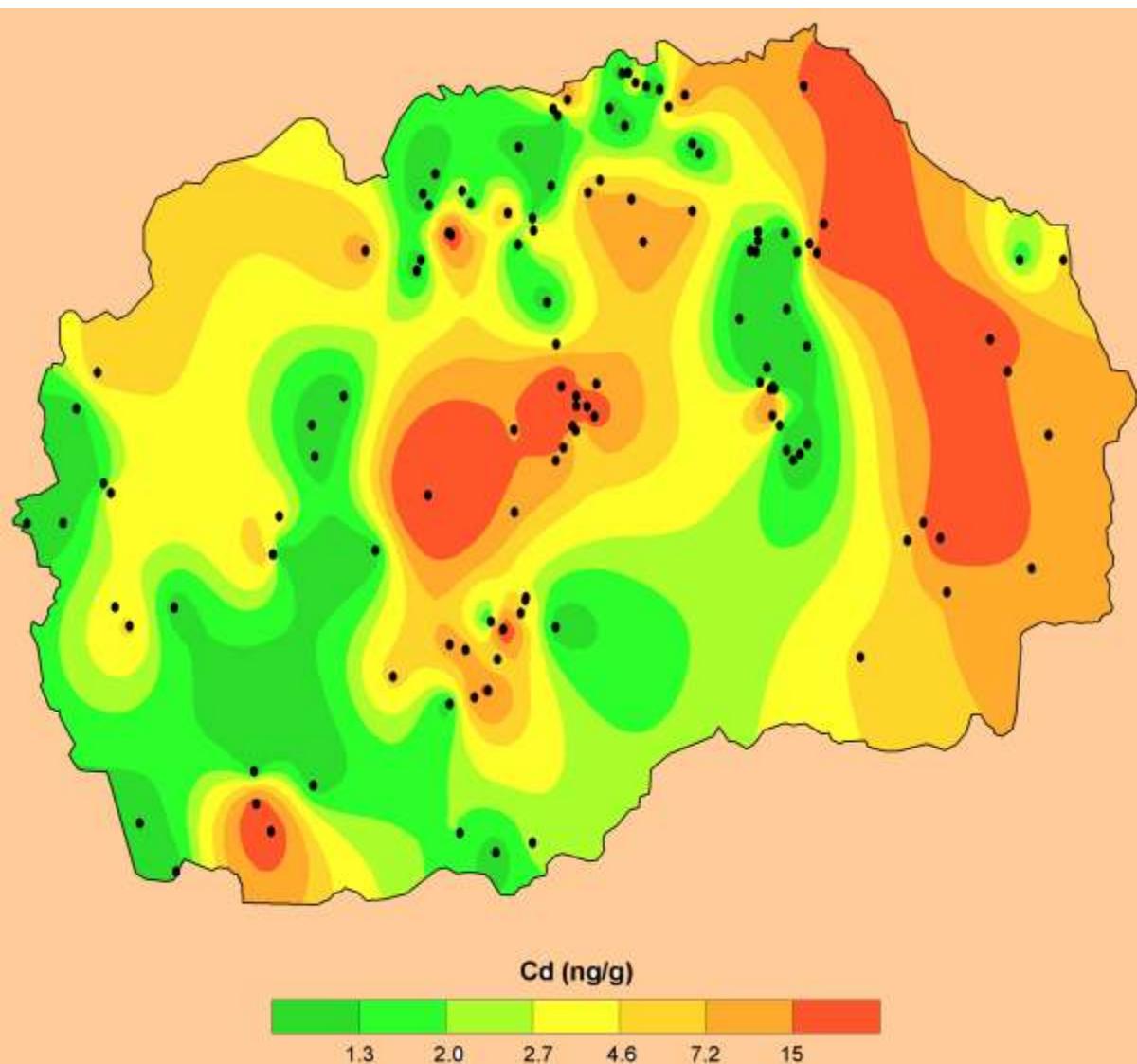
# Soil profiles (II)

## City Park



	Pb, mg/kg	Zn, mg/kg	Cd, mg/kg	As, mg/kg
Referent value	85	140	0.8	29
Intervention value	530	720	12	55

# Distribution of heavy metals in honey samples

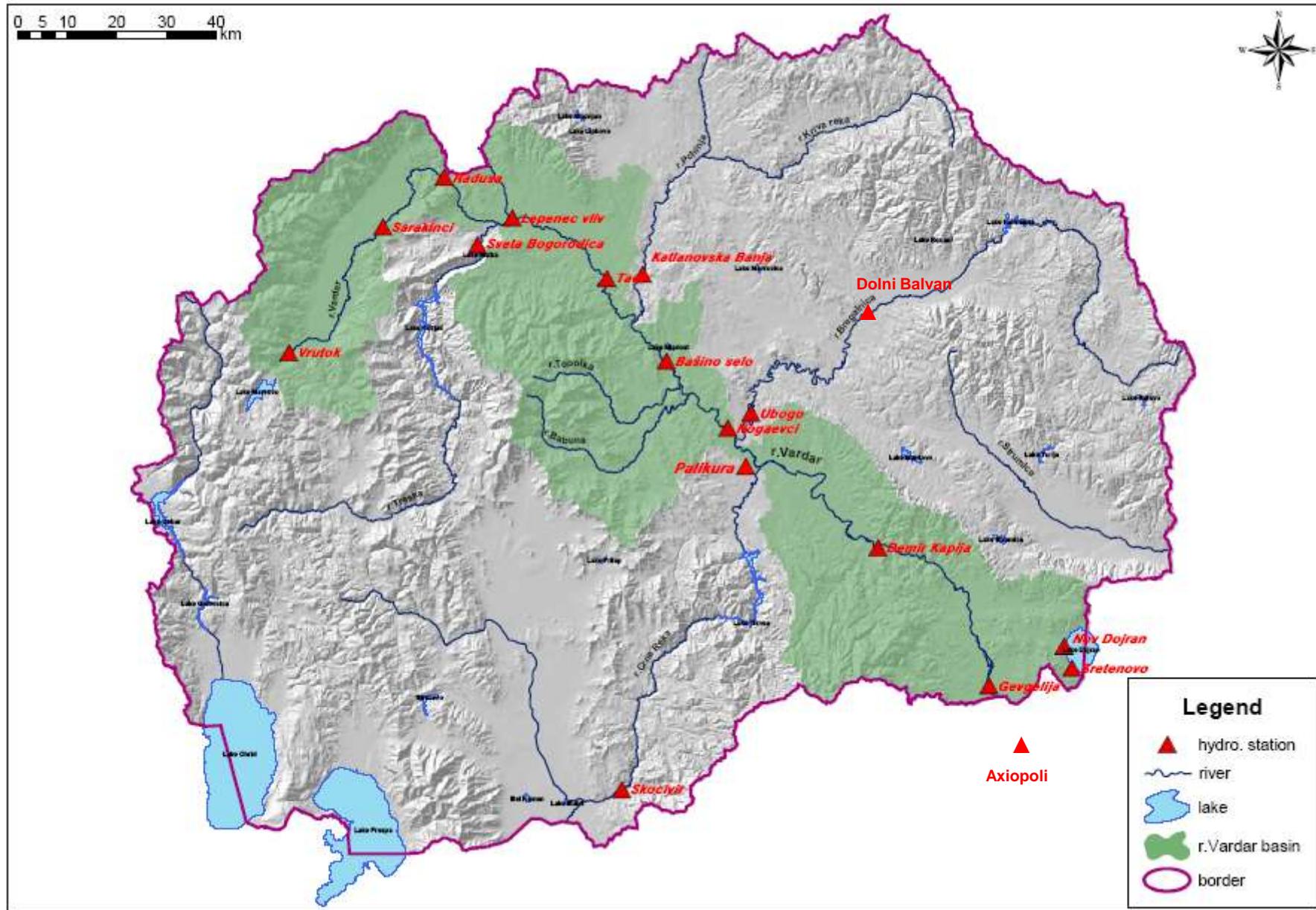


MPC for Cd – 30 ng g<sup>-1</sup>

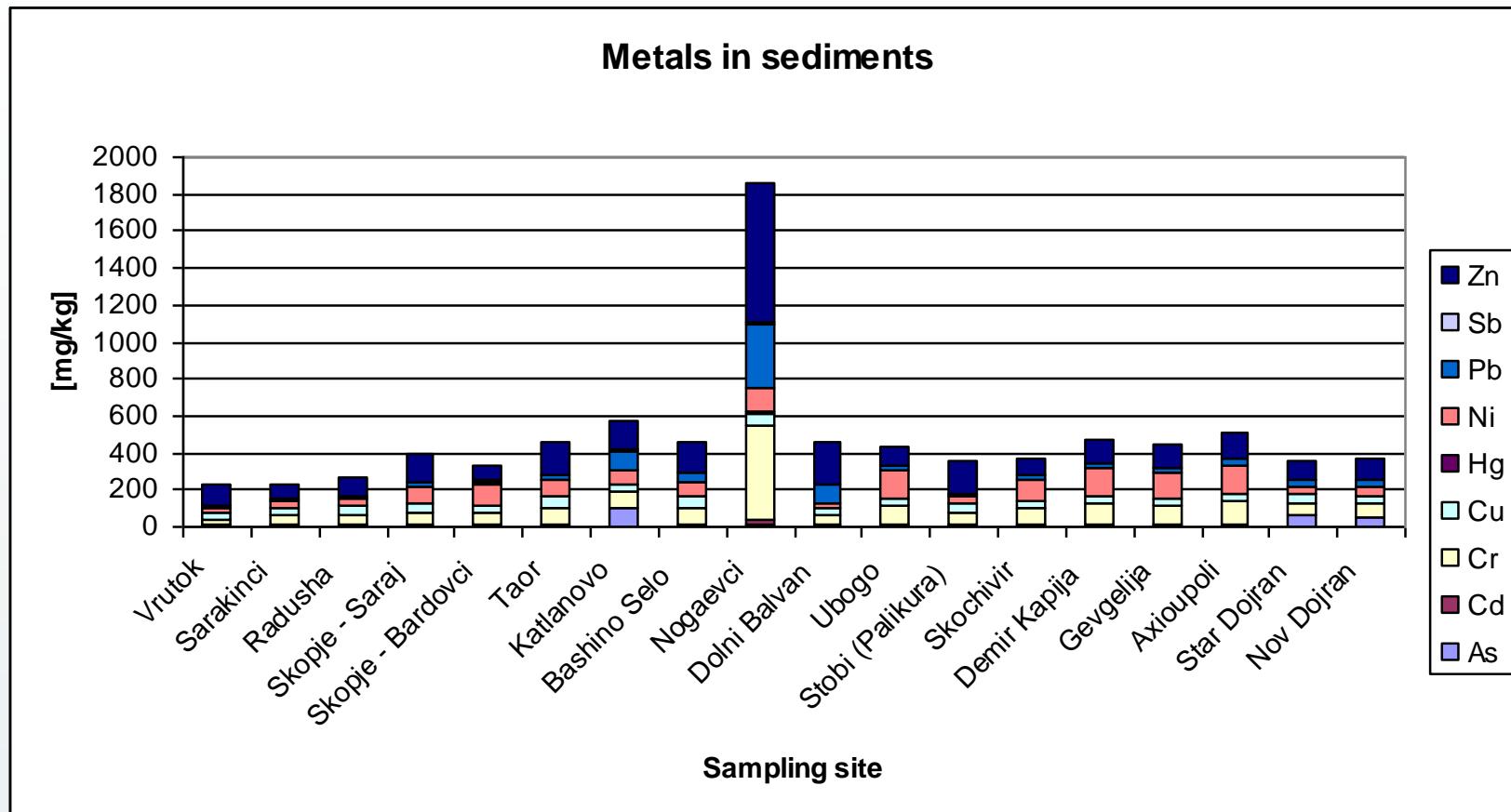
6 samples from Veles region  
over the limit

Distribution of Cd content

## **Improvement of Management of Transboundary Water Resources, EU Project**



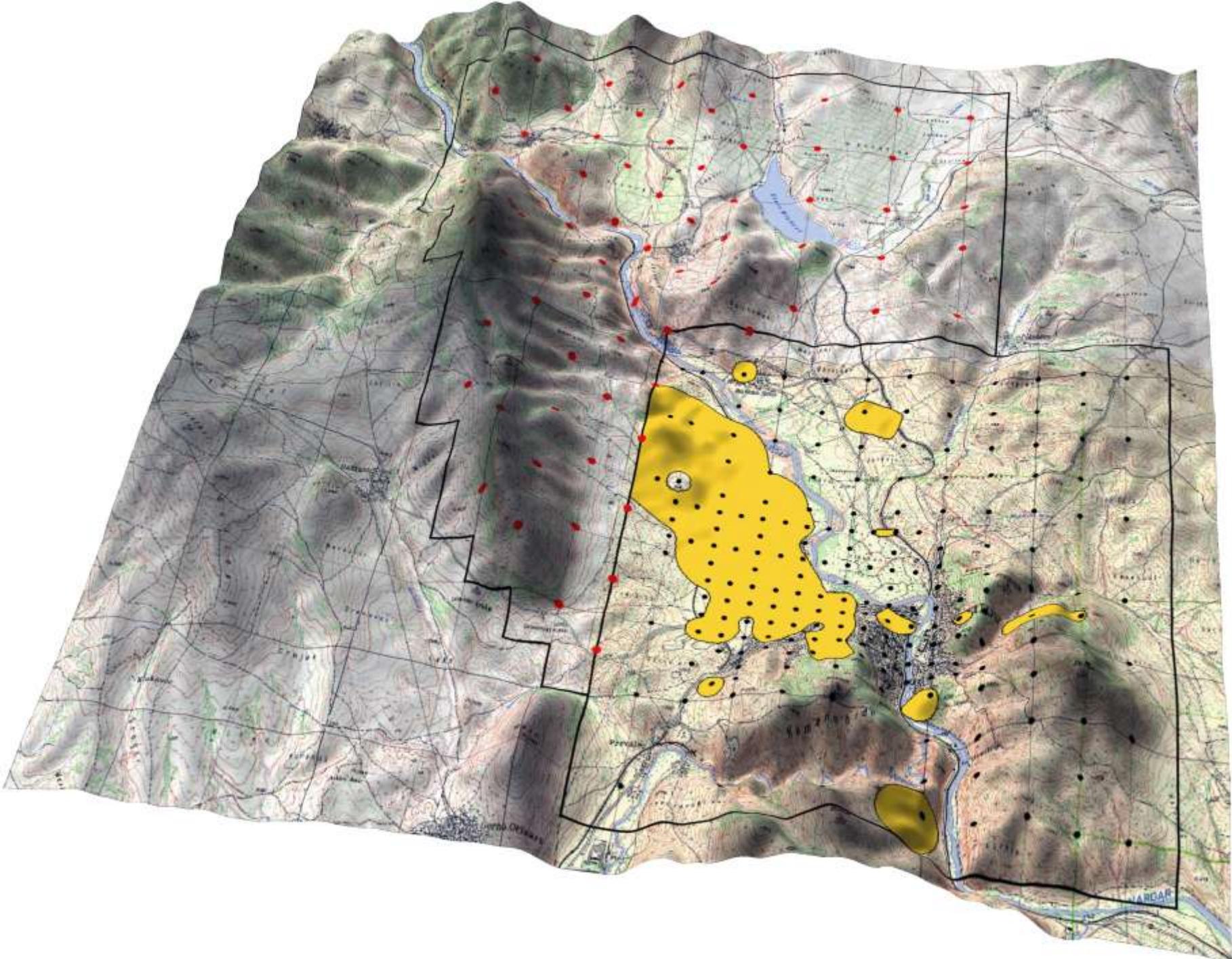
# WFD PS in sediments IV



Dutch EQS As: 55 mg/kg; Cr: 380 mg/kg; Cu: 73 mg/kg

EQS Cd: 2.3 mg/kg; Hg: 9.3 mg/kg; Ni: 3 mg/kg; Pb: 78.4 mg/kg

T. Stafilov, Z. Levkov, Summary of Vardar river basin field survey,  
European Agency for Reconstruction; Ministry of Environment &  
Physical Planning, Republic of Macedonia, Skopje, 2007.

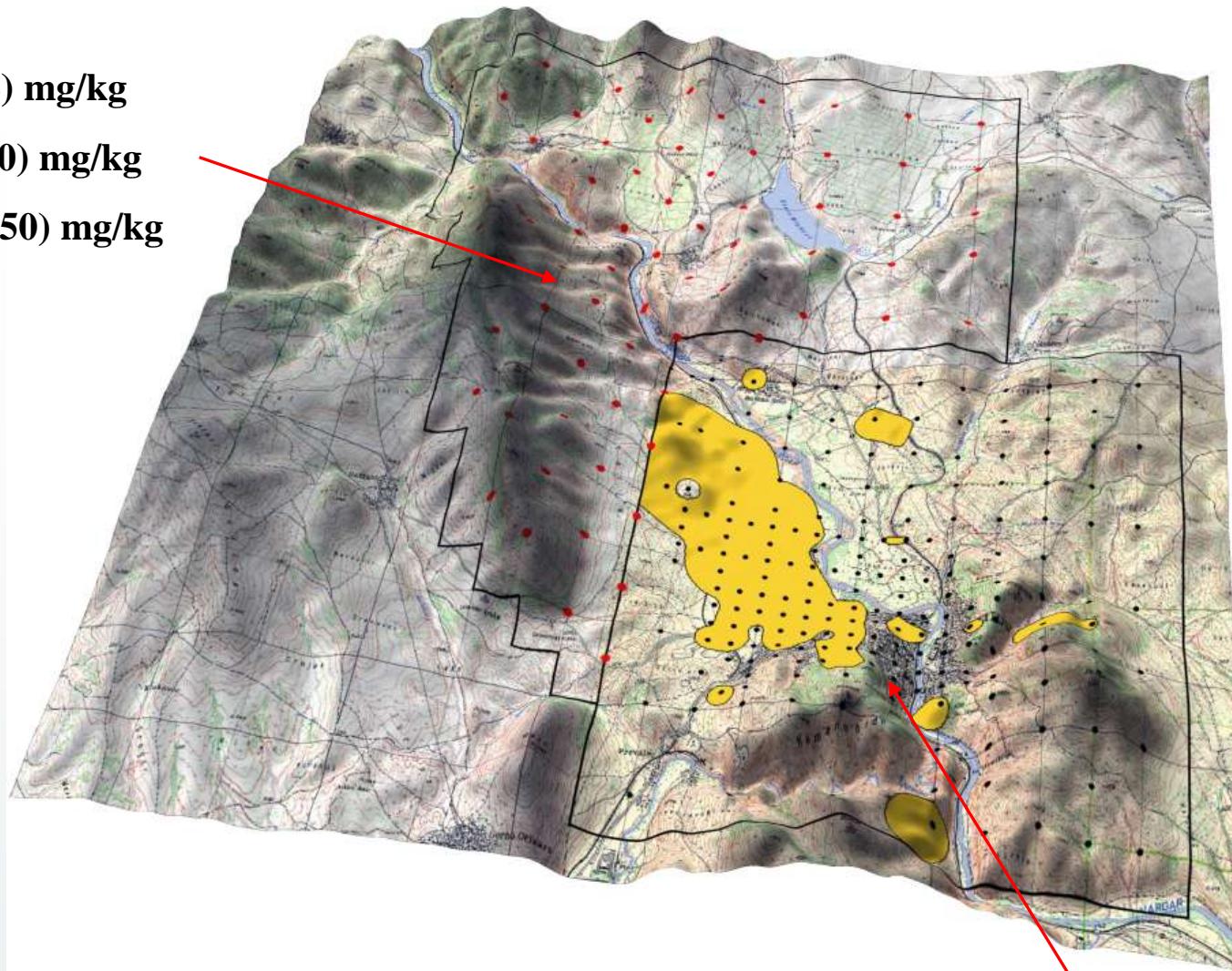


## Average values:

Cd – 8.7 (0.6-42) mg/kg

Pb – 173 (9-1200) mg/kg

Zn – 310 (50-1750) mg/kg



Average value:

Cd – 7.7 (0.3-600) mg/kg

Pb – 220 (13-15000) mg/kg

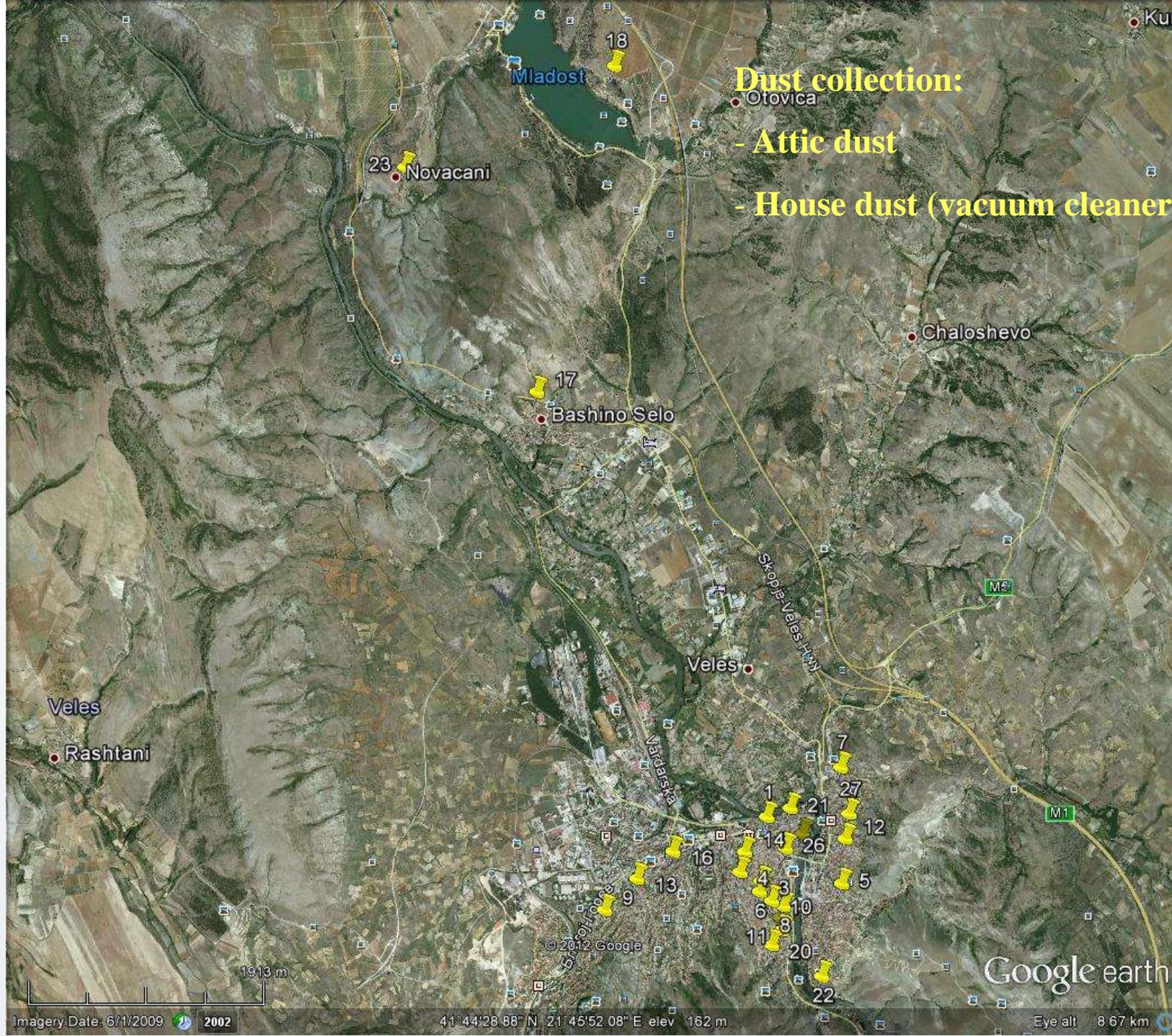
Zn – 280 (22-27000) mg/kg

	Pb	Zn	Cd
Referent value, mg/kg	85	140	0,8
Intervention value, mg/kg	530	720	12

Dust collection:

- Attic dust

- House dust (vacuum cleaner)



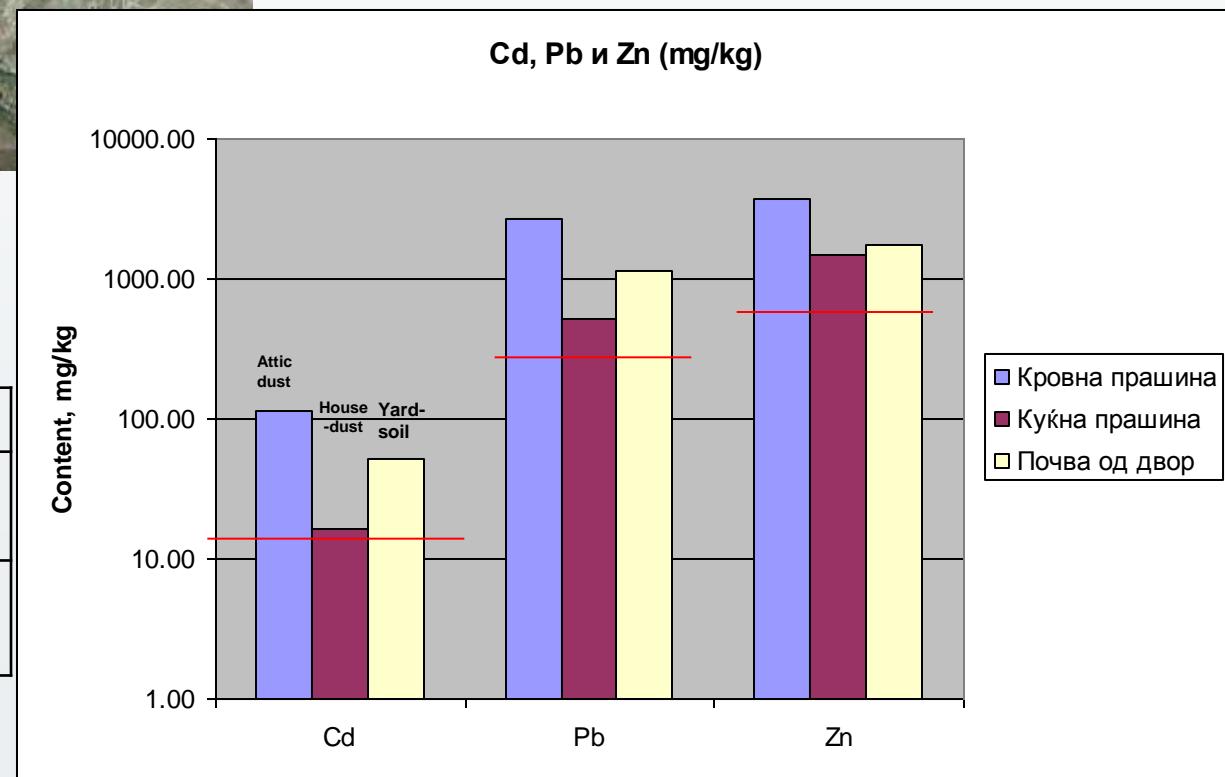
# ATTIC DUST



# Veles



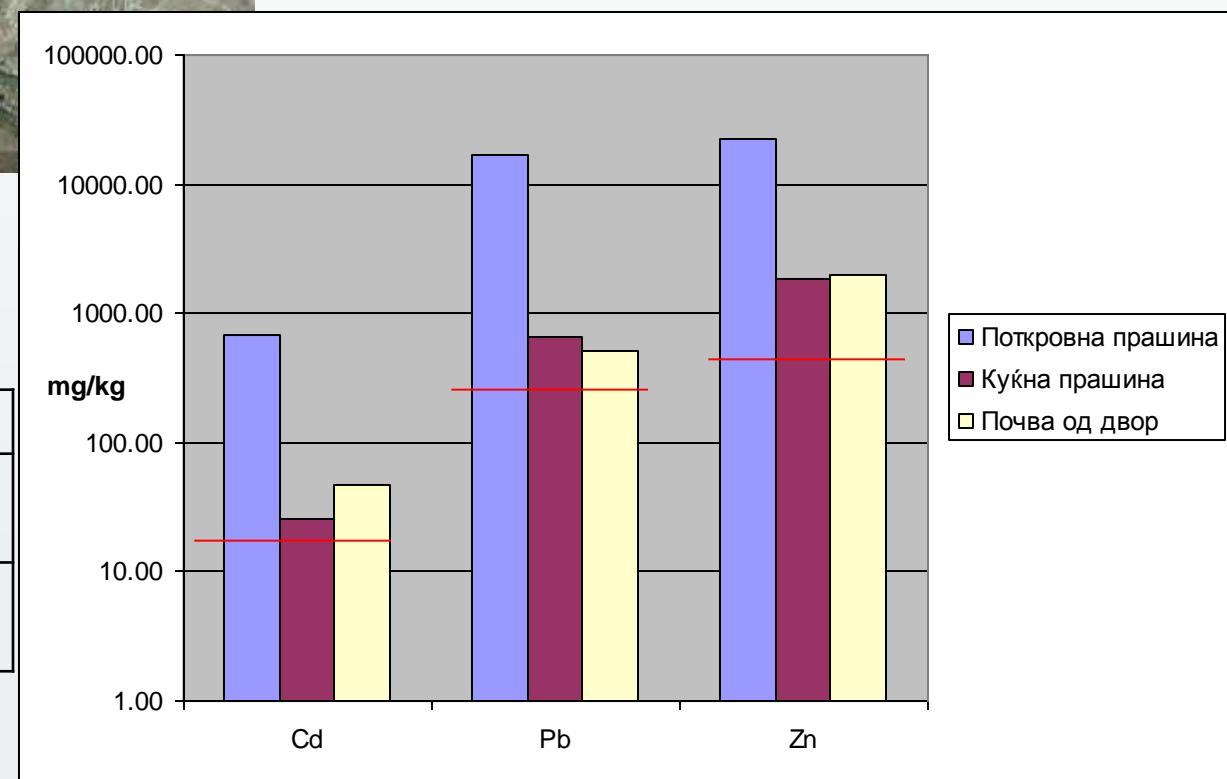
	Pb	Zn	Cd
Referent value, mg/kg	85	140	0.8
Intervention value, mg/kg	530	720	12



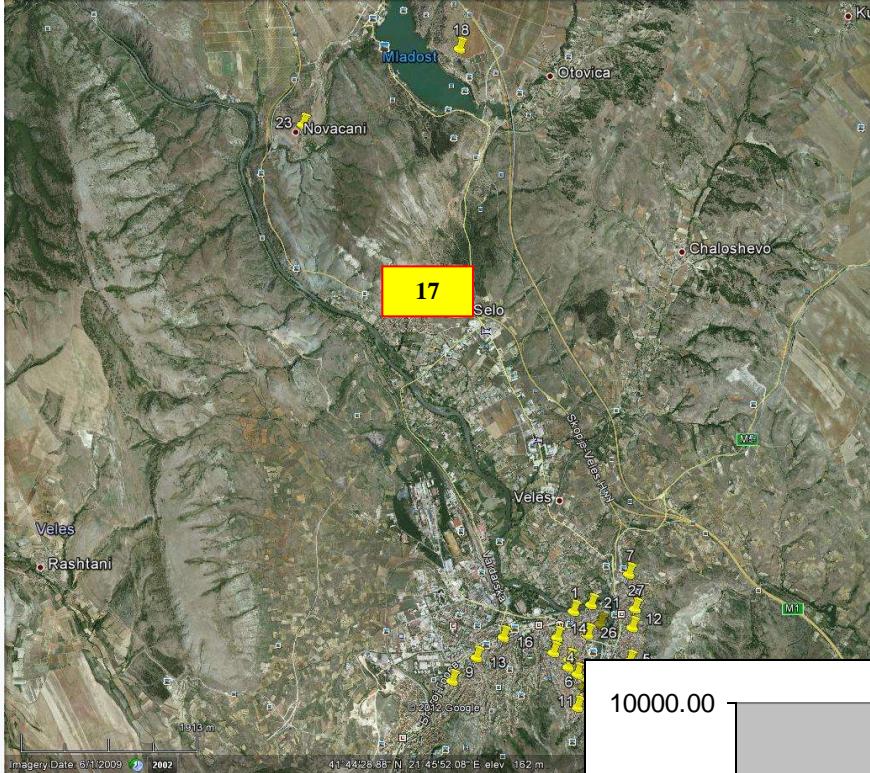


# Veles

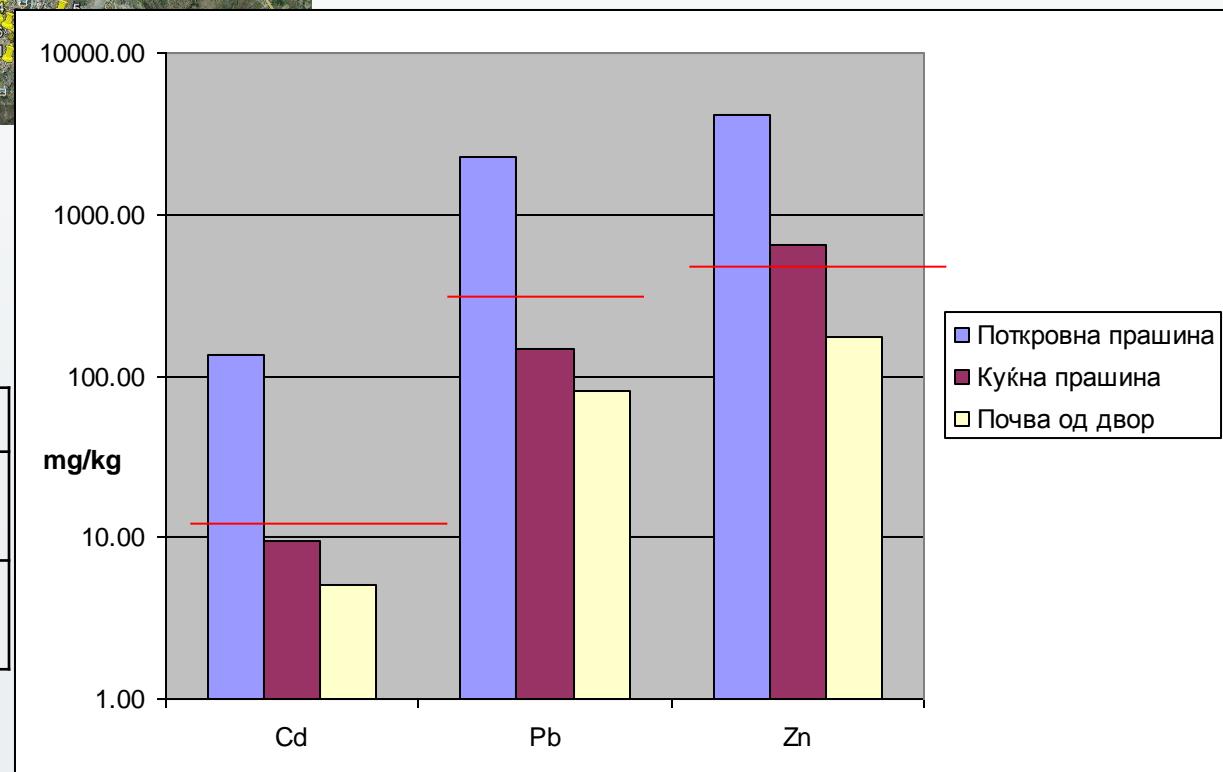
	Pb	Zn	Cd
Referent value, mg/kg	85	140	0.8
Intervention value, mg/kg	530	720	12

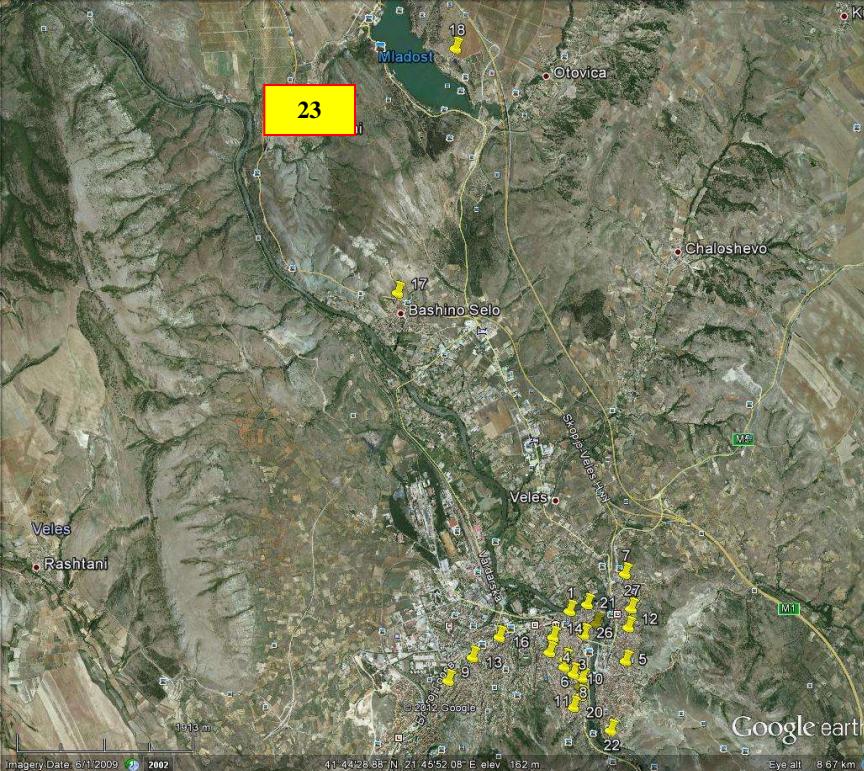


# Bashino Selo



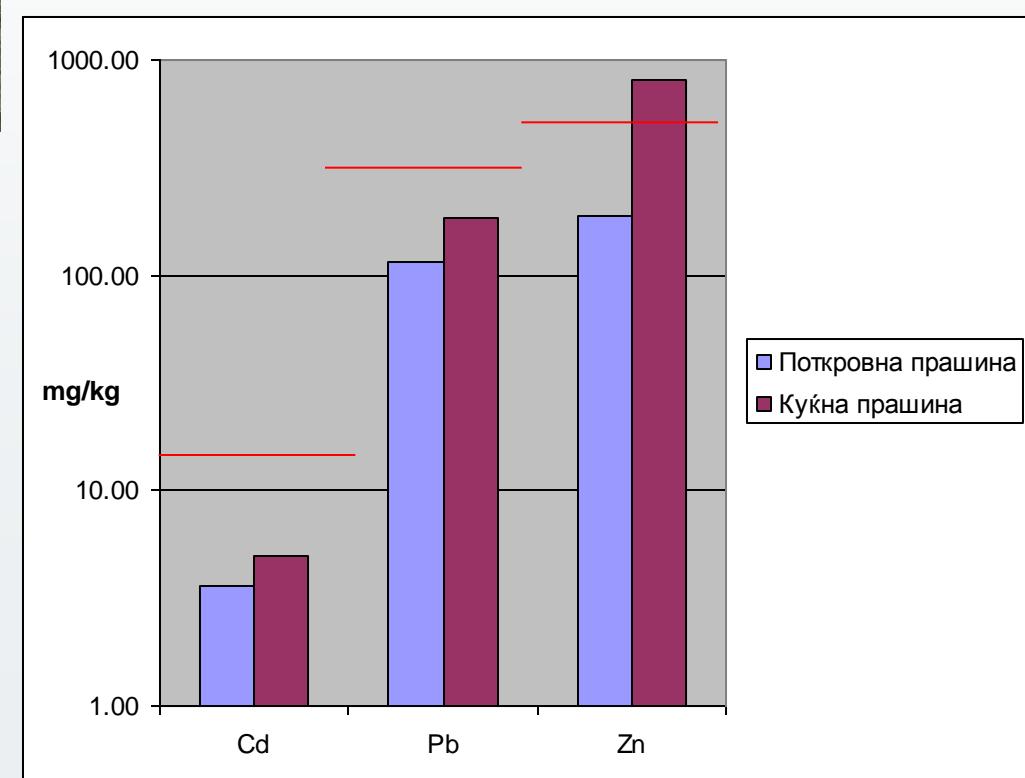
	Pb	Zn	Cd
Referent value, mg/kg	85	140	0,8
Intervention value, mg/kg	530	720	12



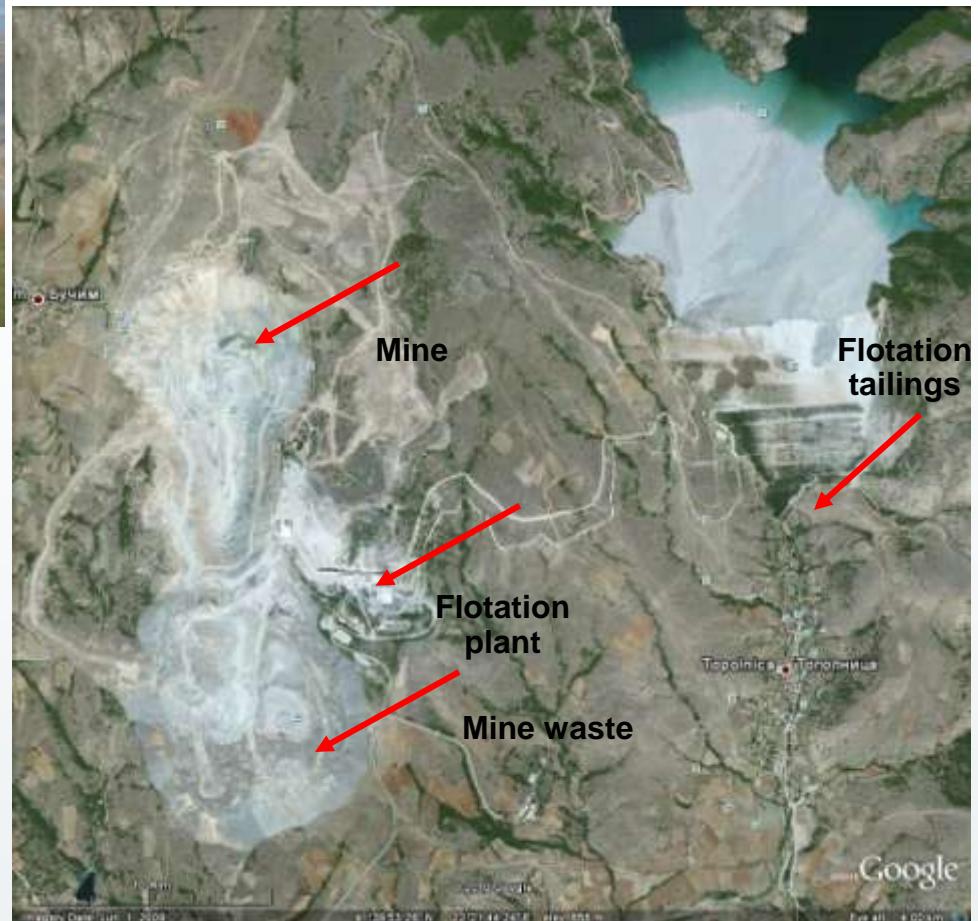
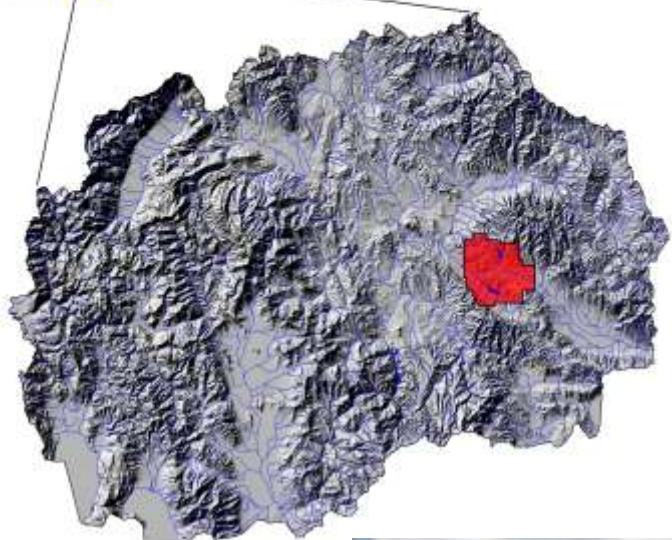


# Novachani

	Pb	Zn	Cd
Referent value, mg/kg	85	140	0,8
Intervention value, mg/kg	530	720	12



# COPPER MINE AND FLOTATION “BUČIM” - RADOVIŠ

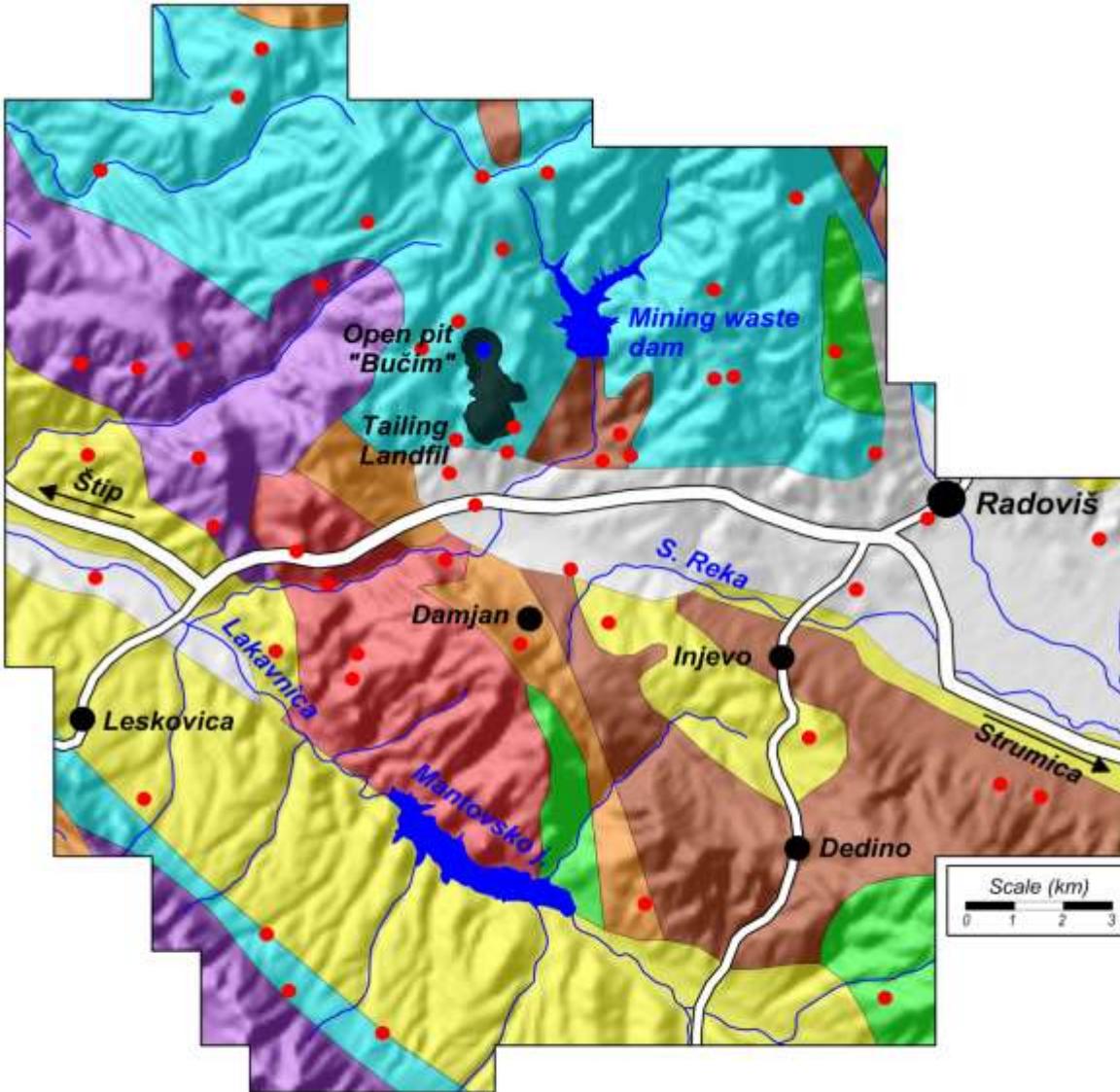


# Moss biomonitoring

January 2009 – May 2009

Al, As, Ba, Ca, Cd, Co, Cr,  
Cu, Fe, K, Mn, Na, Ni, Pb,  
Sr, Zn  
ICP-AES)

52 locations



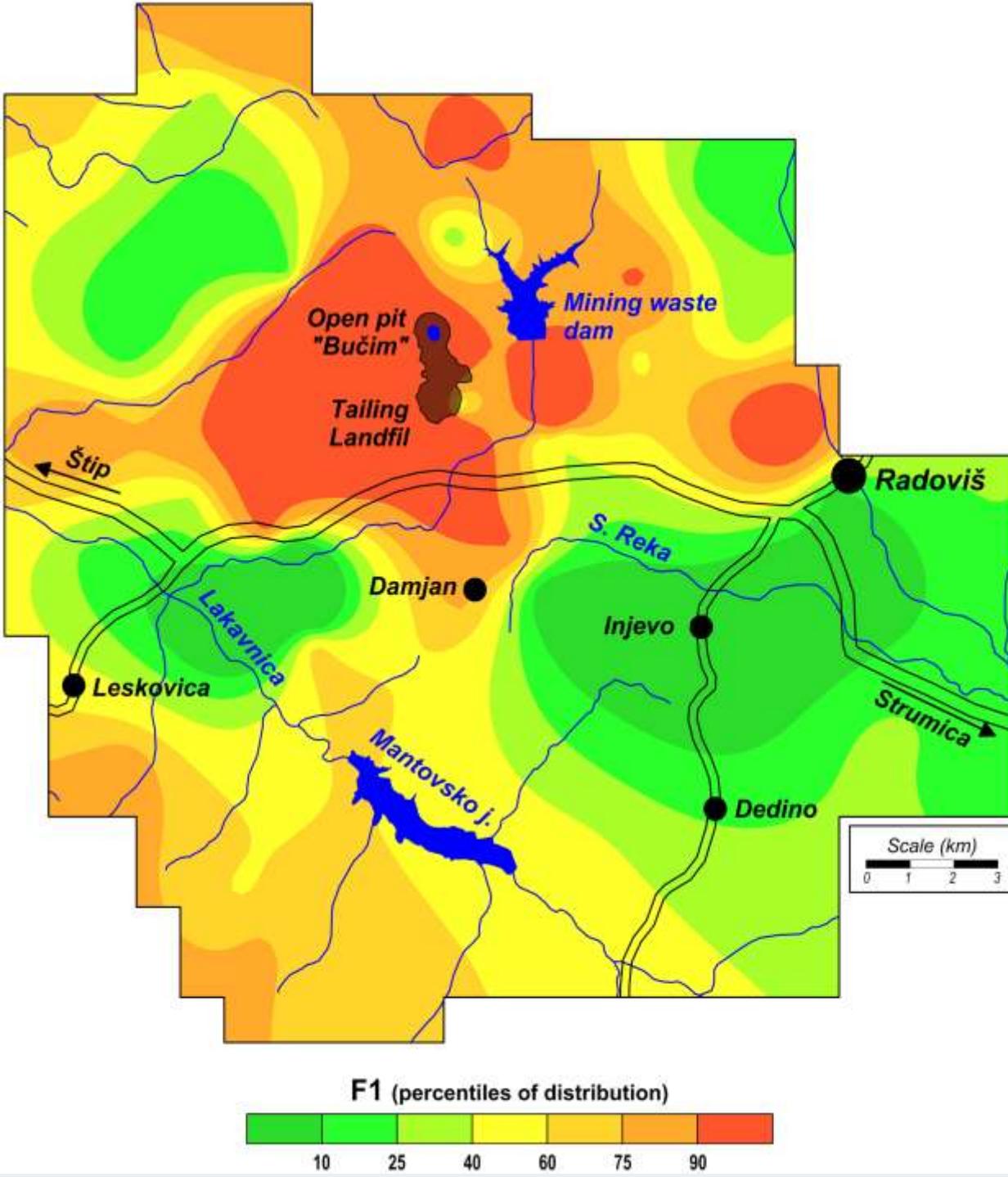
Pleistocene sediments
Pliocene unconsolidated sediments
Eocene flysch and mollase
Neogene dacites, andesites and pyroclastites

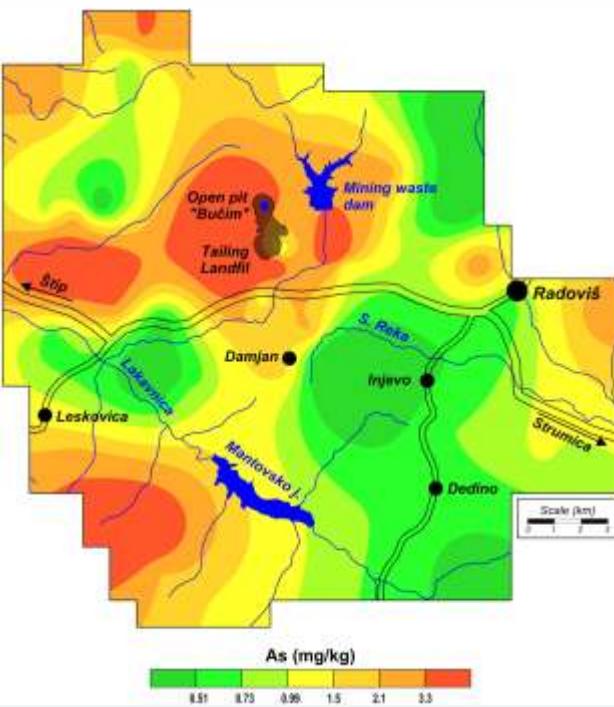
Mesozoic granites and granodiorites
Paleozoic schist
Proterozoic micaschist
Proterozoic gneisses

B. Balabanova, T. Stafilov, K. Bačeva, R. Šajn, Biomonitoring of atmospheric pollution with heavy metals in the copper mine vicinity located near Radoviš, Republic of Macedonia, *Journal of Environmental Science and Health, Part A*, **45**, 1504–15181 (2010).

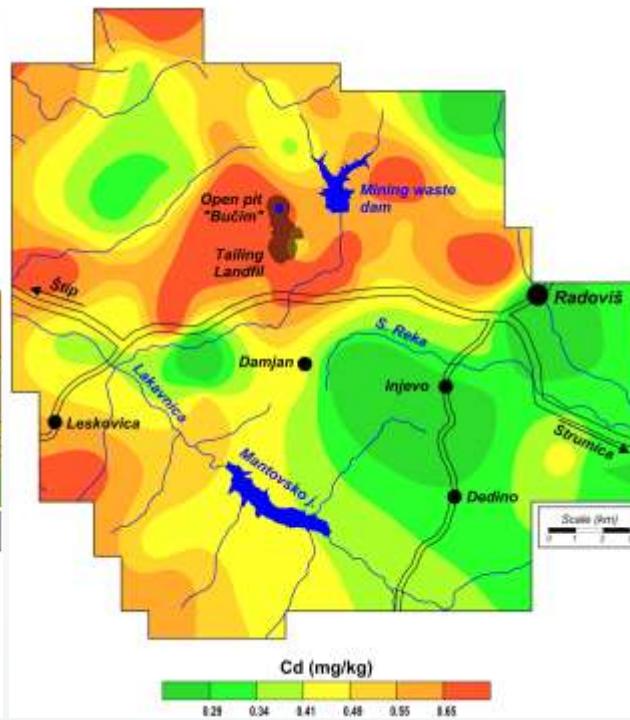
# ANTHROPOGENIC ASSOCIATION

Al, As, Cd, Cu, Fe, Pb, Zn

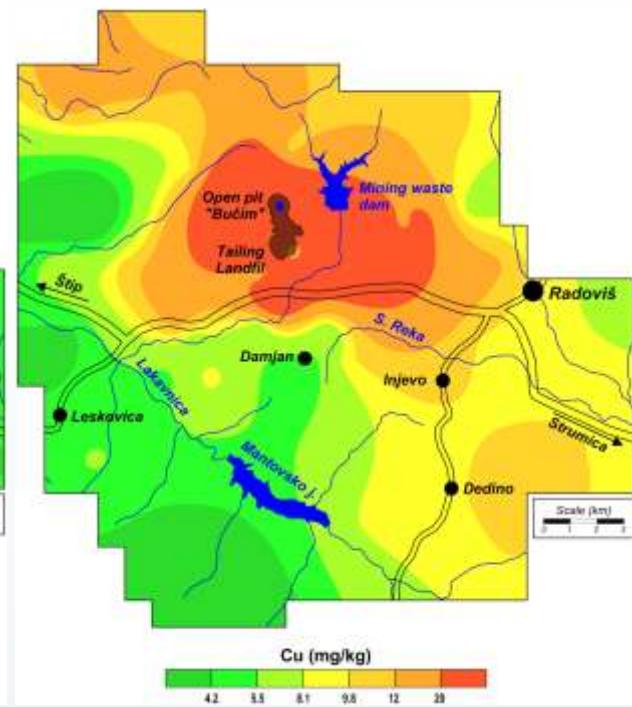




Enrichment factor Bucim/Macedonia  
~ 2 times



Enrichment Factor Bucim/Macedonia  
~ 5 times



Enrichment Factor Bucim/Macedonia  
~ 5 times

# ATIC DUST

64 houses - 29 villages



B. Balabanova, T. Stafilov, R. Šajn, K. Bačeva, Distribution of chemical elements in attic dust as reflection of lithology and anthropogenic influence in the vicinity of copper mine and flotation, *Archives of Environmental Contamination and Toxicology*, 2010, in press.

**Factor 1** (Ca, Li, Mg, Mn, Sr)

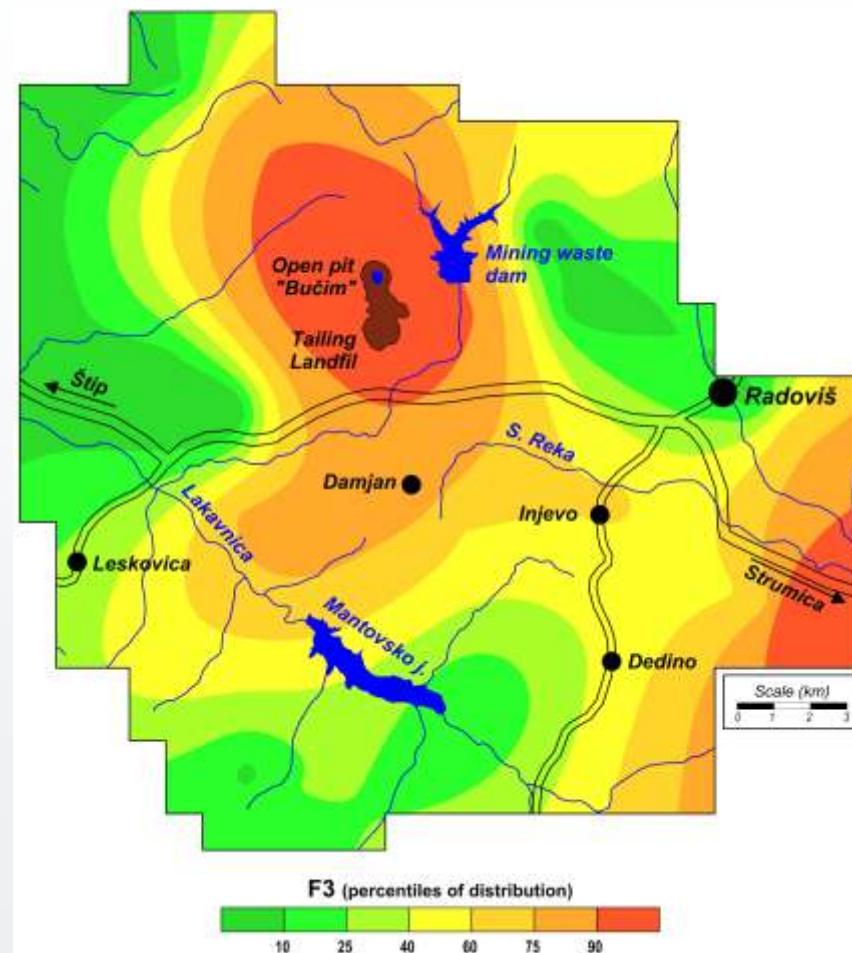
**Factor 2** (Co, Cr, Ni)

Geogenic association of elements

**Factor 3** (As, Cu, Pb) → Anthropogenic association of elements

	F1	F2	F3	Com
As	-0,08	-0,06	0,78	62
Ca	0,80	-0,03	-0,09	70
Cd	0,27	<u>0,51</u>	<u>0,47</u>	67
Co	0,04	0,89	0,09	89
Cr	-0,07	0,90	-0,23	89
Cu	-0,18	-0,07	0,70	57
Li	0,81	-0,18	0,04	80
Mg	0,78	0,21	-0,22	79
Mn	0,76	0,34	0,11	80
Ni	0,19	0,85	0,04	65
Pb	0,27	0,09	0,70	81
Sr	0,72	0,11	0,19	66
Var	31	19	16	67

**Factor 3**  
**As, Cu, Pb**

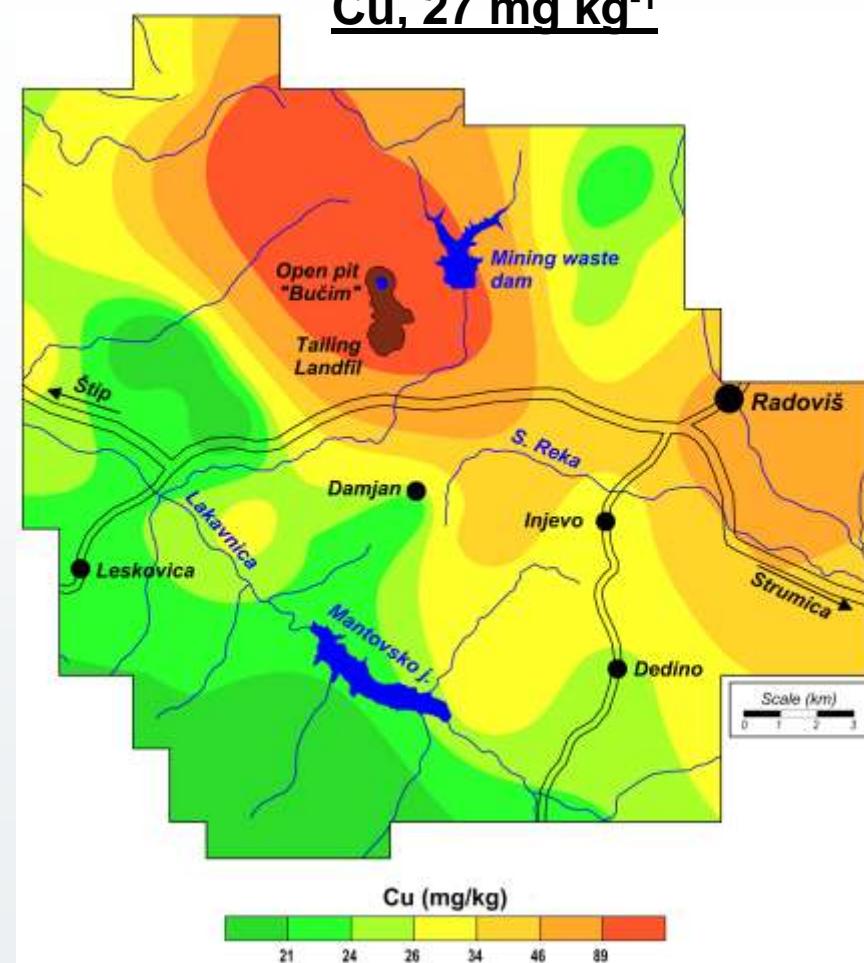


Around the mine and flotation:

**Cu, 180 mg kg<sup>-1</sup>**

Whole investigated region:

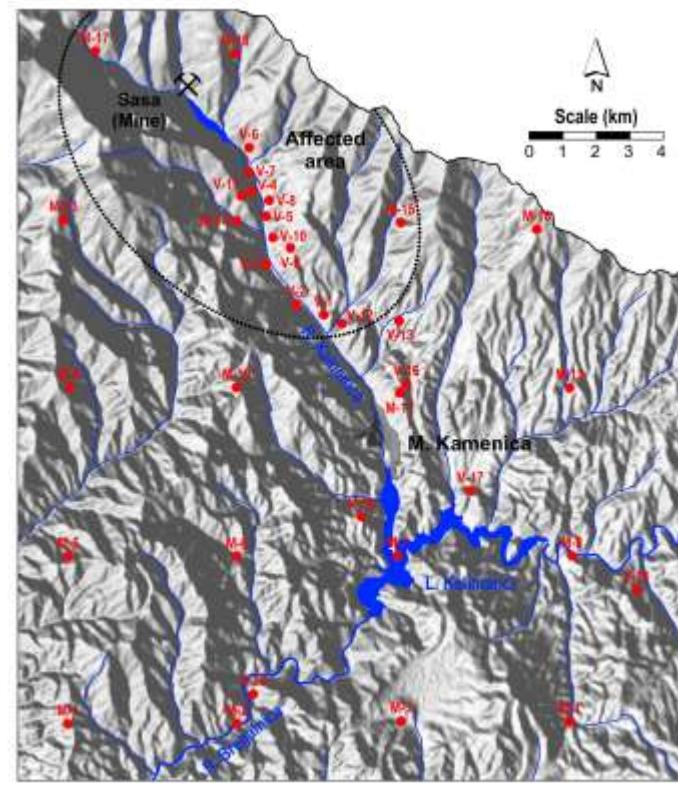
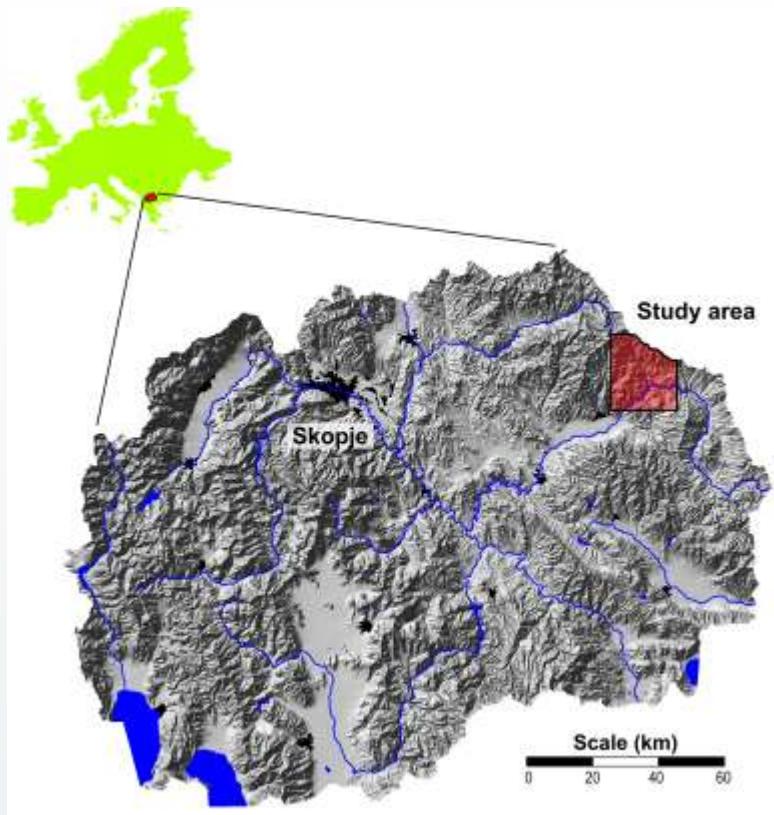
**Cu, 27 mg kg<sup>-1</sup>**



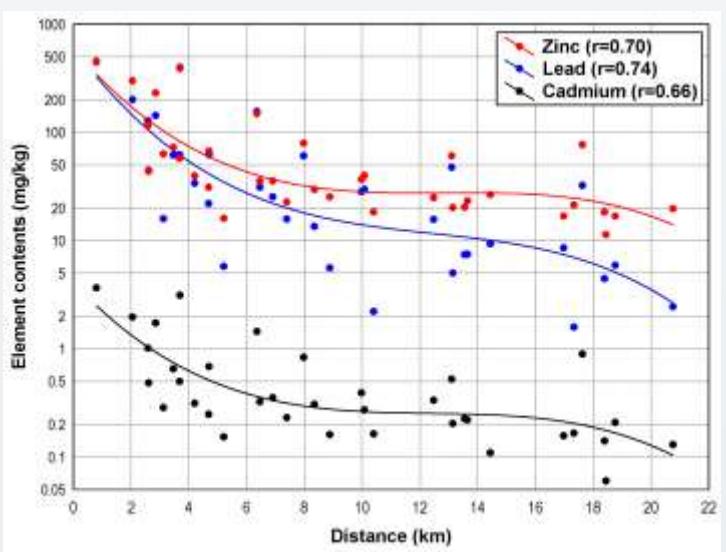
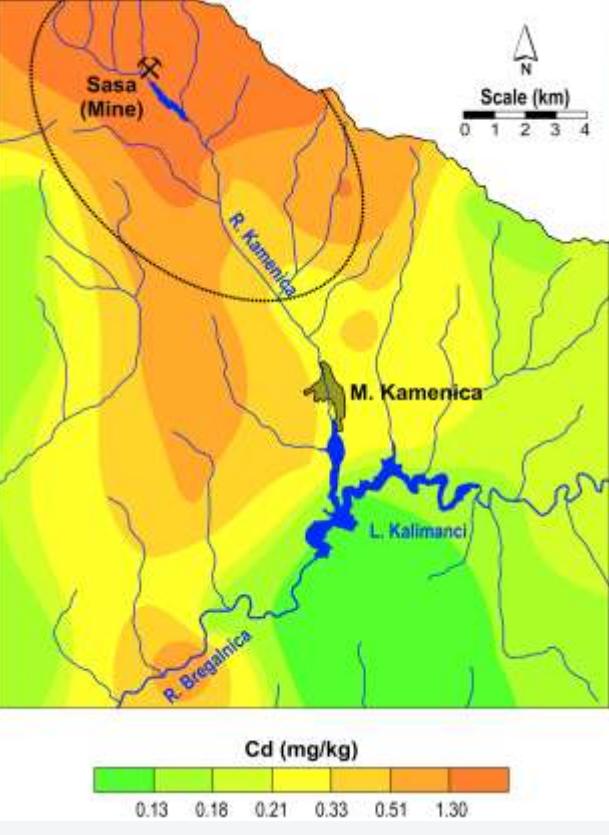
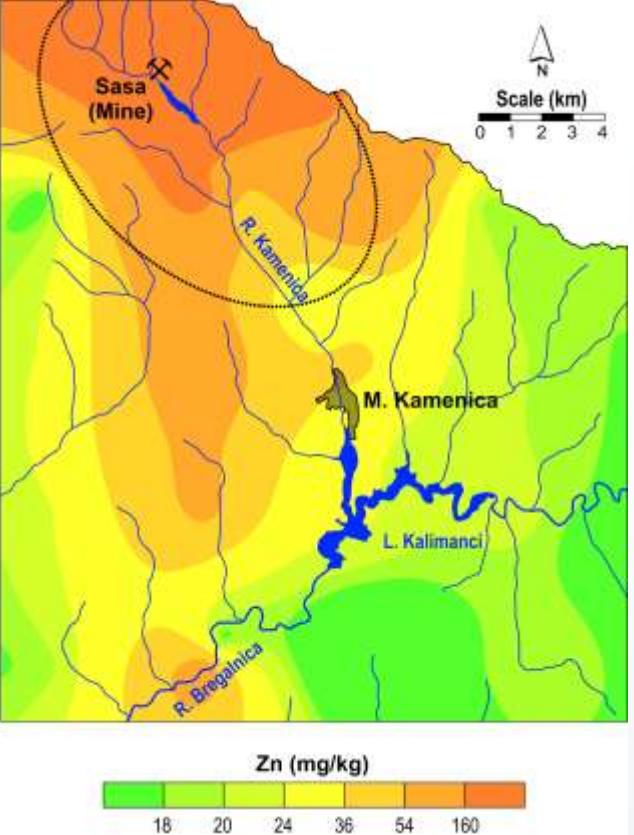
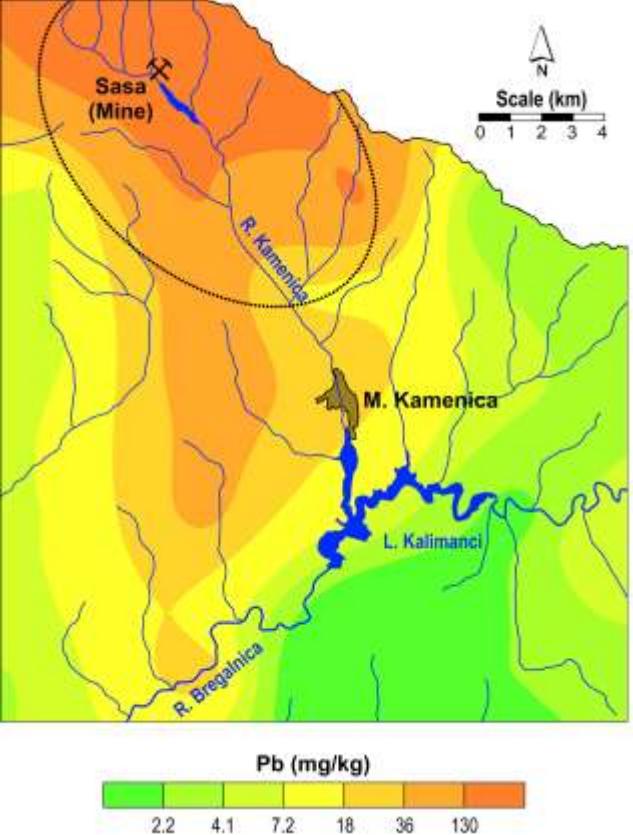
**Enrichment factor ~ 7 times**

# Pb-Zn mine and flotation “Sasa”

## Moss biomonitoring

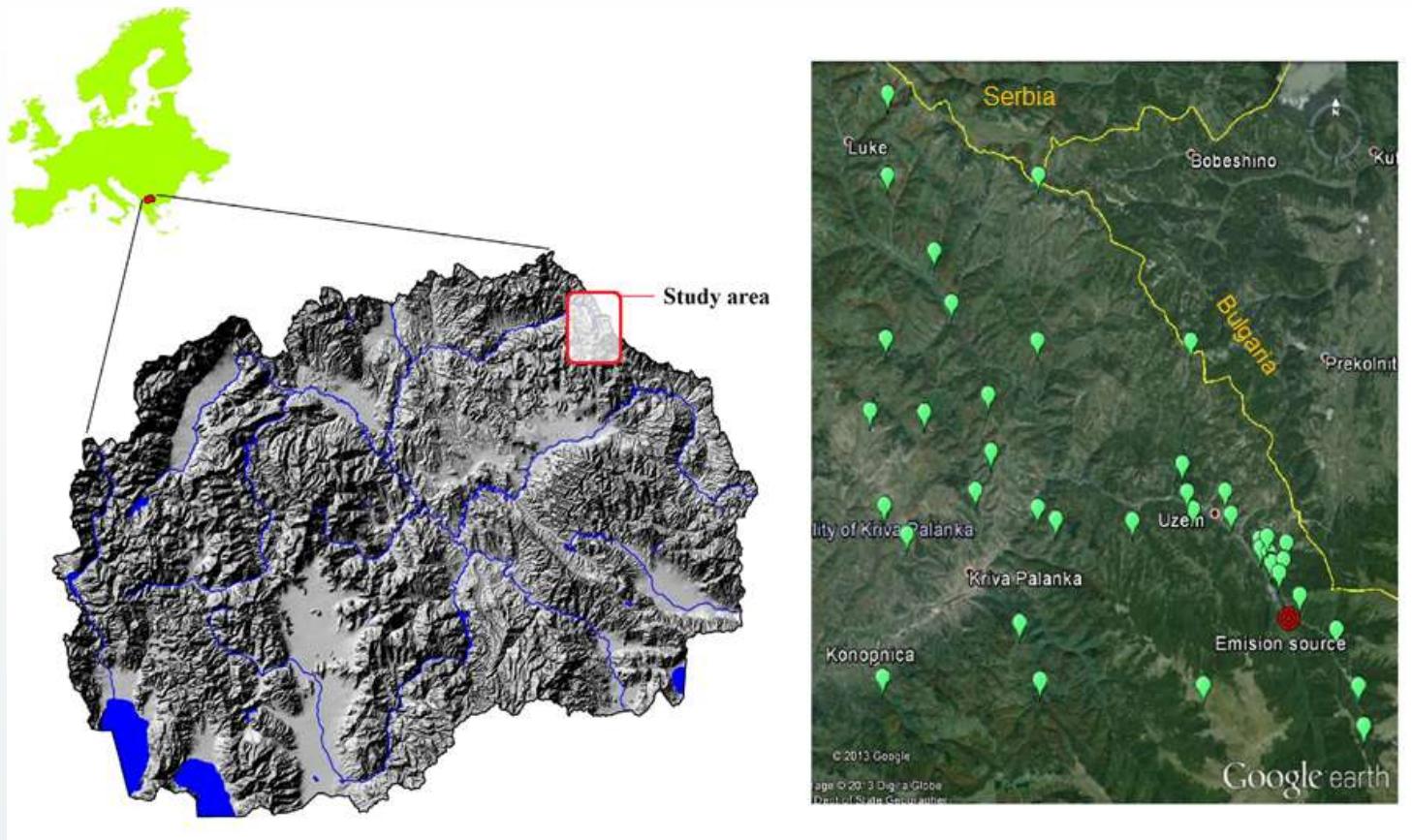


B. Balabanova, T. Stafilov, R. Šajn, K. Baćeva, Quantitative assessment of metal elements using moss species as biomonitorers in downwind area of one lead-zinc mine, *Journal of Environmental Sciences*, **26**(7), (2014); DOI: 10.1016/S1001-0742(13)60561-6

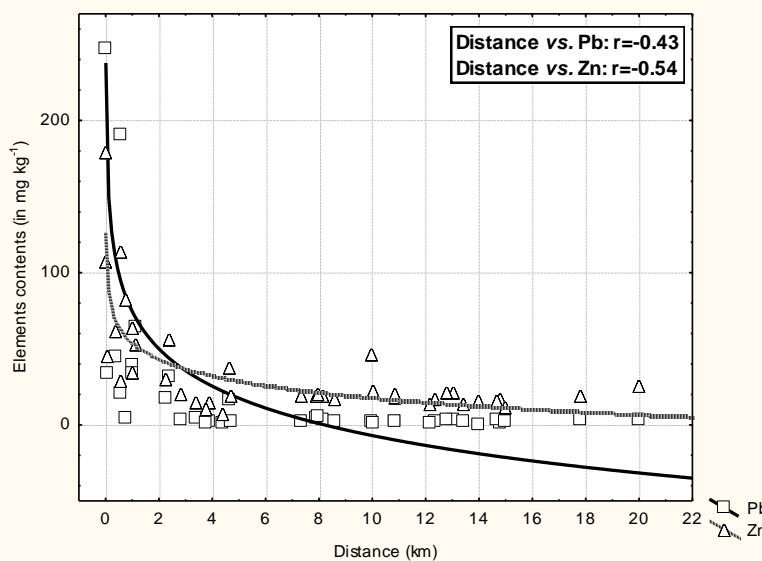
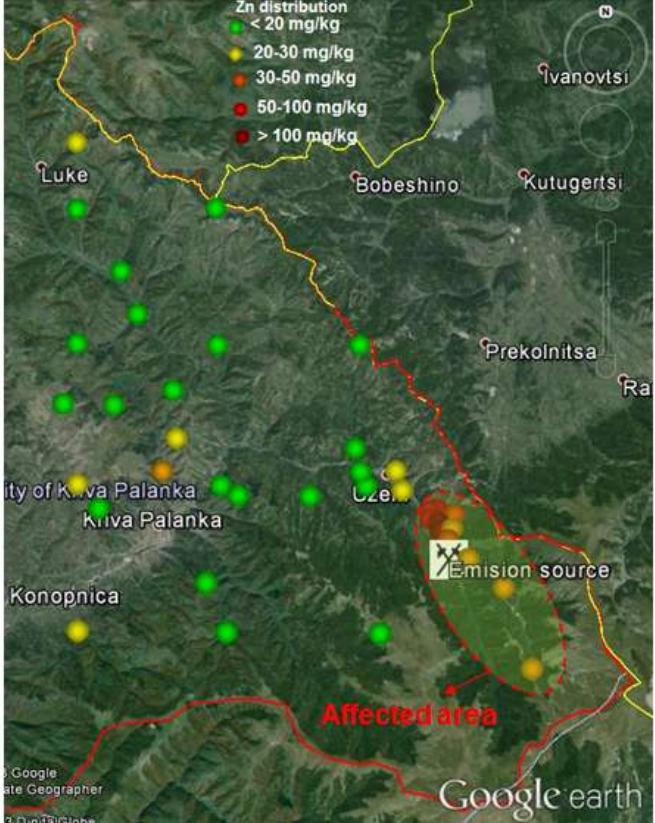


# Pb-Zn mine and flotation “Toranica”

## Moss biomonitoring

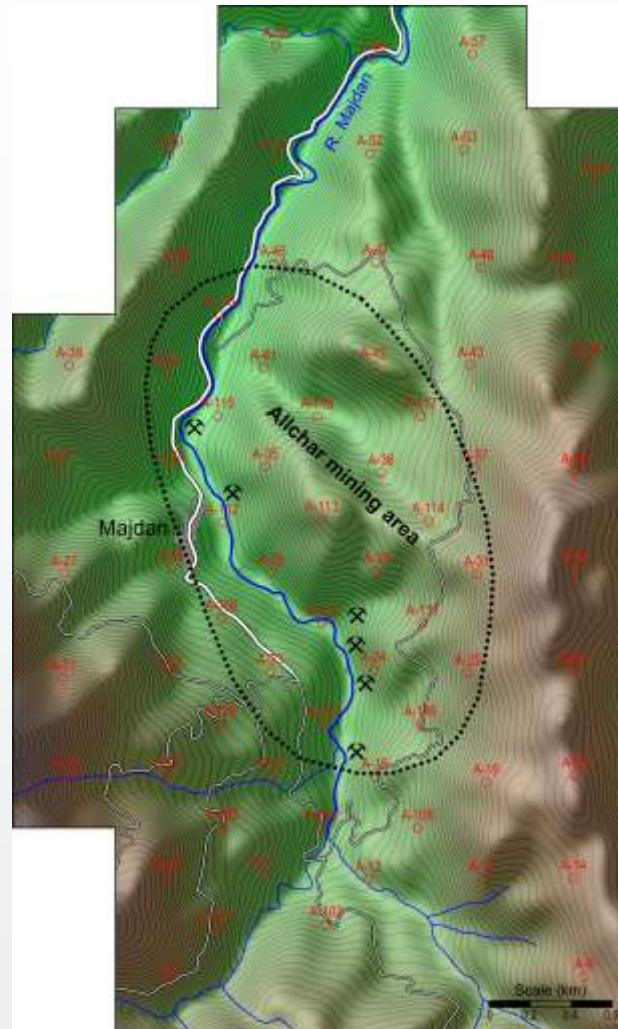
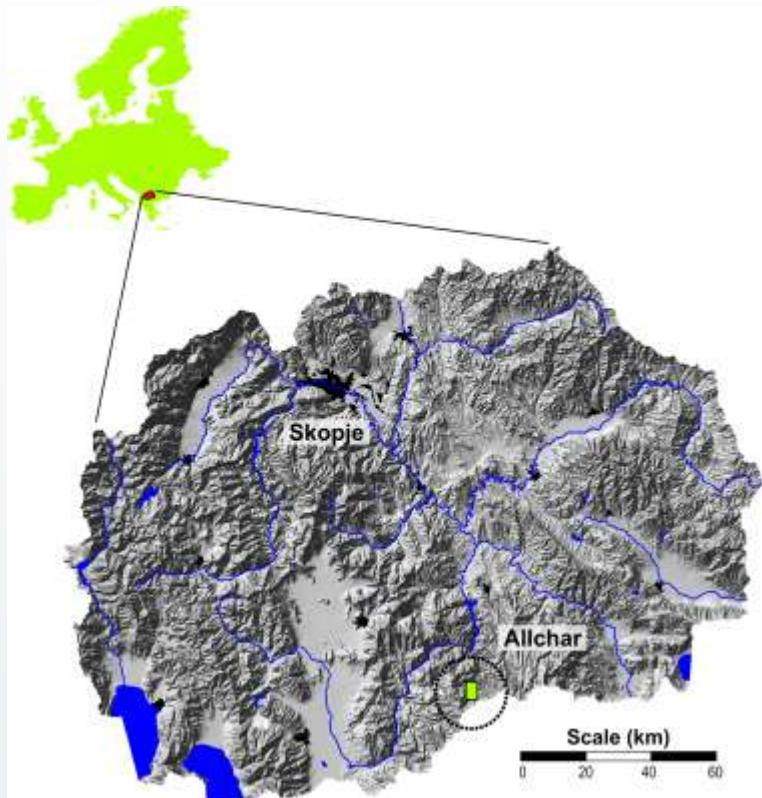


S. Angelovska, T. Stafilov, R. Šajn, K. Bačeva, B. Balabanova, Moss biomonitoring of air pollution with heavy metals in the vicinity of Pb-Zn mine “Toranica” near the town of Kriva Palanka, *Modern Chemistry & Applications*, 2(1), 123, pp. 1-6 (2014).

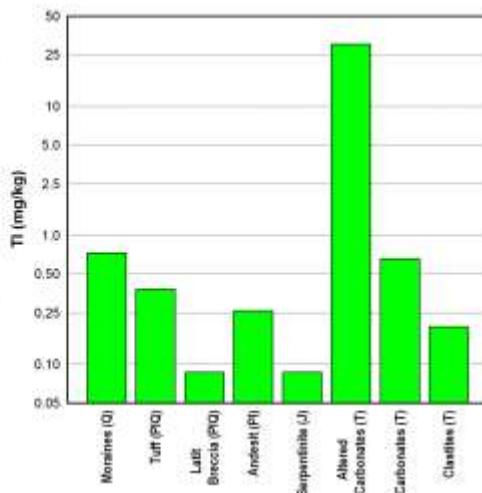
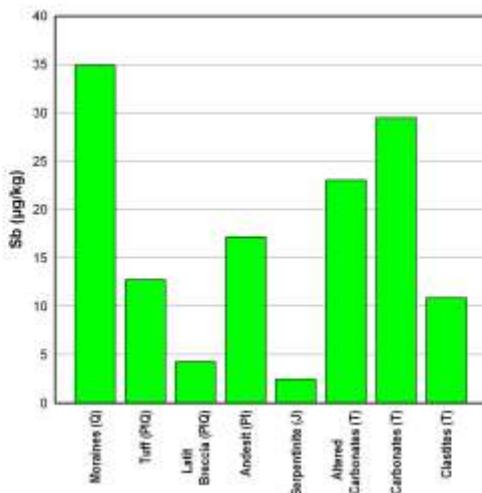
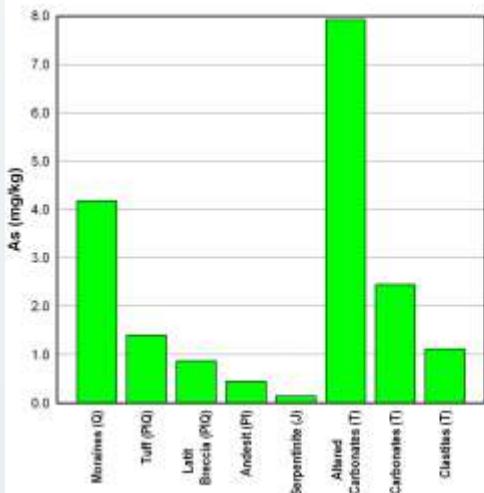
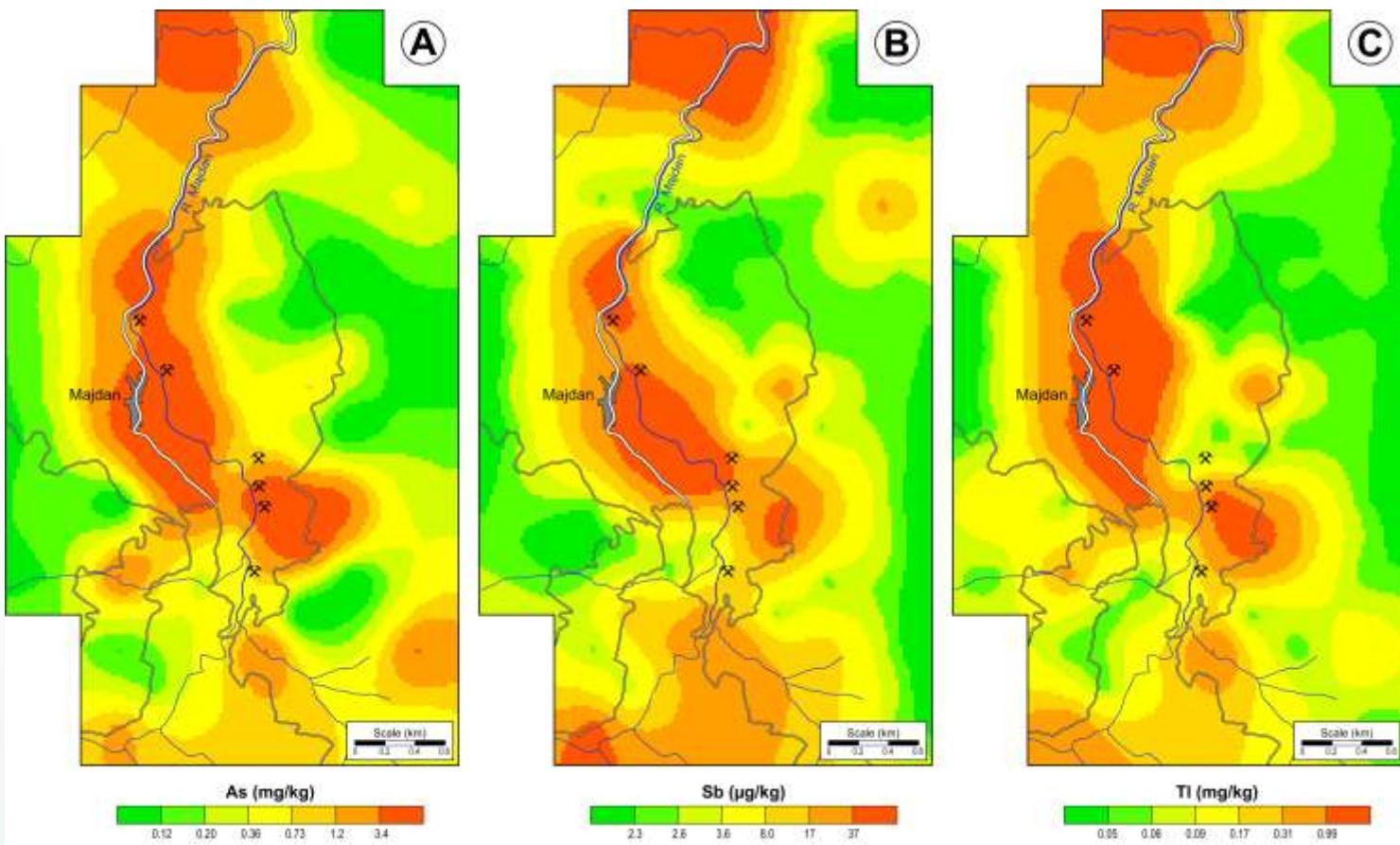


# As-Sb-Tl abounded mine “Allchar”

## Moss biomonitoring

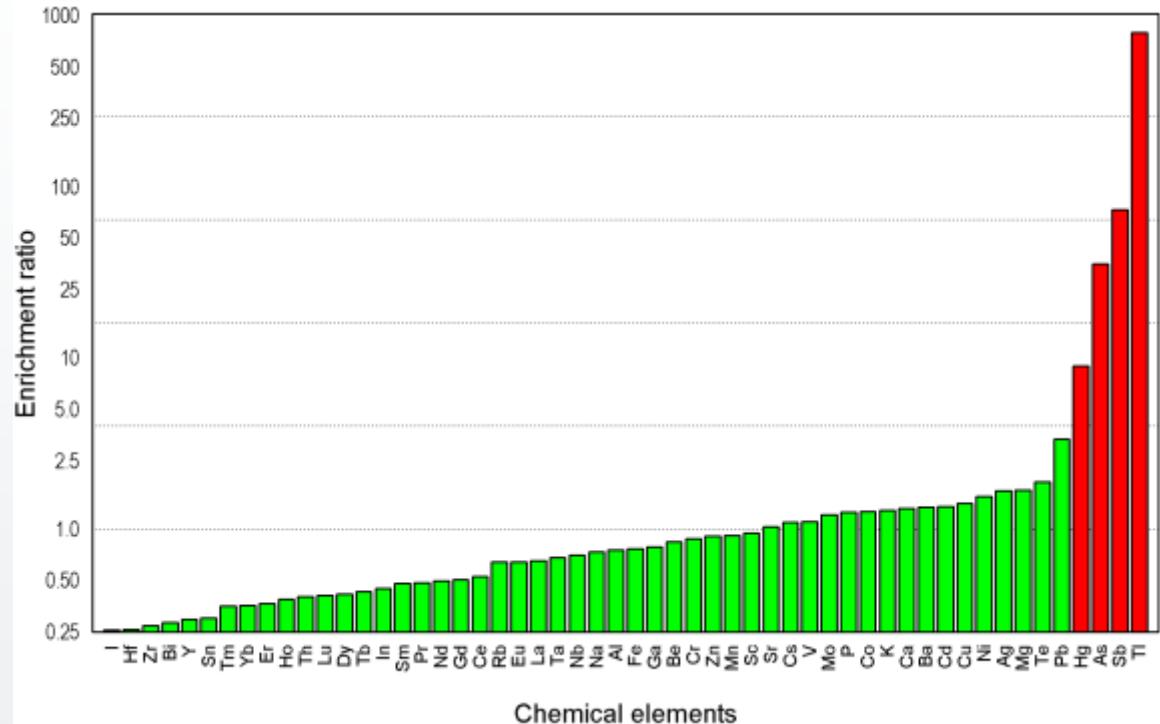
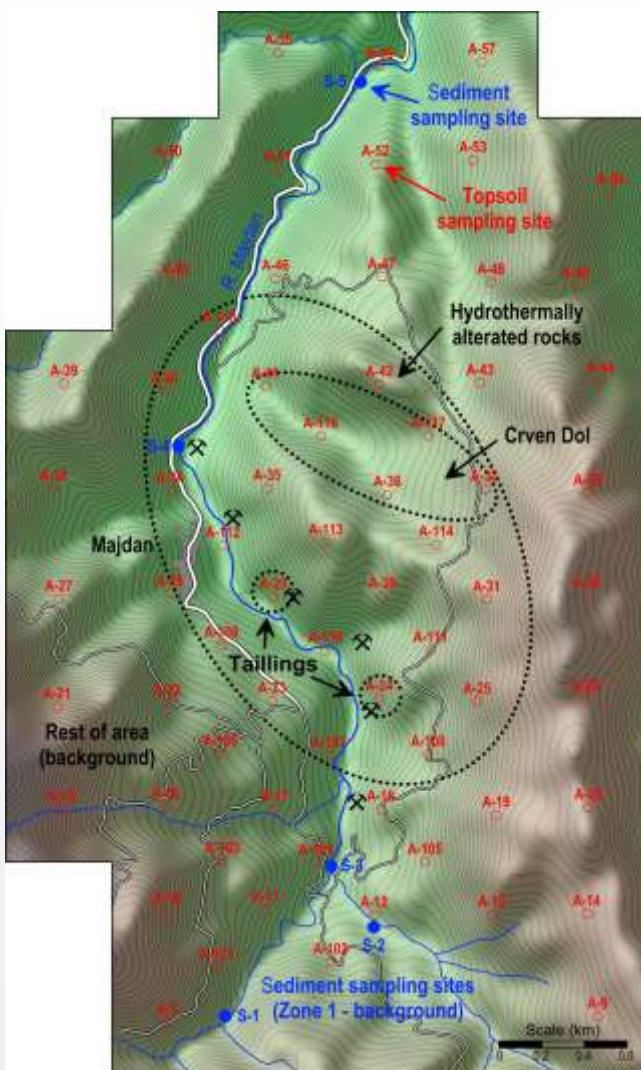


K. Bačeva, T. Stafilov, R. Šajn, C. Tăñăselia, Air dispersion of heavy metals in vicinity of the As-Sb-Tl abounded mine and responsiveness of moss as a biomonitoring media in small scale investigations, *Environmental Science and Pollution Research*, **20**(12), 8763-8779 (2013).

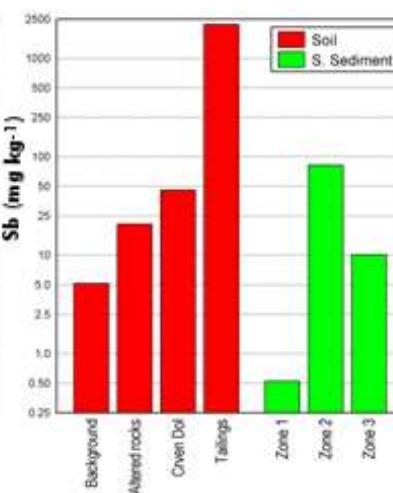
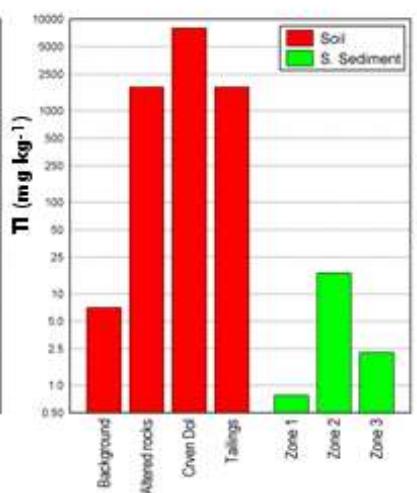
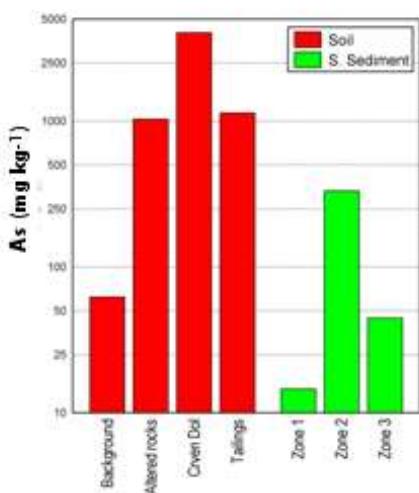
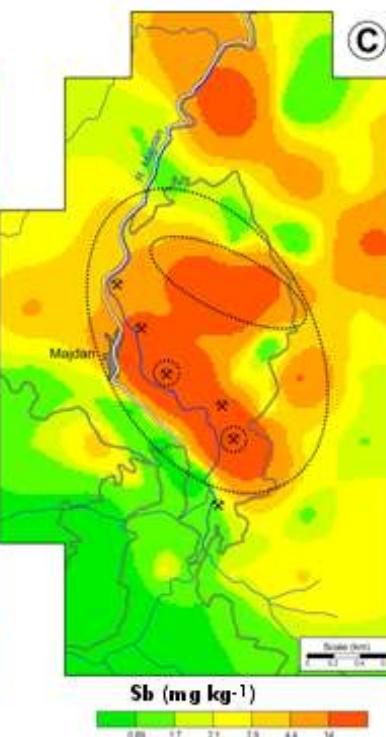
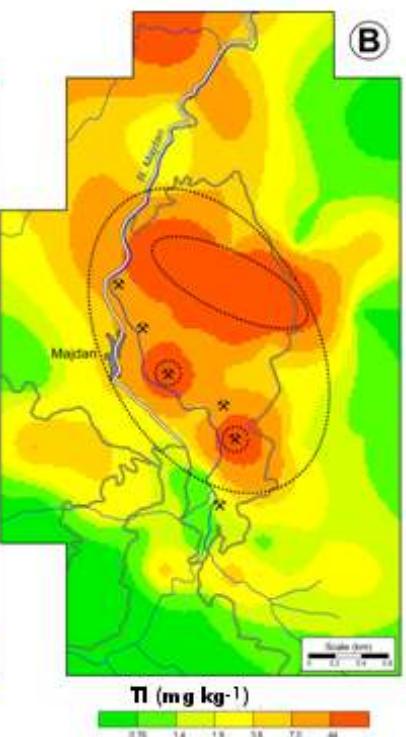
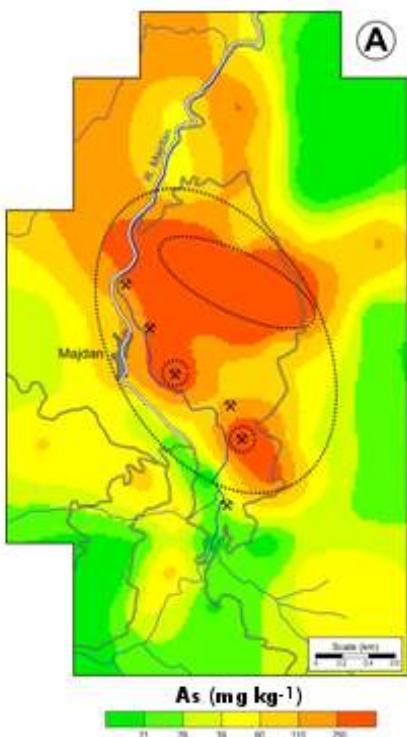


# As-Sb-Tl abounded mine “Allchar”

## Soil monitoring

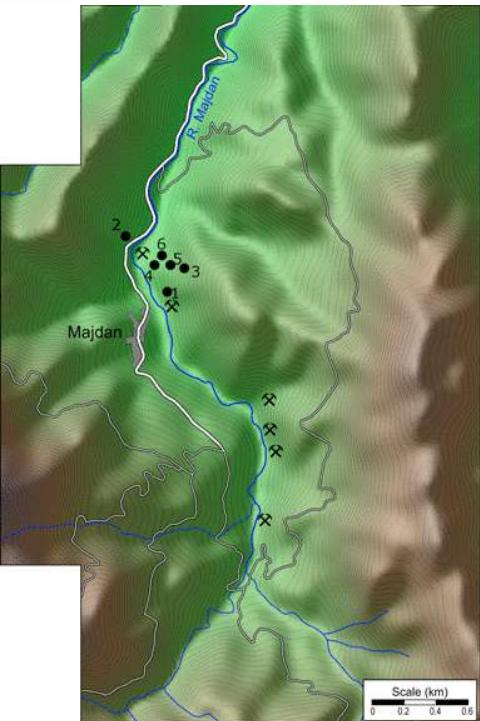


K. Bačeva, T. Stafilov, R. Šajn, C. Tăñăselia, Distribution of chemical elements in soils and stream sediments in the area of rare thallium mineralization and abandoned mine "Allchar", Republic of Macedonia, *Environmental Research*, (2014); DOI: 10.1016/j.envres.2014.03.045.



# As-Sb-Tl abounded mine “Allchar”

## Endemic plant species



*Viola allchariensis*

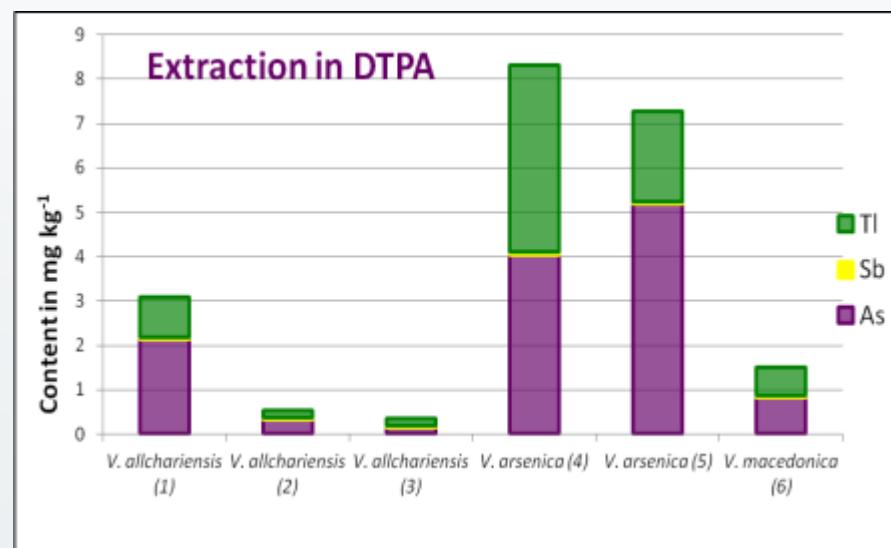
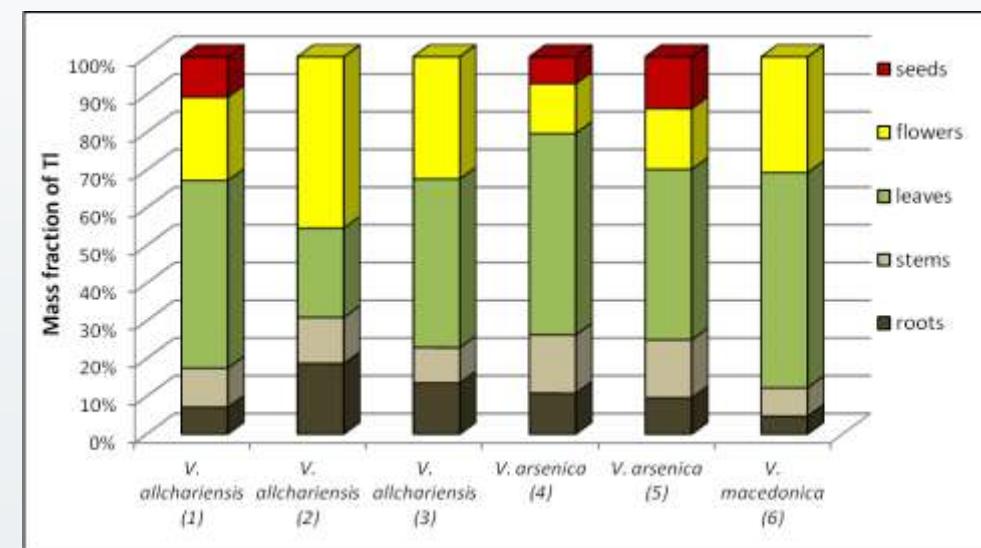
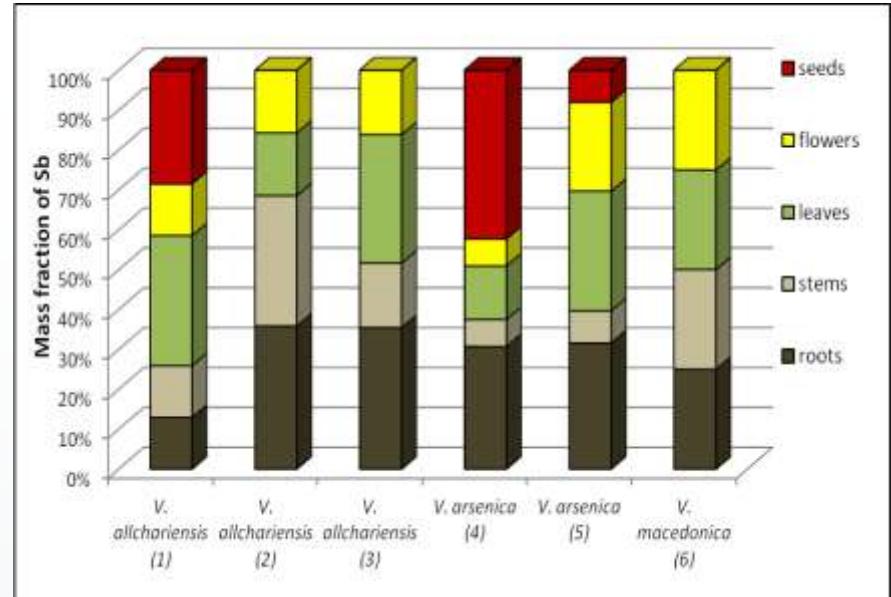
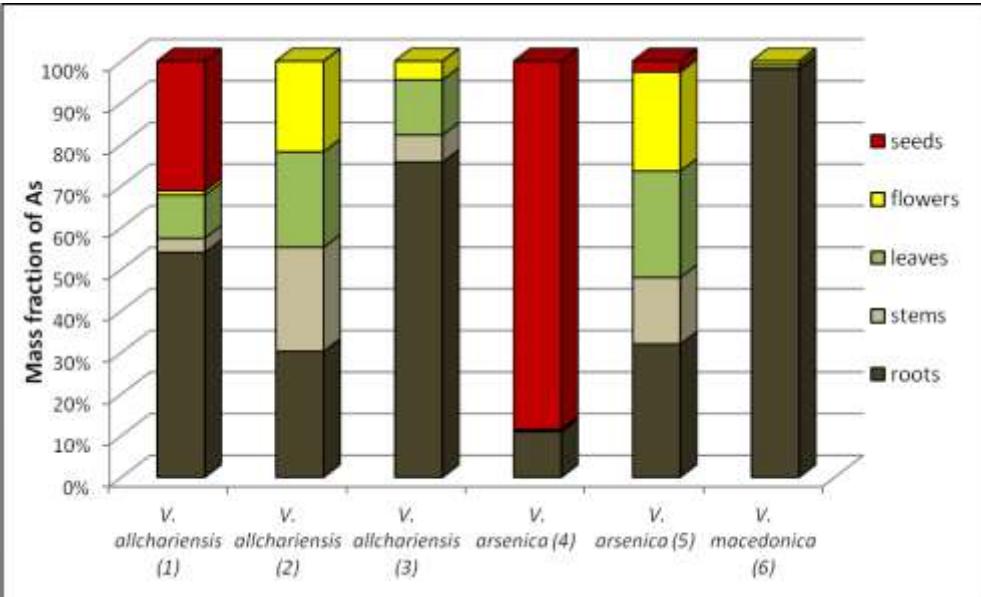


*Viola arsenica*



*Viola macedonica*

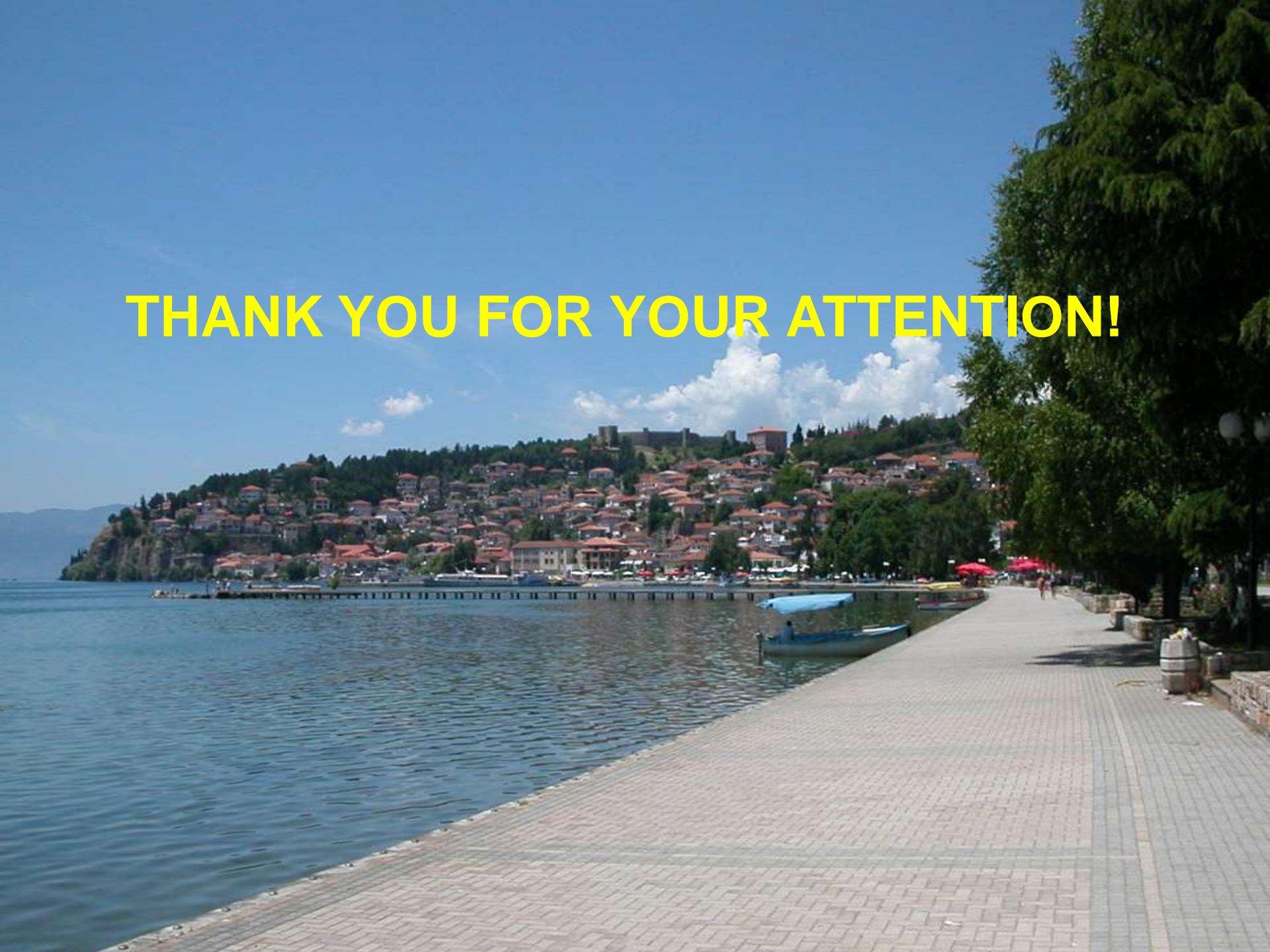
K. Bačeva, T. Stafilov, V. Matevski, Bioaccumulation of heavy metals by endemic *Viola* species from the soil in the vicinity of the As-Sb-Tl mine “Allchar”, Republic of Macedonia, *International Journal of Phytoremediation*, **16**(4), 347-365 (2014).



# The mean content of As, Sb and Tl in plant parts and calculated bioaccumulation and biotransfer factors

Sample	Root	Steam	Leaves	Flowers	Seeds	Sum	Soil	BAF <sup>a</sup>	BTF <sup>b</sup>
As, mg kg <sup>-1</sup>									
<i>V. allchariensis</i>	133.9	9.54	26.3	3.87	108	282	2573	<b>0.11</b>	<b>0.81</b>
<i>V. arsenica</i>	210	21.9	32.35	34.35	1391	1691	10066	<b>0.17</b>	<b>6.61</b>
<i>V. macedonica</i>	158	0.25	1.46	1.38	-	161	4932	<b>0.03</b>	<b>0.01</b>
Sb, mg kg <sup>-1</sup>									
<i>V. allchariensis</i>	0.46	0.34	0.46	0.25	0.40	1.91	33.80	<b>0.06</b>	<b>0.87</b>
<i>V. arsenica</i>	1.06	0.25	0.72	0.47	0.91	3.40	70.85	<b>0.05</b>	<b>0.86</b>
<i>V. macedonica</i>	0.25	0.25	0.25	0.25	-	1.00	30.90	<b>0.03</b>	<b>1.00</b>
Tl, mg kg <sup>-1</sup>									
<i>V. allchariensis</i>	514	437	2075	1306	1690	6022	178	<b>33.80</b>	<b>3.29</b>
<i>V. arsenica</i>	1877	2831	9092	2669	1877	18346	1312	<b>13.98</b>	<b>1.00</b>
<i>V. macedonica</i>	356	567	4292	2310	-	7525	409	<b>18.40</b>	<b>6.49</b>

**THANK YOU FOR YOUR ATTENTION!**





ОДБОРОТ ЗА ДОДЕЛУВАЊЕ НА НАГРАДАТА

"ГОЦЕ ДЕЛЧЕВ"

ЈА ДОДЕЛИ

НАГРАДАТА "ГОЦЕ ДЕЛЧЕВ"

НА

д-р Трајче Ѓтафилов, д-р Роберт Шајн,  
д-р Златко Панчевски, д-р Блаќо Боев,  
д-р Марина Фронтакијева и д-р Мудумла Ѓтрелковска

КАКО ОПШТЕСТВЕНО ПРИЗНАНИЕ ЗА ОСОБЕНО ЗНАЧАЈНИ ОСТВАРУВАЊА  
ОД ИНТЕРЕС ЗА РЕПУБЛИКА МАКЕДОНИЈА ВО ОБЛАСТТА НА НАУКАТА

ЗА ТРУДОТ

"Геохемикарски атлас на Велес и неговата окоина"

СКОПЈЕ

БР 13-607/1

09.04.2009 ГОД



ПРЕТСЕДАТЕЛ

д-р д-р Георги Ѓтадилов  
*Богдан Ѓтадилов*



