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 km². 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 km² 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 NAL-GENE (USA) and nitrocellulose membrane filters SYN-POR (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 determi-

nants. 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 $\sqrt2$ 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.
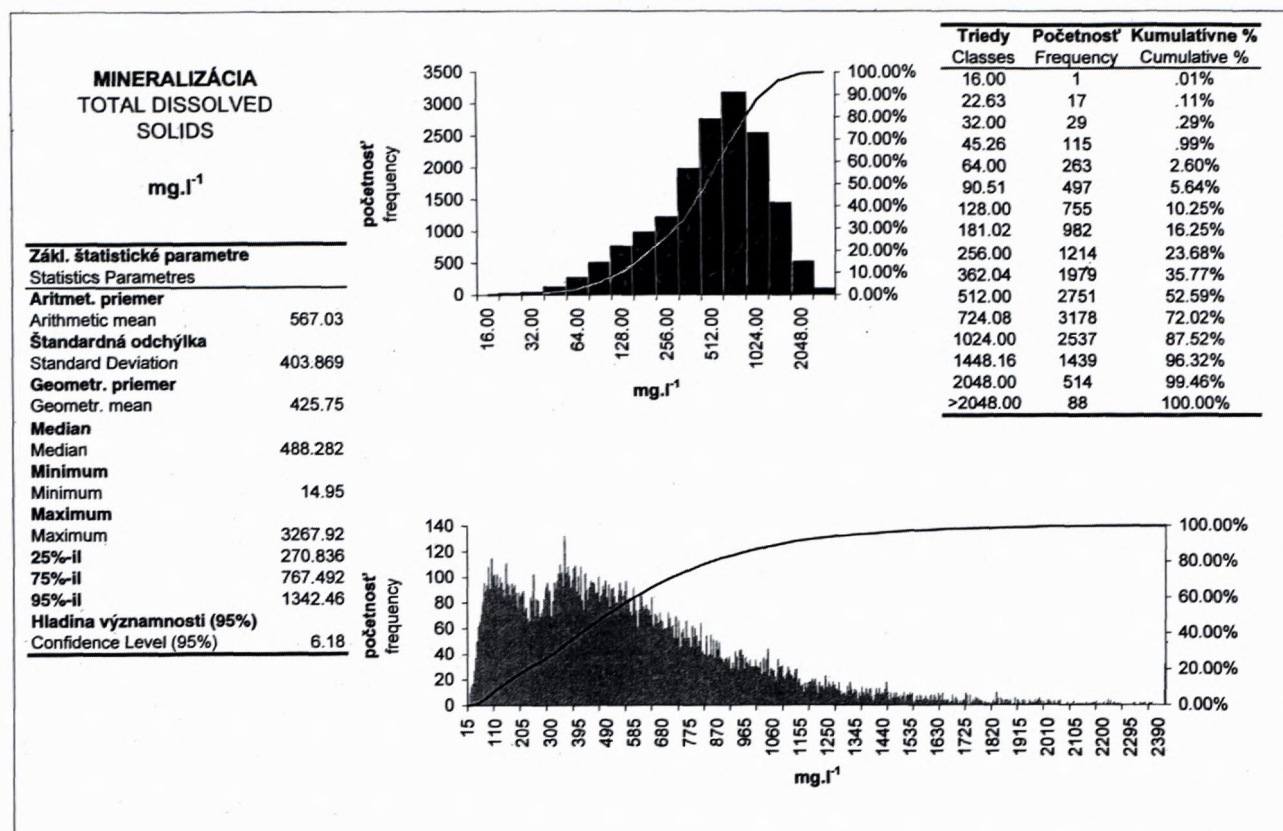
Composition of the Atlas

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

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%

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

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.
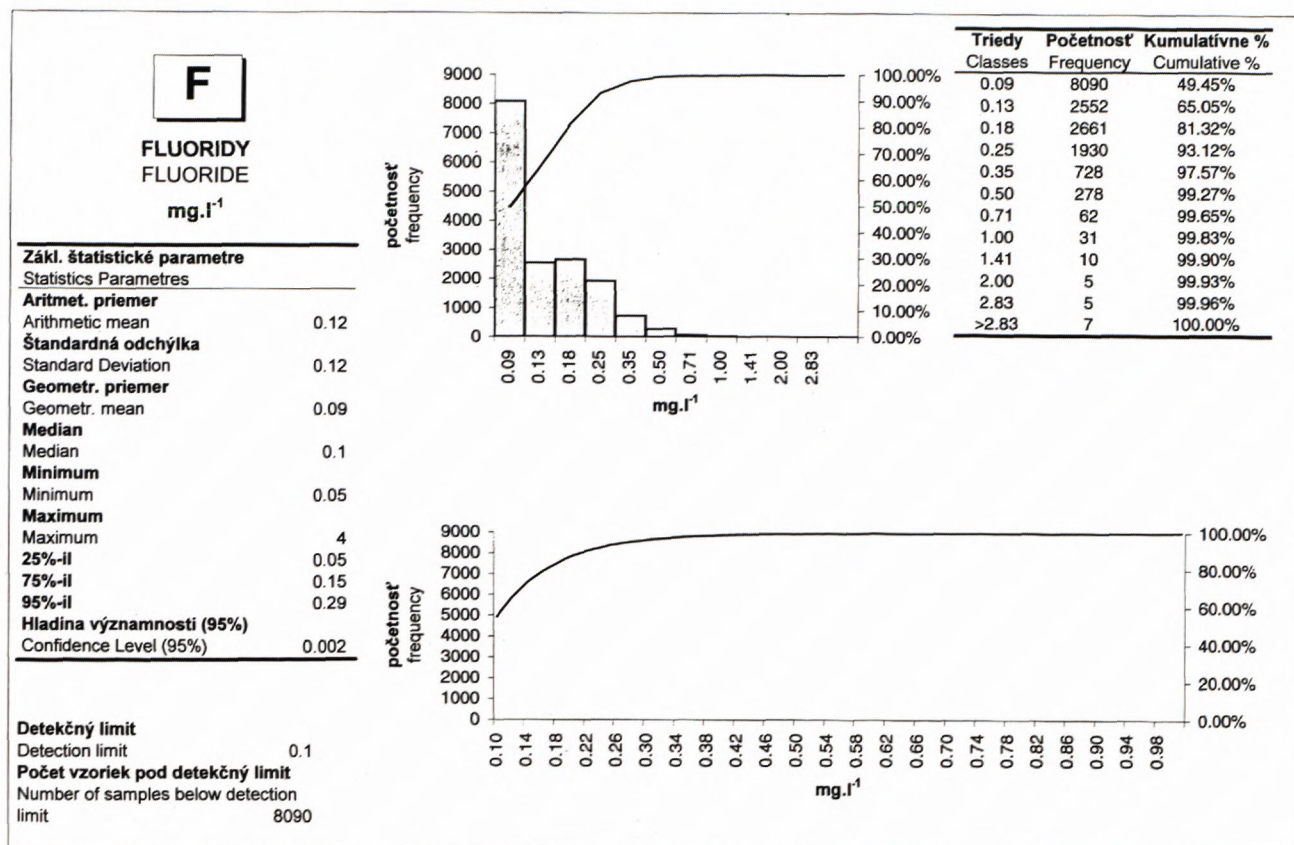
Arsenic (As) (atomic weight 74,921)

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	Početnosť	Kumulatívne %
Classes	Frequency	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.
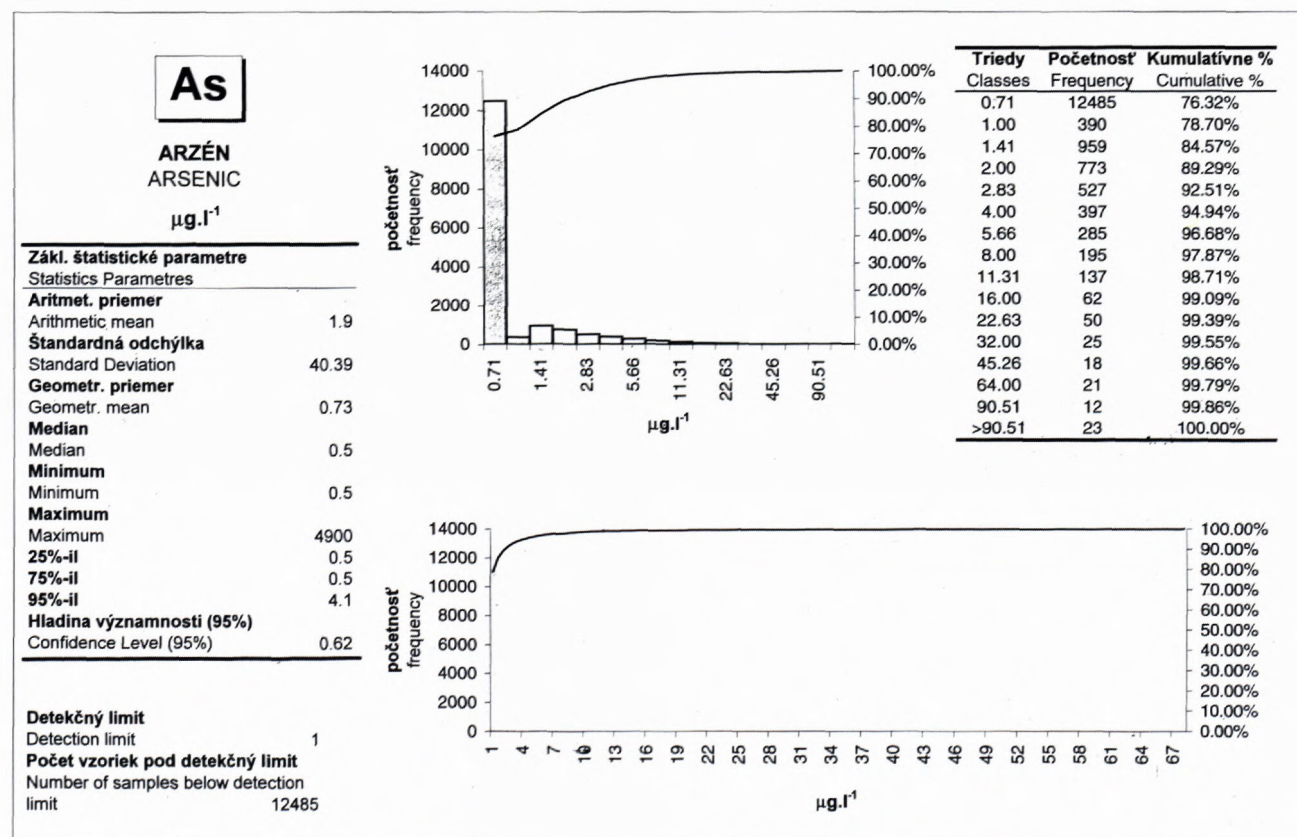
Flouride concentrations are also important from a hygienic point of view. The Slovak standard No. 75 7111 and the WHO standard specify, that the highest permissible fluoride content in potable water is 1,5 mg.l^{-1}. Owing to the mineralogic-petrographic character of rocks in Slovakia, fluorides are 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

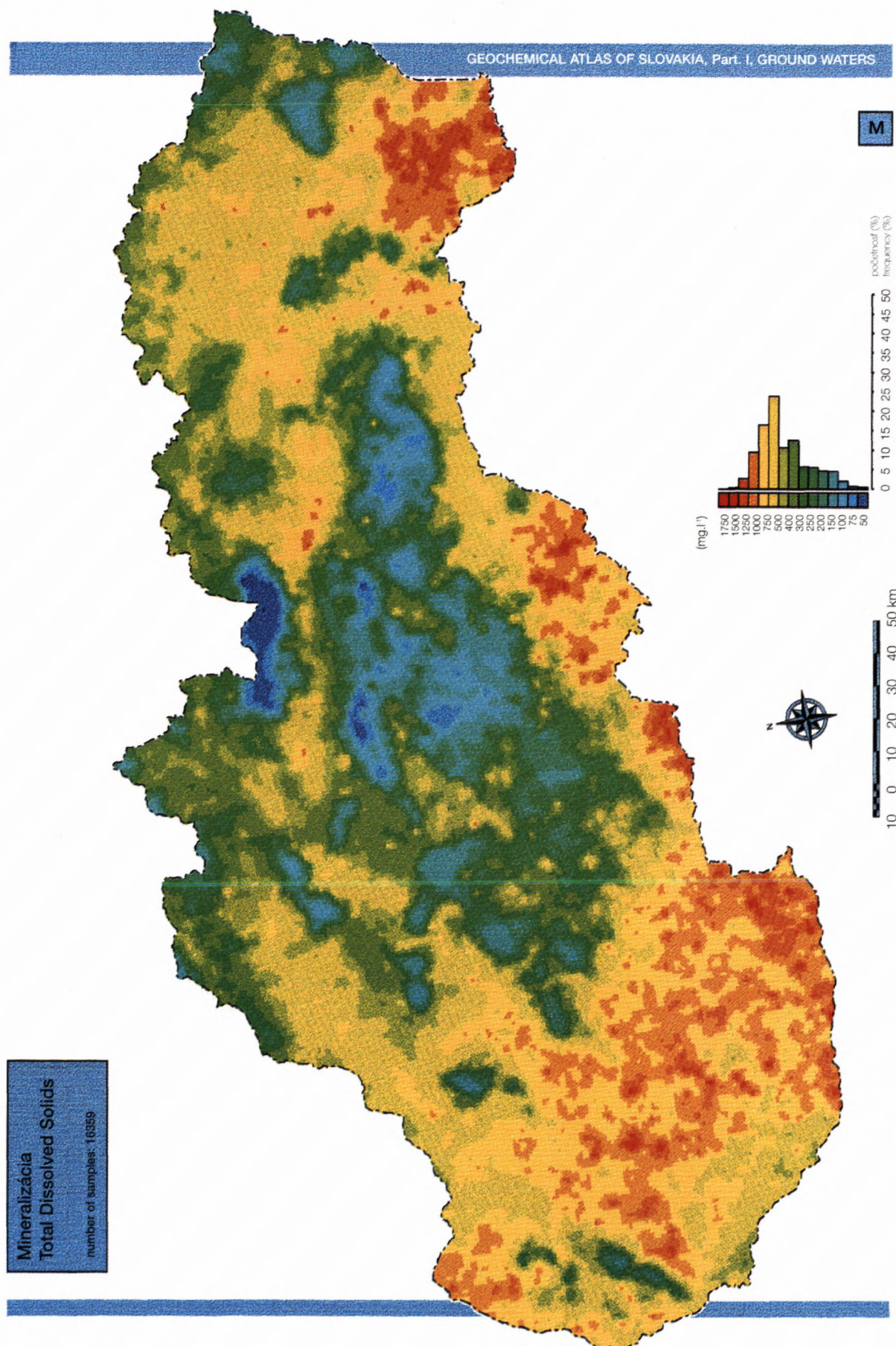| Triedy | Početnosť | Kumulatívne % |
Classes	Frequency	Cumulative %
0.71	12485	76.32%
1.00	390	78.70%
1.41	959	84.57%
2.00	773	89.29%
2.83	527	92.51%
4.00	397	94.94%
5.66	285	96.68%
8.00	195	97.87%
11.31	137	98.71%
16.00	62	99.09%
22.63	50	99.39%
32.00	25	99.55%
45.26	18	99.66%
64.00	21	99.79%
90.51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

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

Tab. 4 Statistical parameters ... As

GEOCHEMICAL ATLAS OF SLOVAKIA, Part. I, GROUND WATERS

M

Mineralizácia
Total Dissolved Solids

number of samples: 16859

Fig. 1 Map of T. D. S.

Fig. 2 Map of F

As

As
(µg. l⁻¹)

> 250
< 250
< 100
< 50
< 25
< 10

50 km

40

30

20

10

0

10

As

Arzén
Arsenic

počet vzoriek
number of samples   16359

počet vzoriek
pod detekčným limitom
(nezobrazené)   12485

number of samples
below detection limit
(not expressed)
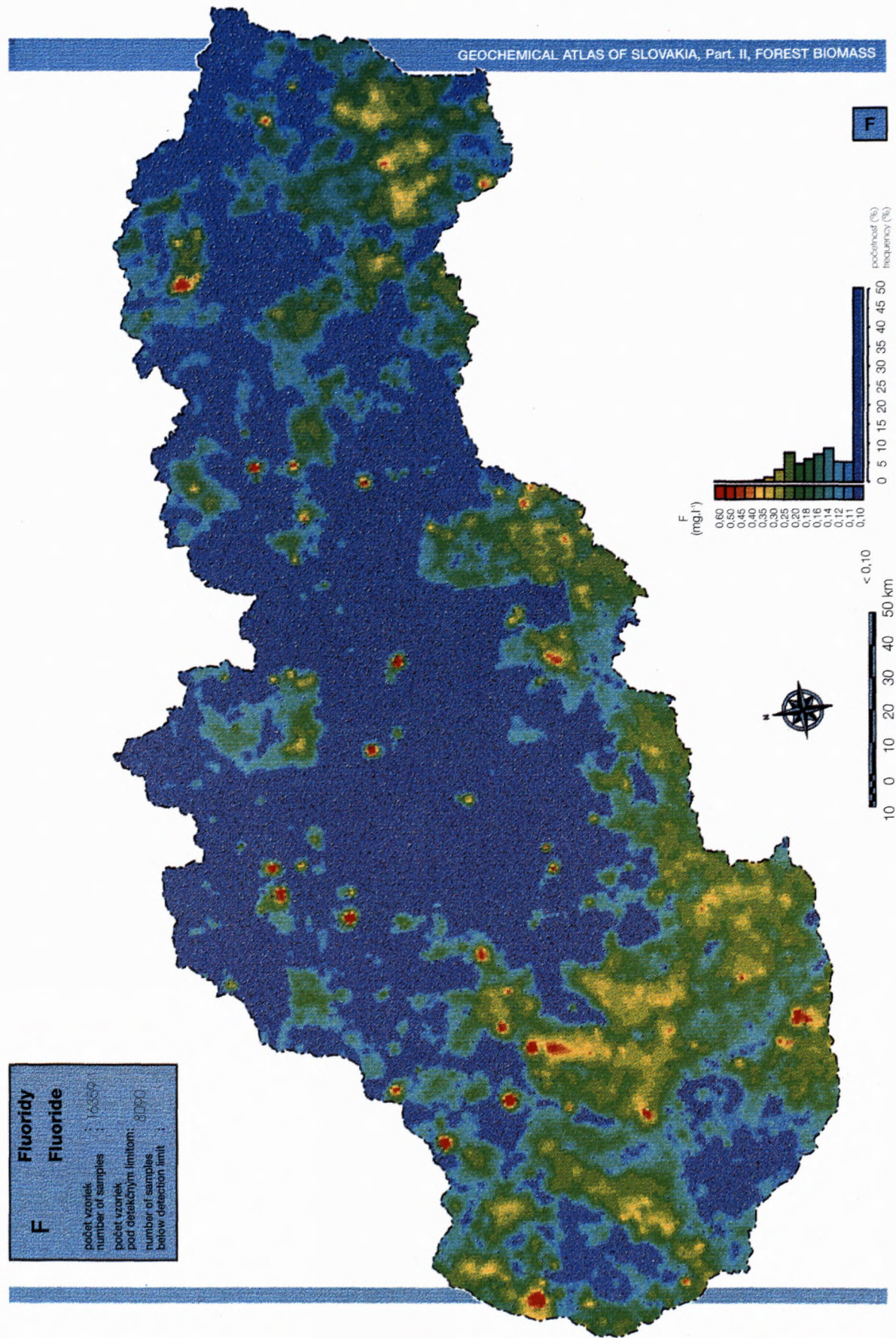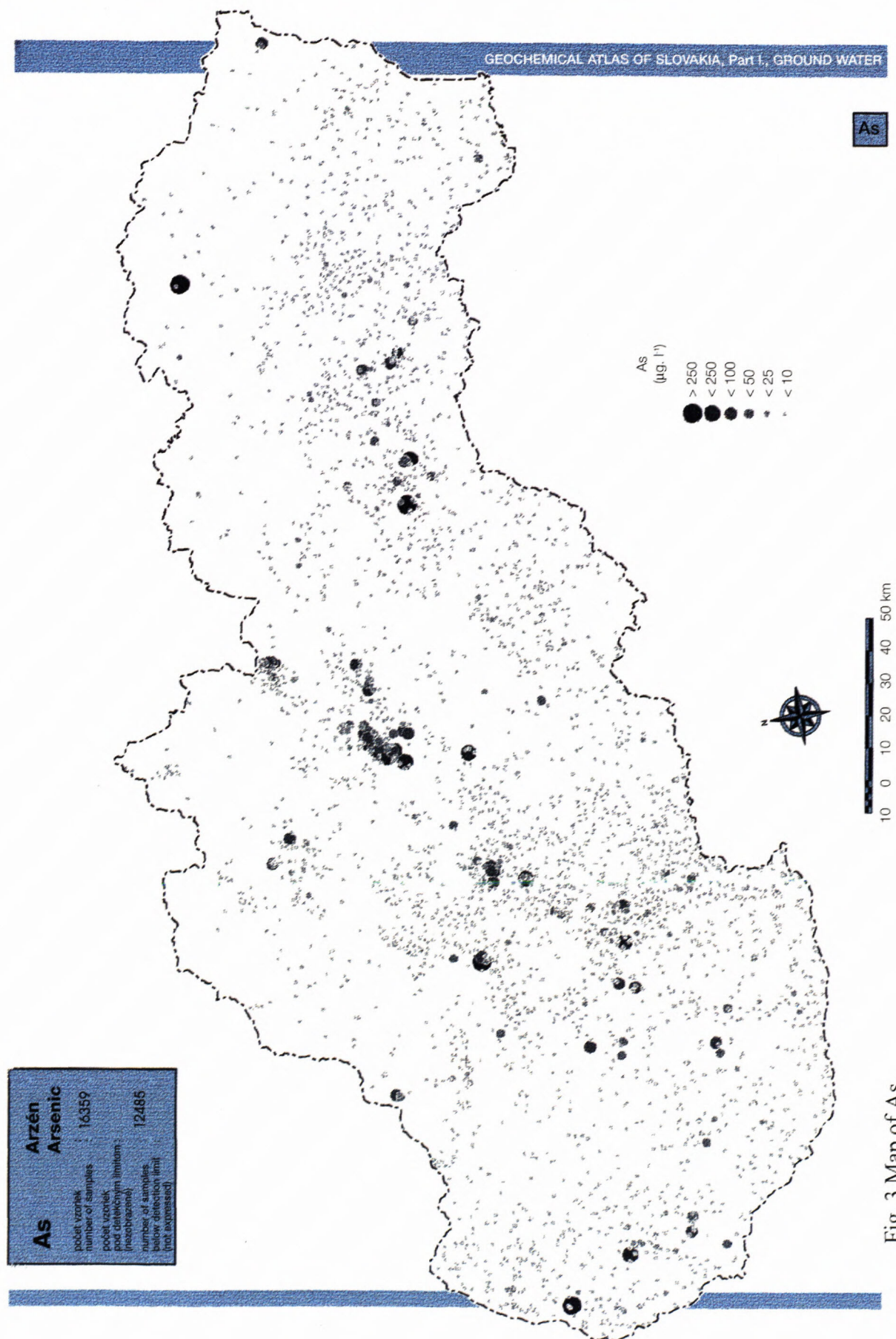
Fig. 3 Map of As

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.

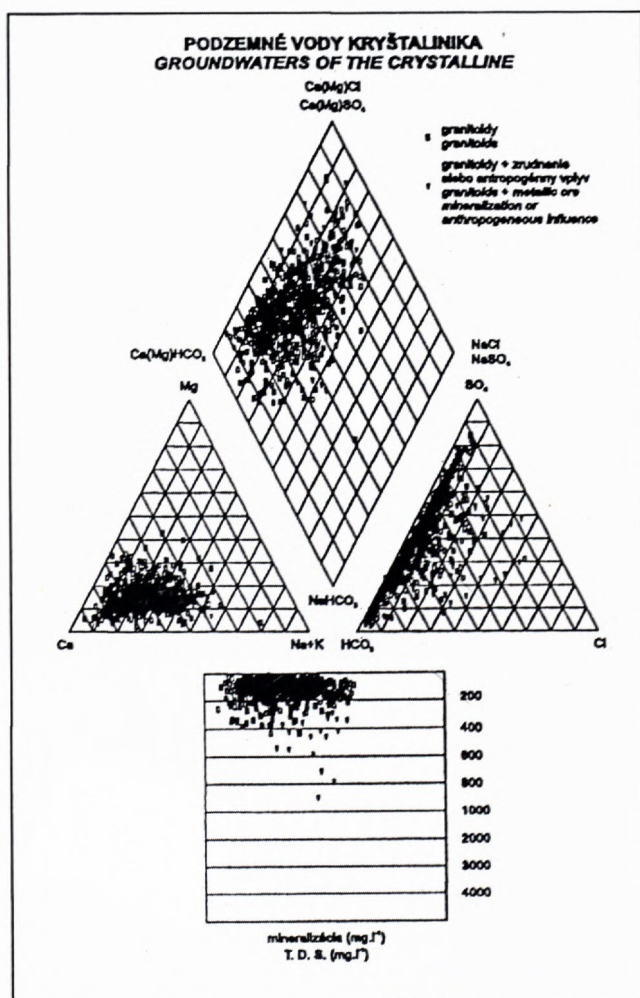The highest concentrations of virtually all trace ele-
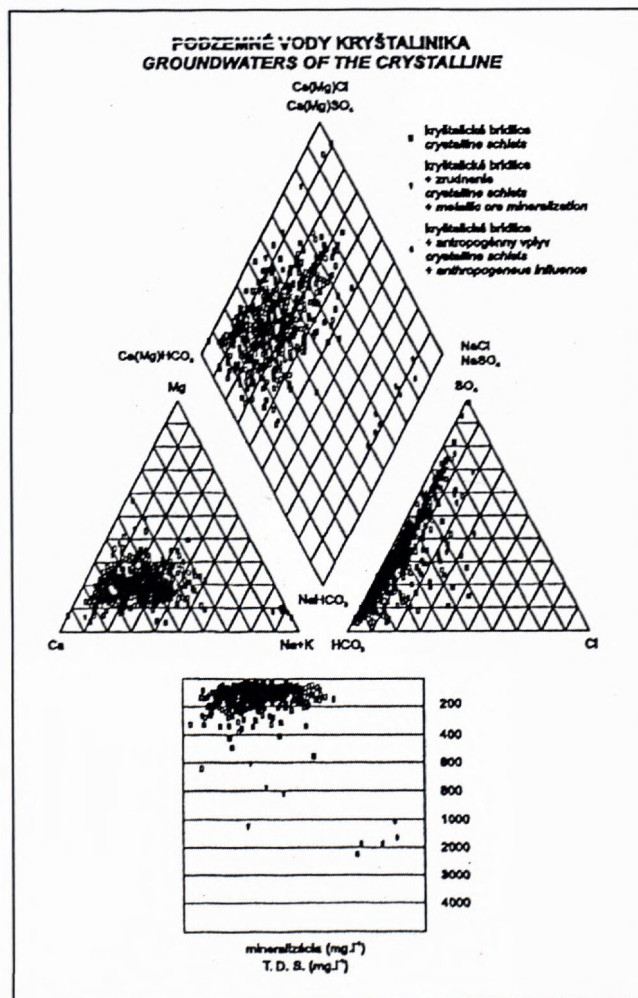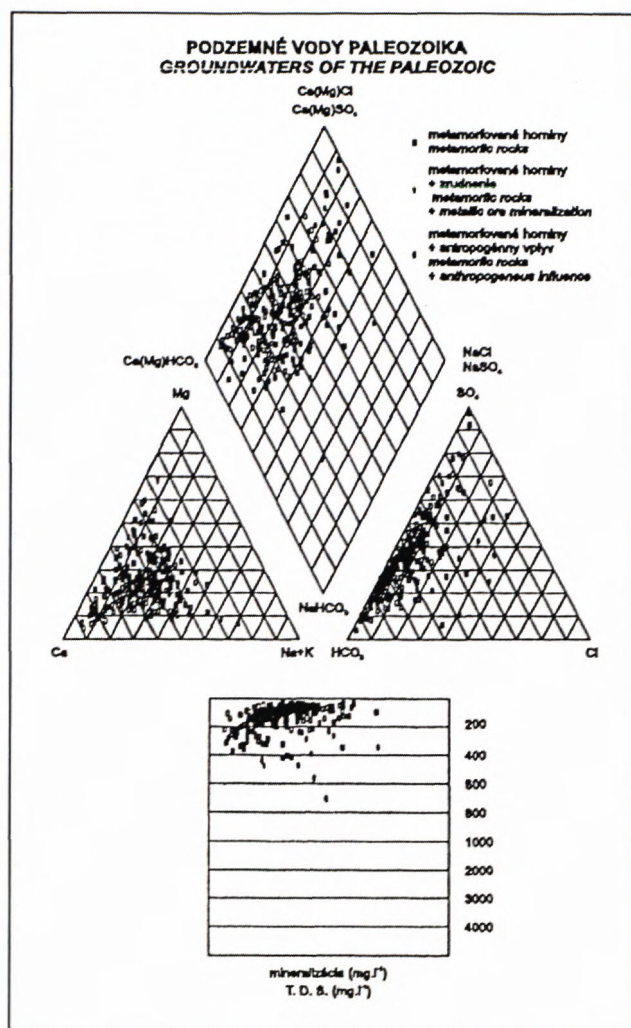

Fig. 4a-h systemization diagrams
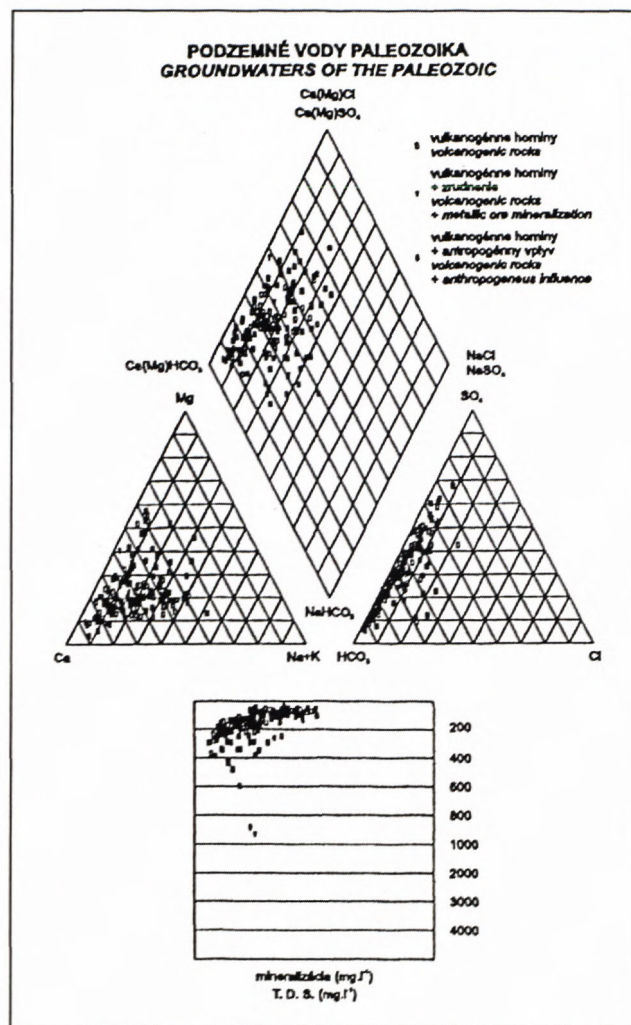
Fig. 4b

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}.
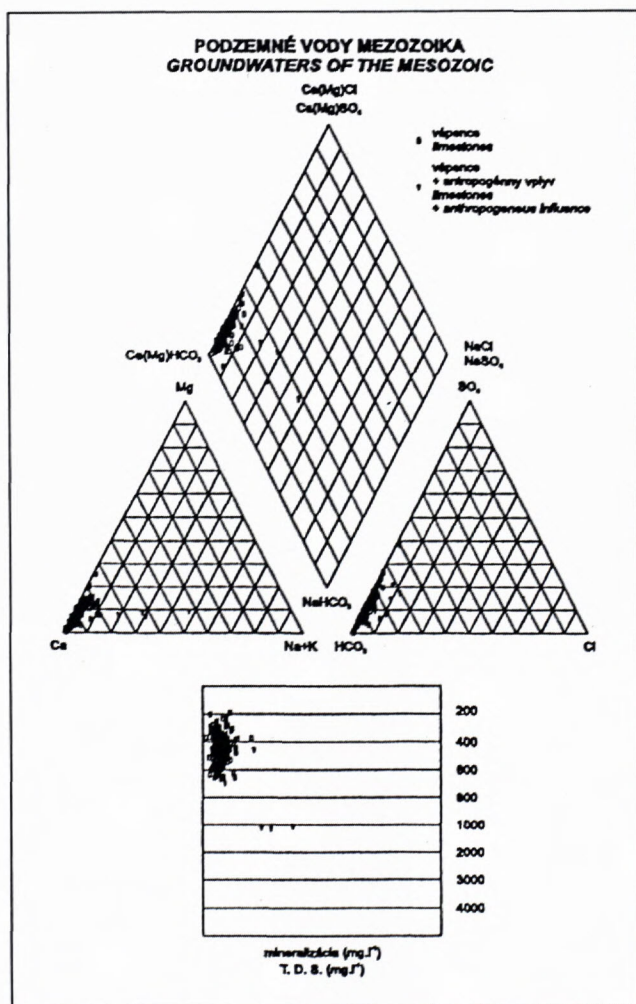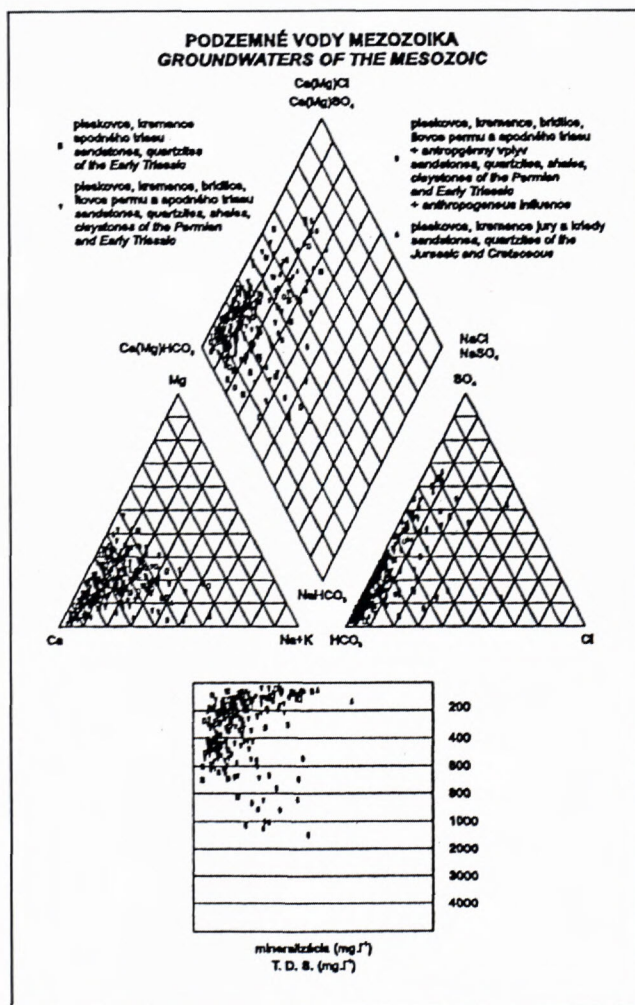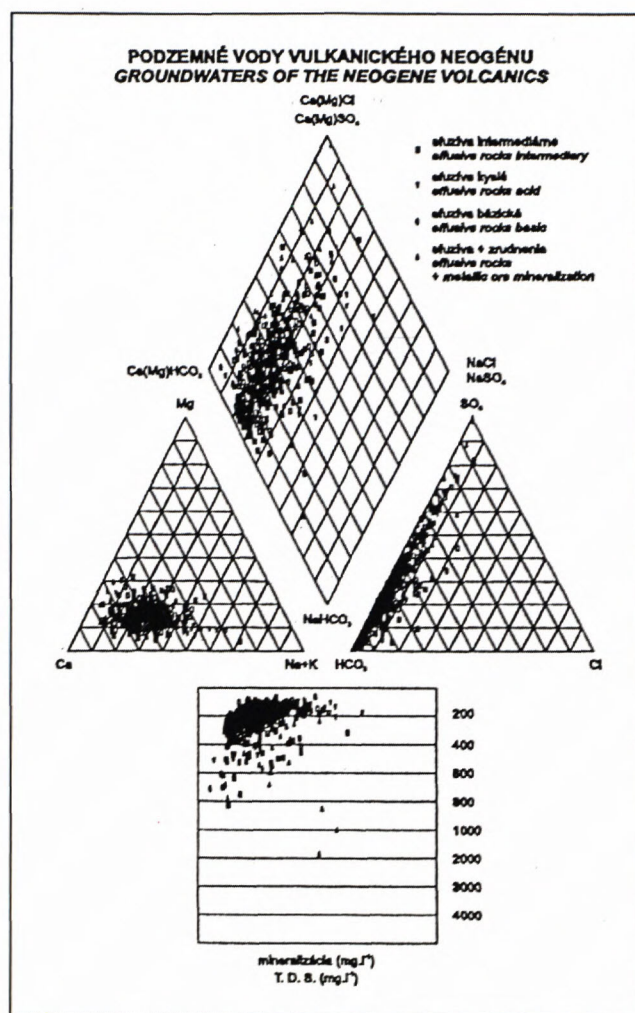

Fig. 4e

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 typicall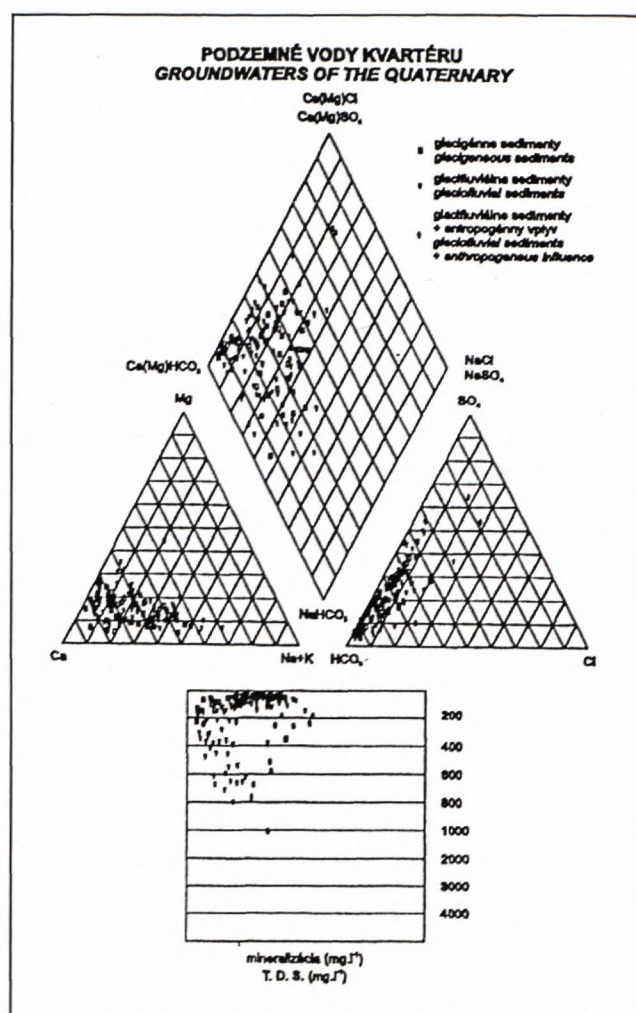y underlies fairly densely populated and industrialized intermontane depressions. The T.D.S. of groundwaters varies from 370 to 560 mg.l⁻¹, locally exceeding 1 000 mg.l⁻¹. The presence of man-made sources is reflected by COD_{Mn} values which sometimes attain around 10 mg.l⁻¹. The content of aggressive 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
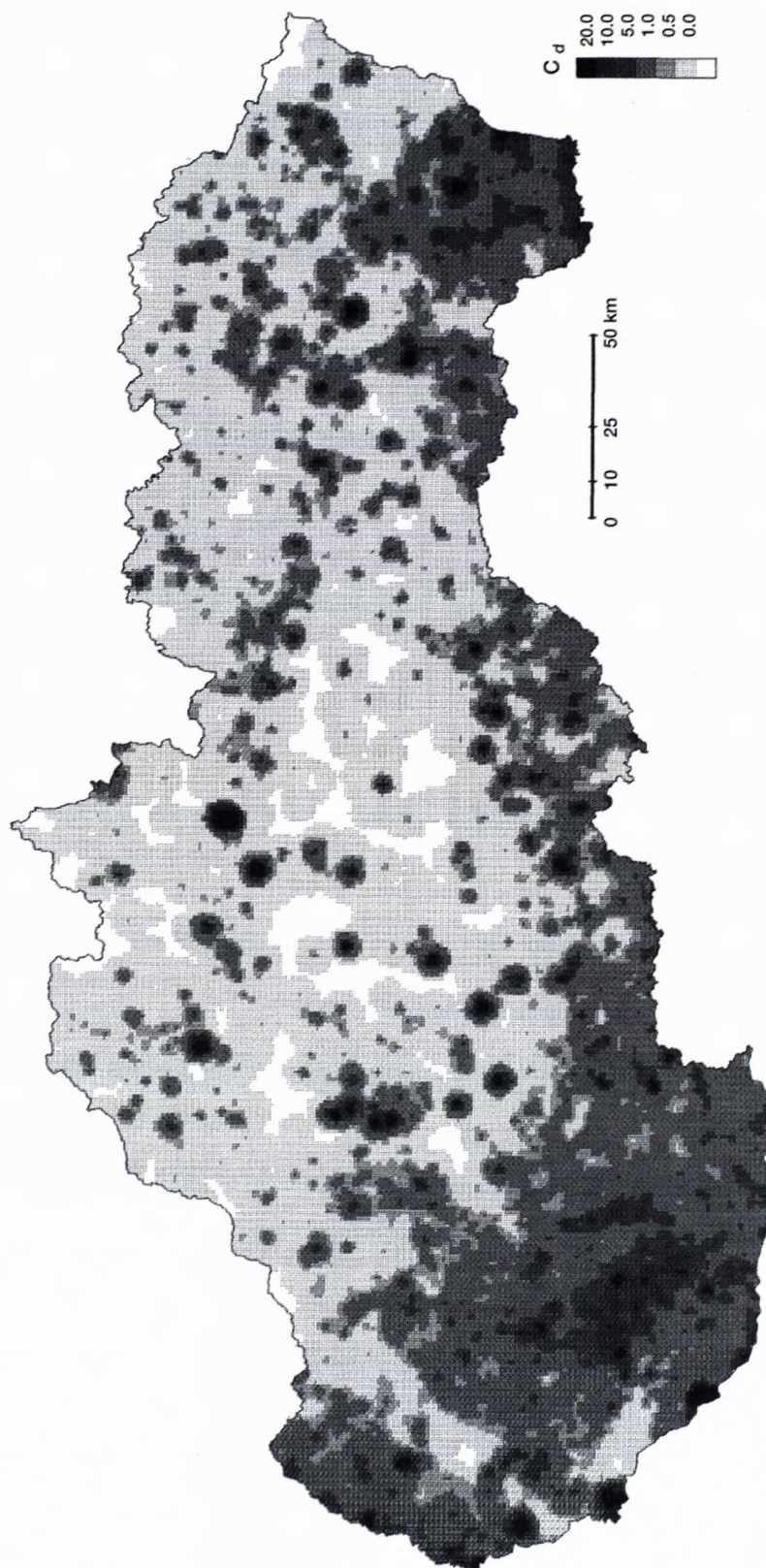
Fig. 5 Grounwater Contamination Degree map of Slovakia

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:
C_d – 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 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%

Number of exceeded limit values

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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