Atmospheric Deposition Trends in Bulgaria Over a 20-year Period of Participation in the European Moss Survey Programme (1995/6-2015/6)

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ICP Vegetation surveys in Bulgaria: Participation since 1995

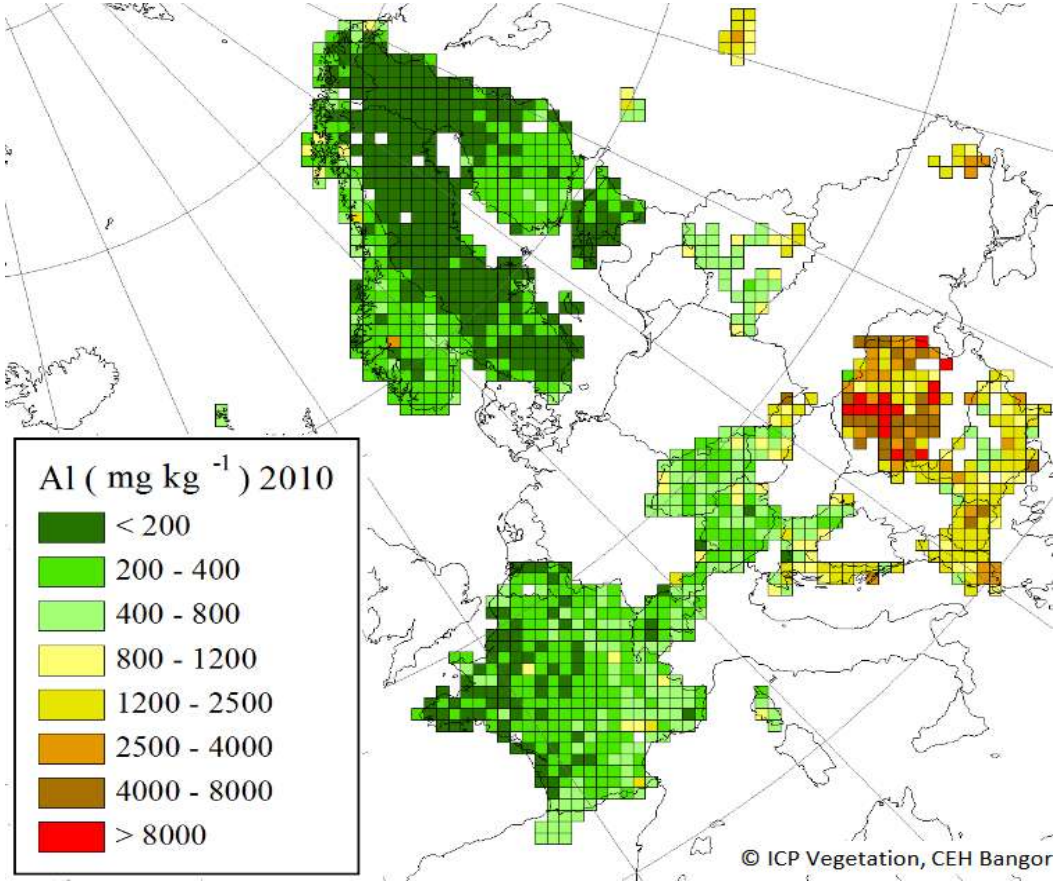
Most abundant moss species: *Hypnum cupressiforme*

Non-uniform sampling networks:

- Hot and dry summers, mountainous terrains, arable land
- Different groups partaking in sample collection
- Financial and time constraints

ICP Vegetation surveys in Europe: east-west gradient for metals

31st TFM discussion: Factors contributing to the gradient include:



- Higher anthropogenic emissions **and sampling in more polluted areas**
- Higher contribution of wind-blown dust from drier mineral soils (Al)
- NAA as analytical method

ICP Vegetation surveys in Bulgaria: Analytical Methods

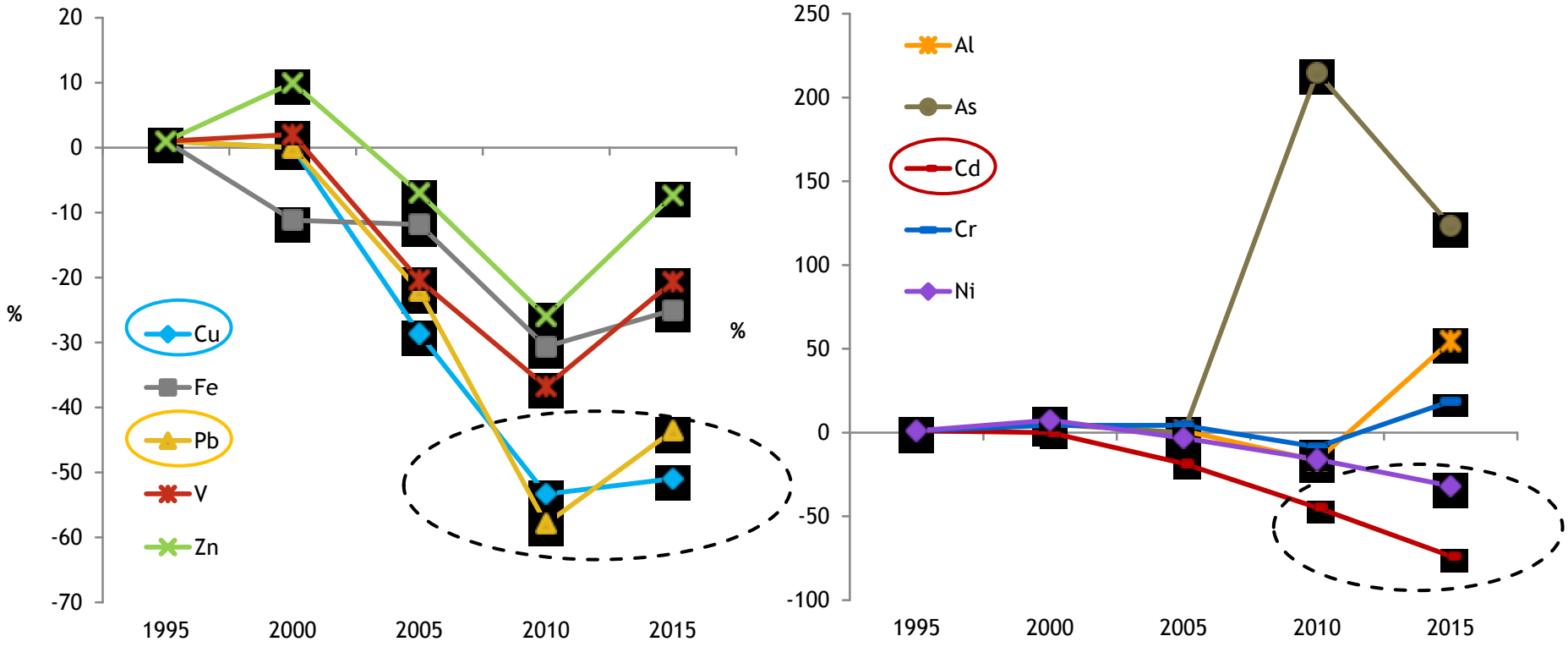
Data submitted: **1995-2010: ICP-AES;** ***2005 additional data: NAA**
2015: NAA + ICP-AES

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**											Rf	Db	Sg	Bh	Hs
	*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
	**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw		

- Retrospective comparison: median values
  - With data from other participants, including neighboring countries
  - With data from surveys conducted in Bulgaria

Retrospective comparison: surveys in Bulgaria
1995 (N=215), 2000 (N=217), 2005 (N=213), 2010 (N=129), 2015 (N=115)

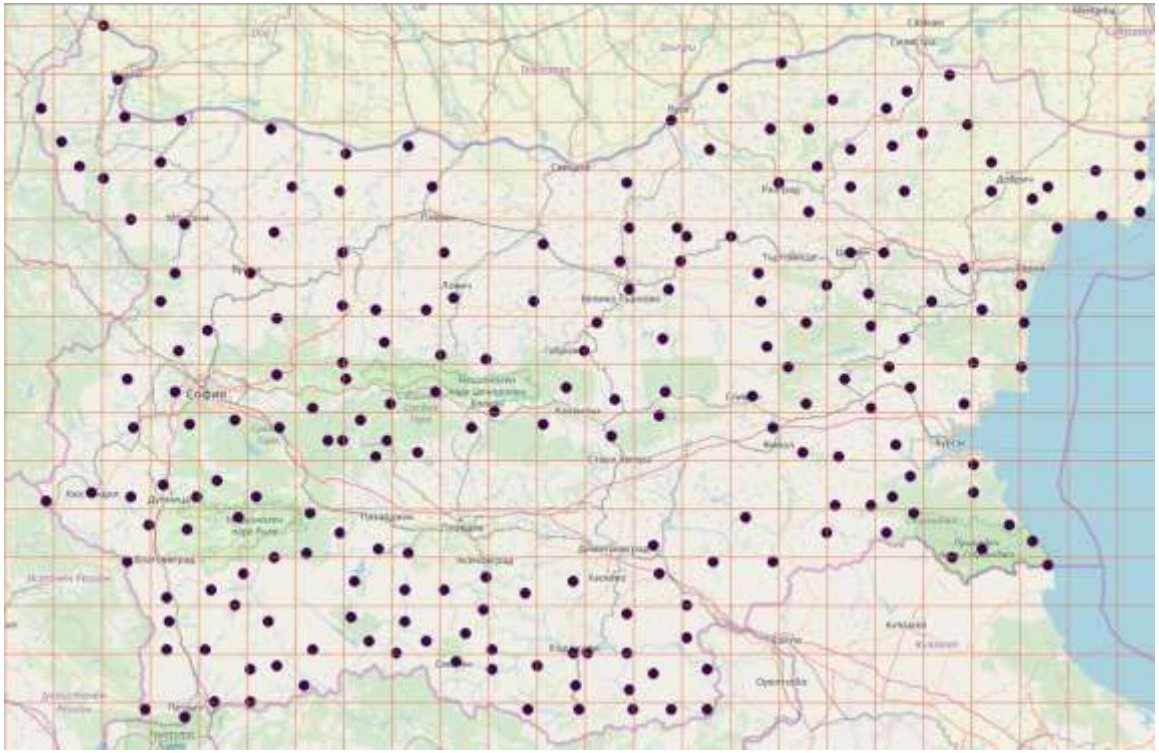
Relative difference [%]: relative to the median concentrations in 1995:



Different accuracies for each element. **In 2015: Cu & Pb medians increased but Cd medians decrease steadily (ICP-AES: 1995-2015); Ni median values decreased (NAA in 2015).**

ICP Vegetation surveys in Bulgaria: Sampling map, 1995, N=215

Moss species: *Hypnum cupressiforme*

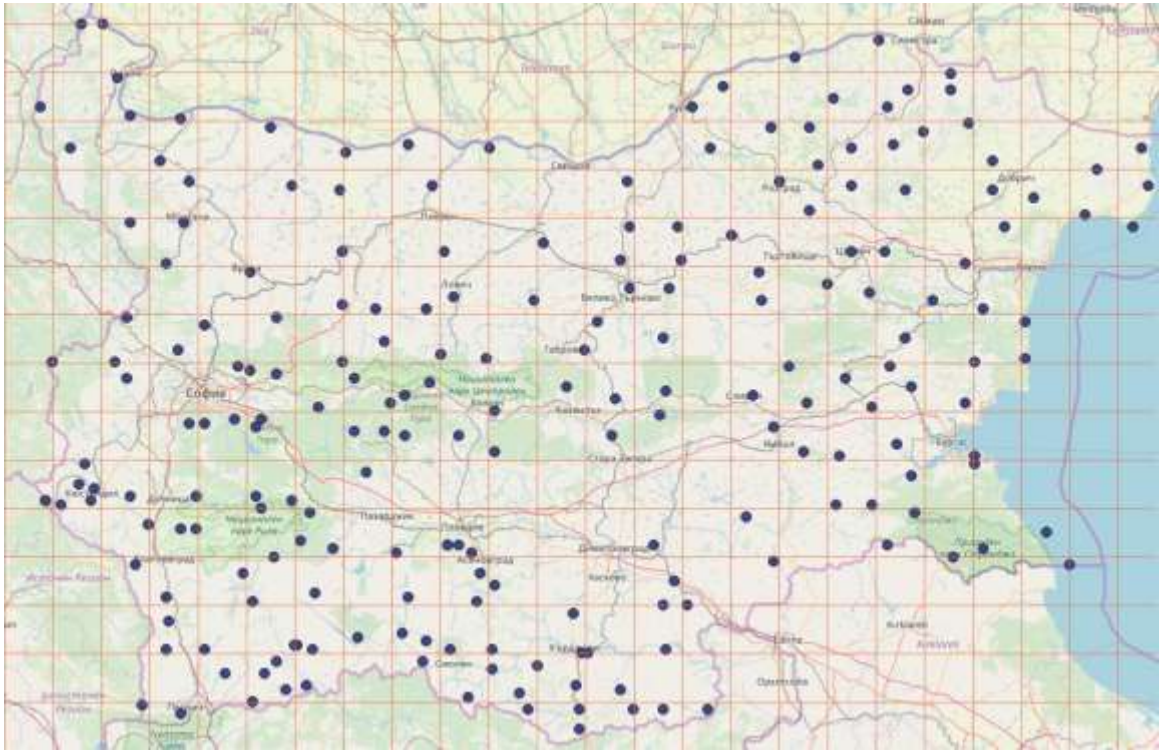


Sampling network:

- A rather uniform grid: 30 x 30 km
- Almost all nature parks and reserves were sampled
- In valleys: proximity to arable land and urban areas

ICP Vegetation surveys in Bulgaria: Sampling map, 2000, N=217

Moss species: *Hypnum cupressiforme*

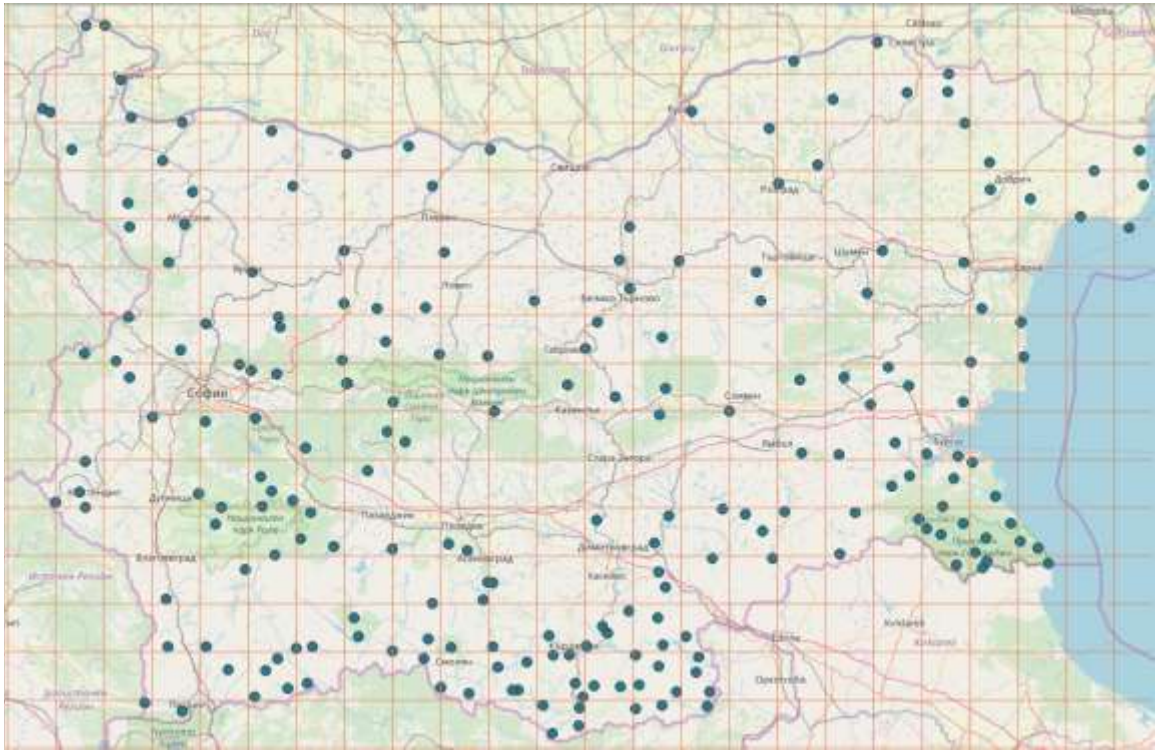


Non-uniform sampling networks:

- The degree of regularity decreased to avoid urbanized areas and arable land
- SS in mountainous regions shifted the most (accessibility)
- Emphasis on all borders

ICP Vegetation surveys in Bulgaria: Sampling map, 2005, N=213

Moss species: *Hypnum cupressiforme* (but also: *Abietinella abietina*, *Brachythecium rutabulum*)

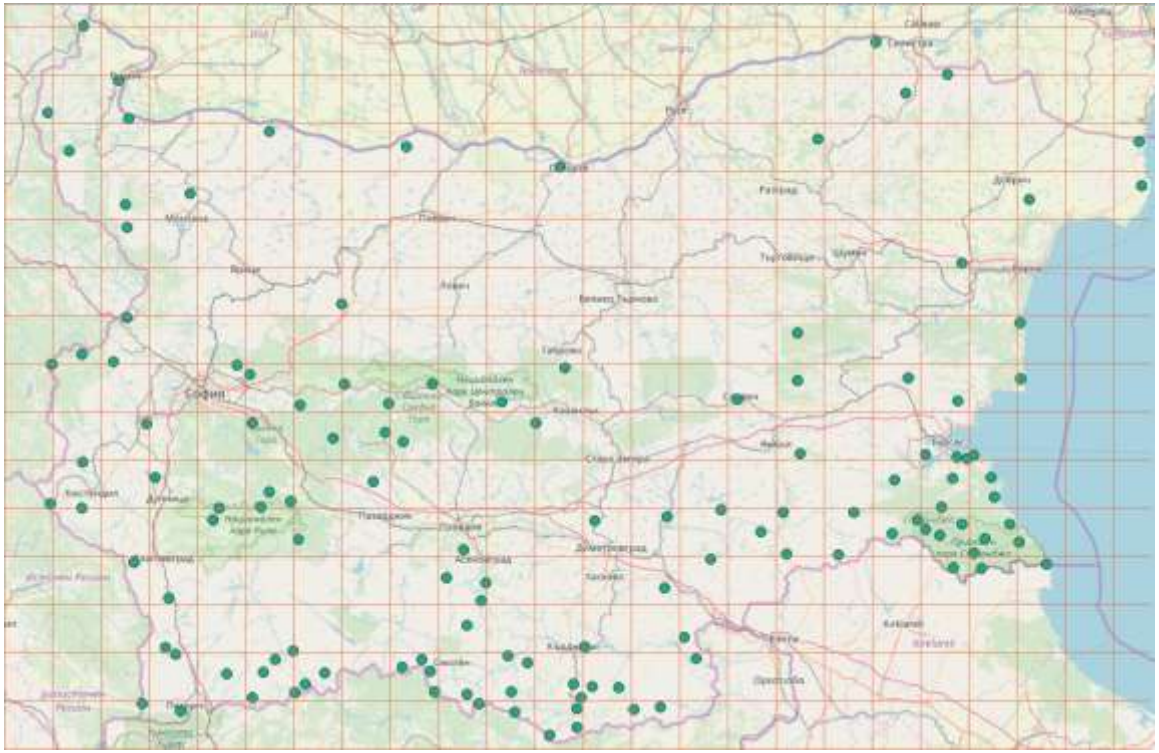


Non-uniform sampling networks:

- Fewer points remaining from the uniform design
- Sampling density increased near the southern borders:
  - Pb-Zn plant
  - Mineral deposits
  - Strandzha Narure park

ICP Vegetation surveys in Bulgaria: Sampling map, 2010, N=129

Moss species: *Hypnum cupressiforme* (but also: *Pseudoscleropodium purum*, *Brachythecium rutabulum*, *Abietinella abietina*, *Rhytidium rugosum*)

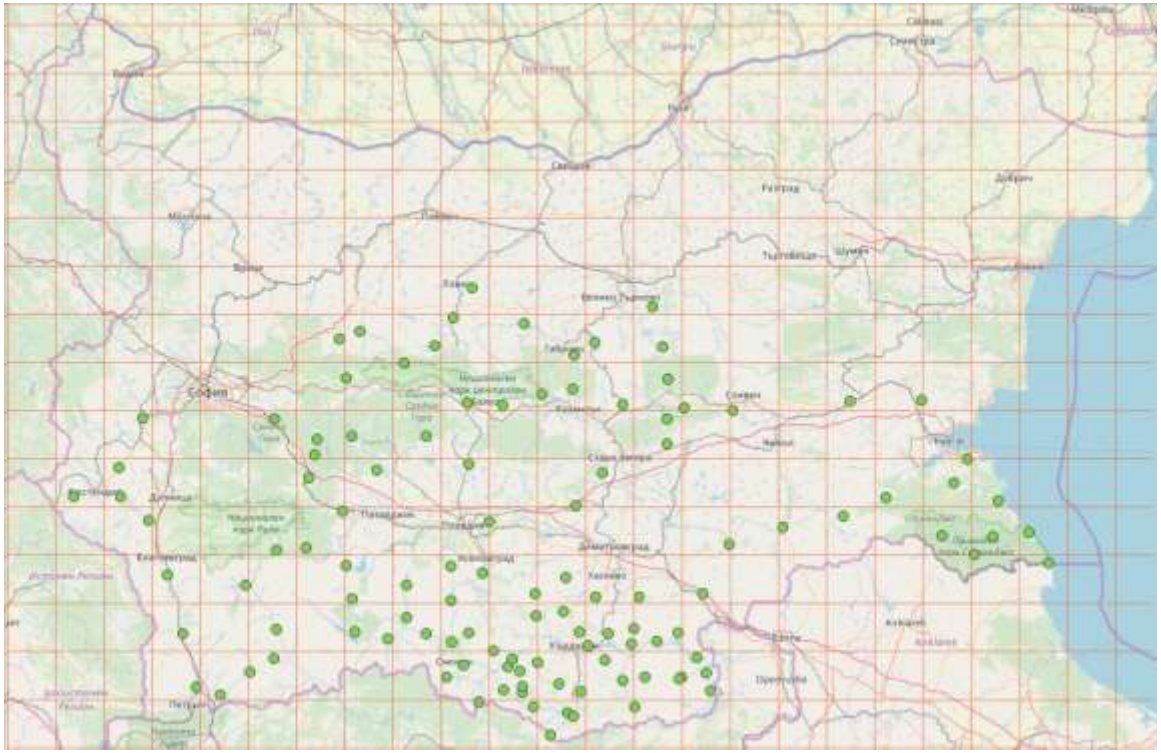


Non-uniform sampling networks:

- Even fewer points retained from the uniform design
- Emphasis only on borders, some nature parks, and some known “hotspost”
- Financial and time constraints

ICP Vegetation surveys in Bulgaria: Sampling map, 2015, N=115

Moss species: *Hypnum cupressiforme* (but also: *Pseudoscleropodium purum*, *Pleurozium schreberi*, *Abietinella abietina*)



Non-uniform sampling networks:

- No samples from the northern border
- Even fewer points from the uniform design + few samples from Nature parks
- Resembles the 2005 sampling network:
  - Increased sampling density near the southern borders

Previous publications: interpretation and discussion excerpts

FYROM, Greece are shown in **Table 2**. Bulgarian maximum concentrations in mosses indicated very high element

Pirdop; or Cd and Cu in Devnya district because of inorganic industry, whereas others showed elevated high content over a

Mountain.

✓ *Sampling in more polluted areas*

✓ Higher contribution of wind-blown dust from drier mineral soils

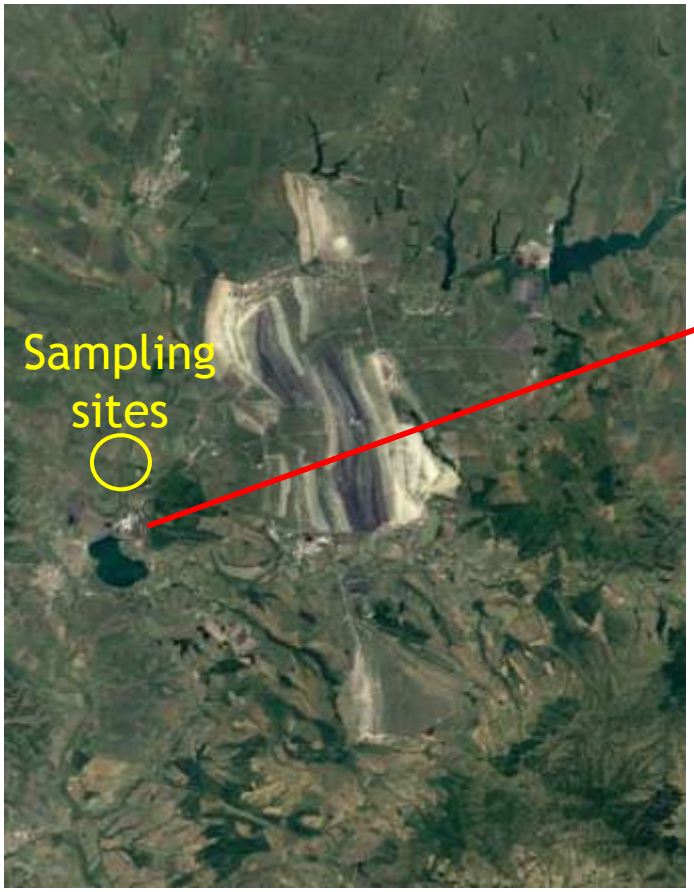
2000, 2003-2005) for the Bulgarian territory. The significant decreasing trend of the element content of As, Cu, V, Zn, Cd and Pb, in most of the European countries involved in the last moss surveys (5), was not proved in the Bulgarian area due to

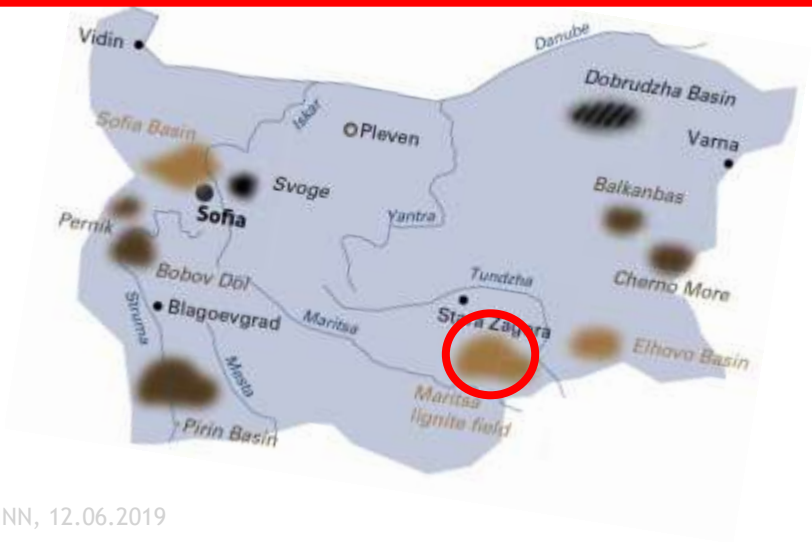
However, all analyzed elements in *Hypnum cupressiforme* showed a small decline in time, the bigger decline between 2000 and 2005 (19).

✓ High anthropogenic emissions (coal combustion)

Considering heavy metal atmospheric deposition in the Balkans specific geographical distribution patterns of several elements are evident. The highest median value for

Maps: Sampling at hotspots: 4 km away from the largest mining site in South East Europe & 4 lignite coal-fired thermal power plants around

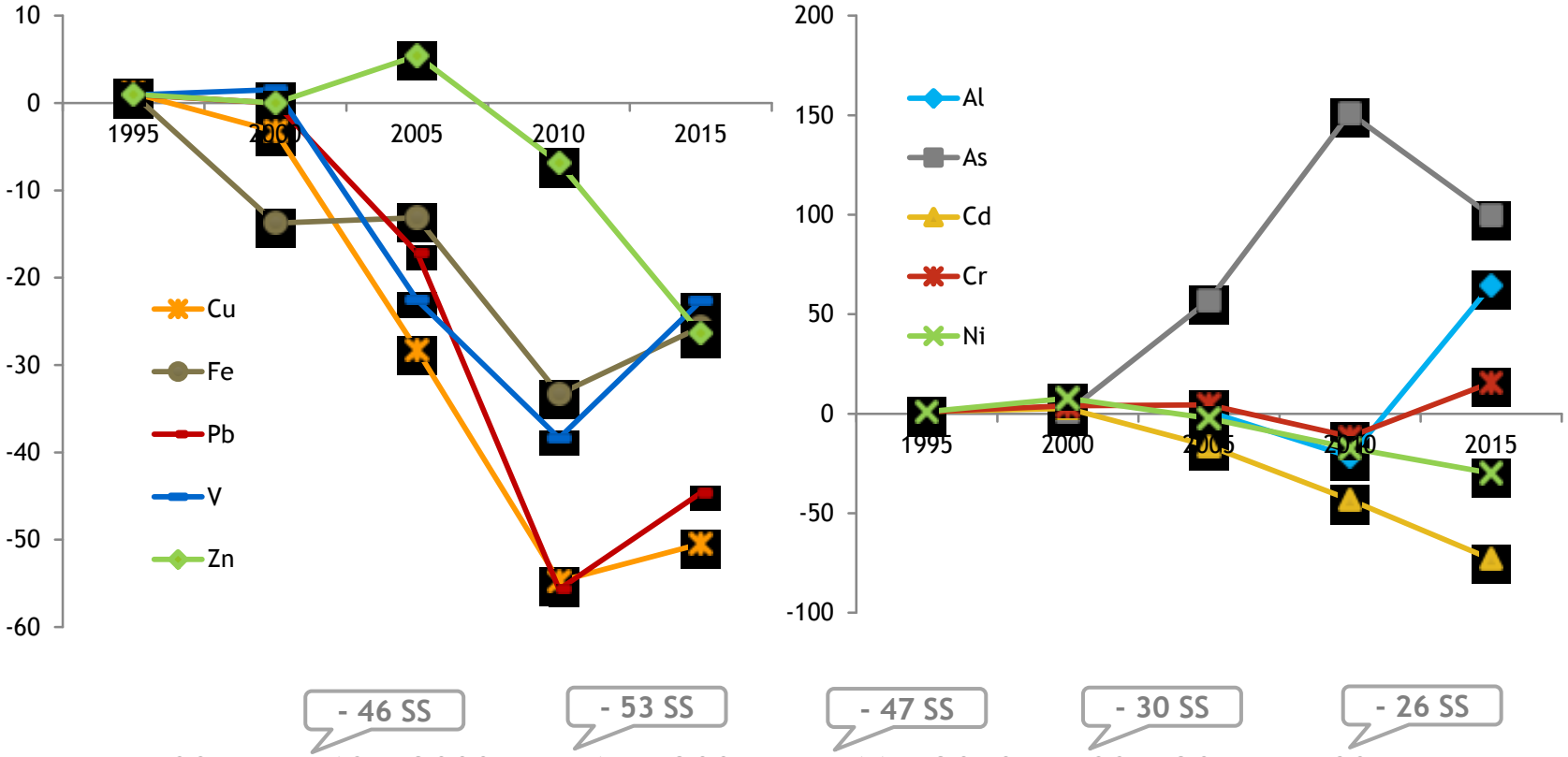




Sample but do not report to the ICP Vegetation? Worst example but not an isolated case.

Excluding sites near known hotspots, trends:

Relative difference [%]: relative to the median concentrations in 1995:

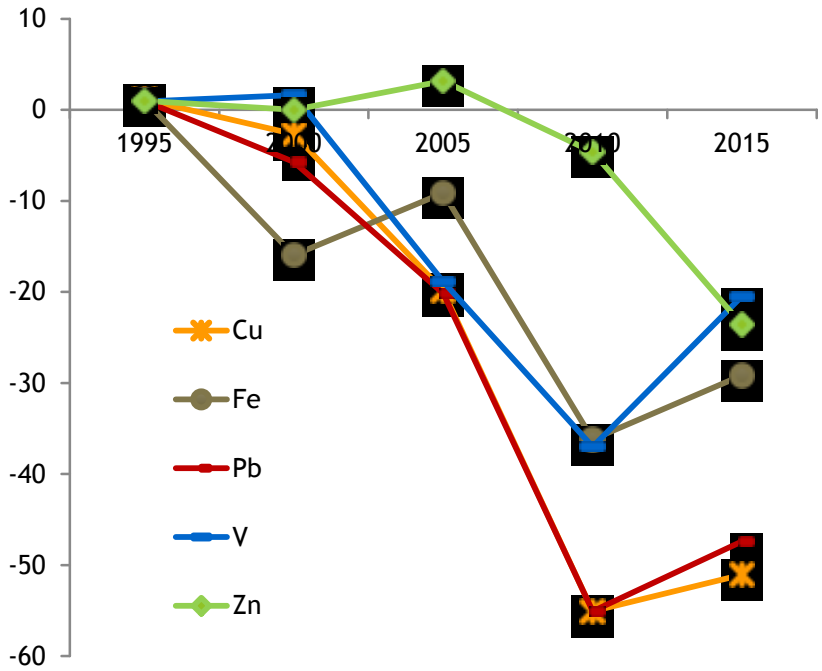


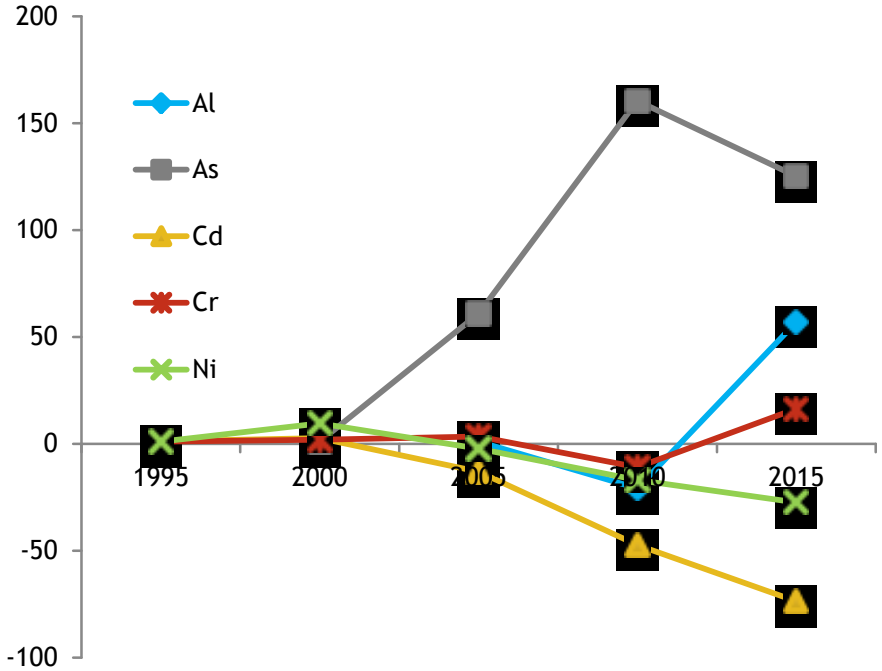
1995 (N=169), 2000 (N=164), 2005 (N=166), 2010 (N=99), 2015 (N=89)

In 2005: Zn median values increased, As follows the same trend.

Excluding sites close to known hotspots, and averaging concentrations from samples within 30x30 km grid, trends:

Relative difference [%]: relative to the median concentrations in 1995:





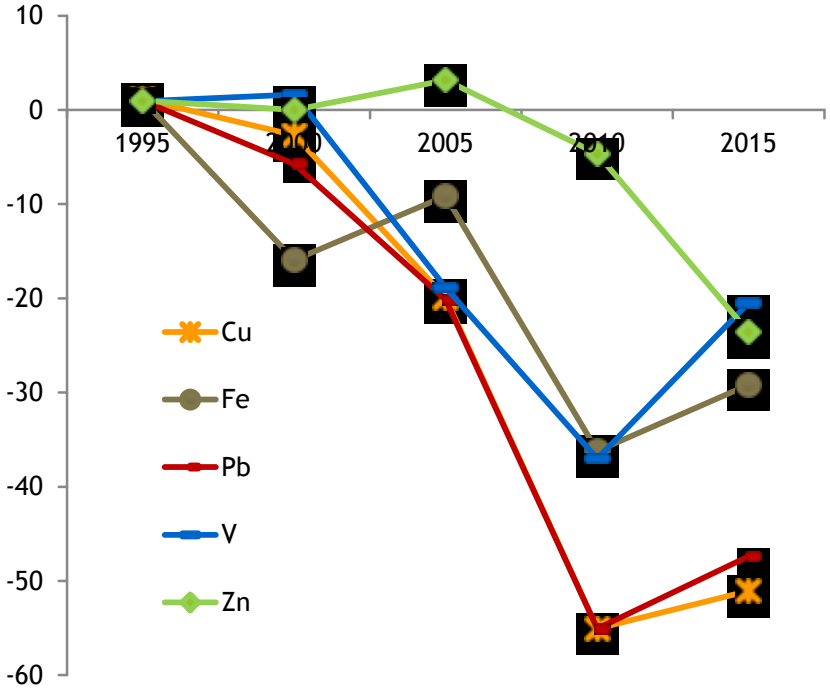
- 109 SS | - 119 SS | - 117 SS | - 69 SS | - 60 SS

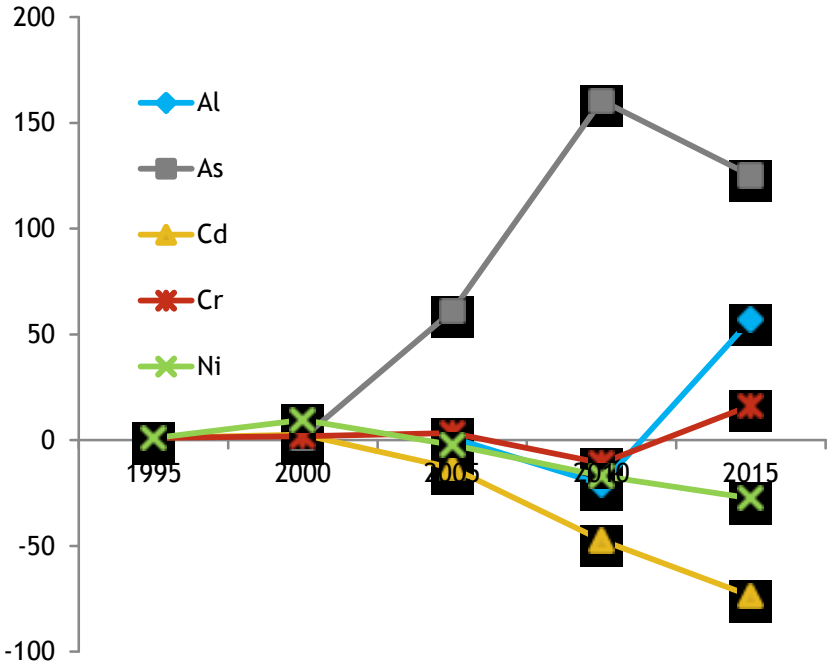
1995 (N=106), 2000 (N=98), 2005 (N=96), 2010 (N=60), 2015 (N=55)

Minimization: combining all collected samples to decrease cost for analyses.

Excluding sites close to known hotspots, filtering just for resampled sites from 1995 to 2015. Trends:

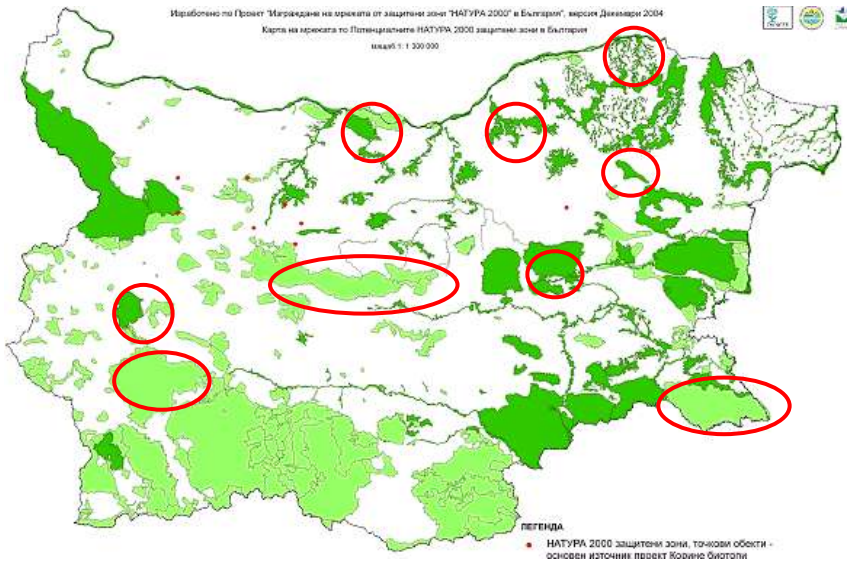
Relative difference [%]: relative to the median concentrations in 1995:

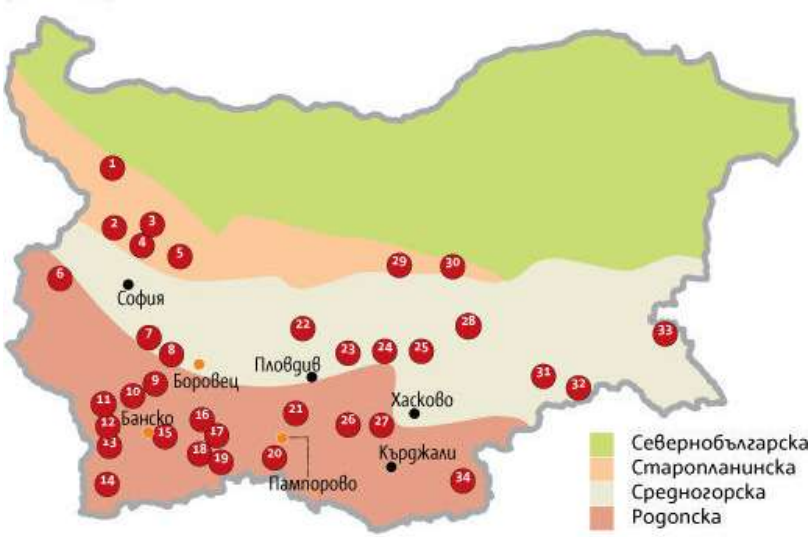




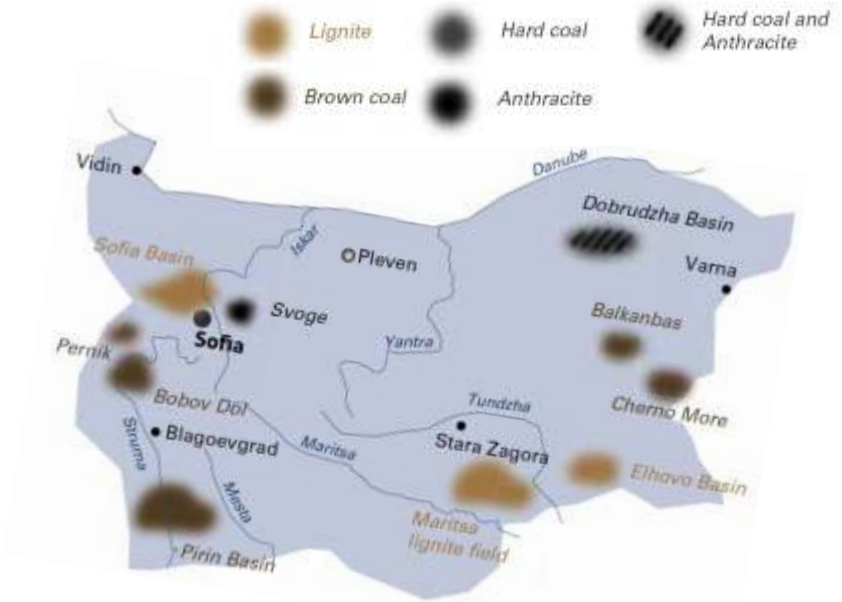
N= 42, very few samples in North Bulgaria. Same trends!

Maps: State monitoring stations, Protected Habitats, Mineral and non-mineral resources. Background?





- State monitoring stations: near roads, on the periphery of protected areas
- Protected habitats: mineral and non-mineral deposits, proximity to the Black Sea, high altitudes,
- Historical and present day mining



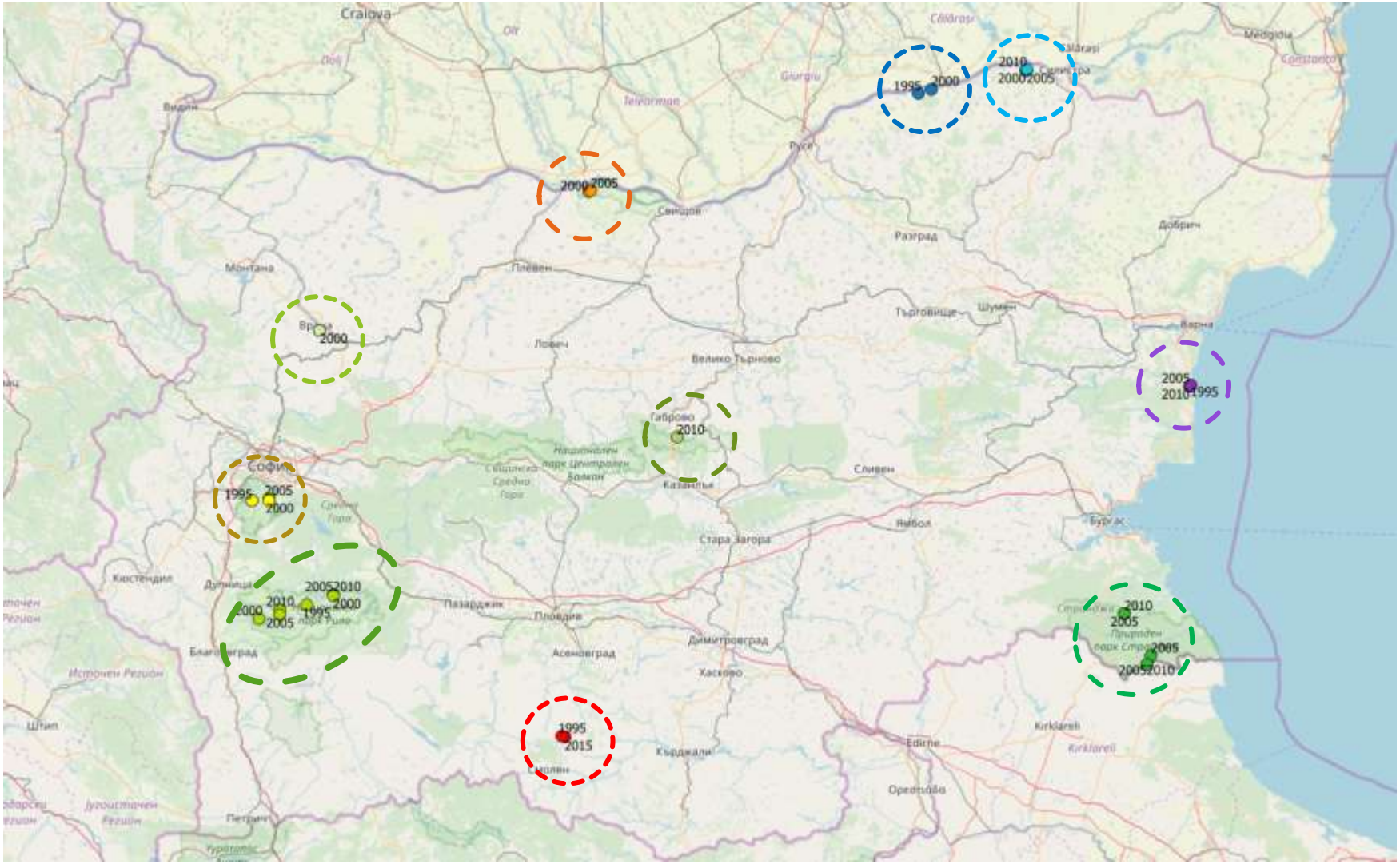
Maps: Sampling in presumably “ecologically clean” areas yet near sources of contamination - 3 examples: 1995, 2000, 2005 surveys

a) **‘95:** in <u>Kalimok-Brashlen protected habitat</u>;
’00: on the banks of the Danube River,
‘05: in the town of Tutrakan

b) **’95 and ’00:** in villa zone,
’10 near a military weapons testing area

c) **‘95:** Between a town and a <u>nature park</u>,
‘00 and ’05: near railroad and an aerodrome

Nature parks and reserves in Bulgaria: Sampling points (1995-2005) for background values estimation



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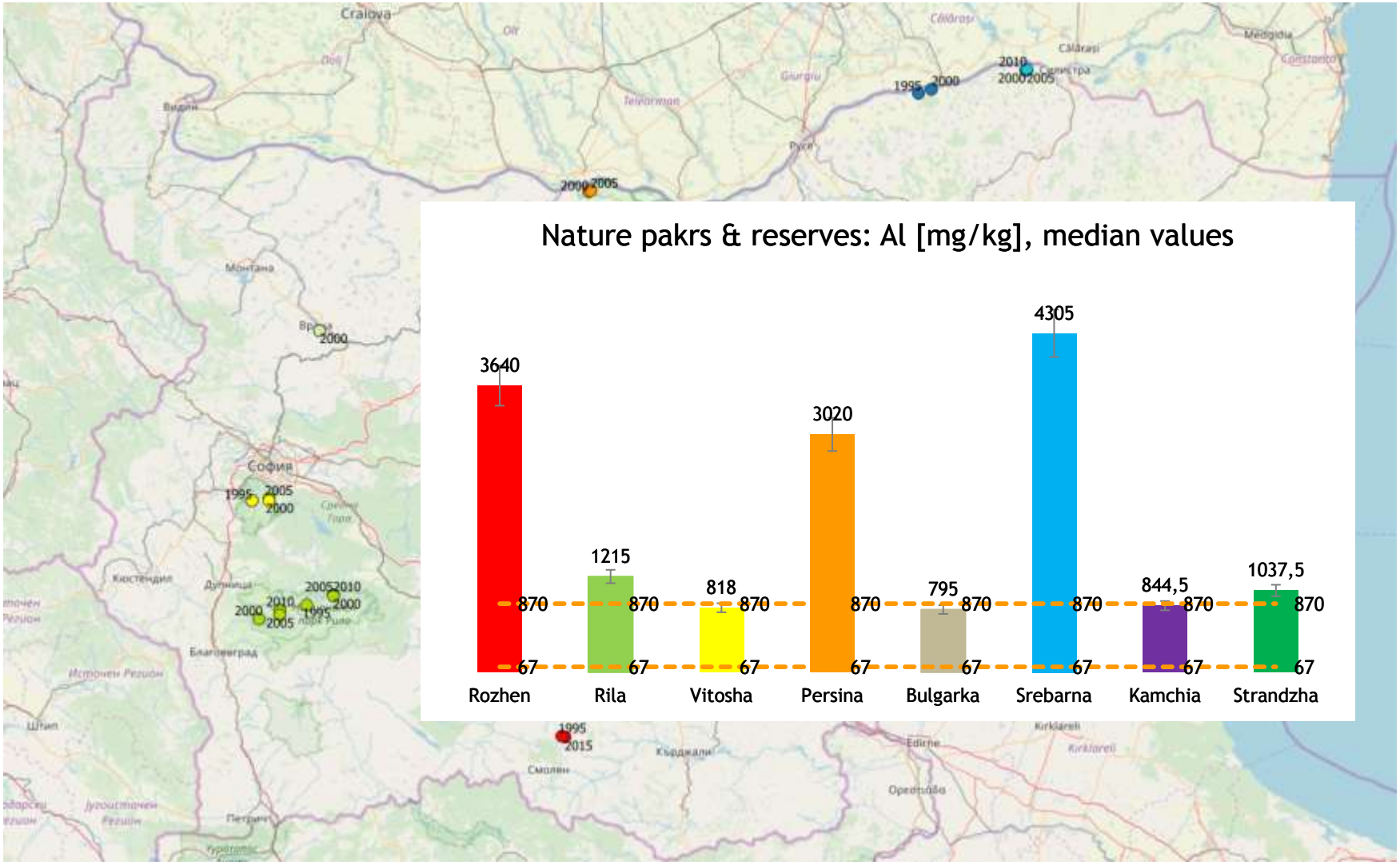

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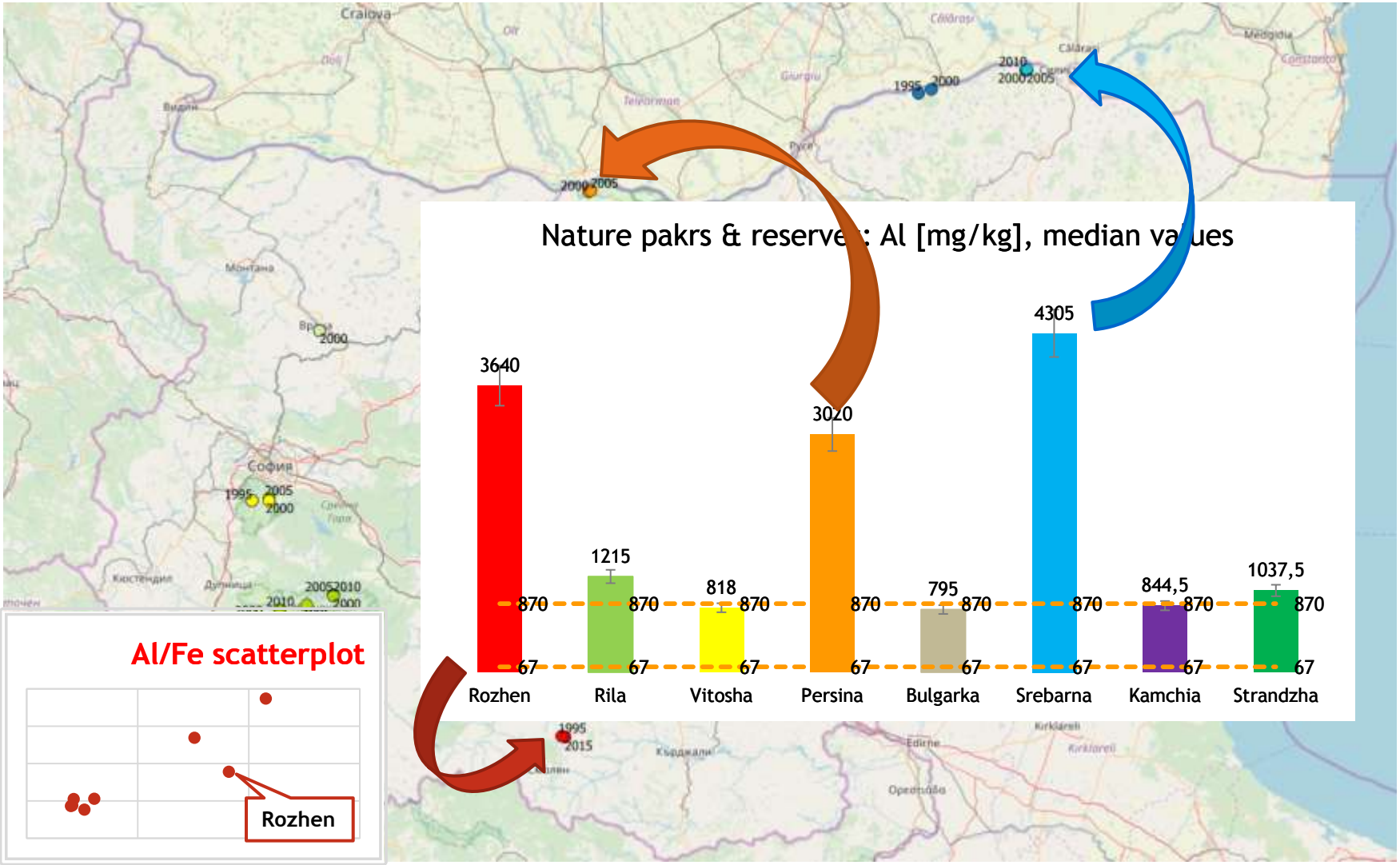

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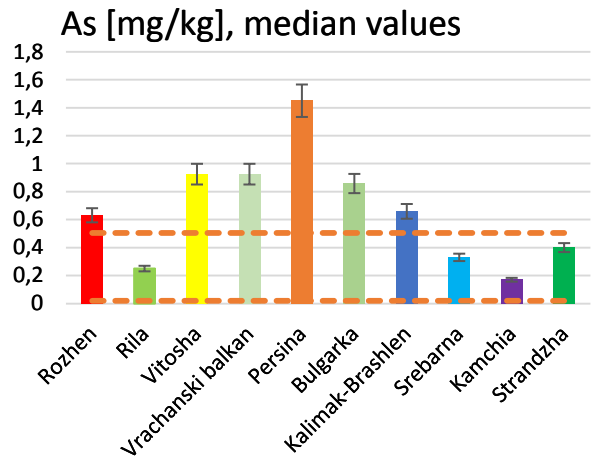
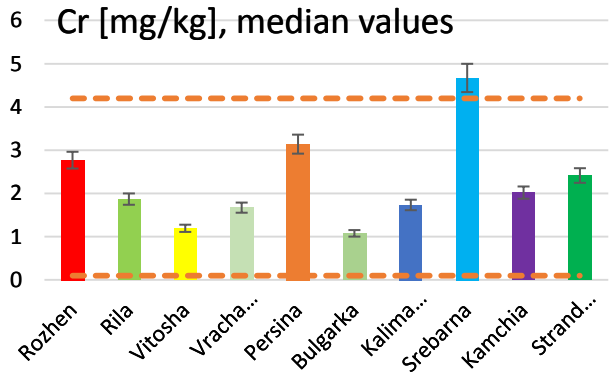
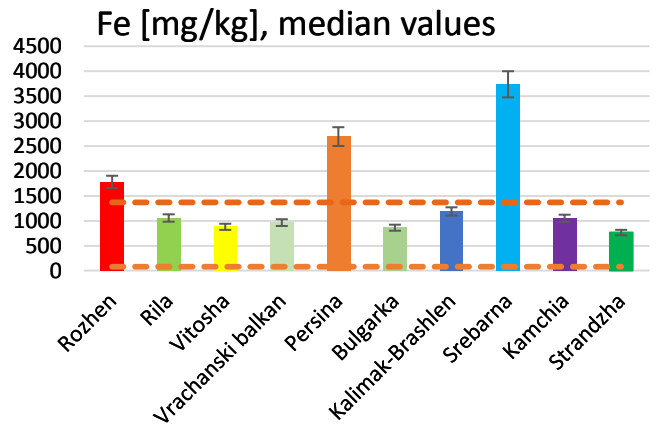
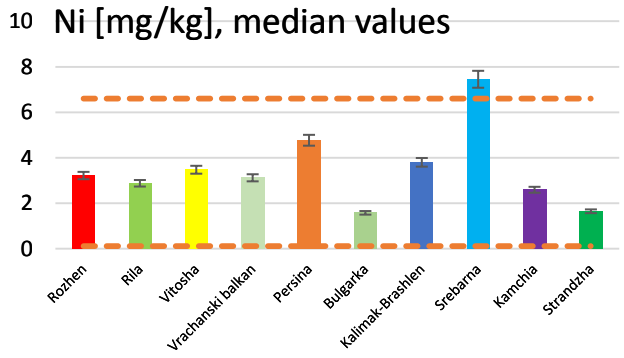
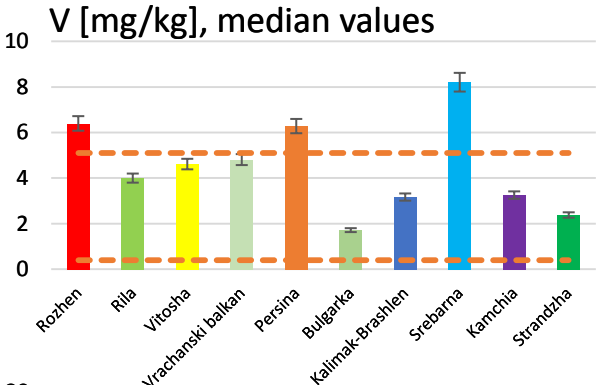
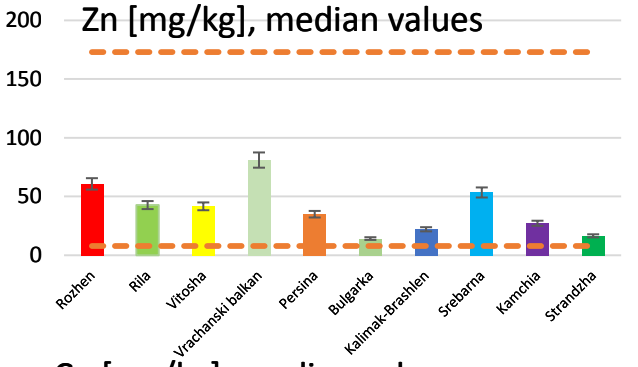


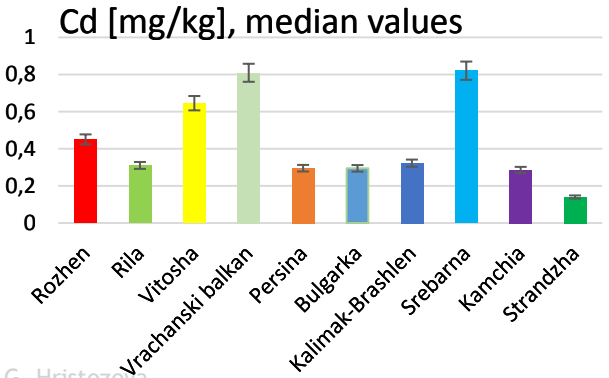


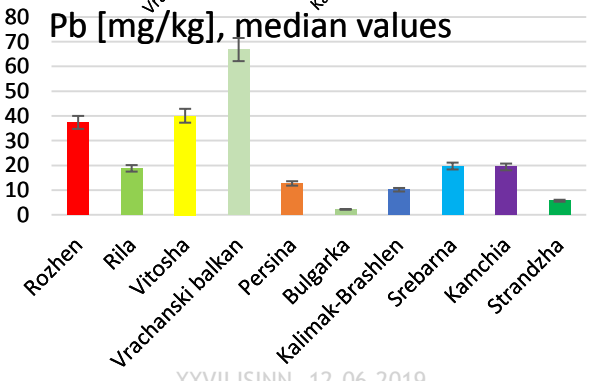


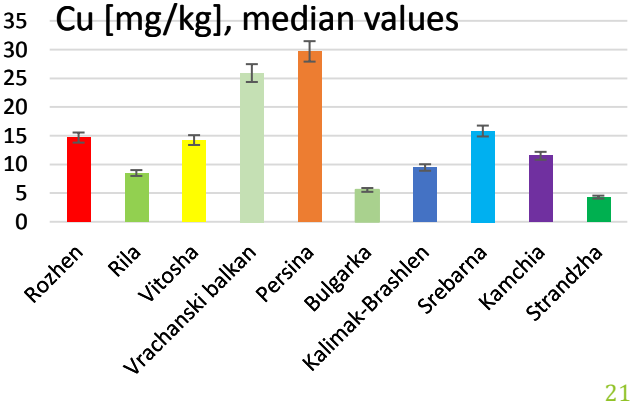




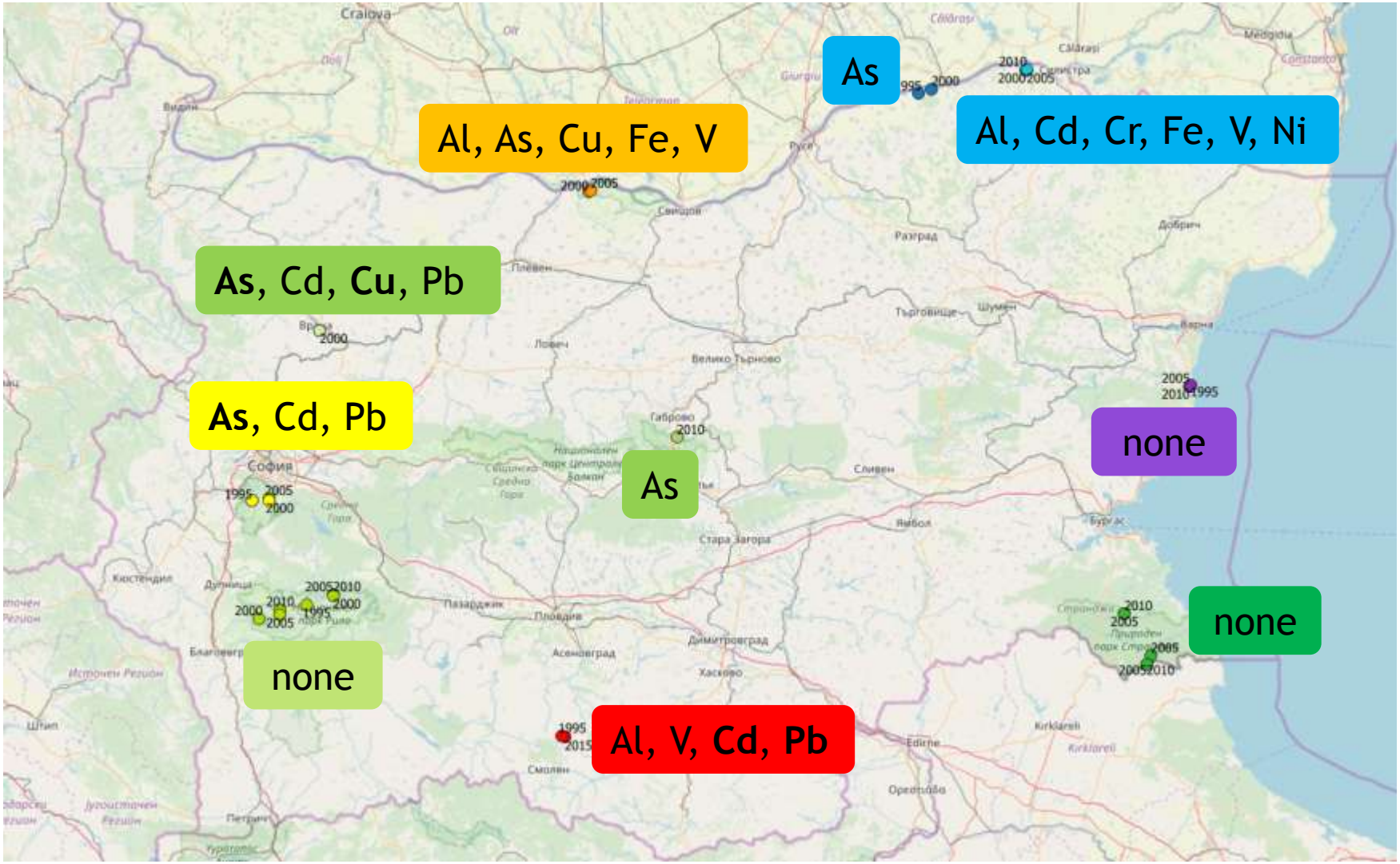








Nature parks and reserves in Bulgaria: Sampling points (1995-2005) for background values estimation



Conclusions

Between 1995 and 2010, for Bulgaria, there was an observation that, in general, **concentrations of metals** deposited from the atmosphere had **steadily decreased by about 30%.** The most recent survey data **does not show continuation of that trend for all elements reported**.

However, the **sampling networks** were **inconsistent** through the 20-year period of participation in the ICP Vegetation European moss survey.

Based entirely **on location criteria**, the datasets from 1995 to 2015 were adjusted to **exclude sites near known sources of pollution**. Then, a grid of 30×30 km was used to further **minimize** the number of sampling sites. For each square of the grid, the concentrations of metals determined in multiple sampling sites were averaged (**treated as if they were subsamples**) or discarded (**as if they had not been collected**).

Conclusions

The resulting datasets were used to show **trends which would have been reported for the ICP Vegetation programme**, were the sampling networks **consistent in time and designed to avoid known local sources of contamination**.

Non-parametic U-test was used to show that the difference in the medians obtained were not significant, **except for the element Zn**. Therefore, **the sampling design alone was not a factor contributing to the east-west gradient for metals in Europe**. Median values prove to be very robust, as they were "unaffected" by the aggressive removal of outliers.

Having in mind the financial and time constraints, and the difficulty of finding living plants from appropriate species, this overview and attempt at optimization based on location criteria should be taken into consideration **for the 2020/21 moss survey in Bulgaria**.


Thank you for your attention!