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Monothematic Issue to summarize results of Geochemical Atlas of Slovak Republic

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An Introduction

KAMIL VRANA

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Key words: Geochemical atlas, groundwater, stream sediments, rocks, soils, forest biomass, natural radioactivity.

Introduction

Most geological results are valuable for environmental studies. This is due to the fact that the natural environment is strongly determined by geological conditions. At the present time there is a strong need to carry out comprehensive and complex geological programmes oriented to ecology because, so far, existing geological data are dispersed and often not fully suitable for ecological studies. Moreover, new and more precise data and complex geological information are needed for ecological studies. That is why the Dionýz Štúr Institute of Geology in Bratislava (since January 1, 1996, a part of the new Geological Survey of the Slovak Republic), in collaboration with 10 other institutions, started an extensive project in 1991 entitled "Investigation of the geological factors in the environment".

The project was covered by two partial tasks. The first of these tasks was aimed at the compilation during the 1991-1995 of the Geochemical Atlas of Slovak Republic at a scale of 1:1 000 000. This map was supplemented by maps of associated geochemical and ecological features at a scale of 1:200 000. Investigations were directed to the evaluation of concentrations and distributions of chemical elements, including the toxic ones (single chemical elements and components maps) in groundwater, stream sediments, rocks, soils and forest biomass. The evaluation also covered the total radioactivity of Slovakia and that of individual elements producing that radioactivity. The result of the first task is the subject of this monothematic volume of the Slovak Geological Magazine.

In the frame of the second task, a set of maps representing geological factors of the environment in Slovakia was compiled based on regional geological maps at a scale of 1:50 000. The set includes maps of geology, mineral resources and forecasts; natural radioactivity of rocks (K, U, Th, U_{Tot} , dose rate), radon risk and in water (U_{nat}, ^{226}Ra, ^{222}Rn); pedology, geochemical reactivity of rocks; hydrogeological map; groundwater quality; geochemical map and a multicomponent engineering geology map showing the complex interactions of the technogenetic sphere and that of the geological environment. In the first stage of the completion of the second task (1991–1993) the compilation concentrated on regions: Upper Nitra river area, Low Tatra Mts., Hornád river Basin with the Eastern Slovak Ore Mts., Košice Basin and Slánske Vrchy Mts., Žiar Basin with the Banská Štiavnica area, Malá Fatra Mts. with the surrounding basins. Together, these areas cover about 9 000 km^2 (fig.1).

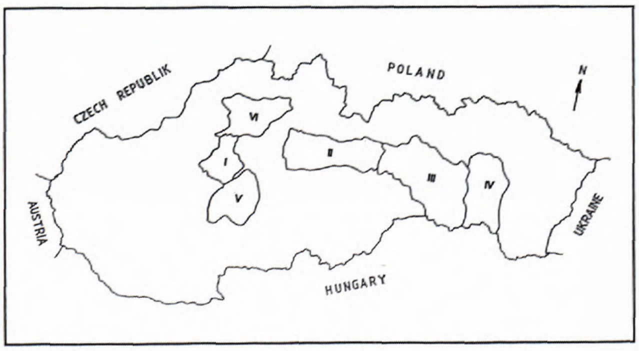

Fig. 1: Regions, studied at scale 1 : 50 000 (I - Upper Nitra river, II - Low Tatra Mts., III - Hornád river Basin with the Eastern Slovak Ore Mts., IV - Košice Basin and Slánske vrchy Mts., V - Žiar Basin with the Banská Štiavnica area, VI - Malá Fatra Mts. with the surrounding basins)

A geochemical atlas of Slovakia is being prepared by the Geological Survey of Slovak Republic mainly in co-operation with the Comenius University, Slovak Academy of Science in Bratislava, INGEO Žilina, the Soil Fertility Research Institute in Bratislava, the Forestry Research Institute in Zvolen and the URANPRES Spišská Nová Ves and with other institutes in lesser ways.

Methodology

a) Sampled media, sampling density

Sampled media	Sampling density	Number of samples	Note
Groundwater	1 sample/3 km^2	16 359	Mostly springs and dug wells; some hydrogeological bore holes
Stream sediments	1 sample/2 km^2	24 422	Active stream sediments <0.125 mm
Rocks	irregular grid	3 839	"main rock types"
Soils	1 profile/10 km^2	9 892	1 profile = 2 samples (A and C horizons)
Forest biomass	1 sample/16 km^2	3 063	Composite sample
Radioactivity	1 point/10 km^2	4 900 (points recorded)	- Total natural radioactivity - individual components of natural radioactivity K, U, Th, Rn

b) Analysed elements, components, measured parameters:

Stream sediments (soils, rocks - modified)

Al, As, Ba, Be, Ca, Ce, Co, Cd, Cs, Cr, Cu, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, Th, U, V, W, Y, Zn, Zr

Groundwater:

Temperature, pH, conductivity, dissolved O_2, acidity, alkalinity (field measurements)

Na, K, Mg, Ca, SiO_2, NH_4, F, Cl, NO_3, SO_4, HCO_3, HPO_4, COD-Mn, Fe, Mn, Li, Sr, Zn, Cu, Cd, Pb, Cr, Hg, As, Se, Tl, Sb, Al, Ba, aggr.CO_2
(metals: filtration – 0.45 μm)

Forest biomass:

Al, As, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, F, Fe, Hg, K, Li, Mg, Mn, N, Na, Ni, Pb, Rb, S, Sb, Sr, V, Zn, (Ba, Ce, Rb - in some samples only)

Radioactivity:

Total natural radioactivity, K, U, Th, Rn

These elements were analysed by following analytical techniques (more in detail see in the following articles).

FAAS:	atomic absorption spectrophotometry, flame atomization
GAAS:	atomic absorption spectrophotometry, electrothermal atomization
CVAAS:	atomic absorption spectrophotometry, atomization by cold vapor generation
HGAAS:	atomic absorption spectrophotometry - hydride-generation method
ICP- OES:	inductively coupled plasma optical emission spectrometry
ICP - AES:	inductively coupled plasma atomic emission spectrometry
XRF:	x-ray fluorescence spectrometry
ISE:	ionselective methods
TMA:	trace mercury analyzer (AAS)
ITPH:	isotachophoresis
T:	acidobasic titrations

Control of analytical processing has been accomplished by an independent group of scientists using internationally acknowledged criteria for the control of analytical results.

The analyses of stream sediment samples collected in the period 1991 – 1994 are incomplete by this time.

The presentation of the more recent data, statistical analysis of all the data, and the interpretation of all these results will be completed by 1998 when this part of the Geochemical Atlas is to be published.

Use of results - environmental aspects

The complex geochemical data obtained on the basic components of the environment are indispensable for the Administration and its Ecology Institutes in their planning for environment protection, urban development, water management, agriculture, food industry, hygiene and other fields. The special goals are:

- Background values and distribution in Slovakia of chemical element concentrations will be established for the main components of the environment.

- Results provide accurate values of contamination of important single-element environmental components.

- Results of geochemical mapping will allow a more effective evaluation of the results in geomedical or geohygienical sciences (regional occurrence of diseases in relation to geochemical provinces or contamination zones), in agriculture and food production (soil fertility and protection, trace elements in the food chain etc.), forestry (establishment of causes of forest and forest soil degradation), as well as in water management (regional distribution of significant features in groundwater for water management).

- Results allow a more efficient establishment of tasks for newly realized research in the indicated scientific areas.

- The results of geochemical mapping of stream sediments and groundwater will be valuable for mineral prospecting that it provides an exact metallogenetic characterization of Slovakia.

The results of geochemical mapping will also be useful in evaluation of Slovak territory in terms of the results of international geochemical mapping project (IGCP No 360, etc.)

Present state of the Geochemical Atlas of Slovak Republic

In 1997 three parts (groundwater, forest biomass, radioactivity) of the Geochemical Atlas of Slovakia will be issued separately. In 1998 other three parts (rocks, soils and stream sediments) will be published, including the compilation of maps focused on anomalous concentrations of the ecologically most important elements at a scale of 1 : 200 000.

Slovak Geol. Mag., 3 (1997) 9–26

Geochemical Atlas of Slovakia
Part Groundwater

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Abstract. In the project Geochemical atlas of Slovakia, Part 1, Groundwater, a total of 16 359 samples were collected and analysed, giving a statistical density of 1 sample per 3 km^2. The data was compiled on maps and interpreted in accordance with procedures accepted in the IGCP Project No. 360 Baseline Geochemical Mapping. The results were published in a bilingual Slovak – English version.

The main part of the Atlas contains maps showing the distribution of chemical elements, components and parameters (T.D.S., pH, conductivity, SiO_2, Na, K, Ca, Mg, Cl, SO_4, NO_3, NO_2, NH_4, PO_4, HCO_3, Sb, As, Ba, Cd, Cu, F, Al, Cr, Li, Mn, Pb, Hg, Se, Sr, Zn, Fe, dissolved O_2, COD_{Mn}, aggr. CO_2) in the groundwaters of the first aquifer in Slovakia's territory at a scale of 1 : 1 000 000.

The Atlas also gives an overall review of regional differences in groundwater chemistry of the first aquifer with detailed data on Slovakia's principal hydrogeological units.

Key words: Hydrogeochemical mapping, Geochemical atlas, Monoelemental maps, Groundwater contamination.

Introduction

Geochemical mapping of Slovakia's groundwaters was one of the tasks incorporated in the project Geochemical atlas of Slovakia which has been accomplished in 1991 –1995. Selecting the part of the hydrosphere to be sampled, so that the representative and interpretable results are obtained is, an essential problem in such type of geochemical mapping. Based on sampling of groundwater of the first aquifer (springs, wells, boreholes), the hydrogeochemical mapping of the Slovak territory was aimed at illustrating the regional distribution of those elements, components and parameters which are most important from environmental and water-management points of view. Sites to be sampled were selected with respect to hydrogeological conditions of the Slovak territory. Moreover, they were consulted with specialists in hydrogeology. The mapping also complied with another essential geochemical requirement – sampling density to ensure acceptable reliability of the resulting maps. The projected and actual sampling density averages 1 sample per 3 km^2 but it varies from one area to another, depending on the significance of its hydrogeologic structures and the complexity of geologic-tectonic and hydrogeologic conditions. Consequently, the results of the groundwater geochemical mapping can be interpreted not only for the whole Slovak territory but also for separate hydrogeologic units whose databases are sufficiently representative as to the quality and quantity of data.

The graphic and interpretative part of the Geochemical Atlas, part Groundwater illustrates the groundwater chemistry of the first aquifer in the Slovak territory at the time of sampling (1991–1994). However, the results of the regional hydrogeochemical mapping are valid more generally as they respect basic hydrogeologic variability of the Slovak territory and assess the role of primary and secondary factors in the formation of groundwater chemistry in a regional scale. Hydrogeochemical data obtained from 16 359 groundwater analyses is used in both national and regional scales to compare changes in groundwater quality in the years ahead. Based on an all-Slovakia project of groundwater quality monitoring carried out by the Slovak Institute of Hydrometeorology /SHMÚ/ in Bratislava since 1982, the results of the regional geochemical mapping will become a complementary part of basic data on Slovakia's groundwater quality.

Research Methods

Sampling

As regards water-sample collection, the Geochemical Atlas of Slovakia's Groundwaters is based on the three following criteria:

1) The first aquifer was sampled,
2) Statistical sampling density was 1 sample per 3 km^2,
3) Samples were collected in summer (broadly speaking), at medium groundwater levels and under stable climatic conditions.

A total of 16 359 groundwater samples were collected in broader summer from May to October in 1991–1994. Given Slovakia's natural conditions, they were collected from springs (8857), drillholes (1537), adits (51), wells (5716) and dewatering systems (198). In mountain areas the samples were taken from abundant springs, whereas in lowlands they were mostly from wells and drillholes. The sampling points were selected on the basis of data from the National register of springs and other groundwater sources (drillholes and wells) of the Slovak Institute of Hydrometeorology and from hydrogeological records of groundwater sources compiled during research and exploration works by Dionýz Štúr Institute of Geology and trhe Slovak water management companies.

Characteristics measured during sample collection comprise: water temperature, pH, content of soluble oxygen, conductivity (adjusted to 25°C) and discharge. Furthermore, acidity 4.5 and alkalinity 8.3 were determined, and membrane filtration to analyse trace elements and chemical stabilization of samples were carried out. The pH, conductivity, soluble oxygen and water temperature were measured with German WTW instruments: LF 92, LF 95, pH 91, pH 192, OXI 96 and OXI 191.

The polysulphone vacuum filtration instrument NALGENE (USA) and nitrocellulose membrane filters SYNPOR (Czech Republic), with 0.45 µm pores were used in membrane filtration. Before the fieldwork started, the whole filtration process was tested in laboratory conditions to reveal possible loss of elements during filtration either by sorption processes on the walls of filtration vessel or by interception on the membrane filter. These experiments proved that no elements were lost due to absorption on the surface of filtration equipment. 5–20 % of the metallic-element contents were lost from true solutions during direct filtration through nitrocellulose filters. But if the filter was flushed by distilled water prior to filtration, the loss of metallic elements always was below 5 %. As a result, the filtering of water samples was always preceded by flushing the membrane filters by 0.5 l of distilled water.

Chemical Analyses

The groundwater samples were analysed for the contents of 32 variables (elements, anions, chemical oxygen demand and aggressive CO$_2$) in a hydrochemical laboratory of INGEO Inc. Žilina. Each variable illustrated on a map of element areal distribution was determined by a single analytical method. A review of analytical techniques applied to individual variables is given in Tab. 1. The table also shows the detection limits of the techniques used, reliability intervals of analytical results at ten times the detection limit and description of analytical instruments used.

The pH and KNK$_{8,3}$ values were repeatedly determined in the laboratory to check the field measurements. As for the analysis accuracy, permissible analytical errors were inferred from cation and anion equivalent balance totals with regard to T.D.S. If the permissible errors were exceeded, the relevant analysis was repeated:

TDS < 50 mg.l^{-1} do 10 %,
TDS $50 - 50$ mg.l^{-1} do 5 %,
TDS >150 mg.l^{-1} do 3 %.

The analytical data accuracy was continuously ensured by the analytical quality assurance (AQA) system corresponding to European standards of the series EN 45 000 and to the principles of good laboratory practice.

The analytical quality assurance system was proposed and organized by an independent group of analysts. Analytical methods and calibration techniques used in the laboratory corresponded to internationally accepted standards. The metrological sequence of calibration procedures was ensured through certified reference materials CDN-SLRS-2, SRM 1643-C and CRM-398.

The regulation diagrams applied as part of the laboratory quality internal checks were themselves regularly scrutinized by an external audit and, throughout the duration of analytical works, the regulatory limit was rarely exceeded. In these rare cases the method used was immediately recalibrated.

The external checks of water sample analysis quality included interlaboratory analyses of water samples, analyses of spiked samples, analyses of certified reference materials and parallel sample analysis. The relabelled check samples were invariably dispersed among common samples to be analysed.

Parallel samples accounted for approximately 6 % of the total number of samples collected throughout the research stage.

The parallel samples were produced by splitting a check sample into 2 - 6 separate samples, which were relabelled and dispersed among common samples. As a comparative criterion for their evaluation we used reliability interval given by the laboratory for individual determinants. Parallel analyses allowed us to divide the determinants into four groups of different measurement reliability:

Group 1 (measurement reliability below 10 %): lithium, calcium, strontium, manganese, ammonium, phosphates, silica, arsenic, cadmium, selenium, lead, mercury, antimony and filtered aluminium.

Group 2 (measurement reliability 10 – 20 %): sodium, potassium, magnesium, chromium, sulphates, bicarbonates, copper, barium, nitrates

Group 3 (measurement reliability 20-50 %): fluorides, chlorides, zinc

Group 4 (measurement reliability above 50 %): iron, chemical oxygen demand, unfiltered aluminium.

Data Presentation and Statistical Data Processing

16 359 water samples were used to compile the Geochemical Atlas of Slovakia's Groundwaters. 35 phy-

Tab. 1 A review of techniques, their detection limits, reliability intervals at concentrations close to ten times their detection limit and analytical instruments used

element compound	*detection limit(DL) (mg.l^{-1})*	*reliability interval (mg.l^{-1})*	*method*	*type of industrument*
Na	0.1	± 0.2	AAS - F	Varian 1 200
K	0.1	± 0.2	AAS - F	Varian 1 200
Mg	1	± 0.5	ICP - OES	Liberty 200,Varian
Ca	1	± 0.75	ICP - OES	Liberty 200,Varian
SiO_2	0.5	± 0.55	SPFM	Spekol 11,Carl Zeiss
NH_4	0.05	± 0.02	SPFM	Spekol 11,Carl Zeiss
F	0.1	± 0.015	ISE	pX, OP 208/1Radelkis
Cl	0.1	± 0.3	T	pX, OP 208/1Radelkis
NO_3	0.5	± 0.4	ITHP	ZKI 02, Labeco
SO_4	0.3	± 0.5	ITHP	ZKI 02, Labeco
HCO_3	0.1	± 2.1	T	-
PO_4	0.05	± 0.01	SPFM	Spekol 11,Carl Zeiss
Fe	0.01	± 0.01	ICP - OES	Liberty 200,Varian
Mn	0.005	± 0.005	ICP - OES	Liberty 200, Varian
Cr	0.0005	± 0.0006	AAS - ETA	4 100 ZL,Perkin Elmer
Mn	0.005	± 0.005	ICP - OES	Liberty 200, Varian
Cr	0.0005	± 0.0006	AAS - ETA	4 100 ZL,Perkin Elmer
Cd	0.0005	± 0.0004	AAS - ETA	Spectr AA 300 s GTA,Perkin Elmer
Pb	0.001	± 0.001	AAS - ETA	4 100 ZL,Perkin Elmer
As	0.001	± 0.0005	AAS - MHS	Spectr AA 300 s GTA,Varian
Se	0.001	± 0.0006	AAS - MHS	Spectr AA 300 s GTA,Varian
Cu	0.0005	± 0.0007	AAS - ETA	Spectr AA 300 s GTA,Varian
Al	0.01	± 0.01	ICP - OES	Liberty 200,Varian
Zn	0.001	± 0.002	AAS - F	Spectr AA 300 s GTA,Varian
Hg	0.0002	± 0.0002	AAS - CV	Varian 1475B s VGA-76
Sb	0.0002	± 0.0003	AAS -MHS	Spectr AA 300 s GTA,Varian
Ba	0.01	± 0.005	ICP - OES	Liberty 200,Varian
Li	0.002	± 0.002	ICP - OES	Liberty 200,Varian
Sr	0.01	± 0.005	ICP - OES	Liberty 200,Varian
COD_{Mn}	0.08	± 0.1	T	-
agr. CO_2	2.2	± 4.62	T	-

AAS - F: flame atomic absorption spectrophotometry; ICP - OES: inductively coupled plasma optical emission spectrometry; SPFM: spectrophotometry; AAS - ETA:atomic absorption spectrophotometry - electrothermic atomization; ISE:ionselective methods; AAS - CV: atomic absorption spectrophotometry - coldvapour; ITPH: isotachophoresis; AAS - MHS: atomic absorption spectrophotometry - hydride-generation method; T: acidobasic titrations sical and chemical parameters were determined in each sample which gives a total of 0,57 million individual data. The data were processed and one-element maps were generated on personal computers PC – Pentium using software MADAM-G for mono-element maps, Excel 5.0 for basic statistics and correlations, and Quatro Pro 5.0 for systemization diagrams. The data obtained during geochemical rersearch of Slovakia's groundwaters are illustrated on one–element maps at a scale of 1 : 1 000 000. With regard to the obtained analytical results, two basic ways of graphic illustrations were used – colour areal maps (more than 50 % of analyses exceeded detection limit) and point maps (more than 50 % of analyses were below detection limit). On the areal maps where more than 5 % of analyses were below detection limit, sample sites where the content of the relevant element was below detection limit were marked by a point. By the compilation of maps and all other mathematic–statistical calculations, all element contents below the detection limit were replaced by half of the detection limit.

Areal Maps

Basic element of the areal one-element map is a 1 x 1 mm cell representing the area of 1 km^2. The content of relevant element in each cell was calculated from primary, irregularly distributed analytical data (1 sample per 3 km^2). The calculation consisted of two steps. In the first one, weighted averages for each cell are calculated from inverse distances (1/D2) from the centre of the cell to the nearest 20 samples. In the second step, the contents in individual cells are locally smoothed by moving–average method from the nine adjacent samples.

The concentrations were marked by 15 different colours ranging from red to blue. The first and last interval are open.

The intervals of individual colour classes are irregular and were determined empirically. They express geochemical characteristics of a given element in Slovakia's natural conditions with respect to the overall distribution of the element. The limits of some intervals correspond to the most important standard values of the investigated element in water management and ecology. The areal maps are accompanied by frequency-distribution histograms showing the distribution of weighted and smoothed geochemical data in individual cells in the same colour spectrum.

Point Maps

These maps express elemental concentrations by circles of different size. Only contents above detection limit are illustrated. 5 or 6 classes of elemental contents are distinguished. The lower limit equals detection limit and the upper one is open. The limits of individual classes were determined empirically with respect to the element's geochemical characteristics, overall distribution and contents in water-management standards.

Basic Statistical Processing

Basic statistical parameters for each element were calcultaed from primary analytical data on 16 359 samples. The parameters include the arithmetic mean with standard deviation and probability at importance level 95%, the median, geometric mean, minimum and maximum values, as well as 25, 75 and 95% importance levels. The detection limit of each element and the number of analyses below the detection limit are given, as well. The distributions of elemental contents are illustrated in two ways. The upper histogram gives the contents in $\sqrt{2}$ logarithmic scale (except for pH), with an open last interval while the lower histogram uses the arithmetic scale with computer-generated intervals up to the 99.8% importance level. Both histograms show cumulative frequency curves.

Composition of the Atlas

The Geochemical Atlas of Slovakia – Part 1, Groundwater includes the comprehensive information on groundwater quality in Slovakia. The composition is based on historical overview of hydrogeochemical research and mapping of the country, which results in goals definition of the new geochemical mapping. The methods used for mapping met all the requirements needed for this specific type of mapping. The atlas includes relevant analysis of natural conditions of Slovakia stressing hydrogeological and hydrological factors important for groundwater quality evaluation.

The edition of the Atlas includes two main kinds of information: the distribution of element content (single element coloured surfaces maps) in groundwater and regional hydrogeochemical evaluation related to main hydrogeological features of the Slovak territory. The interpretation of the hydrogeochemical results took into account natural and man–made factors influencing groundwater quality formation.

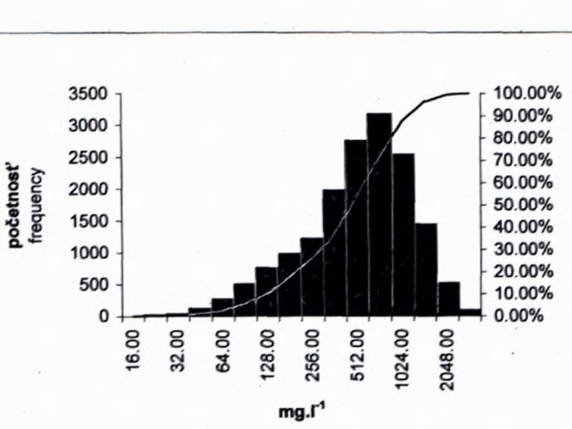
Element and Component Distribution

The following elements, components and parameters were evaluated individually in the Geochemical Atlas of Slovakia – Part 1, Groundwater: T.D.S., pH, conductivity, SiO_2, Na, K, Ca, Mg, Cl, SO_4, NO_3, PO_4, HCO_3, As, Ba, Cd, Cu, F, Al, Cr, Li, Mn, Pb, Hg, Se, Sr, Zn, Fe, dissolved O_2, COD_{Mn}, aggr. CO_2. In this contribution T.D.S., As, and F are presented as an example of geochemical results from regional mapping.

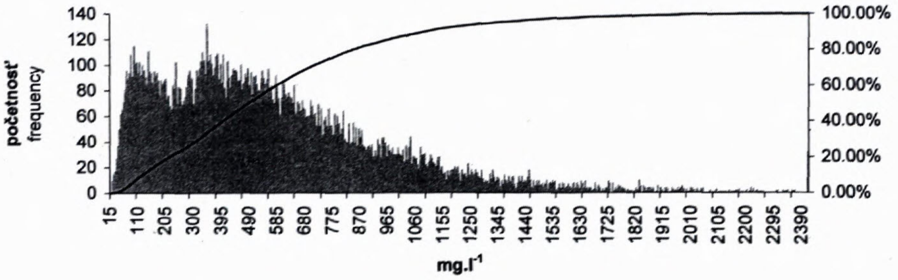
MINERALIZÁCIA
TOTAL DISSOLVED
SOLIDS

mg.l^{-1}

Zákl. štatistické parametre Statistics Parametres	
Aritmet. priemer Arithmetic mean	567.03
Štandardná odchýlka Standard Deviation	403.869
Geometr. priemer Geometr. mean	425.75
Median Median	488.282
Minimum Minimum	14.95
Maximum Maximum	3267.92
25%-il	270.836
75%-il	767.492
95%-il	1342.46
Hladina významnosti (95%) Confidence Level (95%)	6.18



Triedy Classes	**Početnosť** Frequency	**Kumulatívne %** Cumulative %
16.00	1	.01%
22.63	17	.11%
32.00	29	.29%
45.26	115	.99%
64.00	263	2.60%
90.51	497	5.64%
128.00	755	10.25%
181.02	982	16.25%
256.00	1214	23.68%
362.04	1979	35.77%
512.00	2751	52.59%
724.08	3178	72.02%
1024.00	2537	87.52%
1448.16	1439	96.32%
2048.00	514	99.46%
>2048.00	88	100.00%



Tab. 2 Statistical parameters ... T.D.S.

Total dissolved solids (T.D.S.)

The primary source of total dissolved solids in groundwaters is the interaction water – gas – rock environment during water circulation and the secondary one is a wide scale of human activities and waste production (Fig. 1). The value of total dissolved solids has no direct effect on human health. Extremely low–mineralized waters are not suitable for drinking because of bad taste. The Slovak standard 75 7111 Drinking water specifies a limit of total dissolved solids of 1 000 mg.l^{-1}.

The average content of total dissolved solids in the Atlas's samples is 567,03 mg.l^{-1} and the median amounts to 488,28 mg.l^{-1} (tab. 2). The lowest T.D.S. values (below 100 mg.l^{-1}) were noted in the West Carpathian crystalline mountains, largely in their summit sectors. Some differences do also occur in these areas. They result from the character of weathering, morphology and the hydrodynamic conditions of groundwater circulation. For instance, the difference between the values of total dissolved solids in the Malé Karpaty Mts. and Vysoké Tatry Mts. is as much as 200 mg.l^{-1}. The high values reflect human activities largely in fairly densely populated lowland and intermontane depressions.

Arsenic (As) (atomic weight 74,921)

Arsenic occurs in nature in valences +5, +3, +1,0 and -3. Soluble arsenates $H_nAsO_4^{3-n}$ (valence +5) are important for aqueous environments.

The soluble forms of arsenic may be appreciably sorbed by iron oxides. These oxides are very stable and widely distributed in the hypergene zone and, therefore, thanks to their sorbtion properties, they reduce arsenic mobility. However, the element becomes more mobile under reducing conditions in which Fe^{3+} is reduced to Fe^{2+} and As^{5+} to As^{3+}.

Present in oxidizing environments with pH over 4,09, colloidal ferric (Fe^{3+}) oxides sorb arsenic thus reducing its concentrations in solutions. Under strongly reducing conditions in the presence of hydrogen sulphide, arsenic sulphides precipitate along with iron ones. Under medium reducing conditions without hydrogen sulphide, arsenic mobility is the highest as iron is in the soluble form of Fe^{2+} and arsenic migrates in the form of arsenites.

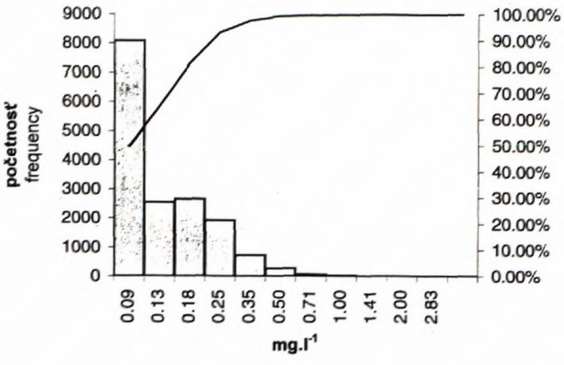
Arsenic is released into the environment predominantly through coal burning and ore processing. In the past it was contained in insecticides and embalmment agents used mainly in war to dispose of corpses. The latter case led to serious groundwater pollution. Despite its strong toxicity, arsenic is also used in modern industries.

F

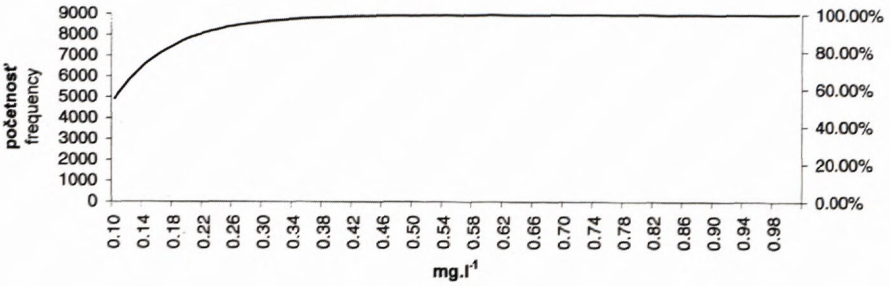
FLUORIDY
FLUORIDE
mg.l^{-1}

Zákl. štatistické parametre Statistics Parametres	
Aritmet. priemer Arithmetic mean	0.12
Štandardná odchýlka Standard Deviation	0.12
Geometr. priemer Geometr. mean	0.09
Median Median	0.1
Minimum Minimum	0.05
Maximum Maximum	4
25%-il	0.05
75%-il	0.15
95%-il	0.29
Hladina významnosti (95%) Confidence Level (95%)	0.002

Detekčný limit Detection limit	0.1
Počet vzoriek pod detekčný limit Number of samples below detection limit	8090



Triedy Classes	**Početnosť** Frequency	**Kumulatívne %** Cumulative %
0.09	8090	49.45%
0.13	2552	65.05%
0.18	2661	81.32%
0.25	1930	93.12%
0.35	728	97.57%
0.50	278	99.27%
0.71	62	99.65%
1.00	31	99.83%
1.41	10	99.90%
2.00	5	99.93%
2.83	5	99.96%
>2.83	7	100.00%



Tab. 3 Statistical parameters ... F

Numerous authors have noted high natural (geogenic) concentrations of arsenic in groundwaters (up to 100 ug.l^{-1}). Weathering of arsenopyrite-bearing mine dumps may increase arsenic concentrations in groundwaters to as much as 5 mg.l^{-1}. Increased As contents in groundwaters commonly occur in some sedimentary rocks of volcanic areas, around geothermal systems and close to gold and uranium mines (above 50 ug.l^{-1}). In some cases, arsenic was released into groundwater as a result of intensive irrigation of farmland, its concentrations attaining as much as 1 mg.l^{-1}.

The Slovak standard No. 75 7111, as well as a WHO standard, limit the maximum As concentrations in potable water to 0,05 mg.l^{-1}. The highest permissible content was derived from the element's direct toxicity. Arsenic is a toxic element of cummulative character, probably carcinogen. It enters the human body mainly in water, and therefore its presence in drinking water is undesirable.

The map of As distribution in Slovakia's groundwater (Fig. 2) shows that high concentrations of this element occur only exceptionally, most analyses being below the detection limit of the analytical method used (1 ug.l^{-1}). The average As concentration was 1.9 ± 40,39 ug.l^{-1} and the median 0,5 ug.l^{-1} (tab. 3). High As contents have two sources: 1. sulphide deposits (Malé Karpaty Mts., Nízke Tatry and Slovenské rudohorie Mts.), i.e. essentially geogenic but As mobilization was accelerated by human activity; and 2. man-made contamination sporadically distributed all over Slovakia's territory sometimes attaining 50–250 ug.l^{-1}.

Fluorides (F) (atomic weight 18,998)

Fluoride concentrations in natural waters are usually below 1,0 mg.l^{-1}, but sometimes they attain several tens of mg.l^{-1}. In rocks, fluorine is bound to minerals, such as fluorspar (CaF_2) and apatite (Ca_5 (Cl, F, OH) $(PO_4)^3$. In the course of weathering, these minerals release fluorides but only in negligible amounts. Waters are also contaminated by industrial waste containing hydrofluoric acid. For example, cryolite (Na_3AlF_6) is used as an agent facilitating aluminium electrolysis. Production of phosphate fertilizers from phosphate-rich rocks are another source of fluorides in groundwater. Fluorides occur in groundwater in the form of the F^- anion. In water they create complexes with a number of cations, including iron ions, aluminium and berylium. Dissolved fluorides can react with calcium to form fluorspar, whose dissolution product is 10–10,4. Fluorspar precipitation may reduce the amount of fluoride in groundwater provided that calcium is available, because fluorides are known to enter into an ion–exchange processes. Gibbsite, kaolinite and halloysite are good sorbents, as well. Fluorides adsorbtion is more intensive at lower pH values.

Children need fluorides for proper tooth growth, but on the other hand fluoride surplus causes tooth defects. The Slovak standard No. 75 7111 recommends that drinking water should contain 0,8–1,0 mg.l^{-1} fluorides, unless fluoride intake from a different source is ensured. The highest limit value was derived for direct toxicity and ignores other fluoride sources.

Flouride concentrations are also important from a hygienic point of view. The Slovak standard No. 75 7111 and the WHO standard specify, that the highest permissible fluoride content in potable water is 1,5 mg.l^{-1}. Owing to the mineralogic-petrographic character of rocks in Slovakia, fluorides are not released to the groundwater from primary sources. The map of fluoride distribution (Fig. 3) indicates that its content in roughly one half of the samples was below the detection limit of the analytical method used (0,1 mg.l^{-1}). Concentrations below the detection limit occur in groundwaters whose T.D.S. attains 250–300 mg.l^{-1}. The average fluoride content in the Atlas's samples was 0.12 ± 0.12 mg.l^{-1} and the median 0,1 mg.l^{-1} (tab. 4). Only about 21 % of samples contained at least 0,18 mg.l^{-1}. The maximum concentration was 4,0 mg.l^{-1}, but it is an exceptional value. The highest values commonly attained only approximately 0,50–0,60 mg.l^{-1}. The increased and maximum concentrations occur in basins in southern Slovakia, the southeastern Danube Basin and East Slovakian Basin. High fluoride concentrations were noted in the Upper Nitra Basin and Žiar Basin. The present information suggests that higher concentrations are caused by secondary sources.

Geochemical characteristics of groundwaters of major hydrogeologic units

The complicated geologic structure of the West Carpathians directly influences the formation of groundwater chemistry and therefore, along with other primary and secondary factors, is responsible for the great variability of Slovakia's groundwater chemical composition. This variability is described in relation to the following major hydrogeologic units:

- crystalline massifs
- Paleozoic
- Klippen Belt
- Inner Carpathian Paleogene
- Neogene sediments
- Neogene volcanic formations
- Mesozoic
- Flysch Belt
- Quaternary sediments

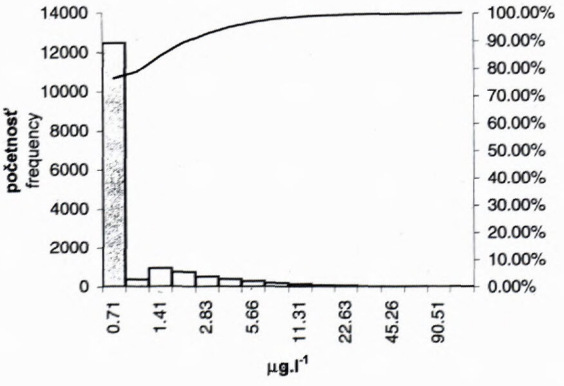
As

ARZÉN
ARSENIC

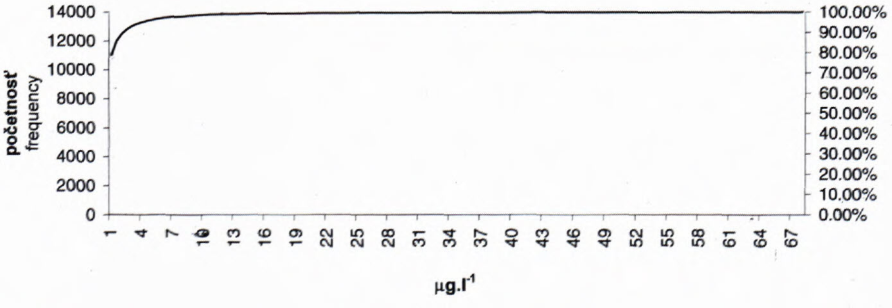
µg.l^{-1}

Zákl. štatistické parametre Statistics Parametres	
Aritmet. priemer Arithmetic mean	1.9
Štandardná odchýlka Standard Deviation	40.39
Geometr. priemer Geometr. mean	0.73
Median Median	0.5
Minimum Minimum	0.5
Maximum Maximum	4900
25%-il	0.5
75%-il	0.5
95%-il	4.1
Hladina významnosti (95%) Confidence Level (95%)	0.62

Detekčný limit Detection limit	1
Počet vzoriek pod detekčný limit Number of samples below detection limit	12485



Triedy Classes	**Početnosť** Frequency	**Kumulatívne %** Cumulative %
0.71	12485	76.32%
1.00	390	78.70%
1.41	959	84.57%
2.00	773	89.29%
2.83	527	92.51%
4.00	397	94.94%
5.66	285	96.68%
8.00	195	97.87%
11.31	137	98.71%
16.00	62	99.09%
22.63	50	99.39%
32.00	25	99.55%
45.26	18	99.66%
64.00	21	99.79%
90.51	12	99.86%
>90.51	23	100.00%



Tab. 4 Statistical parameters ... As

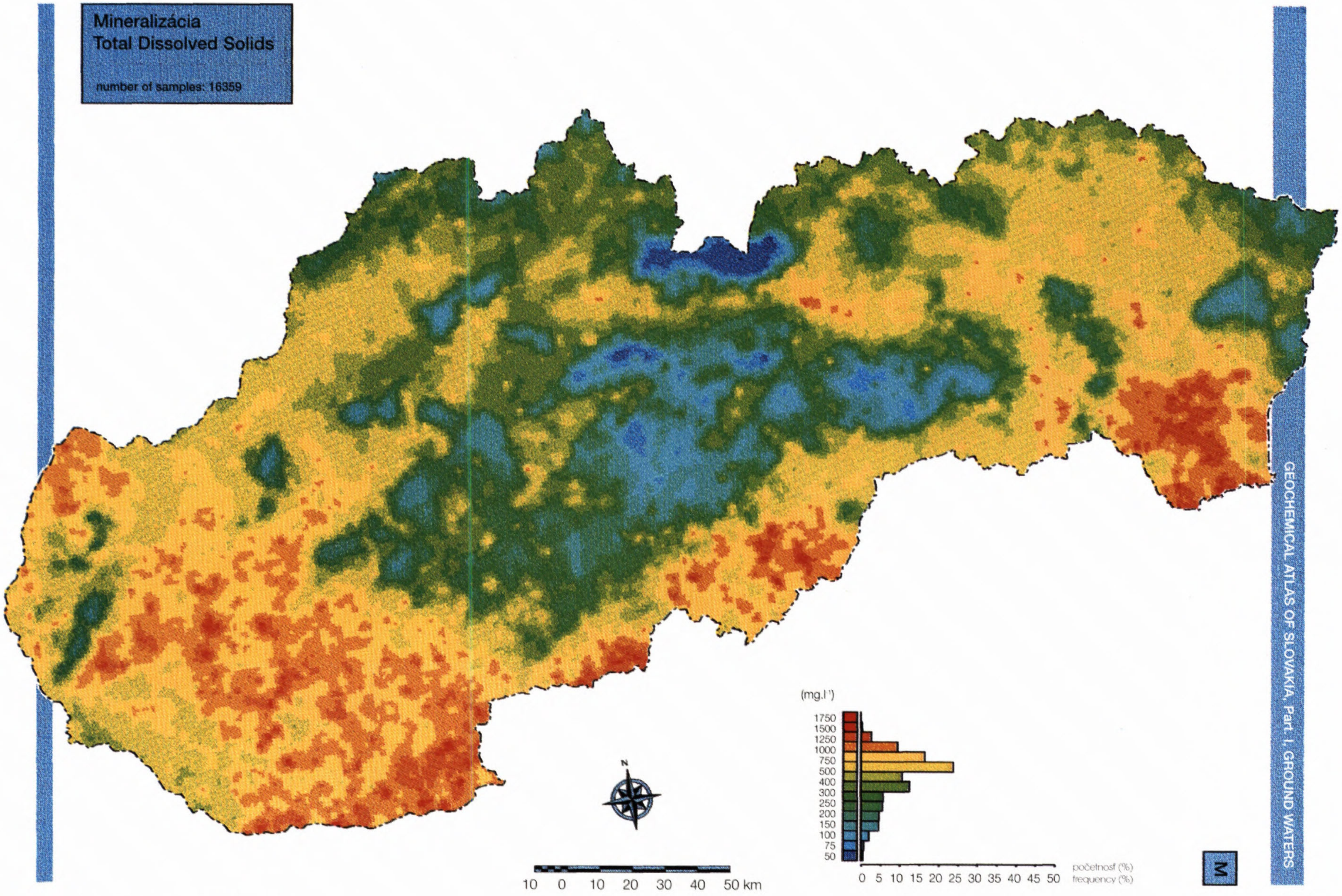


Fig. 1 Map of T. D. S.

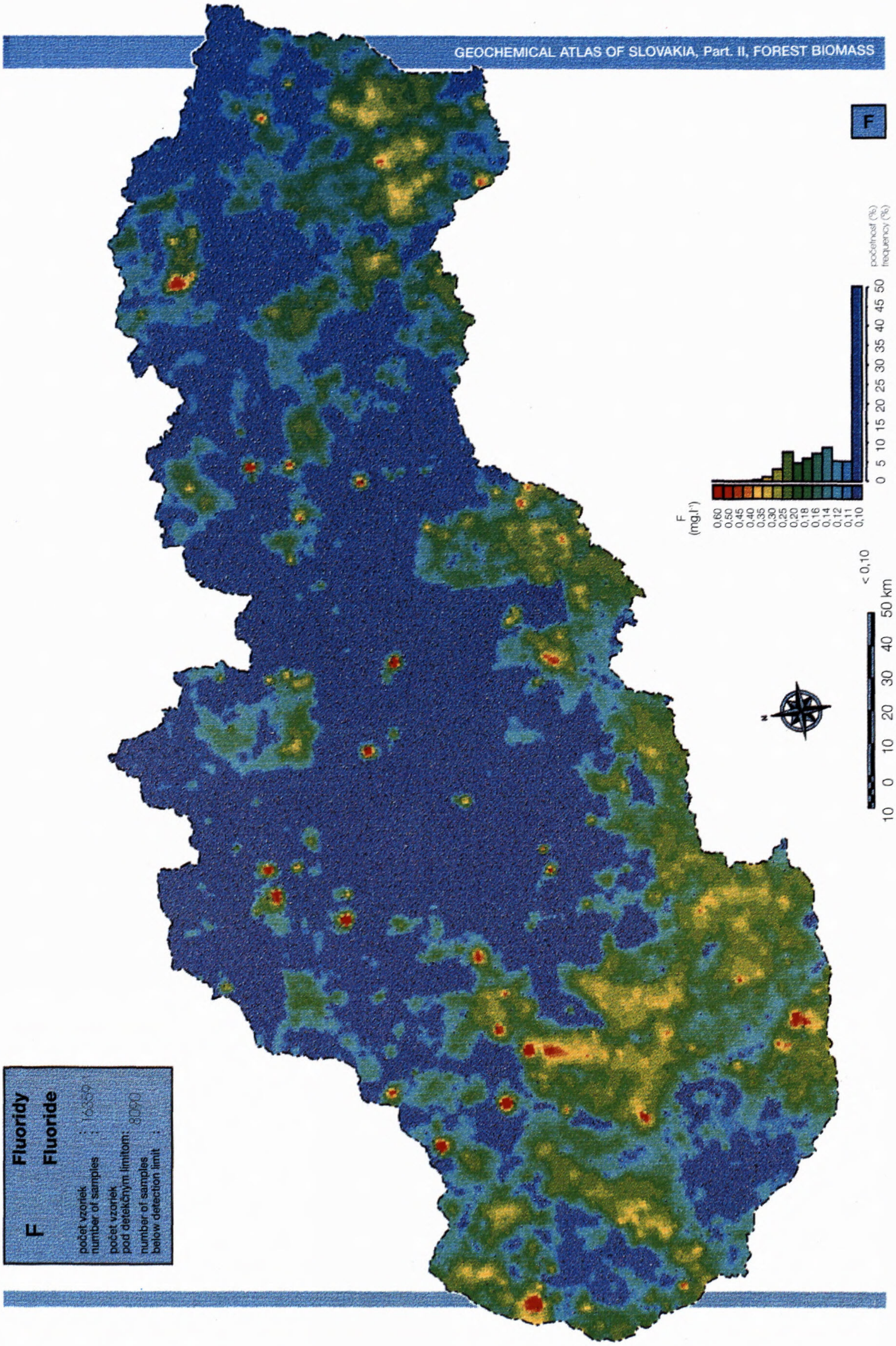

GEOCHEMICAL ATLAS OF SLOVAKIA, Part. II, FOREST BIOMASS
F
Fluoridy
Fluoride
počet vzoriek
number of samples : 16359
počet vzoriek
pod detekčným limitom: 8090
number of samples
below detection limit :
F
(mg.l⁻¹)
0,60
0,50
0,45
0,40
0,35
0,30
0,25
0,20
0,18
0,16
0,14
0,12
0,11
0,10
< 0,10
0 5 10 15 20 25 30 35 40 45 50
početnosť (%)
frequency (%)
10 0 10 20 30 40 50 km
N

Fig. 2 Map of F

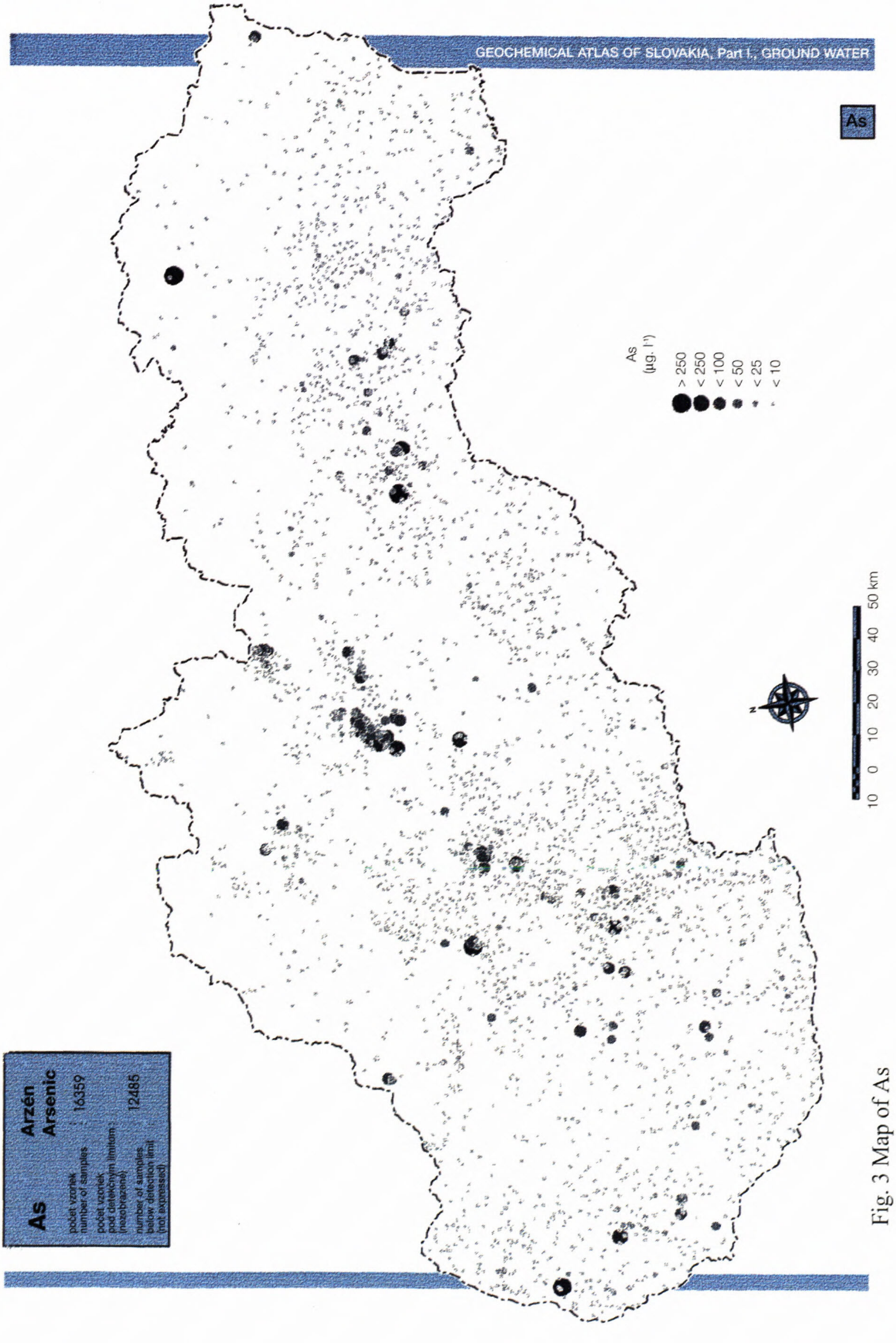


Fig. 3 Map of As

As regards this regional division, it is worth mentioning that major horizontal and vertical inhomogeneities also occur within the above hydrogeologic units. They influence mineralization and metamorphic processes, which in turn have an effect on the formation of groundwater chemistry. That is why anomalies arose, especially local ones, which are virtually unidentifiable at a regional scale. The systemization of groundwater chemistry in selected hydrogeologic units is illustrated through Piper's diagrams in which T.D.S. was added (Fig. 4a-h).

T.D.S. values in groundwaters of some **crystalline massifs** are as low as about 100 mg.l^{-1}. They are clearly controlled by altitude and consequently by the speed and length of groundwater circulation. In the summit sectors of the highest mountain ranges such as Tatry and Nízke Tatry, T.D.S. is commonly about 30 mg.l^{-1}, and locally even less, but in lower mountains whose altitudes do not exceed 1000 m (Malé Karpaty) it attains as much as 200 mg.l^{-1}. In general, T.D.S. values in groundwaters in crystalline schists are by 10 % higher than those in granitoids. This can be explained by the morphological position of both rock types, inasmuch as granitoids largely underlie the summit parts of mountain ranges.

As far as general characteristics are concerned, COD$_{Mn}$ mean values range from 1,0 to 1,5 mg.l^{-1} suggesting a fairly low contamination degree of groundwaters. The aggressive CO_2 content varies between 13 and 23 mg.l^{-1}. Because of their low T.D.S., groundwaters in the crystalline massifs are referred to as so-called "hungry or aggressive waters". Contentrations of major elements are extremely low. Cations are dominated by Ca and Mg, whereas the main anions include HCO_3, SO_4, Cl and NO_3 (Fig. 4a). The main sources of macropollutants (N forms, Cl and SO_4) comprise atmospheric deposition and local tourist and agricultural activities. Trace-element concentrations in groundwaters are characterized by the following regularities:

a) Zn, Cr and Al concentrations are higher in crystalline schists,

b) concentrations of the other trace elements in granitoid rocks roughly equal those in crystalline schists.

The highest concentrations of virtually all trace ele-

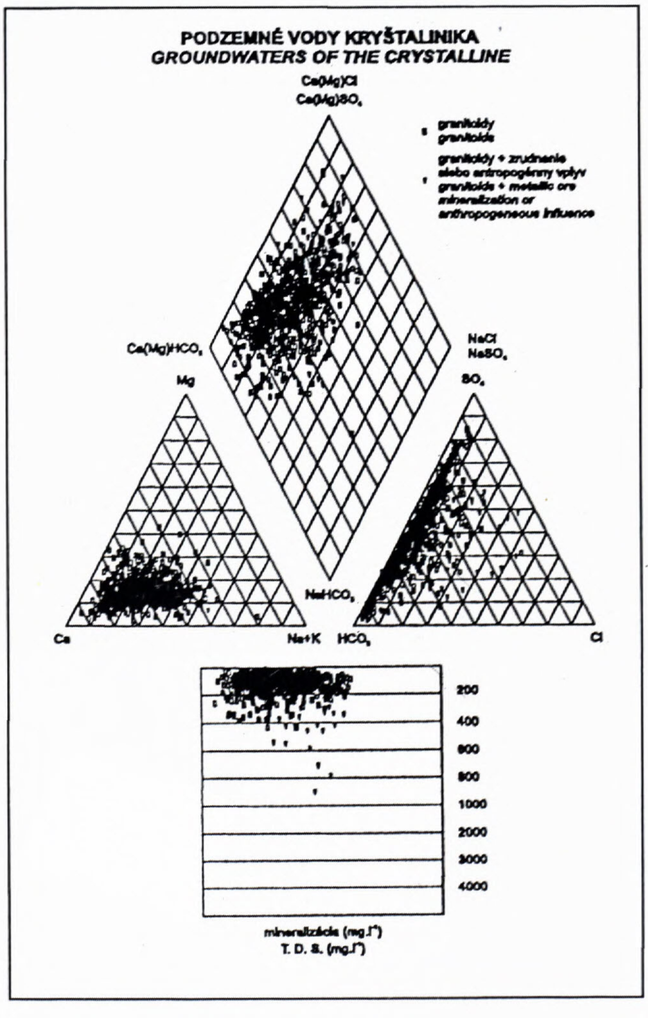


Fig. 4a-h systemization diagrams

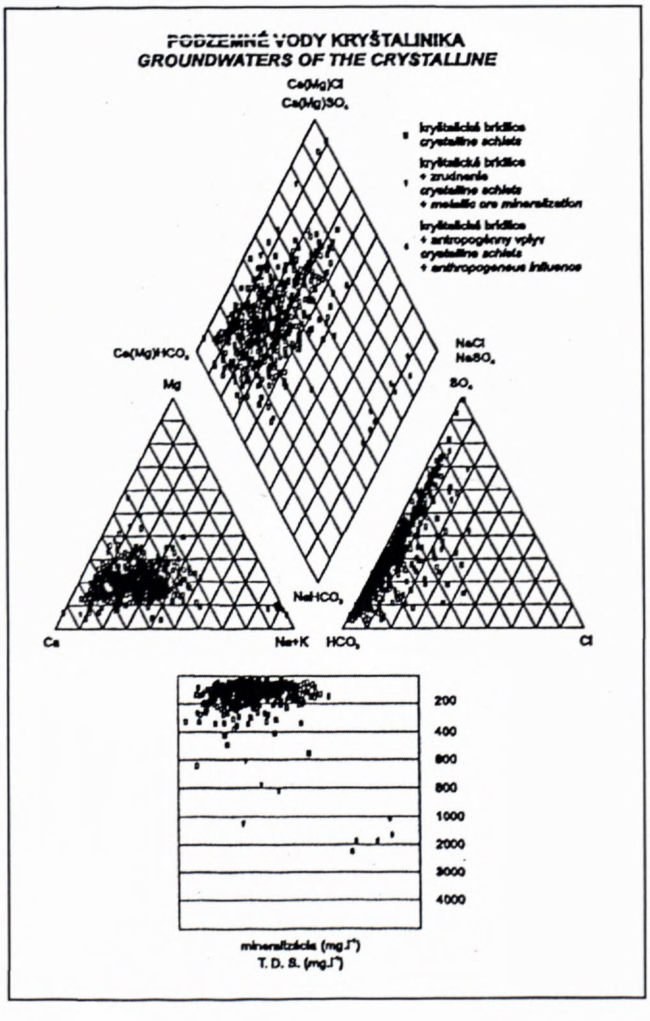


Fig. 4b

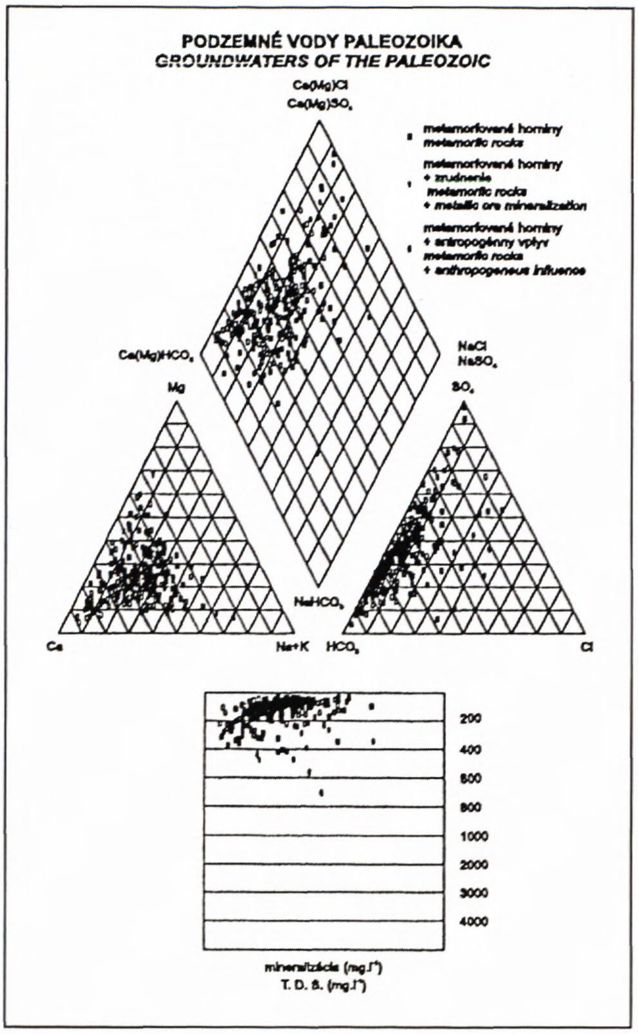


Fig. 4c

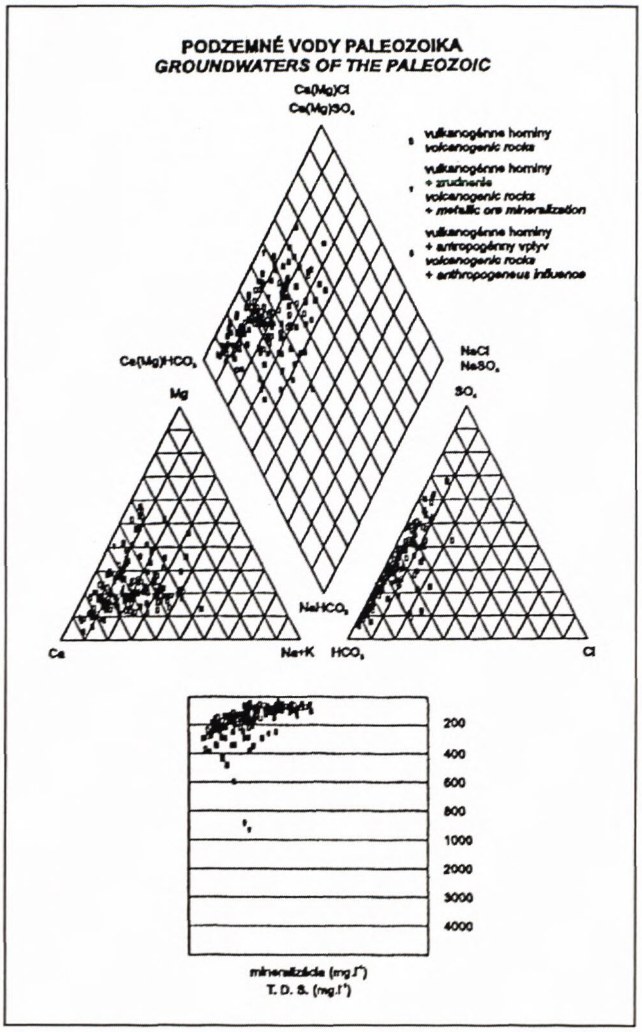


Fig. 4d

ments in the groundwaters of the West Carpathian crystalline massifs occur in the vicinity of ore occurrences. On the basis of the above statement, we presume that the contamination of groundwater in Crystalline rocks due to trace elements is of geogenic - anthropogenic origin.

The variegated lithology in the **Paleozoic hydrogeologic units** gave rise to extremely variegated and diverse groundwater chemistry. It consists virtually of all basic chemical and genetic types of groundwaters. The T.D.S. values in groundwaters of Paleozoic mostly range from 100 to 200 mg.l^{-1}, and increase from metamorphosed rocks through volcanics to sediments. The most widely distributed chemical type is Ca-Mg-HCO_3, Ca-Mg-HCO_3-SO_4 and Ca-Mg-SO_4 types occur only near major gypsum and anhydrite occurrrences or sulphide mineralization. The T.D.S. of these waters is usually several times the normal one, in places even over 1000 mg.l^{-1}, especially in sedimentary Paleozoic rocks and where the water contacts evaporites (Fig. 4b, c, d).

The mean concentrations of aggressive CO_2 are 13–28 mg.l^{-1} and COD_{Mn} oscillates closely around 2 mg.l^{-1}. The major components in Paleozoic groundwaters comprise Ca, Mg and Sr, as well as anions HCO_3, SO_4, NO_3 and Cl, whose increased concentrations are related to human activities (maximum NO_3 concentrations are approx. 35 mg.l^{-1}). As regards minor elements, mean contents of Fe and Mn are around 0,05 and 0,03 mg.l^{-1}, respectively, local highs being located largely near ore occurrences. Trace-element concentrations are usually monotonous, e.g. average concentrations of aluminium are around 0,17 mg.l^{-1} and those of zinc between 0.04 and 0.06 mg.l^{-1}.

In the **Mesozoic**, the T.D.S. varies mostly from 300 to 500 mg.l^{-1}, only in the case of anthropogenic influence and/or at the contact of groundwater with Lower Triassic gypsum containing formation does the T.D.S. content vary from 800 to 1 000 mg.l^{-1}. No major differences between waters from limestones, dolomites and mixed limestone-dolomite circulations were noted. They differ only in their Mg/Ca coefficients (in eq. %), which are below 0,25 in groundwaters from limestones (even below 0,1 in pure, notably organogenic limestones) and above 0,75 in groundwaters circulating in dolomites.

The lowest T.D.S. values in the Mesozoic (often below 50 mg.l^{-1}) occur in the sandstone–quartzite–conglomerate formations. Average COD$_{Mn}$ values amount to 1,9–2,4 mg.l^{-1}. Aggressive CO_2 concentrations are low or absent, owing to the abundant presence of carbonates. Throughout the Mesozoic, cations are dominated by Ca and Mg, while in contrast to other hydrogeological units, there is characteristically the average Sr content around 0,5 mg.l^{-1} and the anions by HCO_3 and SO_4. Groundwaters of typical limestone and dolomite circulations are shown in Piper diagrams on Fig. 4e, f. Because of the vulnerable environment, nitrate concentrations attain as much as 39 mg.l^{-1} the NH_4 over 1 mg.l^{-1}. Groundwaters here typically contain little silica (about 10 mg.l^{-1}) and the average concentrations of trace elements are a mere thousandths or hundredths of mg.l^{-1}. The barium contents are fairly high, its mean value is 0,03–0,08 mg.l^{-1}.

Groundwater chemistry in the **Flysch Belt** depends on the presence of individual lithofacies, i.e. share of claystones and sandstones in a given aquifer (Fig. 4g). The lowest T.D.S. values (366 mg.l^{-1}) are characteristic of the sandstone facies. On the other hand, maximum T.D.S. values (up to 2 000 mg.l^{-1}) are bound to areal or local sources of contamination. COD$_{Mn}$ values vary from 1,8 to 5,6 with respect to human–related impacts. The vast majority of groundwaters is devoid of aggressive CO_2. In addition to Ca and Mg, major components also include Na. Anions are dominated by HCO_3, but sulphates are equally abundant in the vicinity of sulphide occurrences. High chloride contents (as much as 120 mg.l^{-1}) are of geogenic origin as they come from deeper groundwaters dispered in the first aquifer. Widely distributed in the Flysch Belt, anoxic environments give rise to increased concentrations of minor elements, notably iron and manganese, sometimes even hydrogen sulphide (H_2S). Zinc is the most abundant trace element, concentrations of the others are as little as thousandths or tenthousandths of mg.l^{-1}.

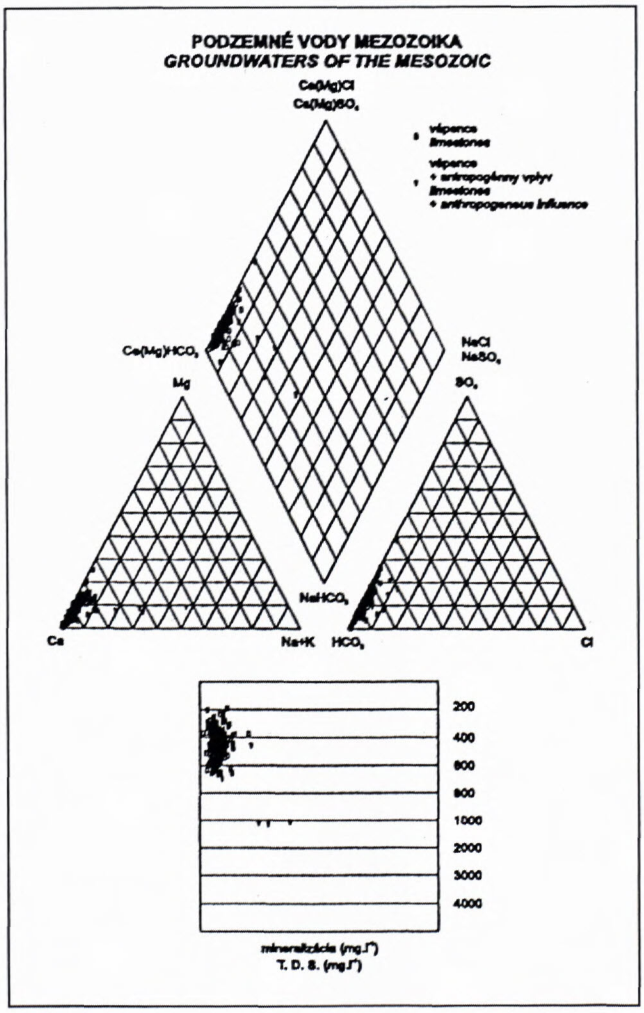
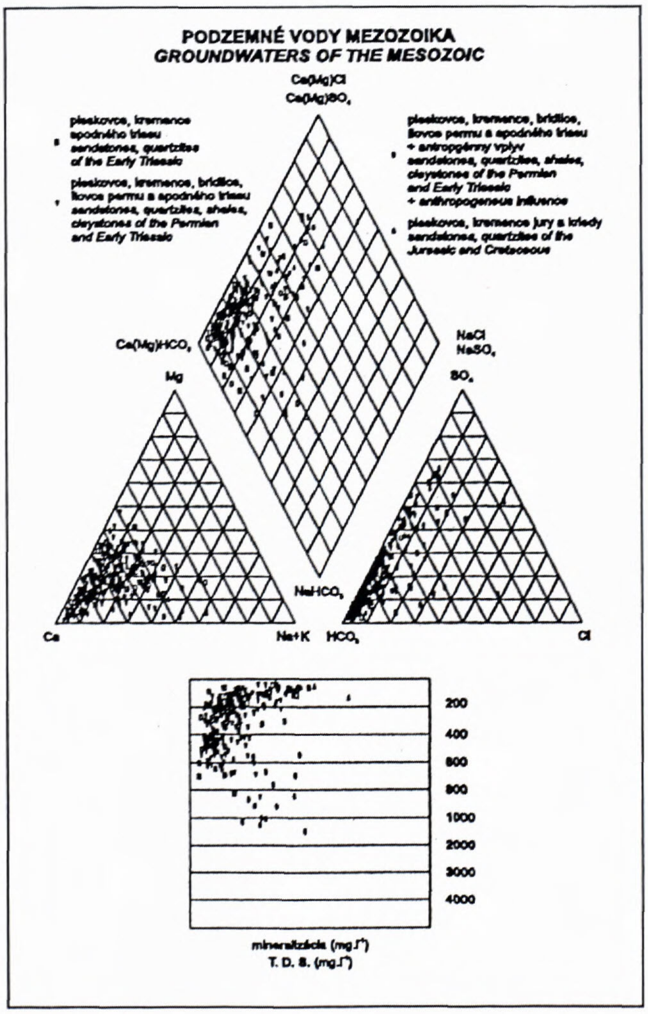


Fig. 4e



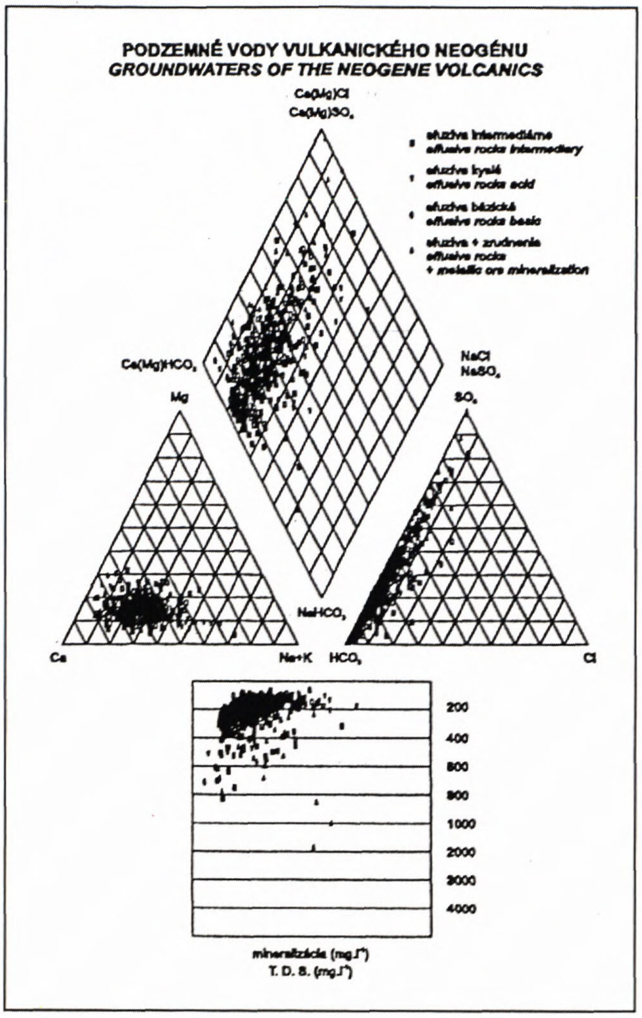


Fig. 4g

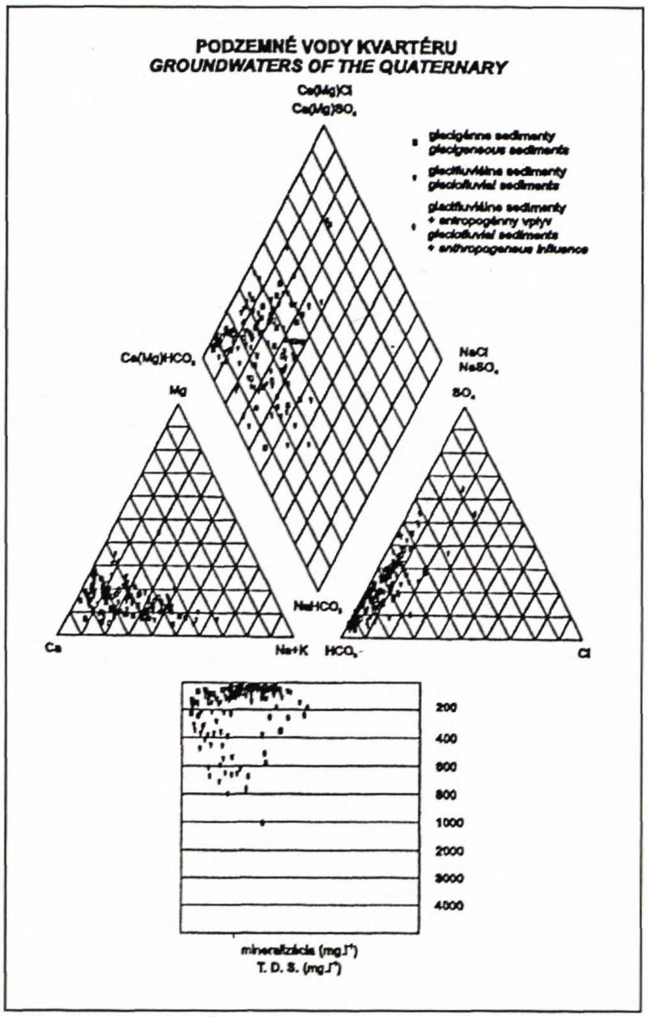


Fig. 4h

Groundwaters in the **Klippen Belt** have T.D.S. between 220 and 1200 mg.l^{-1}. It is controlled mainly by the percentage of carbonate and sandy–clayey–carbonate lithofacies. COD_{Mn} values vary around 2 mg.l^{-1}, but locally around man–made sources up to 14 mg.l^{-1}. The vast majority of groundwaters is devoid of aggreessive CO_2. Cations in these groundwaters are vastly dominated by Ca and Mg, and the anions by bicarbonates and sulphates. As regards the components significant from a water–management point of view, nitrate concentrations attain up to 40 mg.l^{-1} and the maximum NH_4 content is 1,4 mg.l^{-1}. As to trace elements, aluminium concentrations are about 0,1 mg.l^{-1}, zinc 0,02 mg.l^{-1} and barium ones 0.1 mg.l^{-1}, contentrations of the other trace elements amount to thousandths or hundredths of mg.l^{-1}.

The chemical composition of groundwaters in the **Inner Carpathian Paleogene** is similar to that in the Flysch Belt. The only substantial difference is only a higher percentage of man–made sources because the Paleogene typically underlies fairly densely populated and industrialized intermontane depressions. The T.D.S. of groundwaters varies from 370 to 560 mg.l^{-1}, locally exceeding 1 000 mg.l^{-1}. The presence of man-made sources is reflected by COD_{Mn} values which sometimes attain around 10 mg.l^{-1}. The content of aggressive CO_2 is generally low due to carbonate cement in the Paleogene lithofacies. The major components are dominated by calcium and magnesium. Bicarbonates and sulphates are the most plentiful anions in groundwaters. The sodium content is locally increased, notably in the flysch lithofacies of the Paleogene. The average content of nitrates varies around 9 mg.l^{-1}, and locally reaches 40 mg.l^{-1}. Aluminium and zinc are the most abundant trace elements.

Groundwaters in **Neogene sediments** have T.D.S. between 130 and 2 700 mg.l^{-1}. Such big differences are caused by diverse lithofacies of Neogene sediments. Low values typically occur in clayey-gravelly lithofacies, medium in basal Neogene sediments and high near man–made sources of local or areal importance. Associated

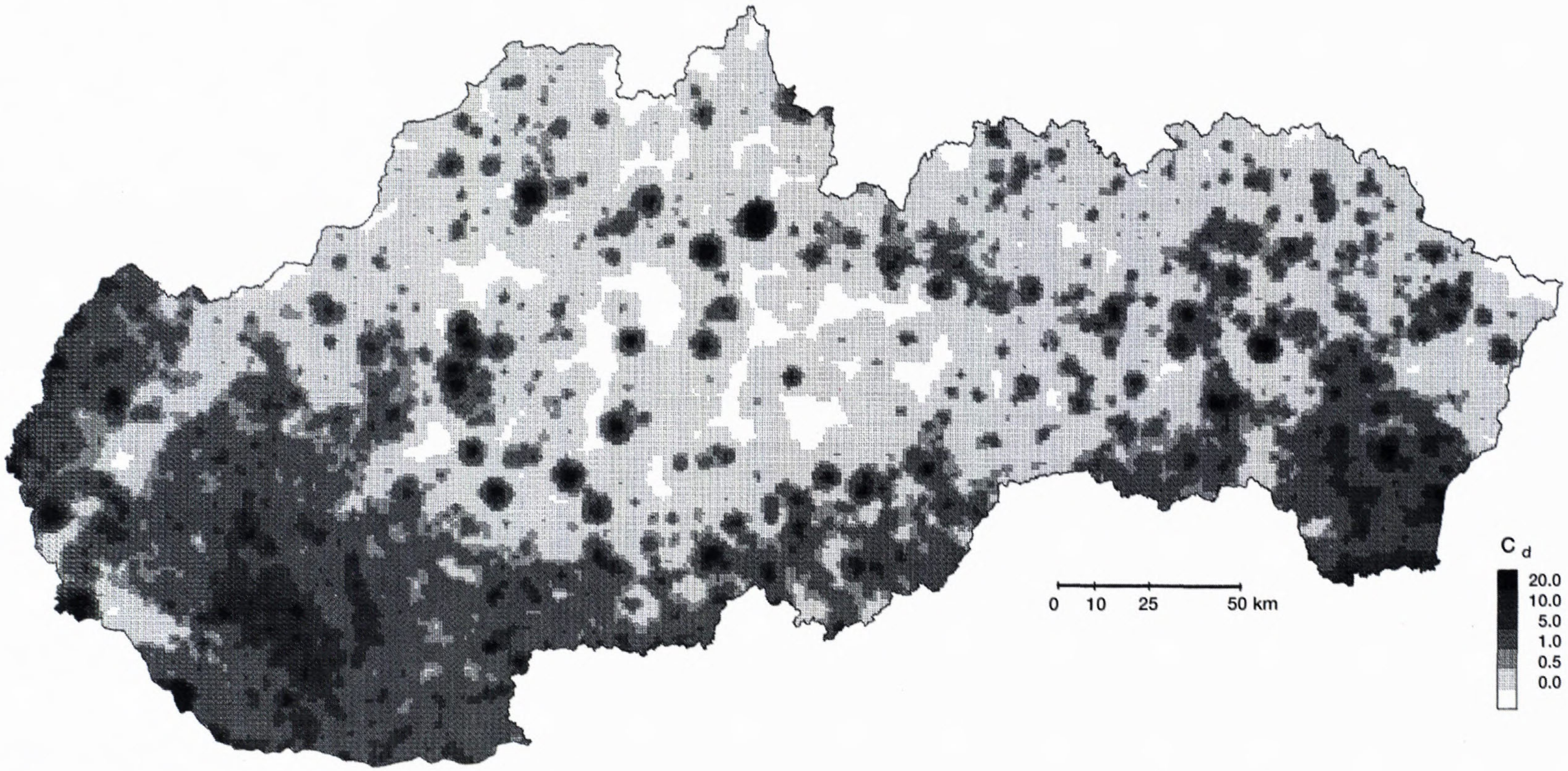


Fig. 5 Grounwater Contamination Degree map of Slovakia

COD_{Mn} values range from 1 to 38 $mg.l^{-1}$. Groundwaters here are little aggressive. The major components are dominated by Ca, Mg and Na. HCO_3 and SO_4 are the most abundant anions in these groundwaters. Another significant geogenic component is chlorides. Nitrate concentration in groundwaters unaffected by human activity varies around 10 $mg.l^{-1}$, but in contaminated groundwaters, particularly in sandy–clayey–gravelly lithofacies, the concentrations are much higher, with a median value 93,3 $mg.l^{-1}$ and a maximum content as much as 862,7 $mg.l^{-1}$. Contents of minor elements are controlled by groundwater contamination. Concentrations of trace elements in groundwaters polluted by human activity are several times higher than in unaffected ones.

Groundwaters in the **Neogene volcanic formations** have T.D.S. between 60 and 1 900 $mg.l^{-1}$. Interestingly, the highest concentrations are found in mineralized areas and not in groundwaters affected by human activity (Fig. 4g). COD_{Mn} values are 2–5 $mg.l^{-1}$. The content of aggressive CO^2 is increased, their mean values ranging from 5 to 16 $mg.l^{-1}$. Ca and Mg are predominant major cations, sodium contents are increased locally. Anions consist mostly of bicarbonates, but sulphates are also widespread, notably in groundwaters associated with effusive volcanics.

Groundwaters bound to Neogene volcanics are typically rich in silica, whose mean content is around 50 $mg.l^{-1}$, except in mineralized effusives. As to trace elements, aluminium contents up to 58 $mg.l^{-1}$ are noteworthy. Ore occurrences gave rise to local anomalies of trace elements.

The chemical composition of groundwaters in **Quaternary sediments** is the most variable in space and is the most affected by human activities. Average T.D.S. values range widely from 50–112 $mg.l^{-1}$ in glacial and glaciofluvial sediments to 600–1 000 $mg.l^{-1}$ in fluvial sediments of flood planes and lowland sediments hydraulically connected with surface streams (Fig. 4h). Quaternary deposits recharged mostly by meteoric precipitation have T.D.S. around 235 $mg.l^{-1}$. As regards groundwater exploitation, Quaternary deposits as much as 400–450 m thick are of prime importance.

In general, we may conclude that groundwaters of the first aquifer or aeration zone in Quaternary sediments are contaminated. In addition to other evidence, this is suggested also by some group indices, such as COD_{Mn} up to 40 $mg.l^{-1}$ and slightly alkaline pH. Least polluted are glacial and glaciofluvial sediments mainly in mountain areas devoid of man-made sources of contamination. Cations are dominated by Ca, Mg, and often also by Na mostly in so-called fluviogenic waters (groundwaters directly hydraulically connected with a surface stream). Bicarbonates are the most widespread anions, but suplhates, chlorides and nitrates are widespread as well, in highly contaminated waters they even affect the water type. As regards minor components, iron and manganese concentrations in anoxic environments exceed 1 $mg.l^{-1}$. Higher concentrations of aggressive CO_2 are typical of groundwaters in glacial and glaciofluvial sediments. Trace-element concentrations in groundwaters of Quaternary deposits are largely of man–made origin. The lowest average concentrations of trace elements occur in groundwaters of glacial and glaciofluvial sediments. Aluminium and zinc have the highest contents.

The outlined regional-hydrogeochemical situation with regard to hazardous areas with occurrences of analysed pollutants, whose contents exceed the limit values of the Slovak standard 75 711 is shown on the Map of groundwater contamination degree (C_d, Fig. 5). Unlike one-element maps, this method allows us to illustrate all ions (components) exceeding the limit values in a single map.

The degree of contamination was calculated as follows:

a) the contamination factor was calculated for each analysed component that exceeds the value permitted by Slovak standard No. 75 7111 for drinking water:

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$$

where:

C_{Ai} – analytical value of the i-th element (component)

C_{Ni} – normative value of the i-th element (component) permitted by Slovak drinking water standard

C_{fi} – contamination factor of the i-th component

b) contamination degree for each sample from individual factors was calculated as follows:

$$C_d = \sum_{i=1}^{n} C_{fi}$$

where:

Cd – degree of contamination

C_{fi}– factor of contamination for i-th element (component)

The number of exceeded limit values of analysed components divided as to types of sampled groundwater sources is given on Tab.5. The table suggests that the worst contaminated water is in wells, drillholes, drainage systems and mine adits. The highest concentrations and consequently also the highest contamination factors for Al, As, Cd, Cu and Hg occur in effluents from adits. Not surprisingly, the highest contamination degrees were noted in centres of human activities in lowlands and locally also in past or present-day mining areas. The latter anomalies can be regarded as geogenic–man–made ones.

Conclusion

In the project Geochemical atlas of Slovakia – Part 1, Grounwater, a total of 16 359 samples were collec- ted and

Tab. 5 Comparison indices of Slovak technical standard No. 75 7111 (Drinking water) and contamination degree of groundwaters in Atlas´s samples

Assessed		*Number of exceeded limit values*											
index	*limit value* $mg.l^{-1}$	*total groundwater* $n = 16359$		*springs* $n = 8857$		*wells* $n = 5716$		*drillholes* $n = 1537$		*drainages* $n = 198$		*adits* $n = 51$	
		n	*%*	*n*	*%*	*n*	*%*	*n*	*%*	*n*	*%*	*n*	*%*
MIN.	1000	2188	13,37%	101	1,14%	1726	30,20%	336	21,86%	21	10,61%	4	7,84%
NO_3	50	3277	20,03%	229	2,59%	2626	45,94%	390	25,37%	31	15,66%	1	1,96%
Cl	100	1100	6,72%	42	0,47%	886	15,50%	160	10,41%	11	5,56%	1	1,96%
SO_4	250	738	4,51%	100	1,13%	469	8,21%	134	8,72%	26	13,13%	9	17,65%
F	1,5	16	0,10%	6	0,07%	6	0,10%	3	0,20%	0	0,00%	1	1,96%
NH_4	0,5	315	1,93%	150	1,69%	86	1,50%	62	4,03%	11	5,56%	6	11,76%
Fe	0,3	732	4,47%	212	2,39%	241	4,22%	255	16,59%	21	10,61%	3	5,88%
Mn	0,1	1988	12,15%	402	4,54%	1029	18,00%	508	33,05%	40	20,20%	9	17,65%
Al	0,2	170	1,04%	94	1,06%	55	0,96%	14	0,91%	4	2,02%	3	5,88%
As	0,05	50	0,31%	31	0,35%	8	0,14%	7	0,46%	1	0,51%	3	5,88%
Ba	1	9	0,06%	3	0,03%	6	0,10%	0	0,00%	0	0,00%	0	0,00%
Cd	0,005	71	0,43%	26	0,29%	32	0,56%	12	0,78%	0	0,00%	1	1,96%
Cu	0,1	12	0,07%	1	0,01%	8	0,14%	2	0,13%	0	0,00%	1	1,96%
Cr	0,05	31	0,19%	15	0,17%	14	0,24%	1	0,07%	1	0,51%	0	0,00%
Hg	0,001	54	0,33%	24	0,27%	21	0,37%	7	0,46%	1	0,51%	1	1,96%
Pb	0,05	5	0,03%	1	0,01%	4	0,07%	0	0,00%	0	0,00%	0	0,00%
Se	0,01	76	0,46%	2	0,02%	64	1,12%	9	0,59%	1	0,51%	0	0,00%
Zn	5	115	0,70%	4	0,05%	95	1,66%	16	1,04%	0	0,00%	0	0,00%
C_d	0	5968	36,48%	1125	12,70%	3775	66,04%	956	62,20%	91	45,96%	21	41,18%

analysed, giving a statistical density of 1 sample per 3 km^2. The maps were compiled and interpreted in accordance with procedures accepted in the IGCP Project No. 360 Baseline Geochemical Mapping. The results have been published in bilingual Slovak–English version.

The main part of the Atlas are maps showing distribution of chemical elements, components and parameters (T.D.S., pH, conductivity, SiO_2, Na, K, Ca, Mg, Cl, SO_4, $NO_3^+NO_2^+NH_4$, PO_4, HCO_3, Sb, As, Ba, Cd, Cu, F, Al, Cr, Li, Mn, Pb, Hg, Se, Sr, Zn, Fe, dissolved O_2, COD_{Mn}, aggr. CO_2) in groundwaters of the first aquifer in Slovakia's territory at scale 1 : 1 000 000.

The Atlas also gives an overall review of regional differences in groundwater chemistry of the first aquifer with detailed data on Slovakia's principal hydrogeological units.

All regional information is evaluated with respect to the importance of primary and secondary factors affecting groundwater chemistry. It has turned out that primary factors over most of Slovakia's territory are overshadowed by man–related factors. Industrial, agricultural and household pollution of groundwater over the past decade created continuous zones of shallow groundwater highly contaminated with sulphates, chlorides, nitrates, phosphates, potassium, some metals (notably iron and manganese), and with increased oxidability, aggressive CO_2, etc. particularly in lowlands and intermontane depressions. All these data will have to undergo an environmental analysis and be applied in a rational and effective solution of Slovakia's ecological problems.

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Geochemical Atlas of Slovak Republic Part Rocks

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Abstract. As a part "Rocks" of the project "Geochemical Atlas of Slovak Republic" 64 main rock types of the Slovak territory (49 036 km^2) were defined during 1991 - 1995 (Marsina et al., 1995). The main rock types are presented through: **unique database** containing 3 839 samples placed in 7 main groups, **Brief text explanations** describing each rock type (geologic-tectonic setting, petrography, modal composition, anomalous element distribution, etc). Basic statistical parameters (mean, standard deviation, median, geometric mean, minimum, maximum, number of values below detection limit, count) were counted for each rock type and **Map of lithogeochemical types of Slovakia at a scale of 1 : 500 000** was constructed.

These data represent an information of the element distribution in the primary lithology. Thereby it is possible to distinguish primary lithogeochemical background and/or anomalies from the anomalies caused by metallogenic processes and anthropogenic impacts.

Key words: Geochemical atlas, rocks, main rock types, lithogeochemical database, lithological parameters, statistical parameters.

Introduction

Main aim of the Geochemical Atlas of the Slovak Republic - part Rocks - was to create the Lithogeochemical database on the distribution of all major and 26 minor elements and on other data, in the main rock types of Slovakia. The obtained geochemical data (Marsina et al, 1995) were needed for the complex characterization of the primary element distribution in all Slovakian main rock types. This knowledge was used as foundation for the distinctions between primary - lithological element distribution and secondary - metallogenicaly or anthropogenicaly caused distribution of the studied elements in other researched media (water, soil, biomass and stream sediments).

About 50 geologists and geochemists contributed to the research in various ways. Besides the Dionýz Štúr Institute of Geology (since January 1, 1996, a part of the Geological Survey of the Slovak Republic) other organizations participated; mainly the Faculty of Natural Sciences of Comenius University and Geological Institute of the Slovak Academy of Science.

During the first stage, all the accesible older rock analyses were collected.

During the second stage, new rock samples were taken on an irregular grid and were analysed to get suffi cient information about each lithotype present on the Geological Map of Slovakia at a scale of 1 : 500 000.

Inasmuch at all the achievements of the subproject "Rocks" will be published during 1998 as the "Catalogue of the Main Rock Types of Slovakia", this paper gives only the basic information dealing with methodology and brief text explanations of 64 main lithotypes including a table with some statistical data.

A brief review of the geological structure of Slovakia

(Hók, Kováč after Biely et al. (1992), in Maňkovská, in press)

Geologically, most of the Slovak territory is covered by the Western Carpathians (fig. 1).

As far as the age of tectonic individualisation of their geological units is concerned the Western Carpathians can be divided into outer and inner parts.

The Outer Western Carpathians are represented by the flysch belt units (the Magura and Krosno flysch), which were thrust over the margin of the European platform during the Tertiary period. Sandstones, mudstones and conglomerates are the predominant lithotypes.

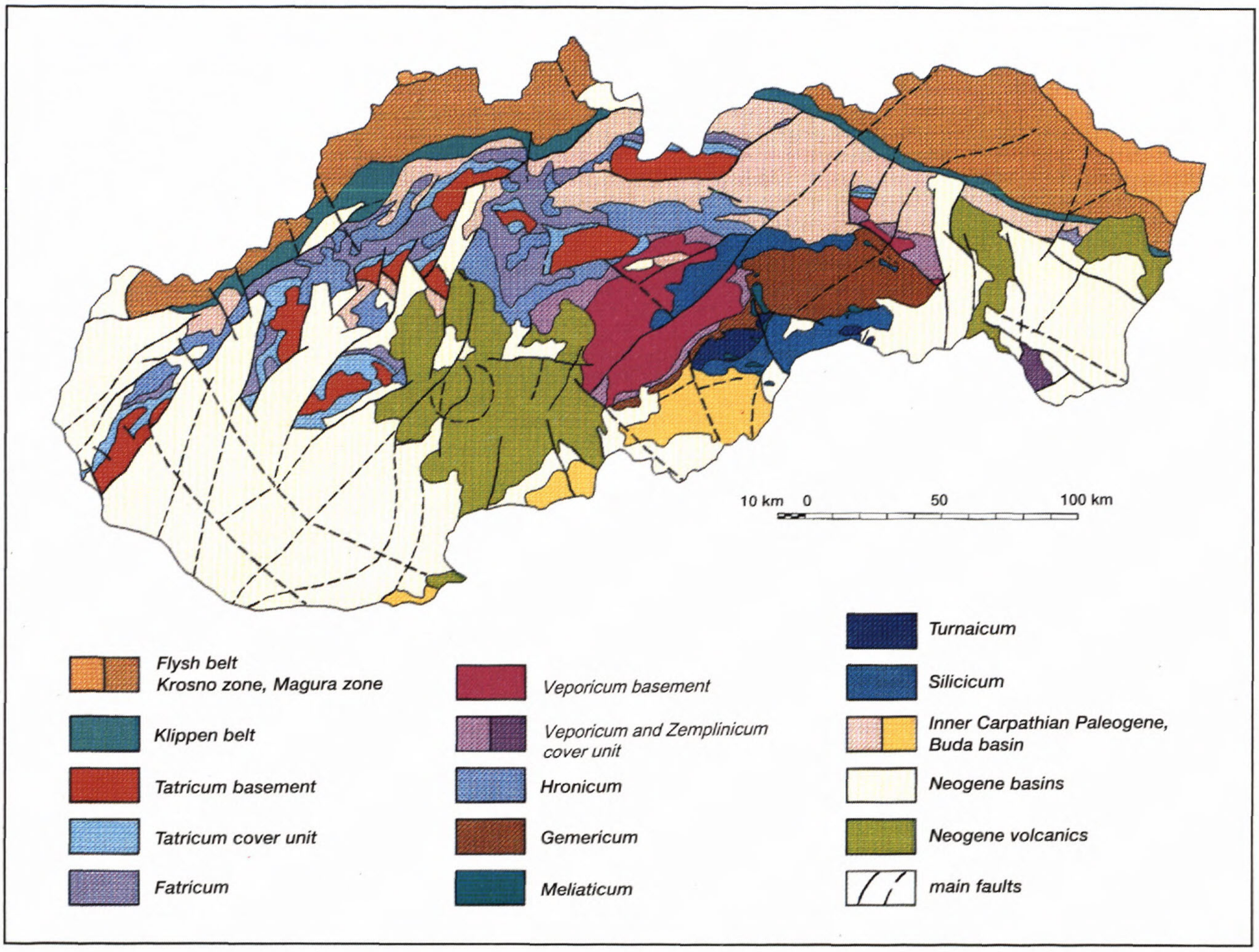

Fig. 1: Geologic-tectonic sketch of the Slovak part of Western Carpathians

The Klippen belt is an independent tectonic unit situated between Outer and Inner Western Carpathians. It comprises two basic units, the Čorštýn Unit, composed of the shallow water carbonate facies and a deep water Kysuce-Pieniny Unit. Both units were involved in several stages of folding, which occurred to some degree in the Inner Western Carpathians, or more intensely, with the Outer Western Carpathians.

Tectonic individualisation of the Inner Western Carpathians took place during the Middle Cretaceous Period. The principal tectonic units of the Outer Western Carpathians are divided, from north to south, into the Core mountain belt, the Veporicum belt and the Gemericum belt.

The Core mountain belt is made of the Tatricum Unit, composed of crystalline rocks, which are mostly granitoids, and of autochthonous cover units. In rising sequence there include Upper Paleozoic rocks, (only locally present) a Lower Triassic clastic arkosic to siliceous quartzite formation, Middle Triassic limestones and dolomites and Upper Triassic and Lower Cretaceous limestones, dolomites, marlstones, shales and sandstones. The Fatricum nappe (composed predominantly of the Križna nappe) and the Hronicum Unit (made of the Choč nappe) are characterised by thin bedding.

The Veporicum belt comprises crystalline rocks (granitoids and crystalline schists) and a considerably reduced Mesozoic cover (siliceous sandstones, shales, limestones and dolomites), making together the Veporicum Unit. This unit is thrust northwards over the Tatricum Unit. The Veporicum Unit is overlain by the Hronicum and Silicicum (Silica nappe) nappes, represented mainly by Triassic limestones and dolomites.

The Gemericum belt is the southernmost unit of the Western Carpathians. Composed of low metamorphosed Early Paleozoic rocks of the flysch character and of Late Paleozoic cover with a strongly reduced Mesozoic development, this rock complex represents, in fact, the Gemericum Unit, thrusted northward over the Veporicum Unit. The Gemericum Unit, as well as the area south of it, are overlain by the Meliaticum, Turnaicum and Silicicum nappes, all composed predominantly of the carbonate rocks.

The Inner Carpathian Paleogene (conglomerates, sandstones, shales) with the relics of Upper Cretaceous sediments and with the Neogene sedimentary basins (conglomerates, sandstones, mudstones, limy mudstones and rare carbonates and coal) represent a tectonic molasse. The Neogene volcanics and volcani-clastic rocks (Miocene) are products of back-arc volcanism, in which the andesites are the predominant lithology.

Methodology

1. Sampling

All new samples were taken predominantly from outcrops (some of them also from boreholes and adits) In general only fresh - unweathered and unaltered samples were taken. The grid sampling was irregular. The weight of samples depended on grain size, as follows: above 30 mm - 5 kg, 10 to 30 mm - 2 kg, below 10 mm - 1 kg. Thin sections were made of all samples, with the exceptions of carbonates, clays and claystones.

2. Analytical procedures

Together, 3 839 samples of three kinds were used for this study: a) archive analysed samples (not all minor elements determined), b) archive samples reanalysed for missing minor elements and c) new samples analysed for all major and 26 minor elements in the Geoanalytical Laboratories of Geological Survey of Slovak Republic at Spišská Nová Ves, with following analytical techniques and detection limits (in brackets, for major elements in %, for minor elements in ppm) :

major elements - SiO_2 - ICP OES (inductively coupled plasma optical emission spectrometry, 0.01), TiO_2 - ICP OES (0.001), Al_2O_3, Fe_2O_3, FeO - ICP OES (0.01), MnO, MgO, CaO - ICP OES (0.001), Na_2O, K_2O, P_2O_5, S_{Total} - ICP OES (0.01), H_2O^+ (350°C) - gravimetry (0.01), CO_2 - coulometry (0.01).

minor elements: Ag - GAAS (atomic absorption spectrophotometry, electrothermal atomization, 0.04), As - HGAAS (atomic absorption spectrophotometry, 0.1), B - ICP OES (3.0), Ba - XRF (x-ray fluorescence spectrometry, 30.0), Be - ICP OES (0.1), Ce - ICP OES (10.0), Cd - GAAS (0.1), Co - ICP OES (1.0), Cr - ICP OES (5.0), Cu - ICP OES (1.0), F - ISE (ionselective methods, 50), Ga - XRF (5.0), Hg - AAS - TMA (trace mercury analyser 0.01), La - ICP OES (1.0), Li - AAS (1.0), Ni - ICP OES (1.0), Pb - GAAS (1.0), Rb - XRF (5.0), Sb - HGAAS (0.1), Se - GAAS (0.05), Sn - GAAS (1.0), Sr - XRF (5.0), V - ICP OES (5.0), Y - XRF (1.0), Zn - ICP OES (1.0), Zr - XRF (1.0).

3. Statistical sets representing rock types

Statistical sets were created in two steps. In the first step, 100 sets - rock types were defined according to lithological, regional geologic and stratigraphic criteria. Several of the sets had shown either small representativity or geochemical similarity with other sets after counting all the basic statistical parameters (see bellow). Therefore, the second stage resulted in joining of several sets and creating of the final 64 sets - rock types. The main criteria used were lithology and the difference in element distribution.

4. Statistics

For each statistical set - rock type the following basic statistical parameters were counted: mean, standard deviation, median, geometric mean, minimum, maximum, number of values below detection limit and count (see example on table 1). Means / counts for each rock type - statistical set is present on table 2.

Mean and geometric mean were not counted in those cases in which more than 40 % values of an element content were below the detection limit. In other cases, half of the value below detection limit was included in the calculation. Extreme values = mean ± 3 standard deviations were exluded from the calculations.

138 samples representing "exotic", transitional or mixed rock types were excluded from the calculations and they were not included in any of the 64 statistical sets - rock types:

Granitoids (Crystalline)	770 samples	6 sets (Gt - 1 to Gt - 6)
Metamorfites (Crystalline)	225 samples	7 sets (Mt - 1 to Mt - 7)
Paleozoic (remaining)	457 samples	15 sets (Pz-1 to Pz -15)
Mesozoic	395 samples	12 sets (Mz - 1 to Mz -12)
Paleogene	258 samples	8 sets (Pg - 1 to Pg - 8)
Sedimentary neogene	237 samples	6 sets (Ne - 1 to Ne - 6)
Neovolcanics	1 359 samples	10 sets (Nv - 1 to Nv - 10)
Together:	3 701 samples	64 sets

64 main rock types of Slovakia - brief description (after Marsina et al., 1995)

1. Granitoids

1a. Tatricum and Veporicum

Gt - 1 consists of amphibole-biotite diorites which generaly constitute fairly small bodies several metres and/or tens of metres in size. They are found mainly in the Malé Karpaty, Nízke Tatry, Vysoké Tatry, Strážovská hornatina, Čierna hora, Žiar and Malá Fatra Mts. Principal rock forming minerals (range in volume %): quartz 3.2 - 26, plagioclase 19 - 62, potassium feldspar 0 - 4, amphibole 9 - 66, biotite 5 - 20, accessory minerals 1.5-7 (apatite, titanite, zircon, diopside, magnetite, allanite, pyrite ± ilmenite).

Table 1: Granitic rocks of the Tatric and Veporic Units

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 %)	Fe_2O_3 (%)	FeO (%)	MnO (%)	MgO (%)	CaO (%)
Mean	70.59	0.43	14.97	1.09	1.42	0.042	0.93	1.90
Standard Deviation	2.13	0.24	1.05	0.53	0.64	0.015	0.36	0.70
Median	70.62	0.38	14.85	1.00	1.40	0.040	0.85	1.95
Geometric Mean	70.56	0.37	14.94	0.96	1.23	0.039	0.86	1.74
Minimum	61.94	0.06	12.09	0.18	0.10	0.010	0.05	0.14
Maximum	75.75	1.50	19.32	3.03	3.23	0.100	2.25	3.52
Detection limit (d.l.)	0.01	0.001	0.01	0.01	0.01	0.001	0.001	0.001
Number of values below d. l.	0	0	0	0	0	0	0	0
Count	378	374	377	360	359	370	343	378

	Na_2O (%)	K_2O (%)	P_2O_5 (%)	CO_2 (%)	S_t. (%)	Ag (ppm)	As (ppm)	B (ppm)
Mean	3.89	3.27	0.19	0.54	0.05		1.6	11.7
Standard Deviation	0.58	0.65	0.09	0.26	0.03		1.4	6.2
Median	3.86	3.25	0.18	0.56	0.04		1.2	10.6
Geometric Mean	3.82	3.21	0.17	0.46	0.04		1.0	9.9
Minimum	0.21	1.32	0.01	0.11	0.005	0.02	0.1	1.7
Maximum	5.63	5.00	0.58	1.23	0.18	2.40	6.2	37.0
Detection limit (d.l.)	0.01	0.01	0.01	0.01	0.010	0.04	0.1	3.0
Number of values below d. l.	0	0	0	0	2	70	15	0
Count	356	328	332	111	107	99	116	258

	Ba (ppm)	Be (ppm)	Ce (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	F (ppm)
Mean	941	2.36	61.0		4.6	21.2	10.2	227
Standard Deviation	335	0.79	19.2		3.5	12.6	14.1	132
Median	910	2.30	58.0		3.8	20.0	5.0	200
Geometric Mean	880	2.23	58.0		3.4	16.8	5.5	185
Minimum	242	0.50	21.0	0.05	0.5	1.0	0.5	25
Maximum	2140	6.20	128.0	1.00	20.0	60.0	87.0	700
Detection limit (d.l.)	30	0.10	10.0	0.10	1.0	5.0	1.0	50
Number of values below d. l.	0	0	0	66	25	0	8	8
Count	347	277	215	124	299	343	319	120

	Ga (ppm)	Hg (ppm)	La (ppm)	Li (ppm)	Ni (ppm)	Pb (ppm)	Rb (ppm)	Sb (ppm)
Mean	16.1	0.08	33.2	31.8	6.8	20.5	91.6	0.76
Standard Deviation	5.7	0.10	12.2	17.6	3.7	10.6	30.0	0.99
Median	17.0	0.04	32.0	26.0	6.0	20.0	92.0	0.49
Geometric Mean	14.9	0.04	30.9	27.6	5.9	17.2	86.3	0.40
Minimum	2.5	0.01	9.4	6.0	1.5	1.0	30.0	0.05
Maximum	40.0	0.47	74.0	88.0	21.0	52.0	161.0	5.30
Detection limit (d.l.)	5.0	0.01	1.0	1.0	1.0	1.0	5.0	0.10
Number of values below d. l.	3	10	0	0	0	0	0	14
Count	205	75	214	268	341	309	305	175

	Se (ppm)	Sn (ppm)	Sr (ppm)	V (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
Mean		2.9	373.8	33.5	13.2	53.9	134.8
Standard Deviation		2.3	168.8	16.5	6.3	17.6	44.7
Median		2.0	357.0	32.0	12.0	55.0	138.0
Geometric Mean		2.0	333.6	28.1	11.8	50.9	125.6
Minimum	0.03	0.5	39.0	1.5	1.0	18.0	10.0
Maximum	0.50	11.0	980.0	93.0	51.0	107.0	263.0
Detection limit (d.l.)	0.05	1.0	5.0	5.0	1.0	1.0	1.0
Number of values below d. l.	80	35	0	0	0	0	0
Count	98	249	347	346	339	270	346

Gt - 3 GRANODIORITES to GRANITES (378 samples)

Due to strong Alpine tectonic and metamorphic overprinting in the whole Veporic unit, the granitoids of Tatric unit are separated into Gt-2 to Gt-4 sets of the granitoids of the Veporic unit.

Gt - 2 includes Tatric biotite tonalites, hybrid biotite tonalites and Veporic Sihla-type granodiorites to biotite tonalites, as well as hybrid biotite tonalites to granodiorites.

a) Tatric unit: biotite tonalites occur in all core mountains except for the Žiar. Small quantities of hybrid biotite tonalites are present in the Čierna hora, Nízke Tatry, Malá Fatra, Malá Magura and Žiar. The principal rock forming minerals (range in volume %): quartz 20 - 40, plagioclase 30 - 60, potassium feldspar 0 - 16, biotite 3 - 21, amphibole 0 - 10, muscovite 0 - 5, accessory minerals 1 - 4 (apatite, zircon, magnetite, sillimanite, garnet ± titanomagnetite ± allanite ± ilmenite ± monazite ± titanite).

b) Veporic unit: Sihla-type granodiorites to biotite tonalites, present mainly in the western sector of the Vepor Massif. On the contrary hybrid biotite tonalites to granodiorites are found on the southeastern edge of the central granitoid body and in the Kohút zone. Principal rock forming minerals (range in volume %): quartz 19 - 35, plagioclase 40 - 60, potassium feldspar 0.5 - 27, biotite 4 - 13, amphibole 0 - 8, muscovite 0.5 - 4, accessory minerals 1 - 3.5.

Gt - 3 are Tatric and Veporic granodiorites to granites composed of four major rock types.

a) Tatric unit: Biotite and two-mica granodiorites, as well as two-mica granites, are present in all core mountains. Principal rock forming minerals (range in volume %): quartz 22 - 42, plagioclase 27 - 49, potassium feldspar 10 - 36, biotite 2.5 - 12, muscovite 0.5 - 7.7, sillimanite 1 - 4, accessory minerals 0.5 - 3.5 (apatite, zircon, ilmenite, ± monazite, ± garnet ± magnetite, ± allanite, ± titanomagnetite ± hematite ± xenotime ± tourmaline).

b) Veporic unit: Vepor-type porphyritic granodiorites to granites dominate in the Vepor pluton (Kohút and Stolica Massifs). Massive tonalites-granodiorites occur in the southernmost Veporicum from Krokava, through Lubeník Dam, as far as Hladomorná. Principal rock forming minerals (range in volume %): quartz 30 - 45, plagioclase 32 - 48, potassium feldspar 4 - 18, biotite 3 - 9, muscovite 0.4 - 3, accessory minerals 0.6 - 2.5.

Gt - 4 comprises Tatric and Veporic leucogranites, which in turn include 3 main rock types.

a) Tatric unit: leucogranitoids widespread in all core mountains.

b) Veporic unit: Leucogranitoids in southern Veporicum (Kohút zone) intrude mildly metamorphosed Paleozoic rocks. Hrončok-type granites are found in the Kamenistá dolina Valley and Hrončok Valley and recently also in the Čierny Balog area.

Principal rock forming minerals (range in volume %) of tatric and veporic leucogranites: quartz 28-40, plagioclase 20-46, potassium feldspar 10-36, biotite 1-8, muscovite 2 - 12, accessory minerals 0.6 - 2.5 (garnet, apatite, zircon, ilmenite, ± monazite, ± tourmaline, ± titanite.

Gt - 5 comprises Tatric pegmatites and aplites. These rocks are present in all core mountains. They form relatively thin veins (several metres to tens of meters) of various len. They occur in the granitoids, as well as in the surrounding metamorphic rocks. Principal rock forming minerals (range in volume %): quartz 30 - 43, plagioclase 20 - 37, potassium feldspar 19 - 42, biotite 0.5 - 12, muscovite 2.5 - 15, accessory minerals 1 - 2.5 (garnet, beryl, pyrochlore, gahnite, columbite - tantalite, fersmite, microlite).

1b. Gemericum

Gt - 6 consists of Gemeric granitoids. They are medium- to coarse-grained, but also slightly porphyritic rocks of pinkish-gray colour. Principal rock forming minerals (range in volume %): quartz 27 - 46, plagioclase 15 - 30, potassium feldspar 25 - 40, biotite 0 - 7, muscovite 2.5 - 10, accessory minerals 0.8 - 2.5 (tourmaline, zircon, apatite, garnet, ±magnetite).

2. Metamorphic rocks

Mt - 1 - Metapelites: low-grade metapelites (chlorite, muscovite and biotite-bearing schists and phyllites) are abundant in the Malé Karpaty crystalline, notably on the edge of the Bratislava Massif and between Pernek and Pezinok. In the Veporicum, they occur in the Paleozoic metasedimentary sequences in the southeastern part at the boundary with Gemericum. Medium-grade mica schists with staurolite, garnet and Al_2SiO_5 polymorphs (andalusite, sillimanite, kyanite) are present in the core mountains of Tatricum (Západné Tatry and Považský Inovec). In the Veporicum, they occur in several "mica schists complexes" (e.g.Hron and Ostrá complex).

Mt - 2 - Metapelites: high-grade paragneisses and migmatites rich in sillimanite and garnet occur in almost all Tatric core mountains (e.g. Západné and Nízke Tatry Tatry, Malá Fatra, Strážovské vrchy), as well as in the Veporicum (Kraľova hoľa complex).

Mt - 3 - Metapsammites: low-grade metasediments (quartz-rich schists and metaquartzites) are most widespread in the Malé Karpaty, they also occur in the SE Veporicum.

Mt - 4 - Metapsammites: quartz-rich gneisses to metaquartzites are common in several core mountains of Tatricum (e.g. Západné Tatry, Nízke Tatry) and they represent higher-grade-metamorphosed equivalents of the psammitic sediments.

Mt - 5 - Metabasites: green schists and amphibolites correspond to various types of metamorphosed basic rocks. They occur in the Tatric core mountains (Malé Karpaty, Západné Tatry, Nízke Tatry, Malá Fatra, Tribeč) as well as Veporicum (Hron and Ľubietová complex).

Mt - 6 - Metavolcanics - acid to intermediate (metarhyolites, metadacites) are represented by samples from the Jánov Grúň complex in the Veporicum.

Mt - 7 - Metagranitoids (orthogneisses, mylonites) represent intensely sheared and metamorphosed rocks of magmatic origin. They are common in high-grade, migmatitized complexes of the Tatricum (Ďumbierske Tatry, Západné Tatry, Malá Fatra) and Veporicum.

3. Paleozoic

3a. Early Paleozoic of the Gemericum

Pz - 1 - Psammites - Early Paleozoic sandstones comprise quartzose and lithic metagraywackes (Vozárová, 1993). Dominant rock forming minerals are (range in volume %): Quartz - 60-95 %; plagioclase - 2-16 %; rock fragments (volcanites - 8-17 %; sediments - 2-3 %), heavy minerals - 0,5 -1 % (zircon, edisonite, tourmaline, titanite, magnetite, ilmenite, anatase, apatite). The grade of metamorphism corresponds with the low-pressure greenschist facies.

Pz - 2 - Pelites, siltstones with variable content of semigraphite. Sericite and chlorite-sericite metapelites are most widespread. Critical metamorphic mineral associations are: muscovite + albite; muscovite + paragonite + albite; quartz + chlorite + muscovite with minor content of epidote, edisonite and graphite. Origin of biotite is linked to the metapelites with high Fe/Mg ratio and higher content of K. Geobarometric estimations ($d_{0,60,\ 311}$ parametres of muscovites) proved P = 2-3 kbar, T= 350 - 370 °C (Sassi, Vozárová, 1987).

Pz - 3 - Acid volcanics and volcanoclastics dominated by rhyolite volcanoclastics. Their composition corresponds with rhyolite and dacite tuffs, tuffites and rarely to quartzose andesite volcanoclastics. They are of calc-alkaline affinity (mainly the Gelnica Group). The only exception are rare layers of subalkaline intermediate and acid volcanics in the basal part of the Rakovec Group. The Gelnica Group calc-alkaline volcanism was related to an active continental margin.

Pz - 4 - Intermediate and basic volcanics and volcanoclastics - occur mainly in the Rakovec Group. The bulk composition and contents of REE of the Rakovec Group metabasalts suggests E-MORB / OIT and partly island arc tholeiites (Bajaník, 1981, Ivan, 1994). Rare fragments of tholeiitic basalts with CAB, E - and N-MORB affinity are associated with thick volcanogenic flysch sequences of the Gelnica Group.

Pz - 5 - Lydites - form thin-bedded bodies along with black phyllites and carbonates. Accumulation of rare earth elements is strongly related to the content of former clayey and organic matter.

3b. Late Paleozoic of the Gemericum

Pz - 6 - Psammites - are widely distributed in Carboniferous and Permian formations. The grade varies of metamorphism from anchizone to low - temperature greenschist facies. Dominant rock forming mineral in Lower Carboniferous metapsammites is quartz (70-80 %, in some cases even more) accompanied by plagioclase, micas and fragments of schists, lydites, volcanites, gneisses and rare granitoids. Westphalian metapsammites contain mainly rock fragments (50 %) together with feldspars (13 %), quartz (36 %) and micas (2 %). The only exception is the Upper Westphalian metapsammites of Hámor Formation, containing predominantly quartz grains (80 %) with minor feldspars (5 %) and rock fragments (15 %) (Vozárová, Vozár, 1988).

Permian metapsammites of the northern and southern Gemeric Units are distinctly different. The north-Gemeric psammites are relatively richer in feldspars (19 %) and rock fragments (20 %) with less content of quartz (50-60 %). Dominant rock forming mineral in the south Gemeric psammites is quartz (in average 90 %) accompanied by feldspars (3-8 %), micas (1-2 %) and rare fragments of acid volcanics.

Pz - 7 - Pelites, siltstones - Carboniferous pelites contain a detrital admixture dominated by quartz and clastic micas. Permian sediments contain, in addition to quartz and micas, also fragments of various rocks. As a consequence of different sedimentary and climatic conditions the Carboniferous metapelites contain organic admixture and Permian shales iron oxides.

Pz - 8 - Acid volcanics and volcanoclastics - are most widespread in Permian sequences of the northern and southern Gemericum and in the Bôrka Nappe. Their chemistry shows calc-alkaline affinity. Felsitic varieties with minor content of quartz, K - feldspar and plagioclase phenocrysts dominate. In general, different types of volcanoclastics prevail.

Pz - 9 - Intermediate and basic volcanics and volcanoclastics - are most widely distributed in Carboniferous sequences of the northern Gemeric zone, in minor quantities also in the Permian of the same zone. Their magmatic affinity is completely different. Carboniferous volcanics are of tholeiitic type with an E-MORB trend and Permian andesite/basalts have calc-alkaline affinity.

Pz - 10 - Limestones - In the Late Paleozoic Gemeric units they occur in the Lower Carboniferous Ochtiná Formation and Črmeľ Group, and in the Upper Carboniferous Zlatník Formation. Among carbonate minerals, calcite is common and dolomite rare. Their chemical composition was influenced by detritic admixture (clayey material, quartz grains).

Pz - 11 - Dolomites and magnesites - These carbonates are associated with limestones. Magnesites occur primarily in the Lower Carboniferous. Principal carbonate minerals comprise dolomite and magnesite. Also talc + quartz, as a part of critical metamorphic mineral association are present.

3c. Late Paleozoic of the Tatricum, Veporicum, Zemplinicum and Hronicum

Pz - 12 - consists of two rock subgroups:

a) Psammites of the Lower Paleozoic in the Tatricum, Zemplinicum and Veporicum. Their composition corresponds to arkoses, arkosic graywackes and lithic graywackes. Content of main rock forming minerals vary in a wide range (in volume %): Quartz (20-65 %), feldspars (18-34 %), micas (8-20 %), rock fragments including synsedimentary volcanites (9-27 %). Metamorphic mineral assemblages indicated anchizone to low - temperature greenschist PT-conditions.

b) Psammites of the Hronic Late Paleozoic.
Sandstones are the most widespread lithotype here. They occur in both Carboniferous and Permian sequences. Quartz (54-66 %); feldspars (20 %), micas (6-4 %) and rock fragments (14-26 %) are their principal constituents (range in volume %).

Psammites of the Hronic Late Paleozoic are mostly unmetamorphosed. Their alteration reached PT conditions of diagenesis or the low - temperature part of anchizone (Plašienka et al., 1989, Šucha, Eberl, 1992).

Pz - 13 - Pelites and siltstones. These include Late Paleozoic pelites and siltstones in the Tatricum, Veporicum and Zemplinicum, as well as Late Paleozoic siltstones in the Hronicum. Their composition, as well as grade of metamorphism, reflects close association with psammite equivalents. In general, the pelites of the Veporicum, Tatricum, Zemplinicum show a low degree of maturity, with the admixture of course detritic material. Pelites and siltstones of the Hronicum are relatively more mature. Carboniferous sediments contain a variable admixture of organic matter. Permian fine grained sediments contain iron oxides or dolomitic concretions.

Pz -14 - Acid volcanics and volcanoclastics of the Veporicum, Zemplinicum and Tatricum. Rhyolite-dacite volcanoclastics and ignimbrites prevail over effusive varieties.

Their chemical composition shows calc - alkaline affinity. The characteristic feature of the volcanics is mainly the felsitic matrix and sparse phenocrysts (mainly 5-10 %, rarely 30 %).

Pz - 15 - Intermediate and basic volcanics of the Hronic Late Paleozoic are part of the Permian sequence. Characteristic is the manifold repeating of lava-flows, intraeffusive volcanoclastics or brecciated lavas in layers. Their bulk chemical composition and distribution of immobile elements indicate their continental tholeiitic affinity (WPB, Vozár, 1977).

4. Mesozoic

Mz - 1 - Limestones are fairly pure rocks of various lithostratigraphic and tectonic units, widespread across Slovakia: calcarenite limestones, reef limestones, lagoonal limestones, crinoidal limestones, nodular limestones, mud limestones and crystalline limestones.

Mz - 2 - Clayey limestones of Triassic to Lower Cretaceous age, mostly Cretaceous limestones in the Veporicum with less abundant Triassic limestones of the higher subtatric nappes.

Mz - 3 - Marlstones of Cretaceous and Paleogene age, accompanied by spotted limestones and minor nodular limestones of the Klippen Belt.

Mz - 4 - Sandy limestones - Jurassic limestones of the Tatricum, assigned to the Orešany, Tribeč and Donovaly Groups and limestones of the Krížna nappe.

Mz - 5 - Siliceous limestones to silicites - a group of Dogger - Malm siliceous limestones and radiolarites in the Veporicum, and cherty limestones of Triassic age in the Hronicum or of Cretaceous age in the Tatricum.

Mz - 6 - Dolomites of Middle to Upper Triassic age in the Tatricum, Veporicum, Hronicum and, less frequently, in the Silicicum. The dolomites are very pure.

Mz - 7 - Dolomites of Carpathian Keuper form layers of primary chemogenic dolomites in the variegated Carpathian Keuper formation. The dolomites are enriched in silica and alumina.

Mz - 8 - Claystones, sandy claystones of Triassic and Jurassic age - Lower Triassic claystones largely in the Tatricum and Silicicum, claystones in the Carpathian Keuper of the Tatricum and Veporicum, and claystones of the Lunz Member in the Hronicum. All these claystones are fairly sandy.

Mz - 9 - Claystones, sandy claystones of Cretaceous to Paleogene age. Unlike Triassic claystones of the Inner Carpathians (Mz-8), these claystones are less sandy, but richer in carbonate admixture.

Mz - 10 - Sandstones, quartzose sandstones to quartzites of Triassic and Jurassic age. This variegated group consists of sandstones and quartzites of the Tatricum, Veporicum and Silicicum, Upper Triassic quartzites of the Tatricum, Upper Triassic sandstones of the Veporicum and Hronicum, and Cretaceous sandstones of the Tatricum. The rocks are rich in silica and poor in CaO.

Mz - 11 - Carbonatic sandstones and conglomerates of Cretaceous and Paleogene age are carbonatic sandstones and conglomerates of Jurassic to Paleogene flysch sequences in the Klippen and Near-Klippen Belt.

Mz - 12 - Metabasalts of the Bôrka nappe include glaucophanites and greenschists.

5. Paleogene

5a. Inner-Carpathian Paleogene

Pg - 1 - Sandstones (except in the Biely Potok Formation). This set comprises sandstones with a variable content of carbonate material, mainly of the Zuberec and Huty formations, less the Borové Formations, in which sandstones are relatively not so abudant.

Pg - 2 - Claystones - This group includes primarily claystones of the Huty and Zuberec Formations which have variable carbonate content.

Pg - 3 - Breccias, conglomerates and carbonates - Mainly in the Borové Formation.

Pg - 4 - Sandstones of the Biely Potok Formation are sandstones with a carbonate admixture. These sandstones are richer in silica and lower in carbonates in comparison with the set Pg - 1.

5b. Outer Carpathian Paleogene

Pg - 5 - Dukla unit sandstones - The set embodies more or less carbonatic sandstones. Most samples come from the Menilite and Submenilite Members, the Lupkov, Čergov and Zboj Members are represented by fewer samples.

Pg - 6 - Dukla unit claystones - These claystones are represented mainly by the samples from Menilite, Submenilite and Čergov Members, sparcer are the samples from the Variegated Submenilite, Lupkov and Zboj Members.

Pg - 7 - Magura unit sandstones - In comparison with the Dukla unit sandstones (Pg - 5), these sandstones contain more quartz and less carbonate. Most samples come from the Zlín and Strihov Members, and less from the Bystrica, Racibor, Lupkov, Vychylovka and some other Members.

Pg - 8 - Magura unit claystones - These rocks are represented mainly by the Zlín Member and to a lesser extent also by the Bystrica, Strihov, Beloveža,Vychylovka and some other Members.

6. Sedimentary Neogene

Ne - 1 - Clays, claystones are widespread across Slovakia, but they occur in Inner Carpathian basins and the Miocene of the Eastern Slovakia Basin. Unlike the Ne - 2 group, these rocks have little or no carbonate admixture.

Ne - 2 - Calcareous claystones, marlstones - A variegated set of rocks occur in all Slovakia's Neogene basins, but mainly in the Miocene of the Eastern Slovakia Basin, Inner-Carpathian basins and in the Miocene of the Danube Basin.

Ne - 3 - Sands, sandstones, silts, siltstones - These occur in the Southern Slovakia Basin, Danube Basin and Inner-Carpathian basins. Unlike the Ne - 4 group, these rocks are mostly devoid of carbonate admixture.

Ne - 4 - Calcareous sandstones and siltstones make up a variegated set of rocks widespread throughout Slovakia, mainly in the Oligocene and Miocene of the Southern Slovakia Basin, and in smaller amounts also in the Miocene and Pliocene of the Danube Basin, in the Miocene of the Eastern Slovakia Basin and in the Vienna Basin.

Ne - 5 - Sandy limestones and limestones - These are present in the Upper Oligocene and Miocene of the Southern Slovakia Basin, Inner-Carpathian basins and the Vienna Basin.

Ne - 6 - Tuffaceous sediments - These comprise tuffaceous claystones, siltstones and sandstones in basins adjacent to Neogene volcanics in central and eastern Slovakia (Southern Slovakia, Upper Nitra, Žiar, Zvolen, Košice and other basins).

7. Neogene volcanics

Nv - 1 - Basalts and basaltic andesites are porphyritic rocks with phenocrysts of basic plagioclase, augite, olivine or hypersthene and titanomagnetite in a groundmass of plagioclase, pyroxene and magnetite. They occur in the form of massive lava, scoraceous breccias, agglomerates and tuffs, mostly as a part of large stratovolcanoes.

Nv - 2 - Pyroxene and hornblende-pyroxene andesites are porphyritic rocks with phenocrysts of plagioclase. augite and/or hypersthene, magnetite and rare olivine or biotite, in a groundmass of plagioclase, pyroxene, magnetite and comonly also altered glass. Rocks of this category dominate in structure of andesite stratovolcanoes in the central and eastern Slovakia alike.

Nv - 3 - Pyroxene-hornblende, hornblende and biotite-hornblende andesites and dacites are porphyritic rocks with phenocrysts of plagioclase, hornblende, biotite and rare hypersthene, augite, olivine, quartz in groundmass of acid plagioclase, sanidine, quartz, pyroxene, magnetite and usually also glass. They mostly form effusive complexes and extrusive domes associated with large stratovolcanoes, and they are associated with pyroclastic breccias, pumice tuffs and epiclastic breccias.

Nv - 4 - Rhyodacites and rhyolites are mostly porphyritic rocks with phenocrysts of acid plagioclase and/or sanidine, quartz, biotite and rare hornblende or hypersthene in a groundmass of sanidine, quartz and glass. They occur in the form of extrusive domes and dome flows associated with tuffs, pumice tuffs and epiclastic volcanic breccias and sandstones.

Nv - 5 - Propylitized andesites and andesite porphyries. This group includes mostly pyroxene and hornblende-pyroxene andesites and andesite porphyry affected by propylitic alterations in surroundings of intrusive stocks and hydrothermal systems in central zones of large andesite stratovolcanoes.

Nv - 6 - Diorites and diorite porphyry are equigranular or porphyritic holocrystalline rocks composed of basic plagioclase, pyroxene, hornblende and rare magnetite, quartz, biotite. They occur as stocks in central zones of andesite stratovolcanoes and are affected by propylitic alteration.

Nv - 7 - Granodiorite is a coarse grained rock composed of intermediate plagioclase, biotite, hornblende, quartz, orthoclase and accessory magnetite, apatite and zircon. It crops out only in the Hodruša sector of the Štiavnica stratovolcano central zone.

Nv - 8 - Granodiorite porphyries are composed of plagioclase, hornblende, biotite and quartz phenocrysts, in a groundmass of quartz and orthoclase. They occur next to Pukanec and in the Štiavnica stratovolcano central zone, variably affected by silicification, sericitization and pyritization.

Nv - 9 - Quartz-diorite porphyries are composed of plagioclase, hornblende, biotite and quartz phenocrysts, in a groundmass of acid plagioclase, quartz and orthoclase. They form dykes and sills in the ćtiavnica stratovolcano central zone.

Nv - 10 - Alkali basalts and basanites are almost aphanitic rocks with sparce phenocrysts of plagioclase, augite, olivine and rare kersutitic hornblende, in a prevailing groundmass of acid plagioclase, pyroxene, magnetite and nepheline. They occur as lava flows, cinder/spatter cones, maars and diatremes in the Cerová Vrchovina Highlands and Lučenec Basin, and rarely also in the Central Slovakia volcanic field.

Lithogeochemical database

For each of the 3 839 samples - records, following information is available in the database: name of the sample, author, year, regional and local geologic setting, x and y coordinates, lithostratigraphy, petrographic data, chemical analyses for all major and 26 minor elements and some other data). dBase IV (dbf format) was used for the lithogeochemical database.

Map of lithogeochemical types of Slovakia at a scale 1 : 500 000

This map will appear as a part of the "Catalogue of the Main Rock Types of Slovakia" in 1998.

All geochemically defined lithotypes / lithofacies are shown on the map either as simple lithotypes or as a set of lithotypes due to their tight bedding. The legend of the map contains 54 items, from which about a half represent two and more lithotypes because of the complicated geological structure of Slovak territory. The map of the lithogeochemical types of Slovakia has a close relation to the Geological map of Slovakia 1 : 500 000 (Biely et al., 1992), from which it takes the majority of contours.

Simple lithotypes are distinguished on the map by numeric indexes and colour. Associated lithotypes are shown by a striped raster, with different colours according to the proportion of the individual component lithotypes.

The colour designation of lithotypes was chosen on the basis of four principal minerals groups, as follows:

carbonates - blue colour
mafic silicates - green colour
feldspars and micas - red colour
silica - yellow colour

Transitional lithotypes are coloured by transitional colours and with different intensity. The colour scale was chosen for the case by which one can distinguish carbonate and mafic rocks with their high buffering capacity (blue and green colours - favourable for the environment) from more acid rocks (red and orange colours) with their low buffering capacity and siliceous rocks (yellow colours - not favourable for the environment).

This map is considered to be a basic body of information on lithology for further regional geochemical mapping.

Summary and Conclusions

The above work, as a part of the Geochemical Atlas of Slovak Republic, presents the results of geochemical mapping of the main rock types on the Slovak territory.

64 main rock types were distinguished mainly according to lithological and geochemical-statistical criteria. The results reflect the very complicated geological structure of Slovakia with its large variety of rock types. The geochemical variability of these rocks is documented by the distribution of all major and 26 minor elements in them. Since the sampling was focused mainly on unaltered and unmineralized rocks, the results reflect the primary lithology.

These new and complex basic statistical data on element distribution of all main rock types represent an information which can be used in various ways:

- for setting the lithological background values for the whole territory of the Slovak Republic
- for distinguishing between geochemical anomalies caused by primary lithology and anomalies caused by metallogenic processes and anthropogenic impacts in

rocks and other researched media (soils, water, stream sediments, biomass)

- as a contribution for other projects dealing with the research of geological factors of environment at regional and local scales

- it provides the data sets, needed for comparison with the data in other countries.

All the primary data are in the Lithogeochemical database (dBase IV format) comprising 3 839 samples - records with chemical analytical data and other information (including geologic setting, x and y co-ordinates, litostratigraphy etc).

As an important part of this work, the Map of Lithogeochemical Types of Slovakia at a scale of 1 : 500 000 was compiled. The colour designation of lithotypes was chosen on the base of four principal minerals groups for rapid distinguishing between rocks favourable (carbonatic and mafic rocks) and not favourable (siliceous rocks) for the environment.

All the achievements of the subproject "Rocks" will be published in more detail during 1998 as "Catalogue of the Main Rock Types of Slovakia".

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Geochemical Atlas of Slovak Republic Part Soils

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Abstract. Soil samples were collected from 5000 soils profiles throughout the country with density of 1 sample per 10 km^2. Samples were tested for 36 chemical elements concentrations. For each element computerised monoelemental map was constructed.

The preliminary results on geochemical mapping of Slovakian soils presented in this paper deal with basic problems of soil pollution in Slovakia documented with few examples of geochemical maps and with background values for the some of the risk elements (As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Zn), in major soil units.

Based on geochemical mapping a first understanding of the distribution of chemical elements in Slovakian soils is outlined. Soils are more highly contaminated around the sites with ore mining, smelting and reworking operations. From the sites with an old mining history the pollution has spread to the alluvial river plains. Some of the highest mountainous parts and some border mountains ranges intercept aerosols and may point to the transboundary air pollution, by trace elements.

***Key words*:** soil- geochemical mapping, soil pollution, soil background values, chemical elements distribution, geochemical atlas

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Introduction

Soil has great significance to all life; vegetation is rooted in it and water infiltrates through it. Geochemical mapping of soils, showing surface distribution of chemical elements and risk substances can contribute to a general awareness on soil deterioration and its possible adverse effects to other environmental constituents.

Subproject "Soils" is guided by Soil Fertility Research Institute (Bratislava). About 5000 soil profile were described, composite samples were collected and analysed from upper (A-) and deep (C-) soil horizons throughout the country. The total content of 36 of major and trace chemical elements has been ascertained. By this way a first understanding of chemical element distribution is established in relative to geology and soil types.

At present, the analytical programme is not finished. Therefore the presented information is preliminary. The present chemical analyses represents extensive data collection (set of 4491 samples from A and 4531 from C horizons). The data set is statistically representative and no statistically significant changes are expected in the final stage. Small corrections in the graphic presentations can, however, occur.

The aim of this paper is to gain an overall picture on the background values for some risk elements in soils and finally approach a first draft of maps of the spatial distribution of some chemical elements in soils. From the above statement is evident that some areas with the elements excesses and deficiencies that could prejudice some environmental problems can be later detected.

Very promising results can be also expected in the following stage by the synthesis of the results obtained from the geochemical mapping of stream sediments, rocks, water and biota which will provide an overall picture on environmental pollution in Slovakia.

Methodology

The primary reference network is based on 10 km^2 grid cells distributed over all country. In these cells the soil samples were taken at random. The samples were taken from A, B and C horizons. From the financial reason only samples from A and C horizons were analysed for the assemblage of 36 elements: Al (AES-ICP, det.lim.:1ppm), As(HG-AS, 0.5ppm), B (AES-ICP, 1ppm), Be (AES-ICP, 0.2ppm), Ca (AES-ICP, 1ppm), Cs (FAAS, 1ppm), Cu (AES-ICP, 0.1ppm), F (ISE, 300ppm), Fe (FAAS, 1ppm), Ga (AES-ICP, 2ppm), Hg (AAS-ETA, 0.01ppm), K (AES-ICP, 20ppm), La (AES-ICP, 1ppm), Li (AES-ICP, 1ppm), Mg (AES-ICP, 10ppm), Mn (AES-ICP, 0.1ppm), Mo (AES-ICP, 0.2ppm), Na (AES-ICP, 1ppm), Ni (AES-ICP, 1ppm), P (AES-ICP, 50ppm), Pb (AES-ICP, 0.5ppm), Rb (FAAS, 1ppm), Sb (HG-AAS, 0.1ppm), Se (HG-AAS, 0.1ppm), Sn (AES-ICP, 1ppm), V (AES-ICP, 3ppm), W (AES-ICP, 1pmm), Y (AES-ICP, 1ppm), and Zn (AES-ICP, 0.2ppm). At each site 3-5 subsamples were collected and one composite sample was prepared for each horizon. The samples were prepared by dry sieving. The fraction < 0.125 mm was then used for the chemical analysis and the fraction < 2 mm was used for the soil analysis (Čurlík and Šefčík 1994).

The analytical requirements are compatible with the international standards and accuracy of the results have been tested. Above mentioned analytical methods were employed in the EL spol. s r.o. Spišská Nová Ves. No changes in the methodology of sample preparation and analytical procedures proceeded during this project.

All data (soil morphology, chemical analyses) are stored in a database. Stored duplicate samples are kept in contaminant free containers for the future use. Basically the principles for the geochemical mapping published in Darnley et al. (1995) have been followed.

Soil analysis (pH, carbonate status, texture) were carried out in Soil Fertility Research Institute (Bratislava) using routine soil analytical methods.

Soils in Slovakia

In regional sense, with respect to the: geological history this territory belongs to the young Alpine - formed mountain ranges of the northern branch of the Alpine - Himalayan belt. This was formed in a complicated nappe - forming process which has reflected in a considerable shortening of the depositional areas, accumulation of rock complexes as well as reduction of tectonic units. This resulted in complicated geology (lithology) and relief.

Due to this development (during late Neogene and Quaternary) the relief of Slovakia is characterised by two marked geological - geomorphological formations: by the (West) Carphatian arc (mountains) and adjacent lowlands.

The main soil units occurring in Slovakia are related to the soil parent material and to the relief (altitudes). The great orographical manifoldness and complicated lithology has influenced soil cover diversity in both formations. The extension of soil units in agriculture and forest lands present the Tables 1 and 2.

Subcarpathian lowlands

Mantle rocks of the lowlands differ from one region to another:

In *Záhorská nížina lowland* (West Slovakia - part of Vienna basin) the main part is covered by Quaternary aeolian sands. Relative low fertile soils as Protic, Haplic and Cambic Arenosols, up to locally Arenic Podzols are present under the forest vegetation. On places with shallow groundwater tables, with present or former hydromorphism so called "black sands" (Histi-Mollic Gleysols and Arenic Gleysols) occur (humus accumulation). In northern of this lowland (Chvojnická pahorkatina hillyland) Luvisols prevail. But on loess some Chernozems are present. Locally also small spots with Haplic Vertisols on heavy clays occur.

Podunajská nížina lowland (Danubian lowland) comprises of alluvial sediments and loess. On young (Holocene) alluvial sediments of the lowland Calcaric Fluvisols and Fluvic Gleysols are evolved. On older alluvial sediments not inundated at present Mollic Gleysols and Mollic Fluvisols (all of them Calcaric) and even Calcaric Haplic Chernozems are developed. In southern part of Danubian lowland with shallow groundwater tables and with highly mineralized water salt affected soils locally occur (Solonchaks and Solonetz). In the depressions, especially in old oxbow lakes, Haplic Histosols are present.

In *Východoslovenská nížina lowland* (East Slovakian lowland) which is covered prevailingly by non-calcareous, heavy textured alluvial sediments, various units of Fluvisols and Gleysols occur, prevailingly Eutric Fluvisols, Vertic Fluvisols and Fluvic Gleysols. Very locally Arenosols are developed on sand dunes. Also salic and sodic soils occur here rarely. On hilly part of this lowland Stagnosols, Stagni-Haplic Luvisols and Stagnic Glossisols predominate. On loess cover Luvi-Haplic Chernozems and Stagni-Haplic Chernozems occur.

Intramountainous basins

Mostly tectonic- erosional basins can be divided in three groups:

Lower basins, Middle basins and Higher basins

Lower basins (up to about 300 m above sea level) are covered partly by loess, loess-like sediments and alluvial sediments. To this type belong Košická kotlina, Lučenecká kotlina basins and middle part of Váh river basin. Luvisols and Luvic Stagnosols with sporadic occurrence of Luvi- and Stagni-Haplic Chernozems and Cambisols are present in Košická kotlina basin. Cambisols can be found also on clayey - gravely Neogene sediments of the Lučenecká kotlina basin and on similar alluvial sediments of river Váh basin.

Middle basins (about 300 to 500 m above sea level) - compresses mostly of colluvial and alluvial sediments (Žilinská, Hornonitrianska, Zvolenská, Žiarska, Pliešovská, Rožňavská and Hornádska kotlina basins). In Stagnosols and Albic Luvisols with Stagnic properties and Eutric Cambisols with Stagni-Eutric Cambisols on stony colluvial sediments are predominant. In Stagnosols and Albic Luvisols with Stagnic properties and Eutric Cambisols with

Stagni-Eutric Cambisols on stony colluvial sediments are predominant. On the calcaric rocks in the Hornádska kotlina basin Rendzic Leptosols are developed.

Higher basins (over 500 m above sea level) like those of Turčianska, Liptovská, Popradská and Oravská kotlina basins as well as the Horehronské podolie basin are typical of higher precipitation and cooler climate. Here Dystric Planosols, Luvic- and Gleyic Stagnosols and Stagni-Dystrc Cambisols predominate. These units are accompanied with other Cambisols, Glossisols, Rendzinic Leptosols and Fluvisols and as inclusions Fibric Histosols. In Turčianská kotlina basin even Calcari-Mollic Fluvisols occur on carbonatic sandy materials.

Soils of Mountains

Geological units of West Carpathian Arc- or better to say- units of internal part of the orogenic zone consist of Mesozoic complexes of the Alpine geosyncline (mostly limestones and dolomites) of the Late and Early Paleozoic, and of crystalline complexes in the core mountains (mostly granitic rocks and crystalline schists). This complexes belong to the internides. Externides are formed by Alpine flysch sequences with nappe structure. Paleogene flysch zone consists of sandstones and claystones. In this zone clayey and loamy-sandy Dystric Cambisols and Stagni-Eutric Cambisols are predominant, but Eutric Cambisols, Stagnic Glossisols and varied Stagnosols are frequent too. In Klippen zone, Rendzic Leptosols and Rendzi-Lithic Leptosols occur.

Tab. 1: Soil units in agricultural land

Soil Units (WRB, 1994)	ha	%
Histosols	4 895	0.2
Anthrosols	129 702	5.3
Rendzic Leptosols	85 652	3.5
other Leptosols	12 236	0.5
Mollic Fluvisols and Mollic Gleysols	178 645	7.3
other Fluvisols	386 658	15.8
other Gleysols	19 578	0.8
Solonchaks and Solonetz	4 894	0.2
Andosols	2 450	0.1
Podzols	2 447	0.1
Planosols	134 596	5.5
Chernozems	291 217	11.9
Phaeozems	4 894	0.2
Haplic Luvisols	286 322	11.7
Albic Luvisols and Glossisols	105 230	4.3
Stagnosols	141 937	5.8
Eutric Cambisols	391 552	16.0
Dystric Cambisols and Umbrisols	239 826	9.8
Arenosols	24 472	1.0
Agricultural Soils of Slovakia	*2 447 203*	*100.0*

On the Crystalline rocks of the West Carpathians changing with altitudes a row of various soils, from Eutric Cambisols over Dystric Cambisols, Cambic Umbrisols, Cambic (Umbric) Podzols up to Haplic Podzols and Leptosols are developed.

On the Mesozoic rocks (mostly limestones and dolomites) Rendzic Leptosols and Rendzi-Lithic Leptosols prevail. On the karst plateaus with preserved Terrae Calcis material Chromic Luvisols and Stagni-Chromic Luvisols are sporadically developed.

On the intermediary to basic volcanic rocks Eutric Cambisols are developed, except of greater heights where Dystric cambisols both with inclusions of Andosols are present.

Tab. 2: Soil units in forest land

Soil Units (WRB, 1994)	ha	%
Lithic Leptosols	7 962	0.4
Rendzic Leptosols	288 611	14.5
other Leptosols	49 760	2.5
chromic soils (Leptosols, Luvisols)	39 809	2.0
Fluvisols	5 971	0.3
Gleysols	39 809	2.0
Andosols	29 856	1.5
Podzols	69 664	3.5
Chernozems	1 990	0.1
Haplic Luvisols	5 971	0.3
Albic Luvisols and Glossisols	238 851	12.0
Planosols and Stagnosols	39 809	2.0
Calcaric Cambisols	19 904	1.0
other Cambisols and Umbrisols	1 144 494	57.5
other soils (salic, sodic, histic, anthropic, etc.)	7 962	0.4
Forest Soils of Slovakia	*1 990 424*	*100.0*

Background values for the main soil units

The soil quality and environmental risk assessment for soil has became one of the important environmental issues. The public concern for soil pollution has recently lead to the approval of a soil legislation also in Slovakia (Soil protection law No. 307/1994) within which Dutch ABC list for risk substances has been adopted (Tab. 3).

This reference list for the large number of pollutants (inorganic and organic) is known from the literature. Meanwhile this list was modified and attention is paid to put it on a scientific basis (ecotoxicological risk concept, no observable adverse effect concentration - NOAEC concept, etc.). But the idea of background values for soils is still the main principle for the target values definition in relation to the metals.

In order to understand the real distribution of risk elements in soils since they are usually natural soil com-

Tab. 3 Reference list for inorganic contaminants in soils used in Slovakia (mg.l)

					Background value	
	A	**A1**	**B**	**C**	**A-horizon**	**C-horizon**
As	29	5	30	50	7,10	6,40
Ba	500		1000	2000		
Be	3		20	30		
Cd	0,8	0,3	5	20	0,30	0,10
Co	20		50	300	9,00	10,00
Cr	130	10	250	800	85,00	86,00
Cu	36	20	100	500	17,00	17,00
Hg	0,3		2	10	0,08	0,04
Mo	1		40	200		
Ni	35	10	100	500	24,00	28,00
Pb	85	30	150	600	20,00	13,00
Se	0,8		5	20	0,10	0,05
Sn	20		50	300		
V	120		200	500		
Zn	140	40	500	3000	61,00	54,00

ponents, the pollutant concentration need to be checked against the background values for unpolluted soils (Baize, 1995; Vanmechelen et al., 1995). It is clear that when more such descriptive soil investigation are carried out for the complicated soil and geological conditions (and Slovakia is one of the examples), a good basis for the comparison could be obtained. Geochemical mapping of Slovakian soils gave us an opportunity to determine the background values for risk elements in ten major soil units.

Informations obtained by sampling of unpolluted soils should be characterised as "current background values" or "present background values for not abnormally polluted soils" because diffuse contamination caused by atmospheric deposition is accounted for, together with the pollution caused by the fertilisers and chemicals which are normally used in the practise (Vanmechelen et al., 1995).

In the table 4 the background values for the A- and C-horizons of major soil units are presented as results obtained from geochemical mapping. They include the assemblage of following chemical elements: As, Ba, Cd. Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Zn, which are considered as risk elements.

Closer look to the values and to the individual chemical elements point to several conclusions:

Tab. 4: Background values of the risk chemical elements in the main soil units (mg.kg^{-1})

Soil units (FAO)	**Horizons**	**Count**	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**
Chernozems	A	344	7,4	395	0,20	9,0	82	20	0,01	28,0	15	0,5	0,10	56
	C	360	6,8	343	0,15	8,0	72	16	0,02	26,0	10	0,4	0,07	45
Orthic Luvisols	A	346	6,7	393	0,20	9,0	89	17	0,10	26,0	16	0,6	0,05	54
	C	352	7,6	395	0,10	10,7	88	17	0,03	29,7	14	0,6	0,06	53
Albic Luvisols	A	224	5,7	360	0,20	7,0	79	12	0,10	19,0	22	0,7	0,10	50
	C	226	7,7	422	0,14	11,0	91	20	0,06	27,0	14	0,8	0,13	55
Dystric Planosol	A	219	5,2	387	0,10	8,0	88	12	0,10	19,0	15	0,4	0,05	44
(Pseudogleys)	C	216	7,3	418	0,10	12,0	98	18	0,05	28,0	14	0,5	0,09	52
Phaeozem	A	204	7,0	390	0,30	9,0	85	25	0,10	32,0	18	0,4	0,10	84
	C	205	7,6	379	0,16	9,5	78	19	0,03	32,0	11	0,5	0,09	52
Rendzinas	A	204	12,5	240	0,85	9,0	69	18	0,30	25,5	42	17,0	0,10	84
	C	206	10,2	225	0,66	9,0	67	19	0,19	32,6	20	0,9	0,10	58
Cambisols	A	1584	6,9	383	0,30	9,0	85	16	0,10	22,0	23	0,8	0,10	65
	C	1607	6,1	398	0,10	11,0	81	18	0,10	29,0	14	0,5	0,05	60
Podzols	A	65	10,0	383	0,40	3,0	44	10	0,30	7,0	61	2,6	0,10	44
	C	64	7,2	444	0,15	6,0	60	10	0,10	16,0	18	0,8	0,10	53
Fluvisols	A	356	7,3	373	0,30	10,0	93	22	0,10	32,0	13	0,6	0,10	70
	C	345	6,9	390	0,20	10,0	92	19	0,01	31,0	14	0,4	0,01	58
Gleysols	A	47	6,4	414	0,30	11,0	109	24	0,10	44,0	23	0,5	0,10	79
	C	49	5,9	464	0,10	10,0	120	28	0,10	44,0	16	0,4	0,05	66

Tab. 5 : Statistical parameters of the risk elements content in A-horizons (mg.k^{-1})

Descriptive statistics		As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	Se	Zn
Agriculture soils	Median	6,70	0,20	9,00	89,00	19,00	0,06	27,00	17,00	0,60	0,05	59,00
	Mode	5,70	0,20	9,00	90,00	18,00	0,04	27,00	16,00	0,40	0,05	56,00
	Minimum	0,25	0,01	0,10	2,50	3,00	0,00	2,50	6,00	0,05	0,05	13,00
	Maximum	732,00	8,90	117,00	6096,00	1240,00	98,00	2066,00	2122,00	247,00	2,50	2160,00
	Count	2822	2822	2822	2822	2822	2822	2822	2822	2822	2822	2822
Forest soils	Median	7,90	0,40	8,00	73,00	14,00	0,13	18,00	31,00	1,10	0,10	65,00
	Mode	6,10	0,20	6,00	69,00	10,00	0,09	2,50	23,00	0,60	0,05	66,00
	Minimum	0,25	0,01	0,10	8,00	2,00	0,01	2,50	5,00	0,20	0,05	9,00
	Maximum	592,00	8,50	43,00	1241,00	22360,00	50,33	275,00	810,00	62,00	1,10	1865,00
	Count	1669	1669	1669	1669	1669	1669	1669	1669	1669	1669	1669
Whole soils	Median	7,10	0,30	9,00	85,00	17,00	0,08	24,00	20,00	0,70	0,10	61,00
	Mode	5,70	0,20	9,00	90,00	17,00	0,04	27,00	16,00	0,50	0,05	56,00
	Minimum	0,25	0,01	0,10	2,50	2,00	0,00	2,50	5,00	0,05	0,05	9,00
	Maximum	732,00	8,90	117,00	6096,00	22360,00	98,00	2066,00	2122,00	247,00	2,50	2160,00
	Count	4491	4491	4491	4491	4491	4491	4491	4491	4491	4491	4491

Tab. 6: Statistical parameters of the risk elements content in C-horizons (mg.kg^{-1})

Descriptive statistics		As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	Se	Zn
Agriculture soils	Median	6,70	0,20	9,00	88,00	18,00	0,04	29,00	13,00	0,40	0,05	54,00
	Mode	5,00	0,20	8,00	80,00	15,00	0,02	28,00	13,00	0,30	0,05	41,00
	Minimum	0,25	0,01	0,10	2,50	1,00	0,00	2,00	1,00	0,05	0,05	0,50
	Maximum	913,00	6,10	90,00	963,00	12500,00	446,00	370,00	3258,00	1165,00	36,00	2380,00
	Count	2854	2854	2854	2854	2854	2854	2854	2854	2854	2854	2854
Forest soils	Median	5,70	0,10	10,00	81,00	15,00	0,06	23,00	14,00	0,60	0,10	55,00
	Mode	4,00	0,01	10,00	91,00	12,00	0,03	2,50	13,00	0,40	0,05	40,00
	Minimum	0,25	0,01	0,10	2,50	1,00	0,00	2,50	1,00	0,05	0,05	4,00
	Maximum	2438,20	17,80	83,00	1084,00	4320,00	26,00	509,00	511,00	522,00	4,70	1056,00
	Count	1677	1677	1677	1677	1677	1677	1677	1677	1677	1667	1677
Whole soils	Median	6,40	0,10	10,00	86,00	17,00	0,04	28,00	13,00	0,50	0,05	54,00
	Mode	5,00	0,01	10,00	89,00	15,00	0,03	27,00	13,00	0,30	0,05	40,00
	Minimum	0,25	0,01	0,10	2,50	1,00	0,00	2,00	1,00	0,05	0,05	0,50
	Maximum	2438,20	17,80	90,00	1084,00	12500,00	446,00	509,00	3258,00	1165,00	36,00	2380,00
	Count	4531	4531	4531	4531	4531	4531	4531	4531	4531	4531	4531

- Some elements as As, Cd and Hg show highest values in such genetically different soils as Rendzinas and Podzols. Both soil are present in the high mountainous positions. This may be an evidence for the airborne origin of these elements brought to the soils by dust deposition no prove is presented.
- The highest values are for the Ba in Podzols which is due to higher content of Ba in feldspars (Podzols are developed mostly on granitic rocks) and partly due to Ba accumulation in sesquioxides (Mn-oxides). Similar reason may be accounted for the higher content of Ba in Gleys (higher content of Fe-Mn oxides in upper part of gley horizons).
- Higher values for Cr and Cu may be due to deposition on reducing geochemical barriers (Gleys and Fluvisols) and due to affinity of these chemical elements to organic matter.
- Cobalt which is leached from the soil profiles is rather uniformly distributed in the main soil units but its content is low.
- Nickel shows some increased values in soils with higher humus (organic matter) content. Grand mean (in sense of the authors Kabata-Pendias and Pendias, 1992 - means "mean" for various soil types) calculated for the world soils 22 mg.kg^{1} is not very much higher in Slovakian soils.

Lead opposite to Ni may be bound to the feldspars which are most abundant in the granitic rocks. The highest values in Podzols may be due to feldspars content but some particulate matter deposition could also contribute to this increase.

- Antimony - background values are higher in Podzols because Sb-mineralisation is found in crystalline rocks of Nízke Tatry Mts. Malé Karpaty Mts. and Spišsko-gemerské rudohorie Mts. The background values in other soil units are similar to the world soils (Kabata-Pendias and Pendias, 1992).
- Selenium content in Slovakian soils is generally low. This values range Slovakian soils to the selenium poor.
- Zinc which is concentrated in clay fraction of the soils does not correlate with the soil units.
- Generally there are some relations to the soil litological units (Pb, Ba content in feldspars) to the airborne pollution (Cd, As, Hg, Pb?) and finally to the supergenne processes in soils.

From the statistical point of view, medians were taken as background values, because there are broad ranges of concentration for the individual chemical elements. When comparing to the Dutch ABC list which is related to the theoretical soils with (with 25% of clay and 10% of humus) some real soils in Slovakia have higher concentration of some chemical elements than reference (A-) value. In this relation the target concentration should be revised.

The spatial distribution of the risk chemical elements

The statistical results on risk elements distribution in the topsoils (in the A-horizons) and in subsoils (in the C-horizons) are presented in the following tables (Tab. 5-6) and graphically in the histograms (Fig. 1-2)

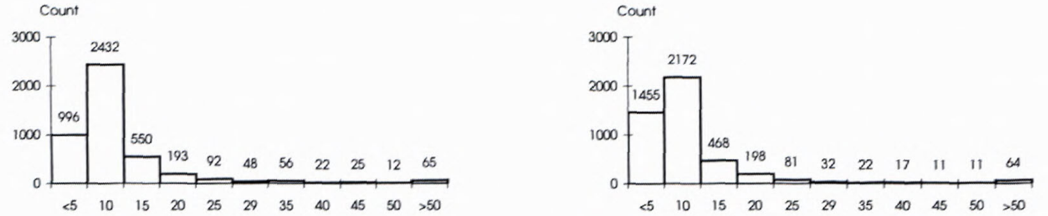
Arsenic in most soils ranges from 1-95 mg.kg^{-1} with mean values about 9 mg.kg^{-1} (Kabata-Pendias and Pendias, 1992). In rocks the content of arsenic is lower and ranged from 0.5-3.0 mg.kg^{-1}. In studied soils arsenic content is higher and median is 7.1 in A and 6.4 in C horizons. When comparing A horizons of forest soils with those in agricultural ones the trend of enrichment in topsoil of the forest soils (medians 7.9/5.7 mg.kg^{-1}) is more evident. This enrichment which is mentioned for the topsoils (Fergusson, 1990) is caused by external sources of arsenic (pollutions). Very high concentrations which reach up to several thousand mg.kg^{-1} (maximum 2438 mg.kg^{-1}) were found in the surrounding of old mining sites. Some above the limit concentrations (above 29 mg.kg^{-1}) were also found in the vicinity of smelters and coal burning facilities (Fig. 3).

Cadmium content in most magmatic and sedimentary rocks does not exceed 1 mg.kg^{-1}, except the clay shales in which can be higher due to affinity to Zn which is also concentrated in the clay. In this respect the median value in A horizon of agricultural soils is 0.2 and forest soils 0.4 which is higher, similar to that reported to the soils of the different countries (Kabata-Pendias and Pendias, 1992). Some enrichment of the topsoils may be due to contamination (fertilizers, smelters). High concentrations of cadmium (up to 18 mg.kg^{-1}) were found near the old mining districts (Fig. 4).

Cobalt content in the rocks is low except the ultramafic rocks. Due to weathering cobalt is leached from the profile. As a result the content of Co in soils is low but principally is inherited from the rocks. The content of cobalt ranges between 0.1-120 mg.kg^{-1}. The medians values in Slovakian soils are 9 mg.kg^{-1} in A and 10 mg.kg^{-1} in C-horizons. Higher concentrations (up to 120 mg.kg^{-1}) are bound with soils on basic and mineralized rocks.

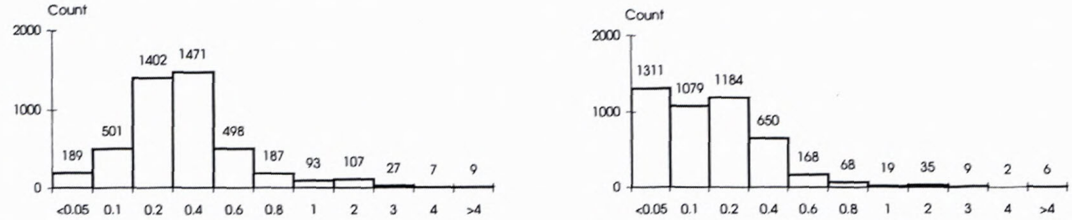
Cromium similarly to Co is bound to ultramafic rocks. In other rocks it ranges from 5 - 120 mg.kg^{-1} (Kabata-Pendias and Pendias, 1992). Mean values range for the different soils of the world from 10 to 200 mg.kg^{-1}. Grand mean for the soils is calculated to be 54 mg.kg^{-1} (Kabata-Pendias and Pendias, 1992). The median values for A horizons are 85 mg.kg^{-1} and 86 mg.kg^{-1} for C horizons, in Slovakian soils. Very high concentration in were found around the smelters and mining works (up to 6000 mg.kg^{-1}) (Fig. 5) . In these soils Cr is mostly fixed to secondary Fe and Mn oxides. Organic matter plays an important role in immobilising the cromium. No significant trends are found in the soils.

Copper similarly to the Co, Cr, Ni and Zn, has the tendency to be concentrated in basic and intermediate



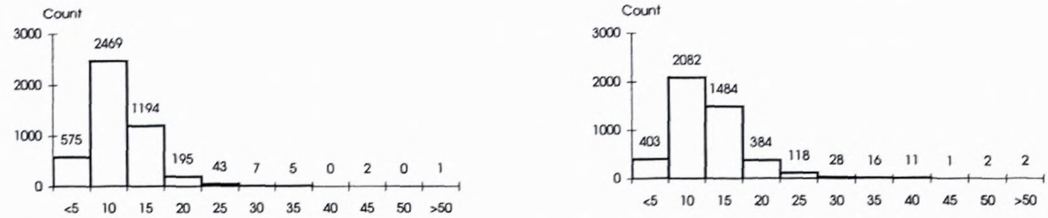
Distribution of As in A-horizons of soils of Slovakia

Distribution of As in C-horizons of soils of Slovakia



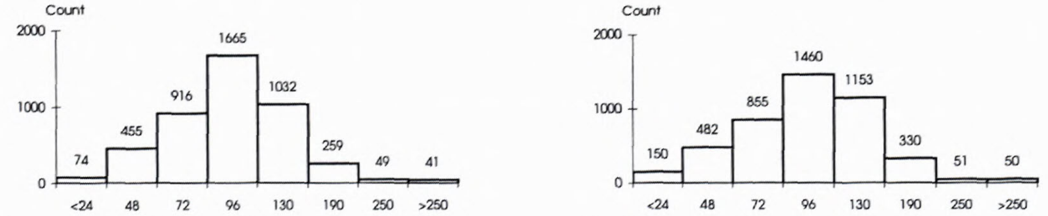
Distribution of Cd in A-horizons of soils of Slovakia

Distribution of Cd in C-horizons of soils of Slovakia



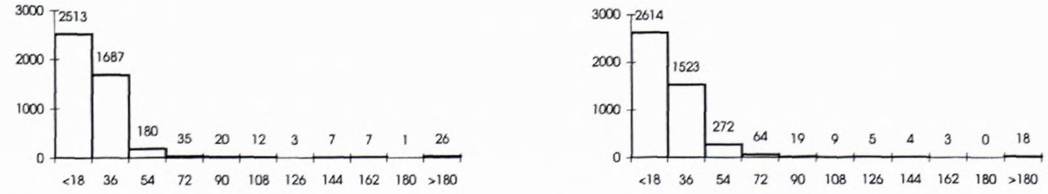
Distribution of Co in A-horizons of soils of Slovakia

Distribution of Co in C-horizons of soils of Slovakia



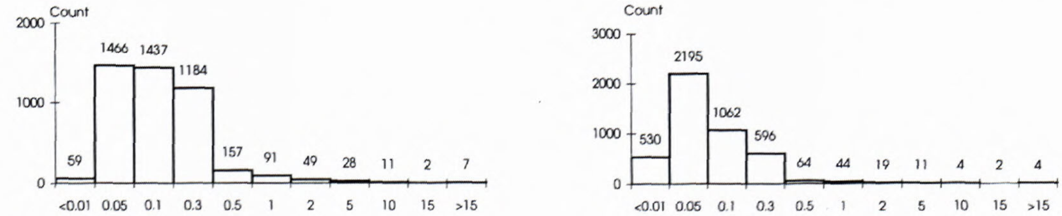
Distribution of Cr in A-horizons of soils of Slovakia

Distribution of Cr in C-horizons of soils of Slovakia



Distribution of Cu in A-horizons of soils of Slovakia

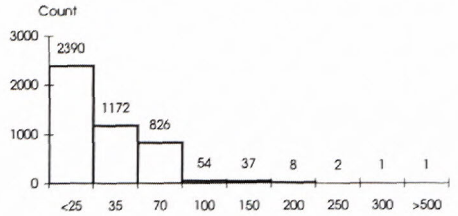
Distribution of Cu in C-horizons of soils of Slovakia



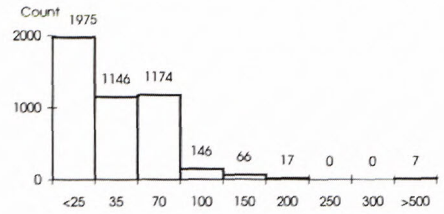
Distribution of Hg in A-horizons of soils of Slovakia

Distribution of Hg in C-horizons of soils of Slovakia

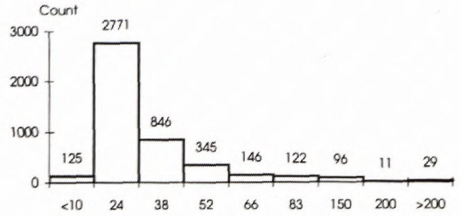
Fig. 1 Frequency distribution of the trace chemical elements (mg.kg^{-1}) in Slovakian soils (As, Cd, Co, Cr, Cu, Hg)



Distribution of Ni in A-horizons of soils of Slovakia



Distribution of Ni in C-horizons of soils of Slovakia



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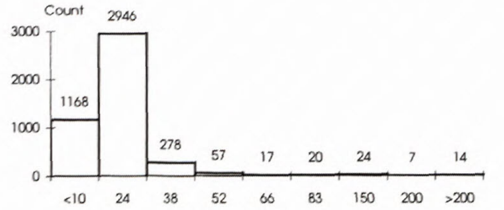
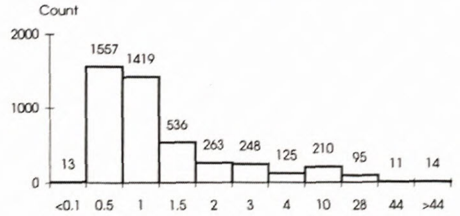
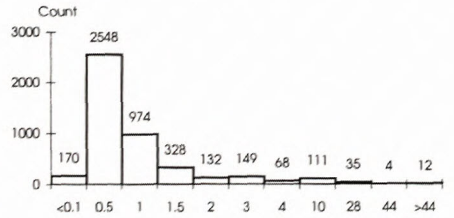


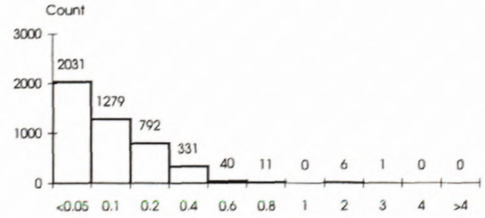
Distribution of Pb in C-horizons of soils of Slovakia



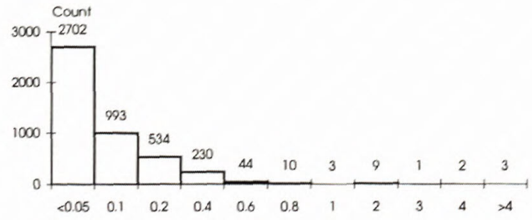
Distribution of Sb in A-horizons of soils of Slovakia



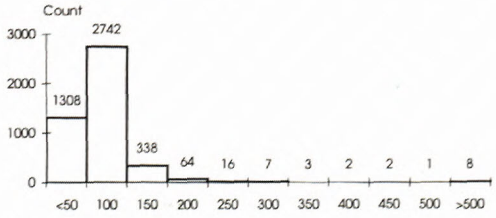
Distribution of Sb in C-horizons of soils of Slovakia



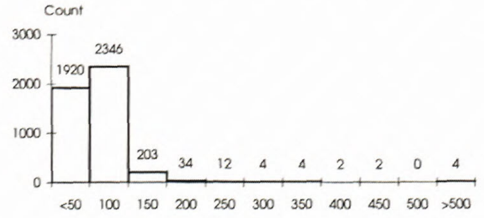
Distribution of Se in A-horizons of soils of Slovakia



Distribution of Se in C-horizons of soils of Slovakia



Distribution of Zn in A-horizons of soils of Slovakia



Distribution of Zn in C-horizons of soils of Slovakia

Fig. 2 Frequency distribution of the trace chemical elements (mg.kg^{-1}) in Slovakian soils (Ni, Pb, Sb, Se, Zn)

Fig. 3 Geochemical atlas of Slovakian soils
Distribution of As in A-horizons

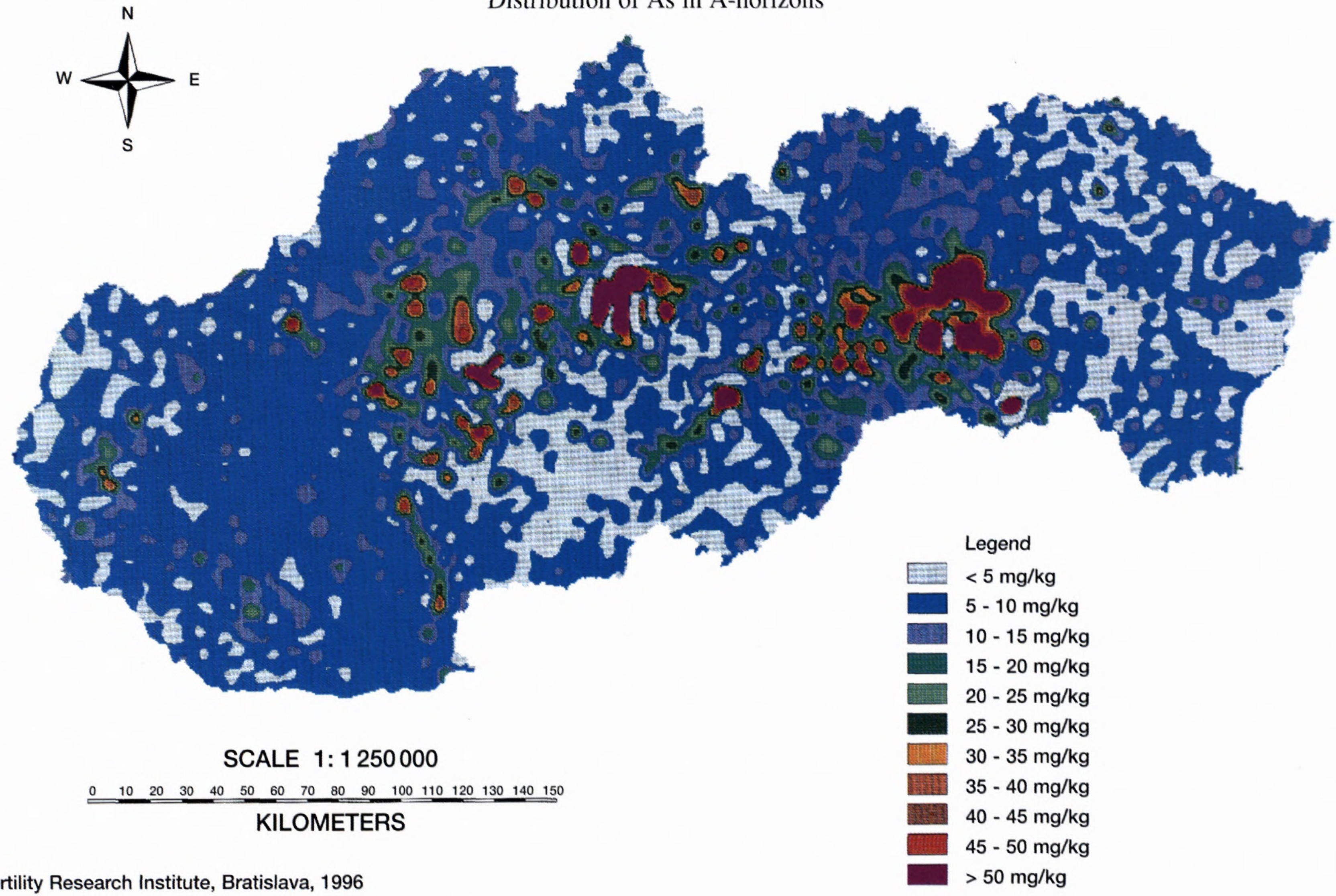


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Fig. 4 Geochemical atlas of Slovakian soils
Distribution of Cd in A-horizons

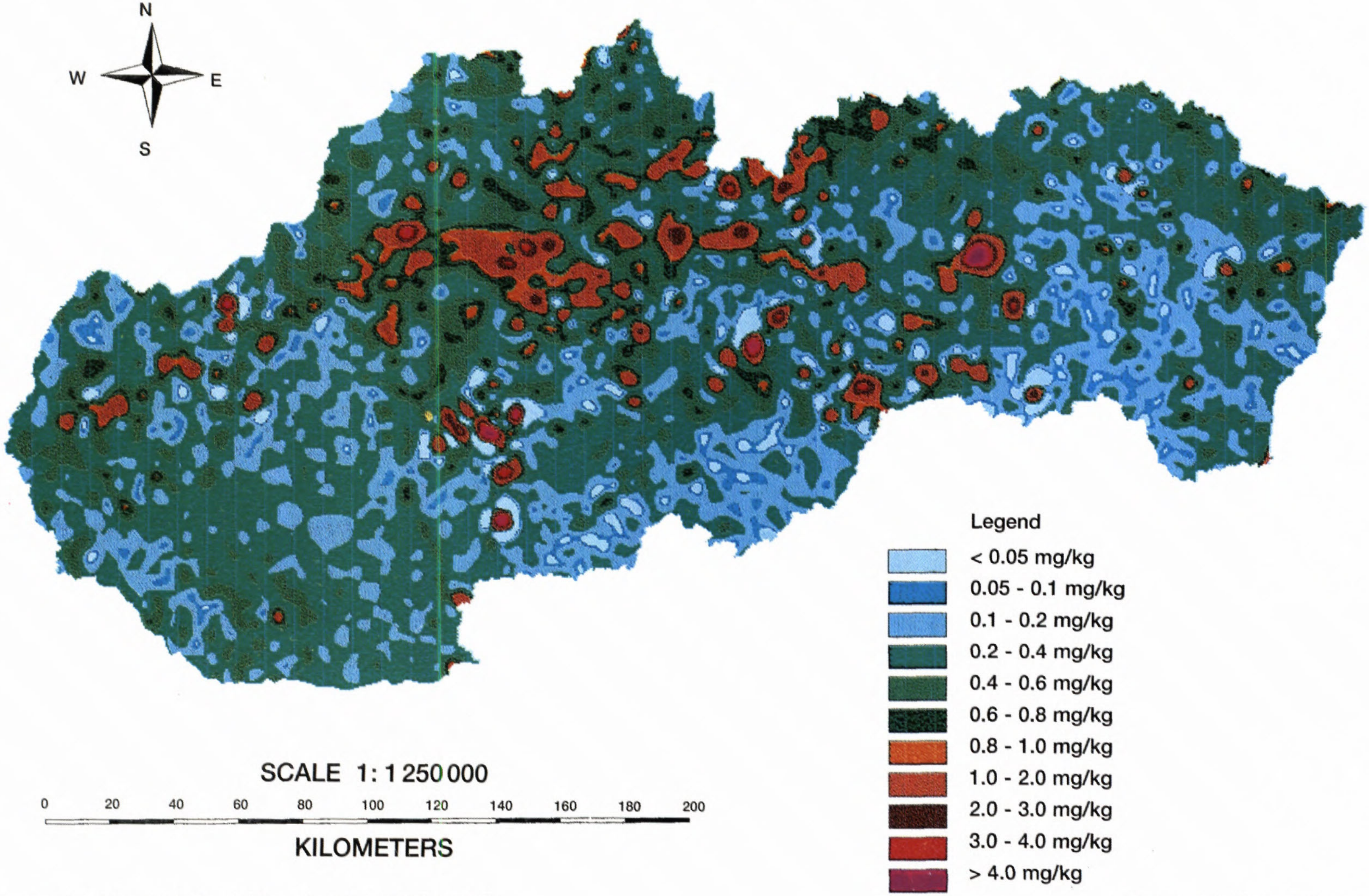

Fig. 5 Geochemical atlas of Slovakian soils
Distribution of Cr in A-horizons

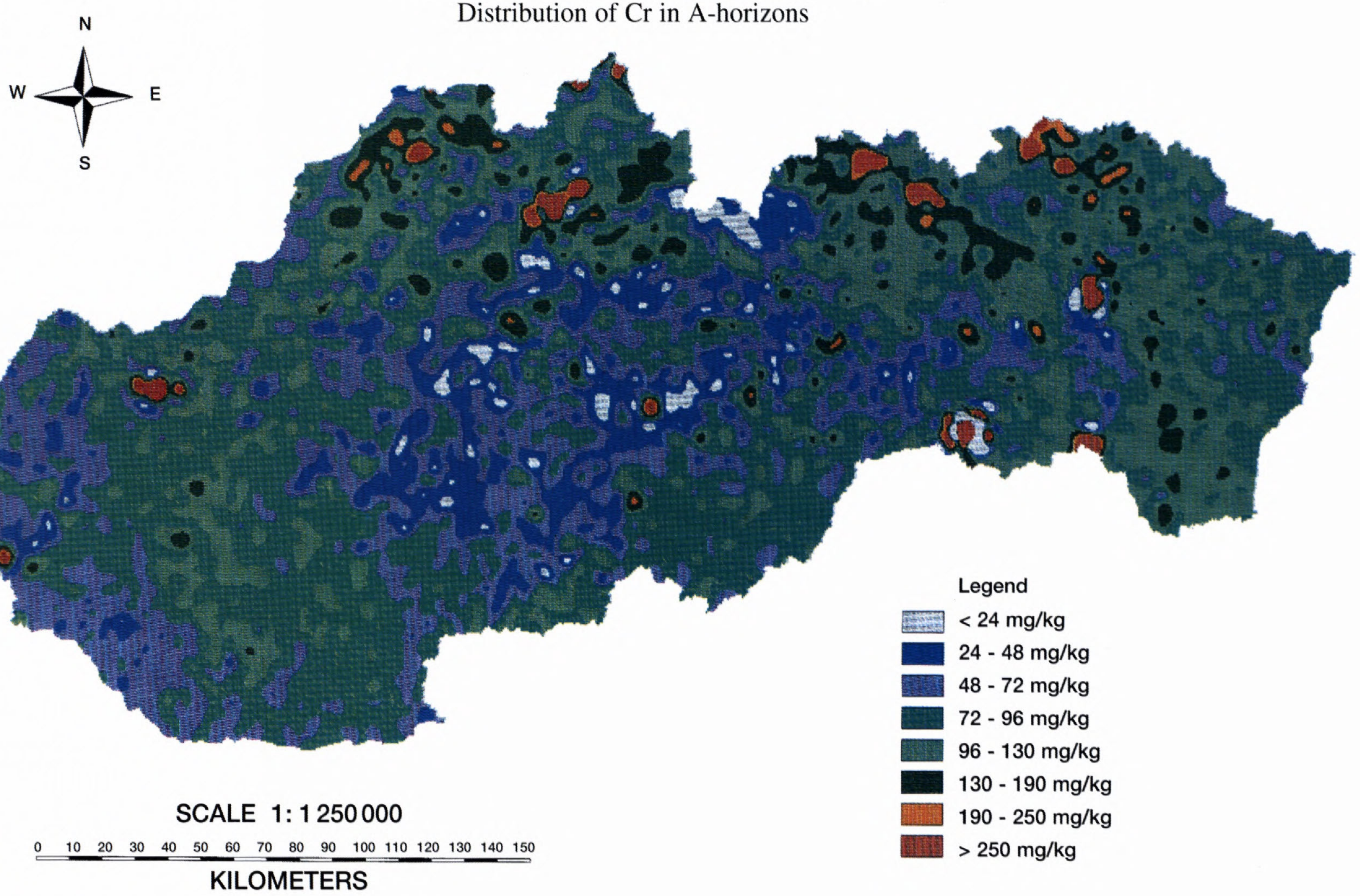

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Fig. 6 Geochemical atlas of Slovakian soils
Distribution of Cu in A-horizons

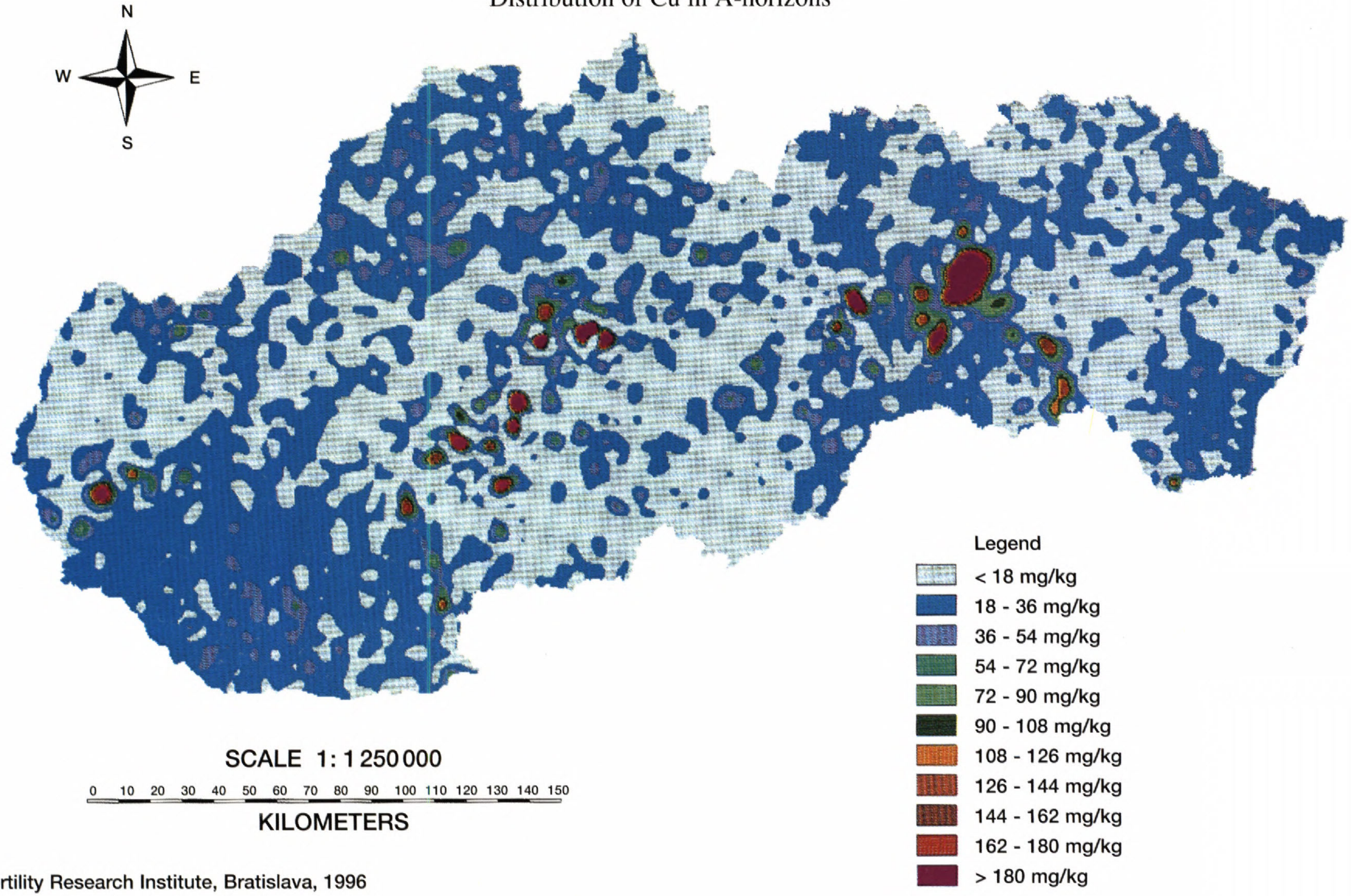

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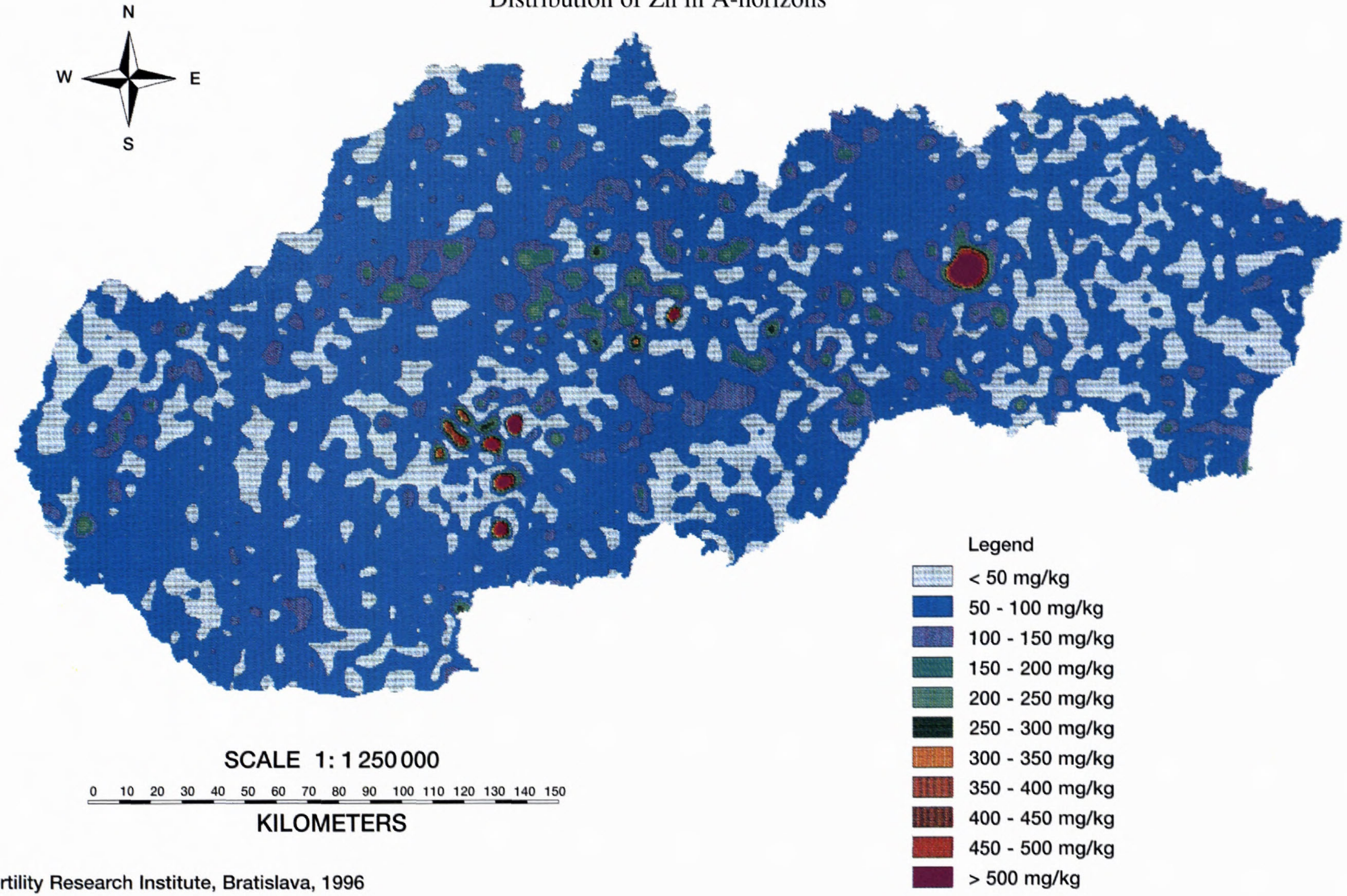
Fig. 7 Geochemical atlas of Slovakian soils
Distribution of Zn in A-horizons



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rocks, and excluded from acid and carbonate rocks. The mean values in the soils vary from 13 - 24 mg.kg^{-1} (Kabata-Pendias and Pendias, 1992). The similar picture is obtained for the Slovakian soils in which median for A and C horizons is 17 mg.kg^{-1} (Fig. 6). Some tendencies of enrichment in A horizons of agricultural land is due to pollution and due to use of chemicals (especially in vineyards). Very high concentrations of Cu are found around the mineralized rocks, mines, smelters and above limit concentrations in the topsoils of the vineyards (Cu-pest).

Mercury content in the soil is generally low and has a tendency to be fixed to the organic complexes. This has been proved for the forest topsoils in which the highest median value 0.13 mg.kg^{-1} was found. When we compare the median of forest soils in A and C horizons (0.04 mg.kg^{-1}), high decrease of Hg content can be also ascribed to some pollution to topsoils. Very high concentrations are accounted to the pollution sources. Especially high concentrations were found around the smelters in which tetraedrite ores with high Hg concentrations have been reworked.

Nickel as it is mentioned above has similar geochemical history as Co, Cu, Cr, Zn, being fixed to ultrabasic and basic rocks. It is easily mobilised during weathering and pedogenesis. But mostly increased content of Ni in soils is bound with increased content in humus and secondary Mn oxides. The mean values for the soils range in rather broad limit but grand mean calculated for the world soils (Kabata-Pendias and Pendias, 1992) is 22 mg.kg^{-1}. The mean values are not much higher in Slovakian soils. But very high local concentrations are bound with mineralized rocks and mining works.

Lead content in the soil can be affected in many ways. It is very common pollutant from the roadside dust, metal processing, mining, battery manufactories and others. Natural content in the soils is included from the parent rocks. The highest content of Pb is in acidic rocks (tens of mg.kg^{-1}). The common trend of enrichment in Pb content in the topsoils due to divergent sources of pollution are proved also for the Slovakian soils. The median for the topsoil is 20 and subsoils 13 mg.kg^{-1}. Very high concentrations (above 0.3%) are connected with old mining activities.

Antimony content in the rocks and thus in the soils is low. It is supposed that antimony can migrate in the water and can be leached from the weathering profile. Not very much data is available in the literature on the antimony (Kabata-Pendias and Pendias, 1992; Fergusson, 1990). Kabata-Pendias and Pendias (1992) gives the grand mean for the soils 0.9 mg.kg^{-1}. The topsoils in Slovakia have median 0.6 and subsoils 0.5 mg.kg^{-1}. Highest median value 1.1 mg.kg^{-1} have been calculated for the forest soils. Higher values are found in mineralized rocks with antimony and around the dumping fields. This gives an opportunity to study the processes of migrations (chemical, mechanical), availability for the plants and possible adverse effects.

Zinc content in soils depends mostly on the parent rocks. Higher concentration in the argillaceous sediments cause the higher content in the soils. The total content in the surface soils according to Kabata-Pendias and Pendias (1992) range from 17-125 mg.kg^{-1} and grand mean was calculated 64 mg.kg^{-1}. The median in the A horizons is 51 mg.kg^{-1} and 54 mg.kg^{-1} in the C horizons which is rather close to this values. The highest concentrations of zinc are found around the mining areas (polymetalic ores) and reach 2160 mg.kg^{-1}. In some vineyards regions (zinc stay wires) above limits concentrations of Zn were found (Fig. 7).

Till now almost no data on *selenium* content in Slovakian soils are available. This is the first picture which is obtained from rather representative samples collections. Selenium is an essential element for human (animal) health in the low range of concentrations. On the other hand can be toxic in elevated concentrations. That is why Se content in soils has received much attention. Surface soils in a world - wide scale contain an average 0.33 mg.kg^{-1} of Se. If we compare the Slovakian soils median value for A horizons and C horizons is rather low and is 0.1 mg.kg^{-1} (0.05 mg.kg^{-1} respectively). Non significant increase in Se content in forests can be with question mark ascribed to some airborne sources of pollution. These values range the Slovakian soils to the selenium poor.

Conclusions

The ranges of natural content of the chosen chemical elements in soils are wide. High values for the most elements are in connection with some point sources of contamination in old mining (reworking) areas. Higher concentration of some risk elements in border parts of high mountains (Malá Fatra Mts., Vysoké Tatry Mts., Nízke Tatry Mts.) may point to the transboundary air pollution. Depending on the wind direction some marginal mountain ranges may play a dominant role in the particular matter deposition.

The natural levels of chemical elements will provide information on their dispersion within the soil profiles. The obtained data will be used to define the threshold limits for some of the risk elements in the soils. They will yield background values to compare with the total content of the chemical elements in European soils.

Soil pollution in Slovakia is connected to mining, smelting and industrial activities. Some of the geochemical anomalies are the secondary halos around mineralized ore bodies.

The great number of the lower "outliers" are connected mostly with analytical limits for which in statistical sense a half of lower detection limits were taken.

Great number of upper "outliers" belong to polluted or mineralized sites.

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Geochemical mapping of environmental stress by selected elements through foliar analysis

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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

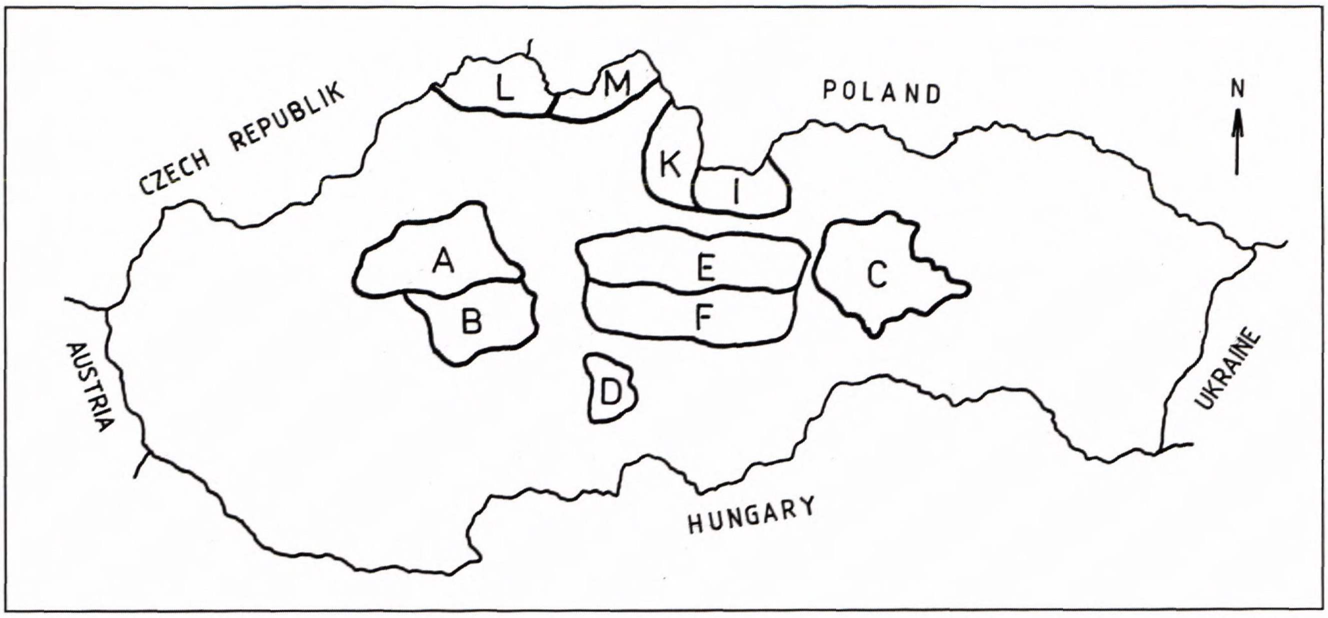

Fig. 1 Sampling locations from three industrial areas, five mountains forests and one military area in Slovakia [A] Horná Nitra area - Thermal power plant; [B] Žiar basin - Aluminium plant; [C] Central Spiš region - Iron mines (production of mercury and barium) and production of non-ferrous metals; [D] 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		Literature values mg.kg^{-1}
		Mean (SD) mg . kg^{-1}	Range 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 region) and Polish (Katowice region)	A_3, A_4
M	Horná Orava mountains	Senonian: marls, sandstones, limestones, conglomerates	2.511	0.469	1.864		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).

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

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:

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

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

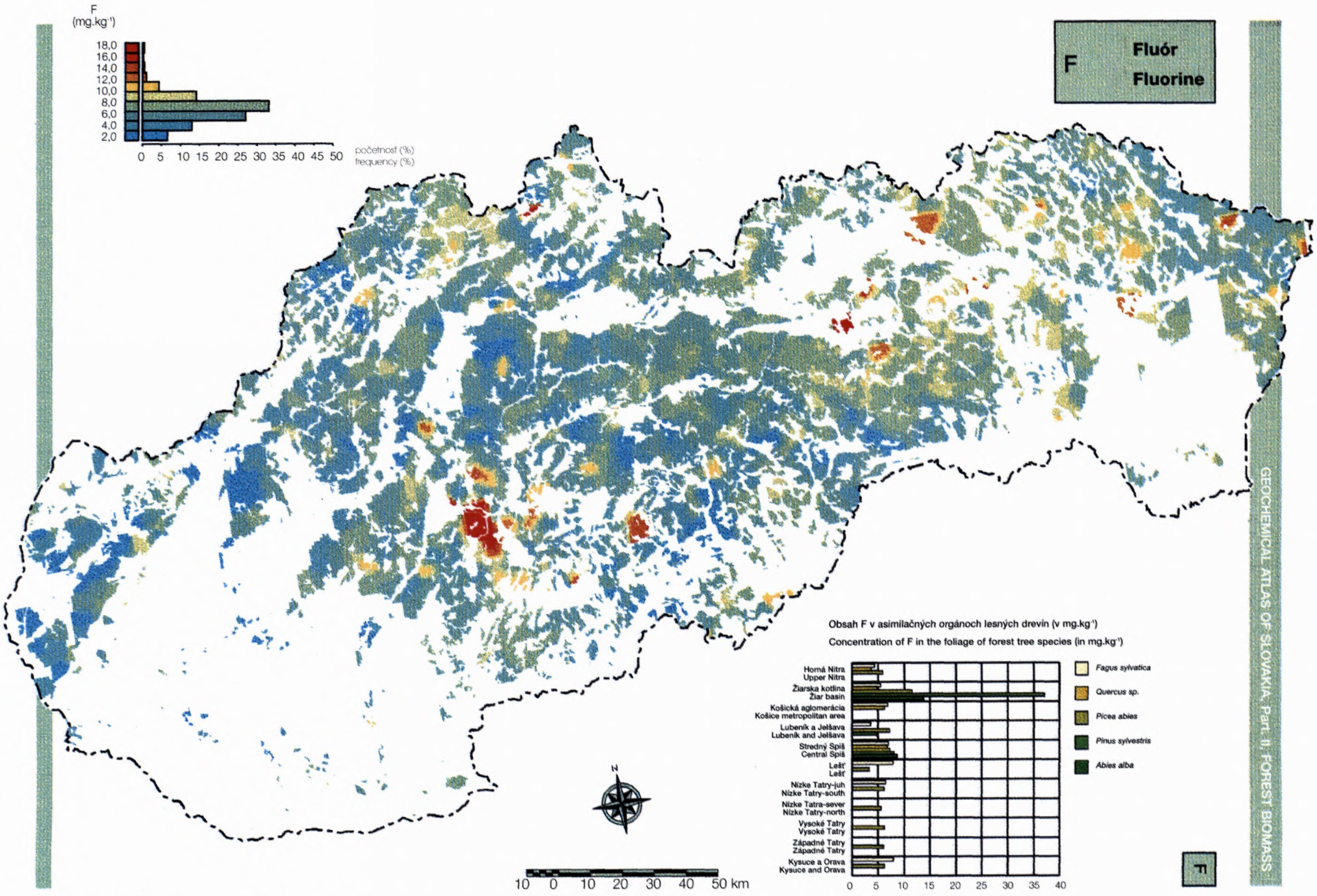

Fig. 2 Concentration on fluorine in the foliage of forest tree species in Slovakia

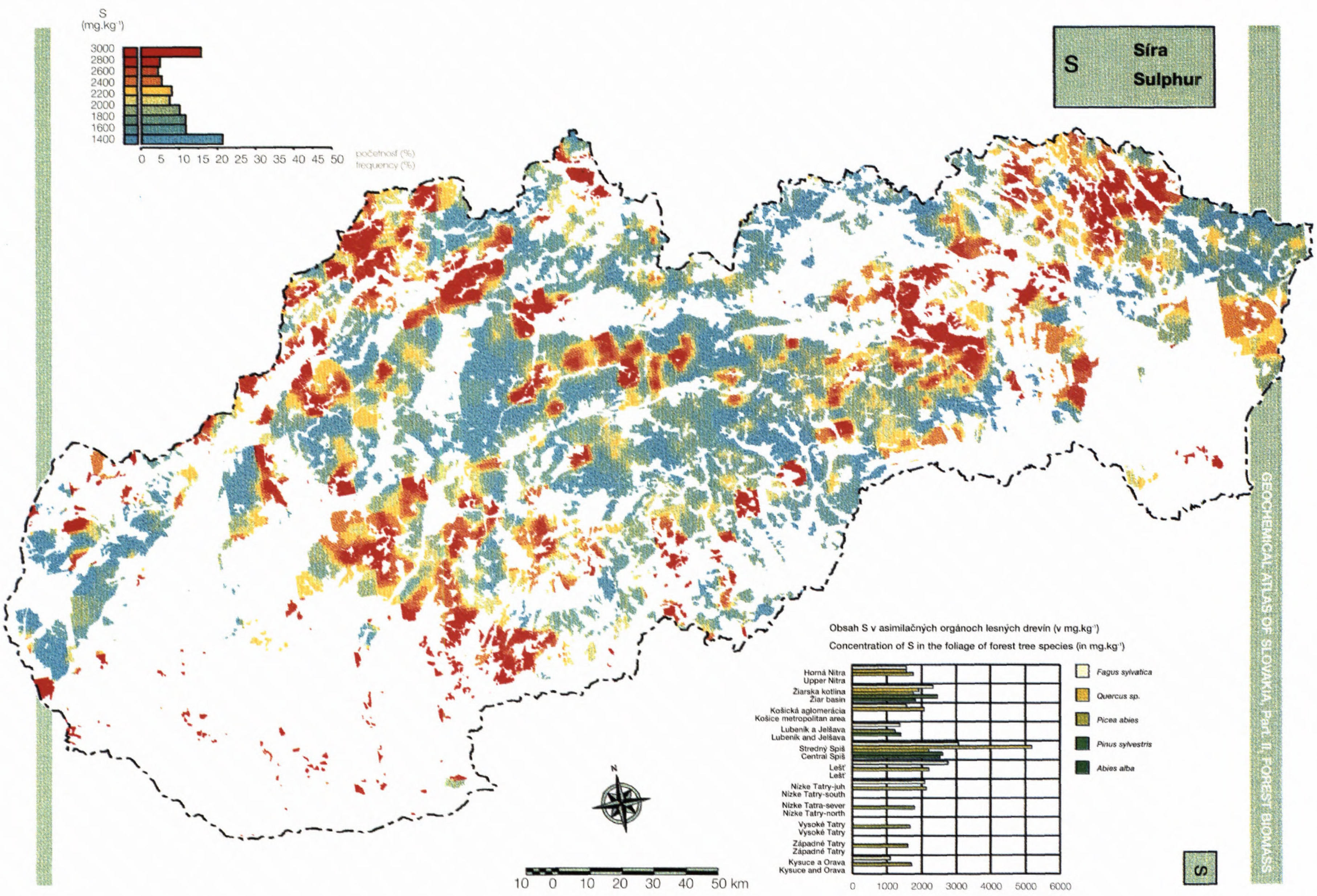

Fig. 3 Concentration on sulphur in the foliage of forest tree species in Slovakia

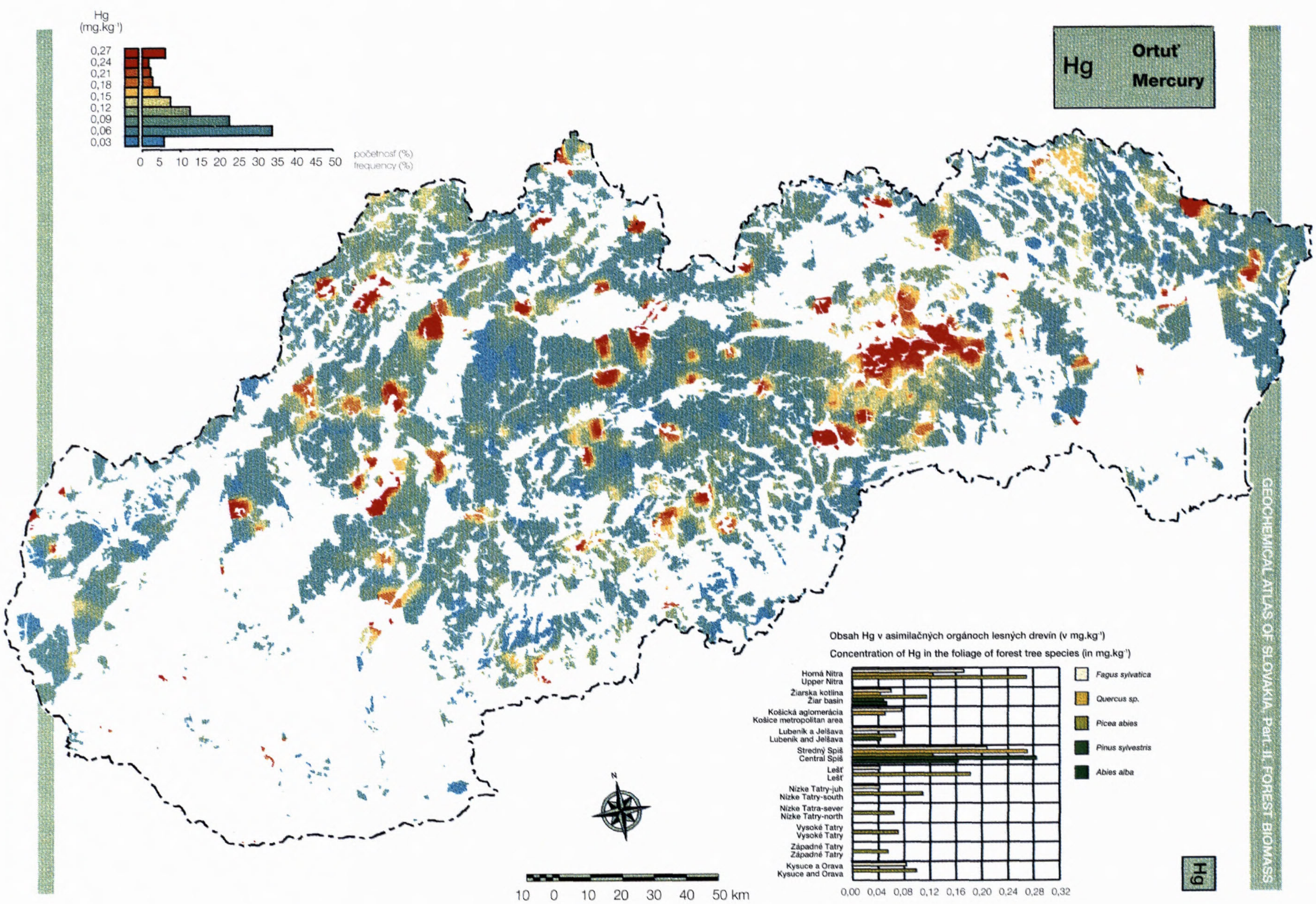

Fig. 4 Concentration on mercury in the foliage of forest tree species in Slovakia

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

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Geochemical Atlas of Slovak Republic
Part Natural Radioactivity

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Abstract. The Atlas of Natural Radioactivity of Slovakia is one of the several separate parts of the Geochemical Atlas of the Slovak Republic prepared at a scale 1 : 1 000 000. The Atlas evaluates natural radioactivity of rocks and waters. Assessed are K, U, Th, U_{total} components and dose rate of natural radioactivity of rocks, Rn on radon-risk maps, as well as U_{nat}, ^{226}Ra and ^{222}Rn components of natural radioactivity of waters. Aside from these maps, the Atlas also includes an assessment of cosmic radiation dose rate.

Key words: Natural radioactivity, rocks, waters, cosmic radiation, Slovakia.

Introduction

The investigations of radioactivity in the natural environment were closely related to the intensive prospecting and exploration of uranium ores after World War II. Geological exploration and mining of radioactive minerals in Slovakia persisted, with short breaks, from 1947 to 1990. They were carried out by a revision detachment of the company Jáchymov Mines, and, since 1960, by the separate Slovak Division of the Uranový pruskum (Uranium Survey). The exploration of radioactive minerals comprised various radiometric techniques (airborne gamma survey, car-borne gamma survey, surface radiometry - mountain-topography measurements, surface gamma survey, gamma survey in pits, gamma spectrometry, emanation survey) and instruments of different kinds, purpose and accuracy.

The surveys were distributed over all of the West Carpathian geological units, but were mainly focussed on the crystalline units of the core mountains, Permian formations, Neogene volcanic mountain ranges and Tertiary basins.

One of the objectives of the project Investigations of Geological Factors of Environment carried out by the Dionýz Štúr Institute of Geology in association with other organizations between 1990 and 1995 was to compile natural-radioactivity maps at a scale of 1 : 200 000 and in some areas of Slovakia at 1: 50 000. The works aimed at radioactivity were performed by URANPRES, Ltd. based at Spišská Nová Ves, Geocomplex, Inc., based in Bratislava, and C & S Radón, Ltd. based at Spišská Nová Ves.

All these works were used to compile the Atlas of Natural Radioactivity of Slovakia at scale 1 : 1 000 000 (Daniel, Lučivjanský & Stercz, 1996).

Natural Radioactivity and Its Measurements

The maps of the natural radioactivity of rocks are based on gamma spectrometric measurements. The investigations were made at a scale of 1 : 200 000 covering Slovakia on a uniform grid 3 x 3 km, i. e. 1 point per 9 km^2. Six selected areas (Upper Nitra Valley, Nízke Tatry Mts., Hornád Basin and the eastern part of the Slovenské rudohorie Mts., Košice Basin and Slánske vrchy Mts., Žiar Basin and Malá Fatra Mts.), which account for 20 % of Slovakia's territory were investigated at scale 1 : 50 000 on a uniform grid 1 x 1 km, i. e. 1 point per 1 km^2. The measurements were taken by a reference-point technique whereby 1 reference point represents 5 cross-like distributed spectrometric measurements located 20 m from the middle of the cross. The average value of these 5 readings corresponds to the value of the relevant reference spectrometric point. The measure-

Tab. 1 Categories of foundation-soil permeability

Categories of foundation-soil permeability	Earth categories acc. to state standard 73 1001
poorly permeable f > 65 %	F5, F6, F7, F8
moderately permeable 15 % < f < 65%	F1, F2, F3, F4, S4, S5, G4, G5
strongly permeable f < 15 %	S1, S2, S3, G1, G2, G3

ments were taken by GS-256 instruments, which were regularly calibrated and checked. Check measurements taken near the border between Slovakia and the Czech Republic revealed that measurements in both countries are highly compatible.

The rock radiometric maps are based on the results of gamma spectrometry. The measurements were taken on a total of 15 573 reference spectrometric points, corresponding to 77 865 gamma-spectrometric measurements points.

The radon-risk derivative map at a scale of 1 : 200 000 was made by the SAN technique designed by the company Uranium Survey, Liberec. The measurement sensitivity was 1 kBq . m^{-3}. More up-to-date measurement techniques, mainly Radon detection through Lucas chambers, are currently being used. The main characteristics to assess radon risk comprise ^{222}Rn volume activity given in kBq . m^{-3} and foundation-soil category (Slovak standard 73 1001) from which gas-permeability of rocks is derived.

The main assessment characteristics are given in Tables 1 and 2.

Tab. 2 Categories of radon risk

Radon risk	^{222}Rn volume activity in soil air (kBq . m^{-3}) in foundation soils according to gas permeability		
	Gas permeability		
	low	medium	high
low	<30	<20	<10
medium	30-100	20-70	10-30
high	>100	>70	>30

The natural radioactivity of waters was investigated by field collecting and laboratory measurements of water samples. The samples were taken from springs, wells, drillholes, outflows from mine workings, rivers, lakes and tailing ponds. The sampling density was 1 sample per 10 km^2 at a scale of 1 : 200 000 and 1 sample per 5 km^2 at a scale of 1 : 50 000.

Natural Radioactivity Maps of Slovakia

The natural radioactivity maps of Slovakia illustrate the distribution of sources of natural radioactivity of rocks, water radioactivity, radon risks and cosmic radiation in Slovakia.

Cosmic Radiation Dose Rate Map (Da_{cosmic})

The cosmic radiation dose rate map was based on C. Murith's and A. Gurtner's (1990-93) investigations. Cosmic radiation dose rate depends on the altitude of the territory. The lowest place in Slovakia near Streda nad Bodrogom (94 m above sea level) has an average cosmic radiation dose rate 38.3 nGy . hr^{-1}. The highest spot is 2 655-m-high Mt. Gerlachovský štít whose cosmic dose rate amounts to 101.5 nGy . hr^{-1}.

Potassium Concentration Map

Potassium is a rock-forming element whose average abundance in the earth's crust is 2.52 weight %. Its abundance in particular rock types are as follows (Polánski & Smulikowski, 1971):

– igneous rocks :	– ultramafic	0.03 %
	– mafic	0.83 %
	– acid	3.34 %
– sedimentary rocks:	– argillaceous	2.66 %
	– arenaceous	1.07 %

Of the three potassium isotopes, only ^{40}K is radioactive.

The potassium concentration map of Slovakia (Fig. 1) reveals that potassium values range from extremely low 0.1 % in Mesozoic limestones and dolomites in the Malá Fatra Mts. to 5.4 % in Lower Triassic rocks of the Melaphyre series.

The average value calculated from all masurements taken in Slovakia amounts to 1.66 %, which is less than the average content in the earth's crust (2.6 %).

Thorium Concentration Map

Of six naturally occurring thorium isotopes, only ^{232}Th (parent element of the thorium series) is significantly radioactive.

The average thorium content in the earth's crust is usually put at 8–12 ppm. It is 18 ppm in acid igneous rocks, 3 ppm in mafic rocks, 11 ppm in shales and clays, 10 ppm in sandstones and 1.8 ppm in limestones.

The average concentration in Slovakia is 9.4 ppm. The measured values range greatly from a few ppm to as much as 26 ppm.

The lowest thorium contents of 6.8 ppm (Fig. 2) occur in the Záhorie – Lower Moravian sector of the Vienna Basin. The contents in the Malé Karpaty Mts. vary from 5 to 12 ppm and in the Central Slovak Neogene Volcanic Mountains they average 9.7 ppm Th. The highest values (21.2 ppm) are found in Neogene rhyolites. Thorium contents amount to 9 ppm in the Nízke Tatry and 9.6 ppm in the eastern part of the Slovenské rudohorie Mts. Low thorium contents occur in the Slovak Paradise (7.9 ppm) and Slovak Karst (10 ppm).

Uranium Concentration Map

The average U content in the earth's crust is put at 2.3 ppm. In igneous rocks the content grows with increasing acidity from 0.5 ppm in mafic rocks to 1.8 ppm in intermediate rocks and to 3.5 ppm in acid igneous rocks (Matolín M., 1994). The average content in shales and clays is 4.0 ppm, in sandstones 3.0 ppm and in limestones only 1.4 ppm U. The mean value is 2.9 ppm (Matolín M., 1976).

Gammaspectrometric measurements yielded an average value of 3.3 ppm, the highest contents exceeding 10 ppm.

Concentrations of uranium minerals form uranium deposits in some places.

Major deposits in Slovakia include those in the Spišská Nová Ves (Novoveská Huta) - Hnilčík - Malý Muráň area, in the Hronicum of the Nízke Tatry, and in the Považský Inovec Mts. (Kálnica, Selec).

The Košice deposit near the tourist resort of Jahodná may be developed in the future.

The lowest U contents of 2.5 ppm are found in the Vienna Basin (windblown sands). The biggest variations occur in the Central Slovak Neogene Volcanic Mountains (0.6–16 ppm eU). Uranium concentrations average 3.1 ppm in the Slovenské rudohorie, 3.3 ppm in the Eastern Slovak Neogene Volcanic Mountains and 3.8 ppm in intramontane basins (Fig. 3).

Map of Gamma Radiation Dose Rate of Rocks

The map of gamma radiation dose rate was compiled from adjusted relationships between the contents of U, Th, K and dose rate (Fig. 4). A look at the dose-rate map reveals that the lowest values occur along the Slovak borders, whereas the highest ones are found in central Slovakia.

The average gamma radiation dose rate value in Slovakia is 63.3 nGy . hr^{-1}.

In most countries, radioactivity measurements are plotted on a map of rock dose rates. The values measured in Slovakia can be compared with an updated table of average dose rate values in some other countries for which the data were available (Tab. 3).

Tab. 3 Average dose rate values in some other countries

Country	Dose rate Ngy . hr^{-1}		Number of measurements	Year of compilation	Measurement technique
	average	range			
Australia	43	20–150	> 1 000	1980	ground
Belgium	43	13–58	272	1987	ground
Czech Republic	66	6–245	100 % of area	1995	airborne
Denmark	38	17–52	14 areas	1980	ground
Eire	42	0–180	264	1980	ground
Finland	65			1980	
France	68	10–250	5 142	1985	ground
Germany (East)	85	24–270	1 005	1969	ground
Germany (West)	53	4–350	24 739	1978	ground
Great Britain	40	0–100	1 400	1984	ground
Hungary	55	20–130	123 areas	1987	ground
India	55	20–1100	2 800	1986	ground
Island	28	11–83		1982	
Italy	57	7–500	1 365	1972	ground
Japan	49	5–100	1 127	1980	ground
Canada	24	18–44	33 areas	1984	airborne
Netherlands	32	10–65	1 049	1985	ground
Norway	73	20–1200	234	1977	ground
Poland	34	10–110	19 528	1994	ground
Romania	81	32–210	2 372	1979	laboratory
Slovakia	63	3–179	15 573	1996	ground
Slovenia	57	4–140	1 052	1993	ground
Sweden	80	18–4000		1979	
Switzerland	48	5–368	805	1995	ground airborne
Taiwan	69		26	1972	laboratory
USA	46	13–100	25 areas	1972	airborne

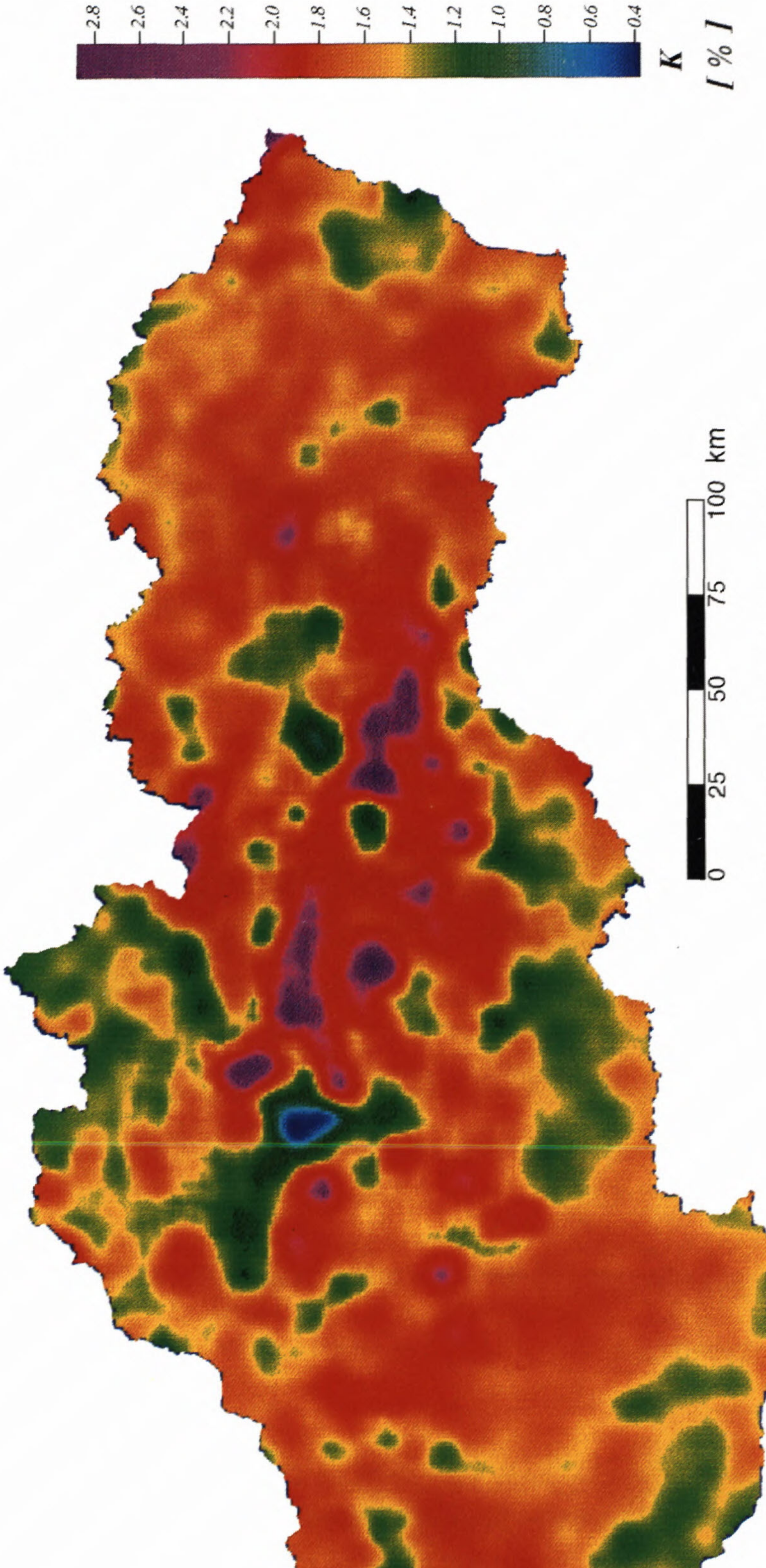

Fig. 1 Map of potassium concentration

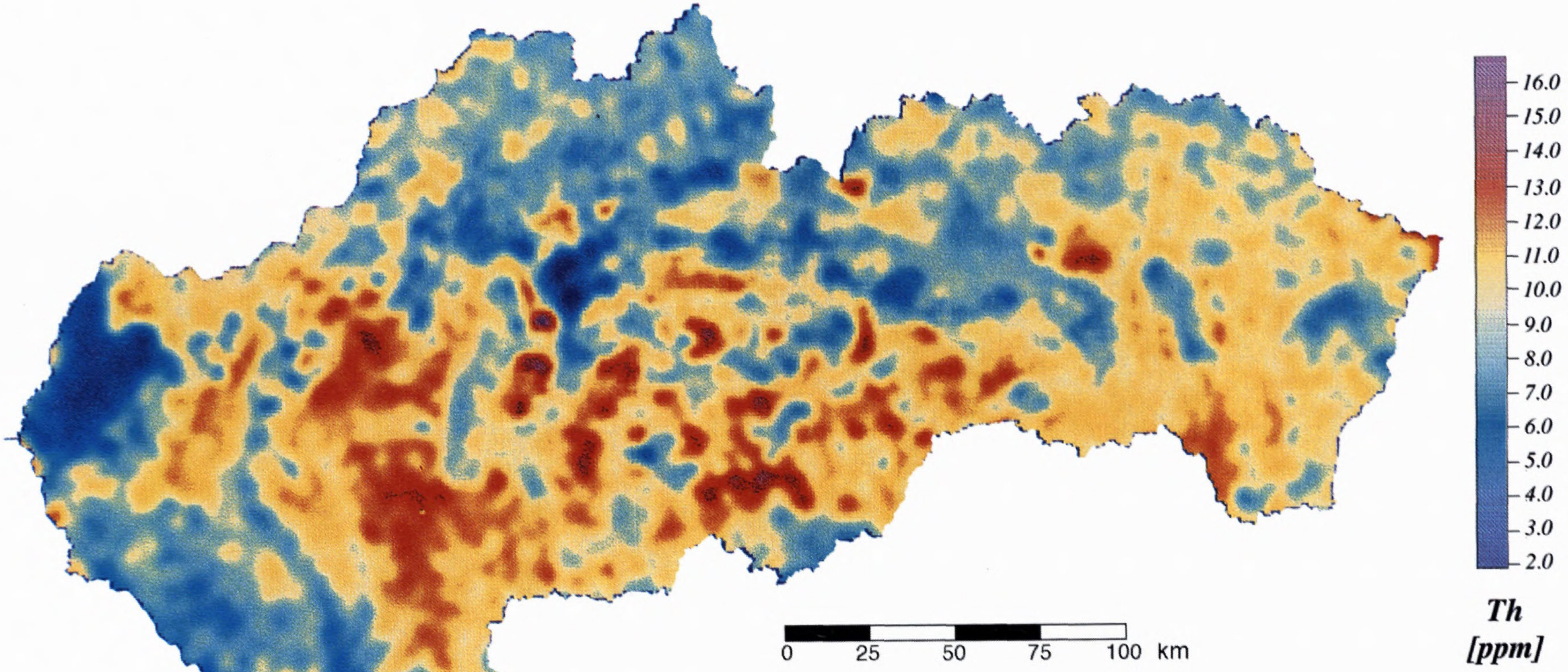

Fig. 2 Map of thorium concentration

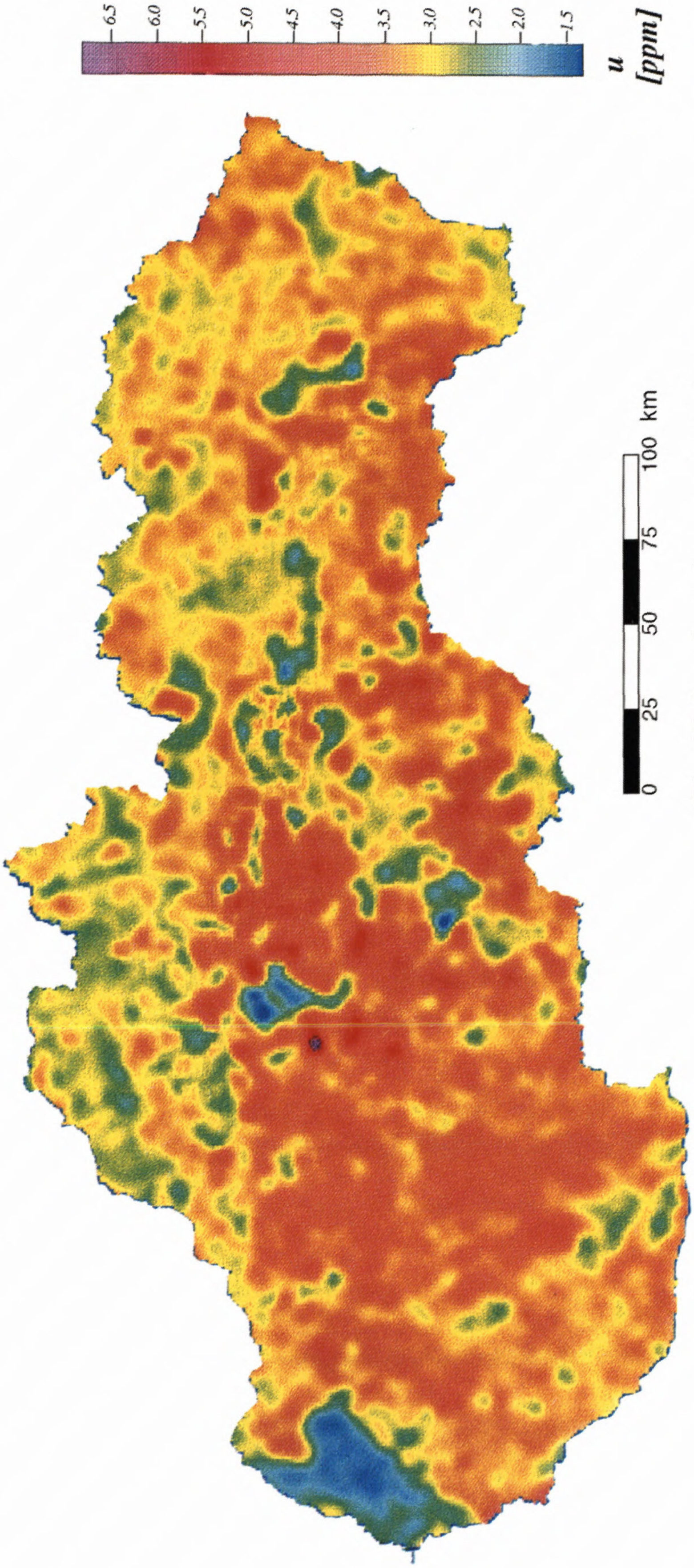

Fig. 3 Map of uranium concentration

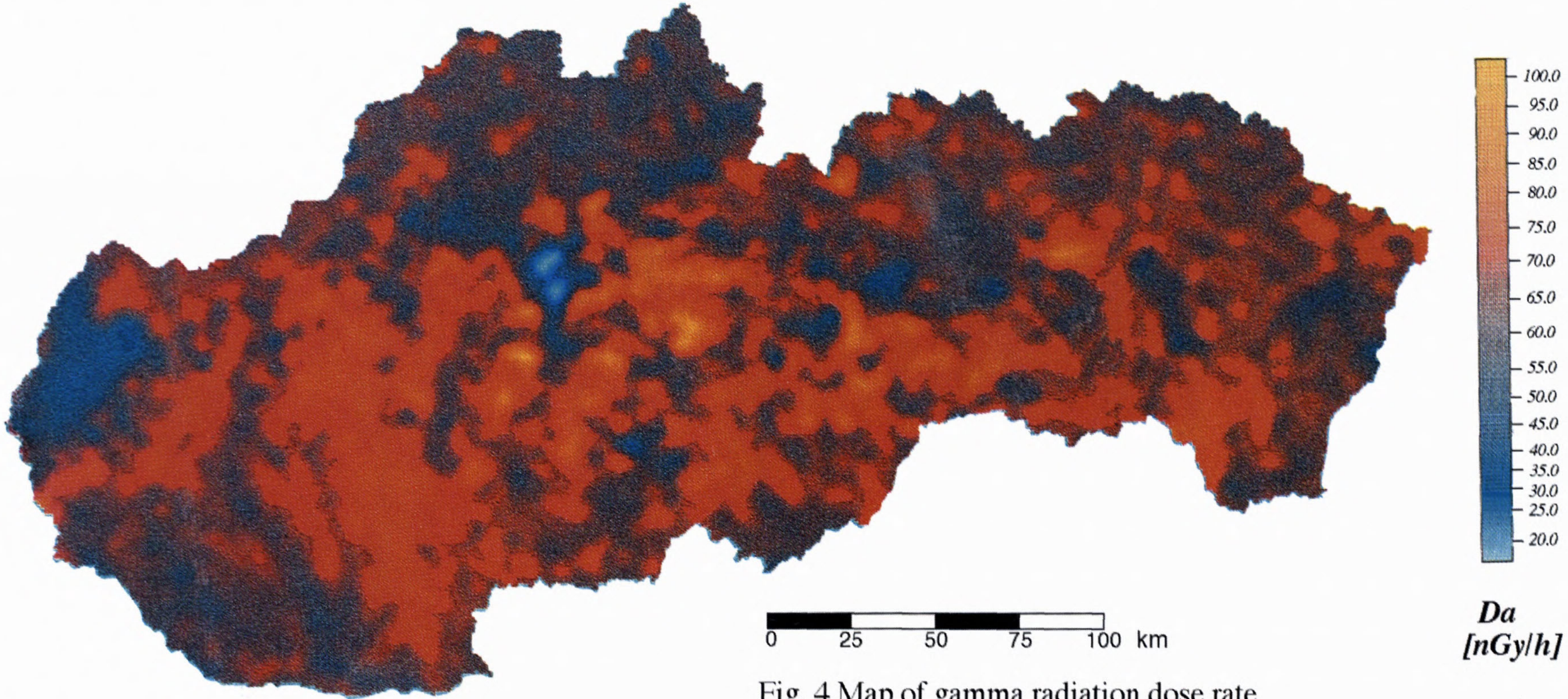

Fig. 4 Map of gamma radiation dose rate

Derived Map of Radon Risk

The derived map of radon risk (Fig. 5) was compiled from measured data and all archive data on natural radioactivity (Čížek P., Smolárová H., 1993).

Slovakia's territory was divided into three categories of radon risk. The shares of respective categories on Slovakia's territory are as follows:

- low radon risk 53.0 %
- medium radon risk 46.7 %
- high radon risk 0.3 %

The highest radon risk in areas measured at a scale of 1 : 50 000 occurs in the area of the town of Levice (15.7 % was in the low, 75.6 % in the medium and 8.7 % in the high radon risk category).

As for geological units, the highest values are found in the Gelnica and Rakovec Groups of the Gemericum in the Slovenské rudohorie. The Middle and Upper Triassic dolomites, called uranium dolomites, are noteworthy in this respect, too.

Maps of Natural Radioactivity of Waters

A total of 5,271 water samples were collected in Slovakia's territory and were used to compile the maps of natural radioactivity of waters.

Map of Uranium Concentration in Waters

Increased uranium concentrations in groundwaters occur largely in waters draining uranium exploration and exploitation mine working (Novoveská Huta, Kálnica), waters in the vicinity of uranium occurrences (Východná) and in some thermal waters (Oravice, Lúčka by Spišské Podhradie). Increased concentrations are also present in waters of some core mountains underlain by the crystalline unit (Považský Inovec, Malá Fatra), in dolomites of the Choč nappe (Nízke Tatry) and in the Danube Lowland and Southern Slovak Basin. The average U_{nat} content in Slovakia's waters amounts to 0.003 $mg . l^{-1}$.

Map of Radium Concentration in Waters

The ^{226}Ra volume activity ranges from 0.001 to as much as 9.7 $Bq . l^{-1}$. The highest values are characteristic of mineral and thermal waters. Increased values also occur in waters of the Záhorie Lowland and western part of the Danube Lowland, in some core mountains (Malé Karpaty, Považský Inovec), Hornád and Poprad Basins, Galmus and the western part of the Volovské vrchy Mts. In Paleogene rocks, radium volume activity grows with increasing depth of groundwater circulation. Radium contents in waters of Neogene volcanics in the Slánske vrchy and Vihorlat Mts. are twice as high as those in waters of Central Slovak Neogene Volcanic Mountains.

Map of Radon Concentration in Waters (Fig. 6)

Radon concentration in water depends on the presence of rocks with uranium minerals, tectonics, water temperature and T. D. S. According to Lange's (1969) classification, several kinds of radon waters can be distinguished.

The first type of radon waters present in nearly all core mountains is radon water formed in fractured weathering crust of crystalline units in core mountains. Such waters are most widespread in the crystalline units of the Veporské vrchy and Stolické vrchy Mts.

Another type consists of radon water bound to clayey-travertine deposits. It includes mineral waters at Sivá Brada near Spišské Podhradie and Bešeňová.

A third type comprises radon waters bound to deep faults, characterized by big discharges and increased temperatures. This type is exemplified by the mineral spring "Carbonic" at Oravice.

Radon water bound to faults is fairly widespread. The type comprises water in the vicinity of the Subtatric fault (Žiar, Starý Smokovec), in the Košice and Hornád Basins.

A fifth genetic type consists of water draining the uranium deposits and springs located near uranium occurrences (Novoveská Huta near Spišská Nová Ves, Kálnica, Východná).

Radioactivity of Mineral and Thermal Waters in Slovakia

In comparison with normal waters, cold mineral waters are enriched in radionuclides, particularly radium and radon. In some thermal waters, radium volume activity is a hundred times as high as in normal waters.

Investigations of natural radioactivity of more than 200 samples of Slovakia's mineral waters allowed us to divide the mineral waters into several categories:

– mineral water bound to Triassic carbonates, mainly those of the Krížna and Choč nappes. Uranium concentrations in these water are low, averaging less than 0.003 $mg . l^{-1}$. Radium volume activity mostly ranges from 0.2 to 0.9 $Bq . l^{-1}$. Radon volume activity largely varies between 20 and 50 $Bq . l^{-1}$ but in some water it attains even higher values. Springs of these waters are frequently coated with travertine.

– mineral water of the crystalline unit is mostly cold acidic. They are enriched in uranium (0.005–0.015 $mg . l^{-1}$), radium (^{226}Ra volume activity largely varies from 0.1 to 0.5 $Bq . l^{-1}$) but mainly radon (often over 200 $Bq . l^{-1}$).

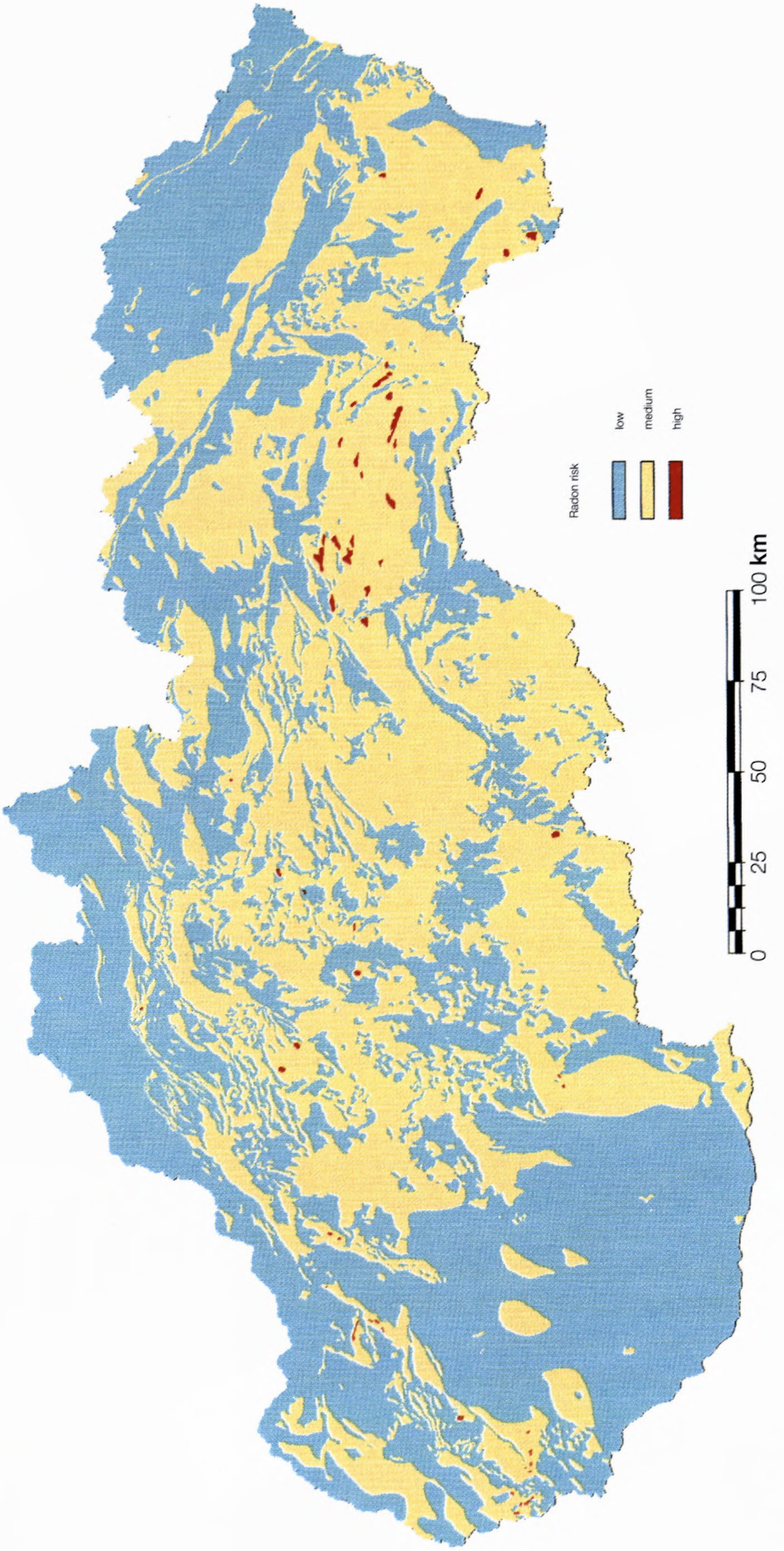

Fig. 5 Derivative map of radon risk

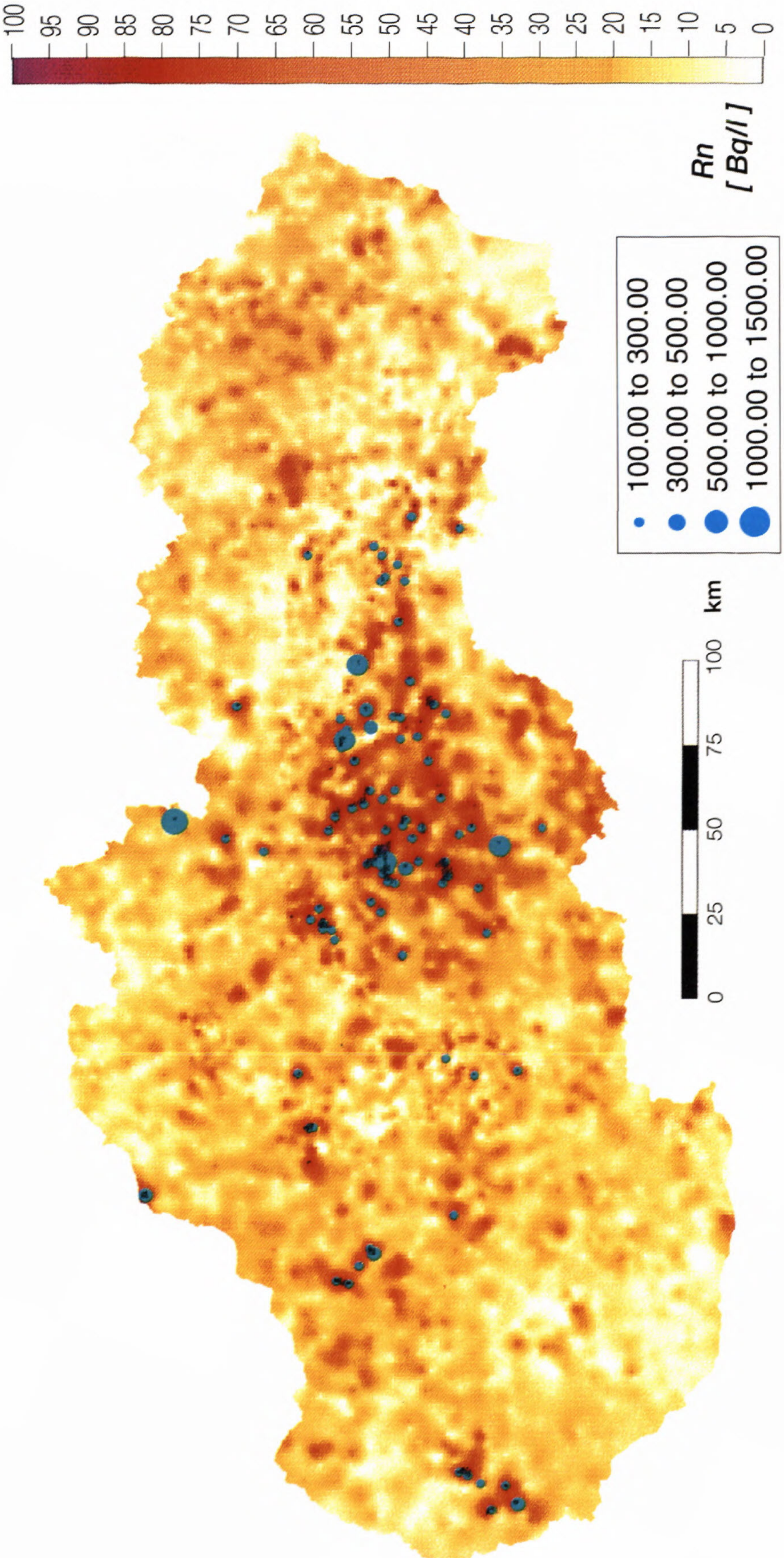

Fig. 6 Map of radon concentration in water

– mineral water of the Flysch Belt - sodium-bicarbonate hydrogensulphide or sodium-bicarbonate acidic water. Water bound to tectonic lines occurs in all partial units of the Flysch Belt. It is typically slightly enriched in uranium (0.004 Bq . l^{-1}), their ^{226}Ra volume activity being medium (0.02–0.08 Bq . l^{-1} only rarely over 0.1 Bq . l^{-1}). ^{222}Rn volume activity varies from 10 to 20 Bq . l^{-1}, only in water enriched in CO_2 does it exceed 20 Bq . l^{-1}.

– mineral water of Neogene volcanic mountains – it is characterized mostly by low uranium (0.002 mg . l^{-1}) and radium contents (up to 0.05 Bq . l^{-1}) and by mildly increased ^{222}Rn volume activities (20–40 Bq . l^{-1}).

With regard to their natural radioactivity, Slovakia's natural water falls into two major categories:

– thermal water of pre-Tertiary units – characterized by high ^{226}Ra volume activity. The category includes water at Bešeňová, Piešťany, Oravice (well OZ-2), Lúčka (well BŠ-1), Vrbov, Kováčová, Lúčky, Trenčianske Teplice, etc. It is largely associated with Triassic rocks of the Krížna and Choč nappes.

– thermal waters of Tertiaty units – characterized by low ^{226}Ra volume activity (up to 0.1 Bq. l^{-1}). This category is exemplified by the thermal waters at Dunajský Klátov, Vlčany, Baloň, Tvrdošovce, Sládkovičovo, Diakovce, Nové Zámky and Topoľníky.

Conclusions

The Atlas of Natural Radioactivity of Rocks was compiled from a multitude of measurements, results and reports. Most data resulted from in-situ field measurements at scales of 1 : 200 000 and 1 : 50 000. Results of works performed by URANPRESS Ltd. Spišská Nová Ves during more than 35 years of exploration for radioactive minerals, the Geological Survey of the Slovak Republic of Bratislava, the C & S Radón Ltd. of Spišská Nová Ves and the Geocomplex of Bratislava were used as well. A further major source of information and instruction was M.Matolín's publication "Radioactivity of West Carpathian Rocks" (1976) which first summarized work on radioactivity in Slovakia. It resulted also in the first map of total radioactivity at a scale of 1 : 500 000.

Natural radioactivity in Slovakia can be characterized by the following average values:

Natural radioactivity of rocks:	
Potassium (K)	1.6 %
Thorium (eTh)	9.4 ppm
Uranium (eU)	3.3 ppm
Dose rate (Da)	63.3 nGy . hr^{-1}
Radon risk:	
– low	53.0 %
– medium	46.7 %
– high	0.3 %
Natural radioactivity of waters:	
Uranium (U_{nat})	0.003 mg . l^{-1}
Radium (Ra)	0.040 Bq . l^{-1}
Radon (Rn)	9.31 Bq . l^{-1}
Cosmic radiation	
Dose rate (Da)	44.3 nGy . hr^{-1}

The natural radioactivity maps are considered to be environmental maps, inasmuch as they can be used to assess human irradiation.

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