Geochemical Atlas of Slovakia and examples of its applications to environmental problems

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Abstract Results of comprehensive geochemical mapping and thematic studies of the Slovak territory (rocks, soils, stream sediments, groundwaters, biomass, and radioactivity) in the first half of the 1990s led to several new research programmes in Slovakia, within the frame of which new methodologies for geochemical data evaluation and map visualization were elaborated. This study describes the application and elaboration of data from the Geochemical Atlas of the Slovak Republic at national and regional levels. Based on the index of environmental risk ($I_{ER} = \Sigma PEC/PNEC$), the level of contamination for the geological component of the environment in Slovakia was evaluated. Approximately 10.5% of Slovakia's territory was characterized as being environmentally disturbed to highly disturbed. In the areas where environmental loadings have accumulated, 14 regions where environmental risks existed due to high element concentrations were defined. The model calculations of health risk estimates based on the databases of the Geochemical Atlas for groundwater and soils indicate that the possible risk occurrence of carcinogenic diseases from groundwater arsenic contents is high in more than 10% of Slovakia, whereas the chronic risk is negligible. To determinate the background and threshold levels a combined statistical–geochemical approach was developed and applied as an example for groundwater at the national level as well as for single groundwater bodies. The results of statistical method application for the whole groundwater body (GBW) were compared with the background values for anthropogenically non-influenced areas in GBW. Final background value took into account time variations and spatial distribution of the element in GBW. Furthermore, based on the database from the Geochemical Atlas for groundwater, groundwater bodies potentially at qualitative risk were delineated for the whole of Slovakia. From a total of 101 groundwater bodies 17 were characterized as being at risk and 22 as being at possible risk.

Keywords Geochemical atlas · Environmental risk assessment · Health risk assessment · Background and threshold values

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Introduction

The last decade of the twentieth century can be characterized from the point of view of trends in geochemistry in Slovakia, as well as in many other countries, as the decade of *Geochemical Atlases*. Although the programmes of geochemical atlas compilation in single countries were essentially based on national mapping programmes reflecting the natural particularities of these countries, from the very beginning their international dimension had been established through harmonization of basic methodological procedures of sampling, laboratory and interpretative procedures (Darnley 1990, 1994; Darnley et al. 1995).

In Slovakia, successful programmes for *Geochemical Atlases* (Vrana et al. 1997) undertaken during the 1990s were followed by a programme of *Environmental-geochemical maps of the regions* (Rapant et al. 1999). This programme has significantly extended and elaborated findings concerning the distribution of chemical elements/

compounds/parameters in geological compartments of the environment. Due to these research activities the Slovak Republic has been ranked in the forefront of worldwide geochemical environmental research involving both national and regional scales. Knowledge of geochemical background for the main compartments of the environment (rocks, soils, groundwater, biomass, stream sediments) in Slovakia is in such detail and of such quality that these national geochemical databases have spurred initialization of additional interpretations of the data in the context of other spheres of research, e.g. critical loads and exceedances (Bodiš et al. 1995), chemical time bombs (Rapant and Bodiš 1995), land use (Bodiš 2006), geomedicine (Khun et al. 2000; Rapant and Krčmová 2007) and risk analysis (Rapant and Kordík 2003). Due to the integrity of their geochemical data, representatives of the Slovak Republic have regularly taken part in international projects dealing with environmental protection and management (Babiaková et al. 1996; Bodiš and Rapant 2000; Vrana and Malík 2003; Brezsnyánszky et. al. 2006; Fordyce et al. 2007). Furthermore, experts from the Slovak Republic have also been involved in preparation of the Geochemical Atlas of Europe (Salminen et al. 2005).

This study presents examples of the use and elaboration of data from the Geochemical Atlases of the Slovak Republic for solving environmental problems at both national and regional scales. Examples are presented of the application of data from the Geochemical Atlases for media not commonly compiled elsewhere and employing methodologies developed by the Geological Survey of the Slovak Republic, or international methodologies adjusted for the natural conditions in Slovakia.

Geochemical Atlas of Slovakia

A description of the single parts of the *Geochemical Atlas of Slovak Republic* (GCHA SR) is summarized in Table 1. All parts of the GCHA SR were compiled based on the collection and analysis of new samples except for part *III—Rocks* for which about 30% of archival data, mainly on major elements, were used. A considerable advantage of the GCHA SR lies in the fact that the sample collection and field measurements were carried out over a relatively short period of time for all evaluated compartments (1991–1995). As a result an integrated national level of

Table 1 The composition of Geochemical Atlas of Slovakia

Part	Statistical sampling density	Number of samples	Analysed parameters	Note
I. Groundwater	1 sample/3 km^2	16,359	Al, As, Ba, Ca, Cd, Cl, COD$_{Mn}$, Cr, Cu, F, Fe, HCO$_3$, Hg, K, Li, Mg, Mn, Na, NH$_4$, NO$_3$, Pb, PO$_4$, Sb, Se, SiO$_2$, SO$_4$, Sr, Zn, pH, TDS, Ca + Mg, conductivity, free CO$_2$, aggressive CO$_2$	Springs, wells, boreholes, drainage
II. Forest biomass	1 sample/16 km^2	3,062	Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, F, Fe, Hg, K, Li, Mg, Mn, N, Na, Ni, Pb, Rb, S, Se, Sr, V, Zn	Leaves, needles
III. Rocks	Irregular net	3,839	Ag, Al, As, Cd, B, Ba, Be, Bi, Ca, Ce, Co, Cu, Cr, Ga, F, Fe^{2+}, Fe^{3+}, Hg, K, Na, P, La, Li, Mg, Mn, Mo, Ni, Pb, Sn, Rb, S, Si, Sb, Se, Sr, V, W, Ti, Y, Zn, Zr, CO$_2$, H$_2$O$^+$, 350°C	"Main rock types"
IV. Natural radioactivity				
Rocks	1 point/3 km^2	15,773	K, eU, eTh, eU$_t$, Da	Gamma activity
Water	1 sample/10 km^2	5,271	U$_{nat}$, ^{226}Ra, ^{222}Rn	Groundwater, surface water, thermal and mineral water
V. Soils	1 profile/10 km^2	10,380	Al, As, B, Ba, Be, Bi, Ca, Ce, Cd, Co, Cr, Cs, Cu, F, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, Sr, V, W, Y, Zn	1 profile = 2 samples (A and C horizons)
VI. Stream sediments	1 sample/2 km^2	24,432	Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Sn, Sr, Ti, V, W, Y, Zn, Zr	Active stream sediments <0.125 mm

understanding of the geochemical environment (geochemical baseline data) for the last decade of the twentieth century was obtained. The Geochemical Atlas of the Slovak Republic is complex from the point of view of its subject matter. Apart from the standard geochemical atlases—*Groundwater* (Rapant et al. 1996), *Soils* (Čurlík and Šefčík 1999) and *Stream sediments* (Bodiš and Rapant eds. 1999), geochemical atlases for *Rocks* (Marsina et al. 1999), *Natural Radioactivity* (Daniel et al. 1996) and *Forest Biomass* (Maňkovská 1996) were also published. The results were presented in a standard form of mono element maps displaying the distribution of analysed elements/compounds/parameters at a scale of 1:1,000,000, except for the geochemical atlas for rocks, in which the chemical composition of the 64 main rock types of Slovakia was characterized in tables of chemical analyses.
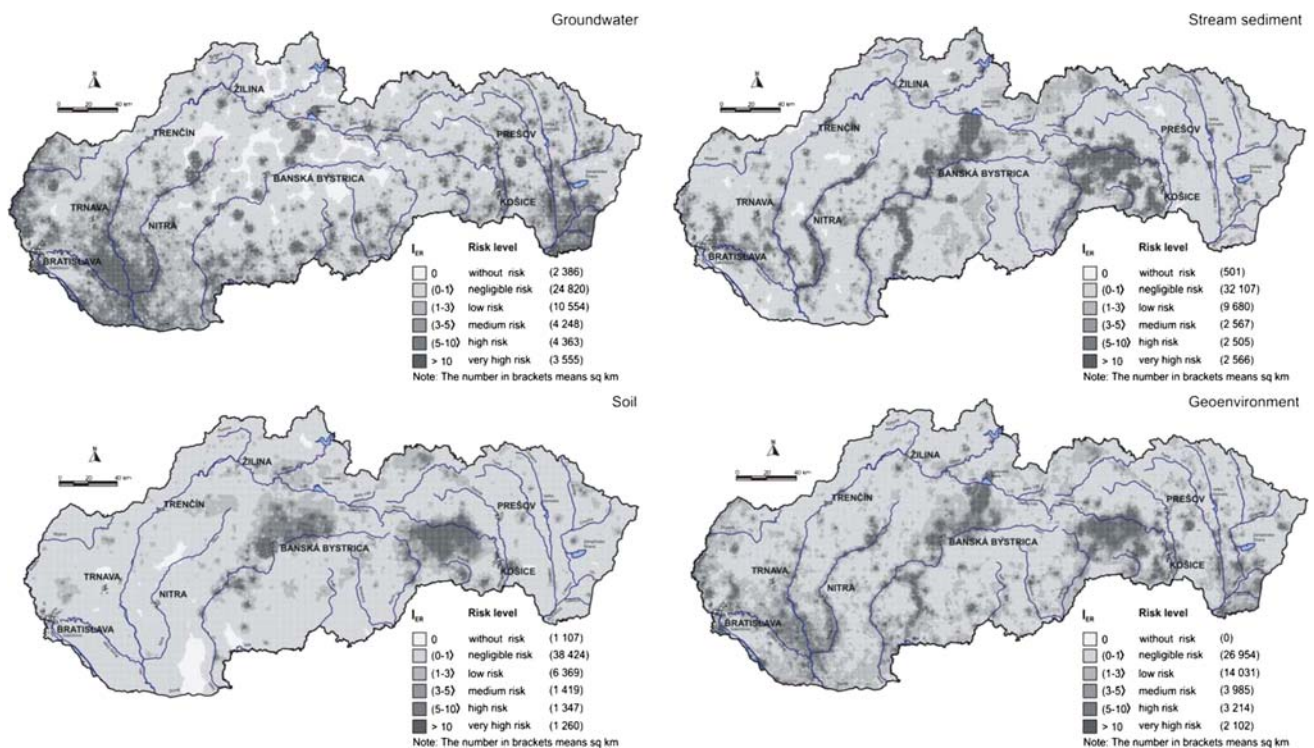
Environmental risk assessment and environmental geochemistry regionalization

Based on the calculation of an index of environmental risk (I_{ER}) following the procedures of Rapant and Kordík (2003) and Rapant et al. (2004) (where I_{ER} = sum of Q [hazard quotient], with Q = Predicted Environmental Concentration [PEC]/Predicted Non Effect Concentration [PNEC]) and using data from the *Geochemical Atlases of the Slovak Republic* maps of the environmental risk (ER) for potentially toxic element/compound contents in groundwater, soils, stream sediments and geoenvironment of the Slovak Republic were compiled (Fig. 1, according to Rapant and Kordík 2003, modified). For PEC, data from the GCHA SR were used, and the PNEC limit values from Slovak environmental directives were used (Anon 1994—soils and stream sediments; Anon 2004—groundwater). Calculation of the environmental risk index value (I_{ER}) for individual analysed water, soil and sediment samples consists of two steps. The first step is the calculation of the environmental risk quotient for each analysed chemical element or compound that exceeds the limit risk values. In the second step, their sum is calculated according to the denoted scheme:

$$I_{ER} = \sum_{i=1}^{n} Q_{Eri} \quad ; \quad Q_{ERi} = \frac{AC_i}{RC_i} - 1$$

Q_{Eri} – environmental risk quotient of the *i*-element, which exceeds the risk (limit) concentration;

AC_i – *i*-element analytical concentration; RC_i—*i*-element risk (limit) concentration;

I_{ER} – environmental risk index of the sample tested.

Fig. 1 Environmental risk for the potentially toxic elements/compounds in geological compartments in the Slovak Republic

The calculations do not discriminate the source of increased levels of the elements. Ultimately it does not matter whether high values are caused by anthropogenic contamination or natural conditions (geochemical background). The real question is the level of environmental risk to which biota and humans are exposed, and that is independent of source.

The above I_{ER} calculations and visualizations of ER indices in the form of pixel maps were used for subsequent environmental risk assessments for individual regional and administrative units of the Slovak Republic. Through the averaging (arithmetic mean) of ER indices for the individual pixels covering the evaluated units (the calculation included also those pixels partially touching the evaluated area), I_{ER} values were calculated for each assessed unit of the Slovak Republic. Subsequently, the ER maps for the individual districts, municipalities, geomorphological units and basic catchments of the Slovak Republic were compiled (Rapant et al. 2004). According to I_{ER} values Slovakia was additionally divided into five main levels of environmental quality (Fig. 2). The first level (high quality with $I_{ER} < 1$) represents the status of an environment with no stress with the least influence of human activities and without increased contents of elements of concern of natural origin in the geological environment, i.e. the nearest to

the status of ecological stability. The last, fifth level (highly disturbed and of poor quality with $I_{ER} > 10$) defines the status of an environment that has undergone extreme changes due to the influence of human activities or with extremely high contents of elements, potentially of concern of geogenic origin, i.e. with the highest levels of environmental stressors and environmental disturbance. The areas where environmental loadings have cumulated were defined and characterized as possible environmental risk regions (Fig. 2). These regions have internal similarity or are distinguished from their surrounding areas by mutual diversity. Within the defined risk areas, in addition to the summary risk factor (I_{ER}) other internal and external factors and features of single elevated element concentrations contributing to the I_{ER} (toxicity or hazard of evaluated element of concern, migration ability, vulnerability of the environment, etc.) have been taken into account. Additionally, risk factors had to be present in more significant amounts in at least two of the three evaluated compartments. The basic characteristics of the areas of concern in Slovakia are reviewed in Table 2, stating the dominant origin of the elements/compounds and the most significant source of each.

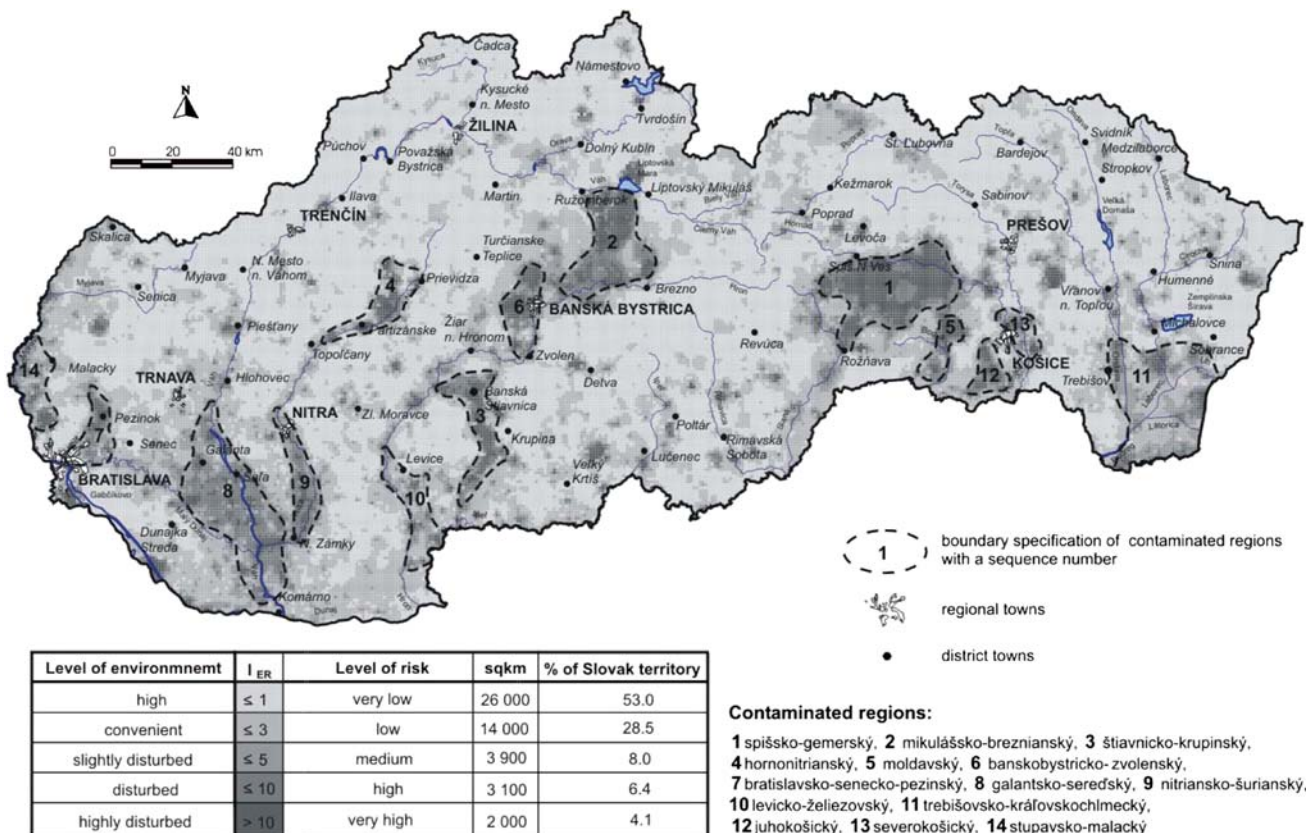The total area of regions of concern in the Slovak Republic is more than 5,000 km², this represents about

Level of environmnemt	I_{ER}	Level of risk	sqkm	% of Slovak territory
high	≤ 1	very low	26 000	53.0
convenient	≤ 3	low	14 000	28.5
slightly disturbed	≤ 5	medium	3 900	8.0
disturbed	≤ 10	high	3 100	6.4
highly disturbed	> 10	very high	2 000	4.1

Contaminated regions:

1 spišsko-gemerský, 2 mikulášsko-breznianský, 3 štiavnicko-krupinský, 4 hornonitrianský, 5 moldavský, 6 banskobystricko-zvolenský, 7 bratislavsko-senecko-pezinský, 8 galantsko-sereďský, 9 nitriansko-šurianský, 10 levicko-želiezovský, 11 trebišovsko-kráľovskochlmecký, 12 juhokošický, 13 severokošický, 14 stupavsko-malacký

Fig. 2 Environmental-geochemical regionalization of Slovakia

Table 2 Basic characteristics of contaminated regions of Slovakia

Contaminated regions	Area (km^2)	I_{ER}	Prevalent origin	The most significant substances of concern			Level of substances of concern		
				Groundwater	Soils	Stream sediments	Groundwater	Soils	Stream sediments
1.	910	20.7	G	As, Sb, Fe, Mn	Hg, Sb, As	Cu, As, Hg, Pb, Sb	++	++++	++++
2.	650	14.5	G	As, Sb, SO$_4$	As, Sb, Cu	As, Sb, Cu, Hg	+++	++++	++++
3.	400	9.0	G	Fe, Mn, SO$_4$, NO$_3$	Pb, Cu, Mo	Cd, Cu, Zn	++	+++	++++
4.	320	8.1	G–A	As, Fe, Mn, NO$_3$	Hg, As	As, Hg	+++	+	+++
5.	150	20.3	G–A	Mn, NO$_3$, Fe	Ni, Cr, Sb, As	Sb, Ni, Cu	++	+++	++++
6.	280	13.8	G–A	Sb, Cd, As	Cu, Sb, Hg	Cu, Hg, As	+	+++	++++
7.	220	7.1	G–A	NO$_3$, SO$_4$, Fe, Mn	Ba, Sb, Cu	Sb, As, Cu, Hg	+++	+	+++
8.	1,100	6.9	A	NO$_3$, SO$_4$, Mn, Fe	Ni, Cu	Hg, Cu, Cd, Zn, Cr	++++	+	++
9.	290	7.0	A	NO$_3$, Mn, NH$_4$, Fe	Mo, Ba	Hg, Cd, Cr	++++	+	++++
10.	350	4.3	A	NO$_3$, Mn, Fe	Cu, Sb, Hg	Zn, Cu, Hg	++++	+	++
11.	1,100	4.3	A	NO$_3$, TDS, Cl, Mn	Ni, Cu, Cr	Cu, Pb, Se, Ni	++++	+	+
12.	150	8.2	A	NO$_3$, Mn,	Sb, As, Ni	Sb, As, Cd	++	++	++++
13.	140	6.5	A	Mn, Fe, NO$_3$	Cu, Sb, Hg	Cu, Ba	+++	++	+
14.	300	6.8	A	Fe, Mn, NO$_3$, SO$_4$	Hg, Ni	Hg, Sb, Zn, Cu	++++	+	++

Note: level of substance of concern: ++++ very high, +++ high, ++ medium, **+** low, A: anthropogenic, G: geogenic, G–A: geogenic–anthropogenic

1. spišsko-gemerský, 2. mikulášsko-breznianský, 3. štiavnicko-krupinský, 4. hornonitriansky, 5. moldavský, 6. banskobystricko-zvolenský, 7. bratislavsko-senecko-pezinský, 8. galantsko-seredský, 9. nitriansko-šurianský, 10. levicko-želiezovský, 11. trebišovsko-kráľovskochlmecký, 12. juhokošický, 13. severokošický, 14. stupavsko-malacký

11% of Slovakia. Two-thirds of these are characterized by intensive land use and relatively dense settlements. About one-third represents mountain areas (almost solely historical mining areas) with a low density of settlement. The transformation of the data from the Geochemical Atlas of the Slovak Republic into the form of maps of environmental risk and environmental geochemical regionalization offers an objective procedure for identifying the contamination of geological compartments by anthropogenic sources, or the presence of geological compartments that are themselves significant sources of elements of concern, for use by appropriate ecological–environmental management authorities.

Health risk assessment

The data from the GCHA SR at both national and regional scales was applied to the calculation and mapping of health risk estimates arising from the contamination of geological environments (groundwater, soils). Health risk, the probability of adverse effects of human exposures due to environmental hazards, was calculated and assessed using the US EPA approach based on quantitative risk level estimates for chronic as well as carcinogenic effects (US EPA 1989a; 1999). Chronic risk was assessed based on the presumption of manifestation of adverse chronic effects until the threshold (tolerance chemical level) expressed as

the so-called reference dose (RfD) was exceeded. Characterization of carcinogenic risk was based on the presumption that there is no toxicological threshold and safe dose, and each level of exposure can generate a carcinogenic response. The risk level was assessed for oral exposure through groundwater and soil ingestion pathway for adults as well as children using the following equations:

Calculation of average daily doses for groundwater/soil ingestion:

$$\text{ADDwater} = \frac{C \times \text{IR} \times \text{ED} \times \text{EF}}{\text{BW} \times \text{AT}}$$
$$\text{ADDsoil} = \frac{C \times \text{IR} \times \text{ED} \times \text{EF} \times \text{FI} \times 10^{-6}}{\text{BW} \times \text{AT}}$$

where ADD is the average daily dose (mg kg^{-1} day^{-1}), C is chemical groundwater or soil concentration (mg l^{-1} or mg kg^{-1}), IR is the ingestion rate (l day^{-1}), ED is the exposure duration (year), EF is the exposure frequency (day year^{-1}), BW is the body weight (kg), AT is the averaging time = average lifetime (day), FI is the fraction of ingested soil (−).

Calculation of chronic risk level was based on the Hazard Quotient method (HQ = ADD/RfD). The existence of chronic risk is assumed if HQ > 1. Carcinogenic risk level (CR = ADDxCSF) was estimated for arsenic (CSF, cancer slope factor = 1.5 [(mg kg^{-1}) day^{-1}]) and expressed as the number of cases of neoplasm occurrence per unit population. Conventionally accepted exposure parameters defined

by US EPA (1989a, b; 1991) were used, including 64 years exposure duration for adults and 6 years for children, exposure frequency 365 days, 70 kg body weight for adults and 15 kg for children, groundwater ingestion rate of 2 L per day for adults and 1 L per day for children, soil ingestion rate 100 mg day^{-1} for adults and 200 mg day^{-1} for children and lifetime 70 years, fraction of ingested soil is conventionally equal to 1. The health risk was estimated based on total contents of the elements in compliance with valid methodologies for quantitative health risk estimation (US EPA 1999), which are available for single element species only in some cases (e.g. Cr^{III}/Cr^{VI}).

Chronic and carcinogenic risk was calculated for all the data from the Geochemical Atlas of the Slovak Republic, for groundwater and soil. The results obtained were subsequently transformed into a health risk assessment map (Fig. 3) using an inverse distance and moving average method for data interpolation.

The model calculations of health risk estimate that the possible risk occurrence of carcinogenic diseases from arsenic groundwater contents is high in more than 10% of Slovakia. However, the majority of the Slovak population is provided with drinking water from public water supplies and so they are not exposed directly to risk from elevated concentrations in natural groundwaters. The maps of health risk estimates for potentially risk element/compound contents in geological environments indicate that the residents of Slovakia are at some risk. The task for geologists in collaboration with other specialists, mainly epidemiologists, is to evaluate the real threat and suggest strategies that can reduce possible negative impacts.

Estimation of background and threshold levels

The estimation of background and threshold levels for single chemicals in groundwater is complicated and also a "sensitive" issue from an economic point of view (implementation of Water Framework Directive [WFD], river basin management plans). Nowadays, there are many background definitions and approaches for estimating its range (e.g. Förstner et al. 1990; Matschullat et al. 2000; Bodiš and Rapant 2000; Reimann and Garrett 2005; Reimann et al. 2005). For the estimation of background and threshold levels for groundwater at the national level as well as for single groundwater bodies a combined procedure was developed (Bodiš 2007) based on both statistical and geochemical approaches. The proposed methodology stems from the availability of input information, conceptual models and hydrogeochemical interpretations of
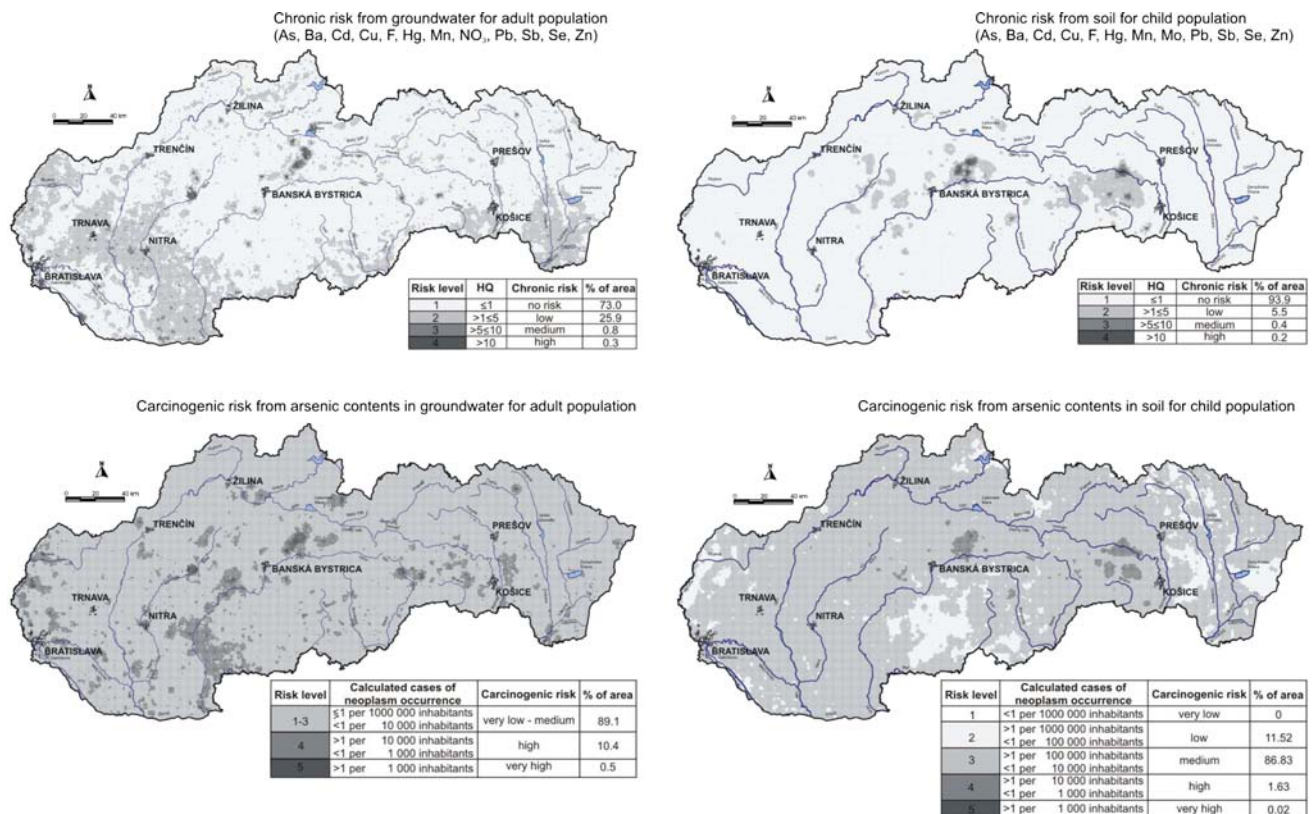
Fig. 3 Health risk for the potentially toxic elements/compounds in groundwater and soil in the Slovak Republic

conditions in the Slovak Republic. For the purposes of the WFD implementation, the background value was defined as the spatially and temporally characteristic concentration range (interval) of the chemical in the groundwater that does not include positive, or even negative anthropogenic or highly contrasting (anomalous) geogenic influences. Then the background value is understood to be the concentration of the upper limit of the background range. To assess groundwater quality it is quite common to make use of background levels and generic reference values and threshold levels according to possible receptors, which are in general ecosystems and human uses. Background and threshold levels are identical when the background level is greater than or equal to the reference value. The input data consists of the database from Geochemical Atlas of the Slovak Republic and the results of geochemical monitoring of groundwater quality in Slovakia.

Statistical approach

- Estimation of summary statistics in the case of data less than the detection limit requires special procedures. For this purpose we have tested some of the convenient methods (US EPA 1998, 2000; Helsel and Hirsch 1992). The criterion for selecting the most suitable method included uncertainties and limitations resulting from the number of values below the detection limit within the dataset. In the case when more than 60% of measurements do not reach the concentrations at the level of detection limit we recommend to elaborate censored data using Kaplan–Maier analysis (Kaplan and Maier 1958) for estimation of the summary statistics. Then the 75th percentile represents the background value. For the datasets with 60–80% censored data we recommend to use maximum likelihood methods. It is recommended that only meaningful values are estimated for the datasets with more than 80% of censored data.
- Determination of the distribution character of the evaluated chemical element/compound (visually, histogram, testing of character of distribution),
- Estimation of background value (identification and elimination of outliers). This step is undertaken for each element/compound and works as a function of the character of the input data. We recommend using an iterative two standard deviation procedure (Erhardt et al. 1998) consisting of repeated elimination of distant data higher or lower than mean $\pm$ 2 s, respectively, until an approximation to the normal distribution is achieved. Then the background value is considered to be mean +2 s from the data induced in the last iteration. This is a relatively radical and mathematically robust method that we have applied, and have found it the most suitable method of those that we have investigated.

Geochemical approach

This represents the estimation of background value with minimal naturally or anthropogenically influenced groundwater in the respective groundwater body. We used the following criteria for the selection of minimally influenced samples:

- Elimination of each sample that does not meet the condition that the concentration is lower than a half of the reference value (drinking water standards). The sample elimination is done also in the case when only one compound does not satisfy this principle.
- From the samples meeting the first condition the background value corresponds to the concentration determined as the 90th percentile.

Furthermore, the final selection of the background value involves a geochemical and hydrogeological review of the statistically and geochemically estimates and the eliminated extreme values. The estimation of geological and anthropogenic influences on the determined background value and its verification was performed using a GIS technique via the comparison with a map of land use and hydrogeological conditions in the groundwater body. For this purpose we used the following hydrogeological parameters:

a. Identification of the areas of groundwater recharge;
b. Identification of the areas of groundwater discharge; and
c. Identification of general directions of groundwater flow within the body.

For synthetic organic compounds (i.e. not of natural origin) the background and threshold value is "zero concentration", and this is in practice the value of the detection limit of a particular organic compound. We propose that in accordance with the background criteria for the identification of groundwater thresholds (BRIDGE) project the threshold, "action value", is a half of the interval between the mean + 2 s value and the reference value (the drinking water standard).

The very strong anthropogenic influence on the concentration of some of the ions can severely distort the determination of their background range and "action level". In this case the background value does not correspond to the definition of spatially and temporally characteristic range of concentration of chemical in groundwater, not including positive or negative anthropogenic and arbitrary (anomalous) geogenic influences. An example of this is the background value for chlorides— 76.26 mg l^{-1} estimated by the mean + 2 s procedure for the Hornád Quaternary groundwater body (Fig. 4).

It is evident that this is an overestimated concentration due to secondary contamination of the aquifers. This stems
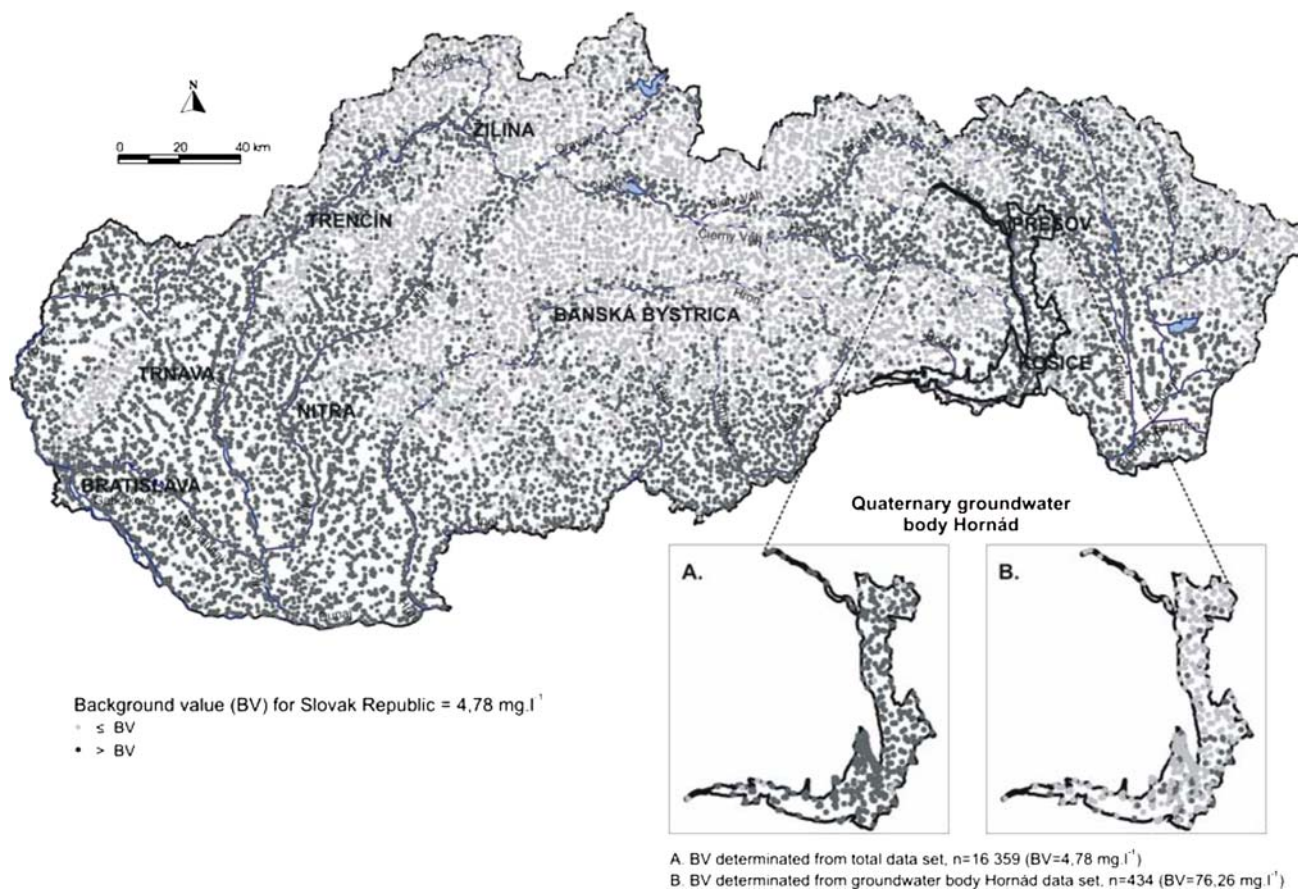
Fig. 4 Distribution of chlorides in groundwater in relation to background value determined from the Geochemical Atlas dataset ($n = 16,359$)

from the fact that the source of chlorides in Slovakia can be atmospheric deposition and, in the case of Quaternary groundwater bodies, also underlying Neogene sediments from which waters with increased chloride contents can infiltrate the Quaternary groundwater bodies. The average content of chlorides in snows derived from the 25-year monitoring of the Slovak territory ranges within 1.45–3.88 mg l^{-1} (Bodiš et al. 2000). There are no data on infiltration from underlying Neogene sediments into the Hornád Quaternary groundwater body. This simple consideration helps us to deduce the calculated background value to be incorrect, or high in relation to the initial water and rock background. Since chlorides represent a conservative ion with a high efficiency of migration and there is an evident difference between their distribution in pre-Quaternary and Quaternary groundwater bodies we use them as an example of an application of the dataset from the Geochemical Atlas of the Slovak Republic for the calculation of the background value. The distribution of chlorides in the Geochemical Atlas of the Slovak Republic is bimodal (Fig. 5), with the right side of the distribution probably being induced by anthropogenic sources. After the application of the mean + 2 s procedure (see Fig. 6)
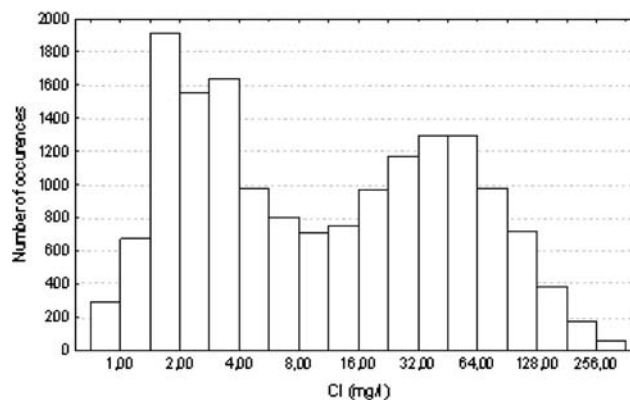
Fig. 5 Histogram of chlorides (before adaptation)

the background value for Slovak groundwater was estimated as 4.78 mg l^{-1}, which could actually correspond to their atmospheric input. Based on this scheme (Fig. 4) it can be supposed that the distribution of chloride contents higher than the background value (4.78 mg l^{-1}) is characteristic for all Quaternary groundwater bodies, and its practical use clearly documents the intensity of anthropogenic influences. In the case of individual estimations of
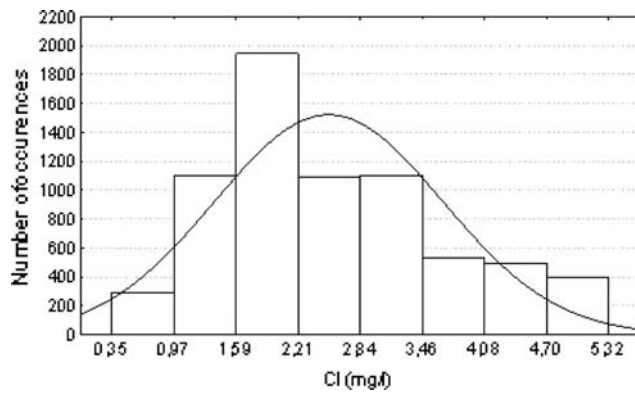
Fig. 6 Histogram of chlorides after adaptation with 2 s-technique

background values for each groundwater body for chlorides almost all of them are overestimated. The examples A and B in Fig. 4 make this evident. For Slovakia it is optimal to determine the background value for chlorides based on the dataset for the whole Slovak territory. Generally, the estimation of background and threshold values requires an individual approach for each chemical and groundwater body. For the majority of elements/compounds it is not possible to determine national background ranges and thresholds. It is necessary to take into account all the specific conditions within each single groundwater bodies, recognizing the possibility of proposing one background range and threshold for several groundwater bodies in the case of close similarity.

Delineation of groundwater bodies potentially at risk

The results of the geochemical mapping of groundwater were utilized for the implementation of WATER FRAMEWORK DIRECTIVE 2000/60/EC (Anon 2000) for the delineation of groundwater bodies (GWB). The estimation of risk of significant differences in GWB quality was taken into account (Bodiš 2007). This consisted of evaluation of the qualitative status of groundwater bodies and the identification of potential risks that would cause the groundwater not to reach "good chemical status". This evaluation for Slovakia was carried out through preparation of "Maps of current chemical status of groundwater bodies" (Bodiš 2003). The input data represented 16,359 groundwater analyses from the Geochemical Atlas and the evaluation parameter was the robust criterion of groundwater quality defined by the level of contamination index derived after Backman et al. (1998). For the update of the data from the Geochemical Atlas (sample collection for geochemical mapping was completed during the years 1991–1994) from the aspect of potential temporal changes, these data were compared with the results of the monitoring network of the Slovak Hydrometeorological Institute

and the monitoring of drinking water sources from the SAVOMW (Water Research Institute) database that are updated on a 10-year cycle. The results of this comparison show very good agreement. Deteriorated groundwater quality in the delineated GWB was identified also in the majority of monitoring objects (ca. 90%).

The identification of potentially at risk groundwater bodies was based on the evaluation of potential impacts of diffuse and point sources of substances of concern and a map of groundwater vulnerability (Malík and Švasta 2006). This approach takes into account and uses all available information of national significance. Potential risk was estimated using an "overlay" method considering several elements simultaneously, where for each element limit values or criteria are defined. The procedure involves map algebra summing over the elements on the basis of the intersection and integration of the individual sets. The estimation of the final potential for cumulative risk is realized via the sum of the point and diffuse potential risks and current chemical groundwater status according to the following criteria:

- deteriorated groundwater quality in terms of map of current chemical status; and
- high potential risk of point sources (overlapping diffuse sources) and diffuse sources of substances of concern from the aspect of their impact and vulnerability.

Furthermore, groundwater bodies at risk are defined as those that contain areas with deteriorated chemical status of groundwater and/or a high potential risk from diffuse and overlapping point sources of contamination (anthropogenic) or substances of concern (natural).

In the case of groundwater bodies impacted by single point sources with high or medium potential risk, groundwater bodies at risk were identified as those that satisfied the following conditions:

- An excess of "permissible" number of point sources with high risk potential in the area of the groundwater body. "Permissible number of point sources" = (body area/79) × 0.5 on the assumption that a point source can contaminate groundwater within a 5 km radius.
- An excess of "permissible" number of point sources with medium risk potential in the area of the groundwater body that results from an expert estimation of the natural conditions of Slovakia. It represents a possible distance of a substance of concern's migration from a point source in the rock environment. "Permissible number of point sources" = (body area/79) × 1.5 on the assumption that a point source can contaminate groundwater within a 5 km radius.

Moreover, groundwater bodies at risk were divided into those at risk (exhibiting all evaluating criteria of chemical status mentioned above as risk) and those at possible risk
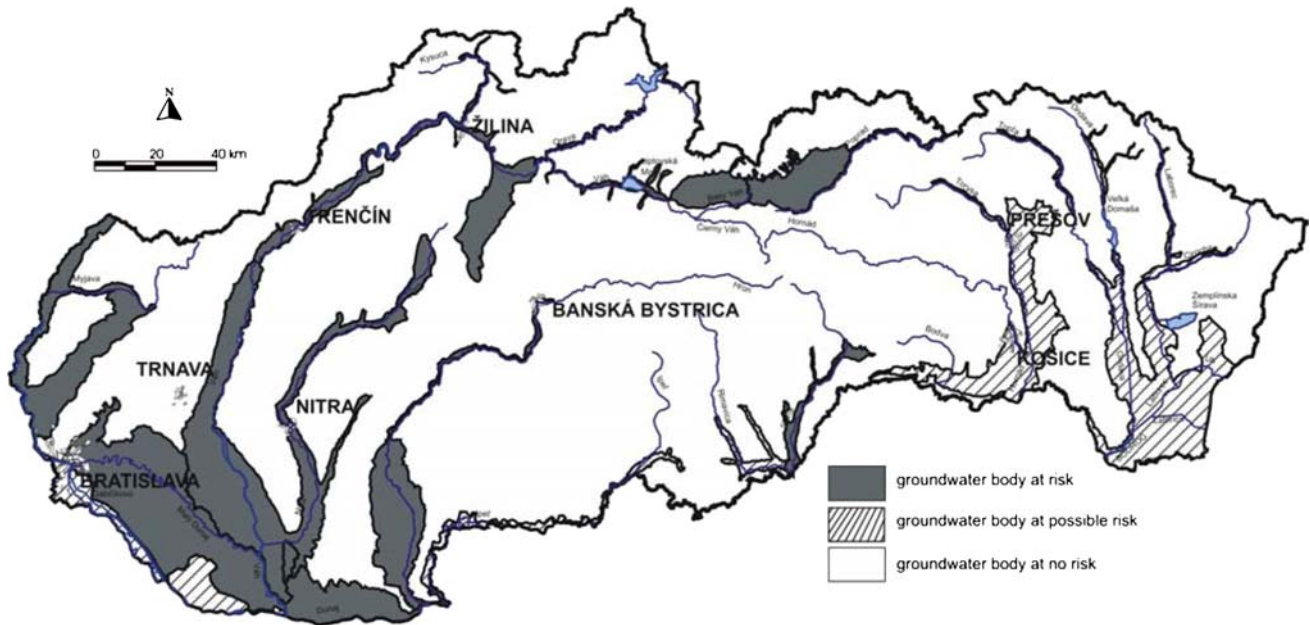
Fig. 7 The delineation of at risk groundwater bodies in Quaternary sediments
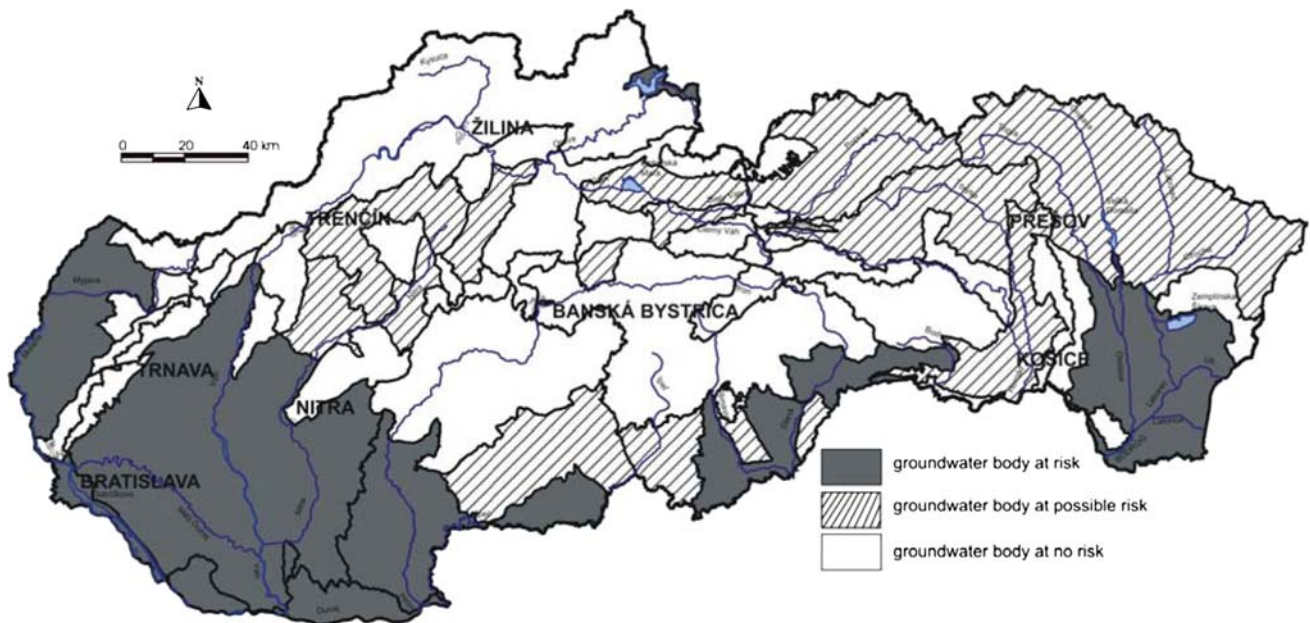
Fig. 8 The delineation of at risk groundwater bodies in pre-Quaternary sediments

(some from the evaluating criteria are risk or data missing for evaluation). From the total number of 101 Quaternary and pre-Quaternary groundwater bodies in Slovakia, 17 are at qualitative risk and 22 at possible qualitative risk (Figs. 7, 8).

Conclusions

Results of comprehensive geochemical mapping and thematic studies of Slovakia (rocks, soils, stream sediments,

groundwater, biomass and radioactivity) in the 1990s of the twentieth century led to several new research tasks in Slovakia. Within this research new international methodologies adjusted to natural Slovak conditions have been developed.

The environmental risk estimation for contamination of geological environment and the environmental–geochemical regionalisation has brought in objective information about the quality of geological components of the environment and has been presented in numeric as well as map

form. In Slovakia 14 most significantly contaminated regions were defined and characterized with the risk elements/compounds in single geological components of the environment.

The health risk assessment has covered up the estimation of health risk for the risk element/compound contents in soils and groundwater in Slovakia. Additionally, the risk areas subject to future studies have also been defined.

The estimation of background and threshold values for single chemicals in groundwater plays a very important role in environmental geochemistry with direct use for the determination of standards within the implementation of the Water Framework Directive. Calculated background and threshold values correspond to different geological bedrock within the groundwater bodies.

The application of data from the Geochemical Atlas of Slovak Republic and monitoring of groundwater quality via point and diffuse sources of contamination allowed the evaluation of chemical status of groundwater bodies as well as the determination of appropriate risk level.

The outcomes of geochemical studies in Slovakia became more significant after the Slovak Republic entered the European Union (April 2004) due to integration of the EU environmental legislation with the Slovak legislative system. Geochemical results were especially valuable in the implementation of the Water Framework, Nitrate and Mining Waste Directives. It is expected that the Geochemical Atlas of the Slovak Republic for Soil will play a key role in the implementation of the new EU Soil Directive in Slovakia.

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