Bioindication of heavy metals atmospheric depositions in Romania

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Moss biomonitoring technique

Using mosses to measure atmospheric heavy metal deposition

Mosses obtain most trace elements and nutrients directly from precipitation and dry deposition; there is little uptake of metals from the substrate.

Moss survey

Provide an indication of the deposition of heavy metals away from pollution sources, primarily in rural areas

Moss survey

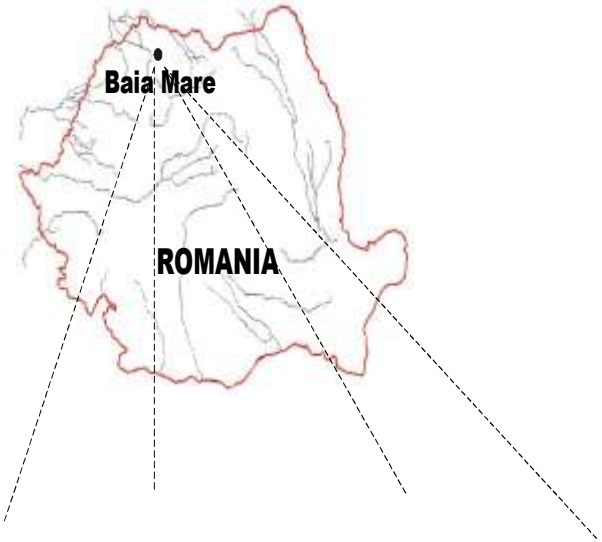
Provide the contribution of long-range transport to heavy metal deposition to vegetation

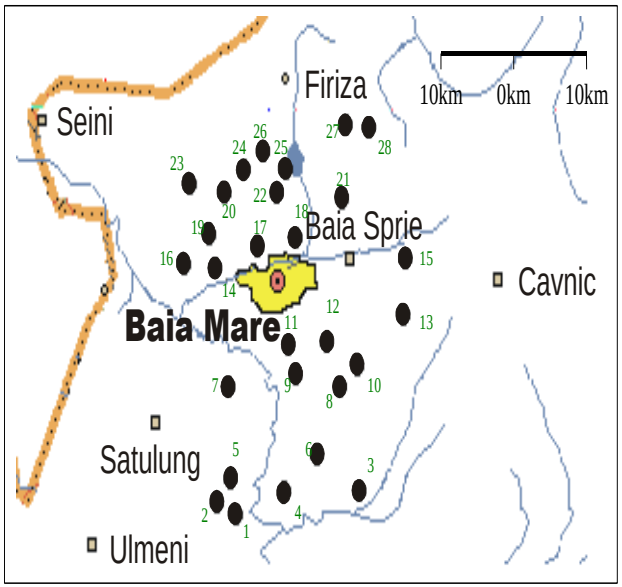
- **The heavy metals in mosses biomonitoring network was originally established in 1980 as a Swedish initiative and has, since then, been repeated at five-yearly intervals;**

- **The first moss survey at the European scale was conducted in 1990 and since then the number of participating countries has greatly expanded.**

- **During 2001, responsibility for the coordination of the survey was handed over to the ICP Vegetation Programme Coordination Centre at the Centre for Ecology and Hydrology (CEH) Bangor, UK (http://icpvegetation.ceh.ac.uk)**

- **From January, 2014, the coordination of the European moss survey was transfer from the ICP Vegetation Coordination Centre at CEH Bangor, UK, to the Joint Institute for Nuclear Research (lead coordinator: Marina Frontasyeva), Dubna, Russian Federation (www.jinr.ru)**

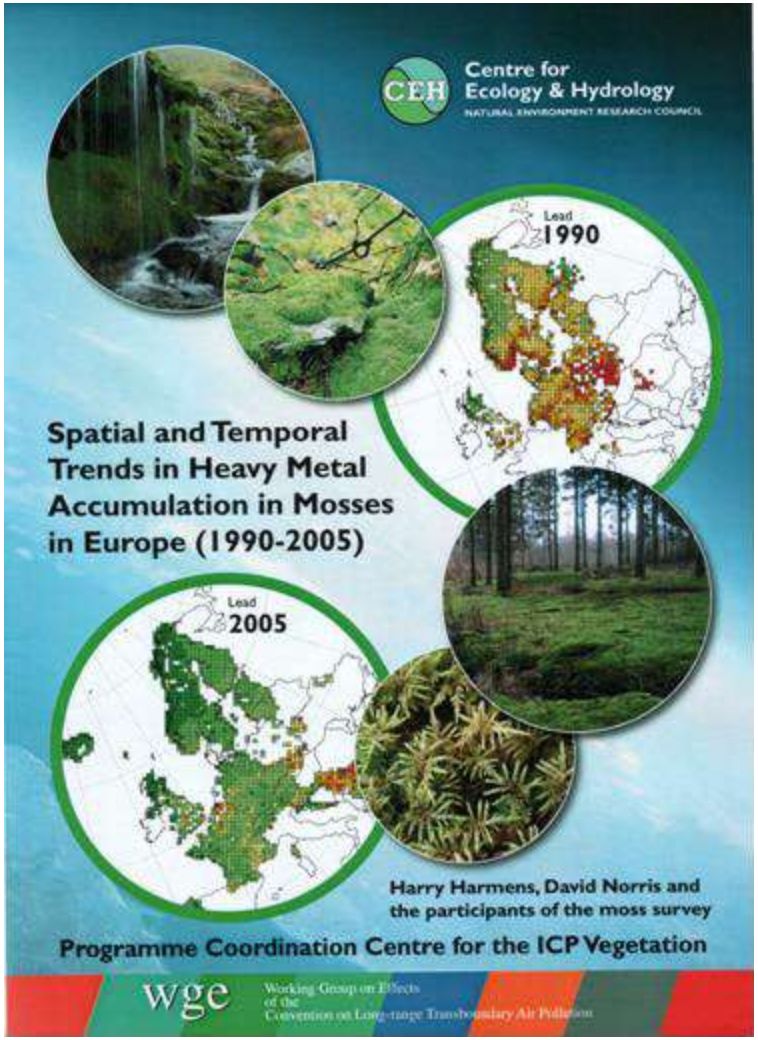




- **In Romania (only in north part of Romania) the first systematic study of atmospheric pollution from heavy metals and other toxic elements based on moss analysis was undertaken as a Romanian–Russian–Norwegian collaboration, in in the period 1995–2001**

(Lucaciu, A., Timofte, L., Culicov, O., Frontasyeva, M.V., Oprea, C., Cucu-Man, S., Mocanu, R., Steinnes, E. (2004), Atmospheric deposition of trace elements in Romania studied by the moss biomonitoring technique, Journal of Atmospheric Chemistry 49: 533–548)

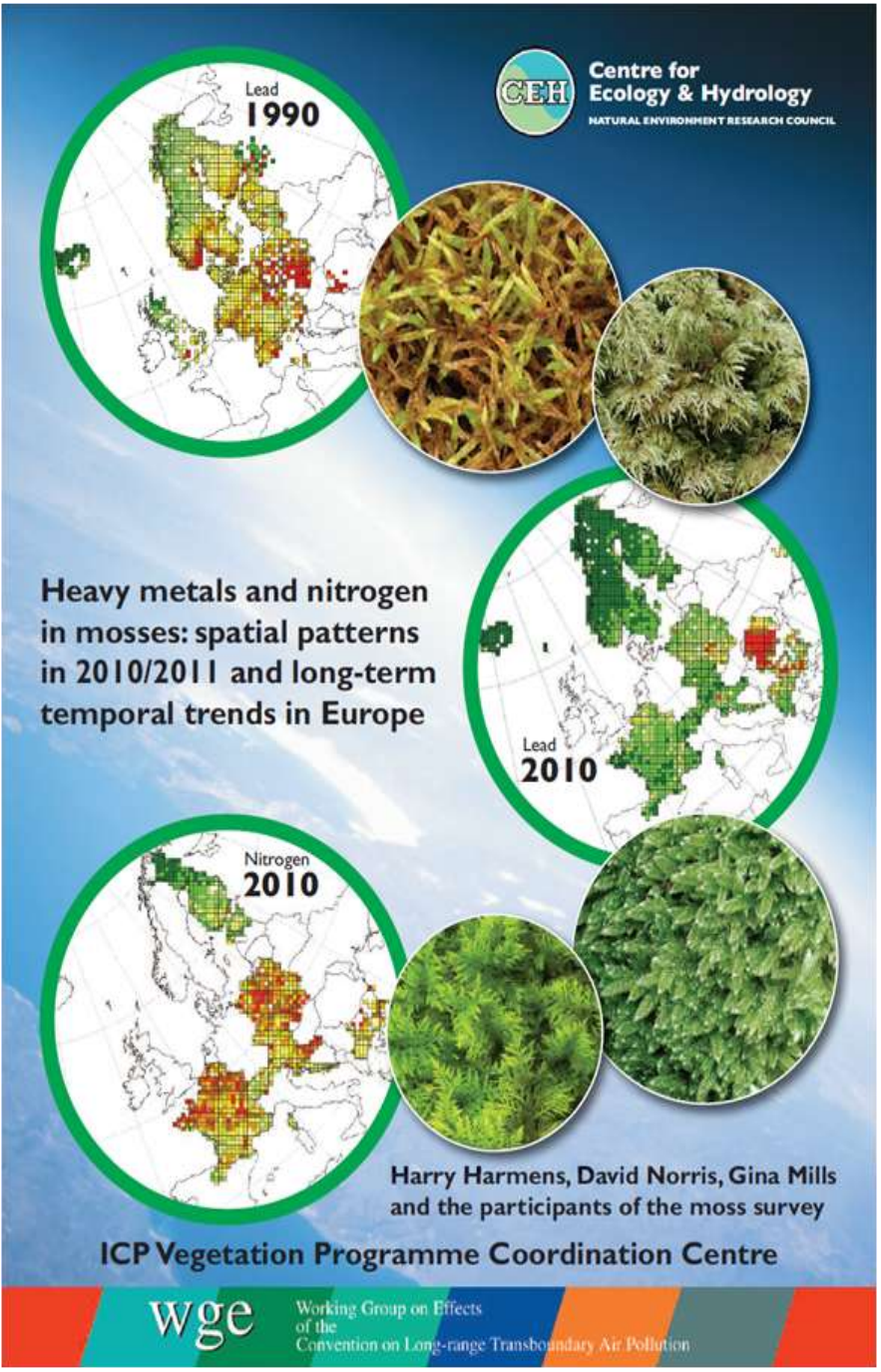
Moss survey in Romania 1995-2001



• The results on moss samples collected in different points of Romania in 1990, 1995 and 2000 were unified and reported by Harmens et al.

(Harmens, H., Norris, D. & the participants of the moss survey (2008), Spatial and temporal trends in heavy metal accumulation in mosses in Europe (1990-2005). Programme Coordination Centre for the ICP Vegetation, Centre for Ecology and Hydrology, Bangor, UK**.;** http://icpvegetation.ceh.ac.uk/publications/documents/ICPVegetationannualreport2008-09WEBversion_000.pdf)

•Romania did not submit data for the 2005/6 European moss survey.

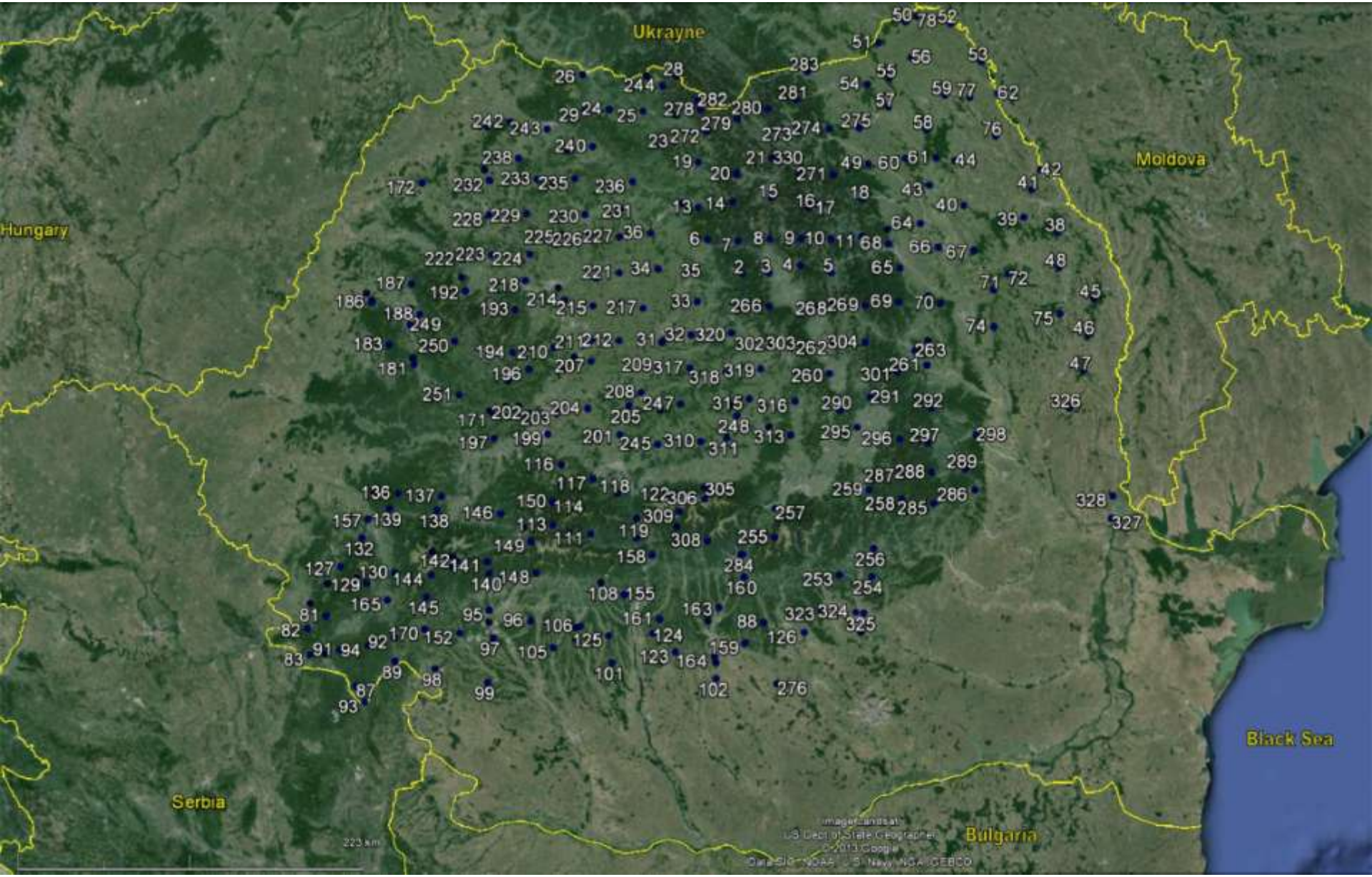


Romania took part in the 2010/2011 European moss survey and reporting data from 330 sampling sites evenly distributed over 75% of the Romanian territory

http://icpvegetation.ceh.ac.uk/publications/documents/Finalmossreport2010-11forweb.pdf

Harmens, H., Norris, D., Mills, G., and the participants of the moss survey (2013), Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe. ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK

Sampling points in 2005/2006 sampling campaign



Four Romanian universities was involved:

• *Valahia University of Targoviste* – coordinator

Leaders: Ion V. Popescu, Claudia Stihi, Cristiana Radulescu

ivpopes@yahoo.com, stihi@valahia.ro, radulescucristiana@yahoo.com

• *Dunarea de Jos University of Galati,* Leader: Antoaneta Ene, aene@ugal.ro

• *Alexandru Ioan Cuza University of Iasi* , Leader: Simona Cucu-Man, sman@uaic.ro

• *Technical University of Cluj-Napoca, North University Center, Baia Mare* , Leader : Radu Todoran, Todoran_radu@yahoo.com

Together with **Frank Laboratory of Neutron Physics–Joint Institute for Nuclear Research, Dubna, Russia** team

Leaders: Marina Frontasyeva and Otilia Culicov

The work was financially supported by bilateral project JINR-Romania: “Nuclear and related analytical techniques for Environmental and Life Sciences” , 2010- today

Moss survey 2010/2011-
Sampling and sample preparation:

- **Moss samples (*Pleurozium schreberi* - the most frequently sampled species, followed by *Hylocomium splendens, Hypnum cupressiforme* and other species (ca. 7 - 9%), were collected during August and September 2010 according to European moss surveys standardised protocol;**
- **The samples were cleaned but not subjected to any further washing and dried to constant weight for 24 hours at 45^0C ;**
- **Green and green-brown parts of the moss were sorted and prepared for analysis**

Moss survey 2010/2011-

Sampling and sample preparation:

1 sample =10 sub-samples

Moss survey 2010/2011-

Analytical Techniques

The elemental concentrations were determined in 2011-2012 using two complementary methods:

- Instrumental epithermal neutron activation analysis (INAA) at the IBR-2 reactor in Joint Institute for Nuclear Research at Dubna, Russian Federation

- Graphite furnace/flame atomic absorption spectrometry (GFAAS /FAAS) in the Multidisciplinary Research Institute for Science and Technologies from Valahia University of Targoviste, Romania

Moss survey 2010/2011-

Results and discussions

- A total of 34 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu*, Zn, As, Br, Rb, Sr, Cd*, Sb, Ba, Cs, La, Ce, Sm, Tb, Hf, Ta, W, Pb*, Th, and U) were determined in the large-scale concentration range — from 10000 mg/kg for Al and K to 0.001 mg/kg for some rare earths;

- Principal component (factor) analysis was used to identify the most polluted areas and characterize different pollution sources.

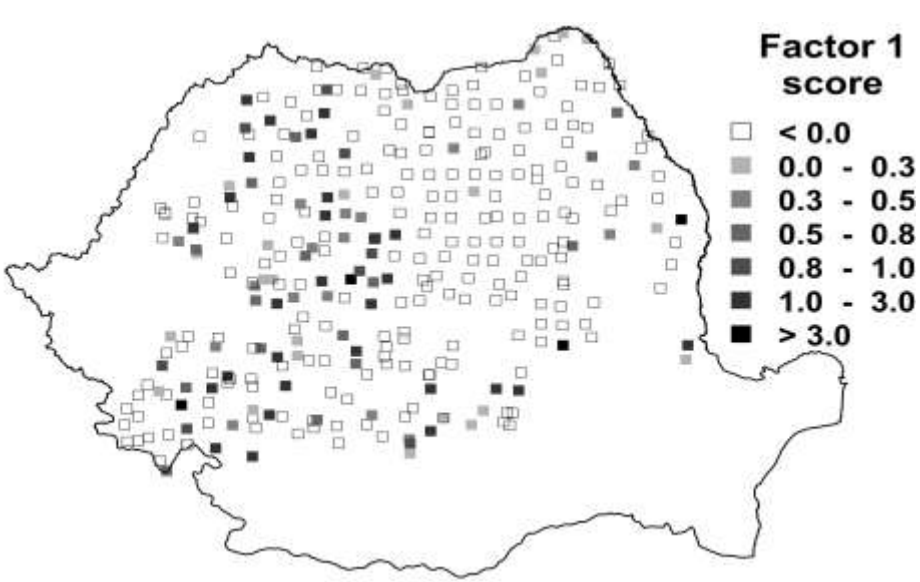
Principal component (factor) analysis

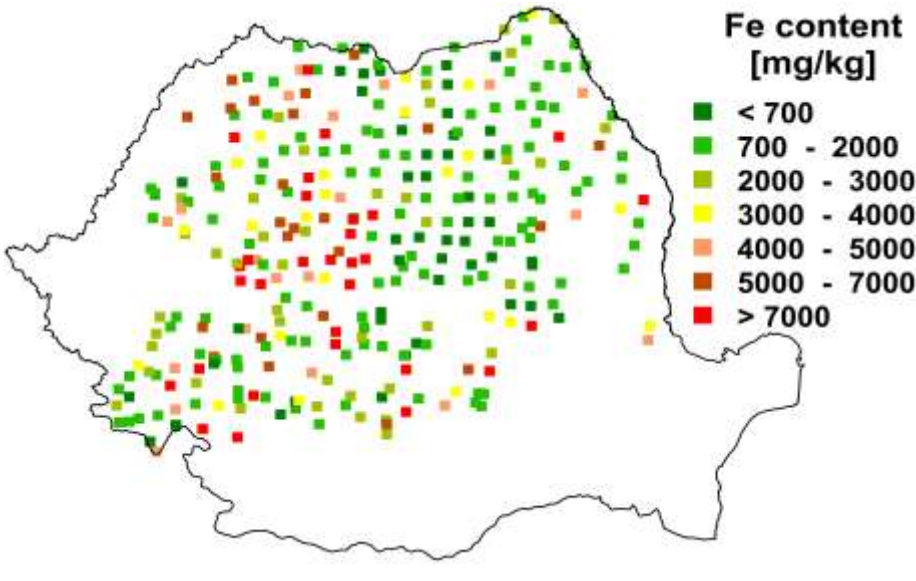
	Factor 1	Factor 2	Factor 3	Factor 4
Na	**0.81**	0.19	0.18	0.07
Mg	0.50	0.08	0.35	–0.15
Al	**0.80**	0.21	0.23	0.14
Cl	0.12	–0.05	**0.79**	–0.04
K	0.25	0.05	**0.57**	0.18
Ca	0.05	0.10	**0.78**	–0.04
Sc	**0.92**	0.15	0.15	0.18
Ti	**0.84**	0.16	0.19	0.08
V	**0.79**	0.19	0.23	0.15
Cr	**0.85**	0.26	0.16	0.18
Mn	0.32	0.08	0.03	–0.31
Fe	**0.90**	0.21	0.14	0.14
Ni	**0.85**	0.16	0.16	0.10
Co	**0.88**	0.15	0.12	0.09
Zn	0.09	**0.82**	0.07	0.05
As	0.24	**0.73**	–0.02	0.04
Br	0.06	–0.04	**0.62**	–0.07
Rb	0.56	0.01	–0.01	0.20
Sr	0.49	0.16	**0.45**	0.15
Sb	0.05	**0.92**	0.03	0.05
Ba	**0.76**	0.11	0.24	–0.15
Cs	0.42	–0.03	0.04	0.30
La	**0.96**	0.00	0.08	–0.02
Ce	**0.95**	–0.01	0.08	–0.01
Sm	**0.92**	–0.02	0.08	0.08
Tb	**0.97**	0.04	0.10	0.03
Hf	**0.92**	–0.02	0.04	–0.08
Ta	**0.97**	0.04	0.09	0.04
W	**0.77**	0.26	0.10	0.18
Th	**0.96**	0.00	0.08	0.03
U	**0.93**	–0.04	0.06	–0.06
Cd	0.09	0.06	0.00	**0.66**
Cu	0.10	–0.04	0.10	**0.64**
Pb	0.11	0.24	–0.15	**0.63**
Expl.Var	*16.16*	*2.57*	*2.71*	*1.80*
Prp.Totl	*0.48*	*0.08*	*0.08*	*0.05*

Moss survey 2010/2011-

Results and discussions

Factor 1 is a mixture of light and heavy crust components (Na, Al, Sc, Ti, V, Cr, Fe, Ni, Co, Ba, La, Ce, Sm, Tb, Hf, Ta, W, Th, U);



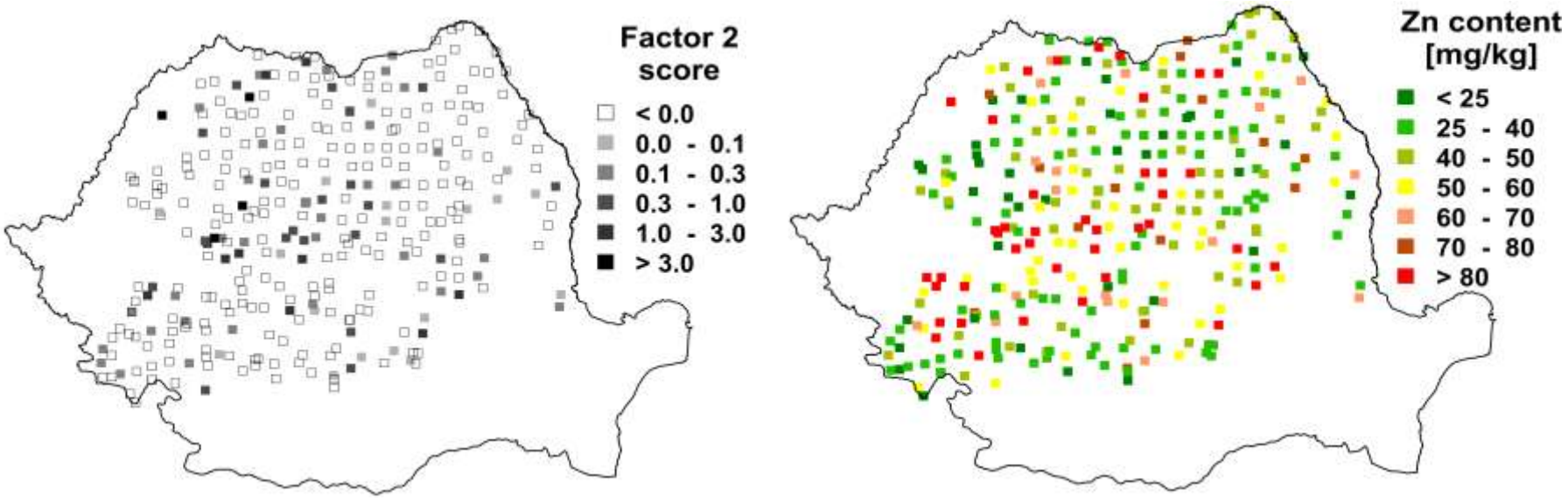


Spatial distribution of Fe and factor 1 based on elemental concentrations in mosses in Romania in 2010

Moss survey 2010/2011-

Results and discussions

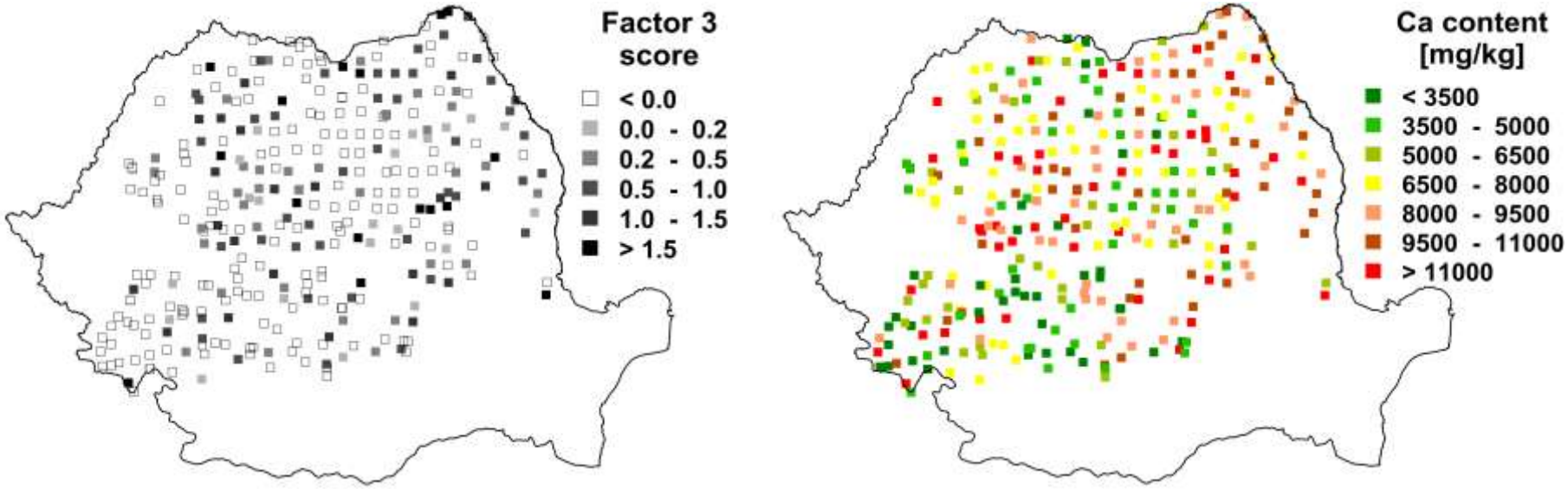
Factor 2 is of anthropogenic origin: Zn (0.82), As (0.73), Sb (0.92), the main contributors to this factor being mining and industrial sites from north-western part of the country;



Spatial distribution of Fe and factor 2 based on elemental concentrations in mosses in Romania in 2010

Moss survey 2010/2011-
Results and discussions

- **Factor 3** is a mixture of "marine elements" Cl (0.79) and Br (0.62); Ca (0.78), K (0.57) and Sr (0.45) may originate from fertilizer components — Sr most probably occurs from phosphate fertilizers in agricultural areas and Ca and K from saltpeter (niter) ones;

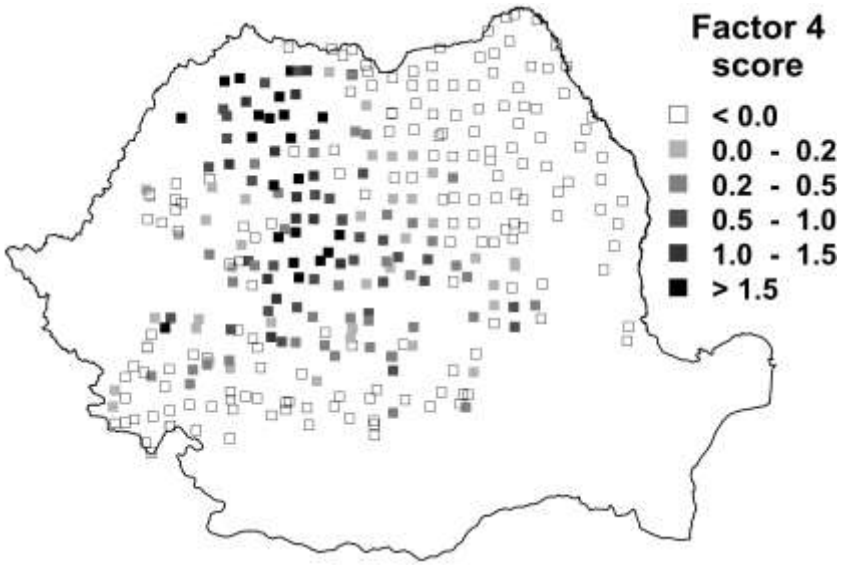


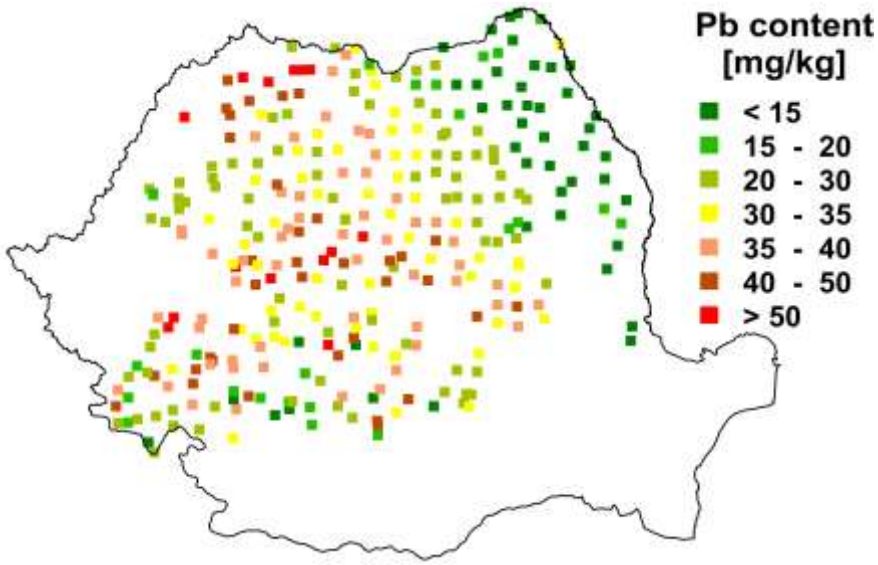
Spatial distribution of Ca and factor 3 based on elemental concentrations in mosses in Romania in 2010

Moss survey 2010/2011-

Results and discussions

Factor 4 comprises Pb (0.63), Cd (0.66), Cu (0.64) which can originate from gasoline or copper mining industry**.**





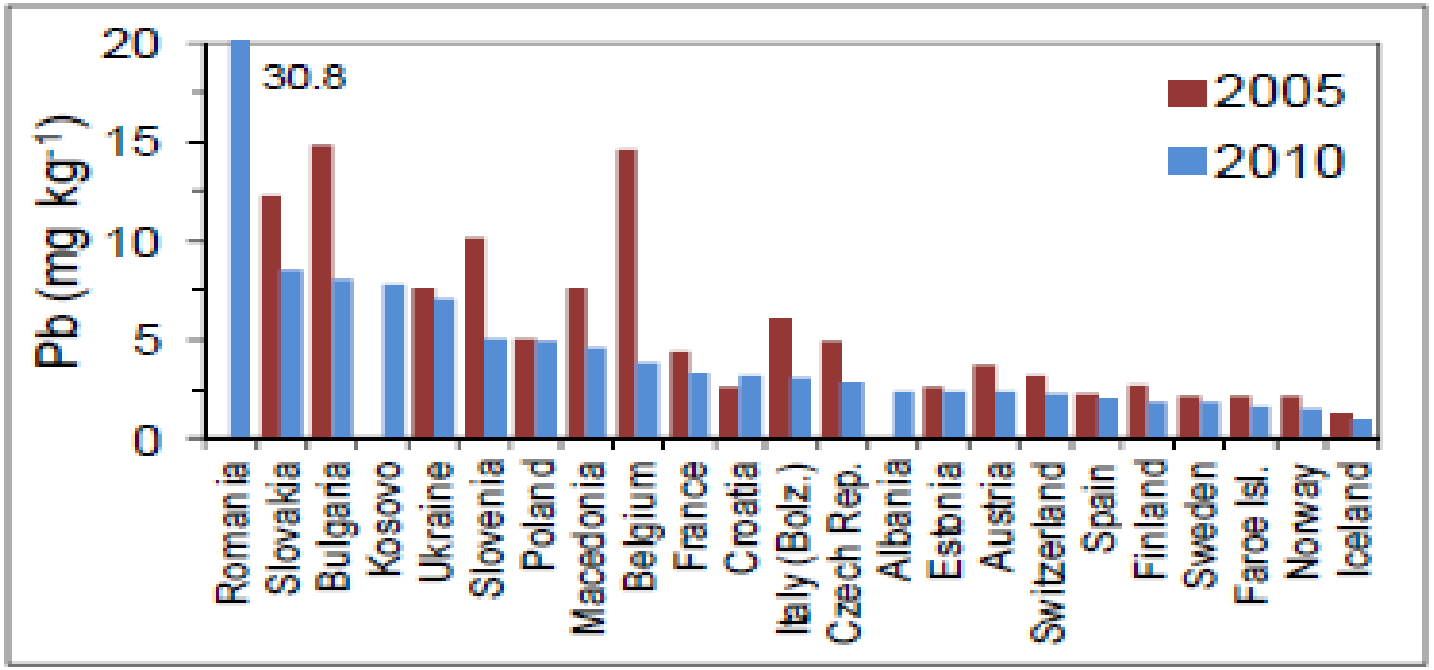
Spatial distribution of Pb and factor 4 based on elemental concentrations

Moss survey 2010/2011-

Results and discussions

The concentrations of heavy metals in mosses collected in Romania are high compared to other European countries (Harmens et al., 2013)

Median Pb concentrations in 2005 and 2010 in European space

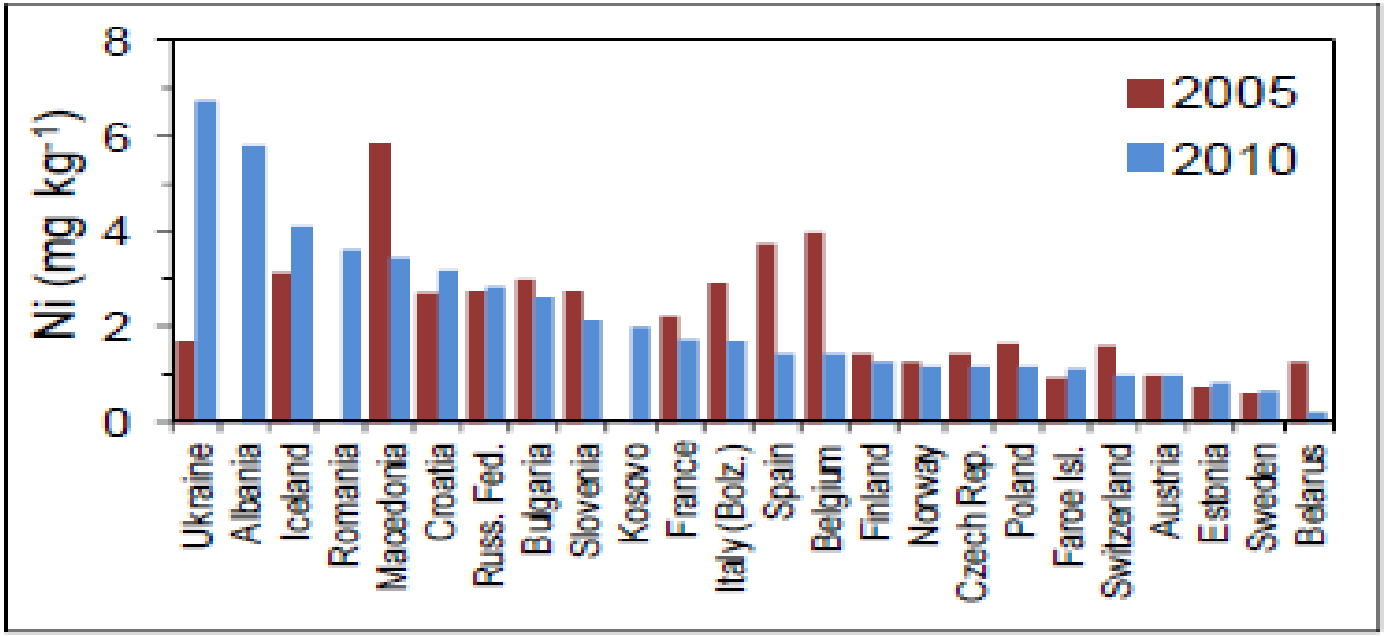


Moss survey 2010/2011-

Results and discussions

The concentrations of heavy metals in mosses collected in Romania are high compared to other European countries (Harmens et al., 2013)

Median Ni concentrations in 2005 and 2010

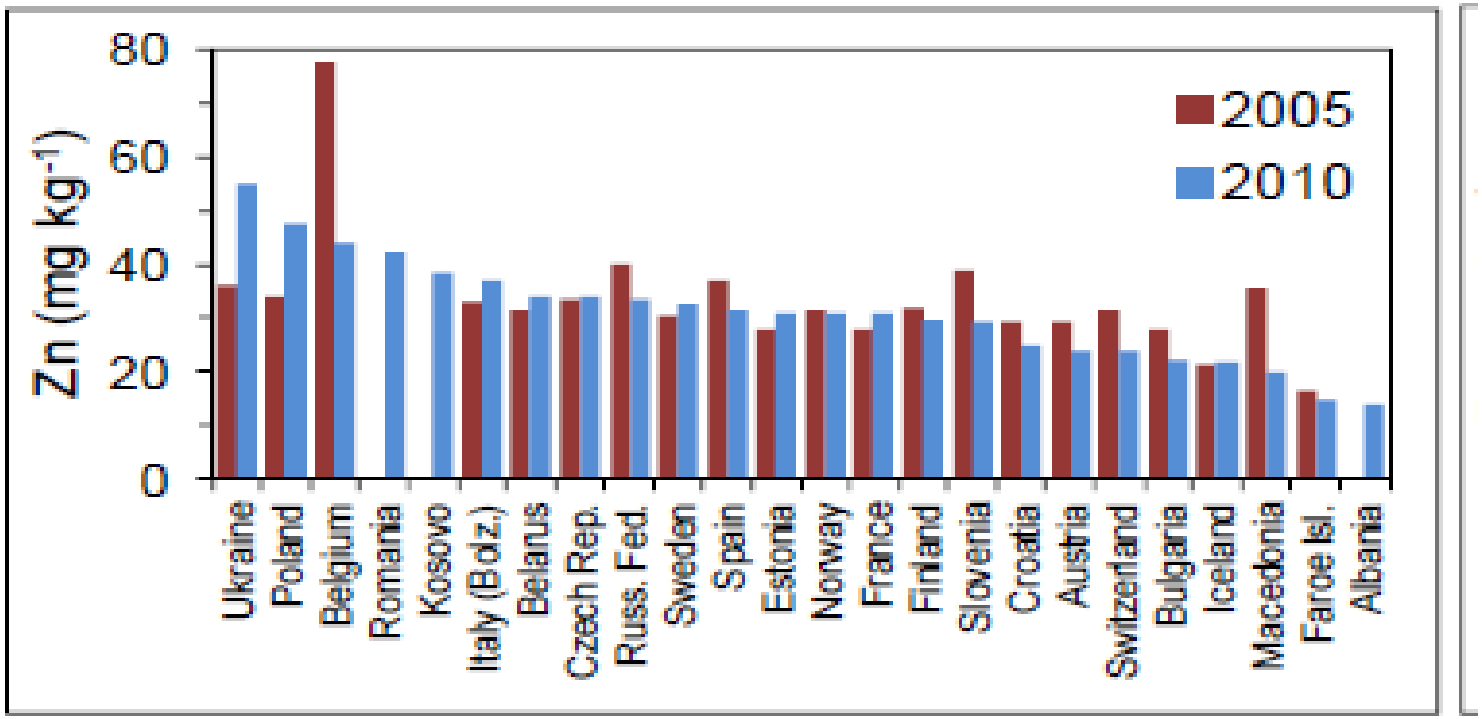


Moss survey 2010/2011-

Results and discussions

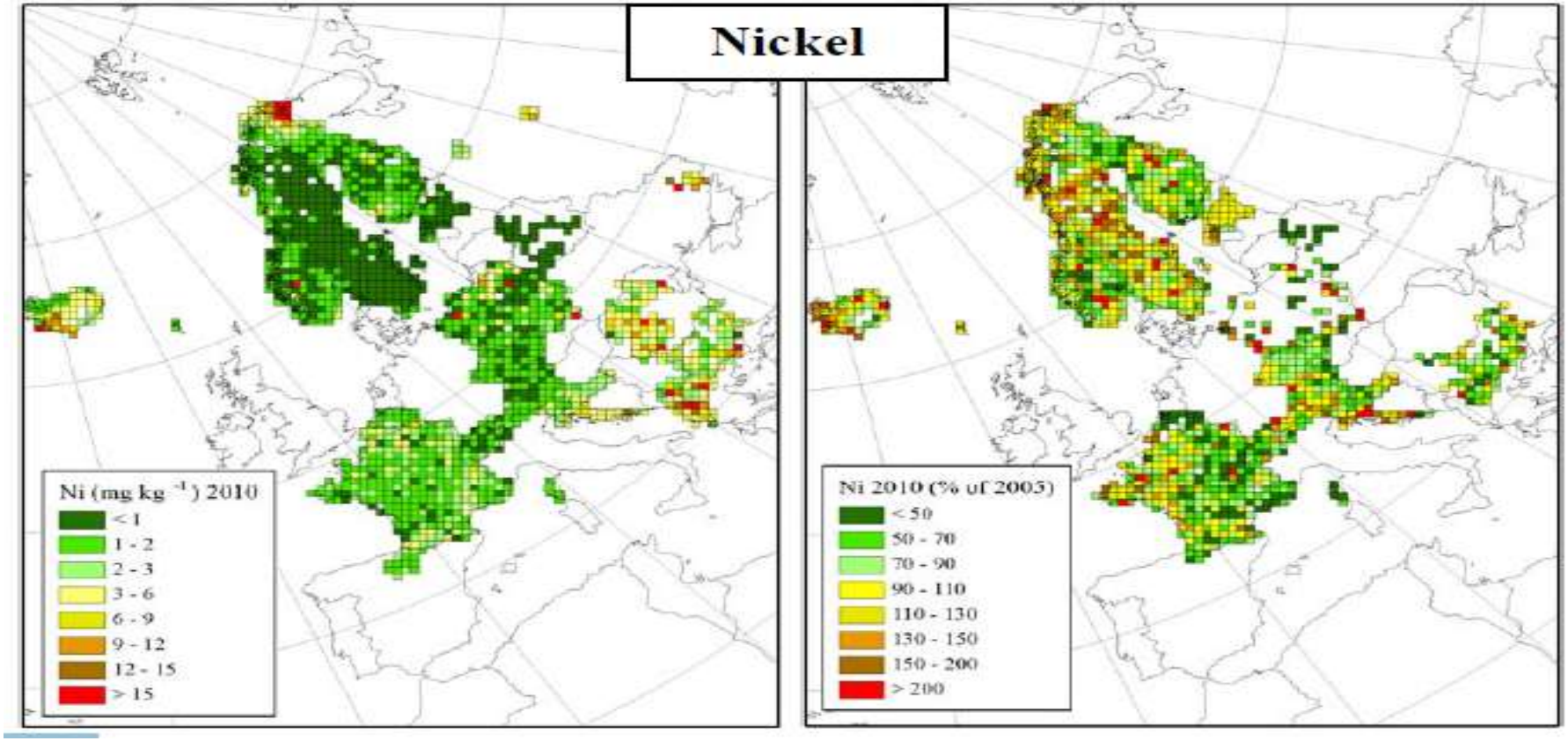
The concentrations of heavy metals in mosses collected in Romania are high compared to other European countries (Harmens et al., 2013)

Median Znconcentrations in 2005 and 2010



Moss survey 2010/2011-

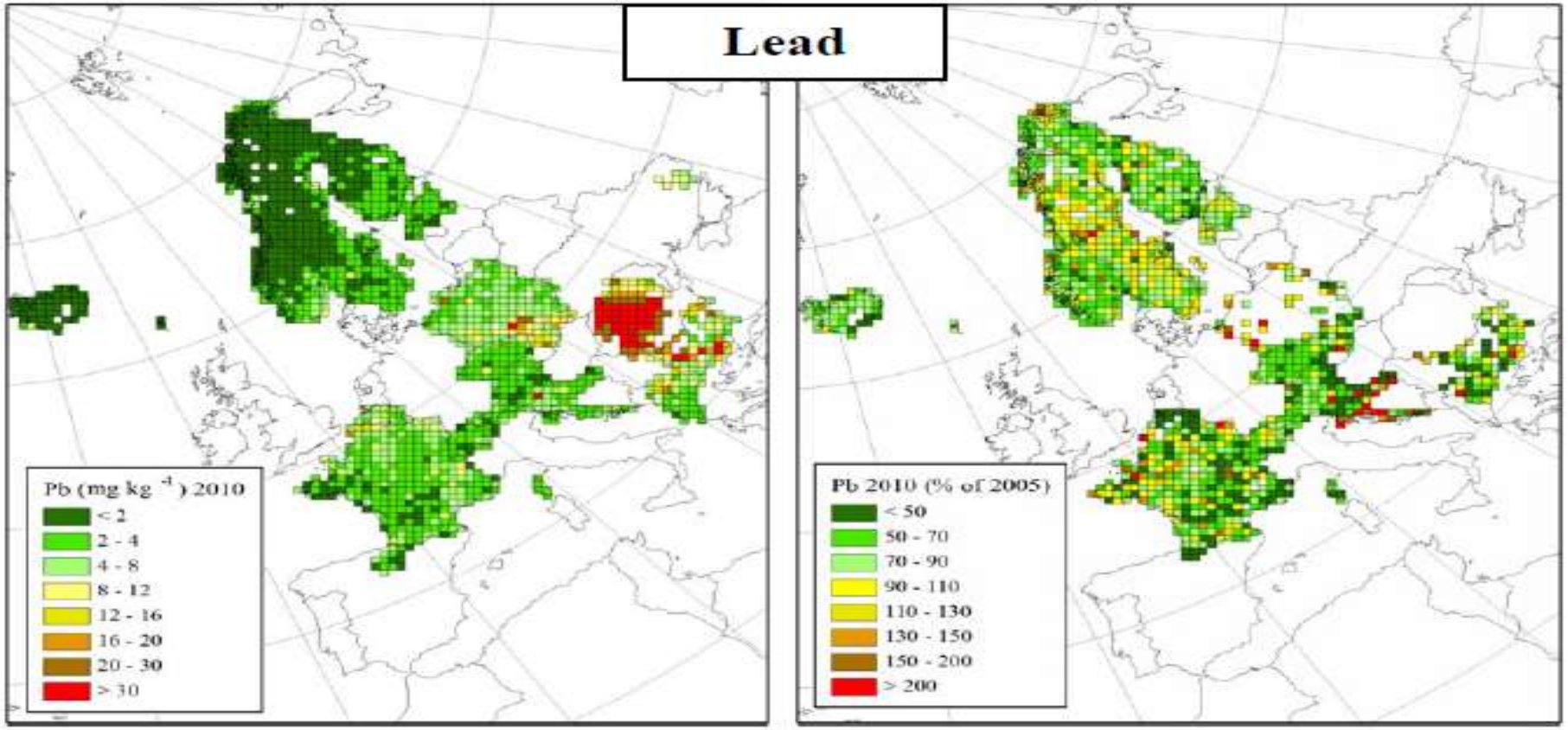
Results and discussions



Highest Ni concentration were found in (south) eastern European countries, Iceland and Norwegian-Finnish-Russian border in the north (due to the presence of very polluting copper-nickel smelters in the Kola Peninsula at the Russian side of the border)

Moss survey 2010/2011-

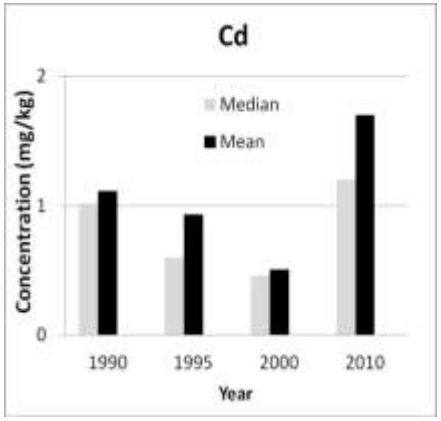
Results and discussions

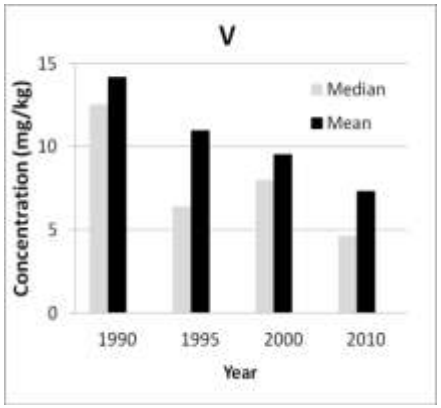


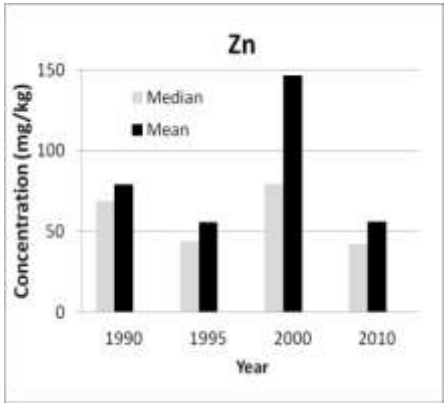
High Pb concentrations in mosses:

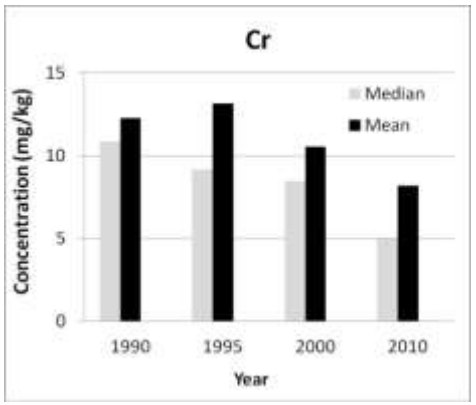
Romania, where the use of leaded petrol was banned completely only since January 2012, in addition, the presence of large industrial areas (including metallurgical works or melting plants) located in Baia Mare, Copsa Mica, contribute to the high concentration of lead in mosses (Lucacia et al., 2010). Relatively high lead concentrations were also found in **Slovakia, Bulgaria, Kosovo, Ukraine and Slovenia**, although the median lead concentration in mosses has declined between 31% and 50% in Slovakia, Bulgaria and Slovenia since 2005.

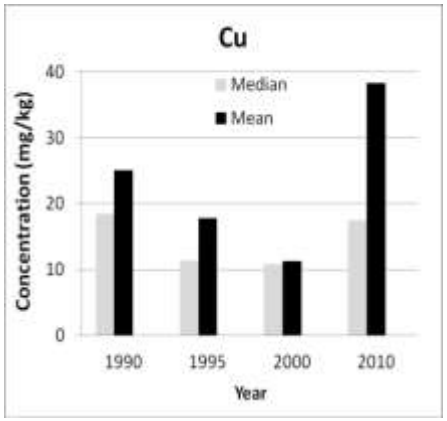
Moss survey 2010/2011-
Results and discussions

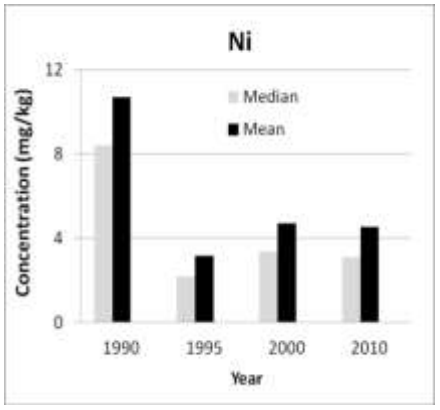


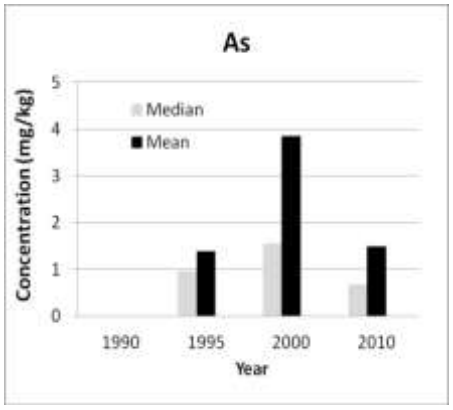


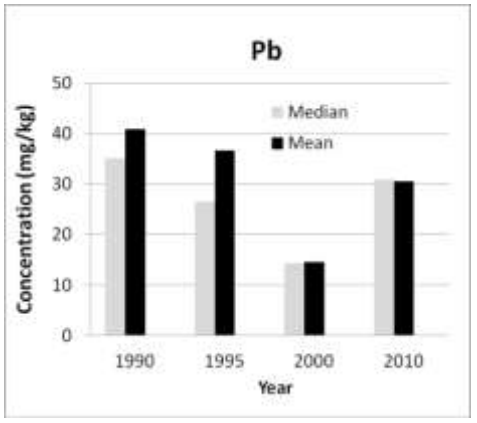












Temporal trends of Cu, Ni, As, Pb, Cd, V, Zn, Cr concentrations in moss in Romania since 1990-2000

Moss survey 2010/2011-
Conclusions

- **Moss biomonitoring provides a cheap and complementary method to deposition analysis for the identification of areas at risk from high atmospheric deposition fluxes of heavy metals for monitoring changes in time;**

- **The atmospheric deposition of trace metals is a considerable problem in the northern and western parts of Romania;**

- **This study contributes to the national monitoring system of Romania for long range transported elements of air pollutants, and along with epidemiological data it may serve for baseline human health risk assessments.**

European moss survey 2015/2016

- **The ecosystems and human health are still predicted to be at risk from adverse effects of heavy metals and nitrogen in the future, the moss survey should be continued to monitor any future trends in heavy metal and nitrogen deposition in Europe, with the next survey 2015/16;**

- **Romania, through the research consortium already created, will continuu to participate at European moss survey and will monitorize also the N concentrations and also radionuclides;**

- **The number of sampling points will increase, trying to cover the entire Romania**

Multidisciplinary Research Institute for Sciences and Technologies – Valahia University of Targoviste (new research location)

September 2011

September 2014

ICP-MS

WDXF spectrometer

SEM-EDX

AAS- GF/FAA

Thank you for attention!

God's Bridge (Ponoarele, Mehedinti County)
a natural protected monument, the largest natural bridge of Romania and the second in Europe (30 metres long, 13 metres wide, 22 metres high and 9 metres thick), being the only one open for road traffic for over 200 years.