MOSS BIOMONITORING OF TRACE ELEMENTS IN SLOVAK INDUSTRIAL AREAS, MINING COUNTRY, AND NATIONAL PARKS EXPERIENCING ENVIRONMENTAL STRESS

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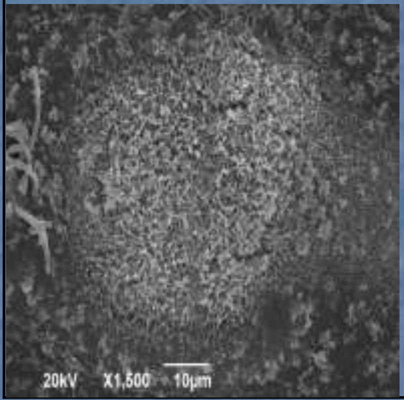
Introduction

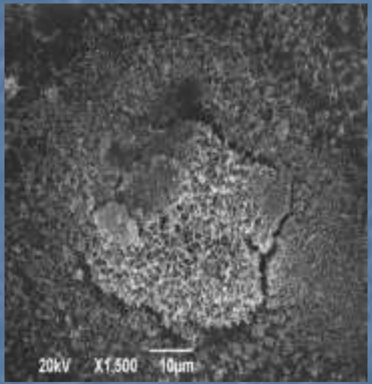
- The application of mosses as biomonitors of trace elements in selected Slovak industrial areas, mining country, and National parks affected by anthropogenic activity is reviewed. Moss was successfully used also to study temporal and spatial deposition of N and S. A combination of analytical data (NAA, and AAS in our case) with principle component analysis and correlation factor allowed pollution source characterization and apportioning in the sampled areas:
- Central Spiš (effect of heavy metalls); Aluminium plant Žiar nad Hronom; Central Nitra (Thermal power plant);
- Central Slovakia (mining area of Staré Hory, Ľubietová, Špania dolina);
- High Tatra National Park (TANAP) and Low Tatra National Park (NAPANT).

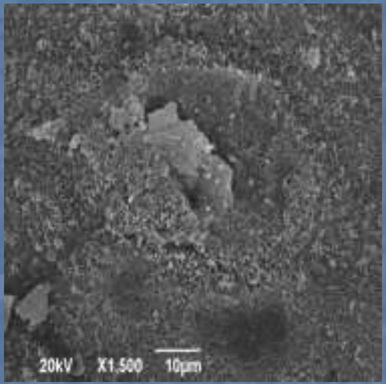
Material and methods

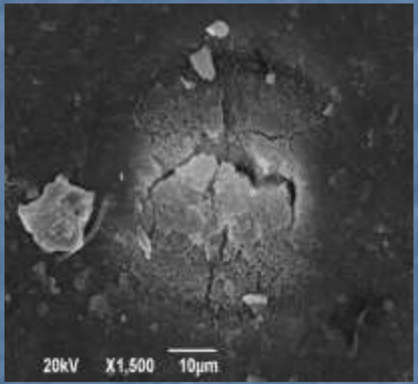
- The environmental samples (spruce needles, mosses, teeth) were not washed before analysis. Elemental analysis was applied to determine the concentration of S (LECO SC 132) and N (LECO SC 228) and the Pulsed fast reactor IBR-2 in FLNP JINR, Dubna, Russia equipped with the fast pneumatic transfer system REGATA and four irradiation channels for Instrumental neutron activation analysis, provides activation with thermal, epithermal and fast neutrons. (Frontasyeva, Pavlov, 2000).
- The foliage of forest tree species was treated on surface by JEOL Ionsputtering. They were assessed by scanning microscope JEOL 840 A and X-ray analyser LINK 10000. The wax surface SEM was done at the Matej Bel University Banská Bystrica. We used Co- Coefficient of occlusion (arithmetical mean of wax quality of 200 stomata per needles/leave).
- The accuracy of data published in paper was verified by 109 separate laboratories and tested by the IUFRO programme (Maňkovská, 1996). The environmental samples were evaluated by common statistical methods (ANOVA).

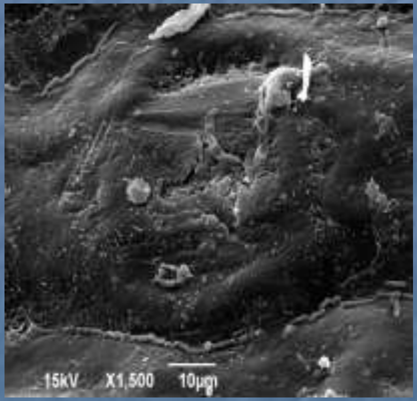
Classification of changes of the epicuticular waxes of *Picea abies* Karst.





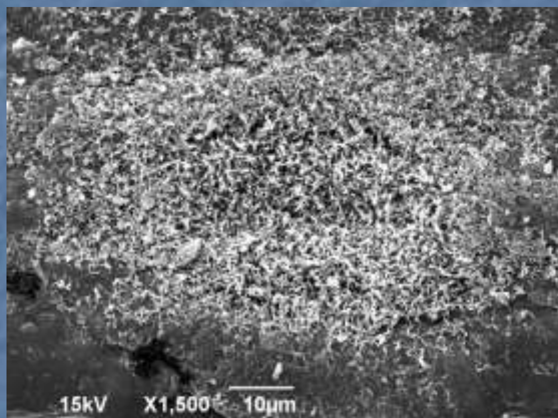


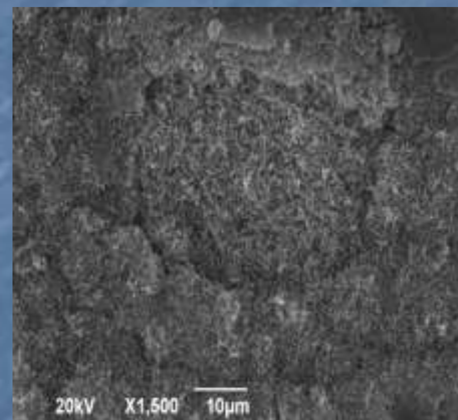


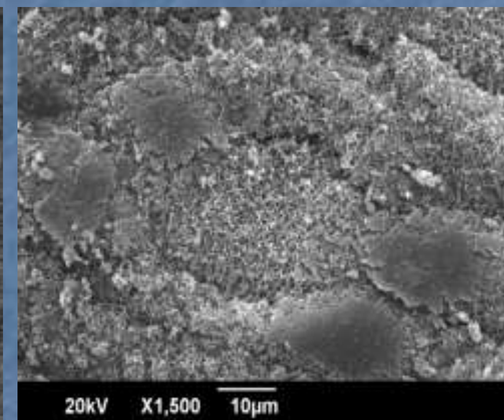


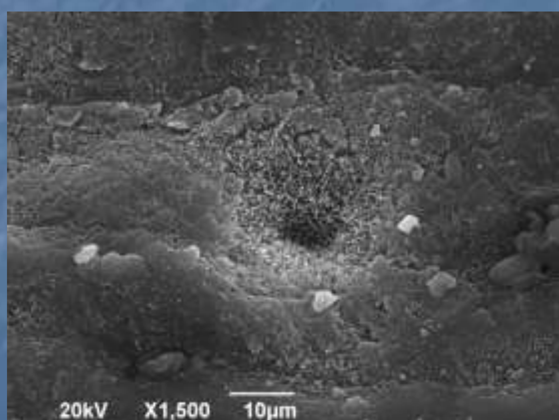
- *Class I* Maximum of 10% of the total stomatal area shows the beginnings of fussion of single wax tubules.
- *Class II* Some of the atypically aggregated wax tubules fuse to small wax tufts at different parts of the stomatal area. The latter cover 10% to 25% of the total stomatal area.
- *Class III* In addition to the wax tufts plate-like wax parts can be found which, in total, cover more than 25% and up to 50% of the total stomatal area.
- *Class IV* More than 50% and up to 75% of the total stomatal area shows small parts of wax tufts as well as large platelet wax forms.
- *Class V* More than 75% of the total stomatal area is characterized by considerably changed wax microstructures. The stomatal antechamber is almost or completely occluded with an amorphous wax plug.

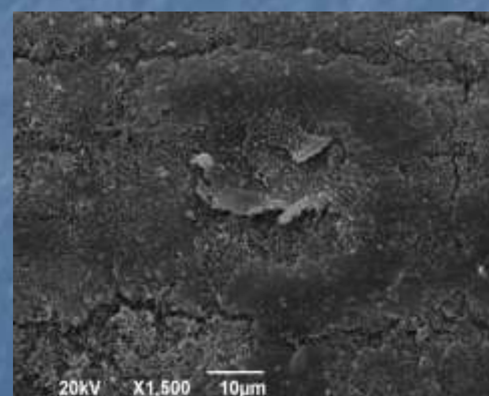
Classification of changes of the epicuticular waxes of *A. abies*





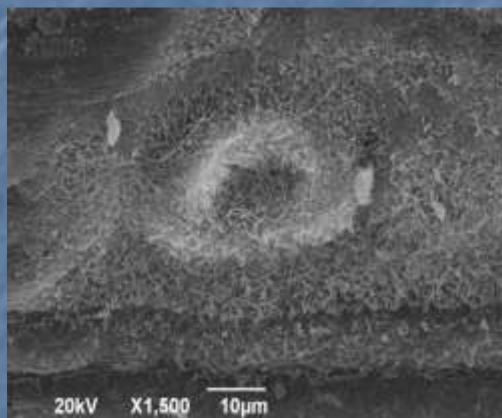


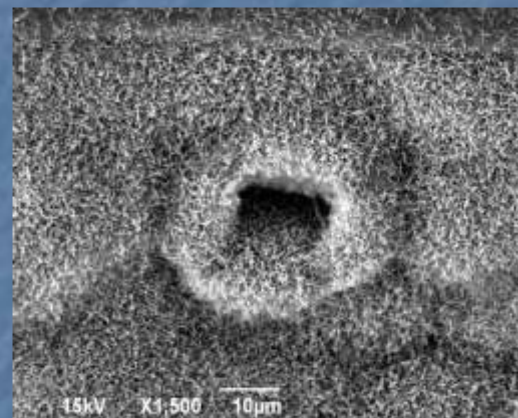


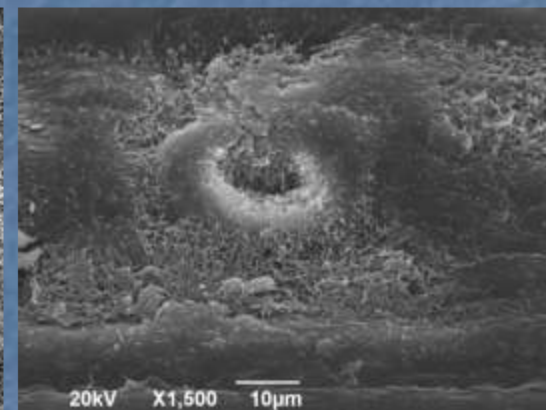


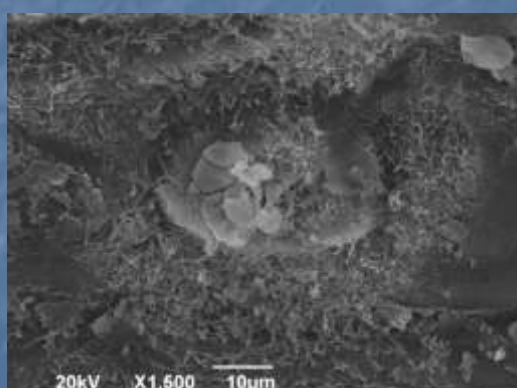
Class 1	Class 2
Class 3	Class 4
Class 5	

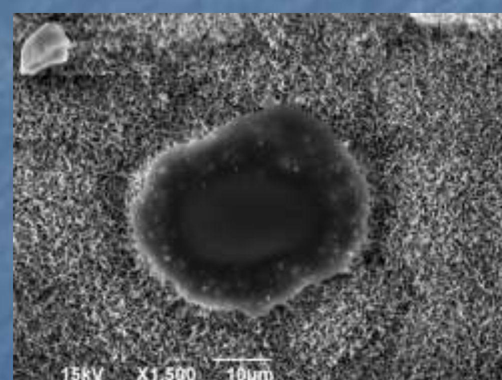
Classification of changes of the epicuticular waxes of *P. silvestris L.*





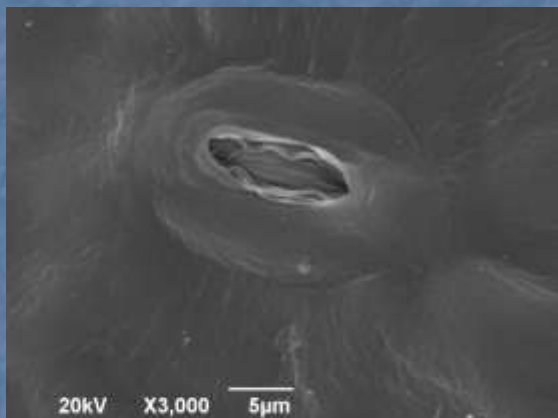


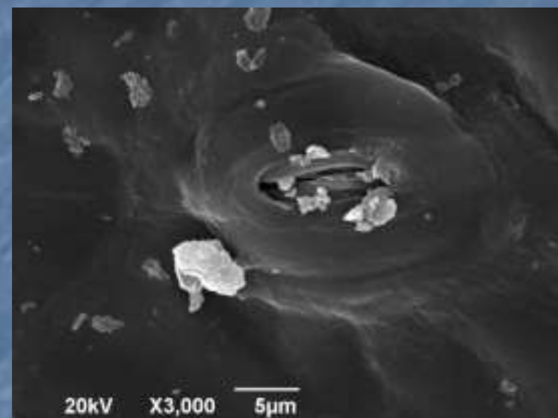


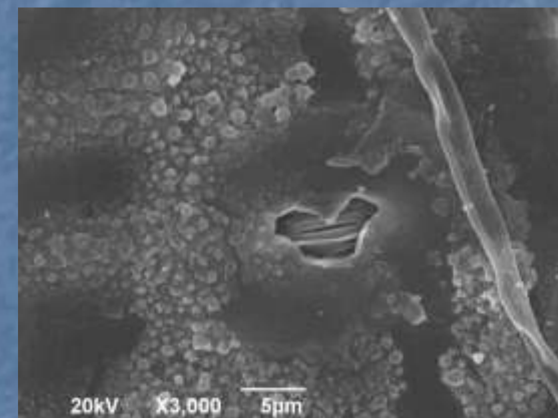


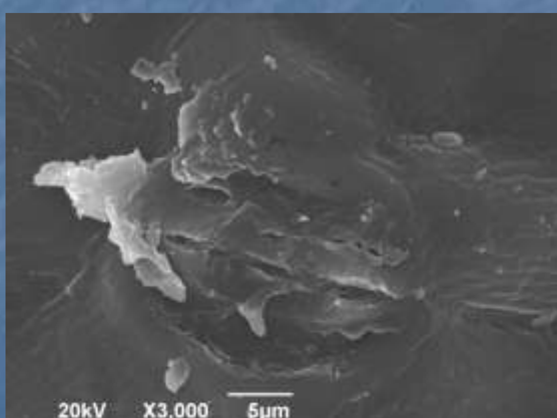
Class 1	Class 2
Class 3	Class 4
Class 5	

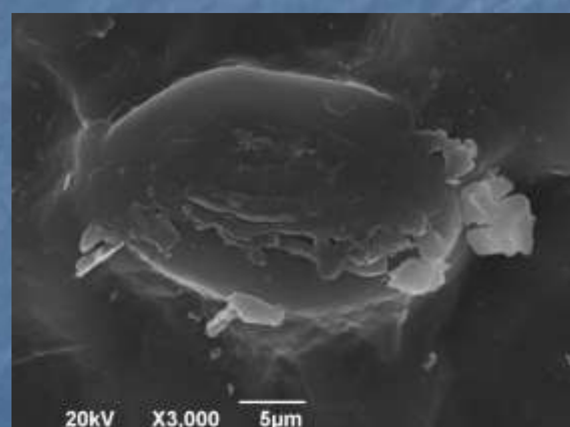
Classification of changes of the epicuticular waxes of *F. sylvatika*.





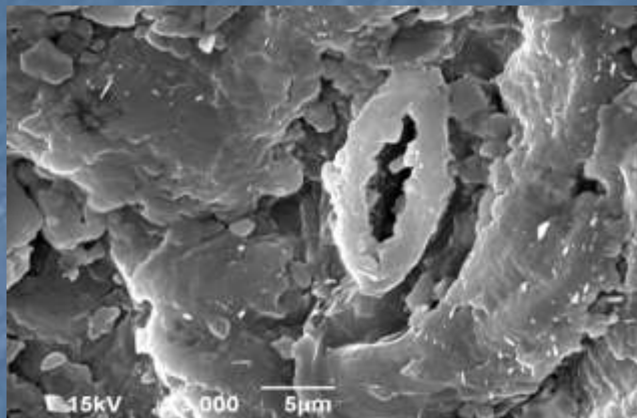


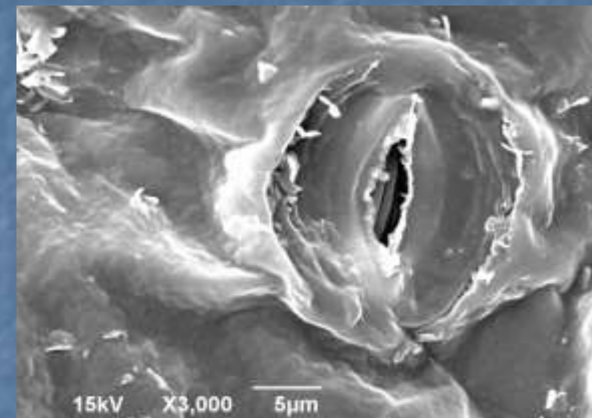


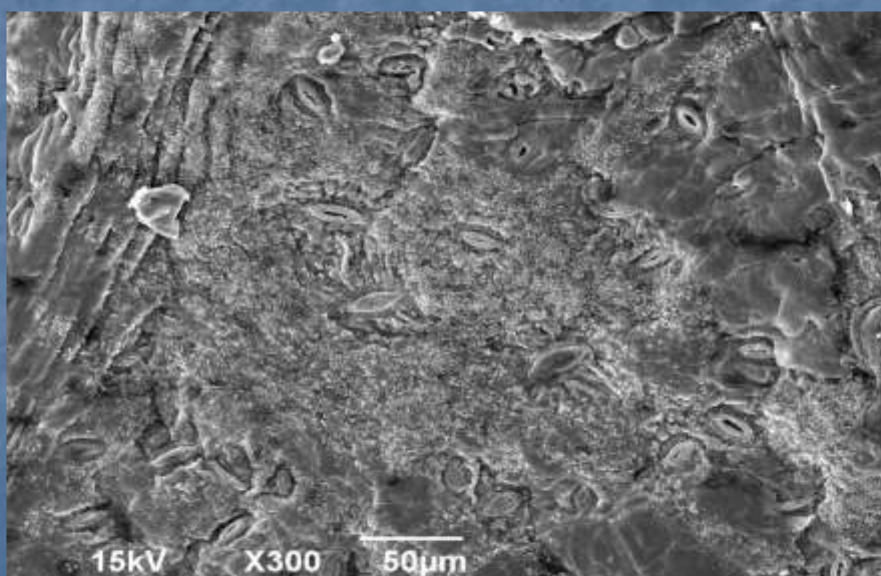


Class 1	Class 2
Class 3	Class 4
Class 5	

Classification of changes of the epicuticular waxes of *B. pendula*



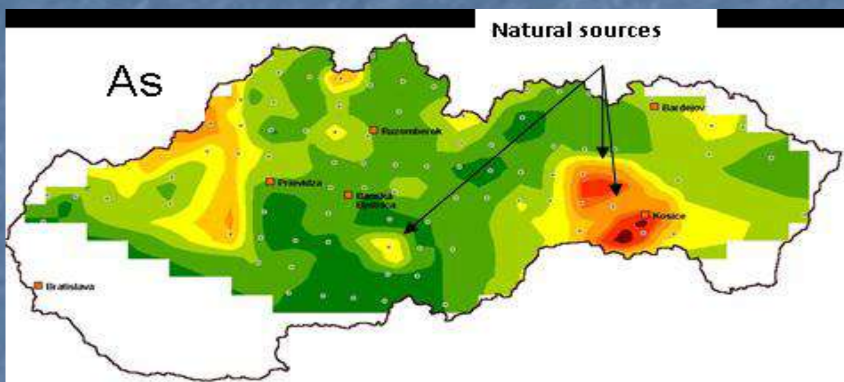


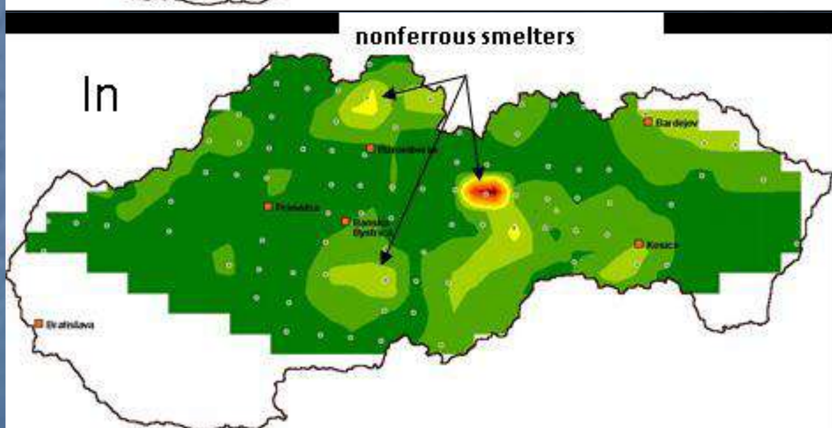


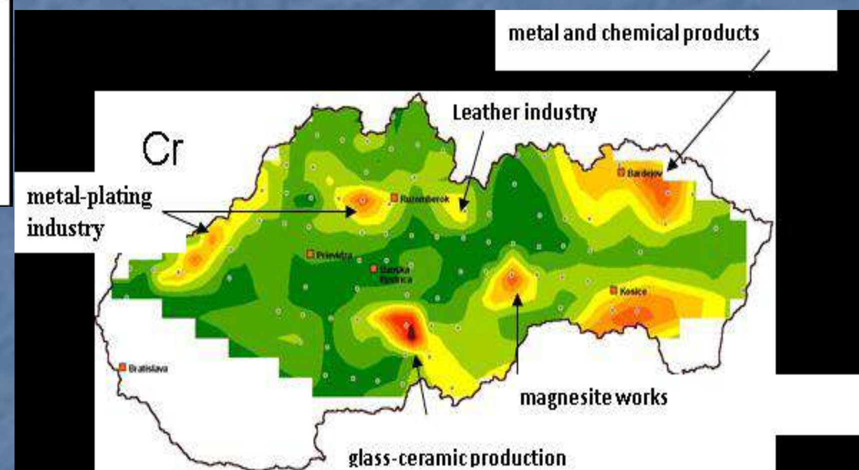
Class 1	Class 3
General view on topsides of birch	

Results and discussion

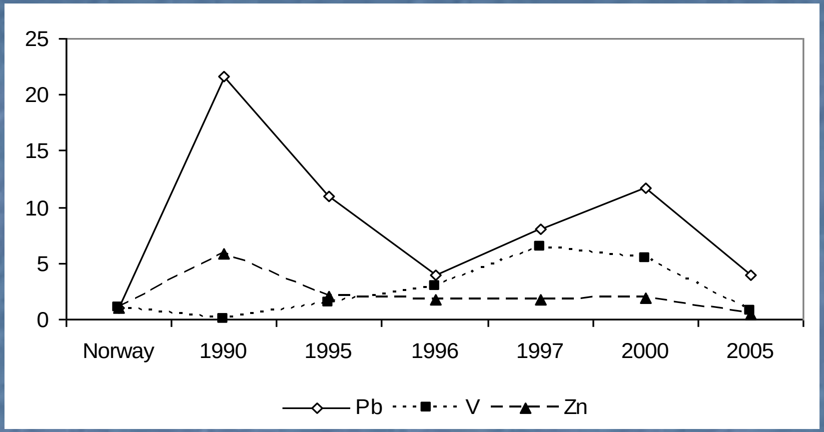
The results of these investigations were presented in the form coloured contour maps for each element

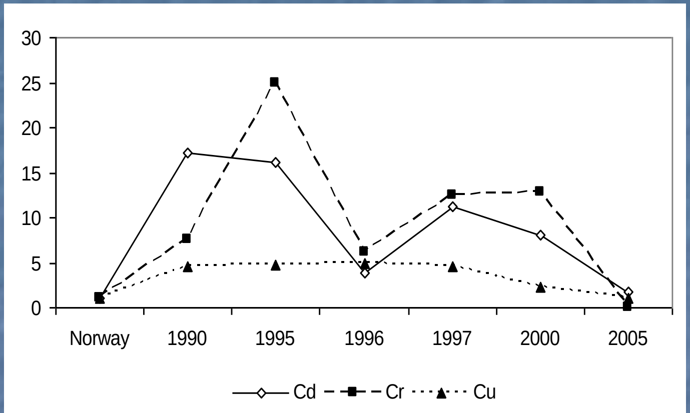


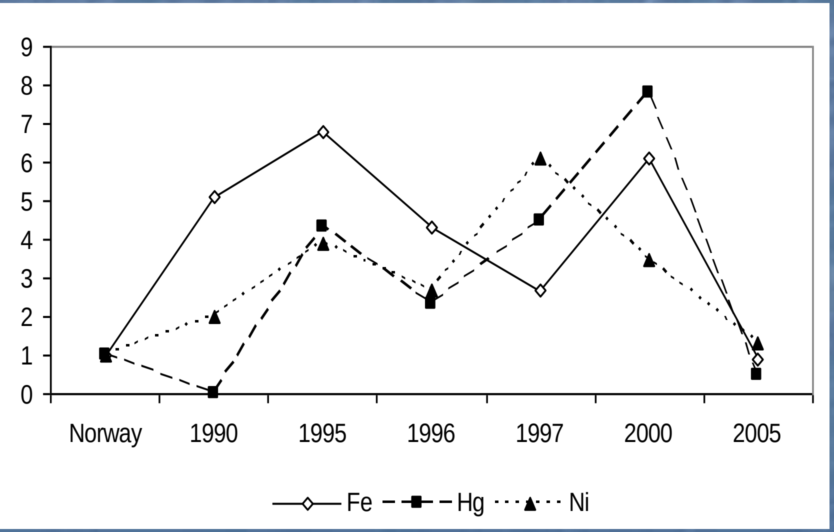




Concentration of Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn (average) in mosses for Slovakia in all survey years







Note:
Year (number of PMP):
1990(58);1995(79); 1996(69); 1997 (74); 2000 (86); 2005(82);
PMP- Permanent monitoring plots

Coefficient of loading by elements KF in the year 2000

Kf=Cx1/Cxn ,Where: **Cx1** –concentration (median) of respective element in l sample of moss in SLovakia
Cxn – concentration (median) of the same element in Norway

Sites	< 1	1-10	10-50	>50	Kf
Low Tatras	Au, Br,I, Mg, S, Se, Sm, Ti	Ag,Al,As,Ba,Ca,Cd,Ce,Cl,Co,Cr,Cs,Cu,Fe,Hg,In,K,La,Mn, Mo,N,Na,Ni,Pb,Rb,Sb,Se,Sr,Ta,Tb,Th,U,V,W,Yb,Zn,Zr	Hf		4.2
Žiar basin	Au, Br,Cl, I, In, Mn	Ag, Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe , Hg, K, La, Mg, Mo, Na Ni, Rb, Sc, Se, Sm, Sr, Tb, Th, Ti, U, V, W, Zn	Hf, Pb,Ta,Yb	F	6,2
High Tatras	Au, Br, Ca, I, Se	Ag, As, Ba, Cd, Ce, Cl, Co, Cs, Cu,Fe, Hg, In, K, La, Mg, Mn, Mo, N,Na, Ni, Pb, Rb, S, Sc, Se, Sm, Sr, Tb, Th, Ti, U, V, W, Zn	Al, Cr, Sb, Ta, Yb, Zr	Hf	6.7
Central Nitra	Au	Br, Ca, Cl, Cu, In, K, Mg, Mn, Na, Rb, Se, Zn	Ag, Al, As, Ba, Cd, Co, Cr, Cs, Fe, Hg, I, La, Mo, Ni, Pb, Rb, Sc, Sr, Ta, Tb, Th, U, V, W, Yb	Sb,Hf	19
Central Spiš	Au	Br, Ca, Cl, In, K, Mg, Mn, Na,Rb,Se	Al, As,Ba,Cd,Co,Cr,Cs,Cu, Fe, Hg,I,La,Mo,Na,Ni,Sc,Sr, Th, U,V,W,Zn	Ag Hf, Pb,Sb,Ta, Tb, Yb	45
Slovakia	Au, Br,In	Ag, As, Ba, Ca, Cd, Cl, Co, Cs, Cu, Fe, Hg, K, La, Mg, Mn, Mo, N, Na, Ni, Rb, S, Sb, Sc, Sm, Sr, Ti, U, V, W, Zn	Al, Ce, Cr, Hf, Pb, Sb, Se, Ta, Tb, Th, Yb, Zr		9.5

High Tatra National Park (TANAP)

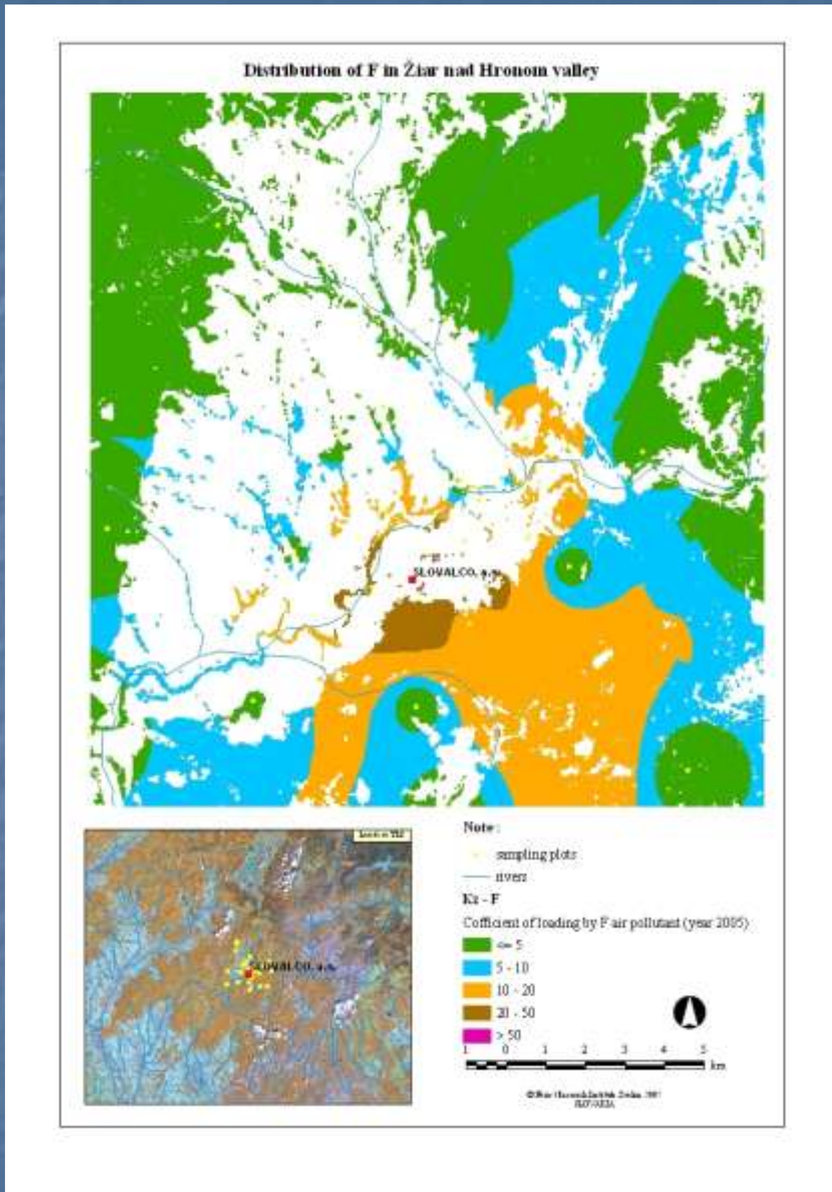
Low Tatra National Park (NAPANT)

Region NAPANT - Wind calamity

Napant Wind Calamity

Region Spiš –Immision Calamity

Žiar basin

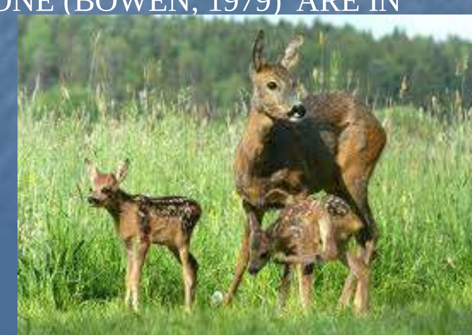

Distribution of F in Žiar nad Hronom valley
SLOVALCO, a.s.
Note:
sampling plots
rivers
Kz - F
Cofficient of loading by F air pollutant (year 2005)
<= 5
5 - 10
10 - 20
20 - 50
> 50
1 0 1 2 3 4 5
km

Concentration of elements in roe deer teeth, soil and mosses in Central Spiš Nálepkovo (in mg.kg-1)

Element	Al	As	Ba	Ca	Cd	Co	Hg	Cu	Fe
soil	47700	13.4	331	16550	0.40	6.3	1.51	21.5	20850
mosses	1605	0.72	81	3825	0.46	0.85	0.16	8.7	964
teeth	15.0	0.055	**218**	250000	4.9	**0.05**	**0.99**	20.8	25
Control bone	4-27	0.08-1.6	3-30	170000	1-8	0.01-0.04	0.45	1-26	3-380

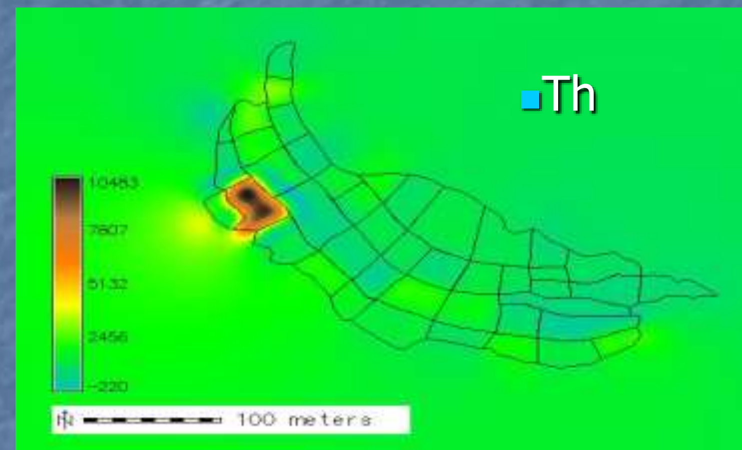
Element	Na	Mg	Mn	Pb	Rb	Sr	Sb	Zn
soil	6875	10828	580	42	77.8	77	4,5	75
mosses	307	1055	198	37	9.4	33	3,1	51
teeth	5890	**6780**	**83.3**	18.9	0.684	**147**	0,005	120
Control bone	10000	700-1800	0.2-14	3.6-30	0.1-5	36-140	0.01-0.6	75-170

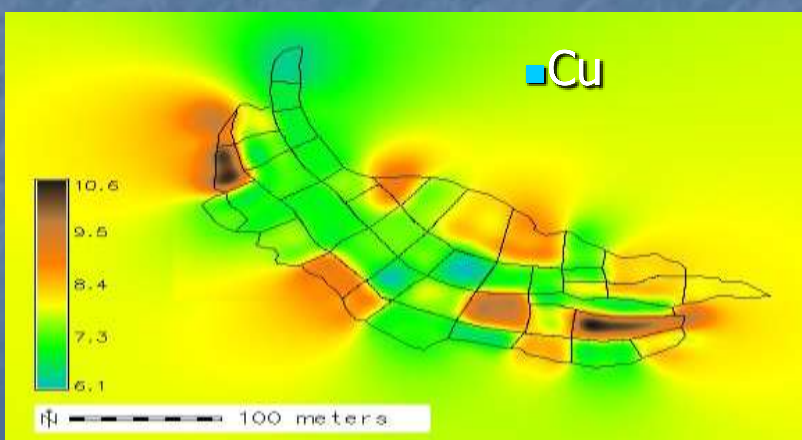
NOTE: CONCENTRATIONS OF ELEMENTS HIGHER THAN THE DATA FROM CONTROL BONE (BOWEN, 1979) ARE IN BOLD FACE.

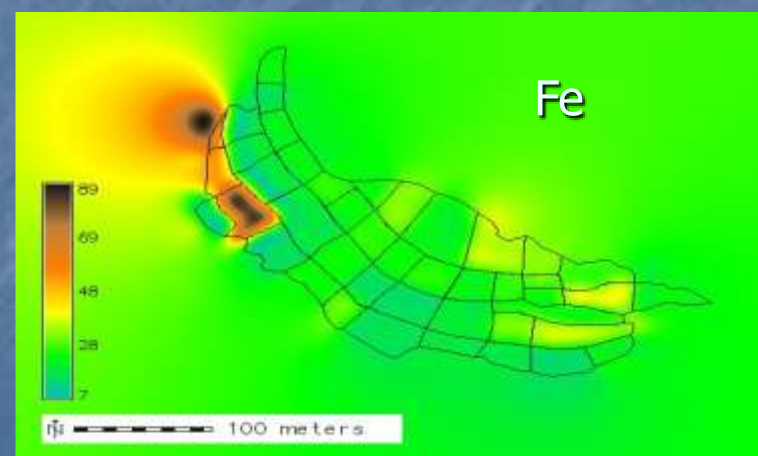


Mining country :Špania Dolina – Piesky, the old dump-field; Staré Hory, dumps at Richterová lokality; Dump-field Podlipa; plant-settlement of dump-sites .

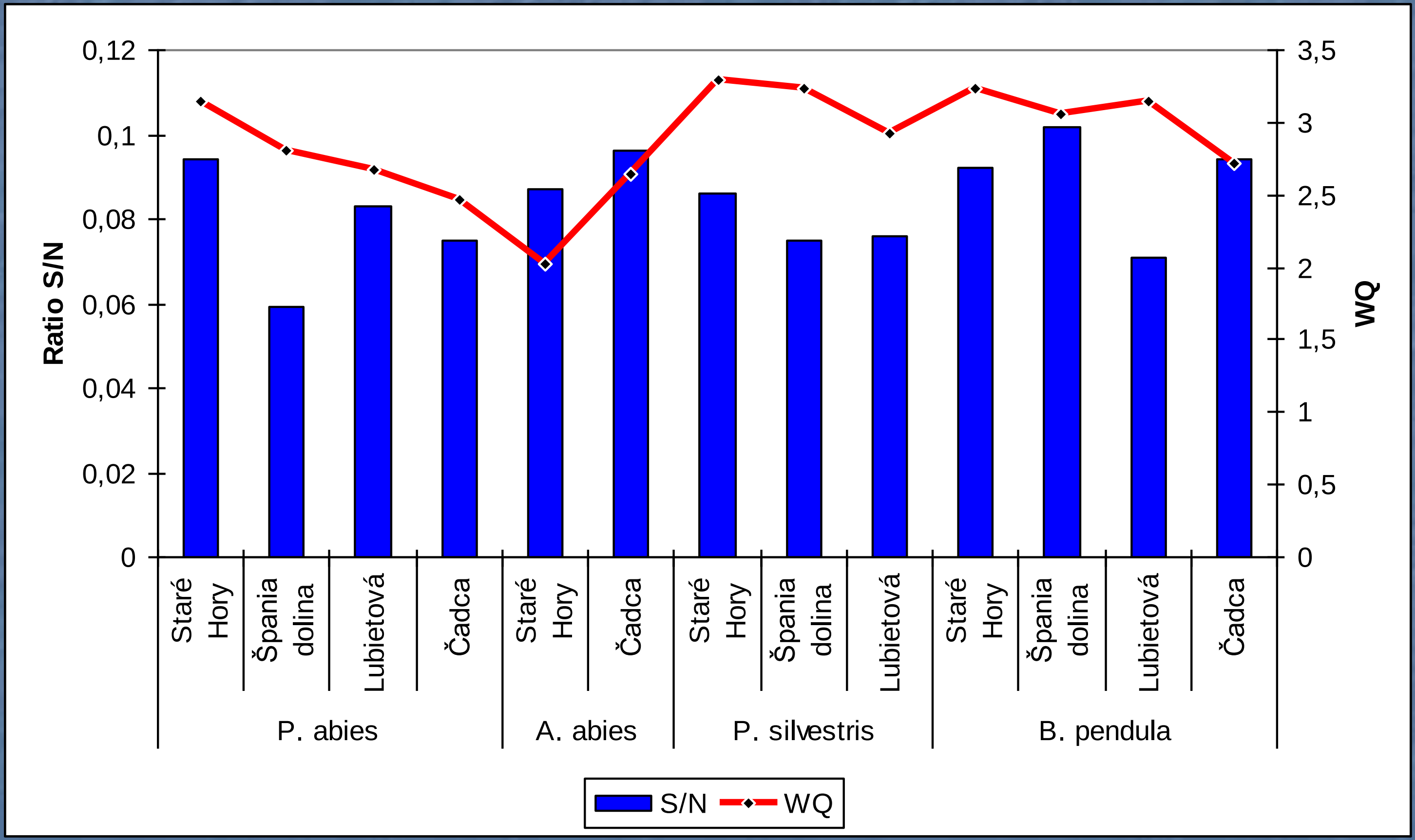
Špania dolina mining country



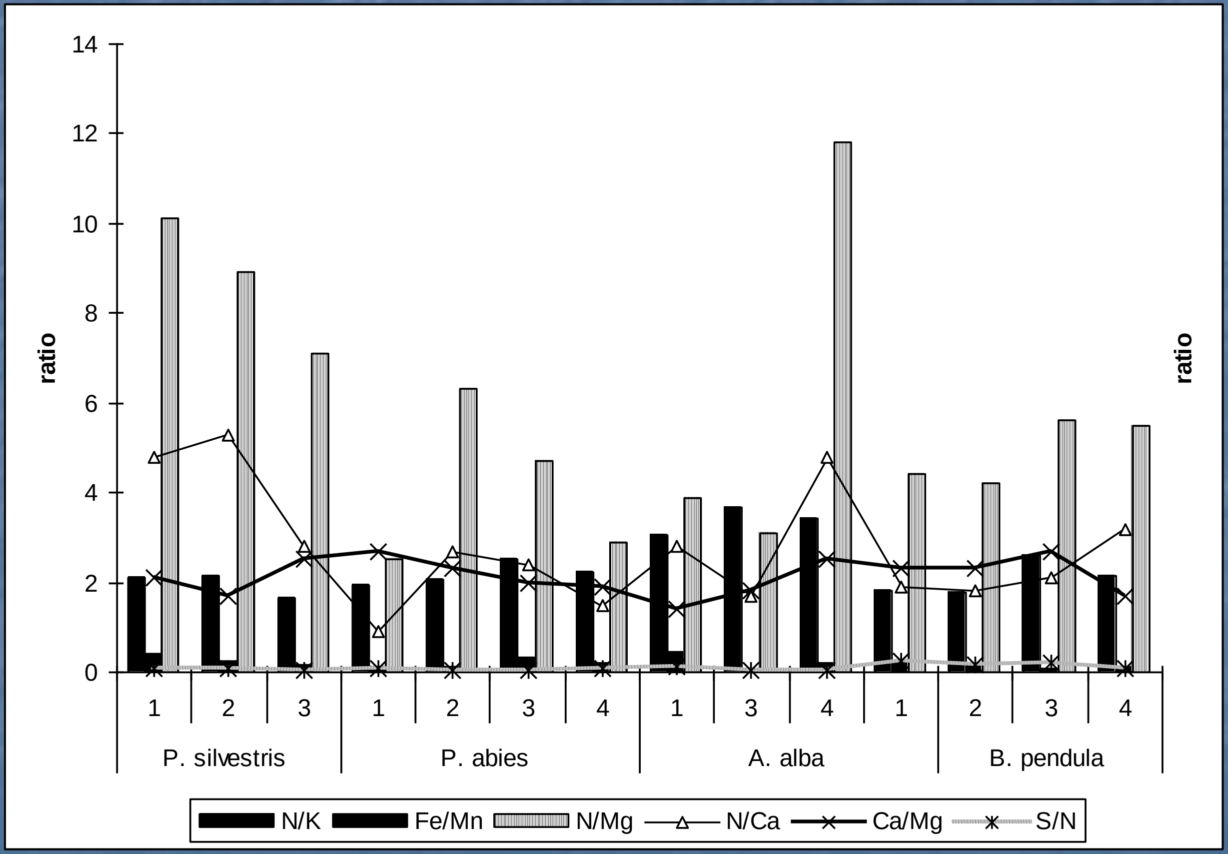




Concentrations of S/N, and changes of the epistomatal wax (WQ) of one year old needles of *P. abies*, *A. alba*, *P. sylvestris* and leaves of *B. pendula*.



Ratio N/K; Fe/Mn, N/Mg, N/Ca, Ca/Mg, S/N



Correlation between tree species (*P. abies, P. silvestris, A.alba, B. pendula)* and 31 elements

- Element Coeficient of correlation
- Tree Cd(0.601); Fe(0.564); La(0.535); Na(0.718);.Pb(0.562); Sc(0.518); Sm(0.572); Th(0.580);U(0.549)
- Ag As(0.535); Sb(0.605); Sm(0.503); U(0.583)
- As Sb(0.630)
- Ca Mg(0.739); Sr(0.533)
- Cd Fe(0.563); Na(0.586); Pb(0.705); Th(0.603); U(0.560)
- Co Pb(0.563); Sb(0.684); Se(0.621); Zn(0.693)
- Cu Fe(0.811); La(0.687); Na(0.566); Pb(0.802); Sb(0.724); Sc(0.744); Sm(0.877); Th(0.824); U(0.935)
- Fe La(0.724); Na(0.734); Pb(0.890); Sb(0.685); Sc(0.806); Sm(0.931); Th(0.927); U(0.909)
- K N(0.551)
- La Na(0.523); Pb(0.653); Sc(0.599); Sm(0.747); Th(0.736); U(0.723)
- Mg S(0.583); Se(0.520); Zn(0.523)
- N S(0.905); Zn(0.607)
- Na Pb(0.699); Sb(0.550); Sc(0.643); Sm(0.686); Th(0.713); U(0.648)
- Ni Zn(0.583)
- Pb Sb(0.652); Sc(0.775); Sm(0.870); Th(0.857); U(0.871)
- S Zn(0.614)
- Sb Sc(0.580); Sm(0.683); Th(0.619); U(0.743)
- Sc Sm(0.818); Th(0.782); U(0.814)
- Se Zn(0.520)
- Sm Zn(0.977); U(0.958)
- Th U(0.920)

- Note: Coefficient of correlation > 0.500

Conclusion

- Spatial trends of heavy metal concentrations in mosses were metal-specific. Coefficient of loading by air pollutants (heavy metals) KF for Slovakia is 9.5 . Since 1990, the metal concentration in mosses has declined for cadmium, chromium, cooper, iron, lead, mercury, nickel, vanadium and zinc. Only the concentration of Au, Br, In, is lower in Slovakia as Norway. Mosses provide an effective method for monitoring trends in heavy metals pollution in Slovakia at a high resolution;
- We found concentration of elements more than 50 times higher: site Žiar basin (F), High Tatras (Hf); Central Nitra (Sb, Hf); Central Spiš (Ag, Hf, Pb, Sb, Ta, Tb,Yb in comparison to the Norway values. Coefficient of loading by air pollutants KF move from 4.2 –Low Tatras; 6.2 –Žiar basin; 6.7 –High Tatras; 19 – Central Nitra and 45 -Central Spiš. The obtained data can be useful as a reference level for comparison with the future measurements of air pollution in the examined area and also for biodiversity study. The significance of transboundary atmospheric transport in this region remains to be studied in the future.
- Quality of epicuticular wax: We recorded differences between forest tree species (*P. abies*, *P. silvestris*, *A.alba*, *B. pendula*, *F. sylvatica*); between sites (Staré Hory, Lubietová, Špania Dolina and control Čadca), and beween treatments (under heap, heap, up healp). Foliage surface of foliage contained solid particulates. From these results it can be assumed that higher trace element concentrations in foliage in the proximity of specific emission sources result to a considerable extent from current atmospheric deposition of particulate matter to the foliage. Fungi effect was observed on foliage from all tree species, treatments and sites, but it was not too important for surface of leaves.
- In the foliage of *P.abies, P.silvestris, A.alba, B. pendula, F. sylvatica* were found the concentration of Ag, Au, As, Ba, Br, Ca, Cd, Cl, Co, Cr, Cs, Cu, Fe, K, Mg, Mn, Mo, N, Na, Ni, Pb, S, Sb, Sc, Se, Sm, Sr, Th, U and Zn in 4 treatments and 3 sites. We found unbalanced ratio for N/K, Fe/Mn, N/Mg, N/Ca, Ca/Mg and S/N, in foliage of for all study tree species. Mutual correlation with r higher or equal to $\pm$ 0.9 existed for following pairs of elements: Sm/Zn, N/S, Cu/U and Fe/U.
- The article present the most important problems connected with the mining wastes and the most often utilised remediation technologies and environmental engineering porocesses used for tle landscape sanitation and revitalisation.

References

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- **Acknowledgements:** This article was realized due the financial support of grant APVV-0663-10.