Heavy metals and radioactive nuclide concentrations in mosses in Greece

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Heavy metals in mosses biomonitoring

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.

Twenty five European countries and over 4,500 sites were involved in the 2010/11 survey.

In 2005, nitrogen was included for the first time, and 15 countries reported on nitrogen concentrations in mosses, collected at ca. 2,400 sites in 2010/11. In addition, six countries determined the concentration of selected persistent organic pollutants (POPs), particularly polycyclic aromatic hydrocarbons (PAHs), at a selected number of sites (data not reported here).

During 2001, responsibility for the coordination of the survey was handed over to the ICP Vegetation1 Programme Coordination Centre at the Centre for Ecology and Hydrology (CEH) Bangor, UK.

The UNECE ICP Vegetation was established in the late 1980s to consider the science for quantifying the impacts of air pollutants on vegetation. It reports to the Working Group on Effects (WGE) of the Convention on Long-range Transboundary Air Pollution (LTRAP). The WGE monitors, models and reviews the effects of atmospheric pollutants on different components of the environment and health.

Heavy metals in mosses biomonitoring

From the start, the European moss survey has provided data on concentrations of ten heavy metals in naturally growing mosses.

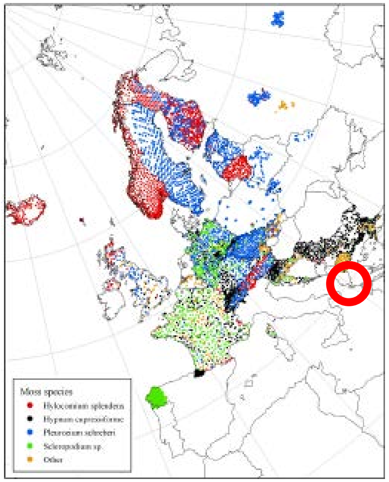
(arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, vanadium and zinc)

Since 2005, the concentration of aluminium (a good indicator of wind-blown dust as it is present in high concentrations in the earth's crust), antimony (a good indicator of anthropogenic pollution as it is present in very low concentrations in the earth's crust) and nitrogen were also determined.

The moss data provide a complementary measure of elemental deposition from the atmosphere to terrestrial systems,

it is easier and cheaper than conventional precipitation analysis,

and therefore enables a high sampling density to be achieved.

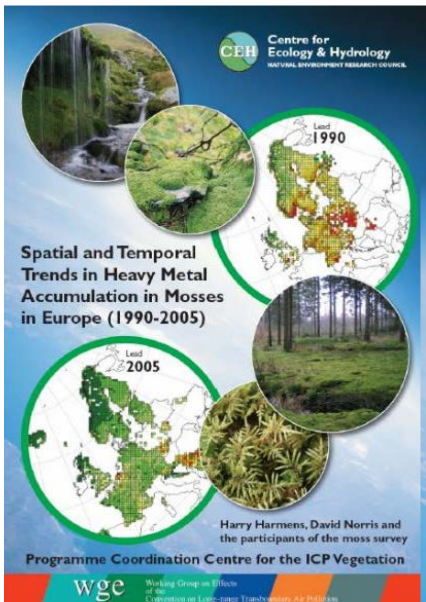


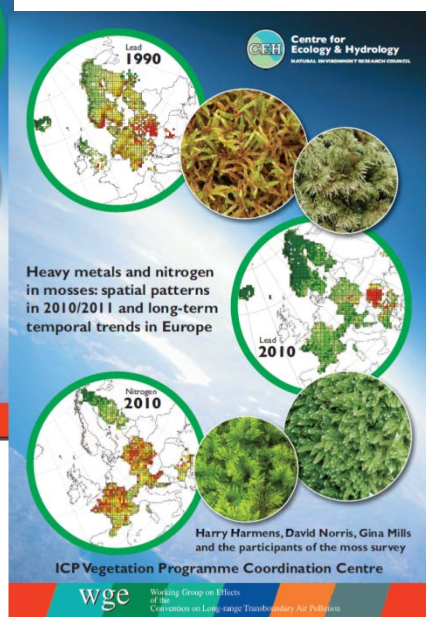
The aim of the survey is to identify the

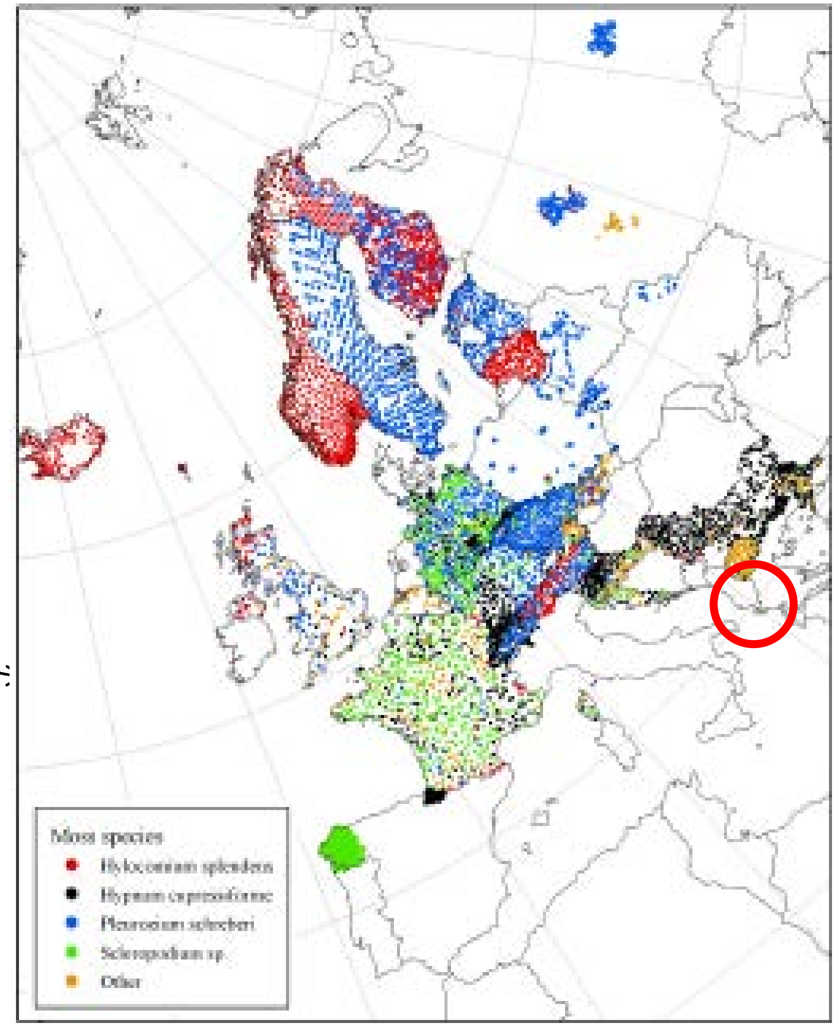
- main polluted areas,
- produce European maps and further develop the understanding of long-range transboundary air pollution of heavy metals and nitrogen.
- Apart from spatial patterns, the repeated surveys also provide an indication of temporal trends of heavy metal and nitrogen deposition.

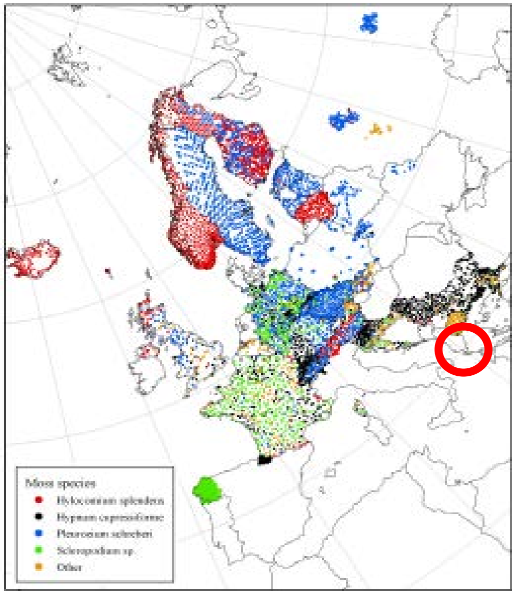
Mosses:

- -Ideal bioindicators
- -Simple sample collection
- -High sampling density
- -Economic sampling medium









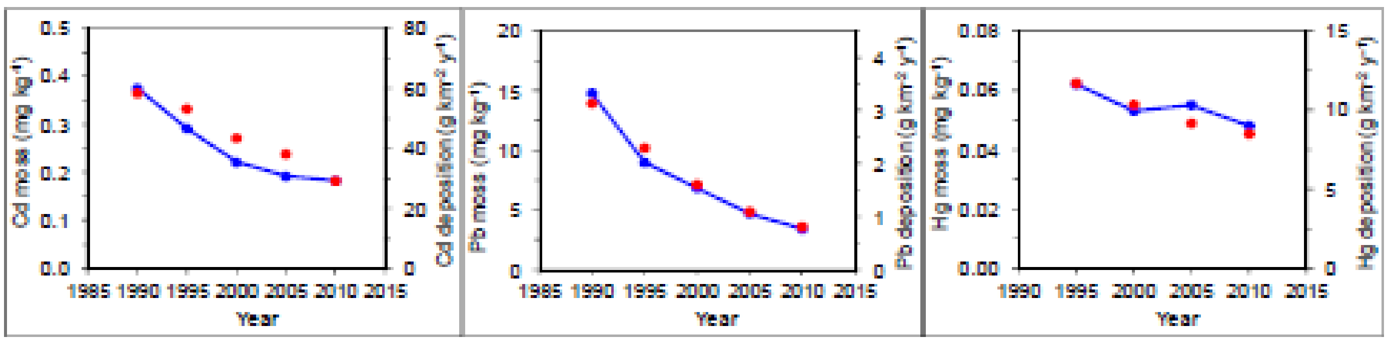
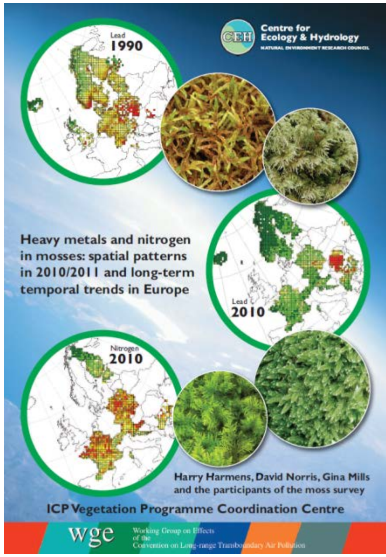


Figure 1. Temporal trend of cadmium (Cd), lead (Pb) and mercury (Hg) concentration in mosses compared to the trend of EMEP-modelled deposition for these heavy metal (red dots).



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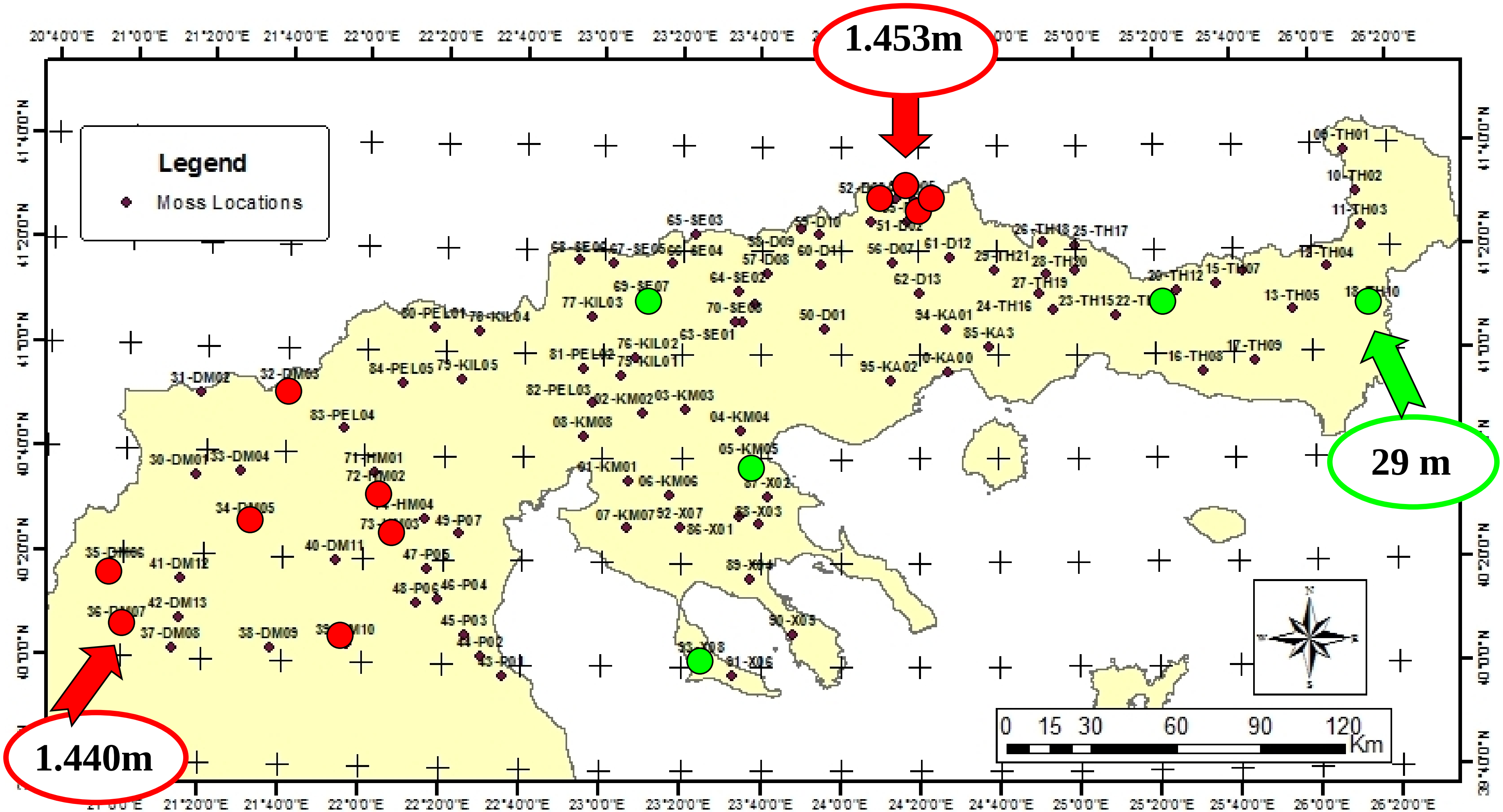
***Hypnum cupressiforme* Hedw.**

Study area - Northern Greece



<u>Samples:</u> moss ***Hypnum cupressiforme*** **Hedw.** <u>Collection:</u> **95 sampling sites** in Northern Greece (<u>regions:</u> W., C., E. Macedonia and Thrace, <u>sampling:</u> July – September 2016).

Collection substrates

Lithotopos, Serres

Neo Petritsi, Serres

Fteri, Pieria

Ano Poroia, Serres

Heavy metals

- Natural constituents of Earth's crust
- Present in all ecosystems
- Affect directly the crops used for animals and human consumption
- Essential nutrients (e.g Fe, Co, Zn) but harmful in larger amounts

Increased due to:

- Urbanization
- Industrial and agricultural activities
- Fossil fuel combustion
- Vehicle emissions and transportation

Heavy metals-sources

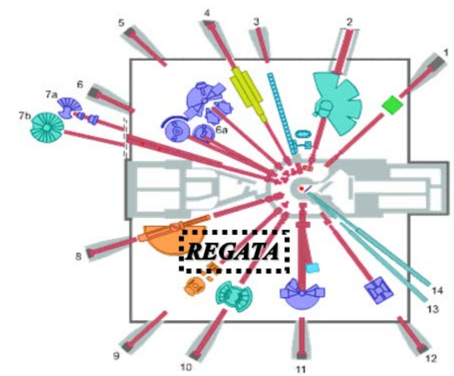
- *Metals Industry* (Al, As, Cr, Cu, Fe, Zn)
- *Manufacturing industry and construction* (As, Cd, Cr, Hg, Ni, Pb)
- *Electricity and heat production* (Ni, Cd, Hg, V)
- *Road transportation* (Zn from tires, Cu and Sb from brake ware)
- *Petroleum refining* (V, Ni)
- *Agricultural activities* (Cd)
- *Earth crust* (U, Th, Fe, Al, La, Ti, Sc, Ba, Nd)
- *Marine elements* (Cl, Br, I , Na)

Sample preparation for INAA

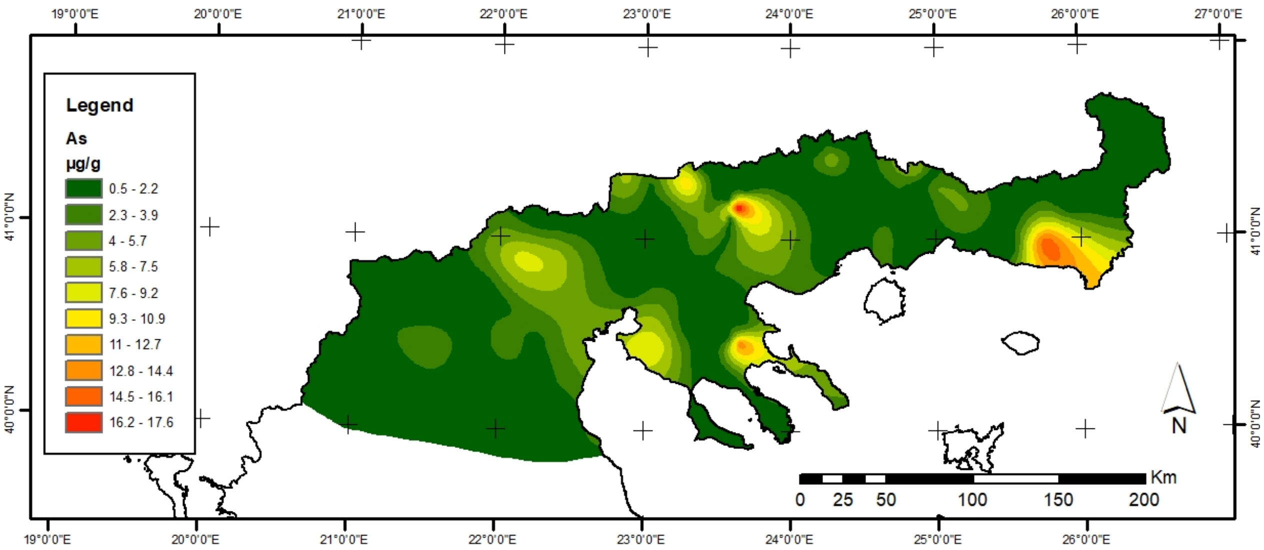
- Sampling preparation: dried and all the impurities were removed manually
- After cleaning and homogenization of the sample, ~ 0.3g of mosses were pelletized in press-forms and were precisely weighed.
- Moss samples for *short-term* irradiation were heat-sealed in polyethylene foil bags, while
- samples for *long term* irradiation were packed in aluminium cups

Measurement with INAA

- Moss samples were irradiated at a pulsed fast reactor IBR-2 of the Frank Laboratory of Neutron Physics, JINR, Dubna, Russia
- Irradiation time varied:
- *-Short* lived (Cl, V, I, Al, Mg) for (3 min)
- *-Long* lived (Br, As, Ba, Mo, K, Na, Zn, Ag, Sc) for (3d 5 h 35 min)
- Sample activities were measured with an HPGe detector with 40% relative efficiency and 1.74 keV FWHM at the 1332 keV line of Co-60
- Analysis of gamma-spectra with GENIE-2000 program
- 33 elements concentrations were determined



Arsenic (As)



Stratoni Gulf: Mining activities (*metal ore and metal processing factory, solid wastes*):

→Fe, As, Pb, Cu, Cr, Cd

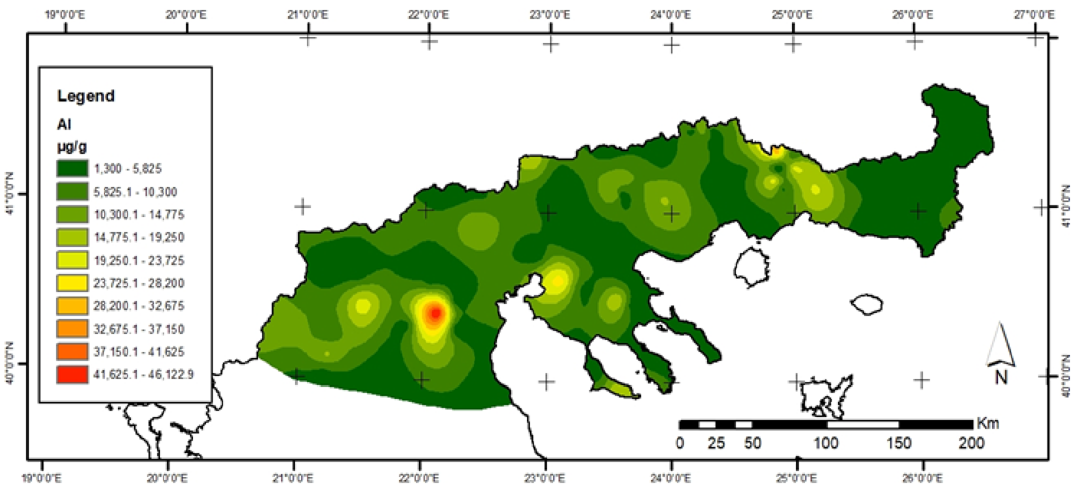
*Pappa, F.K., et al., Radioactivity and metal concentrations in marine sediments associated with mining activities in Ierissos Gulf, North Aegean Sea, Greece. Appl. Radiat. Isotopes (2016), http://dx.doi.org/10.1016/j.apradiso.2016.07.006i

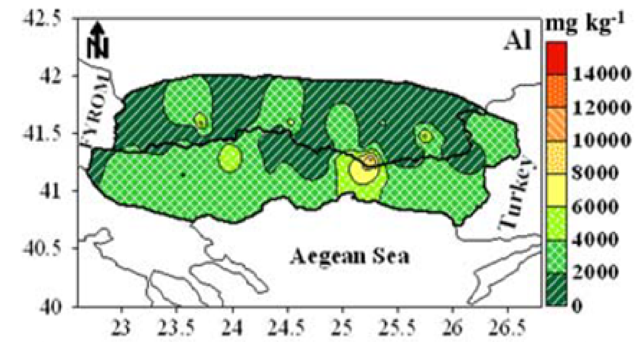
Possible source: Volcanic rocks, industrial and mining activities

As (µg/g)-moss survey 2010/2011

	Greece (2015/16)	Italy	Spain	FYROM (Macedonia)	Bulgaria	Albania	Slovenia	Finland	Norway	Czech Republic	Poland
min	0.517	0.140	0.086	0.077	0.150	0.039	0.130	<0.1	0.020	0.068	0.003
max	17.900	0.950	2.690	3.300	10.800	2.200	0.830	0.380	4.840	1.080	14.300
mean	3.310	0.280	0.390	0.880	1.080	0.420	0.280	0.120	0.180	0.290	0.450
median	1.620	0.220	0.290	0.690	0.630	0.240	0.260	0.100	0.130	0.260	0.300

Aluminum (Al)



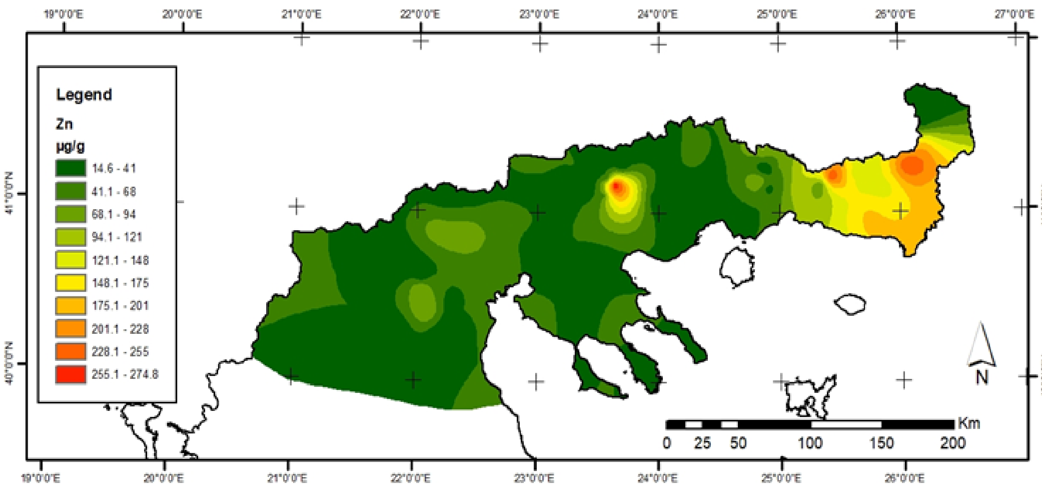


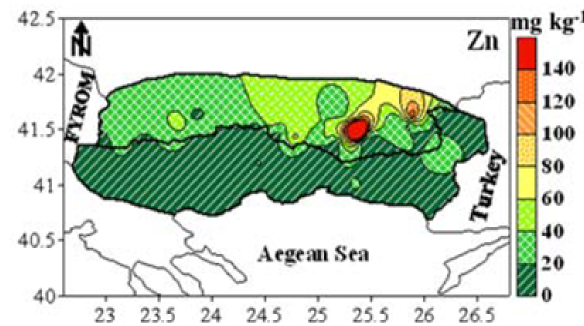
*Yurukova, L. et al., 2009, Cross-Border Response of Moss Hypnum Cupressiforme Hedw., to Atmospheric Deposition in Southern Bulgaria and Northeastern Greece, Bull Environ Contam Toxic 83: 174-179

- -good indicator of mineral particles, mainly windblown soil dust
- -found in Earth's crust
- -connected with local sources: e.g metal industry

Al (μg/g)-moss survey 2010/2011											
	Greece(2015/16)	Italy	Spain	FYROM (Macedonia)	Bulgaria	Albania	Slovenia	Finland	Norway	Czech Republic	Poland
min	1350		173	537	402	535		44	46	184	
max	46100		1459	8679	8886	6974		958	4581	3227	
mean	8240		597	2176	1493	1975		206	346	526	
median	6160		511	1878	1245	1650		187	283	435	

Zinc(Zn)





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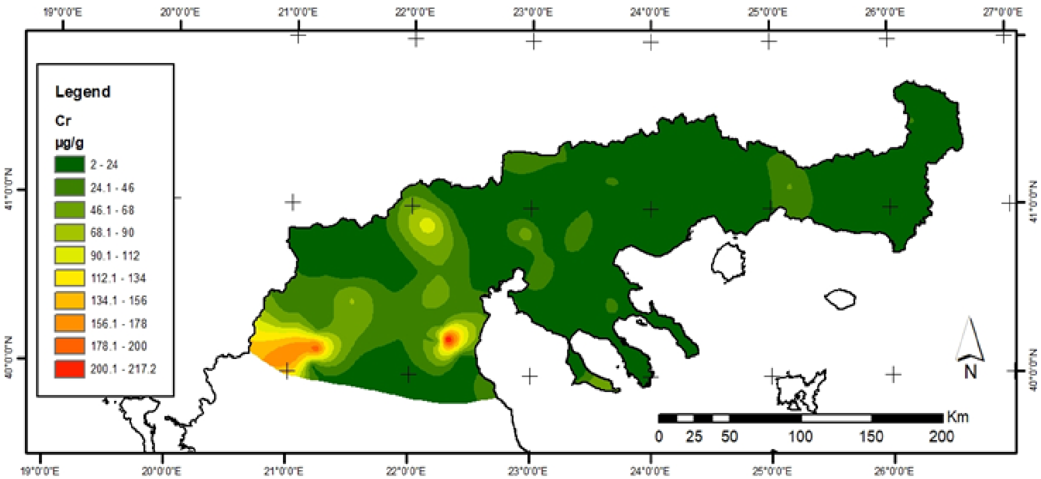
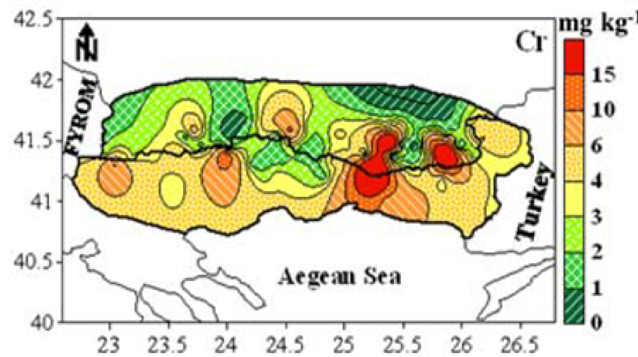
-used in manufacture of rubbers, tires
-traffic source, transportation
- As and Zn follow the same pattern in some areas

Zn (μg/g)-moss survey 2010/2011											
	Greece(2015/16)	Italy	Spain	FYROM (Macedonia)	Bulgaria	Albania	Slovenia	Finland	Norway	Czech Republic	Poland
min	14.60	17.70	12.70	1.00	8.22	1.00	14.70	11.50	7.40	20.10	7.46
max	282.00	68.40	156.00	365.00	286.00	68.10	66.70	102.00	368.00	105.00	211.00
mean	55.70	38.20	32.90	29.70	30.60	14.20	31.50	31.00	35.90	36.50	51.80
median	38.30	37.10	31.50	19.90	22.20	13.80	29.00	29.50	30.70	33.90	47.50

Chromium (Cr)





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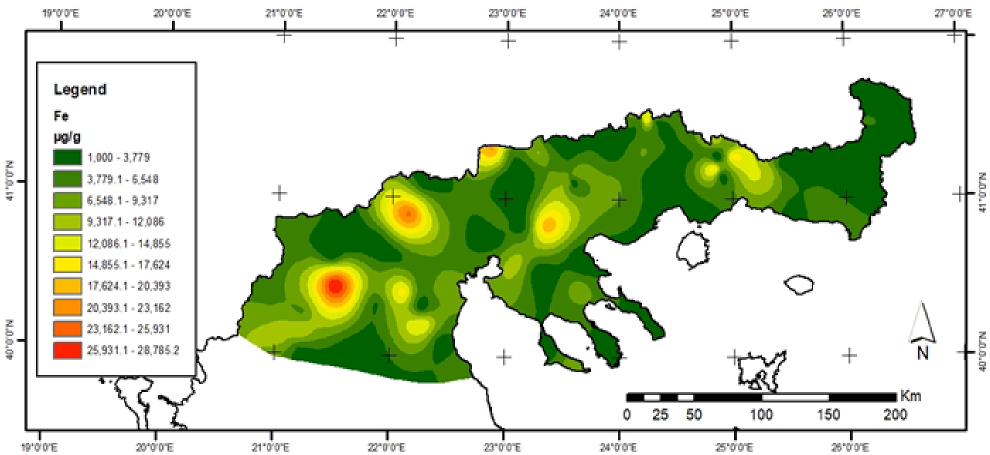
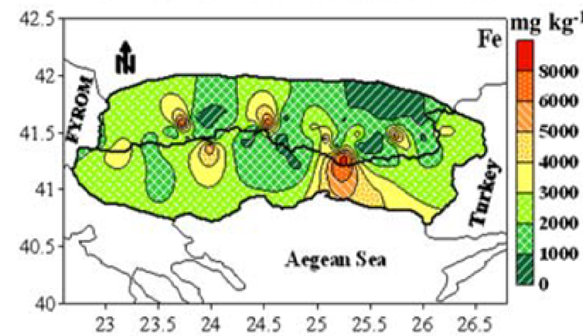
maybe connected with:
-Ophiolites rocks
-industrial activities

Cr (µg/g)-moss survey 2010/2011											
	Greece(2015/16)	Italy	Spain	FYROM (Macedonia)	Bulgaria	Albania	Slovenia	Finland	Norway	Czech Republic	Poland
min	2.04	0.78	0.43	1.03	0.72	1.62	0.72	0.34	0.16	0.46	0.20
max	222.00	3.37	4.77	39.70	38.10	31.80	13.70	14.00	47.90	4.35	293.00
mean	33.01	1.59	1.83	4.68	3.46	6.35	1.94	0.95	0.98	1.21	3.58
median	14.70	1.59	1.46	3.48	2.06	4.83	1.56	0.80	0.59	1.01	1.27

Iron (Fe)





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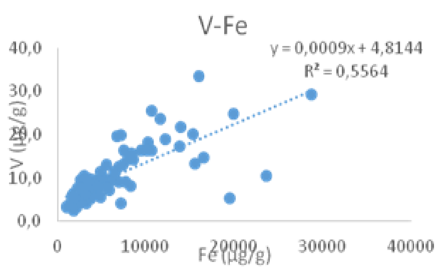
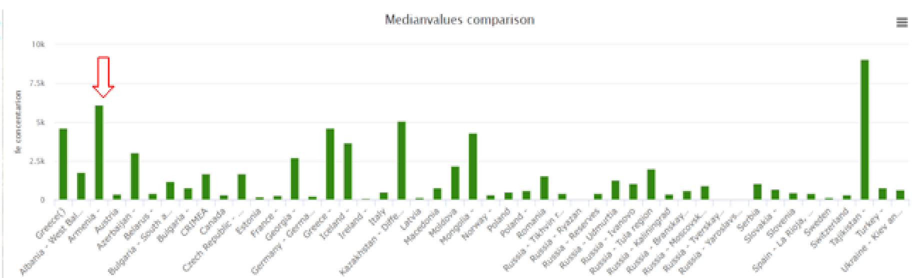
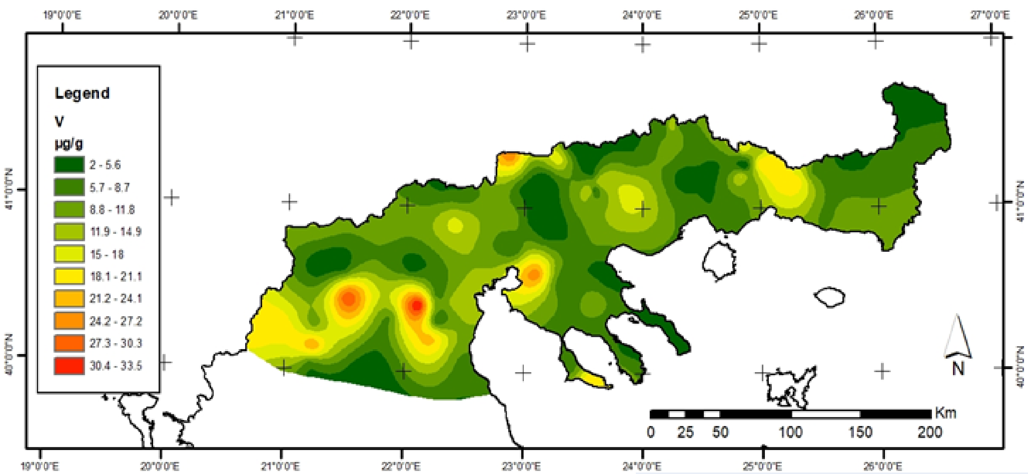
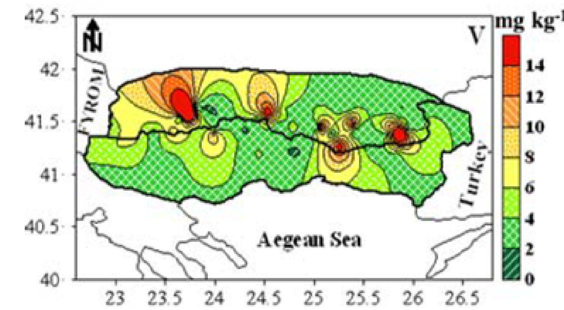


- Found in the Earth's crust
- possible sources: anthropogenic activities and different geological rocks (e.g iron laterites)



Vanadium (V)





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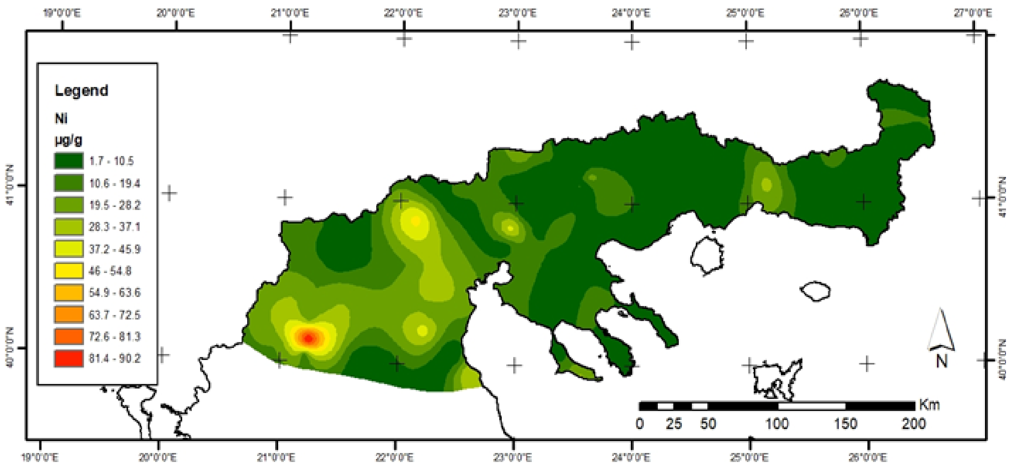
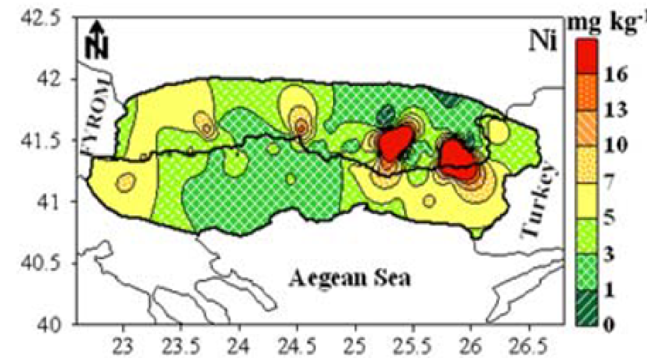
-chemical similar to Ti, Fe, Al, U, P
-due to industrial pollution
-catalyst in production of rubber
-found in oil industry and transportation

V (µg/g) -moss survey 2010/2011

	Greece(2015/16)	Italy	Spain	FYROM (Macedonia)	Bulgaria	Albania	Slovenia	Finland	Norway	Czech Republic	Poland
min	2.61	0.91	0.55	1.00	0.96	1.15	1.00	<1	0.29	0.44	0.11
max	33.40	1.90	4.20	17.40	22.40	16.90	7.00	14.20	25.90	6.10	4.69
mean	11.08	1.39	1.36	3.95	3.96	4.26	2.40	1.28	1.76	1.38	0.77
median	8.66	1.37	1.21	3.49	3.07	3.52	2.30	1.00	1.41	1.18	0.65

Nickel (Ni)





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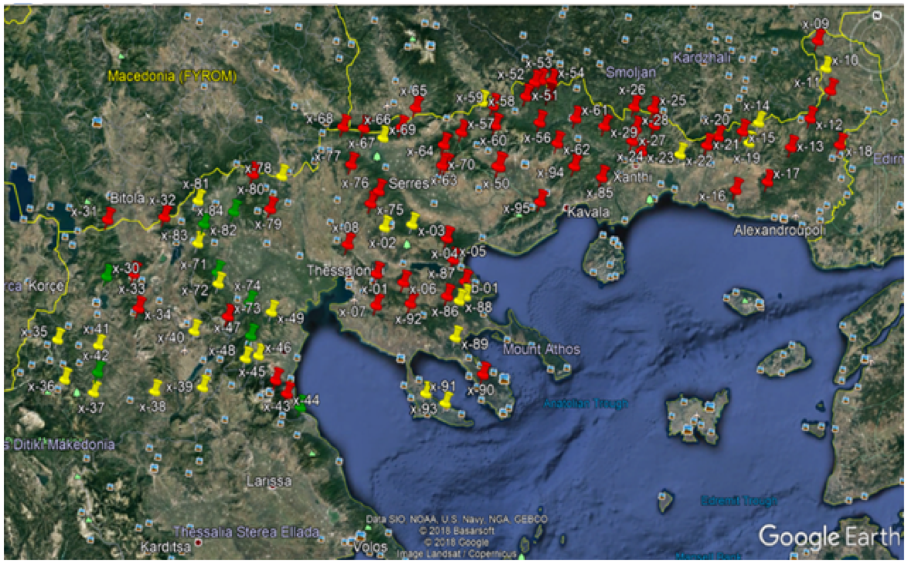
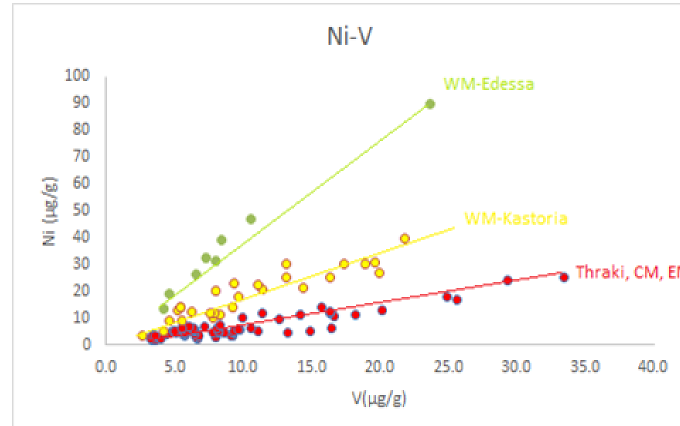
-Chemical similar to Fe, Co, Cu
Possible sources:
oil combustion, Fe-Ni industry, ophiolites rocks(Cr, Ni)

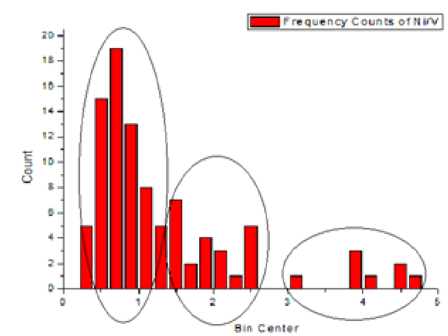
Ni (µg/g)-moss survey 2010/2011											
	Greece(2015/16)	Italy	Spain	FYROM (Macedonia)	Bulgaria	Albania	Slovenia	Finland	Norway	Czech Republic	Poland
min	1.72	0.89	0.58	1.25	0.84	1.56	0.85	0.42	0.15	0.37	0.14
max	138.00	3.36	3.94	51.70	82.10	131.00	8.16	88.20	857.00	4.47	108.00
mean	19.83	1.77	1.60	6.43	4.37	11.20	2.34	2.45	5.40	1.27	2.20
median	10.00	1.69	1.44	3.45	2.61	5.81	2.12	1.24	1.16	1.15	1.15

Ni- V





Usually good correlation between Ni-V →index of heavy oil source



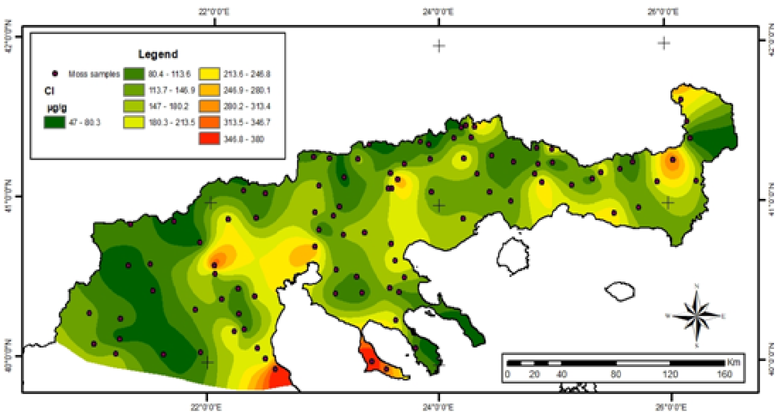
3 groups- regions:

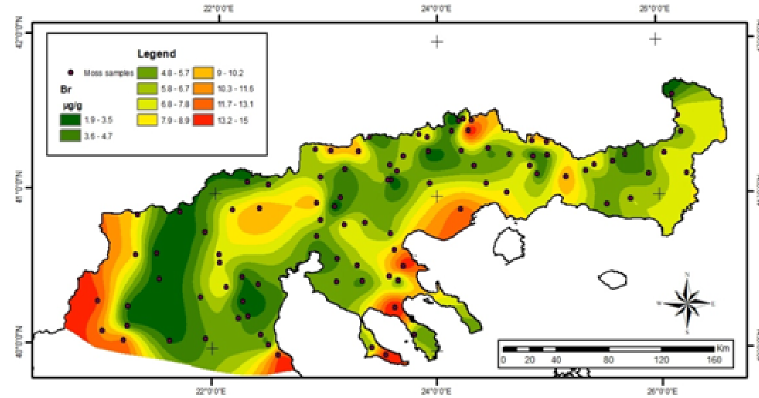
-Central-East Macedonia, Thrace (probably due to oil industry, transportation and geological background)

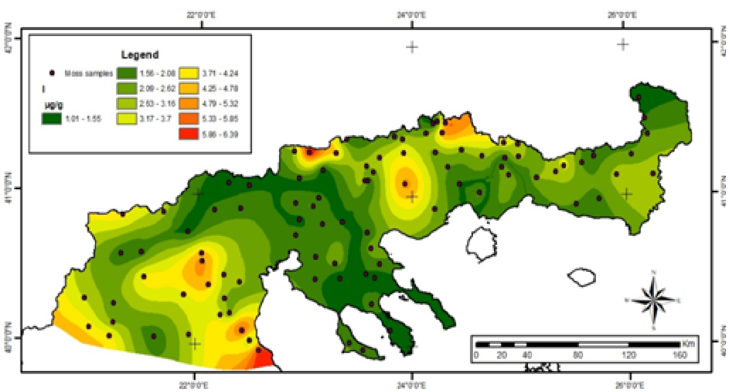
-West Macedonia- Kastoria (probably due to Ni-Fe laterite→ LARKO company- Ni mining and geological background)

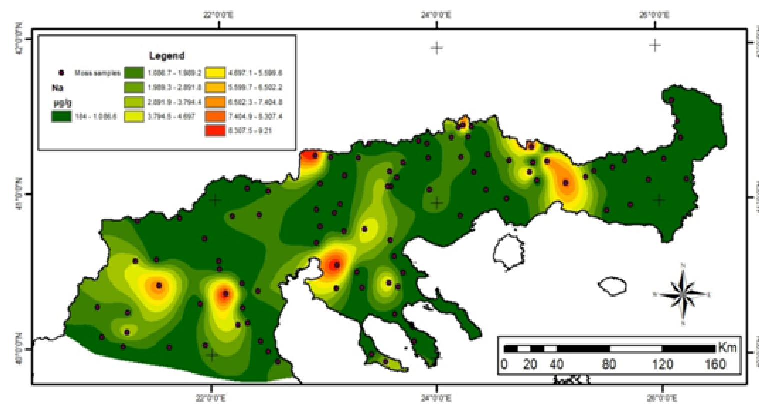
-W.Macedonia- Edessa-Vermio-Olympos (probably due to Ni-Fe laterite)

Distribution of Cl, Br, I, Na

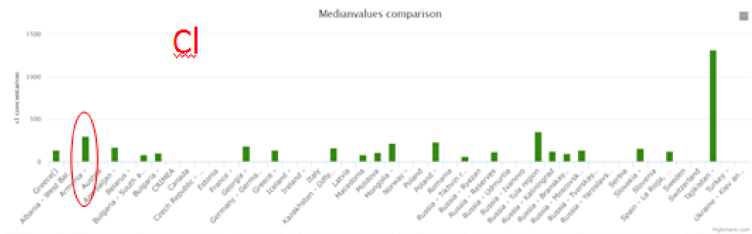


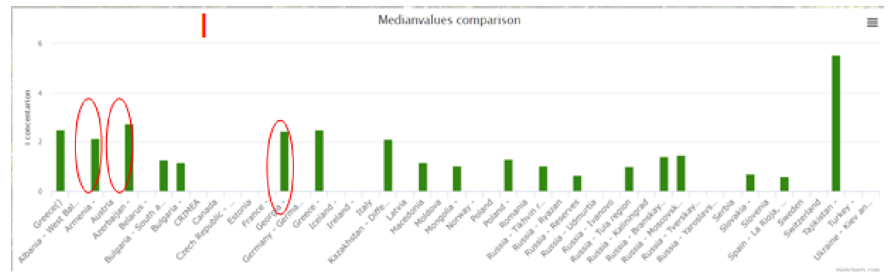


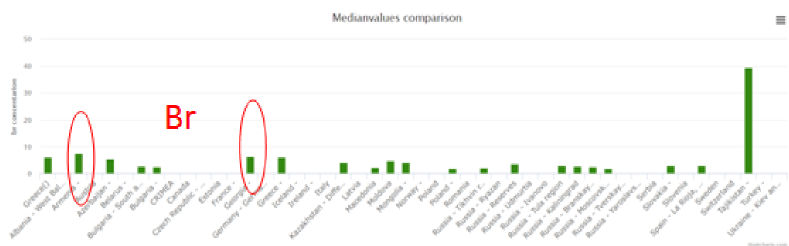




In other countries..



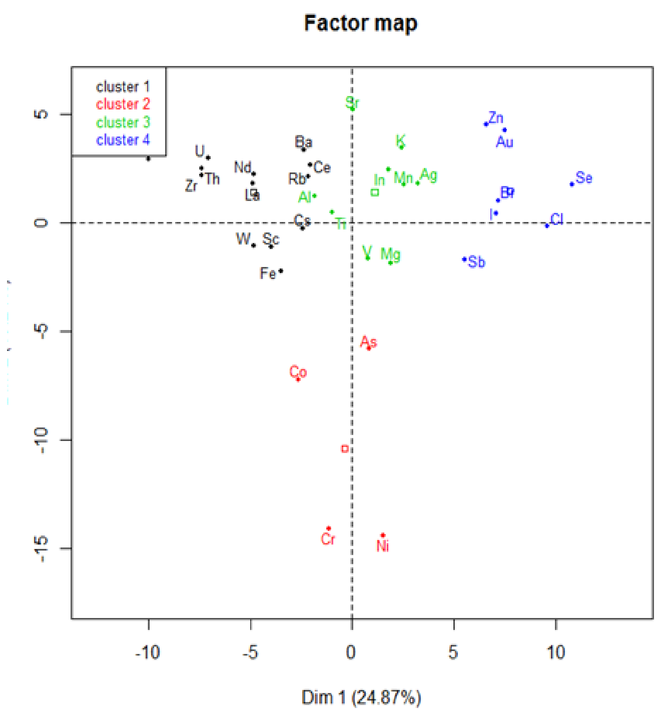




	Cl	Br	I	Na
High	Armenia	Georgia, Armenia	Georgia, Azerbaijan	Kazakhstan, Mongolia, Armenia
low	Macedonia	Poland	Slovakia	Serbia

Cl, Br, I, Na *not* only due to marine environment but also to other local sources

Principle Component Analysis(PCA)

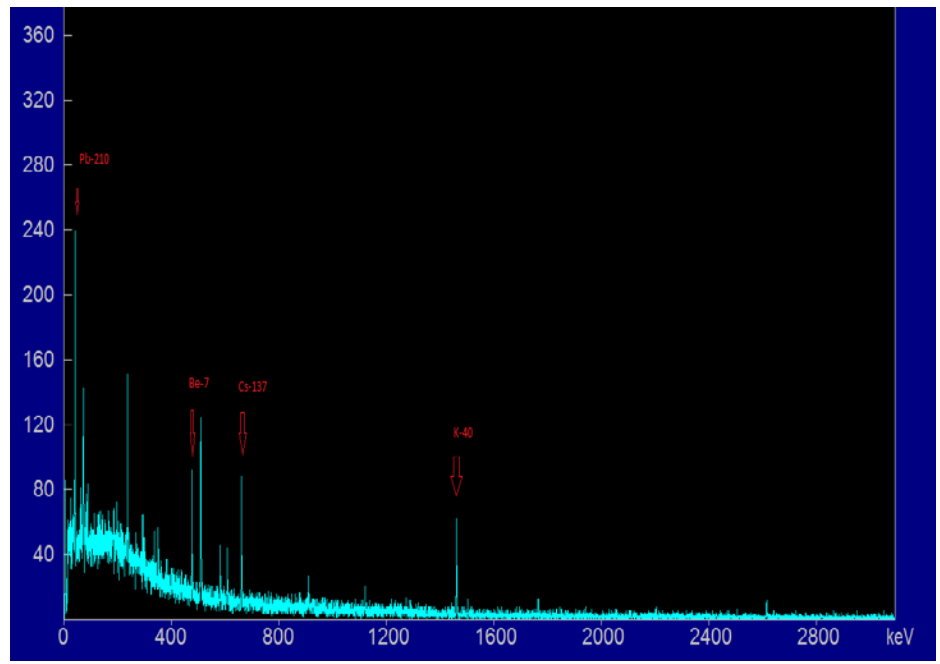


Heavy metals are distributed according to 4 factors:

-deposition of windblown soil dust on the moss surface (Fe, Sc, Ti)
-industry (As, Cr, Ni)
-the "vascular pump" effect,
(root uptake of elements in higher plants→ leaching from living or decaying plant material (e.g. K, Ca, Mn, Zn, ...) →transfer to moss
-constituents from marine environment (Cl, Na, I, Br)

Gamma spectrometry

95 moss samples



Gamma radionuclides

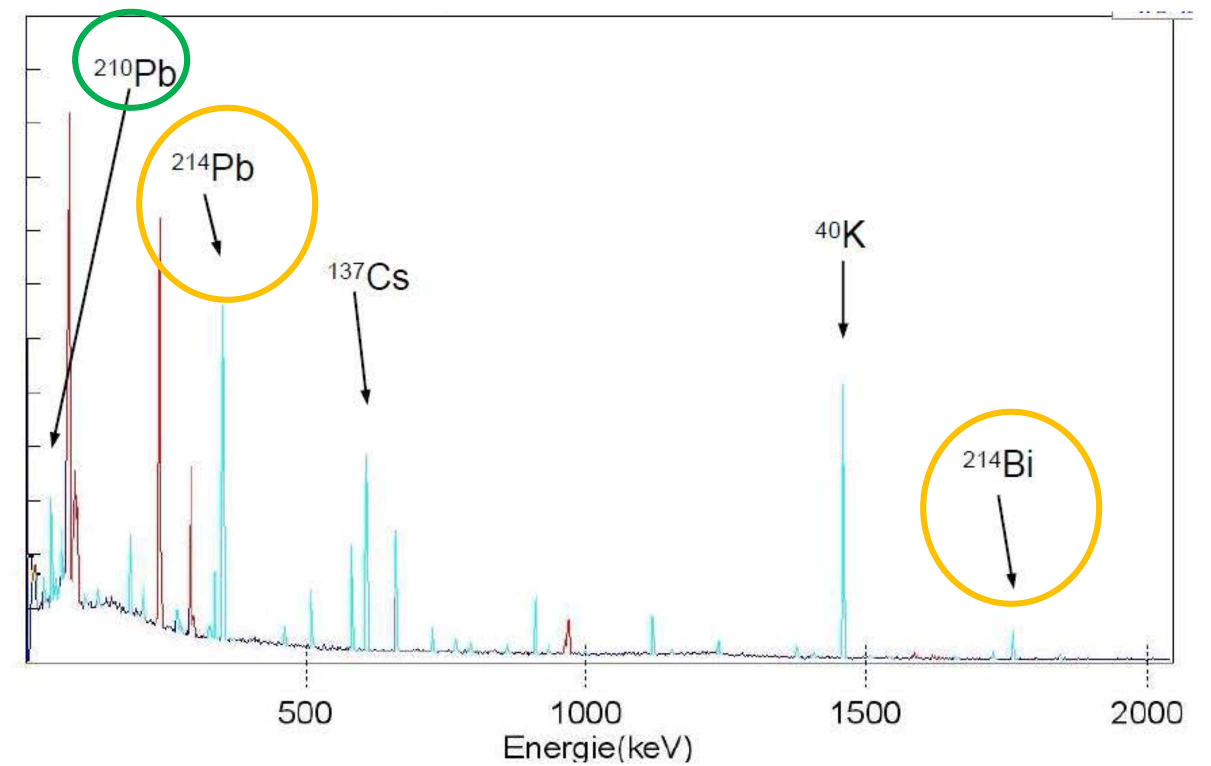
^{210}Pb, ^{7}Be, ^{137}Cs, ^{40}K

^{137}Cs,	$t_{1/2}$ = 30.04 y	(661.65 keV)
^{40}K,	$t_{1/2}$ = 1.25x10^{9} y	(1460.75 keV)
^{7}Be,	$t_{1/2}$ = 53.3 d	(475.5 keV)
^{210}Pb,	$t_{1/2}$ = 22.23 y	(46.5 keV)

Sampling July-Sept 2016

~1 half-life of ^{137}Cs after the Chernobyl accident 1986

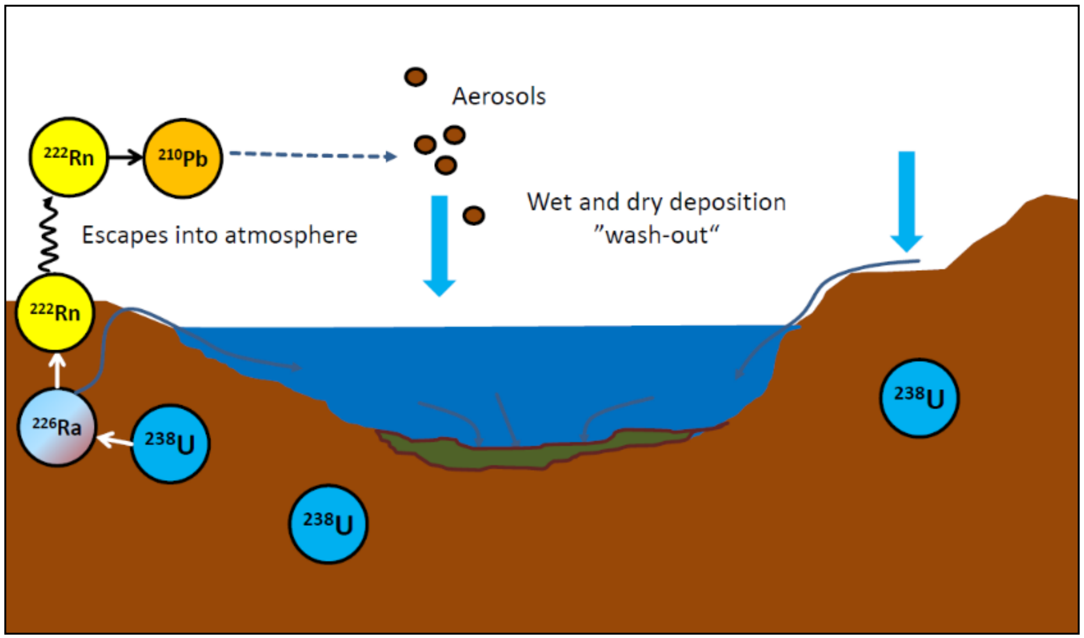
^{210}Pb unsupported



Steps:

1. $^{210}Pb_{total}$ (46.5 keV) determination
2. $^{210}Pb_{sup}$: ^{214}Pb and ^{214}Bi determination (equilibrium with ^{226}Ra)
3. $^{210}Pb_{uns} = {}^{210}Pb_{total} - {}^{210}Pb_{sup}$

^{210}Pb supported & ^{210}Pb unsupported



Supported $^{210}Pb_{sup}$:
In situ from ^{222}Rn decay in sediment *and* ***other*** *matrix where* ^{226}*Ra isotope can be found*

Unsupported (excess) $^{210}Pb_{uns}$:
Dry or wet deposition of ^{210}Pb generated by ^{222}Rn decay in the air or in water column

Sample preparation for gamma-spectrometry

Sampling preparation: dried at 105°C for 24 hours and all the impurities were removed manually.

After the preparation, mosses were put in two cylindrical plastic containers (d = 67 mm, h = 31 mm. Mass: 11-24gr/container, total: ~22-48 gr.

Detector efficiency (reference materials):

-IAEA 372 (grass)
-IAEA 330 (spinach)
-IAEA 447 (moss-soil)

- High resolution gamma spectrometry measurements can be carried out with the moss technique, without any chemical treatment of the samples.

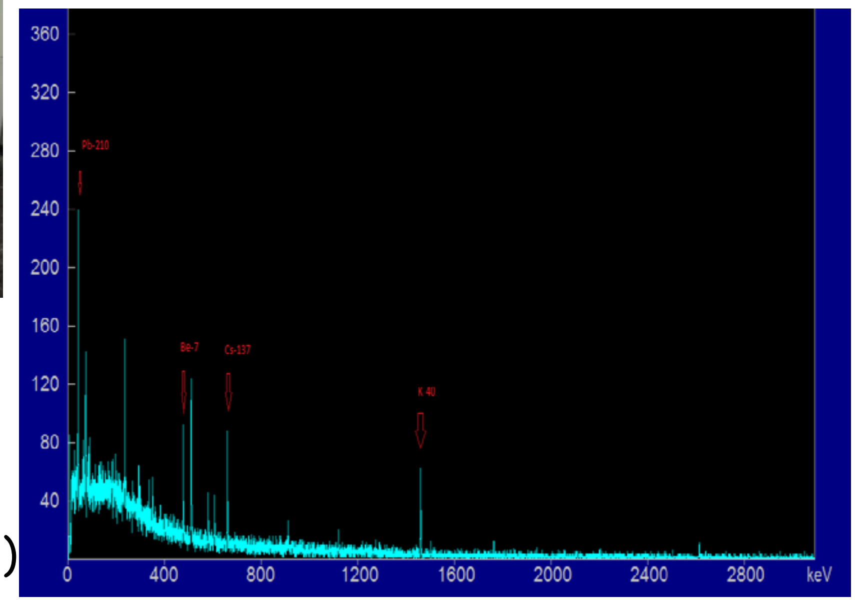
Gamma spectrometry

Measurement:

- low-background HPGe detector (relative efficiency 32%), shielded by 16 cm of Pb (1.5 mm inner Cu shield)
- extended energy range HPGe detector (rel. eff. 100%).

Statistical uncertainty of 46.5 keV ^{210}Pb: up to 5%

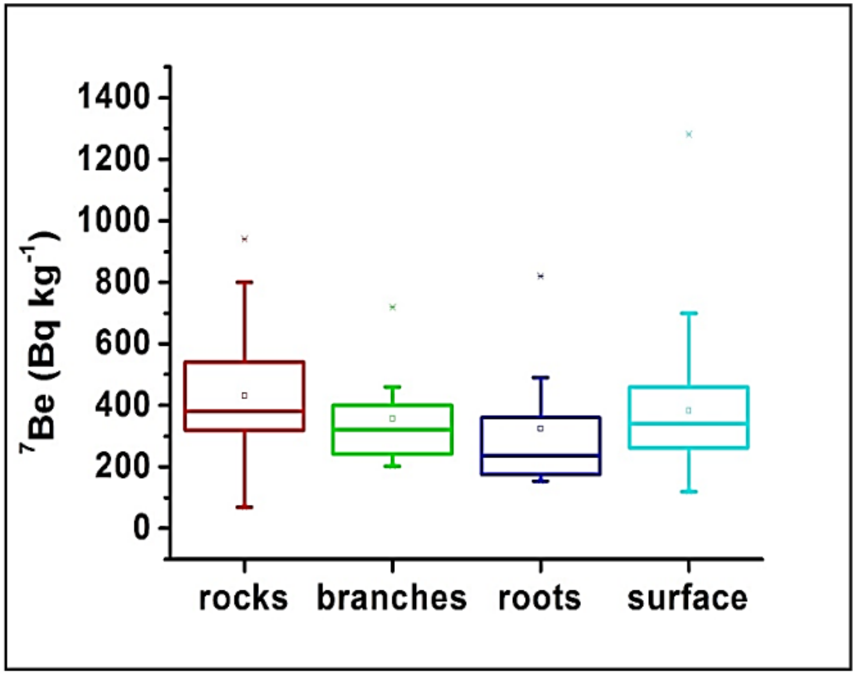
^{137}Cs,	$t_{1/2}$ = 30.04 y	(661.65 keV)
^{40}K,	$t_{1/2}$ = 1.25x10^9 y	(1460.75 keV)
^{7}Be,	$t_{1/2}$ = 53.3 d	(475.5 keV)
^{210}Pb,	$t_{1/2}$ = 22.23 y	(46.5 keV)



Sampling : ~1 half-life of ^{137}Cs (Chernobyl)

SPECTRW (Kalfas et al., 2016)

^{7}Be activity concentrations



^{7}Be (Bq kg^{-1})	
Max	1280
Min	69
mean	392

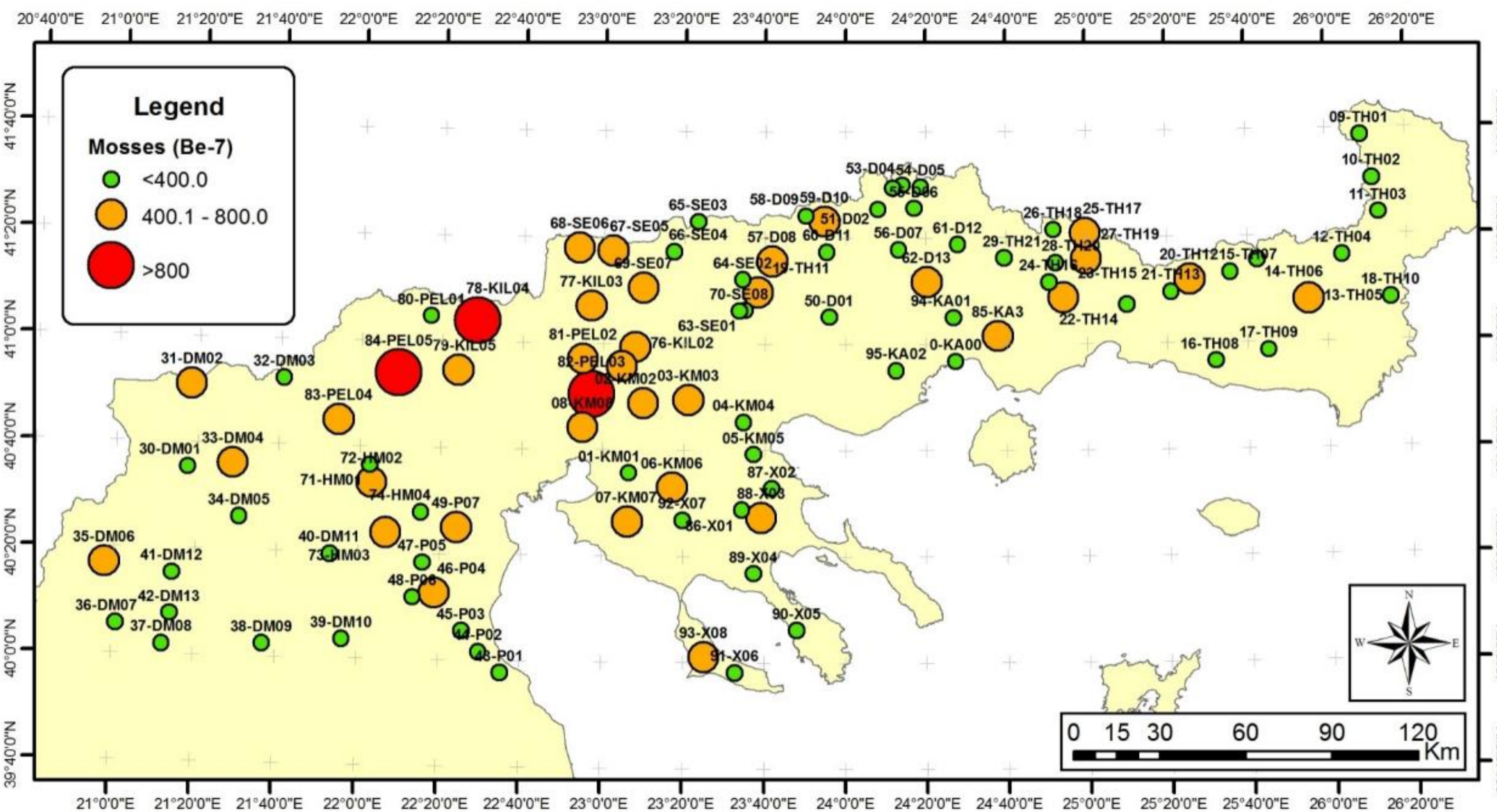
$$\frac{A_{surface}}{A_{roots}} = 1.5$$

collected from different surface type

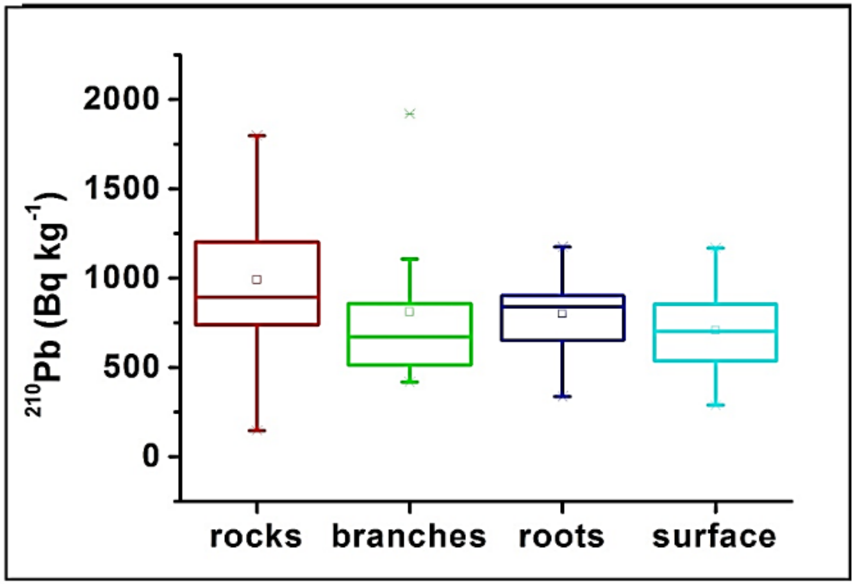
no variances in concentrations due to different altitudes

	^{7}Be (Bq kg^{-1})	
Serbia (winter)	95-360 (195)	(Krmar, 2007)
Serbia (**summer**)	--- (314)	(Krmar, 2013)

^{7}Be activity concentrations in mosses July-Sept 2016



^{210}Pb activity concentrations



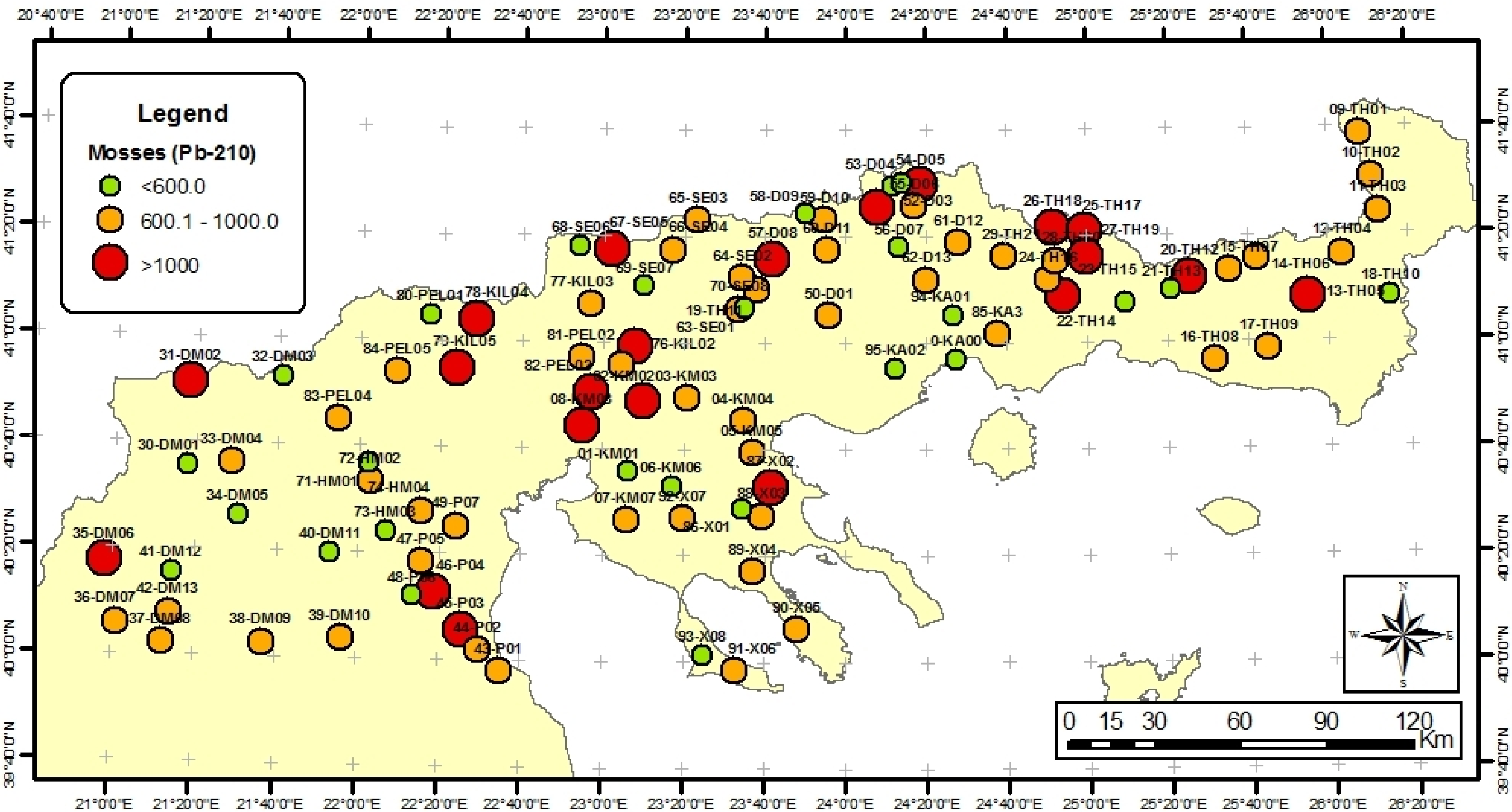
collected from different surface type

^{210}Pb (Bq kg^{-1})	
Max	2049
Min	147
mean	830

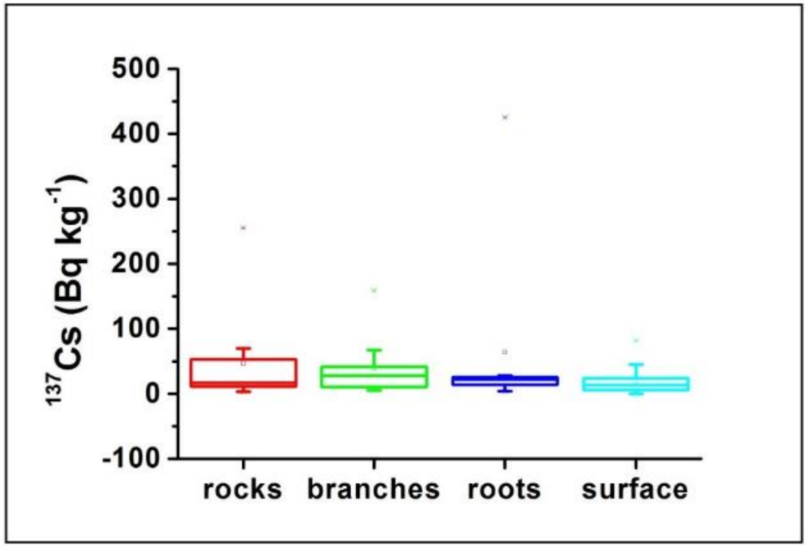
$$\frac{A_{surface}}{A_{roots}} = 0.87$$

	^{210}Pb (Bq kg^{-1})	
Serbia	--- (695)	(Krmar, 2013)
Slovakia	330 - 1521 (771)	(Yu.V.Aleksiayenak, 2013)
Belarus	163 – 575 (312)	

^{210}Pb activity concentrations in mosses July-Sept 2016



^{137}Cs activity concentrations



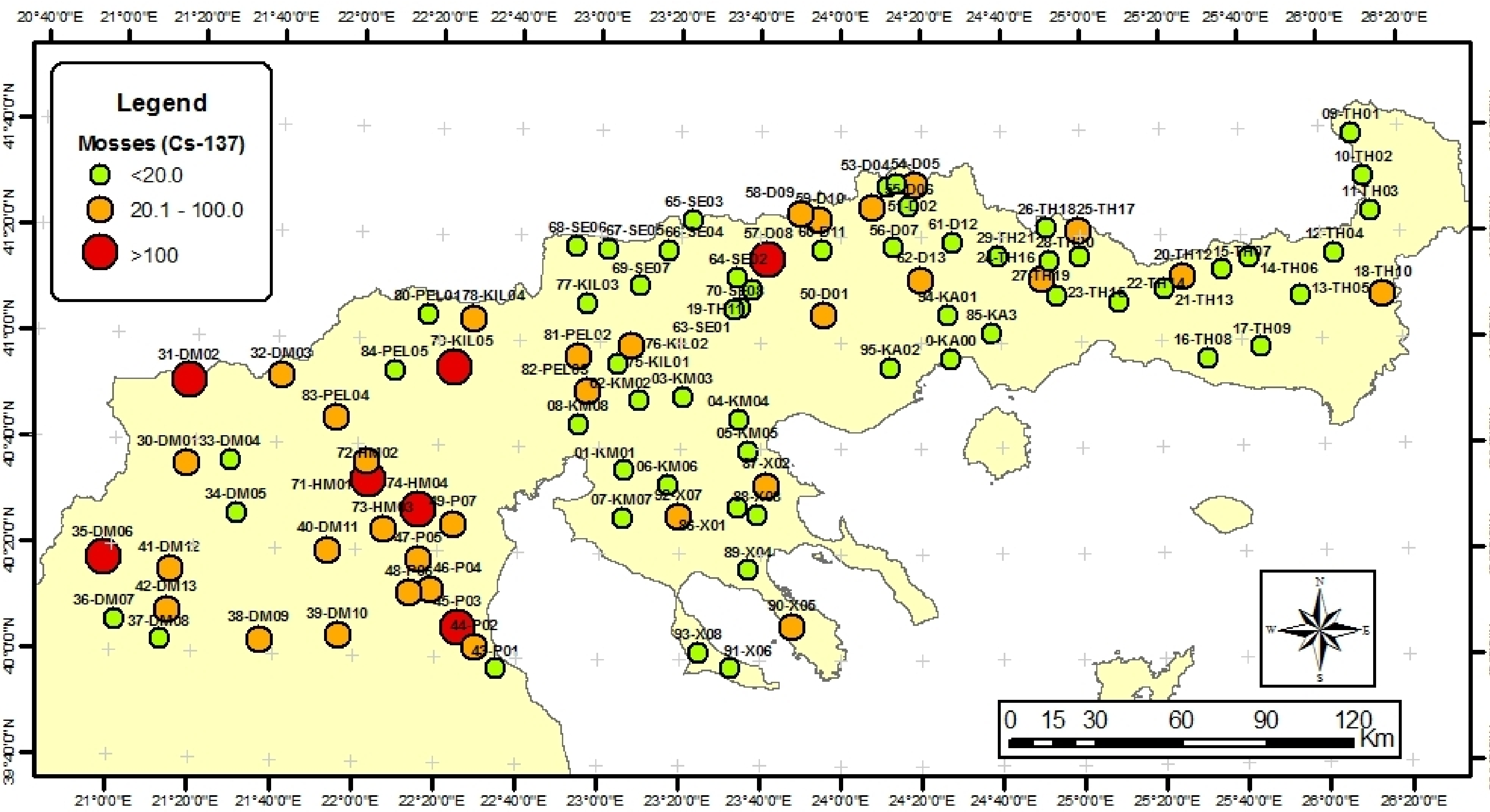
collected from different surface type

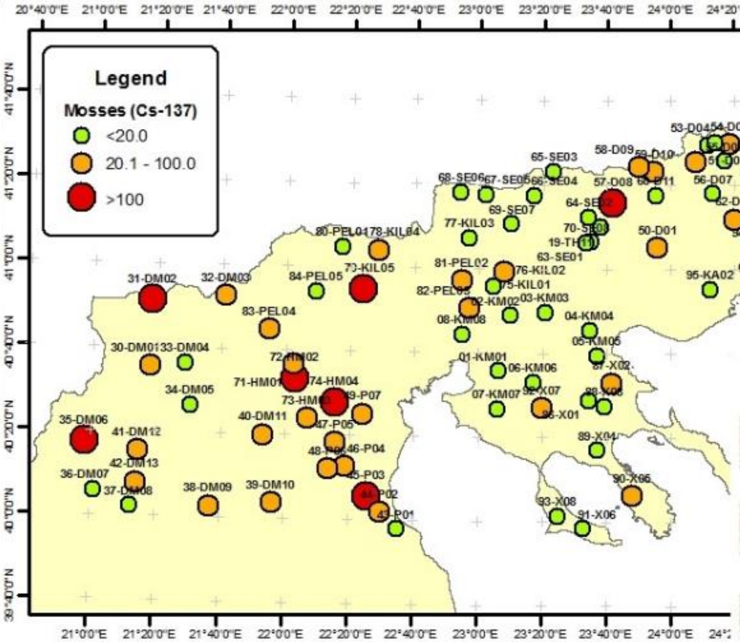
^{137}Cs (Bq kg^{-1})	
Max	425
Min	1.8
mean	35

$$\frac{A_{surface}}{A_{root}} = 0.9$$

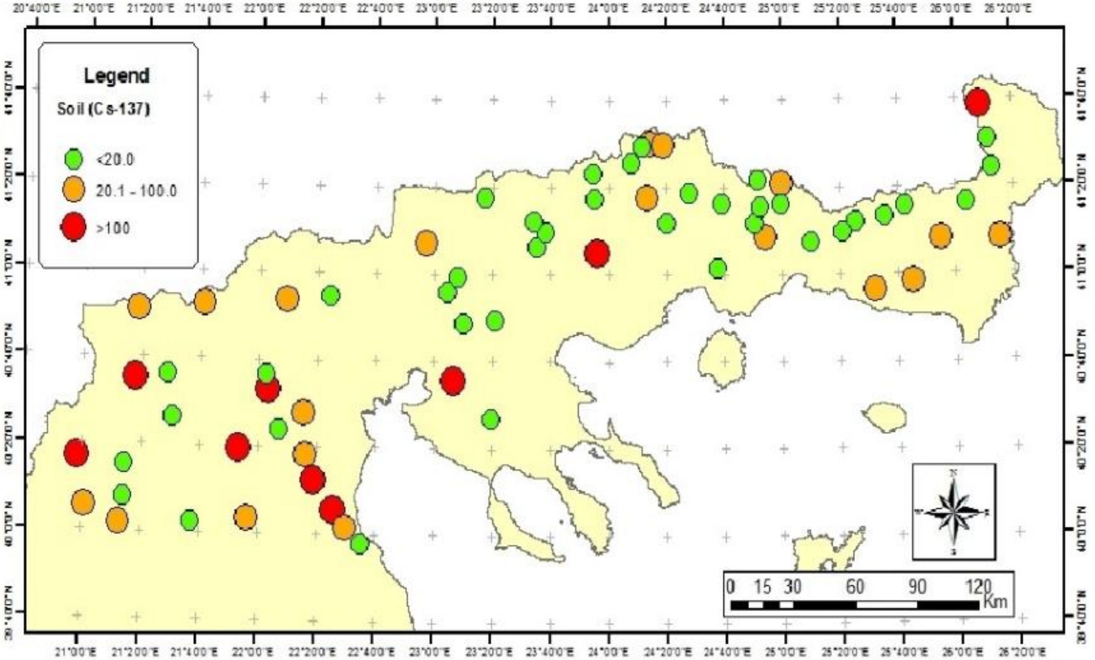
	^{137}Cs (Bq kg^{-1})	
Serbia	--- (34)	(Krmar, 2007)
Slovakia	0.7 - 103 (-)	(Yu.V.Aleksiayenak, 2013)
Belarus	5 – 4833 (-)	

^{137}Cs activity concentrations in mosses July-Sept 2016



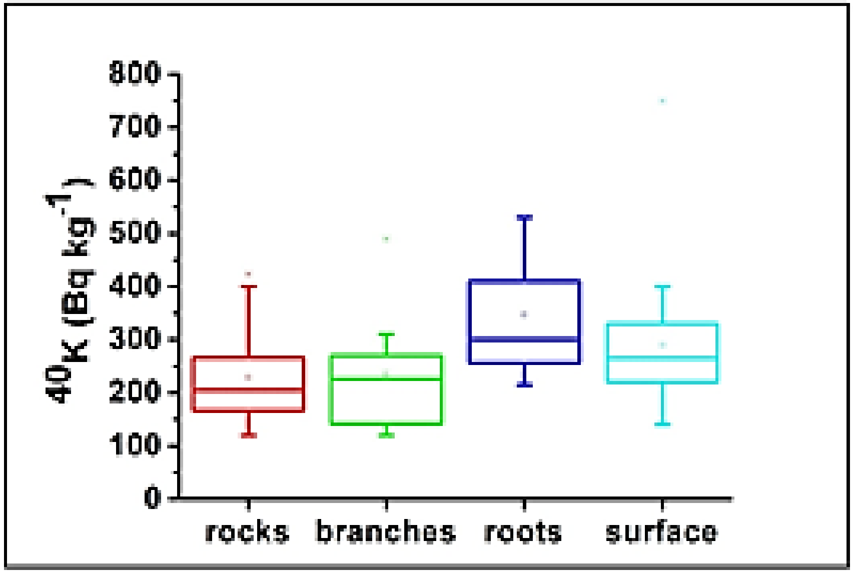


^{137}Cs in mosses
1.8-425 Bq kg^{-1}



^{137}Cs in soil
1-1536 Bq kg^{-1}

^{40}K activity concentrations



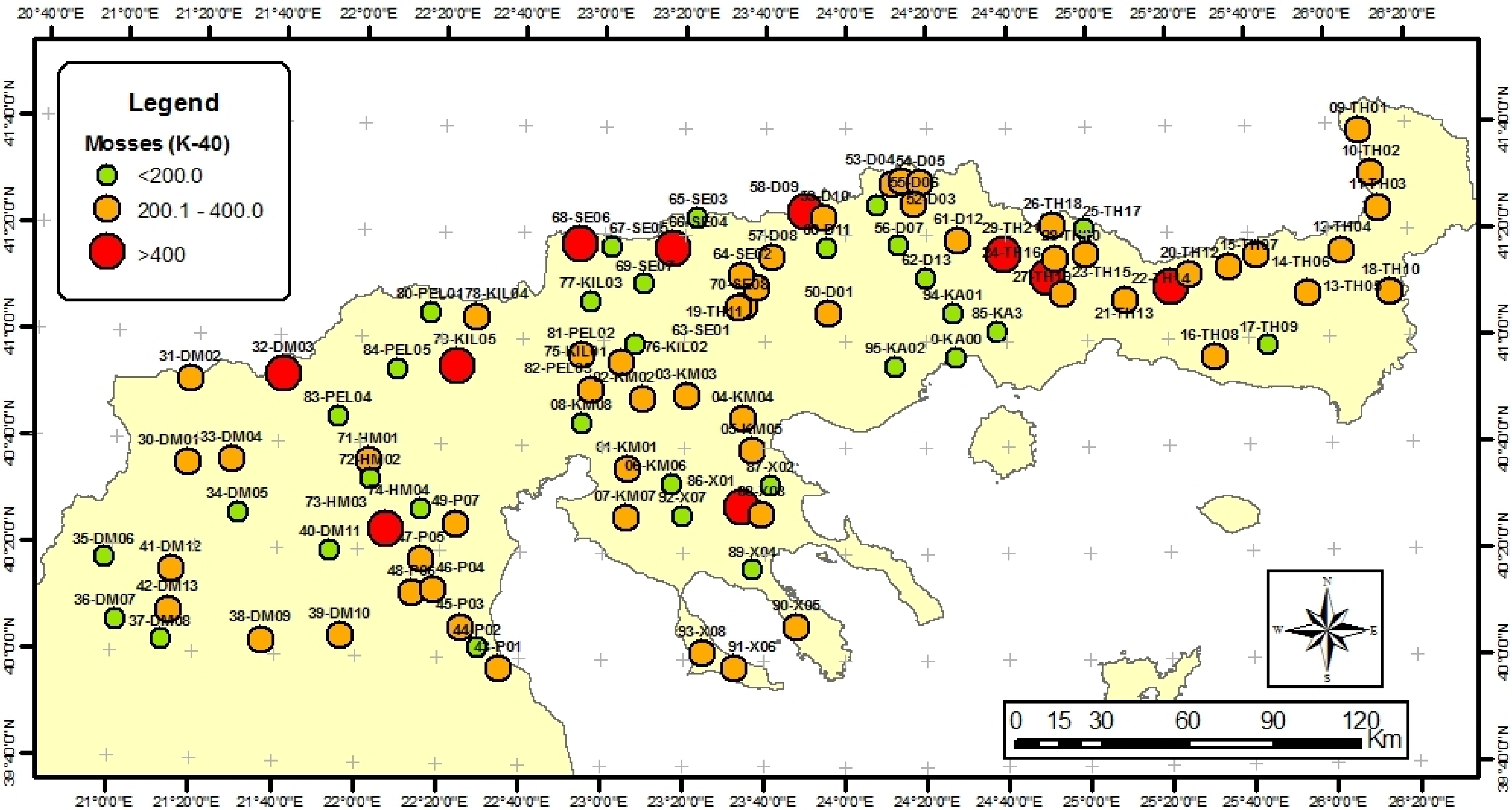
collected from different surface type

^{40}K (Bq kg^{-1})	
Max	750
Min	120
mean	269

$$\frac{A_{surface}}{A_{root}} = 1.2$$

	^{40}K (Bq kg^{-1})	
Serbia	--- (281)	(Krmar, 2007)

^{40}K activity concentrations in mosses July-Sept 2016



Conclusions

- ^{210}Pb, ^{7}Be, ^{137}Cs and ^{40}K activity concentrations determined in 95 moss samples collected from Northern Greece
- No correlation among the concentrations of radionuclides (^{210}Pb, ^{7}Be, ^{137}Cs, ^{40}K)
- The regions in which the activity concentrations of **^{137}Cs** in **moss** samples are **high**, are in a good correlation with the regions where the activity concentrations of ^{137}Cs in **soil** samples are **high**
- The majority of ^{137}Cs in mosses has arrived through re-suspension
- **No great variation** in the concentrations of ^{7}Be due to different altitudes or meteorological conditions (preliminary results)
- Observed **differences** of ^{7}Be concentrations (up to 50%) among **sampling surfaces** (^{210}Pb: 13%, ^{137}Cs: 10%, ^{40}K: 20%)

Conclusions

- The concentrations of 33 heavy metals in mosses were determined
- *Different Factors* according to Principle Component Analysis affect their concentrations
- "Marine elements" don't present systematically higher concentrations in distances closer to the sea→ some contribution from local sources of pollution
- As and Zn present high concentrations in some specific areas→ probably connected with local emission sources or/and geological reasons
- Cr, Ni present high concentrations in the same areas→ possible source ophiolites rocks or/and industrial activities
- ^{210}Pb, ^{7}Be, ^{137}Cs and ^{40}K activity concentrations determined in 95 moss samples collected from Northern Greece
- No correlation among the concentrations of radionuclides (^{210}Pb, ^{7}Be, ^{137}Cs, ^{40}K)
- The regions in which the activity concentrations of **^{137}Cs** in **moss** samples are **high**, are in a good correlation with the regions where the activity concentrations of ^{137}Cs in **soil** samples are **high**
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