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TEMPORAL TRENDS (1990–1997) IN ELEMENT ACCUMULATION IN OAK LEAVES AND SOIL ON BÁB SITES

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Abstract

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Element analysis in the leaves of oak (*Quercus* sp.) and in the soil samples (A horizon) from the research area of the International Biological Programme at Báb sites are discussed in the context of their limit values. We found increased concentrations of Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Ni, Pb, S, V and Zn in the leaves of oak and of Al, As, Be, Ca, Co, Cr, Cs, Cu, F, Fe, Hg, Li, Mg, Ni, P, Rb, Sr, V, Zn in the soil samples (A- horizons). Concentrations of B, Mg, Mn and P in oak leaves and B, Ba, Bi, Cd, Ce, Ga, K, La, Mn, Mo, Na, Pb, Sb, Se, Sn, W and Y in the soil samples (A- horizons) have not exceeded Slovak limit values. 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 too for biodiversity study.

Key words: oak leaves, atmospheric deposition, nutrition elements, heavy metals

Introduction

Tree and shrub species are dominant forms of the research area of the International Biological Programme at Báb. The ecosystem, which represents the semi-natural oak-hornbeam forest on loess, is a typical climatic-zonal unit in this part of Slovakia. Numerous studies were performed on the tree and shrub individuals (Biskupský, 1975; Oszlányi, 2001).

Geochemical mapping of Slovak territory shows that many regions, which have had intense miner activity, are characterized by high concentration of toxic elements, such as As, Al, Mn, Cd, Cr, Cu, Hg, Pb and Sb (Maňkovská, 1996). Their soluble forms presented high environmental risk to nature and man. Over-limited concentrations of these chemical elements are accumulated preferably in soil, water and river sediments (Čurlik, Šefčik, 1999; Rapant et al., 1996; Bodiš, Rapant, 1996). On the territory of Slovakia, 17 000 regions were connected with miner activity. Many of them rank to the past, but the negative effect of their waste heap on the environment has various levels of toxicity. 50 geographical regions from the representative locality have strong negative effects on the environment. Heavy elements and potential toxic ions get in into the environment through atmospheric transfer, direct application and soil contamination.

Air pollutants have impaired the health of Slovak forests. The forest ecosystems break down step by step. Prolonged effects of high concentrations of various air pollutants have resulted in large-scale dying not only of conifers but also deciduous trees. The above-described conditions are not limited to the vicinity of pollution sources, but have spread throughout Slovakia's territory long ago. Huge quantities of pollutants from abroad are also deposited in Slovak territory, mainly from Poland, Austria, Ukraine and Czech Republic from where they are carried by prevailing northern, northwestern and western winds. Furthermore, it must be taken into account that Slovakia has a rugged topography. The highest altitudes reach 2632 m, and the tree limit is (incl. dwarfed pine) 1800 m. All these adverse factors have resulted in a situation when, in the 1990s, 85% of forests displayed symptoms of damage.

No direct measurements of major pollution components ($SO_{2,}$ NO_x) in Slovakia's forest soils are available to characterize the pollution situation. Most data on emissions are estimates based on fuel and material balances. The principal chemical components of air pollutants are reflected in the pollution type. Given the current emission situation in Europe, the whole Slovak territory is affected by air pollutants, and pollution types are unlikely to change substantially in the next years. The Slovak territory has been divided into three major pollution deposition types (PDT) (A – acid, B – basic, and C – ammonia PDT) (Maňkovská, 1996).

The primary task of the present study is to quantitatively characterize the element concentrations over the research area of the International Biological Programme at Báb between 1990 and 1997. An additional aim of this report is to summarise element concentrations in soil samples on sites Báb in 1997.

Material and methods

The leaves of oak (*Quercus* sp.) and soil samples (A horizon) were taken in compliance with international methods (ICP, 1994) in permanent areas situated on the intersections of a 16x16 km pan-European network. The collection of samples in the same localities was performed during the first half of August 1990, 1993, 1995, and 1997. Soil samples were collected from July to August 1997. A collective sample was mixed from 15 samples after their drying. The samples of oak leaves were analysed unwashed. They were dried at a temperature not exceeding 80° C for a period of 24 hours. Leaves were separated 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 a microwave furnace MDS 2000 (CEM company).

Atomic absorption spectrometer (LECO- PLASMA-RAY 2000) was applied to determine concentrations of Al, B, Ca, Fe, K, Mg, Mn, and Na. The atomic absorption spectrometer Varian Techtron was used to determine concentrations of Cd, Cr, Cu, Hg, Ni, Pb and Zn. The LECO SC 132 elementary analyser was applied to determine the concentration of sulphur. The LECO SP 228 elementary analyser was used to determine total the concentration of nitrogen. The results were calculated to dry matter, which was determined separately. The accuracy of data was verified by an analysis of standard plant samples and by a comparison with the results obtained in 109 laboratories within the IUFRO working group for quality assurance (Hunter, 1994).

For the assessment of vegetation material, we used current statistical methods and analysis of variance. For the assessment of total loading on the Báb sites by study elements, we used K_z coefficient of loading by air pollutants, which indicates exceedance of limit values of studied elements in the foliage of forest tree species (Maňkovská, 1996). The 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 n of elements) are given by the relation:

$$Y_i = \frac{M_i}{m_i}$$

valid for i element

where:
M – w concentration of As, Cd, Cr, Cu, Fe, Hg, Mn, N, Ni, Pb, S, V and Zn (in mg.kg^{-1}) in the oak leaves in 1990, 1993, 1995 and 1997
m – 3x concentration of As, Cd, Cr, Cu, Fe, Hg, Mn, N, Ni, Pb, S, V and Zn (in mg.kg^{-1}) in the oak leaves in the oak leaves from control areas – sampling in the years 1974 -1975 (Maňkovská, 1996)
n – number of studied elements

Coefficient of loading by air pollutants K_z is defined:

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

Results

Foliar analysis

The total concentrations of 21 major and trace elements were determined in the leaves of oak (*Quercus* sp.) in Báb between 1990–1997. Our results are presented on Table 1. The background limit concentration of the studied elements in the leaves of oak as given by Bowen, 1979; Maňkovská, 1996; Markert et al. 2003; Stefan et al., 1997 is also in Table 1. We recorded the exceedance of limit values for Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Ni, Pb, S, V and Zn. Statistically significant differences (ANOVA) between concentrations of Cd, Cu, Fe, Ni, Pb and Zn in the leaves of oak were found between all of the studied years

Anthropogenic loading of the foliage of tree species in all sampling locations, within a 30 km distance from the Báb sites, being given by the coefficient of loading by air pollutants Kz is in Table 2. The coefficient K_z represents 3.07 (1990), 1.21 (1993), 0.99(1995) and 1.29 (1997).

Nutrition ratios (S/N, N/P, N/K, N/Mg, K/Ca, K/Mg, Ca/Mg, Fe/Mn) in oak leaves are given in Table 3.

Soil analysis

The concentrations of 36 elements in soil samples (A horizon) from Báb sites for 1998 are given in Table 4. We discovered a statistically significant difference between concentrations

T a b l e 1. Concentration of elements in the leaves of oak (*Quercus* sp.), in Báb between 1990–1997 (median in mg.kg-1) compared with limit values and dispersion analysis (ANOVA).

Element	Al**	As**	B*	Ca***	Cd**	Co**	Cr**	Cu**	Fe**	Hg**	K**
1990	-	-	-	-	1.26	-	1.5	8.1	237	-	-
1993	138	0.224	36	9500	-	-	-	10.1	160	0.059	10240
1995	100	-		13930	-	-	-	8.6	142		10138
1997	77	-	32	10870	0.148	0.357	0.591	13.5	119	0.049	11170
ANOVA	N	-	N	N	***	-	N	***	***	N	N
Theoretical	3.354	-	4.543	3.354	4.667	-	4.667	2.922	2.922	4.543	3.354
Calculated	1.709	-	0.490	3.177	101.8	-	0.257	7.287	8.248	0.198	1.795
Limit values	82	0.21	50	8000	0.10	0.17	0.80	5	200	0.08	10000

Element	Mg**	Mn**	N**	Na**	Ni**	P*	Pb**	S***	V**	Zn**
1990	-	479	-	-	10.7	-	4.9	3030	-	99
1993	2525	869	28438	48	-	1235	-	1955		31
1995	1902	655	19500	42	-	-	0.81	2390		22
1997	2580	235	30340	-	5.03	1420	2.01	3230	0.65	31
ANOVA	N	N	N	N	***	N	***	N	-	***
Theoretical	3.354	2.922	3.354	4.451	4.667	4.543	3.385	2.922		2.922
Calculated	0.354	0.128	2.884	0.110	7.506	0.414	11.55	1.655		13.85
Limit values	2500	1000	25000	40	4.30	1800	0.90	2000	0.30	45

Notes: Limit value: *Bowen (1979), ** Maňkovská (1996), ***Stefan et al. (1997), Markert et al. (2003), values in bold are exceeded Slovak limit values, n = 30 (1990), n = 30 (1993), n = 30 (1995), n = 30 (1997), ***– probability 0.001, N – non statistical difference.

T a b l e 2. The values of the coefficient of loading (Kz) by 13 elements for the oak leaves (*Quercus* sp.) between 1990–1997 within 30 km from the Báb sites.

Element	As	Cd	Cr	Cu	Fe	Hg	Mn	N	Ni	Pb	S	V	Zn	Kz
1990	-	12.6	1.88	1.62	1.19	-	0.48	-	2.49	5.44	1.52	-	2.20	3.07
1993	0.93	-	-	2.02	0.80	0.74	0.87	1.14	-	0.00	0.98	-	0.69	1.21
1995	-	-	-	1.72	0.71	-	0.66	0.78	-	0.90	1.20	-	0.49	0.99
1997	-	1.48	0.74	2.70	0.60	0.61	0.24	1.21	1.17	2.23	1.62	2.17	0.69	1.29
Kz	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Note: Kz – the coefficient of loading (Maňkovská, 1996).

of all study elements (Student test). We discovered a significant correlation r ($p < 0.005$) between toxic elements (As/Cr; As/Hg; Cu/Fe, Cu/Hg, Cu/V, Cu/Zn, Fe/Ni, Fe/Pb, Fe/V, T a b l e 3. Ratio of elements.

Element	S/N	N/P	N/K	N/Mg	K/Ca	K/Mg	Ca/Mg	Fe/Mn
1990	-	-	-	-	-	-	-	0.495
1993	0.069	23.0	2.8	11.3	1.1	4.1	3.8	0.184
1995	0.123		1.9	10.3	0.7	5.3	7.3	0.217
1997	0.106	21.4	2.7	11.8	1.0	4.3	4.2	0.506
Limits	0.052	10.6-25.0	1.8-5.0	12.0-25.0	0.6-2.5	3.3-10.0	3.7-8.0	0.50

Fe/Zn, Hg/Ni, Hg/V, Mn/Cr; Mn/Cu; Mn/Ni; Mn/Pb; Mn/Zn; Ni/Pb, Ni/V) in the soil. The active soil reaction (pH/ H_2O) was moderately alkaline (7.61 to 8.51); and pH/KCL was 6.97 to 7.83. The median values of active pH values in Slovakian soils (A horizons) are 5.10 (Čurlík, Šefčík, 1999).

T a b l e 4. Concentration of elements in the soil samples – Báb sites (area 30 km).

Element	Al	As	B	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs
Conc.	%	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	%	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$
x	5.30	7.74	57.0	327	1.26	0.29	7.54	0.27	51.3	9.11	73.9	5.33
sx	0.47	1.73	3.0	26	0.20	0.08	1.65	0.05	3.0	1.17	9.3	1.00
med	6.27	10.10	63.0	389	1.50	0.30	6.61	0.20	53.0	10.00	89.0	6.00
max	6.27	10.10	63.0	389	1.50	0.40	9.81	0.30	57.0	11.00	89.0	7.00
min	4.84	4.90	52.0	296	0.90	0.20	4.27	0.20	46.0	7.00	59.0	4.00
T test	*	*	*	*	*	*	*	*	*	*	*	*
Calc.	33.70	13.46	51.26	37.4	18.77	11.09	13.69	16.00	51.30	23.40	23.89	16.00
Theor.	2.31	2.31	2.31	2.3	2.31	2.31	2.31	2.31	2.30	2.30	2.31	2.31
SR*	5.88	7.2	61	381	1.3	0.3	0.61	0.3	65	9	85	5

Element	Cu	F	Fe	Ga	Hg	K	La	Li	Mg	Mn	Mo	Na
Conc.	$mg.kg^{-1}$	$mg.kg^{-1}$	%	$mg.kg^{-1}$	$mg.kg^{-1}$	%	$mg.kg^{-1}$	$mg.kg^{-1}$	%	%	$mg.kg^{-1}$	%
x	21	444	2.54	9.44	0.047	1.62	32	33	3.02	0.058	0.38	0.87
sx	3	68	0.19	2.19	0.021	0.09	3	5	0.92	0.003	0.27	0.10
med	26	450	2.86	12.00	0.100	1.64	37	36	2.19	0.055	0.30	0.71
max	26	550	2.86	13.00	0.100	1.80	37	38	4.50	0.062	0.80	1.05
min	16	350	2.25	7.00	0.030	1.52	27	23	1.27	0.054	0.10	0.71
T test	*	*	*	*	*	*	*	*	*	*	*	*
Calc.	18.84	19.50	39.26	12.96	6.60	54.77	32.80	21.40	9.91	56.98	4.23	26.93
Theor.	2.31	2.30	2.31	2.31	2.31	2.31	2.30	2.30	2.31	2.31	2.31	2.31
SR*	17	300	2.64	12	0.08	1.69	38	33	0.64	0.068	0.5	0.85

T a b l e 4. (Continued)

Element	Ni	P	Pb	Rb	Sb	Se	Sn	Sr	V	W	Y	Zn
Conc.	$mg.kg^{-1}$	%	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$	$mg.kg^{-1}$
x	28	0.104	14.44	85	0.57	0.089	3.06	159	69	0.83	22	60
sx	4.4	0.022	2.70	10	0.14	0.065	1.55	19	7	0.66	1.8	7
Med.	36	0.110	18.00	104	0.50	0.100	4.00	170	81	0.50	23	68
Max.	36	0.143	18.00	104	0.80	0.200	6.00	182	81	2.00	26	68
Min.	23	0.075	11.00	65	0.30	0.050	0.50	133	57	0.50	20	51
T test	*	*	*	*	*	*	*	*	*	*	*	*
Calc.	19.27	13.87	16.10	24.50	12.02	4.10	5.91	25.60	29.10	3.78	36.55	27.50
Theor.	2.31	2.31	2.30	2.30	2.31	2.31	2.31	2.30	2.30	2.31	2.31	2.30
SR*	25	0.071	20	84	0.70	0.1	5	93	74	< 1	26	61

Notes: * – median values in bold are exceeded Slovak limit values (Čurlík, Šefčík, 1999); n = 11; Calc. – calculated; Teor. – theoretical.

Discussion

Aluminium (Al) is a metallic non-essential element in foliage of forest trees. The concentrations of Al for oak leaves ranged between 106–192mg.kg^{-1}(1993), between 32–425 mg.kg^{-1}(1995), and between 24–160 mg.kg^{-1}(1997). According to Maňkovská (1996), the allowable limit value for Al in oak leaves is 82 mg.kg^{-1}. Al is released from acid fallout and therefore may damage forests. Plants take up Al from soil, often in excessive quantities. The average Al content in dried soil is 71 000 mg.kg^{-1}(Bowen, 1979; Čurlík, Šefčík, 1999).

Arsenic (As) is a metallic non-essential element in foliage of forest trees. The concentrations of As for oak leaves ranged between 0.200–0.476 mg.kg^{-1}. Maňkovská (1996) and Markert (1993) give a limit value for oak leaves 0.21mg kg^{-1}. Brown coal contains much arsenic, which is released by burning. Average As content in dried soil (A horizons) is 6 mg.kg^{-1}(Bowen, 1979; Čurlík, Šefčík, 1999). Some arsenic forms behave in soil like phosphates.

Boron (B) is an essential element for trees. Its significance is anchored in its positive influence on sugar metabolism, which includes metabolism of nucleic acids, carbohydrate biosynthesis, protein metabolism and cell membrane stability. The concentrations of B for oak leaves ranged between 26–84 mg.kg^{-1} (1993), and between 16–68 mg.kg^{-1} (1997). According to Stefan et al. (1997) and Maňkovská (1996), the allowable limit value for B in the oak leaves trees ranges between 15–50mg.kg^{-1}. The background concentrations of B in Slovakian soils are 61 mg.kg^{-1} for A horizons (Čurlík, Šefčík, 1999).

Calcium (Ca) is an alkali-earth metal, and is an essential element. Concentrations of this element in tree foliage depend on its availability in soil. In principle, the Ca concentrations correlate with Mg levels. The variation range of Ca in oak leaves (in mg.kg^{-1}) was as follows: 3650–17 500 (1993); 6930–39 401 (1995) and 5410–19 450 (1997). In plants, Ca is not as mobile as Mg and thus it is being accumulated in older plant tissues. The highest concentrations were determined for oak in 1995. According to Stefan et al. (1997), the allowable limit value for Ca in the foliage of oak ranges between 4000–8000 mg.kg^{-1}. Its deficiency in plants results in slower growth (small cells), withering of leaf tips, leaf deformations and slower growth of roots. Bowen (1979) puts Ca content in soil at 15 000 mg.kg^{-1}**.** The median values of Ca contents in Slovakian soils (A horizons) are 6100 mg.kg^{-1} (Čurlík, Šefčík, 1999).

Cadmium (Cd) is a heavy metal. It is highly toxic to most organisms, particularly in the form of Cd^{2+} and $CdOH^{+}$. In soil it occurs in the form Cd^{2+}, which is bound in complicated complexes and organic chelates. Cd content in soil, where clay and organic matter readily absorb it, has been estimated by Bowen (1979) at 0.35 mg.kg^{-1}. Cd increased contents in vegetation are important from an environmental point of view. The content of Cd in oak leaves ranged between 0.60–1.37 mg.kg^{-1} in 1990 and between 0.29–0.324 mg.kg^{-1} in 1997. The median values of Cd contents in Slovakian soils (A horizons) are 0.3 mg.kg^{-1} (Čurlík, Šefčík, 1999).

Cobalt (Co) is a metal. In nature, it is always associated with nickel, usually in compound with arsenic. Bowen (1979) gives limit values in soil 8 mg.kg^{-1} and in plants above 0.005 mg.kg^{-1}. The range of Co content in oak leaves was 0.095–0.761 mg.kg^{-1} in 1997. The background level of Co 0.17 mg.kg^{-1} was found to be bellow in about 90% of the SK territory (Maňkovská, 1996). The median values of Co contents in Slovakian soils (A horizons) are 9mg.kg^{-1} (Čurlík, Šefčík, 1999).

Chromium (Cr) is a metal and is not essential to higher plants. Bowen (1979) puts Cr contents in soil at 70 mg.kg^{-1} and in vegetation from 0.03 to 10 mg.kg^{-1}. The content of chromium (Cr) in oak leaves ranged between 0.4–1.7 mg.kg^{-1} in 1990, between 0.118–2.776 mg.kg^{-1} in 1997. The highest total Cr contents exceed 2 mg.kg^{-1} in industrial areas of central and eastern Slovakia (Maňkovská, 1996). The background values of Cr reach 85 mg.kg^{-1} in A horizons (Čurlík, Šefčík, 1999).

Copper (Cu) is an essential microelement. The concentration of Cu for oak leaves ranged (in mg.kg^{-1}): 3.1–10.8 (1990); 8.7–11.9 (1993); 2.7–11.6 (1995) and 6.6–21.1 (1997). According to Maňkovská (1996) the allowable limit value for copper in the foliage of forest tree species is between 2 and 3 mg.kg^{-1}. Stefan et al. (1997) gives a value 2.5–3 mg.kg^{-1} for spruce needles; Maňkovská (1996) considers foliar Cu concentration < 5mg.kg^{-1} as limit level and values >100 mg.kg^{-1} as indicative of extreme load by air pollutants. Total copper concentrations > 5 mg.kg^{-1} are present on about 2/3 of the Slovak territory. Bowen (1979) gave Cu contents 1–80 mg.kg^{-1} in soils. The background values in Slovakian soils attain 17 mg.kg^{-1} for A horizons (Čurlík, Šefčík, 1999).

Iron (Fe) is a typical essential element with physiological enzymatic function. In higher concentrations its effects on plants are toxic. According to Stefan et al. (1997), normal concentrations in healthy oak leaves are about 129 mg.kg^{-1}. The optimal value for Fe in foliage is within the range 50–200 mg.kg^{-1} (Maňkovská 1996). In this study, the concentrations of Fe for oak leaves ranged between 160–399 mg.kg^{-1} (1990); between 117–223 mg.kg^{-1} (1993), between 55–235 mg.kg^{-1} (1995), and between 70–182 mg.kg^{-1} (1997). The concentration of Fe is elevated in all studied tree species and it is obviously connected with the presence of Fe in fly ashes emitted from heating plants. Total Fe concentrations > 200 mg.kg^{-1} are present on about 2/3 of the Slovak territory (Maňkovská, 1996). Bowen (1979) gives Fe content

40 000 mg.kg^{-1} in soil. The median values in Slovakian soils attain 2.64% for A horizons (Čurlík, Šefčík, 1999).

Mercury (Hg) is a heavy metallic element. Maňkovská (1996) puts the critical value for Hg at 0.12 mg.kg^{-1}. Sources of plant and soil contamination with Hg are related to metals processing industries, to some chemical factories, and to the use of fungicides containing Hg. The Hg content in oak leaves ranged between 0.022–0.091 mg.kg^{-1} in 1993 and between 0.018– 0.08 mg.kg^{-1} in 1997. The median values of Hg contents in Slovakian soils (A horizons) are 0.3 mg.kg^{-1} (Čurlík, Šefčík, 1999). Bowen (1979) has determined 0.06 mg.kg^{-1} Hg in soil.

Potassium (K) is an essential element. It can be replaced by rubidium, caesium, barium, lead and thallium. Essential to all organisms, it has electrochemical, catalytic and enzymatic (enzyme activation) functions, and supports osmoregulation and hydration. Oxygen deficiency disturbs water balance (withering tips of leaves. contorted older leaves, premature loss of older needles, rotting roots). Variations in potassium concentration in foliage of forest tree species are controlled by soil. The concentration of K ranged between 8370–12 510 mg.kg^{-1} in 1993; between 5747–20 760 mg.kg^{-1} in 1995 and between 6510–22 020 mg.kg^{-1} in 1997. According to the data, K concentration from 5000 up to 10 000 mg.kg^{-1} is optimal and sufficient (Maňkovská, 1996). Čurlík, Šefčík (1999) gives K content 17 100 ± 4500 mg.kg^{-1} in Slovakian soils (A horizons).

The magnesium (Mg) concentration in foliage of forest trees depends on its soil content. Optimal nutritional values for Mg range from 600 to 1500 mg.kg^{-1} (Stefan et al., 1997). The Mg concentrations are higher in older needle classes of healthy trees. In regions affected by air pollutants, the Mg concentrations increased up to the 3rd year needle class, and then dropped. Low values of Mg correlate with needle yellowing. Maňkovská (1996) showed that concentration of Mg in the needles of older trees (4000 mg.kg^{-1}) was lower in comparison with younger individuals (6200 mg.kg^{-1}). The range of Mg in oak leaves found in this study are as follows: 420–5050 mg.kg^{-1} in 1993; 672–3906 mg.kg^{-1} in 1995 and 890–5690 mg.kg^{-1} in 1997. The Ca concentrations in principle correlate well with the Mg levels. Bowen (1979) gives Mg contents in soil 5000 mg.kg^{-1}. Variations in Mg contents in leaves of oak are controlled by soils. The contents of Ca basically correlate with those of Mg. The median values of Mg contents in Slovakian soils (A horizons) are 6400 mg.kg^{-1} (Čurlík, Šefčík, 1999).

Manganese (Mn) is an essential element that becomes toxic in higher concentrations. Its mobilization indicates the disturbance of a physiological balance leading to a change of the Mn/Fe (normal ratio should be 1:2) (Maňkovská, 1996). According to Markert et al. (1996) Mn concentrations in spruce needles correlate well with needle loss. Therefore, Mn is used as an indicator of tree damage (Maňkovská, 1996). Manganese mobilization indicates an unstable state in the regime of mineral substances of forest stands as well as trees. According to Stefan et al. (1997), regarding needles, the limit of insufficiency of Mn is about 20 mg.kg^{-1} for spruce with an optimal content > 50 mg.kg^{-1}. Stefan et al. (1997) found in healthy 1-year-old spruce needles 320 mg.kg^{-1} and in damaged needles 1300 mg.kg^{-1}, and in healthy beech leaves 940 mg.kg^{-1}. The range of Mn in oak leaves found in this study are as follows: 216–1523 mg.kg^{-1} in 1990; 35–2317 mg.kg^{-1} in 1993; 137–1974 mg.kg^{-1} in 1995, and 67–2757 mg.kg^{-1} in 1997. Bowen (1979) gives Mn contents in soil 1000 mg.kg^{-1}. The median values of Mn contents in Slovakian soils (A horizons) are 640 mg.kg^{-1} (Čurlík, Šefčík, 1999).

N**ickel (Ni)** is considered a risk element. The biological role of Ni is unknown and is presently being debated. 1 mg.kg^{-1} Ni may be regarded as a limit value for vegetation (Maňkovská, 1996). Ni content in oak leaves ranged between 8.8–18.5 mg.kg^{-1} in 1990; and between 0.30–13.31 mg.kg^{-1} in 1997. The background values of Ni contents in Slovakian soils are 25 mg.kg^{-1} (Čurlík, Šefčík, 1999). Usually it is released in surroundings of Ni works and power stations with the increasing combustion of coal and oil.

Sulphur (S) and nitrogen (N) are essential plant nutrients. S and N air pollutants, such as SO_2, H_2S, NO_2, NH_3, or $HNO_{3,}$ can cause increased foliar concentrations of both elements in plants. With regard to damage to forest ecosystems, three main reasons for S toxicity should be considered: damage to roots from elevated concentrations of S in humus complex, damage to foliage by S metabolites resulting from excessive SO_2 and H_2S uptake and redistribution and accumulation of S in older organs (older leaves. wood. etc.). Sulphur is an important nutrient limiting the growth of plants – both excess and deficiency of S may cause growth reduction (Innes, 1995).

Concentrations of S in oak leaves ranged from 2250 to 4450 mg.kg^{-1} (1990); from 1310 –2340 mg.kg^{-1} (1993); from 1090–8440 mg.kg^{-1} (1995), and from 1620–7030 mg.kg^{-1} (1997) (Table 1). The values from 1000 to 2000 mg.kg^{-1} for broadleaved trees are considered to be sufficient (Innes, 1995; Maňkovská, 1988). Higher concentrations should be considered undesirable. These observed high values confirm the marked impact of sulphur oxides in the entire range of the Báb sites.

Concentrations of N in oak leaves ranged from 24 595–33 175 mg.kg^{-1} (1993); from 11 500–38 460 mg.kg^{-1} (1995) and from 15 190–56 690 mg.kg^{-1} (1997) (Table 1). Maňkovská (1996) considers 13 500–17 000 mg.kg^{-1} to be sufficient foliar concentrations for tree species. The S/N ratio in the oak leaves was 0.069 (1993); 0.123 (1995); 0.106 (1997). The S/N ratio is a sensitive indicator of S accumulation in the foliage of forest trees subjected to atmospheric pollution. Molar ratio of protein S and protein N ranges from 0.05 to 0.15 (Stefan et al. 1997), and it is relatively constant for all tree species. The S/N ratio is optimally balanced (Table 2) in all study years when compared with the limit ranges.

Phosphorus (P) is an essential element and its limit values range from 1000 to 2000 mg.kg^{-1} (Stefan et al. 1997; Maňkovská, 1996). P is very important bioelement, often deficient in plants. Plants suffering from P deficiency are retarded in growth fruits and seed formation is depressed. Foliar concentrations of P for oak leaves ranged (mg.kg^{-1}) from 780 to 2050 (1995) and between 640–2830 (1997). The median values of P contents in Slovakian soils are 0.71% (Čurlík, Šefčík, 1999).

Lead (Pb) has no known biological role, is toxic, teratogenic and carcinogenic. The content of lead (Pb) in oak leaves ranged between 2.7–7.1 mg.kg^{-1} in 1990; between 0.01–1.86 mg.kg^{-1} in 1995, and between 1.11–9.64 mg.kg^{-1} in 1997. The median values of Pb contents in Slovakian soils are 20 mg.kg^{-1} (Čurlík, Šefčík, 1999).

Sodium (Na) is an essential element for higher plants and it has an important electrochemical function. But it is well known that Na can substitute isomorphically K in some plants depending on the kind of species. Na concentrations (in $mg.kg^{-1}$) in oak leaves ranged from 15 to 92 in 1993 and from 18 to 112 in 1995. Markert (1993) reported in pine needles 101 $mg.kg^{-1}$ and Maňkovská (1996) found values lower than 100 $mg.kg^{-1}$ in forest trees. The median values of Na contents in Slovakian soils are 8500 $mg.kg^{-1}$ (Čurlík, Šefčík, 1999).

Vanadium (V) is an essential element for alga and higher plants. V can substitute for Mo. Its deficiency leads to stunted growth, changes in lipid metabolism and eventually lower crop. The basic function of V remains is unclear. V concentrations (in $mg.kg^{-1}$) in oak leaves ranged from 0.41 to 1.62 in 1997. The median values of V contents in Slovakian soils are 74 $mg.kg^{-1}$ (Čurlík, Šefčík, 1999).

Zinc (Zn) is an essential element for plants. Zn is a constituent of chlorophyll, activates enzymes, and takes part in dehydrogenase, protein degradation and formation of growth agents (Maňkovská, 1996). In this study, foliar Zn concentrations ranged as follows (in $mg.kg^{-1}$: 57−147 in 1990; 23−50 for 1993; 18−50 for 1995 and 13−116 for 1997). According to Stefan et al. (1997), optimum for Zn concentrations for the foliage of forest tree species are about 50 $mg.kg^{-1}$. The median values of Zn contents in Slovakian soils are 61 $mg.kg^{-1}$ (Čurlík, Šefčík, 1999).

In foliage/leaf diagnoses sometimes comparison of the results with the values of optimal concentrations is made more accurate by giving the ratios of the elements. As, for example, N/P should range from 15 to 20, the ratio N/Mg should be lower than 17.5 (if this is not the case, the concentration of magnesium is low), the ratio K/Ca should be lower than 1.3 and the ratio S/N should be close to 0.069 (higher value means insufficient nitrogen). Thus lack of N in all taken year-classes of needles was confirmed as well as several times increased concentration of Mg (critical level), toxic level of S and critical (subnormal) level of K, increased up to an insufficient level of Fe. Kaupenjohan et al. (1989) notes, that the concentrations of elements in the foliage are not unanimous. The composition of the foliage depends also on site factors (soil, aspect, relief, altitude, climate, etc.). It was proved that high concentrations of sulphur in the soil cause high concentration of sulphur in the foliage, which is in good correspondence with our results as well (Table 3).

Conclusion

The following conclusions were drawn based on evaluation of oak leaves (*Quercus* sp.) and soil samples (A horizons) on Báb sites:

- Báb research sites are subject to air pollution impact. We recorded significant effects of SO_2, which resulted in increased S concentrations in oak leaves in 1990, 1995 and 1997. Sulphur concentration exceeded the European limit values in 3 years. Increased concentration of S in the foliage was also manifested as the disturbed S/N ratio.
- Oak leaves have unbalanced concentrations of nutrition elements and microelements. We found increased concentrations of Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Ni, Pb, S, V and Zn in the leaves of oak. Concentration of B, Mg, Mn and P has not exceeded European limit values. Above-limit and below-limit concentration of nutritionally sig-

nificant elements cause deterioration of the health condition of the studied forest trees and disturb the biogeochemistry of forest stands.

– The coefficient of loading by air pollutants K_z represents 3.07 (1990), 1.21 (1993), 0.99 (1995) and 1.29 (1997).
– We recorded increased concentrations of Al, As, Be, Ca, Co, Cr, Cs, Cu, F, Fe, Hg, Li, Mg, Ni, P, Rb, Sr, V, Zn in the soil samples (A- horizons). The concentration of B, Ba, Bi, Cd, Ce, Ga, K, La, Mn, Mo, Na, Pb, Sb, Se, Sn, W and Y in the soil samples (A- horizons) has not exceeded Slovak limit values.

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