Iqbal M.Z., Shazia Y.: **Redukcia klíčenia a rastu semenáčika** *Leucaena leucocephala* **zapríčinenej olovom a kadmiom a ich kombináciami.**

Klíčenie semien, dĺžka koreňa, výhonu, semenáčika a sušina semenáčika u *Leucaena leucocephala* sa najviac redukovala pri aplikácii olova a kadmia jednotlivo, ako aj pri ich kombinácii. Intenzita vplyvu olova a kadmia na rast *Leuceana leucocephala* bola rozdielna pri rôznych úrovniach a kombináciách aplikácie. V dĺžke koreňa najvyššia redukcia bola pri 30 ppm olova. Kým v dĺžke výhonku a semenáčika sa najvyššia redukcia dosiahla pri 300 ppm Pb + 30 ppm. Cd 100 ppm aplikácie olova preukázalo aj redukciu v sušine semenáčika viacej ako pri iných aplikáciách. Z výskumu vidieť, že 300 ppm Cd v kombinácii s 300 ppm Pb preukázalo pomerne škodlivý účinok na rast semenáčika *Leucaena leucocephala*. Najnižšiu toleranciu sme zistili u *Leucaena leucocephala* pri rovnakej kombinácii olova a kadmia.

BIOMONITORING OF POLLUTION LOAD LOWERING WITH CHANGE OF THE ALUMINIUM PRODUCTION TECHNOLOGY

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Abstract

Maňkovská B.: Biomonitoring of pollution load lowering with change of the aluminium production technology. Ekológia (Bratislava), Vol. 23, No. 2, 169-183, 2004.

Anthropogenic loading of all tree species in Žiarska valley, expressed by means of the coefficient of loading by air pollutants K_z has decreasing trend. Total loading of all tree species by air pollutants in Žiarska valley (pollution zones A, B, C) expressed by means of K_z coefficient represents in 2001 only 5.9 times higher compared with 7.9 higher loading compared with 2000; 19.4 times higher loading compared with in 1997; 22.9 times higher loading compared with 1996 and 29.5 times higher loading compared with 1995. Total loading by air pollutants for all tree species (pollution zones A, B, C, D) within 50 km from SLOVALCO, a.s. given by K_z represents 3.7 times higher loading. We found statistically significant difference for K_z in coniferous tree species (1 and 2 years old) and broadleaved tree species in A zone in comparison with the zone B, C and D. We also found statistically insignificant difference in coniferous tree species (1 and 2 y) and in broadleaved tree species in the zones B, C and D except for broadleaved tree species, for which we found statistically significant increase between the zone B and D.

Key words: biomonitoring, air pollution, mapping of F, S, N

Introduction

Problems of the environment pollution in Žiarska basin are connected with the operation of Aluminium plant from 1953. Abolishment of a municipality Horné Opatovce, which was situated near to the plant, proves of an injurious effect of this emission. Aluminium plant is situated only 2 km from town Žiar nad Hronom. A new chapter in the history started on 29 February 1996. The technology of production was supplied by Norwegian firm Hydro Aluminium. Emission of dust Al_2O_3 dropped from 766 to 243 t.year^{-1}, emission of fluorides dropped from 847 to 65.9 t.year^{-1} and emission of SO_2 have increased from 716 to 974 t.year^{-1}. On that day, the last electrolyser from the old series based on Söderberg technology of aluminium production was shut down. Norwegian company Hydro Aluminium provided a technology for the new production. The implementation of this project contributed to a significant reduction of emission, mainly due to increased efficiency of pollutant's capture. Emission of solid pollutants, fluorine (Fc as HF, Fg as HF, Fs), SO_2, NO_x and CO is being released into the air and measured on emission sources. The mentioned reduction of emission reflected markedly in great reduction of vegetation loading by fluorine (Maňkovská, Kohút, 2002).

Primary aim of the agreement, which is connected with the studies worked out in the years 1995-2000 was solving the effect of polluted air on forest vegetation in Žiarska valley in the year 2001. It was namely evaluation of total concentration of sulphur, nitrogen and fluorine (as the most important air pollutants in broader surroundings) from vegetative organs obtained in sampling on sampling locations in Žiarska valley on average within 50 km from aluminium plant.

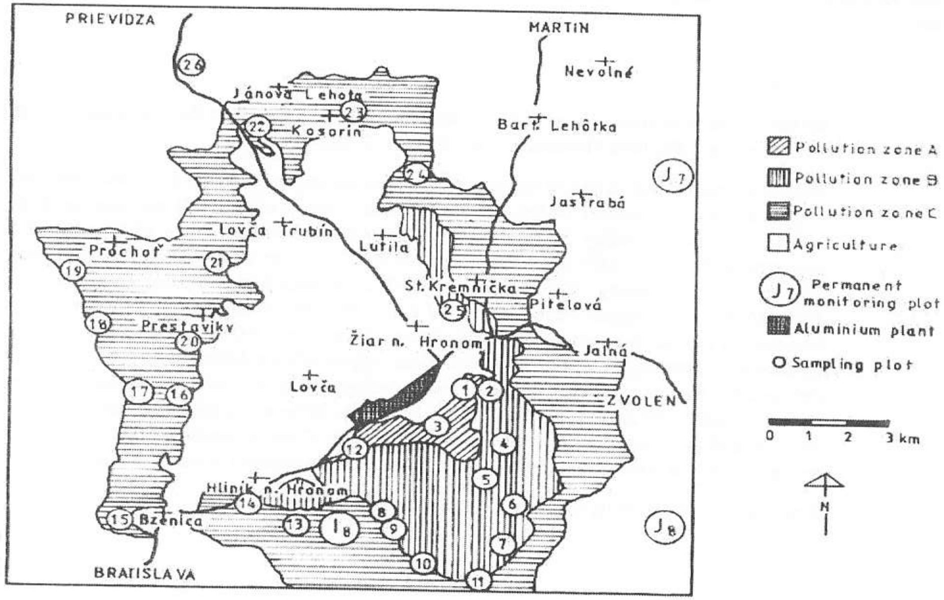

Fig. 1. Sampling location of all tree species and shrubs in three pollution zones from Žiar nad Hronom.

Material and methods

We collected the samples of the foliage of forest trees and fruit trees in 2001 in the same localities as in the years 1970-2000. Then we collected the samples of the foliage of forest tree species within 50 km from aluminium plant using permanent monitoring plots, which are situated in the transects 16x16km of Pan-European network and in denser network (Fig. 1). We had available 200 specimens of samples from 63 localities.

The samples of the foliage of forest trees were taken from the plots, first of all in the stands of the II age class. The trees were distributed on the whole area or in the surroundings of permanent monitoring plot and they represented the health condition of the plot. The trees belonged to pre-dominant and dominant class. They had representative average level of defoliation ±5% and were not infested by insects or fungi. The distance between the trees selected for sampling was 10-15 m and they were mostly the individuals of main tree species. Sampling of forest tree species was carried out in accordance with the international methodology (ICP, 1994).

Foliage selected for sampling came from the part of crown exposed to sunlight, in the upper third of crown, for coniferous species namely from the branches of the 7th whorl spruce (*Picea abies* K a r s t.), for pine (*Pinus sylvestris* L.) from the top or second whorl. For larch (*Larix decidua* L.) samples were taken from the buds of last year. For broadleaved tree species beech (*Fagus sylvatica* L.), oak (*Quercus* sp.), poplar (*Populus* sp.), robinia (*Robinia pseudoacacia* L.), linden (*Tilia* sp.), maple (*Acer* sp.), chestnut (*Castanea sativa* M i l l.), hornbeam (*Carpinus betulus* L), birch (*Betula pendula* R o t h.), willow (*Salix caprea* L.), alder (*Alnus* sp.), hawthorn (*Crataegus* sp.), and fruit trees (apple tree (*Malus domestica* B o r k h.), pear (*Pyrus communis* L.), cherry (*Cerasus* sp.), plum (*Prunus domestica* L.)) and shrubs (hazelnut (*Corylus avellana* L.) and brier bush (*Rosa canina* L.)) leaves from the middle part of annual rings of top parts were taken as samples. The specialists for monitoring from the Forest Research Institute Zvolen in August 2001 carried out sampling. Collective sample was mixed from 15 samples after their drying.

The samples of foliage were analysed unwashed. They were dried at the temperature not exceeding 80°C for the period of 24 hours. Needles were separated from branches and leaves from stems. Dry samples of foliage were perfectly homogenised and aliquot proportions (15 trees per 1 plot) were mixed together. Pressure mineralization was performed in microwave furnace MDS 2000 (CEM company).

Total concentration of fluorine was determined by means of SINTALYZER with fluoride electrode of Orion firm in the laboratories of aluminium plant (SINTEF, Application note AN-07). The concentration of sulphur in the foliage was determined by elementary analyser LECO SC 132. The sample was weighed into ceramic vessel and burnt in oxygen atmosphere in the induction furnace at the temperature 1371°C. Sulphur concentration (as SO_2) in gas was measured by infrared detector and compared with standard samples. Elementary analyser LECO SP 228 determined total concentration of nitrogen in the foliage. The sample was weighed into tin capsule and burnt in argon atmosphere in the induction furnace at the temperature 950°C. Aliquot proportion of burnt products was made free of CO_2 and H_2O. Nitrogen oxides were reduced to N_2 and the concentration was determined on heat conductive cell. Disturbing effects of matrix and its suppression by suitable additives of buffering solutions and modifiers were studied. The results were calculated to dry matter, which was determined separately.

The accuracy of used chemical analytical methods given in the work was verified by 109 independent laboratories and tested within IUFRO (Hunter, 1994). The accuracy of fluorine determination was tested separately in the laboratories of aluminium plant in Žiar nad Hronom and Hydro-Aluminium plant in Norway. The results are comparable (Maňkovská, Kohút, 2002).

For the assessment of vegetation material we used current statistical methods, correlation analysis and analysis of main components (PCA), which is included into factor analysis. For the assessment of total loading in the surroundings of aluminium plant by F, and S pollutants we used K_z coefficient of loading by air pollutants, which gives exceedance of limit values of studied elements in the foliage of forest tree species (Maňkovská, 1996).

Coefficient of loading by air pollutants K_z is defined as an arithmetical mean of n elements, which are cumulated in the foliage of forest tree species. Standard values (Y_i of n elements) results from the formula:

$$Y_i = \frac{M_i}{m_i} + \frac{M_1}{m_1} + ...+ \frac{M_n}{m_n} ,$$

where M – concentration of F and S (in mg.kg^{-1}) in the foliage of studied forest trees in 2000
m – concentration of F and S (in mg.kg^{-1}) in the foliage of studied forest trees from control areas – sampling in the years 1974-1975 (Maňkovská, 1996): F (2); S (1000)
n – number of studied elements.

Coefficient of loading by air pollutants K_z is defined

$$K_z = 1/n \sum_{i=1}^{n} Y_i.$$

Analytical data were stored, processed and checked in the database. It was mainly checking of the accuracy of primary data, including localization of samples after the digitisation of sampling locations. Primary analytical data were taken in an irregular network and served the preparation of the maps of the distribution of loading coefficients by F, S and N concentration. These values were calculated into regular network 1.5x1.5 km. For the centre of each square it was calculated its value on the basis of the values of the closest 12 samples by weighed square of inverse distance from the centre of calculated square (Maňkovská, 1996). The data processed in this way are illustrated in the maps of distribution of individual coefficients of loading by F, S and N concentration. For the illustration of the distribution of F, S and N concentration we selected two up to five degree scale in the colours of red and green with growing value of the coefficient of loading. The classes used in the maps of distribution of studied elements are based on primary data and they reflect their geo-chemical characteristics.

T a b l e 1. The course of fluorine concentrations in 4 groups of tree species for the years 1970–2001

Tree species	Coniferous tree species 1y old	Coniferous tree species 2 y old	Broadleaved tree species	Fruit tree species	Shrubs	Limits*
Element	x (SD)	x(SD)	x (SD)	x (SD)	x(SD)	from–to
Fluor						
1970	**142(97)**	–	–	–	–	< 2.0
1990	**194(67)**	–	–	–	–	
1995	**50.1(89.5)**	–	**167(410)**	**75.2(51.1)**	**106(176)**	
1996	**35.4(50.4)**	–	**115(184)**	**64(58.5)**	**130(174)**	
1997	**18.2(12.8)**	–	**94(175)**	**62.7(27.2)**	**128(138)**	
2000	**10.0(18.1)**	**13.3(18.4)**	**36.7(61.0)**	**31.1(8.6)**	**40.1(45.4)**	
2001	**8.0(10.4)**	**10.9(19.9)**	**27.2(52.3)**	**26.4(12.8)**	–	
Nitrogen						
1995	16825(3818)	–	**30093(5775)**	**24275(5909)**	**28603(6430)**	12000–17000
1996	14279(4270)	–	**24612(6396)**	**18369(6582)**	**22138(5164)**	
1997	15247(3926)	–	**25367(5109)**	**19726(5241)**	**25689(3598)**	
2000	14338(2005)	14152(2756)	**25117(5454)**	**20100(2986)**	**24517(7264)**	
2001	14023(3096)	13588(3001)	**26354(4604)**	**21440(3968)**	–	
Sulphur						
1970	**2548(605)**	–	–	–	–	1000–1800
1990	1703(351)	–	–	–	–	
1995	**1999(468)**	–	**2886(1234)**	**2115(600)**	**3658(2019)**	
1996	**2415(851)**	–	**3503(1618)**	**2735(1172)**	**4279(1874)**	
1997	**2493(566)**	–	**3458(1315)**	**2478(747)**	**7779(3393)**	
2000	1762(214)	1689(265)	**3296(1281)**	**2928(518)**	**4517(1540)**	
2001	1583(358)	1506(379)	**2990 (606)**	**2612(408)**	–	

Note: *Innes (1995); Maňkovská (1996); values in bold are exceeded limit values

x – arithmetical mean; SD – standard deviation

Results and disscusion

Forest stands in this region are formed by forest types as follows: *Fageto-Quercetum, Querceto-Fagetum* and *Fagetum pauper*. In the whole region 10.4% of forests are conifers (5% spruce, 1.1% fir, 3.2% pine, 0.1% larch) and 89.6% broadleaved species (56.4% beech, 15.2% oak, 14.9% hornbeam and 3.1% others). The distribution of forest tree species is altered due to operation of aluminium plant due to a change in biodiversity. In 1995 in the A zone conifers formed 36.6% of vegetation while in 1978 they were reduced to 3.0%. Sampling of foliage was conducted on the same plots as in 1970 (pollution zone A, B, and C) (Maňkovská, Steinnes, 1995) (Fig.1) and on other plots (pollution zone D) within the distance of 50 km from the plant.

The course of fluorine concentrations in 4 groups of tree species for the years 1970-2001 is in Table 1 and for three pollution zone in Fig. 2. In all tree species reduction of fluorine concentration is evidently apparent. The course of sulphur concentration in 4 groups of tree species for the years 1970-2001 is in Table 1 and for three pollution zone in Fig.3. Sulphur concentration in all studied tree species have slightly decreasing trend, whilst sulphur emission is also from other emission sources. The course of nitrogen concentration in

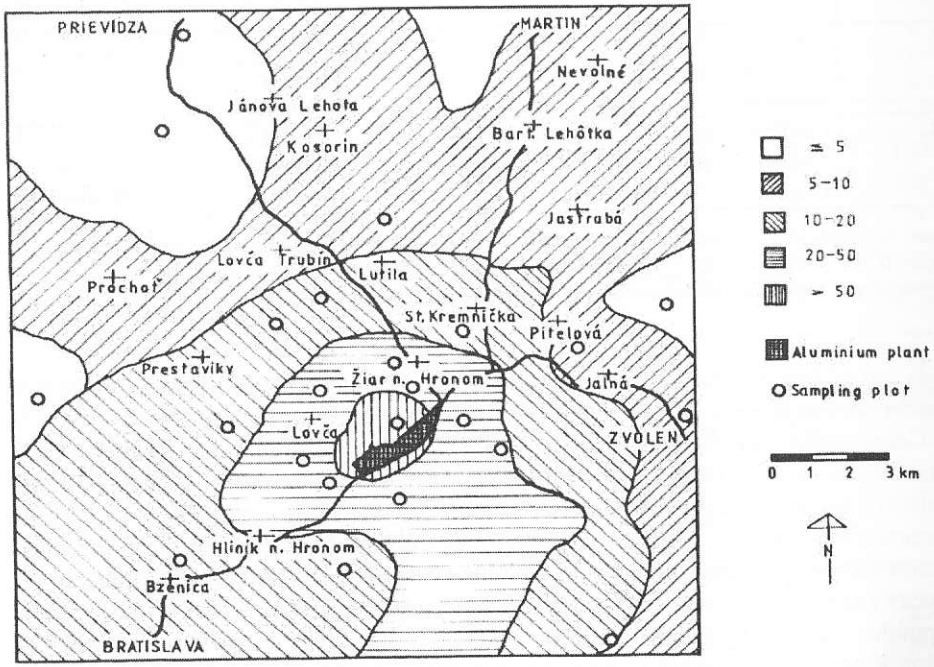

Fig. 2. Course of F concentrations (K_z) in 4 groups of tree species for pollution zone A,B,C.

Table 2. Concentration of F, S, N [in mg.kg^{-1}] and N/S ratio for 4 pollution zones in the year 2001

Element	x	SD	x_{min}	x_{max}	x	SD	x_{min}	x_{max}
Tree species	Coniferous tree species 1 year old				Coniferous tree species 2 years old			
F	5.4	6.9	0.1	46.6	10.9	19.9	2.7	75.3
S	1505	337	920	2850	1506	379	750	2210
N	13208	2772	9300	22100	13588	3001	8900	19200
S/N	0.11	0.01	0.09	0.16	0.11	0.02	0.06	0.14
Tree species	Broadleaved tree species				Fruit tree species			
F	12.3	33.5	0.6	254.3	26.4	12.8	9.3	41.2
S	2807	705	1250	4990	2612	408	2020	3110
N	24501	5814	10900	40800	21440	3968	17900	27700
S/N	0.12	0.02	0.07	0.27	0.12	0.02	0.11	0.15

Note: x –arithmetical mean; x_{min}–minimal value; x_{max}–maximal value; SD–standard deviation

Table 3. Variance analysis between pollution zones in the year 2001 according to separate groups of tree species

Element	Tree species	Testing criterion F	Element	Tree species	Testing criterion F
F	Coniferous 1 yr	8.73***	N	Coniferous 1 yr	2.02^{N}
	Coniferous 2 yr	7.10**		Coniferous 2 yr	0.29^{N}
	Broadleaved	23.18***		Broadleaved	3.68*
S	Coniferous 1 yr	0.91^{N}	K_z	Coniferous 1 yr	9.29***
	Coniferous 2 yr	0.17^{N}		Coniferous 2 yr	7.27**
	Broadleaved	3.23*		Broadleaved	23.49***

Note: N statistically insignificant differences between zones,*statistically significant differences between zones at the level a < 0.05, **statistically significant differences between zones at the level a < 0.01 ***statistically significant differences between zones at the level a < 0.001

4 groups of tree species for the years 1995-2001 is in the Table 1, whilst in addition to coniferous tree species a slight increase was recorded for other tree species.

Concentration of F, S, N and ratio N/S in coniferous, broadleaved and fruit trees for 4 pollution zones (A, B, C, D) in the year 2001 are given in Table 2. In Table 3 there are given the results of variance analysis between 4 pollution zones according to separate groups of tree species in the year 2001. We found statistically significant difference in the fluorine concentration between coniferous tree species (as well as needles year classes) and broadleaved tree species and pollution zones. Statistically insignificant difference in sulphur and nitrogen concentration was found between coniferous tree species (needles year classes as well) and pollution zones on the contrary of broadleaved tree species, for which we found statistically significant difference. We found statistically significant difference also between coefficients of loading by air pollutants K_z for all studied tree species and pollution zones.

In Table 4 there are given the results of testing the significance of the differences between arithmetical means of the concentration of fluorine, sulphur and nitrogen in the year 2001 for respective level of factor (Tuckey-test). We found statistically significant difference in the concentration of fluorine between pollution zone A and pollution zones B, C and D for coniferous and broadleaved tree species. Statistically insignificant difference in the concentration of sulphur and nitrogen we found between the zones A, B, C and D for coniferous tree species (1 and 2 years old) and for broadleaved tree species between the zone A, B and C. Statistically significant difference in sulphur and nitrogen concentration was found only in broadleaved tree species between the zone C and D. We found also statistically significant difference for K_z in coniferous tree species (1 and 2 years old) mutually in the zones B, C and D except for broadleaved tree species, for which statistically significant increase were found between the zone B and D.

Comparison of fluorine and sulphur concentration, as main injurious factors, according to individual tree species, 4 pollution zones and the years 1995-2001 is in the Table 5. In

Table 4. Testing of the significant of the differences between arithmetical means (x) of F, S, N concentration and K_z in 4 pollution zones for respective level of factors (Tuckey-test) – year 2001

Pollution zone	A	B	C	D
F – coniferous tree species 1 yr				
x	18.9	7.5	2.6	4.0
A	–	**	***	***
B	–	N	N	N
C	–	–	–	N
F – coniferous tree species 2 yr				
x	37.0	5.3	4.6	–
A	–	*	**	–
B	–	–	N	–
C	–	–	–	–
F – broadleaved tree species				
x	67.4	5.9	6.9	3.7
A	–	***	***	***
B	–	–	N	N
C	–	–	–	N
S – broadleaved tree species				
x	3008	2717	3112	2701
A	–	N	N	N
B	–	–	N	N
C	–	–	–	*
N –broadleaved tree species				
x	26407	24393	28742	23431
A	–	N	N	N
B	–	–	N	N
C	–	–	–	*
K_z – coniferous tree species 1 yr				
x	5.6	2.6	1.4	1.7
A	–	**	***	***
B	–	–	N	N
C	–	–	–	N
K_z – coniferous tree species 2 yr				
x	10.0	2.0	1.9	–
A	–	*	**	–
B	–	–	N	–
C	–	–	–	–
K_z – broadleaved tree species				
x	18.4	2.8	3.4	2.3
A	–	***	***	***
B	–	–	N	N
C	–	–	–	N

T a b l e 5. Concentration of F and S (x) in the foliage of tree species according to the pollution zones for the years 1995–2001

Element	F [mg.kg^{-1}]					S[mg.kg^{-1}]				
Tree species/ Year	1995	1996	1997	2000	2001	1995	1996	1997	2000	2001
A pollution zone										
Robin	372	254	190	131	–	2510	3413	3460	4251	–
Birch	829	511	429	199	254	2835	5150	2860	2665	2700
Beech	81	29	50	61	23	2450	1060	2530	2138	2530
Oak	79	98	62	39	38	1830	2270	2840	3331	3450
Maple	72	45	71	24	23	2680	4750	2470	3160	2050
Linden	226	82	214	72	42	3760	4295	3885	2918	2967
Poplar	5989	341	320	56	60	5256	6673	6340	3581	3425
Cherry	73	100	37	23	35	1580	2005	1420	3700	2450
Pear	140	148	30	33	18	1985	1610	3150	2693	2020
Apple	65	20	75	40	9.3	2490	1520	2060	2629	2800
Plum	105	33	79	35	41	3320	3380	2590	2468	2680
Walnut	129	63	92	38	28.4	2690	4350	3170	3468	3110
Willow	489	265	280	107	104	7250	6790	7930	4671	3160
Pine	63	119	36	35	23	2027	1753	2353	1783	1673
Larch	317	112	16	17	6.7	2710	3520	4040	2205	1890
B pollution zone										
Oak	10.4	11.0	13.4	4.3	1.9	2133	2967	3020	1873	2980
Alder	7.2	15.4	12.6	7.3	4.6	2570	4210	3450	2180	3050
Hazel	10.7	38.6	62.2	13.9	–	2910	2100	3460	1752	–
Willow	40.4	45.8	85.3	21.3	9.3	5458	4853	8966	4418	2736
Pine	19.0	19.6	19.4	4.9	7.9	2116	2271	2544	1717	1760
Douglas fir	17.2	16.5	13.2	9.5	7.0	2540	2150	2410	1641	990
Spruce	30.2	20.9	15.2	7.5	7.2	1722	2010	2316	1980	1422
Beech	–	–	–	–	7.5	–	–	–	–	2600
Birch	–	–	–	–	3.9	–	–	–	–	2427
Walnut	–	–	–	–	5.7	–	–	–	–	2560
C pollution zone										
Beech	12.6	29.8	13.0	8.3	6.7	1915	2785	2490	2610	2977
Oak	7.4	7.6	6.9	5.9	9.5	2148	1670	2916	3050	3130
Maple	15.1	27.0	24.2	6.6	4.8	2790	4040	2960	2843	2930
Pine	11.0	12.0	11.6	4.1	2.3	1800	2526	2492	1667	1587
Spruce	23.7	8.3	18.4	7.7	4.4	1975	2340	2100	1696	1490
Alder	–	–	–	–	3.7	–	–	–	–	4200
Willow	–	–	–	–	5.3	–	–	–	–	3720
D pollution zone										
Beech	–	–	–	–	3.4	–	–	–	–	2470
Oak	–	–	–	–	3.2	–	–	–	–	2750
Hornbeam	–	–	–	–	3.8	–	–	–	–	2213
Alder	–	–	–	–	5.2	–	–	–	–	4135
Ash	–	–	–	–	2.9	–	–	–	–	2160
Poplar	–	–	–	–	4.7	–	–	–	–	2516
Robin	–	–	–	–	4.1	–	–	–	–	3572
Poplar	–	–	–	–	5.1	–	–	–	–	3050
Willow	–	–	–	–	11.1	–	–	–	–	3140

Note: x – arithmetical mean

2001 we did not analyse *Robinia* the pollution zone A due its removal in this zone. In 2001 we analysed in the B pollution zone in addition to mentioned tree species beech, birch and walnut, and C pollution zone alder and willow. In 2001 we analysed in the D pollution zone (within 50 km from the plant) beech, oak, hornbeam, alder, aspen, maple, robinia, poplar and willow. This zone was not analysed in the years 1995-2000.

Fluorine is a non-metallic, negatively univalent element, one of the most reactive. It naturally occurs in compounds, mainly fluorite, cryolite and apatite. It is also naturally found in fluoro-acids and **nucleocidine.** It is indispensable to animals, but is not essential to bacteria, algae, fungi and higher plants. The element accumulates in *Acacia georginae, Dichapetalum* ssp., *Gastrolobium grandiflorum, Porifere Dysidea crawshayi*, bones and teeth. Its increased amount indicates the presence of emission, which comes from aluminium production, or other production technologies, as glass production, etc. Fluorine is also a part of emission arising from the combustion of fossil fuels. Mammals need it to strengthen their teeth. Excessive fluorine, however, gives rise to tooth fluorosis of cattle and game – e.g. tooth fluorosis of deer in the Žiar nad Hronom area. Its deficiency causes chlorosis or yellowing of young leaves, anaemia, haemolysis and growth reduction. Fluorine has a structural function in apatite, has antibiotic effects and correlates with heart disease. Concentration above 5 mg.kg^{-1}, especially in the form of F^- and HF, is toxic to plants, and the dose of 2 g a day is lethal to human beings.

Total fluorine concentration in the world plant biomass is estimated by Markert (1991) at 3.682 .10^6 t. Maňkovská (1996) gives a limit value for spruce needles 8.7 mg.kg^{-1} F and Markert (1993) for pine tree 2.0 mg.kg^{-1} F. Horntved(1995) found linear dependence between fluorine concentration in the air and the leaves of *Sorbus aucuparia.* The values of fluorine ranged from 16 to 53 mg.kg^{-1} in the surroundings of 5 Norwegian aluminium plants, whereas he determined 4 mg.kg^{-1} as a limit value. Innes (1995) found in 2 years old needles of *Picea abies* the values within 2.8-27.5 mg.kg^{-1} and in *Pinus sylvestris* within 3-11.5 mg.kg^{-1}. The concentration lower than 2 mg.kg^{-1} should be considered as a limit value (Maňkovská, 1996).

Arithmetic mean of total fluorine concentration in leaves of all woody plants mentioned in the Atlas is 6.2+4.8 mg.kg^{-1} (median 6.1 mg.kg^{-1}). Average concentration in leaves of individual species are as follows (in mg.kg^{-1}): *Fagus sylvatica* 5.8±2.6 (median 5.9), *Quercus robur* 4.7±2.1 (median-4.9), *Picea abies* 6.3±4.2 (median 6.2), *Pinus sylvestris* 7.8±14.9 (median 6.3) and *Abies alba* 8.3±5.1 (median 8.0). The atlas of the maps of all woody plants (Maňkovská, 1996) shows, that fluorine concentration exceeds 5 mg.kg^{-1} in two-thirds of Slovak territory and are clearly associated with industrial plants. Total fluorine concentration above 10 mg.kg^{-1} has been determined in leaves of *Picea abies, Pinus sylvestris* and *Abies alba* in the Žiar valley and Central Spiš (Maňkovská, 1996).

Concentration of fluorine in Žiarska valley was reduced in comparison with the years 2001/1995 in all studied groups of tree species. In the year 2001 the concentration of fluorine (in mg.kg^{-1}) ranged in broadleaved tree species within 0 .60-254; coniferous tree species 0 .10-46 .6 (1yr), 2.7-75.3 (2 yr) resp. and within 9.3-41.2 in fruit tree species. The highest values of fluorine were found in the area very close to the aluminium plant (A pollution zone), Fig. 2. The differences between F concentration and pollution zones B, C and D were statistically insignificant. A marked drop of fluorine concentration was recorded for all studied tree species when compared the years 2001 and 1995.

Sulphur and nitrogen are structural elements. Increased concentration of both elements in plants is caused by polluted air. Sulphur is an important element in biogeochemistry of forest ecosystems on the basis of its role as essential plant nutrition. With damage to forest ecosystem it is necessary to consider three main reasons: damage to roots from humus complex, damage to foliage and redistribution of sulphur into older organs (older leaves, wood, etc.) (Rennenberger, 1994). Sulphur is important nutrient limiting the growth of plants (Innes, 1995). Sulphur is a non-metallic element, which naturally occurs in valences (-2), (+3), +4, (+5) and (+6). The most widespread states are -2 (sulphides) and +6 (sulphates). Sulphur is essential element to all organisms and it forms proteins. Its ecologically toxic forms are SO_4^{2-} and HSO_4^-. The element accumulates in noxious plants *Cruciferae, Alium* ssp., in sulphur bacteria, vertebrate hair and feathers. Sulphur is a constituent of amino acids (cysteine and methionine), coenzymes, muco-polysaccharide acids and sulphuric-acid esters. Its deficiency very much resembles the deficiency of nitrogen as it gives rise to interrib chlorosis of young leaves and yellowing of leaves. Considerably high concentration of sulphur in soil (gypsum) is well known. The effect of anthropogenic SO_2 emission on latest damage to forest and soil acidification is well known as well.

Total sulphur concentration in world plant biomass has been estimated by Markert (1991) at 5.523. 10^{10} t. According to Bowen (1979), plants contain 1000-9000 mg.kg^{-1} S. Bublinec (1990) says that a sufficient concentration in spruce is 1100-1800 mg.kg^{-1} S and in oak and beech 1000-2000 mg.kg^{-1}. Innes (1995) found 750-1620 mg.kg^{-1} S in two-year-old needles of *Picea abies* and 970-1950 mg.kg^{-1} in *Pinus sylvestris*. Higher values should be considered undesirable. Materna, Mejstřík (1987) say that sulphur concentration in spruce needles ranges within 800-1000 mg.kg^{-1}, what corresponds to our data (Maňkovská,1996). In air-polluted areas, sulphur concentration in needles is considerably increasing up to 5000 mg.kg^{-1} in the dry matter of 1 year old needles, what has already an unfavourable effect. Arithmetic mean of total sulphur concentration in the foliage of all tree species in the Geo-chemical atlas (Maňkovská, 1996) is 2163+1056 mg.kg^{-1} (median 1910 mg.kg^{-1}). Average sulphur concentration in the foliage of individual tree species are as follows (in mg.kg^{-1}): *Fagus sylvatica* 2242±923 (median 2090), *Quercus robur* 2236±1088 (median 2120), *Picea abies* 1959±851 (median 1750), *Pinus sylvestris* 1952±1010 (median 1730) and *Abies alba* 2203±943 (median 1940). Exogeneous sulphur was found on 0.4% of the surface of analysed foliage of forest tree species. The obtained data on total sulphur concentration in the foliage of forest tree species are surprisingly high in comparison with our data obtained in 1975 (Maňkovská, 1995). They confirm increasing impact of sulphur oxides throughout Slovakia's territory. The concentration of total sulphur higher than 1000 mg.kg^{-1} is present on more than 4/5 of the Slovakia's territory. This concentration is exceeded for all tree species in all industrial areas, military area Lešť and in 5 selected mountainous forests.

Concentrations of **sulphur** (mg.kg^{-1}) in coniferous trees ranged within 920-2850 (1 yr), 750–2210 (2 yr) resp., in broadleaved trees within 1250–4990 and fruit trees within 2020–3110. They confirm a marked impact of sulphur oxides in the whole Žiarska valley. Ac-

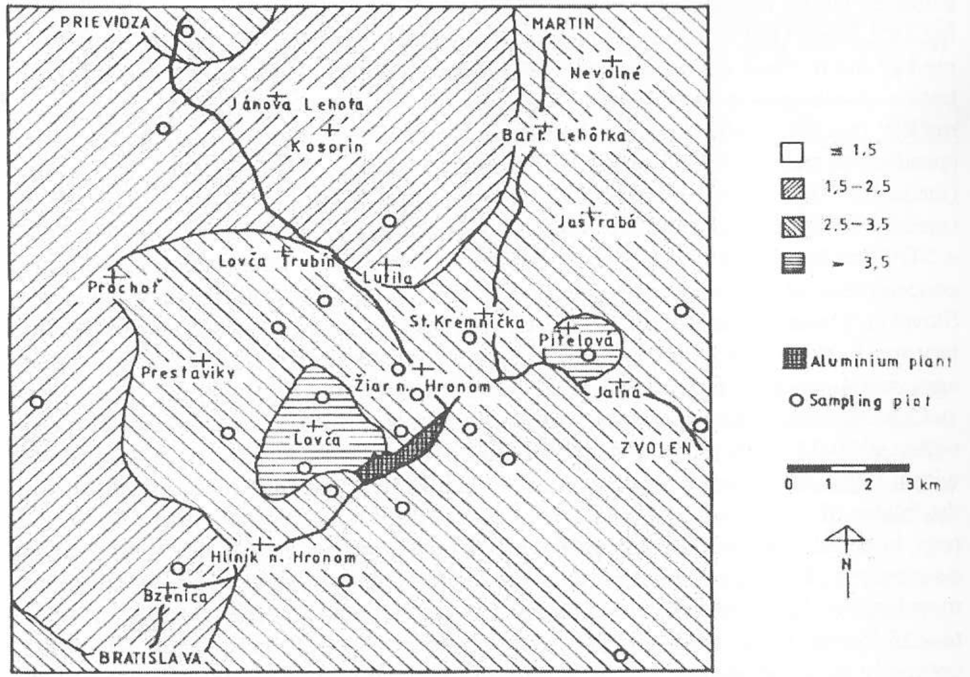

Fig. 3. Course of S concentrations (Kz) in 4 groups of tree species for pollution zone A,B,C.

cording to the assessment by means of the coefficient of loading by sulphur air pollutants, the concentration of sulphur in the foliage of forest trees is higher more than 3.5 times to the east from heating plant and in the surroundings of the plant (Fig. 3). For all studied tree species a marked drop of sulphur was recorded in comparison of the years 2001/1995.

Atmospheric air is composed of about 4/5 volume proportions of elementary nitrogen. Inorganic compounds of nitrogen occur in nature in higher concentration only rarely with except for $NaNO_3$. Nitrogen is indispensable for living organisms, as it is one of elements forming proteins. Nitrogen is structural element and occurs in many organic compounds. Nitrogen is essential for bacteria, algae, fungi, higher plants as well as animals. It is a basic component of protoplasm and enzymes with a majority of metabolic functions. Its deficiency causes dwarfed growth or dwarfish growth, spindly growth of plant, scleromorphosis, yellowing of older foliage. Simple compounds of nitrogen today represent an extensive eco-toxicological problem, e.g. problem of sodium nitrites for animals, NO_2-emission, N_2O as greenhouse gas in the atmosphere. It is ecologically toxic in the form NO_3^- and NH_4^-. Total concentration of nitrogen in plant biomass all over the world is estimated by Markert (1991) at 4.602 .10^{10} t. Markert (1991) gives for the soils the values 2000 mg.kg^{-1} and for plants 12000 up to 38000 mg.kg^{-1}. Bergman (1986) considers 13500-17000 mg.kg^{-1} sufficient for spruce what is in accordance with the data by Bublinec (1990). For beech foliage

Bublinec (1990) considers the values 19000-26000 mg.kg^{-1} for oak foliage 18000-30000 mg.kg^{-1}. Innes (1995) found out in 2 yr needles of *Picea abies* the values 11010-16400 mg.kg^{-1} and in *Pinus sylvestris* 12 500-23 200 mg.kg^{-1}. Arithmetical mean of total concentration of nitrogen in the foliage of all tree species according to Atlas is 18165 ± 6432 mg.kg^{-1} (median 15900 mg.kg^{-1}). Average concentration of nitrogen in the foliage of respective tree species (Maňkovská, 1996) represents in mg.kg^{-1}: *Fagus sylvatica* 19750 ± 6755 (median 17800), *Quercus robur* 20923 ± 6170 (median 21180), *Picea abies* 16640 ± 5220 (median 15300), *Pinus sylvestris* 16630 ± 5 431 (median 15600) and *Abies alba* 17920 ± 5470 (median 16900). In the atlas map of all tree species (Maňkovská, 1996) higher concentration of total nitrogen higher than 20000 mg.kg^{-1} is obvious in south and eastern Slovakia. These concentrations are exceeded in the foliage of *Fagus sylvatica* in the military area Lešť, in Central Spiš and industrial agglomeration Košice; *Quercus robur* in Košice agglomeration and in Central Spiš and *Picea abies* in Central Spiš.

Concentration of **nitrogen** (in mg.kg^{-1}) in coniferous tree species in Žiarska valley ranged within 9300-22100 (1 year old) and 8900-19200 (2 years old); in broadleaved tree species within 10900-40800 and fruit trees within 17900-27700. Coefficient of molar ratio S/N in the foliage of coniferous trees ranged from 0.09 to 0.16 (1 year old) or within 0.06 to 0.140 resp; in broadleaved trees within 0.07-0.27, and fruit trees within 0.11-0.150. S/N ratio is a sensitive indicator of sulphur accumulation in the foliage of forest trees subjected to atmospheric pollution. Molar ratio of protein sulphur and protein nitrogen ranges from 0.05 to 0.15 (Stefan et al., 1997) and it is relatively constant for all tree species. S/N ratio is optimally balanced in more than 90% of coniferous tree species when compared with the limit range. In other tree species it is redundant and our results showed that capability of sulphur to increase exceeded in all cases the need of plants regarding protein synthesis.

Anthropogenic loading of the foliage of tree species in all sampling locations within the distance 50 km from the plant, being given by the coefficient of loading by air pollutants K_z is in Table 6. Sampling locations are illustrated in Fig.1, loading by fluorine in Fig. 2, by sulphur in Fig. 3.

Table 6. The values of the coefficient of loading by F and S air pollutants for the group of tree species in the year 2001 in 4 pollution zones (A, B, C, D) within 50 km from the plant

Group of tree species	Coniferous-1yr x(SD)	Coniferous-2yr x(SD)	Broadleaved x(SD)	Fruit tree sp. x(SD)	Together x(SD)	Limits x(SD)
K_z-F	2.7	5.5	6.2	13.2	5.2	1
K_z-S	1.6	1.5	3.0	2.6	2.3	1
Together	2.8	3.5	8.3	7.9	3.7	1

Comparison of K_z for the years 1995, 1996, 1997, 2000 and 2001 is given in Table 7 (for pollution zones A, B, C). For the year 2001 fluorine level was exceeded 9.5 times and sulphur level 2.3 times. Total air pollutant's loading of all tree species in Žiarska valley (A, B, C zone) given by coefficient K_z represents in the year 2001 a 5.9 times higher loading compared with the year 2000, 19.4 times higher loading compared with 1997, 22.9 times higher loading compared with 1996 and 29.5 times higher loading when compared with 1995.

Table 7. The values of the coefficient of loading by air pollutants K_z according to F, S a total loading for the years 1995, 1996, 1997, 2000 a 2001 in 3 pollution zones

K_z	1995	1996	1997	2000	2001
K_z-F	56.5	42.5	35.0	12.7	9.5
K_z-S	2.8	3.2	3.8	3.1	2.3
K_z -total	29.5	22.9	19.4	7.9	5.9

Conclusion

Air pollution was reduced due to the introduction of a new technology of aluminium production. Substances polluting forest stands accumulated in the soil during more than 40 years. It cannot be expected that after the introduction of more modern technology this problem shall be fully eliminated. Only long-term monitoring can show the response of plants to substantial reduction of fluorine concentration in the air, particularly when the concentrations of other pollutants remain still quite high in the soil.

1. Studied tree species in Žiarska valley are more subjected to the impact of a complex of factors connected with polluted air and soil, which are even increased due to unfavourable effects of biotic and abiotic injurious agents. The foliage of studied groups of tree species in the year 2001 contained following concentrations (in mg.kg^{-1}):
   - coniferous trees (1 year old): fluorine (10.0 ± 18.1), sulphur (1762 ± 214), nitrogen (1312 ± 287), resp. fluorine (10.0 ± 18.1), sulphur (1762 ± 214), nitrogen (1312 ± 287)
   - broadleaved trees – fluorine (10.0 ± 18.1), sulphur (1762 ± 214), nitrogen (1312 ± 287)
   - fruit trees – fluorine (10.0 ± 8.1), sulphur (1762 ± 214), nitrogen (1312 ± 287)
   - in comparison of the year 2001 with 1995 the concentration of F has dropped significantly. The concentration of sulphur was slightly lower as well
   - by means of nutrition ratios S/N we evaluated the state of the nutrition for studied tree species. Nutrition ratio S/N shows in all cases exceeding of plant need for sulphur in all cases for broadleaved, fruit trees and shrubs. In coniferous tree species the ratio S/N is balanced.
2. Anthropogenic loading of all tree species in Žiarska valley, expressed by means of the coefficient of loading by air pollutants was as follows:
   - in 1995 the level of fluorine was exceeded 71 times, of arsenic 3.2 times, sulphur 2.2 times. Total loading of tree species by air pollutants in Žiarska valley expressed by means of K_z coefficient represented 29.5 times higher loading
   - in 1996 the level of fluorine was exceeded 42.5 times, arsenic 4.8 times, sulphur 3.2 times. Total loading of tree species by air pollutants in Žiarska valley expressed by K_z coefficient represented 22.9 times higher loading
   - in 1997 the level of fluorine was exceeded 35 times, of arsenic 10 times and sulphur 3.8 times. Total loading of all tree species by air pollutants in Žiarska valley expressed by the coefficient K_z represented 19.4 times higher loading;

- in 2000 the level of fluorine was exceeded 12.7 times, and of sulphur 3.1 times. Total loading of all tree species by air pollutants in Žiarska valley expressed by K_z coefficient represented 7.9 fold loading
- in 2001 the level of fluorine was exceeded 9.5 times, of sulphur 2.3 times. Total loading of all tree species by air pollutants in Žiarska valley expressed by K_z coefficient represented 5.9 times higher loading.

3. Anthropogenic loading of all tree species in Žiarska valley (pollution zone A, B, C) and then within 50 km distance from the plant (pollution zone D) expressed by the coefficient of loading by air pollutants represented:
   - Sexceeding of fluorine concentration 5.2 times. Statistically significant difference in fluorine concentration was found only between pollution zone A and zones B, C and D for coniferous and broadleaved tree species. Statistically insignificant difference in the concentration of fluorine was found between zones B, C and D mutually for coniferous and broadleaved tree species. It proves of significant effect of fluorine air pollutants only in pollution zone A
   - Exceeding of sulphur concentration was 2.3 times. Statistically insignificant difference in sulphur and nitrogen concentration was sound between zones A, B, C and D mutually for coniferous tree species (1 and 2 years old) and for broadleaved tree species between the zone A, B and C. Statistically significant difference in sulphur and nitrogen concentration was found only for broadleaved tree species between C and D zone. It proves of the presence of other sources of sulphur emission in the studied area
   - total loading of tree species by air pollutants within 50 km from aluminium plant expressed by means of coefficient K_z represented 3.7 times higher loading. Statistically significant difference for K_z was found in coniferous tree species (1 and 2 years old) and broadleaved tree species in A zone in comparison with the zones B, C and D. Statistically insignificant difference we found in coniferous tree species (1 and 2 years old) and broadleaved tree species mutually in the zones B, C and D except for broadleaved tree species where statistically significant increase between B and D zone was found. It proves of a significant effect of fluorine air pollutants in A pollution zone.

Translated by the author

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Maňkovská B.: **Biomonitoring zníženia znečistenia so zmenou technológie výroby hliníka.**

Antropogenické zaťaženie všetkých drevín v Žiarskej kotline, ktoré sme vyjadrili pomocou koeficientu zaťaženia imisiami K_z, má klesajúci trend. Celkové zaťaženie všetkých drevín imisiami v Žiarskej kotline (zóny znečistenia A, B, C) vyjadrené ako koeficient K_z predstavuje v 2001 iba 5,9 násobné zvýšenie v porovnaní so 7,9 násobným zvýšením s rokom 2000; 19,4 násobné zvýšenie v porovnaní s 1997; 22,9 násobné zvýšenie v porovnaní s 1996 a 29,5 násobné zvýšenie v porovnaní s 1995. Celkové zaťaženie imisiami pre všetky dreviny (zóny znečistenia A, B, C, D) do 50 km od SLOVALCA, a.s. vyjadrené pomocou K_z predstavuje 3,7 násobné zaťaženie. Štatisticky významný rozdiel existoval pre K_z u ihličnatých druhov (1 a 2 ročné ihličie) a listnatých druhov v A zóne v porovnaní so zónou B, C a D. Štatisticky nevýznamný rozdiel sme zistili u ihličnatých drevín (1 a 2 ročné ihličie) a u listnatých drevín v zónach B, C a D s výnimkou listnatých drevín; pre ktoré sme našli štatisticky významné zvýšenie medzi zónou B a D.