LONG TERM MAPPING AS METHOD FOR CRITICAL EVALUATION OF ECOSYSTEM POLLUTION

Maňkovská B.[1], Oszlányi J. [1], Tučeková A. [2], Florek M.[3], Frontasyeva M. V.[4], Pavlov S.S.[4]

[1]*Institute of landscape ecology, Slovak Academy of Science, Bratislava, Slovak Republic,*

[2]*NFC, Forest Research Institute, Zvolen, Slovak Republic*

[3]*Department of Nuclear Physics and Biophysics of Comenius University, Bratislava, Slovak Republic,*

[4]*Frank Laboratory of Neutron Physics, JINR, Dubna, Russia*

Pollution problems in the forest ecosystems resulting from 100year of operation of three smelter complexes in the Central Spiš are reviewed. Original data are presented with respect to temporal and spatial trends of nitrogen, sulphur, and heavy metal pollution. INAA at the IBR-2 reactor has made it possible to determine the content of 40 elements in mosses, foliage of forest tree species, lime and spruce wood, soil and wildlife in marginal Slovak hot spot - Central Spiš. Instrumental neutron activation analysis (INAA) at the IBR-2 reactor has made it possible to determine the content of 40 elements in mosses, foliage of forest tree species, lime and spruce wood, soil and wildlife in the marginal Slovak hot spot – the Central Spiš. In addition to NAA, flame atomic absorption spectrometry (AAS) was applied to determine the contents of S, Cd, Cu, Hg and Pb.

1 Introduction

Central Spiš is historically linked with exploitation and processing of non-ferrous metals. Since bronze period it had been the place of the exploitation of copper and later also ferrous ores. The history of exploitation has been documented since 1290. In the year 1903 there was constructed, in addition to ferrous metals exploitation, also parching mill for ores in Bindt and own ironworks in Markušovce. Pollution problems in Central Spiš forest ecosystems (area 5 km^2) resulting from 100 year long operation of three smelter complexes (Krompachy, Rudňany a Spišská Nová Ves) and on northern aspects there is evident the effect of transboundary air pollutants from Poland (Katowice).

In 1980 mass decline of spruce stands has started in the region of Central Spiš, still high volume of incidental felling, which culminated in 1995, proves of it. Catastrophic consequences resulting in total collapse of forest ecosystems were manifested mainly in the Hnilec River valley. A typical case is the forest of the village Nálepkovo. Almost 75% of stands older than 65 years of the total extent of about 3,200 ha of forests were destructed by the mass decline of spruce (Maňkovská, B., 1996).

The aim of this paper is to present actual data of the first survey of the chemical composition of mosses, lichens, foliage, bark, wood, soil and wildlife.

2 Experimental

The environmental samples (spruce needles, mosses, wood, lichens, teeth) were not washed before analysis. Elemental analysis was applied to determine the concentration of S (LECO SC 132) and N (LECO SC 228). 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 analysed for determination of study elements 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. Two channels are cadmium screened for activation with epithermal neutrons. The neutron flux density (for thermal or epithermal neutrons) inside the channels is of the order 10^{12} $cm^{-2}.s^{-1}$. The induced activity can be measured using spectrometers with Ge (Li) ORTEC electronics. The software developed at FLNP JINR is used for data processing (Frontasyeva, Pavlov, 2000). The environmental samples were evaluated by common statistical methods (ANOVA).

3 Results

Total concentration of the elements studied in the environmental samples collected from Central Spiš – Nálepkovo are given in Table 1.

Table 1. Concentration of elements in environmental samples from Central Spiš (n=10) Nálepkovo (in mg. kg^{-1})

No	Environmental samples	Al	As	Au	Ba	Br	Ca	Cd	Ce	Cl	Co
1	3 year old needles-	148	0.078	0.0037	23.5	0.16	4903	0.8	0.67	559	0.25
2	2 year old needles	116	0.119	0.0040	23.6	0.21	4165	0.8	2.07	514	0.42
3	1 year old needles	79	0.056	0.0032	14.3	0.13	2816	0.8	0.42	531	0.36
4	roots <2 mm	670	1.10	0.0049	22.3	3.0	5644	1.16	1.77	691	1.74
5	soil (0-5 cm)	45750	38.2	0.0010	388	8.7	5340	0.8	54.0	228	4.85
6	lichens on bark	973	2.16	0.0010	34.7	7.2	2295	0.8	1.62	1069	0.23
7	bark	325	0.25	0.0017	51.3	2.0	3937	0.30	0.4	84	0.1
8	Wood- average	6.9	0.16	0.0086	9.9	0.11	609	0.18	0.4	38.1	0.14
9	mosses	3040	0.76	0.0012	105	2.94	2730	0.109	4.99	133	1.12

No	Cr	Cs	Fe	Hf	Hg	K	La	Mg	Mn	Mo	Na	Ni	Pb	Rb
1	2.0	0.082	79	0.01	0.194	5654	0.026	65	1073	0.02	18	0.90	18.4	10.9
2	2.0	0.077	95	0.01	0.187	7664	0.062	2018	1086	0.02	33	1.91	8.1	14.4
3	2.0	0.148	74	0.012	0.157	5896	0.049	785	779	0.02	24	2.06	7.4	26.0
4	2.0	0.132	346	0.01	0.452	3580	0.42	1931	500	0.02	86	1.97	6.3	12.2
5	23.0	6.603	21700	4.006	0.591	13240	25.18	14490	355	0.75	4654	5.67	60.2	75.0
6	1.94	0.298	979	0.070	0.559	2701	0.78	900	97	0.16	167	1.0	45.3	12.0
7	2.0	0.029	135	0.01	0.498	330	0.092	184	96	0.02	33	1.0	45.9	1.6
8	2.0	0.017	142	0.01	0.134	560	0.04	104	71	0.03	40	1.1	12.6	1.8
9	8.2	0.62	2199	0.78	0.504	4823	2.32	1040	232	0.67	251	3.1	43.9	17.1

No	S	Sb	Sc	Sm	Sr	Ta	Tb	Th	U	V	W	Zn
1	2500	0.135	0.02	0.0082	10.2	0.007	0.003	0.008	0.02	0.1	0.29	22.8
2	2200	0.125	0.02	0.0103	13.9	0.005	0.003	0.010	0.02	0.1	0.77	28.6
3	2300	0.058	0.02	0.0068	7.1	0.005	0.003	0.014	0.02	0.30	0.25	34.2
4	3400	0.367	0.041	0.0688	18.1	0.005	0.003	0.071	0.02	0.96	0.69	76.2
5	700	10.6	12.8	3.7000	2.5	1.035	0.520	6.60	2.6	71.4	13.10	75.0
6	2500	2.277	0.327	0.1438	7.3	0.039	0.024	0.221	0.076	2.80	0.50	75.7
7	1500	0.606	0.030	0.0271	8.4	0.012	0.007	0.033	0.02	1.43	0.37	27.1
8	900	0.009	0.122	0.0021	9.6	0.005	0.003	0.010	0.01	0.24	1.57	10.9
9	2120	3.31	0.56	0.35	34	0.081	0.071	0.58	0.10	5.8	0.17	61

Atmospheric deposition of elements in three mosses species in studied PMP in Spiš and control, compared with results of 2000 in Slovakia, Ural and Norway is given in Table 2.

Table 2. Atmospheric deposition of elements (in $mg.m^{-2}.rok^{-1}$) from Central Spiš (PMP R_5 and P_5); control (PMP L_5); Slovakia; Ural Mountains and Norway calculated from concentration of elements in 3 year old segments of *P. schreberi; H. splendens* and *Dicranum* sp.

Element	Central Spiš		Control	Ural Mts.*	Slovakia **	Norway***
	PMP - R_5	PMP -P_5	PMP - L_5			
Al	**583**	**490**	**300**	702	618	88
As	**0.21**	**0.15**	**0.12**	0.26	0.18	0.08
Ba	**<u>22.5</u>**	5.8	**<u>20.5</u>**	13.6	12.9	6.0
Br	0.61	0.59	0.85	0.77	0.88	1.25
Ca	**<u>1175</u>**	**653**	**<u>7590</u>**	883	1231	375
Cd	**<u>0.14</u>**	**<u>0.35</u>**	**<u>0.18</u>**	0.065	0.15	0.02
Cl	**<u>111</u>**	**<u>76</u>**	23	32	62	50
Co	**<u>0.31</u>**	**<u>0.20</u>**	**<u>0.40</u>**	0.09	0.21	0.08
Cr	**1.10**	**0.70**	**0.65**	-	1.62	0.38
Cu	**<u>3.13</u>**	**1.49**	**<u>2.31</u>**	1.65	2.19	1.05
Fe	**340**	**184**	**<u>742</u>**	677	390	100
Hg	**0.18**	**0.05**	**0.03**	-	0.04	0.03
K	**<u>1925</u>**	**<u>1818</u>**	**<u>1199</u>**	1088	1747	750
Hg	**0.18**	**0.05**	**0.03**	-	0.04	0.03
K	**<u>1925</u>**	**<u>1818</u>**	**<u>1199</u>**	1088	1747	750
Mn	**<u>378</u>**	**<u>93</u>**	**<u>101</u>**	43	88	50
Mo	0.32	0.12	0.11	-	0.23	-
Na	**<u>125</u>**	**<u>117</u>**	**<u>180</u>**	111	90	50
Ni	0.38	0.40	**0.93**	0.93	0.80	0.40
Pb	**7.08**	**7.48**	**5.78**	-	7.10	1.25
Rb	**<u>2.56</u>**	**<u>2.93</u>**	1.90	2.13	3.35	2.50
Sb	**1.94**	**0.72**	**0.15**	4.74	0.22	0.02
S	555	455	560	-	300	-
Sr	**10.3**	**8.50**	**37.8**	-	15.5	2.88
U	**0.025**	**0.013**	0.010	-	0.025	0.012
V	**0.90**	**0.60**	**0.80**	-	1.43	0.50
W	**<u>0.073</u>**	**0.048**	**<u>0.065</u>**	0.050	0.063	0.010
Zn	**<u>16.5</u>**	**<u>12.3</u>**	**9.50**	9.80	13.9	9.0

Note: Slovakia ** - average from 78 PMP; *** Norway (Central Norway belongs to the least polluted regions in Europe) (Suchara et al.2007). Concentrations of elements higher than the data from Norway are in bold face; concentrations higher than in Ural* (Magnitogorsk belongs to the most polluted regions in Europe) are in bold face and underlined.

Total concentration of the 26 elements ($mg. kg^{-1}$) studied in the 2 years needles of *P. abies,* collected from Central Spiš and NAPANT and literature value of studied elements in the foliage are given in Table 3.

Table 3. Concentration of elements in 2 year old needles of *P. abies* from industrial locality Central Spiš (n=282) and control- NAPANT (n=70) (in $mg.kg^{-1}$)

Element	Central Spiš	Control	Limit .	**Element**	Central Spiš	control	Limit
	x (SD)	x(SD)	min-max		x(SD)	x(SD)	min-max
Al	117(50.6)	105 (108)	50-150	**As**	**0.68(2.14)**	0.19(0.15)	<0.2
Ba	39.9(31.3)	46.8(32.6)	<100	**Be**	0.005(0.01)	0.009(0.02)	<0.04
Ca	5711(5344)	**9567 (4427)**	4000-8000	**Cd**	0.18(0.14)	0.12(0.09)	<0.5
Co	0.21(0.17)	0.062(0.09)	<1.0	**Cr**	0.55(0.65)	**1.02(2.50)**	<1.0
Cu	**5.85(5.18)**	**3.41(1.19)**	2-3	**F**	**6.90(2.40)**	**5.35(1.74)**	<2
Fe	**147(406)**	94 (64.8)	50-100	**Hg**	**0.13(0.09)**	**0.09(0.11)**	<0.06
K	6396(1861)	5136(1331)	5000-10000	**Li**	0.17(0.12)	0.23(0.33)	<0.5
Mg	998(602)	1110(551)	1000-5000	**Mn**	**1166(742)**	**738(809)**	500
N	17920(5610)	14930(2404)	18000-25000	**Na**	34.9(55.3)	40.9(81.5)	<100
Ni	**2.64(1.70)**	1.49(1.16)	<2	**Pb**	1.99(3.31)	2.6(7.1)	<6
Rb	**12.1(10.0)**	8.3(5.9)	<10	**S**	**2093(785)**	**1846(837)**	<1000
Se	**0.053(0.038)**	**0.038(0.026)**	<0.03	**Sr**	**12.1(9.9)**	**21.4(20.7)**	<10
V	**1.12(3.50)**	0.47(0.91)	<1	**Zn**	39.1(23.2)	43.2(16.9)	35-45
K_z	**1.74(1.31)**	**1.29(0.59)**	1				

Note: x - arithmetical mean; SD - standard deviation in parentheses; n- number of samples from permanent monitoring plots NAPANT (in 4x4km) and Central Spiš (in 1x1 km);
K_z- Pollution impact coefficient; Limit values (Maňkovská, 1996; Stefan et al. 1997).

The principal component analysis for Central Spiš and NAPANT is in Table 4.

Table 4. Percentage of explained variance for eight factors obtained in the principal component analysis (Varimax analyse) for Central Spiš and control NAPANT

Localities		Factors								
		1	2	3	4	5	6	7	8	Together
Central Spiš	EV	1.82	1.66	1.50	1.24	1.08	0.99	0.92	0.88	
	% var.	15.2	13.8	12.2	10.3	9.0	8.2	7.7	7.3	83.7
Control	EV	2.37	2.01	1.63	1.47	1.12	0.90	0.70	0.56	
	% var.	19.6	16.7	13.6	12.3	9.3	7.5	5.9	4.6	89.5

Note: EV-Eigen values: % of variability

Total concentration of the elements (mg. kg^{-1}) studied in the teeth of roe deers collected from Central Spiš – Nálepkovo and literature value are given in Table 5. In Table 5 are listed also concentration of elements in soil and bryophyte.

Table 5. 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.

4 Conclusion

It was determined on the basis of monitoring performed in *P. abies* needles on 282 plots in industrial areas Central Spiš and 80 plots in control localities (Low Tatras National Park)

Spruce stands: The absolutely highest values of Al, As, Cd, Co, Cu, F, Hg, Mn, N, Ni, Rb, S, Se, and V were found in the industrial area of Central Spiš and Ba, Be, Ca, Cr, Li, Mg, Na, Sr and Zn from the National Park Low Tatras. The overall loading to the K_z represented 1.74 increase in Central Spiš and 1.3 in NAPANT .1.7-fold exceeding of critical values and the highest concentrations of As, Fe, Hg, and N were found in this region. Low Tatras National Park (control) was the cleanest region where no element maxima were found.

Soil: In comparison with limit values the concentration of Hg in humus and horizon A_0 and As is increased markedly. Other analysed elements (Cd, Co, Cu, Ni, Pb and Zn) do not exceed the limits. We found the highest concentration of Al, As, Ba, Br, Ce, Co, Cr, Cs, Fe, Hf, Hg, K, La, Mg, Mo, Na, Ni, Pb, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, V and W in soil samples; the highest concentration of Ca, Cd, Cl and S in spruce roots; Mn and S in spruce needles; Sr in mosses and Zn in lichens.

Atmospheric deposition with moss bio-monitoring technique: In the area of Central Spiš we found in comparison with Norwegian limit values (Central Norway- as relatively the cleanest region) exceeded levels for Al, As, Ca, Cd, Cl, Co, Fe, K, Mn, Sb, Sm, Sr, W and Zn. In comparison with Magnitogorsk in Ural Mountains (the most polluted area in Europe) we found in Spiš higher values for Ca, Cl, Co, K and Mn.

Spruce wood: We found the highest concentrations of Au, Br, Co, and Sb in the oldest 70-80 years old wood. 60-70 years old wood had the highest concentration of As, Ca, Cd, K, Mn, Rb, Sm, and Sr; 40-50 years old wood had the highest concentration of Ba, Fe, W and Zn; 30-40 years old wood had the highest concentration of Al, Cl, and Na in comparison with younger wood. The highest concentration of Ni was found in 20-30 years old wood.

Lime wood: We found the highest concentrations of Al, As, Au, Br, Cl, K, Na, Rb, Sb and Sm in the oldest 80-90 years old wood. 70-80 years old wood had the highest concentration of Cd, Co, Fe, Mn, Sr and Zn in comparison with younger wood. The highest concentration of Ca and Ni was found in 10-20 years old wood, and W in wood until 10 years. The lowest concentrations of Al, Br, Ca, Mn, Rb and Sr were found in 10 years old lime wood.

Wildlife: In comparison with limit values the concentration of Ba, Co, Hg, Mg, Mn, and Sr in the teeth of roe deers is increased markedly. Other analysed elements (Al, As, Ca, Cd, Cu, Fe, Na, Pb and Rb) do not exceed the limits.

Rerefences

1. Bowen, H.J.M., 1979: Environmental Chemistry of the elements. Academic Press, London, New York, Toronto, Sydney, San Francisko, ISBN 0-12-120450-2, p.237-273.
2. Frontasyeva, M.V., Pavlov, S.S., 2000: Analytical investigation at the IBR-2 reactor in Dubna. Proceedings of the VII International Seminar on Interaction of Neutrons with Nuclei,Dubna, May 17-20, 2000, E3-2000-192. p. 219-227.
3. Maňkovská, B., 1996: Geochemical atlas of Slovakia. Forest biomass. Geological Service of Slovak republic,Bratislava. ISBN 80-85314-51-7, 87 pp.
4. Stefan, K., Fűrst, A., Hacker, R., Bartles, U. 1997: Forest Foliar Condition in Europe. Technical Report. EC and UN/ECE, Brussels, Geneva, 207 pp.
5. Suchara, I.,Florek, M., Godzik, B., Maňkovská, B., Rabnecz, G., Sucharová, J., Tuba, Z., Kapusta, P., 2007: Mapping of main sources of pollutants and their transport in the Visegrad space. Project 11007-2006-IVF, ISBN 978-80-85116-53-3, ISBN 978-80-85116-55-7; ISBN 978-80-85116-54-00, 127 pp