Slovak Geol. Mag., 3 (1997) 53–66

Geochemical mapping of environmental stress by selected elements through foliar analysis

BLANKA MAŇKOVSKÁ

Forest Research Institute, T. G. Masaryka street 2195, 960 92 Zvolen, Slovakia

Abstract. Concentrations of Al, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, N, Na, Ni, Pb, Rb, S, Sr, V and Zn were determined in the foliage of forest tree species of 3063 plots throughout the whole of Slovakia. The median foliage content was ($mg.kg^{-1}$): Al - 106; As - 0.24 ; Ba - 47; Be - 0.01 ; Ca - 9260; Cd - 0.15 ; Co - 0.11; Cr - 0.51; Cu - 5.9; F - 6.1; Fe - 111; Hg - 0.07; K - 6808; Li - 0.13; Mg - 1164; Mn - 864; N - 15900; Na - 34; Ni - 2.4; Pb - 1.4; Rb - 7.2; S - 1750; Se - 0.04; Sr - 18; V - 0.3 and Zn - 36. The maximum values of fluorine and heavy metals were found in industrial areas. The principal component analysis was used for data treatment to establish the general relationships among element amounts accumulated in the 2-year-old needles from three industrial centres, six mountain forests and one military area.

Key words: Geochemical mapping, forest trees, nutritive elements, heavy metals.

Introduction

The possibility to monitor metal contents and essential nutrient elements in the environment through foliar analysis instead of through the direct measurement of emissions in the ecosystem has been intensively studied for more than 25 years. Higher plants are suitable for this purpose because they are bigger and because their foliage is much easier to separate than those of mosses and lichens. Higher plants have well developed vascular systems to transport all mobile elements. The selection of the forest tree species to be investigated was based on the knowledge of biologic variability among individual species, individual plants of the same species and their organs. Higher plants are better accumulation monitors than lower plants, because the physiology, ecology and morphology of the former are known in greater detail. Woody plants suitable for geochemical mapping include *Pinus sylvestris* L., *Picea abiest* Karst., *Fagus sylvatica* L. and *Quercus robur* L. All these species are widely distributed in Europe and therefore it is useful to investigate them in Slovakia, too.

Forest areas in Slovakia exhibit decline symptoms in various degrees. Prolonged effects of high concentrations of various pollutants resulted in large-scale dying, not only of conifers, but also of deciduous trees. These conditions are not limited to the vicinity of the source of industrial pollution, but spread throughout Slovakia long ago. Huge quantities of pollutants from abroad are also deposited in Slovakia, mainly from Poland (Grodzinska et al.,1993) and Czech Republic from where they are carried by prevailing north, north-west and west winds. The forestry lacks details of the concentrations of the main pollutants, SO_2, No_x , in forest stands. Most of the data on pollution are estimates based on fuel balance and mass balance. During 1994 in Slovakia, SHMÚ (1995) calculated that a total of 235.763 t of SO_2, 173.015 t of NO_x, 374.682 t of CO, 87,301 t of solid matter, 55.00 t of arsenic, 6.86 t of cadmium, 12.76 t of chromium, 54.27 t of copper, 2.46 t of mercury, 18.71 t of nickel, 79.03 t of lead and 75.98 t of zinc were emitted. Slovakia, with specific emission of SO_2 over 11 t/km^2, annually ranks sixth in Europe in the amount emitted.

The aim of this paper is to present (1) the actual data on the concentration of Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, F, Fe, Hg, K, Li, Mg, Mn,N, Na, Ni, Pb, S, Se, Sr, Rb, V, Zn in the foliage of forest tree species, based on the results for all Slovakia, and the differences in element concentration

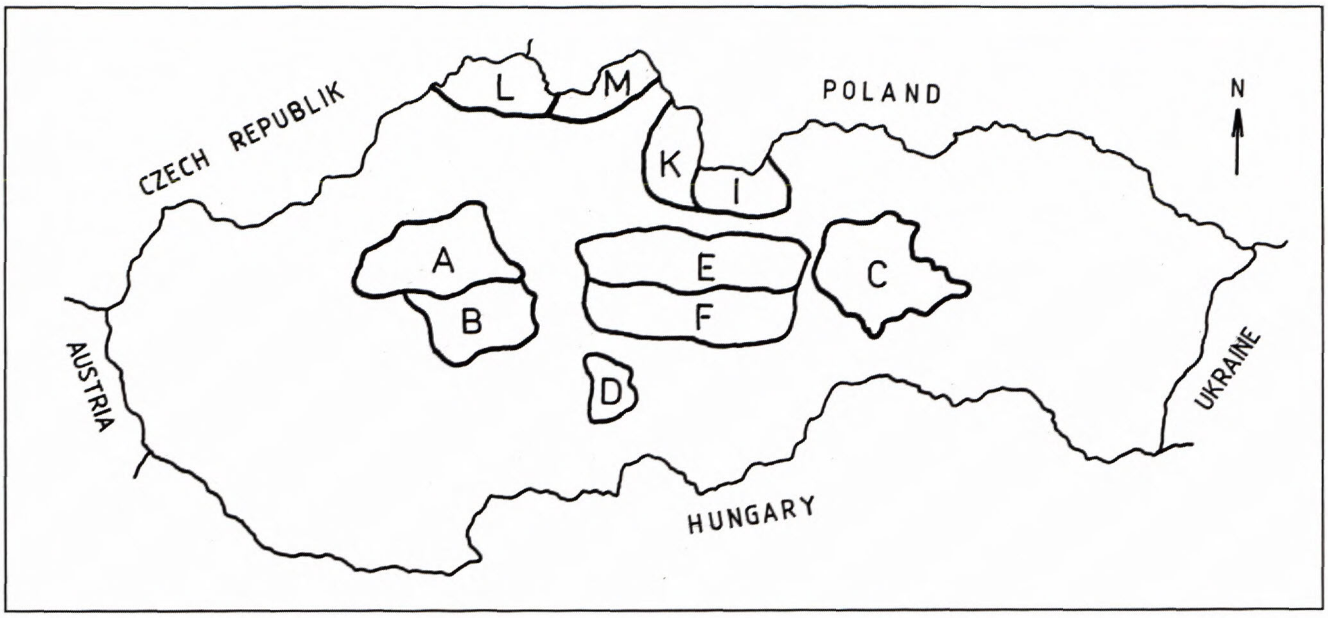

Fig. 1 Sampling locations from three industrial areas, five mountains forests and one military area in Slovakia [A] Horná Nitra area - Thermal power plant; [B] Žiar basin - Aluminium plant; [C] Central Spiš region - Iron mines (production of mercury and barium) and production of non-ferrous metals; [D] Military area; [E] Low Tatras National Park - southern part of mountain forests; [F] Low Tatras National Park - northern part of mountain forests; [I] High Tatras National Park - mountain forests; [K] West Tatras National Park - mountain forests; [L] Beskydy - mountain forests; [M] Horná Orava - mountain forests

in 2-year-old spruce needles among three industrial centres, six mountain forests and one military area.

Material sampled and chemical analyses

The forests of Slovakia cover about 20 000 km^2 representing 40.2 % of the country (49 036 km^2). In Slovakia there are five national parks (4.07 % of Slovakia) and sixteen LPA (13.47 %). About 65 % of Slovakia and a large proportion of its forests are mountainous (Green Report, 1994). The tree assemblage is as follows: deciduous trees 57.7 % (beech 29.8 %, oak 14.3 %, valuable hardwoods 2.7 %, other hardwoods 8.6 %, other deciduous trees 2.2 %), coniferous trees 42.3 % (Norway spruce 27.2 %, silver fir 5 %, pines 7.0 %, larch 2.0 %, mountain dwarf pine 1.1 %) according to the National Forest Inventory (1988).

The samples of foliage of forest tree species were taken in permanent monitoring plots situated on the intersections of a 16 x 16 km Pan-European grid. Additionally, the foliage of forest tree species were taken at a more detailed 4 x 4 km grid, and near the sources of airborne pollution of Central Spiš, on a 1 x 1 km grid plots. These sites were selected for biomonitoring after a detailed review of meteorological data, forest inventory records and documented areas of forest dieback. Three industrial regions were assessed separately (A - Upper Nitra - thermal power plant; B - Žiar basin - aluminium plant; C- Central Spiš - iron ore mines, producing mercury, barium and non-ferrous metals). Also studied was one military area (D) and six mountain forests (E - Nízke Tatry National Park - southern part, F- Nízke Tatry National Park - northern part; I - the Vysoké Tatry National Park; K - Západné Tatry National Park; L - Beskydy and M - Upper Orava). The Table 1 and Figure 1 show the distribution of localities, information on parent rocks, SO_2, NO_x emissions and solid fallouts, main sources of emissions and pollution deposition type.

A total of 3 063 areas were sampled in this manner. Most are covered by trees of the second age category (21–40 year old trees). Trees were distributed all over the entire permanent monitored areas or in their vicinity and represent their state of health. The trees tested belonged to the dominant class of each site. The trees had a representative medium defoliation of +5 % and were not affected by insects or fungi. In each study area, 15 trees were sampled 10–15 m apart (ICP, 1994). The samples were taken by monitoring specialists from the Forestry Research Institute in Zvolen and Lesoprojekt Zvolen during August 1994.

The samples of needles were not washed before the analysis. They were dried for 24 hours at a temperature not exceeding 80 °C. Needles were separated from twigs. Dried foliage was carefully pulverized to a fine powder and its proportional shares were carefully homogenized.

Table 1: Concentration of elements in the foliage of forest tree species (in mg . kg^{-1})

Element	*Picea abies* KARST.		*Pinus sylvestris* L.		*Abies alba* L.		*Fagus sylvatica* L.		*Quercus* sp.	
	mean (SD)	n	mean (SD)	n	mean (SD)	n	mean (SD)	n	mean (SD)	n
Al	116 (89)	1 114	280 (194)	105	366 (181)	178	119 (84)	574	92(53)	126
As	0.41 (1.51)	987	1.21 (3.58)	96	1.15 (2.61)	171	0.68 (1.44)	539	0.44 (1.11)	126
Ba	53.2 (43.8)	1 114	15.8 (25.9)	104	35.6 (23.9)	178	100 (83.8)	574	82.3 (51.9)	125
Be	0.010 (0.035)	976	0.012 (0.013)	96	0.012 (0.013)	171	0.027 (0.034)	538	0.029 (0.064)	126
Ca	8 078 (5 815)	1 114	5 950 (2 498)	105	12 774 (642)	178	13 534 (7 829)	574	12 136 (5 182)	126
Cd	0.19 (0.16)	966	0.22 (0.21)	95	0.26 (0.17)	170	0.19 (0.13)	537	0.12 (0.11)	125
Co	0.16 (0.16)	985	0.22 (37)	96	0.24 (019)	171	0.12 (0.17)	539	0.17 (0.16)	126
Cr	0.68 (0.96)	974	0.59 (37)	96	0.61 (0.76)	170	1.06 (2.89)	536	0.82 (1.11)	126
Cu	5.09 (.81)	1 114	8.67 (12.4)	105	8.15 (7.12)	178	10.0 (6.15)	573	9.30 (13.6)	126
F	6.28 (4.15)	1 113	7.80 (1.9)	104	8.34 (5.07)	178	5.84 (2.56)	572	4.74 (2.10)	126
Fe	123 (370)	1 114	146 (111)	105	246 (105)	178	216 (1 635)	574	131 (79)	126
Hg	0.10 (0.10)	1 118	0.15 (0.40)	105	0.13 (0.15)	178	0.11 (0.11)	577	0.08 (0.09)	126
K	6 178 (3 209)	1 114	5 609 (1 356)	105	5 639 (1 487)	105	9 504 (2 761)	574	9 259 (2 093)	126
Li	0.18 (0.18)	1 113	0.19 (0.25)	105	0.17 (0.25)	105	0.16 (0.14)	575	0.20 (0.18)	126
Mg	966 (479)	1 114	1 161 (422)	105	1 088 (455)	105	1892 (771)	574	2 003 (890)	126
Mn	977 (783)	1 114	635 (865)	105	1 934 (1 636)	105	1 026 (970)	574	1 650 (1 079)	126
N	16 645 (5 221)	1 123	16 631 (5 431)	105	17 921 (5 470)	177	19 754 (6 755)	578	20 923 (6 170)	127
Na	32.2 (38.5)	1 114	42.7 (57.1)	105	43.4 (48.3)	178	58.5 (28.2)	574	39.8 (20.8)	126
Ni	2.60 (2.45)	1 114	3.06 (3.44)	105	3.80 (2.38)	178	3.87 (3.38)	574	4.28 (3.08)	126
Pb	1.73 (2.70)	1 102	3.68 (4.48)	104	2.61 (3.06)	176	3.66 (11.3)	571	1.80 (3.85)	124
Rb	10.2 (10.0)	1 114	6.0 (5.0)	105	6.1 (7.3)	178	14.3 (15.3)	573	10.5 (7.5)	126
S	1 959 (851)	1 122	1 952 (1 010)	105	2 203 (943)	177	2 242 (923)	578	2 236 (1 088)	127
Se	0.048 (0.203)	983	0.069 (0.046)	96	0.074 (0.068)	171	0.058 (0.043)	536	0.053 (0.0447)	126
Sr	22.7 (23.9)	1 114	10.0 (35.4)	105	19.9 (35.4)	178	29.3 (20.3)	573	21.3 (12.7)	126
V	0.94 (3.20)	979	0.98 (4.19)	96	1.03 (2.10)	171	0.72 (2.19)	539	0.44 (1.10)	126
Zn	42.3 (21.3)	1 114	57.7 (43.8)	105	56.9 (37.5)	178	41.0 (46.5)	574	25.6 (21.7)	126

Note: mean - arithmetic mean; SD - standard deviation in parentheses; n - number of samples

Table 2: Internal element concentration in the foliage of forest tree species in 3 063 monitoring plots of Slovakia and literature values

Element	Median (Slovakia)	Internal concentration Mean (SD) mg . kg^{-1}	Range mg . kg^{-1}	Literature values mg.kg^{-1}
Al	106	151 (139)	5 - 1 669	50 - 150
As	0.24	0.57 (1.69)	0.003 - 34.2	< 0.2
Ba	47.0	64.8 (60.9)	0.020 - 603	<100
Be	0.008	0.024 (0.066)	0.0001 - 1.09	< 0.04
Ca	9 260	11 021 (8 086)	931 - 140 012	4 000 - 8 000
Cd	0.153	0.196 (0.199)	0.001 - 3.90	< 0.5
Co	0.114	0.175 (0.239)	0.0005 - 3.91	<1.0
Cr	0.512	0.795 (1.767)	0.002 - 47.12	< 1.0
Cu	5.91	7.27 (7.02)	0.30 - 154	6 - 14
F	6.10	6.24 (4.84)	0.10 - 153	< 2
Fe	111	159 (901)	11.20 - 39 300	200 - 2 000
Hg	0.07	0.10 (0.13)	0.008 - 4.008	< 0.06
K	6 808	7 503 (3 564)	1 752 - 94 782	5 000 - 10 000
Li	0.13	0.18 (0.19)	0.007 - 2.82	< 0.5
Mg	1 164	1 458 (1 013)	255 - 19 132	1 000 - 1 500
Mn	846	1 121 (1 060)	7.20 - 9 773	1 000
N	15 900	18165 (6 432)	5 500 - 57 400	18 000 - 25 000
Na	33.5	42.0 (41.3)	0.40 - 849	< 100
Ni	2.44	3.44 (3.33)	0.02 - 36.6	1 - 2
Pb	1.44	2.42 (6.31)	0.005 - 238	2 - 6
Rb	7.19	10.80 (11.49)	0.32 - 161	<10
S	1 910	2 163 (1 056)	440 - 11 400	1 300 - 2 000
Se	0.04	0.06 (0.15)	0.0003 - 6.34	0.03
Sr	17.99	25.85 (25.61)	0.33 - 360	< 10
V	0.267	0.813 (0.612)	0.001 - 46.95	< 1
Zn	35.8	42.7 (34.9)	4.01 - 691	20 - 80

Note: mean - arithmetic mean; SD - standard deviation in parentheses; range - $x_{minimum}$ - $x_{maximum}$. Internal concentration - arithmetic mean element concentration in all forest tree species (P. abies, P. sylvestris, A. alba, F. sylvatica, Quercus sp.) and literature values (Bowen, 1979; Bublinec, 1992; Innes, 1995; Kaupenjohan, 1991; Maňkovská,1996; Markert, 1992, 1993; Rennenberger, 1984; Stefan, 1989; Wyttenbach & Bajo, et al., 1995).

Atomic absorption spectrometry was applied to determine the contents of (detection limits in ppm are in brackets): Al (4), Ba (2), Ca (0.1), Cu (0.1), Fe (0.3), Mn (0.1), Mg (0.05), Na (0.05), Sr (0.8), Rb (0.8), Zn (0.1, model 3030B Perkin-Elmer); Co (0.03), Cd (0.003), Cr (0.02), Be (0.001), Ni (0.025), Pb (0.07), V (0.07, model 3100, HGA-600); As (0.01), Se (0.01, AAS 3030B, MHS-20 Perkin-Elmer).

The total mercury content (0.01) was determined in all samples directly from a solid sample by a single-purpose atomic absorption spectrometer TMA-254 (trace mercury analyser) manufactured by Tesla Holešovice. Sample weight reached 50–100 mg, with a sensitivity of 0.001 ppm Hg.

Fluorine in all samples was determined spectrophotometrically with lanthanum alizarincomplex following microdiffusive separation from an environment of perchloric acid. Absorption of blue coloration was compared with a calibration curve within a range 0–5 µg F/10 ml by spectrophotometer SPECOL 11 Carl Zeiss Jena in a 1 cm cell.

The total sulphur concentration in spruce needles was determined by elemental analyser LECO SC 132. The samples were weighed, put into a ceramic vessel and burnt in an oxygen atmosphere, in an induction furnace at 1371°C. The sulphur concentration (as SO_2) was measured by an infrared detector and compared with standard samples.

The total nitrogen concentration in spruce needles species was determined by elemental analyser LECO SC 228. The samples were weighed, put into a tin capsule and burnt in an argon atmosphere in an induction furnace at 950 °C. CO_2 and H_2O were removed from a proportional part of the burnt products. Nitrogen oxides were reduced to N_2 and the concentration was determined on a thermally-conductive cell.

The accuracy of the analytical results was checked in two ways. The accuracy and precision of the analytical data was verified during the analysis. Moreover, the accuracy of the results was checked after every ten analyses by the measuring of international reference material (SRM 1575 Pine Needles, USA; KALE SRM (cabbage) USA; GBV 07604 (GSV-3) certified values of reference material for vegetable and human hair MNA). The relative standard deviation of the check analyses was always below 5 %. The accuracy of data published in this paper was verified by 109 separate laboratories and tested by the IUFRO programme (Hunter,1994).

Statistical evaluation

The vegetation samples were evaluated by common statistical methods (calculation of basic statistical characteristics) and Factor analysis. Factor analysis, which included principal component analysis (PCA), consists of

Table 3: List of localities, parent rocks, specific rated emissions, main sources of emision and pollution deposition types (PDT)

No	Locality	Parent rock	Specific rated emissions in t . km^{-2}			Main sources of emissions	Pollution deposition type
			SO_2	NO_x	solid fallouts		
A	Horná Nitra	Miocene - claystones, tuffs Middle-Upper Triasic - mainly dolomites	43.156	16.449	6.331	Thermal power plant	A_1
B	Žiar basin	Tithonian -Neokomian - marly limestones, marlstones, shales	3.992	1.237	1.635	Aluminium plant + Thermal power plant	A_2
C	Central Spiš	Middle - Upper Triassic mainly dolomites, locally limestones and shales	11.317	0.305	2.381	Non-ferrous metallurgy plants + Mercury plant + Barium plant	A_3
D	Military area	Miocene - andesites and their volcanoclastics	1.535	1.118	1.254	Military area	A_1, A_4
E	Low Tatras Nation. Park-northern part	Gneisses, metamorphosed volcanics, schists, granites	3.810	1.561	1.416	Regional pollution Non-point source	A_3
F	Low Tatras Nation. Park-southern part	Amphibolites, granites, variegated limestones	2.038	1.255	1.012	Ferrous metallurgy plants	A_1
I	High Tatras National Park	Eocene - sandstones, calcareous claystones-flysch	0.670	0.466	0.457	Regional pollution Non-point source	A_1
K	High Tatras National Park-western part	Upper Eocene-Oligocene sandstones, claystones, marlstones	0.670	0.466	0.457	Regional pollution Non-point source	A_1
L	Beskydy mountains	Paleocene - Eocene: sandstones, flysch with reef limestone blocks	2.986	0.520	2.103	Heavilly polluted by the industry in the neighbouring Czech Republic (Ostrava	A_3, A_4
M	Horná Orava mountains	Senonian: marls, sandstones, limestones, conglomerates	2.511	0.469	1.864	region) and Polish (Katowice region)	A_3

Note: A_1 = acid Pollution deposition type with fly ash; A_2 = acid Pollution deposition type with fly ash, fluorine and chloride; A_3 = acid Pollution deposition type with smelter dust; A_4 = acid Pollution deposition type with organic matter

Table 4: Concentration of elements in 2 year old needles of P. abies from ten localities - arithmetic mean (standard deviation) [in mg . kg^{-1}]

Element	A	B	C	D	E	F	I	K	L	M
Al	88.5 (25.8)	101 (49.4)	117 (50.6)	125 (53)	105 (108)	121 (62)	151 (78.3)	164 (84)	90 (31.6)	103 (42)
As	0.34 (0.27)	0.31 (0.17)	0.68 (2.14)	0.18 (0.21)	0.19 (0.15)	0.16 (0.17)	0.62 (3.74)	0.12 (0.06)	0.20 (0.11)	0.14 (0.11)
Ba	67.4 (63.9)	109 (80)	39.9 (31.3)	124 (62)	46.8 (32.6)	55 (36)	41.5 (39.2)	35.6 (22.3)	68.7 (38.0)	55.5 (34.1)
Be	0.004 (0.005)	0.009 (0.008)	0.005 (0.009)	0.082 (0.137)	0.009 (0.017)	0.007 (0.007)	0.020 (0.05)	0.014 (0.059)	0.01 (0.02)	0.006 (0.007)
Ca	13 623 (7 339)	11 376 (6 500)	5 711(5 344)	16 262 (3 697)	9 567 (4 427)	8 491 (5 311)	7 316 (5 649)	6 449 (2 715)	9 450 (3 785)	5 287 (2 015)
Cd	0.12 (0.12)	0.19 (0.11)	0.18 (0.14)	0.15 (0.12)	0.12 (0.09)	0.13 (0.12)	0.19 (0.12)	0.17 (0.62)	0.29 (0.26)	0.38 (0.23)
Co	0.078 (0.053)	0.13 (0.21)	0.21 (0.17)	0.24 (0.16)	0.062 (0.088)	0.10 (0.09)	0.13 (0.20)	0.12 (0.14)	0.18 (0.14)	0.14 (0.10)
Cr	0.86 (0.92)	0.71 (0.89)	0.55 (0.65)	0.55 (0.25)	1.02 (2.50)	0.63 (0.61)	0.79 (0.74)	0.83 (0.56)	0.50 (0.28)	1.10 (0.90)
Cu	4.49 (2.28)	4.52 (1.67)	5.85 (5.18)	3.30 (0.79)	3.41 (1.19)	3.63 (1.45)	7.54 (10.9)	10.7 (7.55)	3.56 (2.16)	3.71 (2.03)
F	5.83 (1.65)	7.87 (9.44)	6.90 (2.40)	4.22 (3.24)	5.35 (1.74)	5.78 (2.61)	6.39 (2.04)	5.83 (1.92)	6.95 (2.38)	5.51 (4.06)
Fe	111 (40.3)	103 (51.8)	147 (406)	81 (26.9)	94 (64.8)	94 (53.1)	102 (56.4)	91 (49.8)	102 (24.9)	74 (30.5)
Hg	0.19 (0.40)	0.08 (0.10)	0.13 (0.09)	0.11 (0.10)	0.09 (0.11)	0.10 (0.13)	0.06 (0.06)	0.05 (0.06)	0.07 (0.03)	0.10 (0.10)
K	7 004 (2 220)	7 410 (2 070)	6 396 (1 861)	6 055 (1 170)	5 136 (1 331)	5 753 (1 400)	5 913 (1 909)	5 520 (1320)	5 433 (1 132)	6 652 (1 639)
Li	0.19 (0.11)	0.24 (0.30)	0.17 (0.12)	0.16 (0.11)	0.23 (0.33)	0.28 (0.27)	0.15 (0.10)	0.15 (0.11)	0.19 (0.08)	0.14(0.10)
Mg	1 153 (546)	864 (210)	998 (602)	879 (224)	1 110 (551)	933 (318)	1 009 (777)	867 (292)	730 (283)	728 (170)
Mn	669 (914)	503 (396)	1 166 (742)	1 144 (731)	738 (809)	893 (800)	949 (593)	769 (472)	1 694 (970)	906 (464)
N	15 950 (2 580)	14 660 (3 395)	17 920 (5 610)	15 510 (2 210)	14 930 (2 404)	16 380 (5 384)	15 681 (2 377)	13 818 (1939)	14 632 (2753)	15 517 (2019)
Na	42.4 (36.4)	32.4 (28.3)	34.9 (55.3)	23.9 (12.7)	40.9 (81.5)	28.1 (19.2)	28.3 (11.7)	29.0 (14.4)	30.2 (18.4)	34.6 (17.2)
2i	1.95 (1.86)	2.84 (2.32)	2.64 (1.70)	1.16 (1.40)	1.49 (1.16)	2.12 (1.43)	2.64 (2.78)	2.33 (2.23)	5.84 (3.90)	3.02 (1.86)
Pb	3.0 (3.9)	2.23 (2.41)	1.99 (3.31)	1.42 (0.66)	2.6 (7.1)	1.57 (1.49)	1.26 (1.21)	1.38 (0.86)	2.60 (2.07)	1.33 (0.58)
Rb	4.3 (4.2)	21.4 (25.9)	12.1 (10.0)	7.2 (5.2)	8.3 (5.9)	11.6 (11.2)	12.8 (9.5)	12.4 (9.0)	6.32 (6.11)	13.7 (9.8)
S	1 720 (470)	1654 (449)	2 093 (785)	2 185 (744)	1 846 (837)	2 125 (1 556)	1 606 (520)	1 690 (917)	1 940 (837)	1 855 (877)
Se	0.039 (0.027)	0.027 (0.016)	0.053 (0.038)	0.049 (0.023)	0.038 (0.026)	0.030 (0.022)	0.033 (0.027)	0.032 (0.026)	0.057 (0.040)	0.043 (0.024)
Sr	56.2 (55.3)	55.7 (39.3)	12.1 (9.9)	75.0 (29.2)	21.4 (20.7)	24.2 (15.8)	23.1 (16.4)	23.3 (26.4)	19.9 (17.9)	13.5 (8.6)
V	0.56 (1.31)	0.34 (0.38)	1.12 (3.50)	0.19 (0.07)	0.47 (0.91)	2.09 (6.89)	0.93 (1.90)	0.37 (0.60)	0.18 (0.11)	0.17 (0.08)
Zn	41.7 (12.5)	53 (27.2)	39.1 (23.2)	36.3 (10.9)	43.2 (16.9)	45.7 (23.0)	34.6 (19.0)	38.7 (13.5)	40.8 (15.7)	40.6 (12.3)
Kz	1.57 (0.76)	1.60 (0.67)	1.74 (1.31)	1.70 (1.11)	1.29 (0.59)	1.46 (0.69)	1.71 (2.25)	1.44 (0.65)	1.72 (0.42)	1.41 (0.34)
n	15	16	282	31	70	44	58	69	27	31

Note: n - number of samples; Permanent monitoring plots (4 x 4 km) - localities A, B, D, E, F, I, K, L, M; (1 x 1 km) - locality C, K_z - Pollution impact coefficient the procedures for removing the redundancy from a set of correlated variables and representing the variables with a smaller set of "derived" variables or factors (Kachigan, 1986).

If there are n characteristic variables V_1, V_2....Vn, PCA means the determination of m (<n) synthetic variables Z_1, Z_2......Zm the correlation between two of which is 0. Here, Z_1 is known as the first principal component or first factor, Y_2 as the second principal component or second factor,...... (Suzuki et al., 1994).

$$Z_1 = a_{11}V_1 + a_{12}V_2 + ...+ a_{1n}V_n$$
$$Z_2 = a_{21}V_1 + a_{22}V_2 + ...+ a_{2n}V_n$$
$$Z_m = a_{m1}V_1 + a_{m2}V_2 + ...+ a_{mn}V_n$$

This methodology was selected in order to identify factors underlying our set of variables and in order to screen our variables to obtain relationships among them. Factor rotation was performed by the varimax method (Kachigan, 1986) in order to redefine the factors such that the loading on the various factors tends to be very high (near 1.0 or -1.0), eliminating as many medium-sized loadings as possible. Thus, sharper distinctions in the meanings of the factors will be observed. The number of factors was restricted to eight, and the percentage of explained variance was greater than 90 %.

To calculate the total pollution impact on Slovakia, we applied a pollution-impact coefficient Kz which expresses to what extent the limits of evaluated elements in 2-year-old needles of Picea abies Karst. were exceeded (Maňkovská, 1984). The Kz coefficient is defined as an arithmetic mean of n elements accumulated in foliage of forest tree species. Standard values (Yi of n elements) result from the formula:

$$Yi = \frac{M_i}{m_i} + \frac{M_i}{m_i} + ... + \frac{M_n}{m_n}$$

where

M – is the content of investigated elements (in mg . kg^{-1}) in 2-year-old needles of Picea abies Karst sampled in 1994

m – is the content of investigated elements (in mg . kg^{-1}) in 2-year-old needles of Picea abies Karst collected in checked areas during 1974–1975 (Maňkovská, 1984) As (0.2); Cd (0.5); Cr (1.5); Cu (3); F (2); Hg (0.12); Ni(1); Pb (6); Rb (8); S (1,000); Sr (1); V (0.6); Zn (45), and

n – is the number of investigated elements.

The pollution-impact coefficient Kz is defined as follows:

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

Results

The total (internal) concentrations of Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, F, Fe, Hg, K, Li, Mg, Mn, N, Na, Ni, Pb, Rb, S, Se, Se, V and Zn (arithmetic mean and standard deviations) in the foliage of five forest tree species (*P. abies*, *P. sylvestris*, *A. alba*, *F. sylvatica* and *Quercus* sp.) collected from 3,063 sampling plots are given on Table 2, and illustrated in Fig. 2 (fluorine), Fig. 3 (sulphur) and Fig. 4 (mercury). The total (internal) concentrations of Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, F, Fe, Hg, K, Li, Mg, Mn, N, Na, Ni, Pb, Rb, S, Se, Se, V and Zn (arithmetical mean and standard deviations) from ten localities (three industrial, one military and six mountain forest areas) in 2 year-old needles of *P. abies* are given in Tab. 3. Total (internal) concentrations (arithmetical mean, standard deviation) and literature value of Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, F, Fe, Hg, K, Li, Mg, Mn, N, Na, Ni, Pb, Rb, S, Se, V and Zn in the foliage of forest tree species collected from 3,063 plots are given on Tab. 4.

Discussion

Seven discrete pollutant deposition types (PDT) were identified in Slovakia on the basis of air concentration of SO_2, wet deposition of SO_4^{2-}, NO_3^- and NH^{4+}, meteorological data, soil changes, and observations regarding forest health (Maňkovská,1991). PDT characteristic for 10 localities are given on Table 1. The central part of the Spiš region [C] (Fig. 1) receives a large quantity of emmissions. The highest value of Kz = 1.74 means that critical values (limits) are exceeded about 1.7 fold. At this locality spruce needles contained the highest concentrations of As, Fe, Hg and N. In the region of the aluminium plant [B] spruce needles had the highest concentrations of F, K, Rb and Zn. The highest values of Mg, Na and Pb are near the thermal plant (A). The cleanest mountainous regions include the norther part of the Nízke Tatry National Park [E] with lowest Kz, where like in the Vysoké Tatry National Park [I] no element maxima were found. The southern part of Nízke Tatry National Park [F] is affected by emissions from local sources where the maximum values of S, Li and V in spruce needles were recorded. In the Západné Tatry National Park [K] Al and Cu reach a maximum, at Beskydy [L] Mn, Ni and Se reach a maximum, at Upper Orava [M] a Cd maximum occurs. These areas are under a great impact of emmissions from foreign sources for there are no important industrial sources in this part of Slovakia. It is interesting to note that the highest concentrations of Ba, Be, Ca, Co and Sr in spruce needles were found in military area [D].

The equilibrium of individual elements in plants is a precondition for their normal growth. Similar chemical properties due to roughly equal ion radicals and charges probably cause interactions between individual elements in plant organisms. Synergic and antagonistic relationships between individual elements are disturbed by a polluted atmosphere. Markert (1993) was the first who explained correlations among P, N, K, Ca and Mg in 54 higher and lower plant species. P and N play role in protein biosynthesis, while Ca and Mg are common enzymatic activators in metabolic physiological processes. Markert (1993) identified high correlations between P, N, Ca, Mg and Sr and between Co/Mo and Cr/Co in needles of *P. sylvestris*. He also stated that Al/Ca, Mn/Ca and B/Sb are typical antagonistic pairs of elements. Correlations among individual elemental pairs of elements in spruce needles have been investigated separately in three industrial areas, one military area and six mountain forests.

Surprisingly, in contrast to data put forward by Markert (1993), only highly positive correlatable pairs of locally emitted elements were found around the aluminium plant for Cr/Pb (0.994) and in the military area for Cu/Na (0.912). In the southern part of Nízke Tatry only a positive correlation between Cr and Fe (0.999) and in the Vysoké Tatry National Park between As and Cu (0.970) was found. No negative correlation was found among pairs of elements with r exceeding or equalling -0.9.

Principal component analysis (Kachigan 1986, Suzuki et al.,1994) was used as a method for data processing to establish general relationships among element amounts accumulated in the 2-year-old spruce needles of the three polluted areas, six mountain forests and one military area. We compared the ratios of N/S, Ca/Sr, Fe/Mn, K/Rb, N/Mg, coefficient Kz (As, Be, Cd, Cr, Cu, F, Hg, Ni, Pb, V and Zn) and individual elements (Al, Ba, Co, Na, S, Se, Tab.7).

All weights of the components in PC1 exhibit the highest positive values for the group of elements in the order S and S/N ratio for all investigated localities, with the exception of the industrial localities of the Žiar basin [B] and Central Spiš [C]. In the above two regions, the highest positive values exhibited the elements As, Be,

Table 5: Percentage of explained variance for eight factors obtained in the principal component analysis (Varimax method) for three industrial areas (A, B, C), six mountain areas (E, F, I, K, L, M) and one military area (D)

Localities		Factors								Together
		1	2	3	4	5	6	7	8	
A	EV	2.96	2.44	2.01	1.48	1.22	0.72	0.58	0.26	
	% var.	24.6	20.3	16.7	12.3	10.2	6.0	4.8	2.2	97.1
B	EV	3.21	2.38	1.69	1.43	1.04	0.69	0.63	0.34	
	% var.	26.8	19.8	14.1	11.9	8.7	5.8	5.3	2.8	95.2
C	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
D	EV	2.98	2.50	2.90	1.90	1.16	0.90	0.72	0.57	
	% var.	24.9	20.8	15.9	9.6	7.5	6.0	4.7	3.5	92.9
E	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
F	EV	2.29	1.90	1.61	1.32	1.19	0.93	0.82	0.65	
	% var.	19.1	15.9	13.4	11.0	9.9	7.7	6.9	5.4	89.3
I	EV	2.59	1.82	1.46	1.31	1.12	0.94	0.79	0.59	
	% var.	21.6	15.2	12.2	10.9	9.3	7.9	6.6	4.9	88.6
K	EV	2.67	1.85	1.52	1.47	1.02	0.86	0.79	0.60	
	% var.	24.6	20.3	16.7	12.3	10.2	6.0	4.8	2.2	97.1
L	EV	3.55	2.01	1.42	1.18	1.01	0.82	0.64	0.42	
	% var.	29.6	16.8	11.9	9.9	8.4	6.8	5.3	3.5	92.2
M	EV	3.01	2.36	1.48	1.18	1.11	0.87	0.66	0.51	
	% var.	25.1	19.7	12.4	9.9	9.2	7.3	5.5	4.2	93.3

Note: EV - Eigen values: % of variability

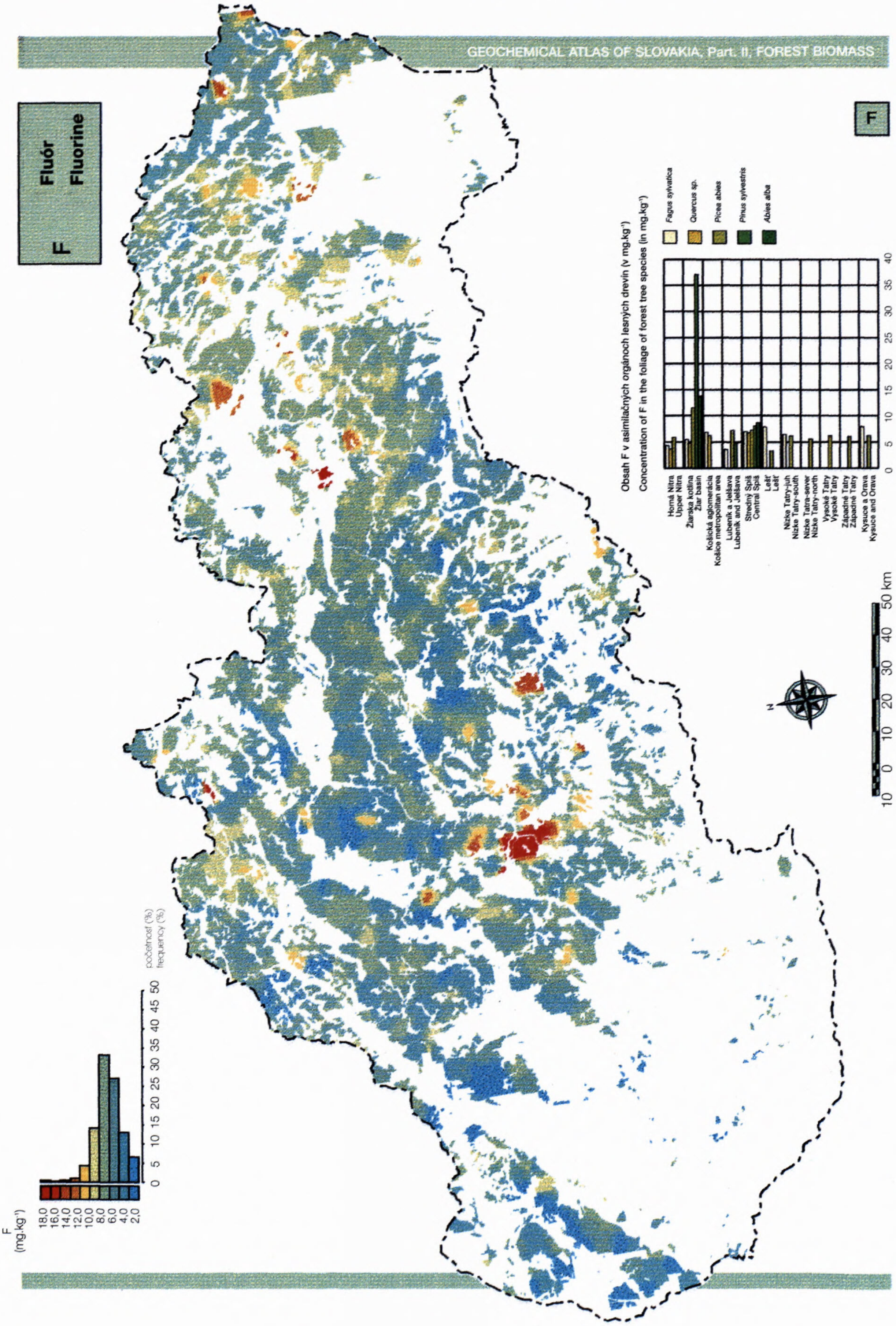

Fig. 2 Concentration on fluorine in the foliage of forest tree species in Slovakia

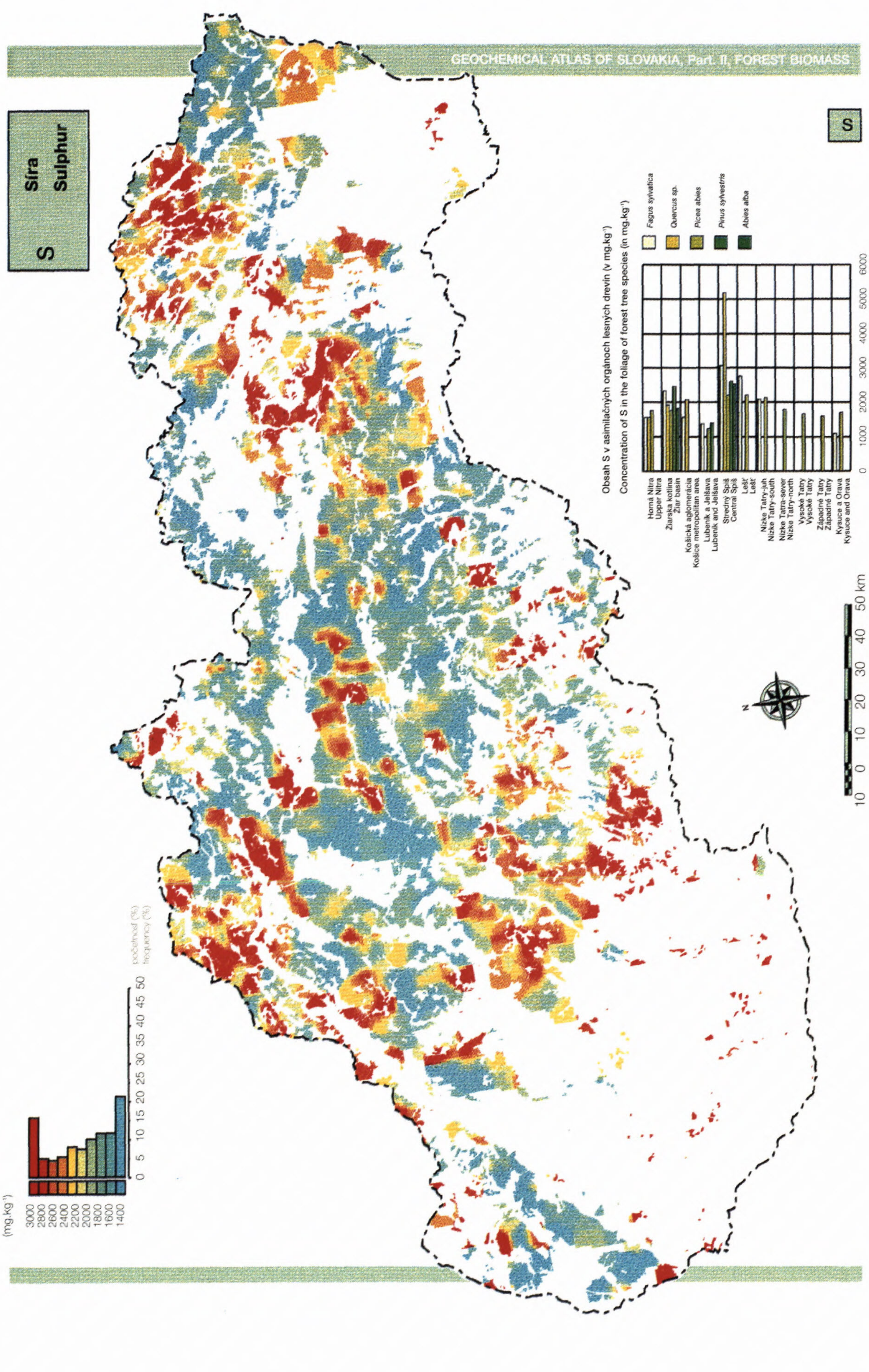

Fig. 3 Concentration on sulphur in the foliage of forest tree species in Slovakia

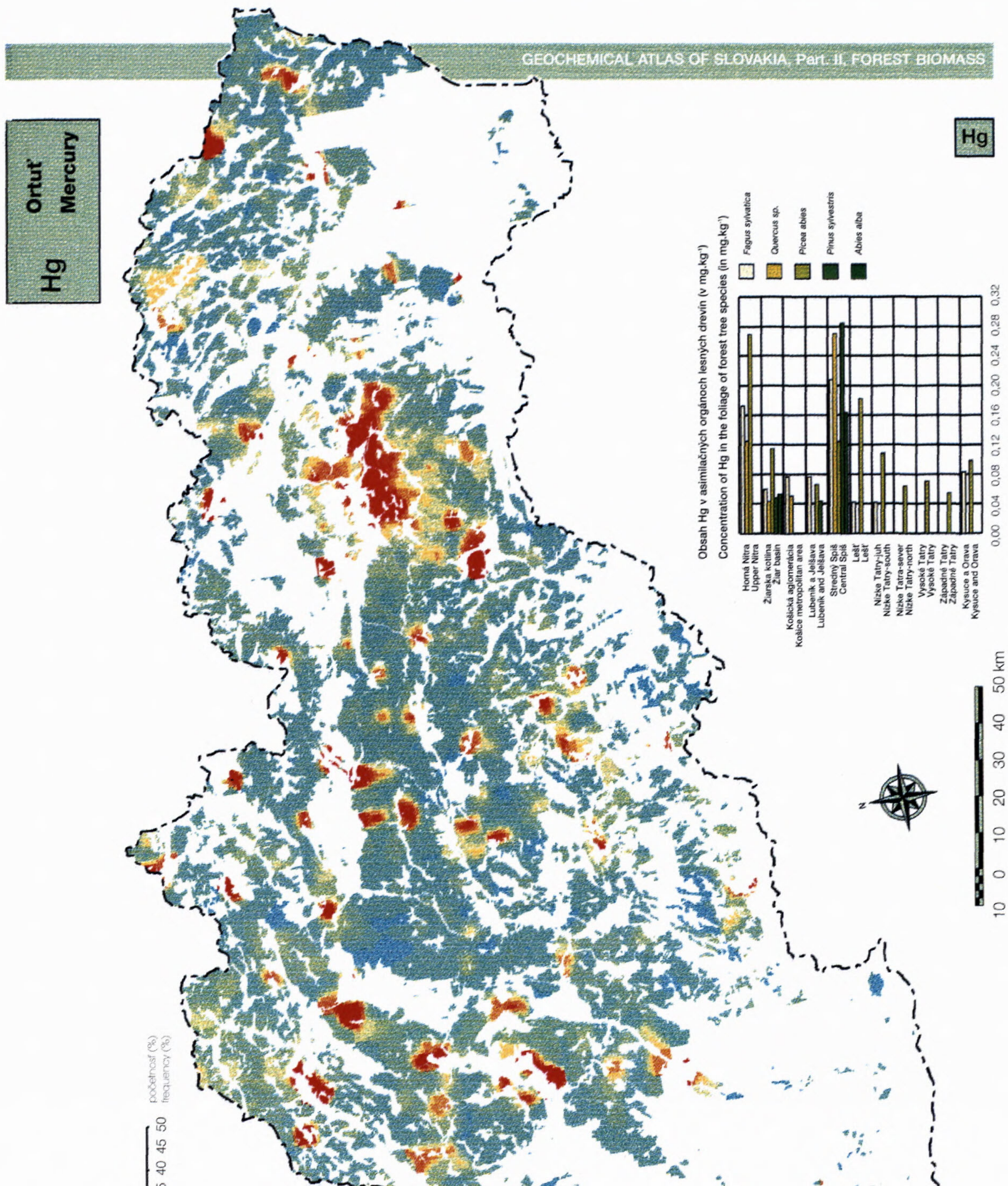

Fig. 4 Concentration on mercury in the foliage of forest tree species in Slovakia

Cd, Cr, Cu, F, Hg, Li, Ni, Pb, V, Zn expressed as Kz and Ba, Se, and they explain 19.1–26.8% of total variability.

The individual PC1 components significance is different. Sulphur is an important element in the biogeochemistry of forest ecosystems, with regard to its role as an essential plant nutrient. S requirements for current growth can be met from three potential sources: uptake by roots from the soil-humus complex, intake by the foliage, and redistribution from older tissues (older leaves, wood etc. Rennenberger, 1994). S is not usually regarded as a nutrient that limits the growth of forests (Innes, 1995). The values of 1100-1800 mg . kg^{-1} are considered as a sufficient content of sulphur for spruce (Bublinec, 1992; Stefan, 1989). In 2 year old needles of *P. abies,* Innes (1995) found the values of 750–1,620 mg . kg^{-1}. Materna a Mejstřík (1987) give the content of sulphur in spruce needles in the range 800–1,000 mg . kg^{-1}, which corresponds well with our data (Maňkovská, 1996). In emmission regions the level of sulphur is markedly increased, up to 5000 mg . kg^{-1}, which represents an unfavourable effect. The arithmetic mean of the total content of sulphur in the samples examined reaches 1,959 ± 851 mg . kg^{-1}. The variation range of sulphur is from 550 to 11,400 mg/kg for 2-year-old spruce needles. Data obtained on the total amount of sulphur in spruce needles are surprisingly high, compared with our data of 1975 (Maňkovská,1996). They confirm the marked effect of sulphur oxides on all of Slovakia. The S/N ratio is a more sensitive indicator of the accumulation of S in conifer foliage exposed to atmospheric pollution than are the analyses of elemental S or for the SO_4 ion alone (Maňkovská, 1996).

As, Ba, Be, Cd, F, Hg, Li, Pb, V are non-essential for higher plants. Arsenic is a typical pollutant being formed in the combustion of Slovak bituminous coal (industrial localities A, B and C). Mercury is emitted in the surroundings of the mercury plant [C] and the military area [D]. Fluorine in plants is of insignificant biological function. Its increase indicates the presence of emission sources, especially in the region of the aluminium plant [locality B]. The higher concentration of lead can be explained through emission from industry and mainly through exhaust gases. The increased amount of lithium in spruce needles is attributed to the emissions from local industrial sources, e. g. glass works and ceramic works. Vanadium and nickel are typical emission components from the combustion of heavy oils. Cadmium is non-essential for higher plants. The increased amount of cadmium in spruce needles is important from an environmental point of view. Cadmium is emitted from the metals-producing plants, cities, combustion of refuse at incinerating plants, cigarette smoke, mineral fertilizers and waste, as well as cars with diesel engines. Cadmium uptake can be passive as well as metabolic. It is very mobile in plants. Zinc, copper and selenium reduce the cadmium uptake and its toxicity. It is easily transportable into different parts of plants, with the highest concentrations found in the roots and parts of leaves. Chromium, copper, nickel and zinc are essential elements, but in higher concentrations they are harmful. Beryllium and aluminium are formed from emission sources and earth dust.

PC2 explains 15.2–20.8 % of total variability and contains the weights of components for elements As, Be, Cd, Cr, Cu, F, Hg, Li, Ni, Pb, V and Zn expressed as Kz for the localities of Horná Nitra [A], and the mountain forests [I, K and M]; cobalt for Žiar basin [B] and mountain forests [E]; Fe/Mn ratio for Žiar basin [B] and mountain forests [K], S/N ratio and sulphur for the thermal power plant [C]; barium for Central Spiš [A] and aluminium for the mountain forests [M]; selenium and sodium for military area [D]. Manganese, cobalt and iron are essential elements but in higher concentrations are harmful. Manganese mobilization indicates the disturbance of equiliubrium in spruce physiology leading to imbalance with iron (the ratio should be 1:2, KAUPENJOHAN et al., 1989). The highest mobilization of manganese appeared at higher altitudes. Barium and selenium are unessential for plants. Selenium is accompanied by sulphur in nature.

The main elements in PC3 are cobalt in the mountain forests [I, K, M]; aluminium at the thermal power plant [A] and mountain forests [K], selenium at the thermal power plant [A] and mountain forests [M]; the ratio Fe/Mn for mountain forests [F, I]; K/Rb ratio for military area [D] and mountain forest [E]; S and S/N ratio for Aluminium plant[B] and they explain the 11.9-16.7% of total variability. Whether cobalt is essential for higher plants or not is unclear yet, in spite of that it is indispensable for N_2 fixation of bacteria *Rhyzobium* living in symbiosis with *Leguminosae.* A small addition of cobalt frequently increases crop yield (Markert, 1992). Increased amounts of aluminium are connected with its industrial manufacture from bauxite, kaolin processing and aluminium processes, and deposited in stomata, as well as on the surface of foliage. Potassium is an essential element. Rubidium has no biological role and is nontoxic. It is similar to potassium. It can substitute for potassium but without having its physiological effect (Wyttenbach et al., 1995).

The forth PC contains the Ca/Sr ratio for mountain forests [E, K, M]; the Fe/Mn ratio for industrial area [A,B]; the K/Rb ratio for the aluminium plant [B] and mountain forests [I]; the Kz for the military area [D] and mountain forests [E]; aluminium for the military area [D] and mountain forests [I], barium for Central Spiš [C] and mountain forests [M] and sodium for the localities of Central Spiš [C] and the mountain forests [F], and it explains the 9.6–12.3% of total variability. Calcium and magnesium are essential for plants but in higher concentrations they are harmful. Strontium is a nontoxic element with exception of its radioactive form ^{90}Sr. As it is chemically related to calcium it frequently can substitute calcium in biological processes. Sodium is essential for higher organisms and is relatively nontoxic, damage to plants can cause the ionization of Na^+. The electrochemical function of sodium causes enzymes to activate, which is significant in plants.

The PC5 explains the 7.5–10.2% of total variability and is formed by cobalt in industrial localities [A, C] and military area [D], and the Ca/Sr for the aluminium plant [B] a mountain forests [F, I].

PC6 contains positive values of the N/Mg ratio for the Žiar basin [B] and the military area [D] and barium for mountain forests [F, K, L] and it explains the 5.8–8.2 % of total variability.

The PC7 has the highest positive value for selenium for the aluminium plant [B] and mountain forests [E] and sodium for mountain forests [I, K] and it explains the 4.8–7.7 % of total variability.

The PC8 has the highest positive values for K_z for the Beskydy mountains [L] and it explains the 3.5 % of total variability.

The 88.6–97.1 % of total variability of the 26 elements in 2 year old spruce needles at the ten localities studied was explained by means of 8 factors.

Conclusion

The main results of the monitoring performed on 3,063 plots in the foliage of forest tree species in Slovakia are as follows:

1. The average element concentrations in the foliage of forest tree species are (in mg . kg^{-1}): Al (151), As (0.57), Ba (65), Be (0.02), Ca (11,021), Cd (0.20), Co (0.18), Cr (0.80), Cu (7.3), F (6.2), Fe (159), Hg (0.10), K (7,503), Li (0.18), Mg (1458), Mn (1,121), N (18,165), Na (42.0), Ni (3.44), Pb (2.42), Rb (10.8), S (2163), Se (0.06), Sr (25.9), V (0.81) and Zn (42.7).

2. Spruce stands in Central Spiš [C] are most heavily loaded by elements introduced by emissions. The highest concentrations of As, Fe, Hg, and N were found in this region to exceed the critical values 1.7 fold. In the region of the aluminium plant [B] occur the highest concentrations of F, K, Rb and Zn in spruce needles, and around the thermal power plant [A] Mg, Na and Pb are at their greatest abundance. The northern part of Nízke Tatry National Park [E] was the cleanest region with the lowest Kz, similarly, the Vysoké Tatry National Park [I] had no element maximum. The southern part of the Nízke Tatry National Park [F] is affected by emissions from local sources and the spruce needles contained maximal values of S, Li and V. The Západné Tatry National Park [K) with Al and Cu maxima. The Beskydy mountains [L] Mn, Ni and Se maxima and Upper Orava [M] Cd maximum are all attributed to emissions. The highest concentrations of Ba, Be, Ca, Co a Sr were found in spruce needles from the military area [D].

Acknowledgements

This work was funded by the Ministry of Environment of Slovak Republic through the Dionýz Štúr Institute of Geology (since January 1, 1996 Geological Survey of Slovak Republic). I would like to thank also Dr. I. Zvara for the elements maps construction and the chief analyst Ing. M. Klinčeková and her staff for making the analytical works.

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