Mosses as biomonitors of trace elements in Greece

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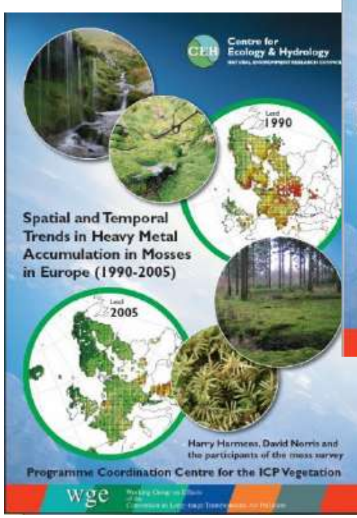
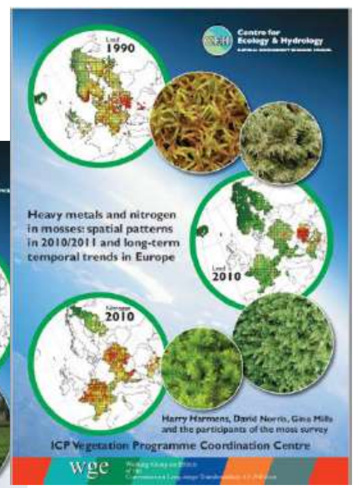
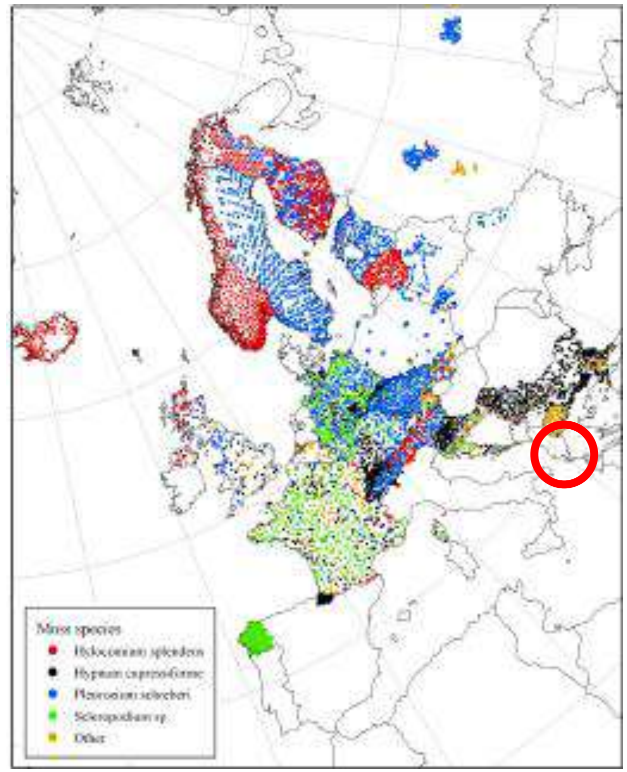
Mosses:

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







Collection substrates

Lithotopos, Serres

Neo Petritsi, Serres

Fteri, Pieria

Ano Poroia, Serres

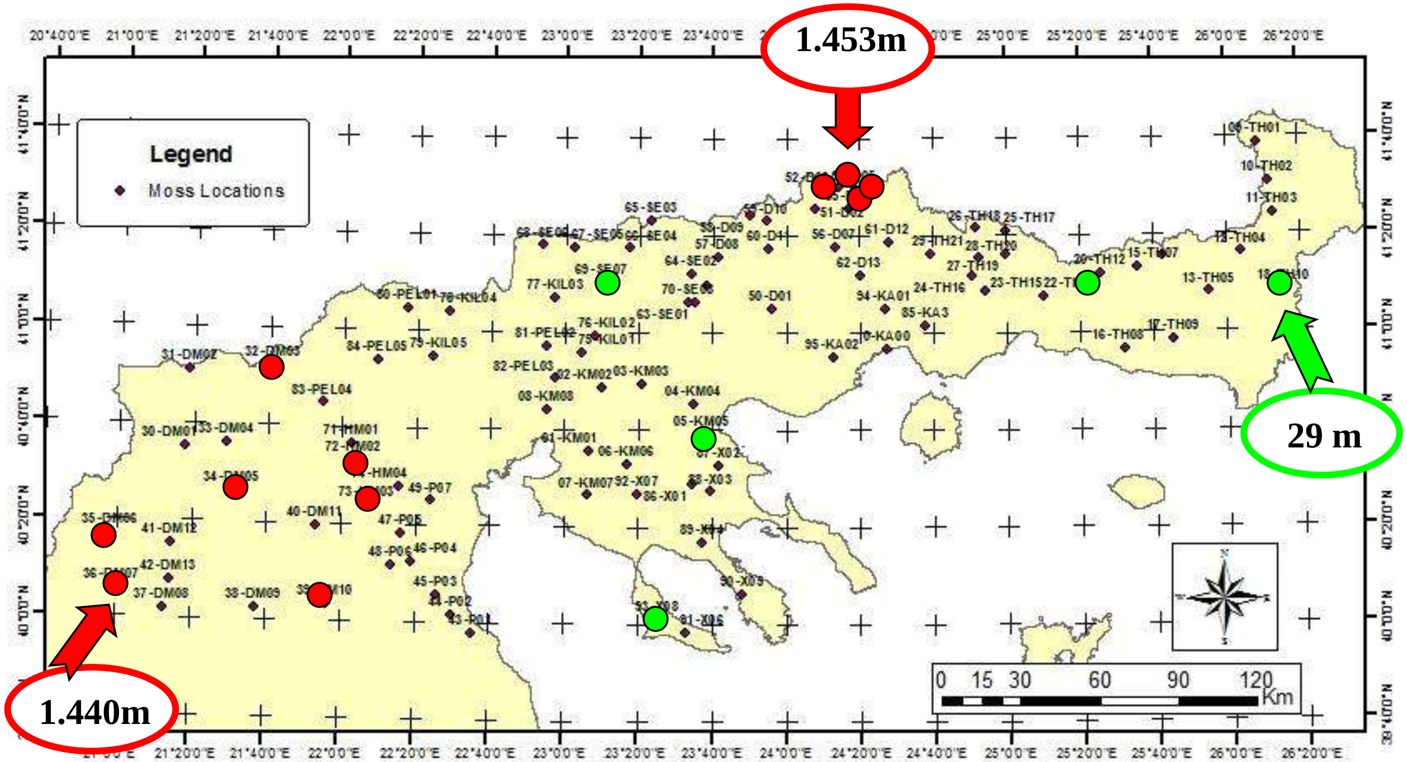
Moss species

***Hypnum cupressiforme* Hedw.**

Hylocomium splendens

Annual segments

Study area - Northern Greece



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

Trace Elements

- **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 & agricultural activities
- Fossil fuel combustion
- Vehicle emissions & transportation

- ***Metal*** *Industry* (Al, As, Cr, Cu, Fe, Zn)
- ***Manufacturing*** *industry & construction* (As, Cd, Cr, Hg, Ni, Pb)
- ***Electricity*** *&* ***heat*** *production* (Ni, Cd, Hg, V)
- *Road* ***transportation*** (Zn from tires, Cu & 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: drainage (40^{o} C), cleaning of impurities, homogenization, pellets

Measurement

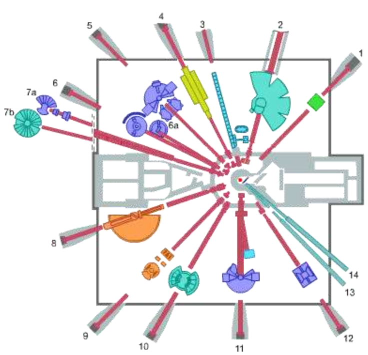
- Irradiation: **IBR-2 fast pulsed reactor** (Frank Laboratory of Neutron Physics, JINR, Dubna, Russia)
- *Irradiation* time :

  -***Short* lived isotopes** (Cl, V, I, Al, Mg e.t.c) for (180 sec)

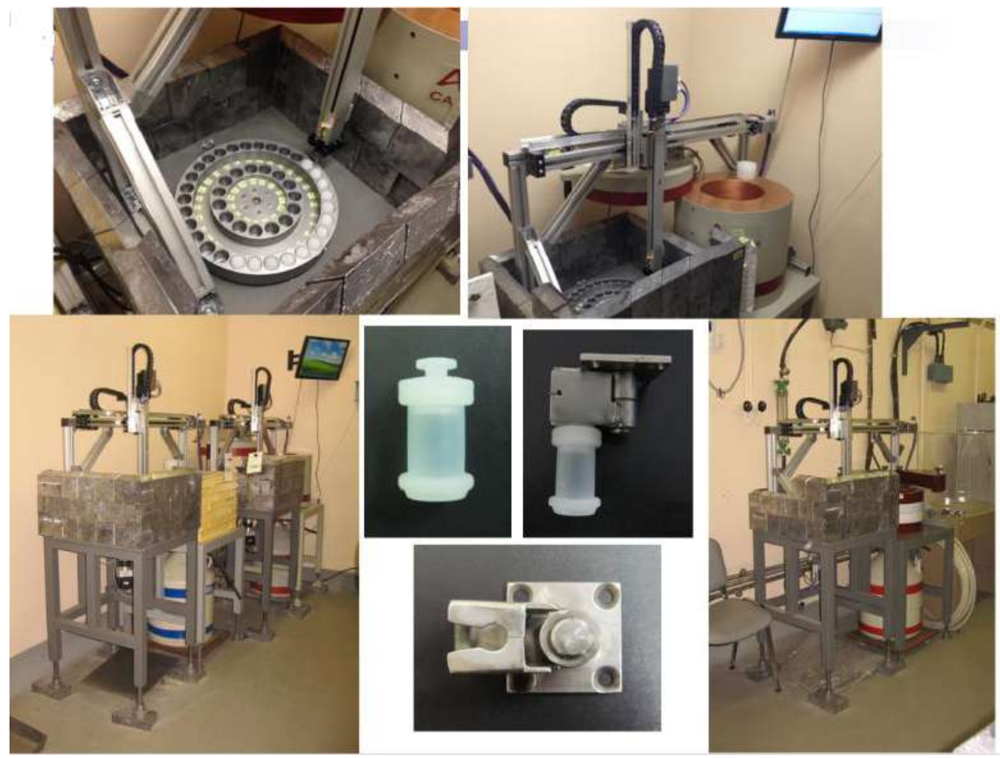
  -***Long* lived isotopes** (Br, As, Ba, Mo, K, Na, Zn, Ag, Sc e.t.c) for (4-5 days)

- Sample activities were measured with HPGe detectors (40% relative efficiency) and 33 elements concentrations were determined

Experimental facility: REGATA at IBR-2 reactor



Automation of reactor



Methodology - Source apportionment (I)

- The chemical composition data of the moss samples was used for the application of **Positive Matrix Factorization (PMF)**, for the source apportionment of the measured chemical species.

The method is based on the assumption that the concentration (C_{ij}) of a chemical species *j* measured during the time period *i* may be expressed as the sum of the contributions of its different emission sources:

$$C_{ij} = \sum_{k=1}^{p} g_{ik} \cdot f_{kj} + e_{ij}$$

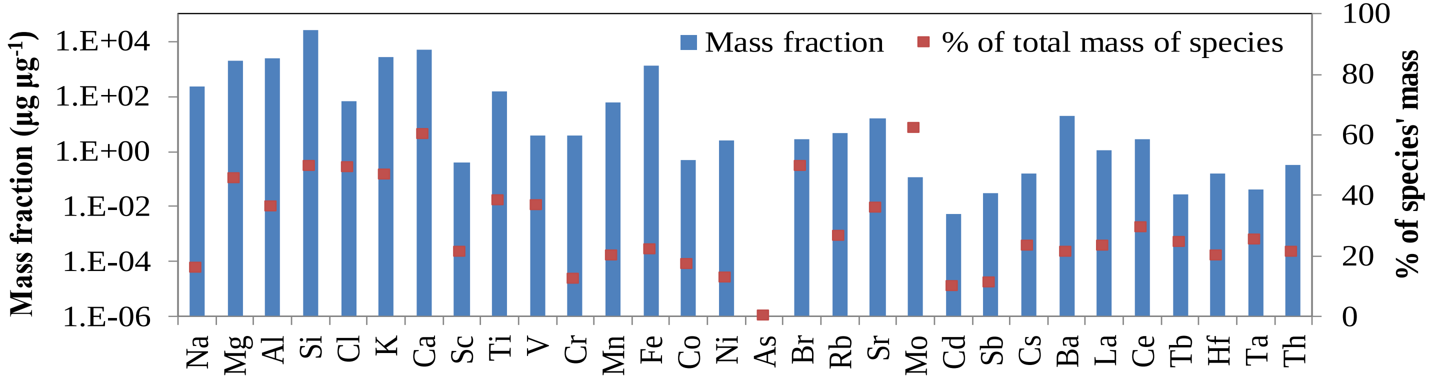
- f_{kj}: Mass fraction of species *j* in the chemical profile of source *k*
- e_{ij}: Residual (the difference between the measured and fitted value).
- g_{ik}: Contribution of source *k* during time period *i*

Methodology - Source apportionment (II)

Model applied:	EPA PMF 5.0
Number of samples:	105
Strong species (26):	Na, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, As, Br, Rb, Sr, Mo , Sb, Cs, Ba, La, Ce, Tb, Hf, Ta
Weak species (4):	Mg, Al, Cd, Th
Extra modelling uncertainty:	10%
Number of runs:	100

- The EPA PMF5.0 model was run for the case of 4-10 sources. The optimum solution was found for **5 sources**, based on the distribution of residuals, G-space plots and Q values.
- The rotational ambiguity of the solution was assessed through the use of different Fpeak values (in the range -1.0 to 1.5). The best solution was found for **Fpeak = -0.5.**

Results – Chemical profiles of identified sources

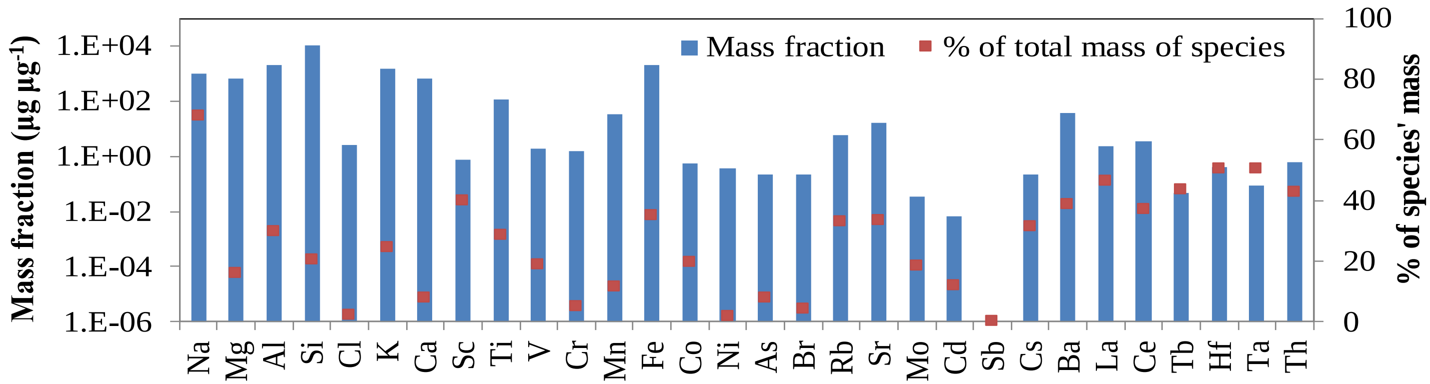


Soil dust

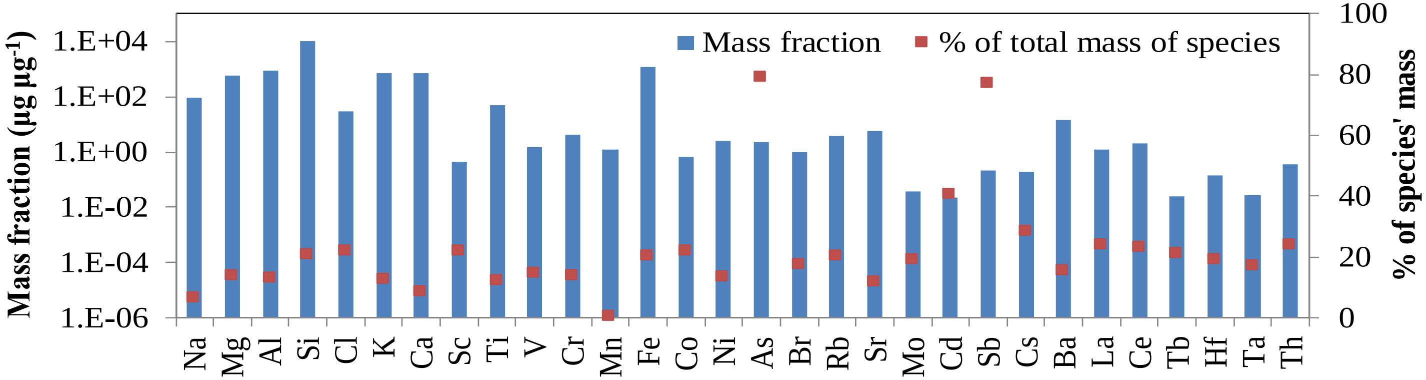
Mainly crustal components contribute to this source (Mg, Al, Si, Ca, K, Ti, Fe)

Aged sea salt

High contribution from Na
Cl/Na ratio << 1.8 (sea water ratio)
→
Cl depletion due to the ageing of sea salt particles



Results – Chemical profiles of identified sources



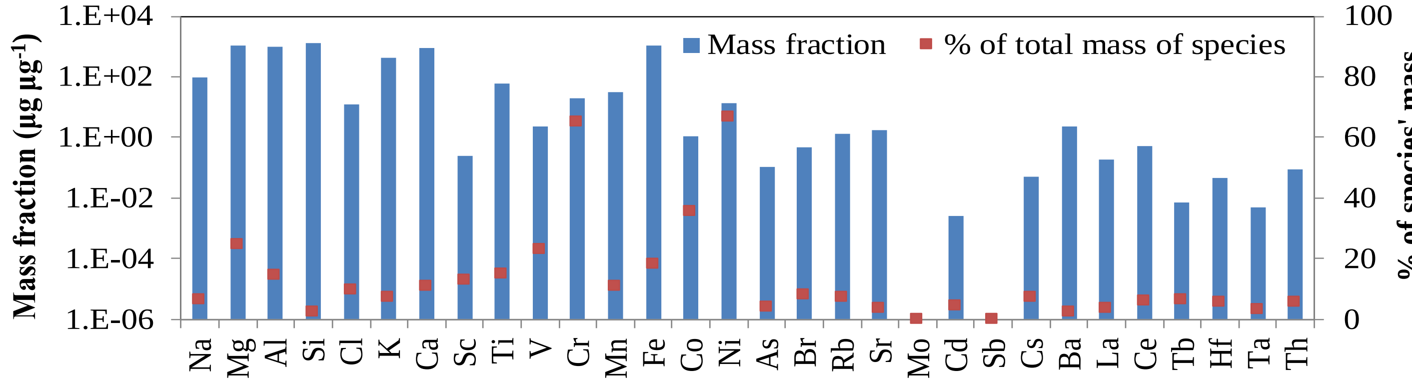
Road dust

Source related to vehicular traffic and identified by common traffic tracers (such as Sb and Fe)

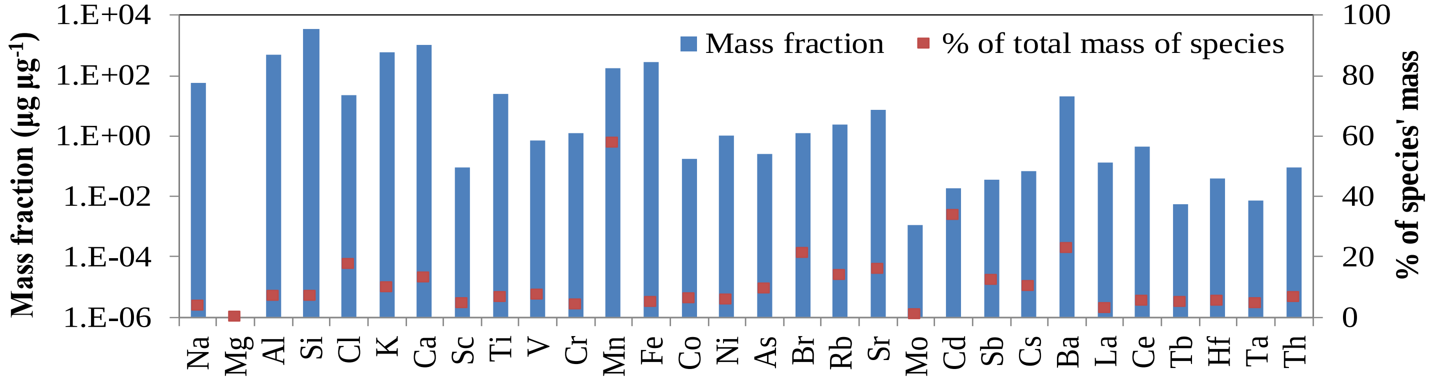
Lignite power plant

Identified by the high contribution of Ni and Cr

Could be also related to heavy oil combustion



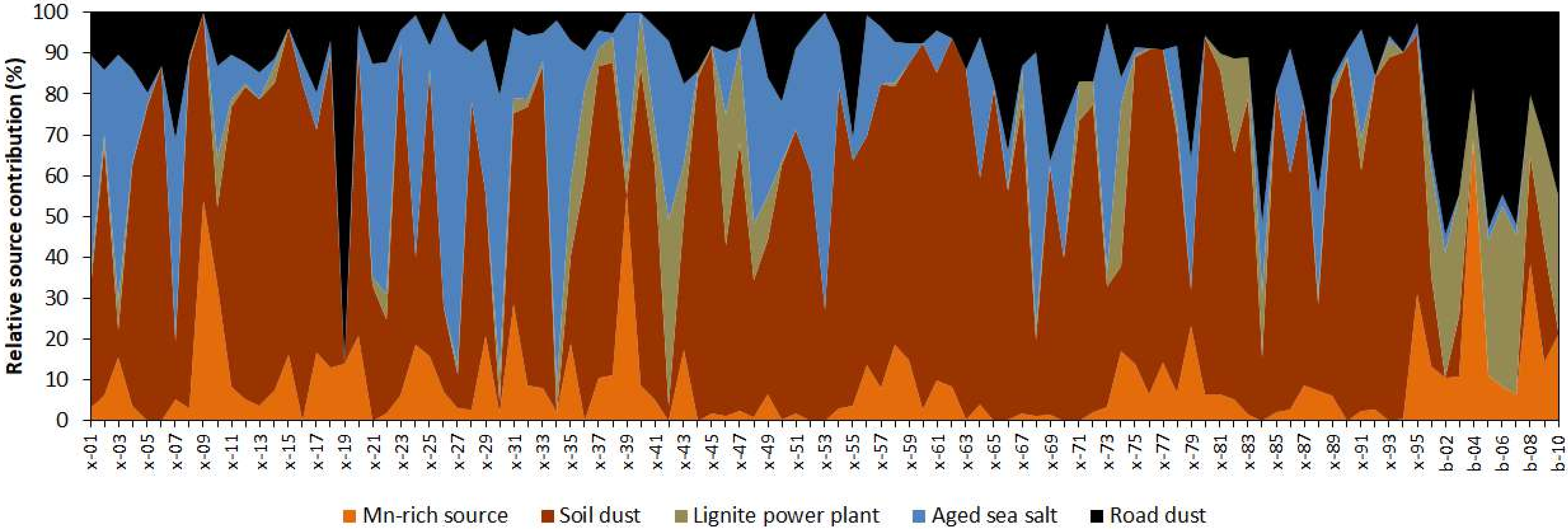
Results – Chemical profiles of identified sources



Mn-rich source

Possibly related to mining activities

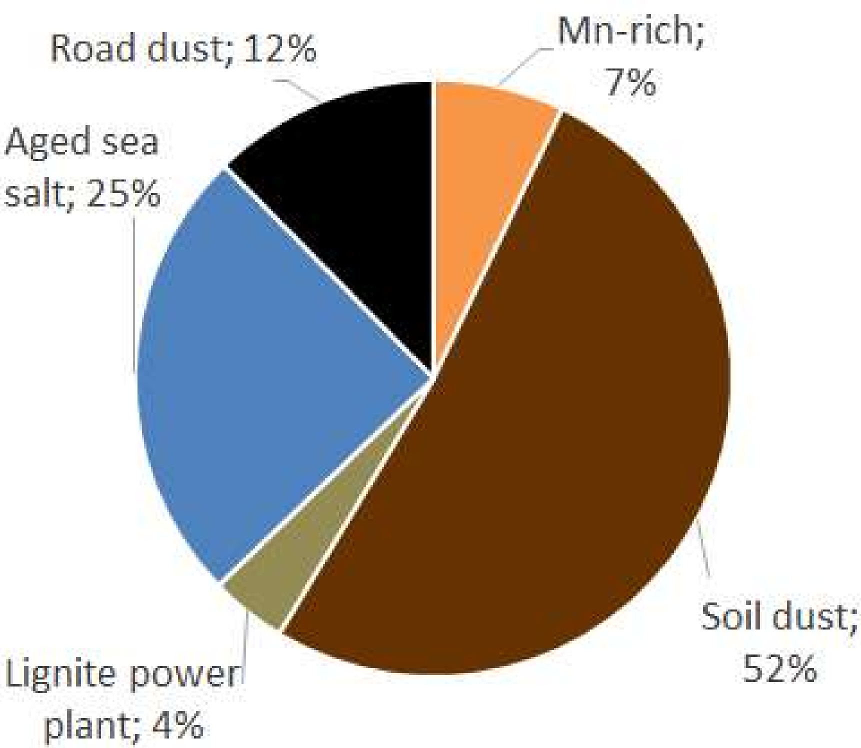
Results – Relative source contributions per sample



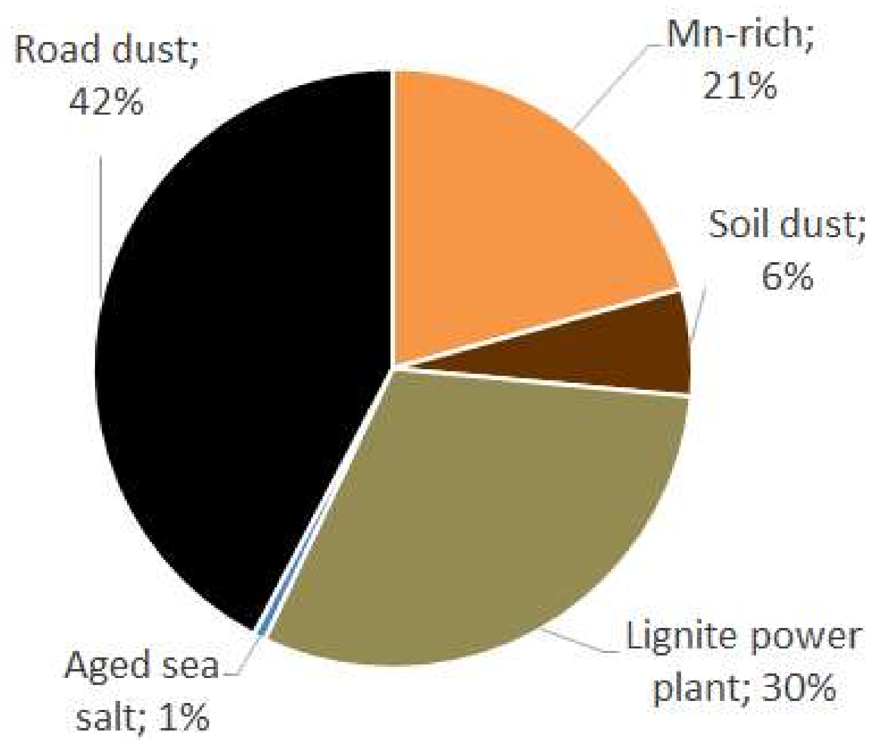
- High contribution from Road dust and Mn-rich source for samples b-01 – b-10, which are collected from sites close to mining activities
- High contribution from the Lignite power plant source was found in Western Macedonia, where the Ptolemaida-Amyntaio complex of lignite power plants is located.

Results – Average source contributions

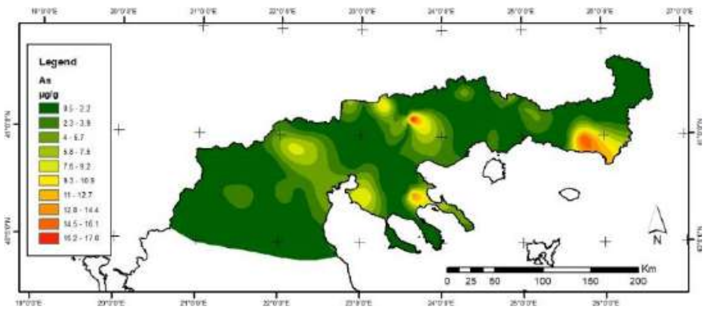
Northern Greece

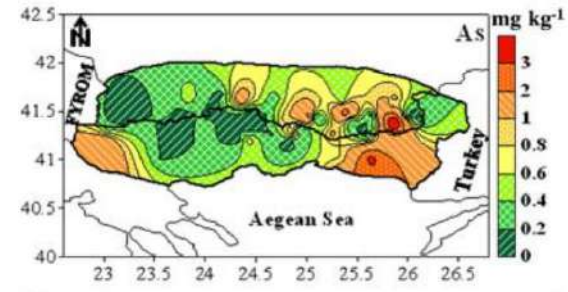


Stratoni, Chalkidiki



Arsenic (As)





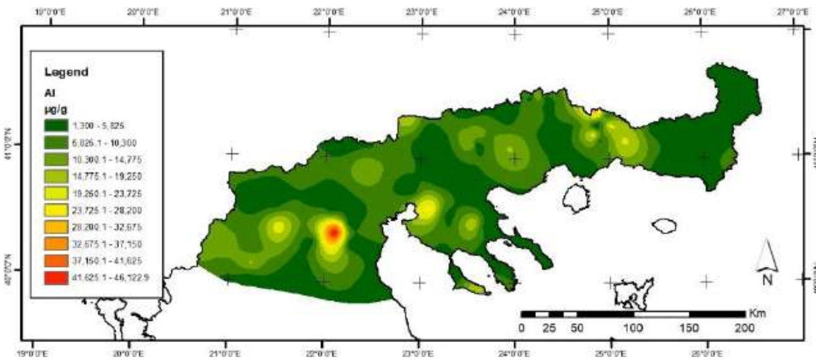
*Yurukova et al., 2009

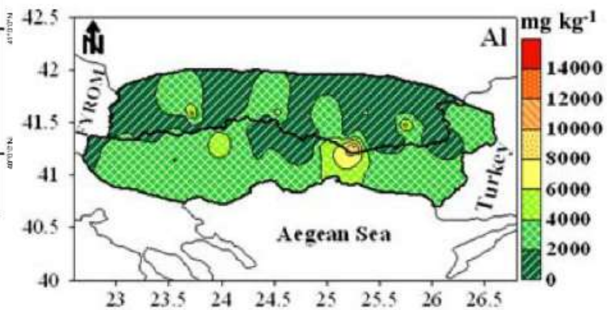
Stratoni Gulf: Mining activities (*metal ore and metal processing factory, solid wastes*):
→ Fe, As, Pb, Cu, Cr, Cd *Pappa et al., 2016

Sources:
-*soil* dust (*geological* formations: volcanic rocks)
- *industrial* and *mining* activities

As (μg/g)-moss survey 2010/2011											
	Greece (2015/16)	Italy	Spain	North 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)





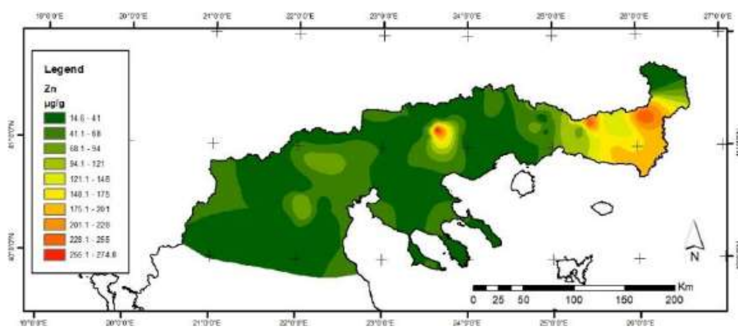
*Yurukova et al., 2009

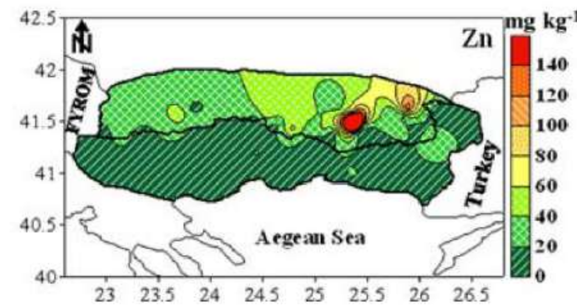
-good indicator of mineral particles, -found in Earth's crust

sources:
- windblown *soil* dust
- *Road* dust

Al (µg/g)-moss survey 2010/2011											
	Greece(2015/16)	Italy	Spain	North 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)





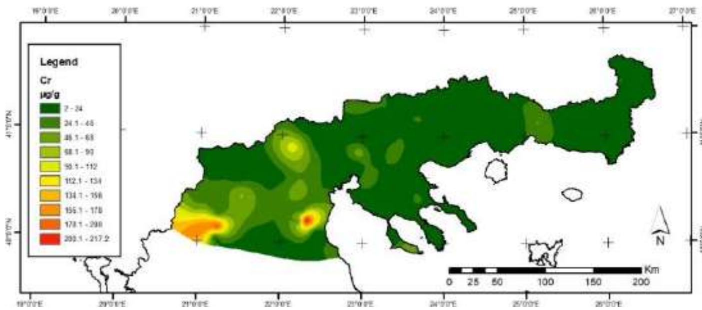
*Yurukova et al., 2009

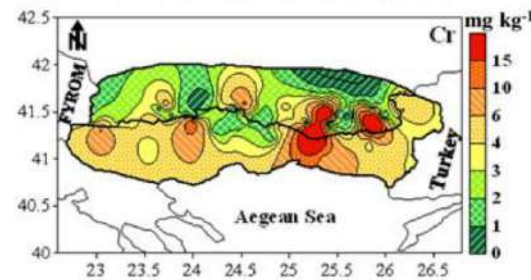
-used in manufacture of rubbers, tires
- *As* and *Zn* follow the *same* pattern in some areas (maybe the same geological formations)

Sources:
-*soil* dust
-*Vehicular* traffic

Zn (µg/g)-moss survey 2010/2011											
	Greece(2015/16)	Italy	Spain	North 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)



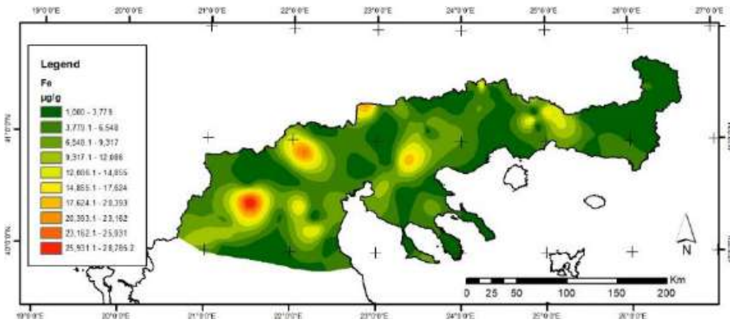


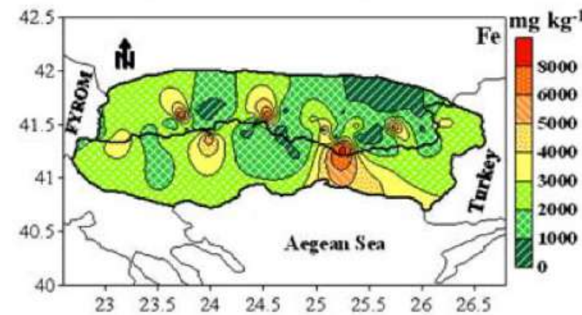
*Yurukova et al., 2009

Sources:
-heavy oil combustion
-*soil* dust (maybe ophiolites rocks)

Cr (µg/g)-moss survey 2010/2011											
	Greece(2015 /16)	Italy	Spain	North 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)





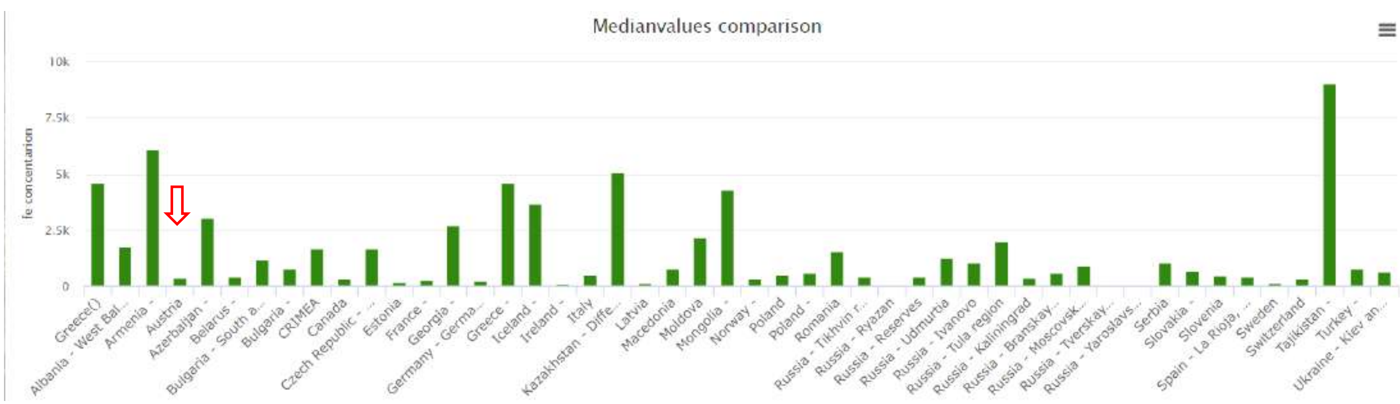
*Yurukova et al., 2009

-Found in the Earth's crust

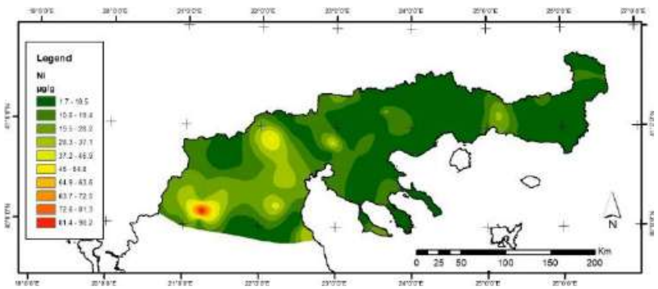
sources:

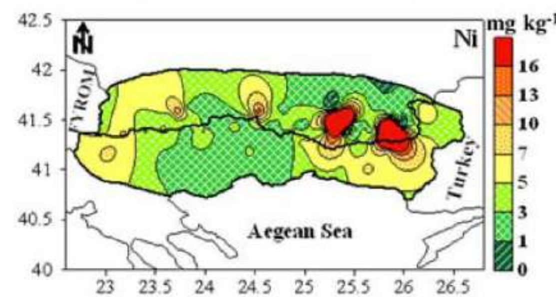
-*soil* dust (geological rocks-iron laterites)

-Aged sea salt factor



Nickel (Ni)





*Yurukova et al., 2009

Chemical similar to Fe, Co, Cu
sources:
-*heavy oil combustion*,
-*soil* dust (ophiolites rocks: Cr, Ni)

Ni (μg/g)-moss survey 2010/2011											
	Greece(2015 /16)	Italy	Spain	North 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

Summary & Conclusions

- The concentrations of **33** elements in mosses were determined
- **PMF** model was applied for source apportionment
- <u>**Five (5)** sources </u>were identified:

  -soil dust

  -road dust

  -aged sea salt

  -Lignite power plant

  -Mn rich source (mining activities)
- ***Stratoni area*** (close to mining activities) *related to Road dust and Mn rich source*
- ***Ptolemaida region*** → *high contribution from Lignite Power Plant*

Next steps:

- **Transfer factor** (TF) of trace elements from the atmosphere to mosses
- Study of the **transboundary transport** of trace elements
- Study of the elemental concentrations in soil
- Correlation between soil & moss elemental concentrations

Thank you!

EXTRA

Literature

-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

-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

PMF technique

-Variant of factor analysis with non-negative factor elements
-takes into account uncertainties in observed data values
-the number of sources are specified initially

Two products-matrices of the technique:
-one that gives the contribution of each of the source factors to each measurement
-one that gives the contribution of each independent measurement (elemental concentrations) to each of the sources

INAA measurements-details

- Short lived nuclides:
- *Irradiation time*: 180 sec
- *Neutron type*: thermal (0-0.055 eV)
- *Flux*: $1.5*10^{12}$ n s^{-1} cm^{-2}
- *γ-measurement*: 15 min

INAA measurements-details

Long lived nuclides:

- *Irradiation time*: 4-5 days
- *Neutron type*: epithermal (0.055-10^5 eV)
- *Flux*: 3.6*10^{11} n s^{-1} cm^{-2}
- *γ-measurement*:

5 h(after 3 days of irradiat.)

20h (after 20days of irradiat.)

Calculation of the elemental concentrations

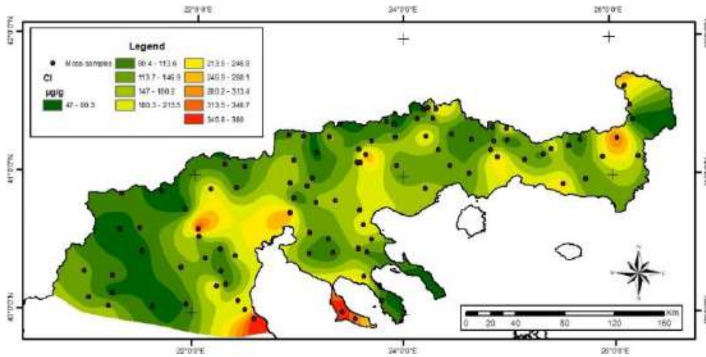
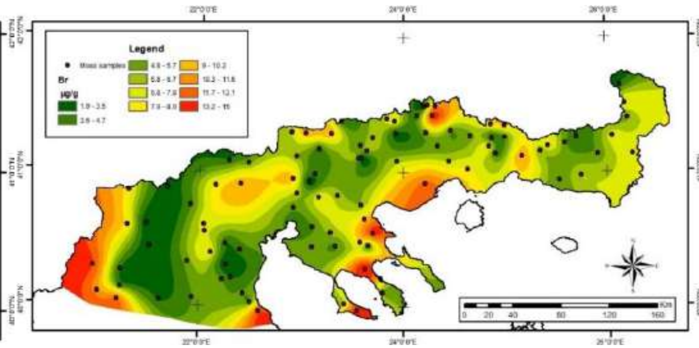
- Simultaneously irradiation of sample and standard
- Spectra analysis of sample and standard
- Calculation of elemental concentrations in sample through proportional comparison of the same isotopes in the sample and standard:
- $C_{sample} = \frac{A_{sample} * C_{stand.}}{A_{stand.}}$

- *Dmitriev A.Y., Pavlov S.S. (2013) Phys. Part. Nuclei Lett 10: 33. DOI:10.*

Descriptive Analysis

	Al	As	Cr	Fe	Ni	Sb	V	Zn	Ba	Co
Min	1350	0.52	2.04	1010	1.72	0.02	2.61	14.60	15.90	0.43
Max	46100	17.90	222	28700	138	3.23	33.40	282	519	20.30
Median	6160	1.62	14.70	4630	10	0.20	8.66	38.30	76.30	1.99

Distribution of Cl, Br, I, Na

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