

## 5. Hydrogeochemistry of Surface Water in Slovakia

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**Abstract:** The paper provides information on characteristics and genesis of surface water in Slovakia. The focus is in the chemical and isotopic analyses of samples of surface water. The input data are represented by 10,960 samples within the geochemical mapping of Slovakia. The interpretation is based on a conceptual model of the formation of the chemical composition of the surface water in the conditions of the Western Carpathians. Based on its end members formation, the surface water is divided on the basis of five dominant types of lithochemical environs in watersheds. Individual earmarked end types are characterized on the basis of statistical methods and thermodynamic modelling. According to composition of oxygen and deuterium isotopes the molecule of water itself is clearly of meteoric origin. Approximately 6.5% of the main ions content is of the same origin. The rest of the chemical composition of a surface stream is caused by the interaction of water – rock – gas. Its source is the direct interaction in the bed, and wash-off and inflow of groundwater into a surface stream. The last factor of the chemical composition formation are anthropogenic impacts of different nature.

**Key words:** surface water, atmospheric deposition, stream water chemistry, stream water isotope composition, thermodynamic modelling

### 5.1 Introduction

Hydrogeochemical research focused on natural waters has a long tradition in Slovakia. It is focused in absolute majority on assessment of groundwater (fresh, mineral and geothermal), its chemical and isotopic composition, genesis, anthropogenic influence, protection, etc.

In the scope of the project of geochemical mapping of Slovakia there was obtained a large amount of initial information on the distribution of elements in groundwater, rocks, soils, river sediments, natural radioactivity and forest biomass. These data were published in the edition of Geochemical atlases of Slovakia at scale 1:1,000,000 (Rapant et al., 1996, Marsina et al., 1999, Čurlík and Šefčík, 1999, Bodiš et al., 1999, Daniel et al., 1996, Maňkovská, 1996). The latest edition of this series was the Geochemical Atlas of the Slovak Republic – Surface Water (Bodiš et al., 2015). Chemical analyses of the Atlas have given a momentum to hydrogeochemical assessment of surface water in Slovakia.

The surface water plays an important role in the hydrological cycle. The genesis and the chemical composition of surface water have been studied already for many decades in order to obtain knowledge of the distribution of components and elements in the water, their mobility and the processes influencing them. In addition, there was also an effort to learn the processes, extent and rate of chemical and physical weathering and transport of continental weathering products into the world ocean. These

studies provide important information on the consumption of CO<sub>2</sub> at the acidic degradation of continental rocks (e.g. Stallard & Edmond, 1983; Meybeck, 1987; Probst et al., 1992; Gaillardet et al., 1997; Roy et al., 1999; Picouet et al., 2002). In terms of hydrogeochemistry there is important to learn also the quality of surface water flows due to the possibility of its use as a source of water for drinking, irrigation, industrial use, etc.

Globally, we can say that in the process of the Earth's hydrological cycle, the chemical composition of the water is formed in the environment interconnecting the hydrosphere with the atmosphere, lithosphere and biosphere. As a result of interaction of all these components with the nature of the country and anthropogenic activities, the water contains a wide range of various components, gases, colloids, etc. Regarding the physical-chemical water properties the above stated interactions are conditioning the large variability of the water chemical composition.

Already in the 20<sup>th</sup> century, the scientists have tried to compile models of the key processes, forming the chemical composition of the surface water (rivers and lakes). The geochemical model, being one of the earliest and also the most criticized, is so-called boomerang model (Gibbs, 1970).

The boomerang shape of the Gibbs' model is formed by the graphic representation of cations and anions in mg·l<sup>-1</sup>. At cations it was a ratio Na/(Na + Ca) to the TDS and at anions Cl/(Cl + HCO<sub>3</sub>) to the TDS of the water. The resulting model has provided a ground for a hypothesis, which reflected the relative significance of three fundamental mechanisms controlling the chemical composition of the world's surface water.

The bivariate model assumes, that water with low TDS and high content of sodium and chlorides has a chemical composition with the dominant representation of atmospheric precipitation. The water with a medium value of TDS and high calcium and bicarbonate content originates by the water-rock interaction and the water with a high value of TDS and high contents of sodium and chlorides originates by evaporation.

The Gibbs' model was controversial. It distinguished only three factors of formation of the chemical composition of surface water. Feth (1971) responded by opinion that bivariate model does not distinguish between input sources with salt water and evaporation. Similarly according to Stallard & Edmond (1983), the water from the Amazon River has a high value of TDS and high sodium content. Their origin is attributed preferably to the dissolution of evaporites than the evaporation process. These authors also identified other water formations, which

chemical composition of the water was a result of weathering of silicate rocks, while the bivariate model assumes that their composition is a product of atmospheric precipitation. The data by Kilham (1990) of the rivers and lakes in Africa, which due to geological environment were alkaline and salt, have indicated a significant divergence from the boomerang shape of the Gibbs' model. It was just a modification of the model, resp. its shape.

Numerous authors (Eilers et al., 1992; Armengol et al., 1991; Gibson et al., 1995; Baca & Threlkeld, 2000, etc.) suppose that Gibbs' model is not an appropriate model for the expression of the key processes, controlling the chemical composition of the world's surface streams and lakes. For these reasons, this bivariate model is currently used as a null model for comparing the regional chemical composition of the surface water.

The problem is mainly that the model does not consider the other ions, which play an important role in identifying the geochemical processes forming the surface water, especially in complicated geological conditions, such as those in the Western Carpathians. Another disadvantage represents the distance of the drainage basin of the surface flow from the ocean.

The ternary diagrams that take into account a combination of several cations and anions of chemical composition of the surface water seem to be more suitable. Chemical composition of the surface water is often subject to multivariate statistical analysis as e.g. cluster analysis, the method of principal components or factor analysis. These analyses also allow to find hidden relationships between the analysed ions as well as the trace elements. At the trace elements, however, there is a problem at a high representation of values below a limit of determination. Just datasets of trace elements in the surface water are characteristic in many cases with very low concentration. The advantage of the statistical processing is that it allows evaluation of the complex data as e.g. inorganic and organic substances, flow volume, water temperature, etc., altogether in one file (e.g. Shrestha & Kazama, 2007).

According to Garrels & MacKenzie (1971), in the global concept the dissolved solids in water surface flows originate from different sources, such as rainwater and weathering of siliceous, carboniferous and evaporitic rocks. It can be said that in the vast majority of large rivers the direct access of precipitation is less significant (less than 5%), except for the flows influenced by evaporation (Gaillardet et al., 1999).

Generally the hydrogeochemical models of chemical composition of the surface flows are based on analysis of the end members, the composition of which is derived from the data from small basins with homogeneous geological environment (silicates, carbonates, evaporites, etc.). The resulting chemical composition of surface water is assessed by mixing of these end members. Often, there is used a combination of Sr isotope and the molar ratios Ca/Sr, Mg/Na and Ca/Na or  $\text{HCO}_3/\text{Na}$  and Ca/Na (e.g. Négrel et al., 1993).

For various reasons, many authors tried to estimate the average chemical composition of the world's surface waters. It was mostly a compilation of chemical composition

of large rivers. Obviously, the chemical composition of the surface water of the Earth is very variable. The high variability is due to many reasons. On the one hand they are represented by climatic conditions, distance from the ocean, the composition of the geological environment, topography, etc. This shows that a mean value represents mainly the first comparison with the data from a particular river basin. On the other hand, this variability is caused by the time factor and seasonality, and differing from the average ocean water; it is not possible to suppose its stability.

Often referred to average chemical composition of the surface water according to Livingstone (1963) is presented in Table 5.1. Meybeck (1979) has compiled newer data about the surface waters in the world (Table 5.1). These average values of the total concentration are lower, as the values published by Livingstone (1963). Both averages are strongly influenced by the chemical composition of large rivers. For comparison, the Table 5.1 presents the chemical composition of the largest river, the Amazon, from a single sample taken before reaching its delta in the Obidos (Oltman, 1968). When compared to the average chemical composition of the world's rivers, Amazon has a lower content of all ions. This is more or less due to the time of sampling, when its flow rate was maximum and reached  $216,000 \text{ m}^3 \cdot \text{s}^{-1}$ . An important factor is also an inactive rock environment of the river basin and low population. Oltman (1968) has estimated the average annual flow rate of the Amazon River at the mouth to Atlantic Ocean  $175,000 \text{ m}^3 \cdot \text{s}^{-1}$ .

Tab. 5.1 The average chemical composition of surface waters in the world.

Component	1	2	3	4
$\text{SiO}_2$	13.1	10.4	13.5	7
Ca	15	13.4	35.9	4.3
Mg	4.1	3.35	8.7	1.1
Na	6.3	5.15	4	1.8
K	2.3	1.3	1.3	
$\text{HCO}_3$	58.4	52	123.1	19
$\text{SO}_4$	11.2	8.25	25.8	3
Cl	7.8	5.75	2.4	1.9
TDS	118.2	89.2	208.9	38.1

Note: 1 – according to Livingstone (1963); 2 – according to Meybeck (1979); 3 – Slovakia after Bodiš et al. (2015); 4 – composition of the Amazon River at the locality Obidos (Brazil) according to Oltman (1968); values are in  $\text{mg} \cdot \text{l}^{-1}$ .

The Table 5.1 presents also the average composition of the surface water in Slovakia (column 3). The values are calculated from the 7,862 samples of chemical analyses of the surface flows, which relevant part of the basin consists of homogeneous rock environment and there is an assumption of minimum anthropogenic impact. They represent so-called clean water or end members of the streams.

Compared to the average chemical composition of the global surface water according to Livingstone (1963), resp. Meybeck (1979), the Slovak surface waters have higher value of the total dissolved solids. From indivi-

dual ions they most distinctly differ by the concentration of bicarbonates, calcium, magnesium and sulphate, which have higher average values. On the other side, there is interesting that average contents of  $\text{SiO}_2$  and potassium are nearly similar and concentration of sodium and chlorides is in Slovak surface water lower. However, such comparisons are only indicative, because of strong influence by numerous factors.

## 5.2 Share of Slovakia on the global and European water cycle

The estimate of the total amount of the water in the hydrosphere is necessary for understanding the role of water in the Earth system, as well as for providing the base data for rational water management fulfilling the needs of a man and environmental protection. Recently existing several global estimates mutually differ to some extent. Based on the UNESCO (1978) data, the total evaporation from the seas ( $505 \cdot 10^3 \text{ km}^3$ ) returns to continents  $50 \cdot 10^3 \text{ km}^3$  of the water. The rest of the water returns back into the sea by rainfalls. The total amount of precipitation fallen on the continents is around  $110 \cdot 10^3 \text{ km}^3$ , but app.  $45 \cdot 10^3 \text{ km}^3$  returns back to sea by the water flows.

Leaving the global balance estimates, the European continent registers an average rainfall 657 mm. From this amount, 306 mm flow away and the rest 351 mm evaporates. Area of Slovakia represents only three hundredths percent of the world mainland and less than half percent of total European area (0.47%). The outflow from Slovakia participates in the mainland runoff amount less than by three hundredths percent (0.027%) and within European continent the outflow represents 0.4%. Specific runoff in Slovakia, compared with the mainland value ( $10.0 \text{ l} \cdot \text{s}^{-1} \cdot \text{km}^{-2}$ ) and the value from the whole European continent ( $9.7 \text{ l} \cdot \text{s}^{-1} \cdot \text{km}^{-2}$ ) is lower and reaches only  $8.26 \text{ l} \cdot \text{s}^{-1} \cdot \text{km}^{-2}$ . This is caused by relatively large lowland areas with lower amount of water in the southern Slovakia. The catchment areas where the total available water sources in Slovakia have been formed, represent 0.16% of the mainland and 2.28 % of the area of European continent.

The runoff from this area is represented with approximately the same percentage. In the first case it is up to 0.2% and in the second case 2.9%. Disproportional higher is the specific runoff from this territory ( $12.5 \text{ l} \cdot \text{s}^{-1} \cdot \text{km}^{-2}$ ), mainly due to a high specific runoff of the Danube River.

The existence of water sources and population density in certain area represent principal determinants of its development. The population growth and increasing demands on the standards of living, the pollution of water sources and devastation of the natural environment generally cause the decrease of the ratio of usable water sources per inhabitant. According to WMO data (Shiklomanov, 1991), this ratio lowers in the Europe from  $5.9 \cdot 10^3 \text{ m}^3$  in 1950 to  $4.6 \cdot 10^3 \text{ m}^3$  in 1980. In Central Europe it is the decrease from  $3.0 \cdot 10^3 \text{ m}^3$  to  $2.4 \cdot 10^3 \text{ m}^3$  for inhabitant per year. For illustration there is perhaps worth to state known extreme values: e.g. in Canada it is  $384 \cdot 10^3 \text{ m}^3$  and  $219 \cdot 10^3 \text{ m}^3$  and in the northern Africa  $2.3 \cdot 10^3 \text{ m}^3$  and  $0.69 \cdot 10^3 \text{ m}^3$ . These values simultaneously document also irregular macrospatial distribution of water sources on the mainland.

In this spatial division there is interesting a position of Slovakia. If we take into account only sources generated in the Slovak territory, then dated to 1990 it is  $2.4 \cdot 10^3 \text{ m}^3$  for one inhabitant per year. It corresponds with value in the Central Europe region. If we take into consideration also the water sources formed outside Slovakia, which are inflowing to our territory, or they touch it along borders, then this ratio represents  $17.74 \cdot 10^3 \text{ m}^3$  for an inhabitant per year. The data represent estimates as the long-term averages, greater or lesser temporal variability.

## 5.3 Material and methods

Input for hydrogeochemical assessment of surface water database of Slovakia were 10,960 samples of Geochemical Atlas, part Surface Water (Bodiš et al., 2015). The Atlas compiling was based on the chemical analyses of surface water acquired by own collection of 2,400 samples, combined with chemical analyses obtained by archive retrievals. These contained 169 analyses from the Partial Monitoring System in the national monitoring network

Tab. 5.2 Summary of the determined indicators, limits of determination, analytical methods and applied equipments.

Indicator	Limit of determination	Unit	Analytical method	Equipment type
pH	1.0		E	electrochemical analyser EP-100, laboratory pH meter InoLab pH 730
conductivity $\mu\text{S} \cdot \text{cm}^{-1}$	1	$\mu\text{S} \cdot \text{cm}^{-1}$	E	laboratory conductometer InoLab 730, conductometer Multi 340i
$\text{O}_2$	0.2	$\text{mg} \cdot \text{l}^{-1}$	E	oximeter InoLab 730 OXI
$\text{O}_2$	0.1	%	E	oximeter InoLab 730 OXI
Acidity ( $\text{ZNK}_{8,3}$ )	0.04	$\text{mmol} \cdot \text{l}^{-1}$	OA	
Alkalinity ( $\text{KNK}_{4,3}$ )	0.04	$\text{mmol} \cdot \text{l}^{-1}$	OA	
(Ca + Mg)	0.05	$\text{mmol} \cdot \text{l}^{-1}$	OA	
Total dissolved solids		$\text{mg} \cdot \text{l}^{-1}$	calculation	
$\text{COD}_{\text{Mn}}$	0.5	$\text{mg} \cdot \text{l}^{-1}$	OA	
Li	0.01	$\text{mg} \cdot \text{l}^{-1}$	AES-ICP	Varian – Vista MPX
Na	0.05	$\text{mg} \cdot \text{l}^{-1}$	AES-ICP	Varian – Vista MPX

Indicator	Limit of determination	Unit	Analytical method	Equipment type
<b>K</b>	0.1	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Ca</b>	0.2	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Mg</b>	0.2	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Sr</b>	0.002	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Fe</b>	0.007	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Mn</b>	0.002	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>NH<sub>4</sub></b>	0.05	mg·l <sup>-1</sup>	F	spectrophotometer UV-VIS-DR 500
<b>F</b>	0.1	mg·l <sup>-1</sup>	IC	ion chromatograph Dionex DX-120, Dionex ICS 900
<b>Cl</b>	1	mg·l <sup>-1</sup>	IC	ion chromatograph Dionex DX-120, Dionex ICS 900
<b>SO<sub>4</sub></b>	2	mg·l <sup>-1</sup>	IC	ion chromatograph Dionex DX-120, Dionex ICS 900
<b>NO<sub>2</sub></b>	0.01	mg·l <sup>-1</sup>	F	spectrophotometer UV-VIS-DR 500
<b>NO<sub>3</sub></b>	1	mg·l <sup>-1</sup>	IC	ion chromatograph Dionex DX-120, Dionex ICS 900
<b>PO<sub>4</sub></b>	0.03	mg·l <sup>-1</sup>	F	spectrophotometer UV-VIS-DR 500
<b>HCO<sub>3</sub></b>	0.05	mg·l <sup>-1</sup>	OA	
<b>CO<sub>3</sub></b>	0.05	mg·l <sup>-1</sup>	OA	
<b>OH</b>	0.05	mg·l <sup>-1</sup>	OA	
<b>SiO<sub>2</sub></b>	0.2	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Free CO<sub>2</sub></b>	0.05	mg·l <sup>-1</sup>	calculation	
<b>Aggressive CO<sub>2</sub></b>	1.1	mg·l <sup>-1</sup>	calculation	
<b>Cr</b>	0.002	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Cu</b>	0.002	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Zn</b>	0.002	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>As</b>	0.001	mg·l <sup>-1</sup>	AAS-GH	Atomic absorption spectrophotometer SPECTR AA 220
<b>Cd</b>	0.0003	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Se</b>	0.001	mg·l <sup>-1</sup>	AAS-GH	Atomic absorption spectrophotometer SPECTR AA 220
<b>Pb</b>	0.005	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Hg</b>	0.0001	mg·l <sup>-1</sup>	AAS	mercury analyzer AMA - 254
<b>Ba</b>	0.002	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Al</b>	0.02	mg·l <sup>-1</sup>	AES-ICP	Varian – Vista MPX
<b>Sb</b>	0.001	mg·l <sup>-1</sup>	AAS-GH	Atomic absorption spectrophotometer SPECTR AA 220

## Notes:

<ul style="list-style-type: none"> <li>• AAS</li> <li>• AAS-GH</li> <li>• AES-ICP</li> <li>• OA</li> <li>• E</li> <li>• VTO</li> <li>• ISE</li> <li>• ITP</li> <li>• IC</li> <li>• F</li> </ul>	<ul style="list-style-type: none"> <li>• atomic absorption spectrometry</li> <li>• atomic absorption spectrometry with hydrides generating</li> <li>• atomic absorption spectrometry with inductively coupled plasma</li> <li>• volumetric analysis</li> <li>• electrochemistry</li> <li>• high-temperature combustion with non-dispersive infrared detector</li> <li>• ion selective electrode</li> <li>• isotachopheresis</li> <li>• ion chromatography</li> <li>• spectrophotometry</li> </ul>
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of surface water, 6,463 chemical analyses from the map sets of the geological factors of the environment, as well as 1,928 analyses from other works. The main requirement for the inclusion of the sample into the database was a complete chemical analysis of the main compounds. The analysis error must not exceed 5% and the sampling sites must have known coordinates. The total number of the samples in the database has reached the number of 10,960 chemical analyses. As for the laboratory work, approximately 80% of chemical analyses were done in the accred-

ited Geoanalytical Laboratories of the State Geological Institute of Dionýz Štúr Spišská Nová Ves, operating as a reference laboratory for the water analyses in Slovakia.

A list of rated indicators with the Limits of determination, applied analytical method and equipment is presented in Table 5.2.

The quality control of analytical data was expressed in two levels: internal and external. The internal quality control was assured by analysis of reference material, repeated sample analysis of single and multiple sampling.

External quality control was ensured by participation in interlaboratory comparison tests.

The quality policy of the laboratory represents a systematic care about the services quality in securing, maintaining and improving quality in all activities, relating to the implementation of accredited tests.

The samples for the stable isotopes analyses were taken into the glass bottles with the double bell (medicine bottles) with a volume of 0.05 or 0.1 litre. The samples were collected as possible beneath the water surface from a depth of 10 – 30 cm, to prevent against possible sampling of evaporated water. Samples from the collection in August 2013 were transported to the Laboratory of Isotope Geology in SGIDS Bratislava. Each sample was filtered, and aliquot parts were poured into two sample bottles (glass bottles with a volume of 0.01 l with a double seal). One was postponed into the register and the second was used for isotopic analysis. The samples are stored in a refrigerator at ~ 4 °C.

New samples were analysed by the Liquid-Water Isotope Analyser (LWIA; *Los Gatos Research Inc.*), which uses a highly-resolved laser absorption spectroscopy for the simultaneous measurement of ratios of stable isotopes deuterium/hydrogen ( $^2\text{H}/^1\text{H}$ ) and  $^{18}\text{O}/^{16}\text{O}$  oxygen in the water samples. The laser beam passes through an evacuated cavity, into which an aqueous sample is injected. Laser Absorption Spectroscopy uses the Beer-Lambert Law, which relates the absorbance of laser radiation with the water vapour isotopic composition of the samples (Ricci, 1994). For the preparation of the measurement there is used 1 ml of the water dispensed in 1.5 ml vials with screw lids with a penetrable septum (PTFE/silicone/PTFE). To the analysis there is used about 600 to 850  $\mu\text{l}$  of the sample in six injections and double repetition. Samples are analysed in a sequence with the three internal standards calibrated in comparison with the commercially available standards from the firm Iso-Analytical Limited (IA-R052 –  $\delta^2\text{H}_{\text{V-SMOW}} = -157.12 \pm 1.35\text{‰}$ ,  $\delta^{18}\text{O}_{\text{V-SMOW}} = -19.64 \pm 0.11\text{‰}$ ; IA-R053 –  $\delta^2\text{H}_{\text{V-SMOW}} = -61.97 \pm 2.1\text{‰}$ ,  $\delta^{18}\text{O}_{\text{V-SMOW}} = -10.18 \pm 0.20\text{‰}$ ; IA-R054 –  $\delta^2\text{H}_{\text{V-SMOW}} = 4.93 \pm 0.85\text{‰}$ ,  $\delta^{18}\text{O}_{\text{V-SMOW}} = 0.56 \pm 0.23\text{‰}$ ). Set values are in an established  $\delta$ -notation –  $\delta$  (‰) =  $[(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1,000$ , where R represents a molar ratio of the heavier isotope in relation to easier isotope (e.g.  $^{18}\text{O}/^{16}\text{O}$ ) in sample and standard. The standard inaccuracy at  $\delta^2\text{H}$  is 2‰ and at  $\delta^{18}\text{O}$  it is  $\pm 0.2\text{‰}$ .

In a part about the isotopic composition of the surface water there is stated that the water molecule itself has clearly meteoric origin. In the formation of the chemical composition of the surface water, the initial water is represented by rainwater, but its share on the total dissolved solids content is only 6.5%. The conceptual model of end members of chemical composition of the surface water contains a lot of other factors, constituting a source of ions in the final composition of the surface water at a certain time and space. This are particularly the interactions of the rainwater with the vegetation cover, soil profile and the rock environment. Such model is considerably simplified, but sufficient for evaluating the results of the nationwide geochemical mapping in Slovakia at a scale 1:1,000,000.

Under the end members of the formation of chemical composition of the surface water we mean the water samples, bound to relevant catchments area, being built of homogeneous geological environment. At the same time, these samples do not show signs of anthropogenic influence.

The selection of the sample sets, which meet these criteria, took place in several steps. The first one was the upstream assigning of each water sample to the appropriate catchment area, which formed the anticipated space of its chemical composition formation. Given assignment was done by a macro application in the MapInfo Professional 10.0 software environment (Slaninka, 2006).

To generate a relevant part of the catchment area with a homogenous rock environment, after testing there suits best (in terms of the water-rock interaction) the division based on the rock types (lithotypes). This simplification is mainly based on petrographic and geochemical properties. Lithotypes do not take into account the age of rocks, only their composition, allowing by this way to characterize the geochemical processes (interactions) with this environment. There is also important that this categorization of the rock (geological) environment includes the age and genetically undivided rocks from Palaeozoic ones up to Quaternary sediments. Obviously, it is difficult or impossible to name allocated rock groups generally according to the area, tectonic unit, etc., because in terms of petrographic and geochemical characteristics in many cases they overlap.

In simple substantiation, the geological environment is divided into five groups, named A, B, C, D and E, which are characterized by petrography and geochemistry with examples of the main rock types representation. In Table 5.3 these five types have allocated all 54 pre-Quaternary and 3 Quaternary lithotypes sensu Marsina et al. (1999). Division into five groups:

- A) Acid aluminosilicate rocks and siliciclastic sediments, as well as their metamorphic rock equivalents (represented mainly by: granites and granitoids, rhyolites, eolian sands, gneisses, etc.)
- B) Basic and intermediary rocks (represented mainly by andesites, diorites, intermediary and mafic volcanites, etc.)
- C) Dominantly pelitic sediments (represented mainly by clays and claystones, loamy swamp sediments, etc.)
- D) Dominantly siliciclastic rocks (represented mainly by sandstones, sandy shales, sandy and gravel sediments, etc.)
- E) Carbonate rocks (represented mainly by limestones and dolomites, clay and sandy limestones, conglomerates, etc.)

Tab. 5.3 Selection of lithotypes.

	<b>Geochemical type of rocks</b>
	Quaternary
A	Eolian siliceous sands
C	Humic alluvial clay and argillaceous sediments
D	Sand, sandy gravel, loess
	Neogene
E	Freshwater limestone – travertine
C	Clays, sand, gravel, lignite interbeds
C	Clays, sands, and tuffite volcanomictic sediments, lignite interbeds
C	Calcareous claystones and siltstones
C	Calcareous clays, sandstone, gravel, limestone, lignite interbeds
C	Calcareous clays, sandstone, gravel, limestone, tuffite and volcanomict sediments
C	Calcareous clays, sandstone, gravel, limestone and gravel
	Neogene volcanites
B	Alkaline basalts
B	Basalts and basaltic andesites
B	Pyroxene and amphibole-pyroxene andesites
B	Pyroxene-amphibole, amphibole and biotite-amphibole andesites to dacites
B	Propylitized andesites, andesite porphyry, diorite, porphyry and diorite
A	Granodiorite, granodiorite porphyry, quartz diorite, porphyries
A	Rhyodacites and rhyolites
	Inner Carpathian Palaeogene
C	Claystones, marlstones, sandstones, conglomerates, limestone and coal, Palaeogene of the Buda Development
D	Sandstones, sporadic clays, Biely Potok Formation
C	Calcareous claystones, sandstones, Huty and Zuberec formations
D	Sandstones, conglomerates, breccias, limestones, Borové Formation
	Cretaceous and Palaeogene of Outer Carpathians
D	Prevailing sandstones, sporadic claystones, flysch of the Magura Unit
D	Sandstones and claystones, flysch of Magura Unit
D	Predominant claystones, sporadic sandstones, flysch of the Magura Unit
D	Prevailing sandstones, sporadic claystones, flysch of the Dukla (Silesia) units
D	Sandstones and claystones, flysch of the Dukla (Silesia) units
D	Predominant claystones, sporadic sandstones, flysch of the Dukla Unit
	Clayey-sandy sediments of the Cretaceous and Palaeogene of Klippen Belt, Tatricum and Hronicum
C	Marls, carbonatic sandstones, conglomerates, limestones, prevailingly calcareous flysch
C	Variogated marlstones
	Mesozoic of the Klippen Belt and the Central Western Carpathians
E	Limestones
E	Limestones and dolomites
E	Dolomites
E	Limestones, dolomites and shales (phyllites)
E	Limestones, dolomites, shales (phyllites) and mafic volcanites
E	Prevailing clayey limestones, marlstones, sandy and quartz limestones
E	Sandy, patchy, nodular, quartz and chert limestones and silicites
E	Breccia limestones, shales and sandstones
D	Slates, sandstones, limestones, radiolarites, evaporites
D	Variogated slates, sandstones, dolomites, evaporites, Carpathian Keuper
D	Quartzites, sandstones, clayey shales, Lunz and Lower Triassic beds of Tatricum and Veporicum
D	Sandstones, calcareous shales, limestones, evaporites and Lower Triassic of Hronicum and Silicicum
	Upper Palaeozoic of the Central Western Carpathians
A	Shales, sandstones, conglomerates, acid volcanites, Upper Palaeozoic of Tatricum, Veporicum, Hronicum and Zemplinicum
B	Intermediary and mafic volcanites
B	Conglomerates, sandstones, shales, volcanites, carbonates
	Lower Palaeozoic of Gemericum
B	Prevailing sandstones, phyllites, mafic volcanites
B	Prevailing mafic volcanites
A	Prevailing metasandstones, phyllites and acid volcanites, carbonates, lydites
A	Prevailing acid volcanites

Geochemical type of rocks	
	Crystalline basement of Tatricum and Veporicum
A	Metapsammites, phyllites, micaschists, metavolcanites, carbonates
A	Gneisses to migmatites, phyllonites
B	Amphibolites, amphibolic gneisses
A	Prevailing acid to intermediary volcanites, Jánov grúň Complex
	Plutonites of the Central Western Carpathians
B	Diorites
A	Tonalites
A	Granodiorites to granites
A	Leucocratic granites
A	Gemic granites

The information layer with areally divided five lithological types was covered with a layer with generated catchments areas (Fig. 5.1). The dominant lithotype was determined on the basis of the prevailing surface representation (percentage over 90%). Of course, many generated catchment areas did not meet this criterion.

The next step consisted of the separation of anthropogenically unaffected samples in five distinguished sets. It can be stated that the simplest qualitative criterion encompasses the content of chlorides, representing so-called conservative element owing to a high solubility of their compounds in the water. The initial rainwater, represented by the samples from the monitoring of snow pack quality, has an average concentration of chlorides  $1.74 \text{ mg}\cdot\text{l}^{-1}$  with a maximum  $45.2 \text{ mg}\cdot\text{l}^{-1}$  and 90<sup>th</sup> quantile  $4.01 \text{ mg}\cdot\text{l}^{-1}$ . As a criterion, based on these results there was selected a wider border, less than  $10 \text{ mg}\cdot\text{l}^{-1}$ , and the best suited to  $6 \text{ mg}\cdot\text{l}^{-1}$  of chlorides in the chemical composition of the surface water flow.

The result consisted of five sets of chemical composition of the surface water, divided according to environment of their formation. The total number of selected samples was 7,826, while the number of samples in individual files was not the same. In the group A, the number of samples was 1,631, in B 1,307, in C 2,472, in D 1,810 and the group E 642.

In terms of chemical composition, the surface water is characterized by the predominance of constituents  $\text{Ca-HCO}_3$ . In the cation composition there prevails the calcium content and in different representation in individual lithotypes there alternate magnesium and sodium. In the anion composition the bicarbonates dominate. The sulphates represent second most frequent component. In individual groups  $\text{SiO}_2$  is represented in varying proportions. In general, these are the biggest differences in the chemical composition of the surface water. In contrast to the groundwater, the surface water is less variable, which can be observed in the domination of individual ions. This difference can be explained mainly by the shorter interaction (retention time) of the surface water with the environment, and thereby the preference of reactions with mineral phases, more soluble in the water, which run kinetically faster.

Despite certain monotony in chemical composition, there is possible to observe certain differences in the formation of the surface waters, related to the nature of the environment and the conditions of their formation. These differences and the genesis of surface water are interpreted in other parts of the text using various tools. There were used the descriptive statistics, correlation coefficients and the factor analysis with the software package STATISTICA, version 7. Descriptive statistical methods allow to

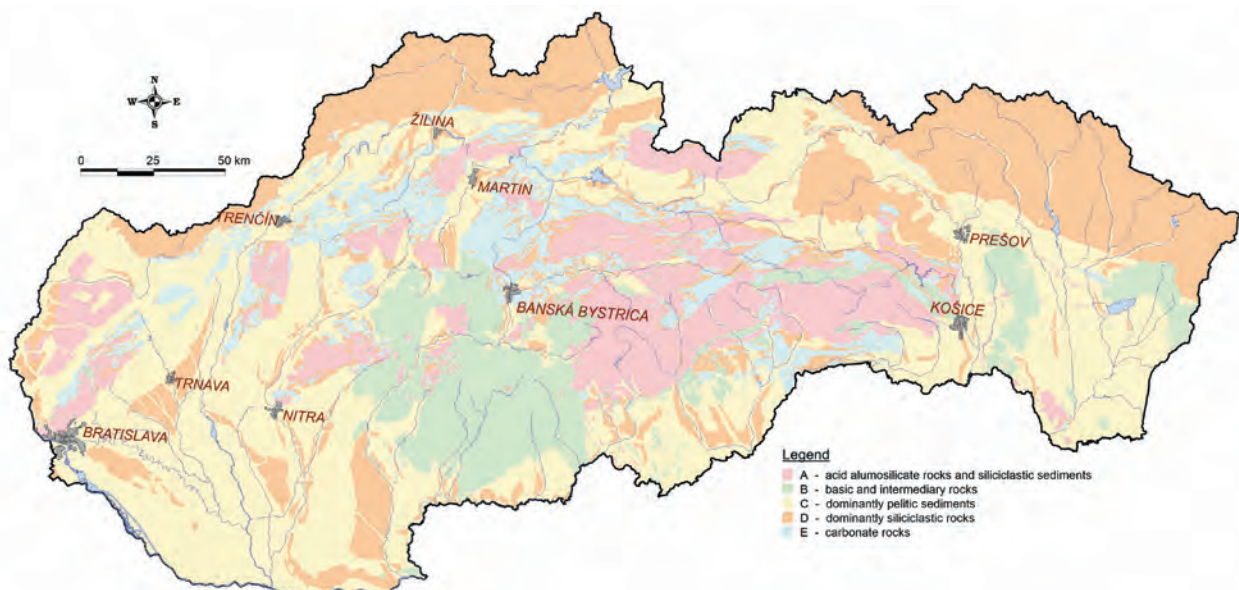


Fig.5.1 Allocated catchments areas of end members of the formation of chemical composition of the surface water.

compare mean values and the concentration range of selected ions in distinguished groups of surface water. Factor analysis facilitates the interpretation of the relationship between individual ions and allows to outline the main mineralisation processes in formation of the surface water. The extraction at the factor analysis was done by the method of main components. There was used the Varimax rotation type, the selection of the number of final factors was made using the scree-test. The ternary diagrams of the main cationic and anionic representation (used concentration unit was  $\text{mmol}\cdot\text{l}^{-1}$ ) were constructed using the HydroOffice software (Gregor, 2013). As to cations, diagrams are drawn up of calcium, magnesium and the sum of sodium with potassium, of anions there were bicarbonates, sulphates, chlorides and amounts of nitrates. These ions prevail in the chemical composition of the surface water in Slovakia. The interaction water–mineral phase was calculated by the program PHREEQC 3.0.6 (Parkhurst & Appelo, 1999) with a database of thermodynamic data *phreeqc*.

#### 5.4 Formation of chemical composition of surface water

According to the conceptual model the formation of the chemical composition of the surface water is very complex mechanism. Moreover, the surface flow is open, dynamic, and it is affected by a large number of factors. A simplified approach represents the initial water – atmospheric precipitation (solid and liquid), which provides input for the formation of surface and groundwater. In this system it is clear that the natural conditions of Slovakia the interaction of water – rock – gas is the most important factor. The resulting chemical composition of surface water then most depends on the composition of the ground, altitude and climatic periods. The chemical composition of surface water quickly reacts to climatic period (spring snow melt, torrential rainfall, etc.), which leads to significant changes in water quality. Temporal changes in the chemical composition of surface water are not the topic of this paper (this is focus of the surface water quality monitoring).

Hereinafter, we will characterise five main types of end members of a surface flow that are typical for Slovakia.

##### Surface water group A

The catchment areas of surface flows are mostly tied on acid aluminosilicate rocks and siliciclastic sediments, as well as their metamorphic equivalents. They mostly represent the surface flows that are located in the upper parts of catchment areas (it is characteristic especially for crystalline massifs). Due to this fact and relatively inactive geological envi-

ronment, their TDS is lowest of all distinguished groups. Calcium is the prevailing component in their cationic composition, in roughly similar representation there is magnesium and sum of sodium with potassium (Fig. 5.2).

In the anion composition there prevail bicarbonates, followed by sulphates and the sum of chlorides with nitrates (Fig. 5.3). The total mineralisation of the water varies within the range  $8 - 192 \text{ mg}\cdot\text{l}^{-1}$  (Table 5.4), and especially in the upper parts of the catchment areas formed by the crystalline basement its chemical composition is similar to the groundwater present in these areas. It is interesting that in the case of higher representation of bicarbonates

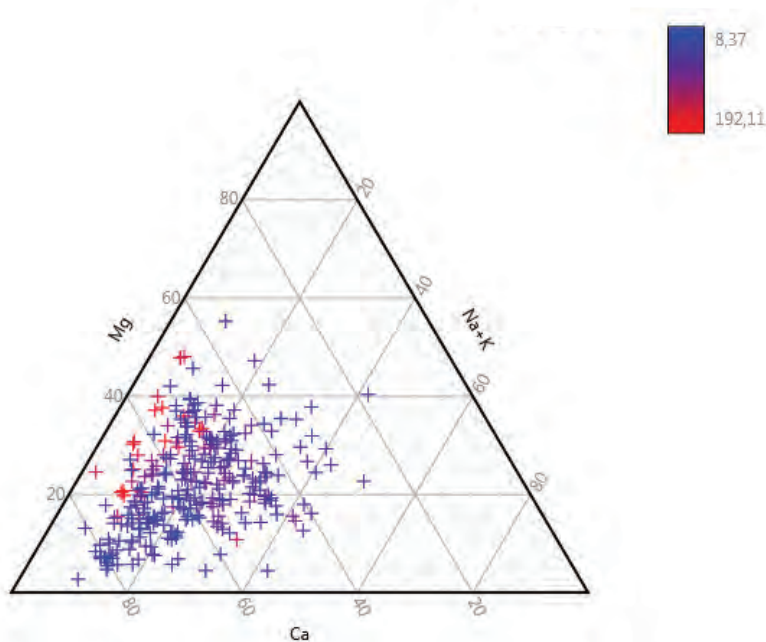


Fig.5.2 Cationic composition of surface water of the group A.

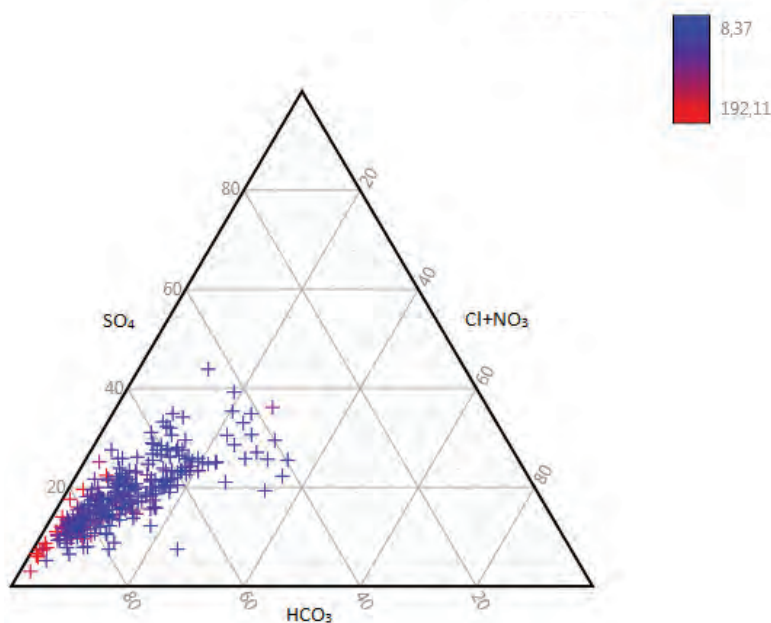


Fig.5.3 Anionic composition of surface water of the group A.



in the anion composition, their mineralisation increases (Fig. 5.3). At low mineralisation close to the minimum value, there is assumed a substantial proportion of virtually all major ions from the rainwater. This is the reason, why in comparison with other selected groups they have the lowest values of water hardness.

The summary of values of the chemical composition of surface water of the group A is stated in the Table 5.4. The certain anomalous concentration values are the values of the lower and upper quartiles. At the water with low TDS, the proportion of individual ions is quite variable and changes already at the small changes in concentration.

The final factor matrix consists of four factors (Table 5.5). The first factor manifests a high saturation of the sodium and silica. This factor is likely to constitute one of the most important mineralisation processes, namely the dissolution of the Na-plagioclase, with the accompanied release of Na and SiO<sub>2</sub> into water. The second factor is represented by the saturation by calcium, magnesium and sodium and can be interpreted as dissolution of Ca-plagioclases. Of course, other sources of these ions can be dissolved, e.g. micas and other present aluminosilicate minerals of this rock environment. Scattered pyrite and its oxidation degradation are probably the source of the third factor. The

Tab. 5.4 The descriptive statistical parameters of surface water of the group A.

	Average	Median	Minimum	Maximum	Lower quartile	Upper quartile	St. deviation
pH	7.6	7.6	5.4	9.0	7.3	7.9	0.5
Na	3.23	2.80	0.02	17.30	1.80	4.10	2.14
K	1.07	0.76	0.05	17.50	0.40	1.48	1.12
Ca	13.18	11.72	1.60	38.88	8.02	17.64	6.60
Mg	4.09	3.55	0.10	14.52	2.33	5.47	2.49
Sr	0.074	0.050	0.010	5.400	0.037	0.070	0.260
Fe	0.090	0.036	0.004	4.660	0.016	0.080	0.223
Mn	0.029	0.005	0.001	7.000	0.003	0.014	0.229
NH <sub>4</sub>	0.07	0.03	0.03	3.83	0.03	0.05	0.16
F	0.08	0.05	0.05	3.14	0.05	0.10	0.11
Cl	2.6	2.0	0.5	33.3	1.2	3.1	2.7
SO <sub>4</sub>	19.2	16.7	1.0	114.0	12.0	24.2	11.5
NO <sub>3</sub>	5.2	4.4	0.5	34.5	1.9	7.6	4.2
PO <sub>4</sub>	0.05	0.02	0.02	2.80	0.02	0.04	0.13
HCO <sub>3</sub>	39.48	33.55	1.22	121.43	20.14	52.48	24.25
SiO <sub>2</sub>	11.22	9.96	0.83	58.07	7.61	12.54	6.10
Ca + Mg (mmol.l <sup>-1</sup> )	0.50	0.45	0.04	1.19	0.31	0.66	0.24
TDS	91.09	84.18	8.37	192.11	59.00	121.03	41.54

Note: Values besides pH are stated in mg.l<sup>-1</sup>.

Tab. 5.5 Factor matrix – surface water of the group A.

	Factor 1	Factor 2	Factor 3	Factor 4
pH	-0.196	0.497	-0.148	0.500
Na	<b>0.769</b>	0.253	0.121	0.382
K	0.648	0.251	0.117	0.399
Ca	0.075	<b>0.883</b>	0.078	0.201
Mg	0.150	<b>0.770</b>	0.186	0.328
Sr	0.103	0.616	-0.074	-0.307
Fe	0.045	0.058	<b>0.855</b>	0.009
Mn	0.094	0.069	<b>0.840</b>	0.063
NH <sub>4</sub>	0.240	-0.095	0.029	0.124
F	0.612	-0.008	0.132	-0.152
Cl	0.345	0.136	0.094	0.646
SO <sub>4</sub>	0.427	0.499	0.234	0.410
NO <sub>3</sub>	0.142	-0.027	0.042	<b>0.807</b>
PO <sub>4</sub>	0.314	0.033	-0.136	0.227
HCO <sub>3</sub>	0.011	<b>0.916</b>	0.057	-0.028
SiO <sub>2</sub>	<b>0.787</b>	0.110	-0.017	0.006

fourth factor represents the high saturation of nitrate. The forms of nitrogen and its role in the formation of this water were discussed in the previous section. In the group A it

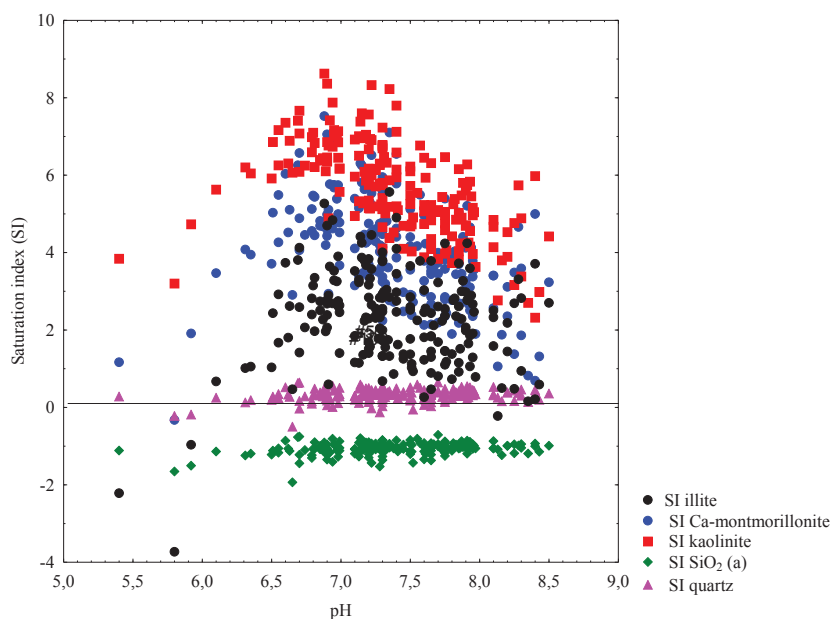


Fig. 5.4 Saturation index of selected mineral phases.

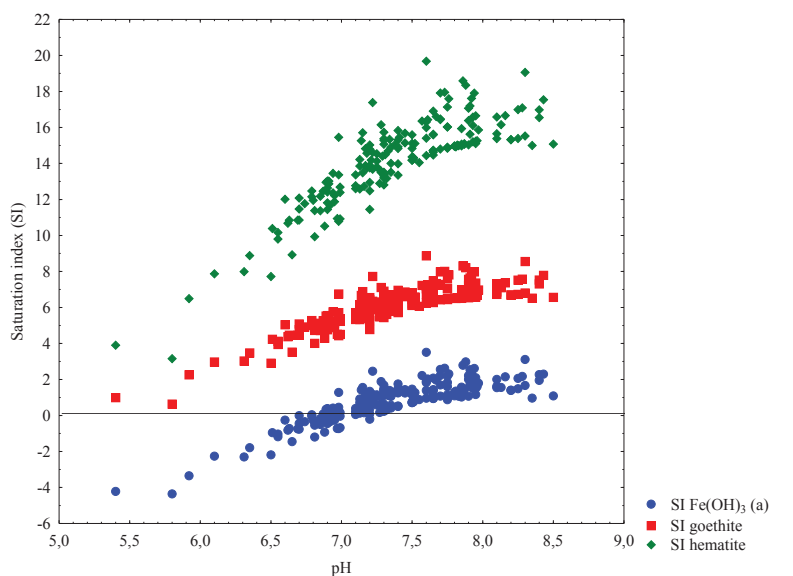


Fig. 5.5 Saturation index of selected mineral phases.

represents a nitrogen form of natural origin, which source is mainly biomass.

In terms of thermodynamic equilibrium there are interesting the weathering products of aluminosilicate minerals. Saturation index of selected plausible mineral phases (Fig. 5.4) documents that amorphous quartz in solution is not sufficiently saturated, but a substantial part of quartz is more or less in equilibrium with the water surface flows. At higher pH values it may lead to oversaturation. By

contrast, kaolinite, montmorillonite and Ca-illite mineral phases are supersaturated and will fall out of solution.

In terms of iron minerals (Fig. 5.5) its trivalent form (in flows the oxidizing environment is prevailing), the amorphous ferric hydroxide is not sufficiently saturated below a pH range of about 7.5 in a solution, resp. it is in equilibrium, and above pH 7.5 it becomes oversaturated and in the surface water it will be most likely in colloidal form. Saturation indexes of hematite and goethite indicate oversaturation of these mineral phases.

The surface water of this group may be in the groundwater genetic classification by Gazda (1971, 1974) classified as silicatogene. This water is mainly formed by interactions of the water with aluminosilicate minerals. A proportion of mainly low-mineralised surface water can have a relatively large share of major ions from atmospheric precipitation.

#### Surface water of the group B

This group of surface water is linked to the catchment area built of basic and intermediary rocks. They represent the surface flows which chemical composition of the water is mainly formed in the environment of Neogene volcanic complexes. Their cationic composition (Fig. 5.6) is characterized by a predominance of calcium ions, presence of magnesium in the range of 40 – 60% and the sum of sodium and potassium 20 – 40%.

In the anion composition the bicarbonates are dominating, in this case it is the highest TDS in the surface water of this group (Fig. 5.7). A relatively large proportion of this water contains a lower amount of bicarbonates, present are the remaining major anions. It is characteristic especially at the lowest levels of TDS.

The overview of the chemical composition of the surface water of the B group is in Table 5.6. In addition to the above stated representation of the main ions, this water is different from all selected groups by the highest concentration of  $\text{SiO}_2$ . It can be assumed that this is caused by the low stability of rock-forming minerals (indicatively it is governed by the reverse Bowen reaction scheme) in their environment at the weathering processes. In comparison with the surface water A and C, the  $\text{SiO}_2$  content in group B is up to three times higher. In terms of TDS from the aforementioned reasons, the surface flows of Neogene volcanic complexes have higher values than the water bound to the crystalline rock environment.

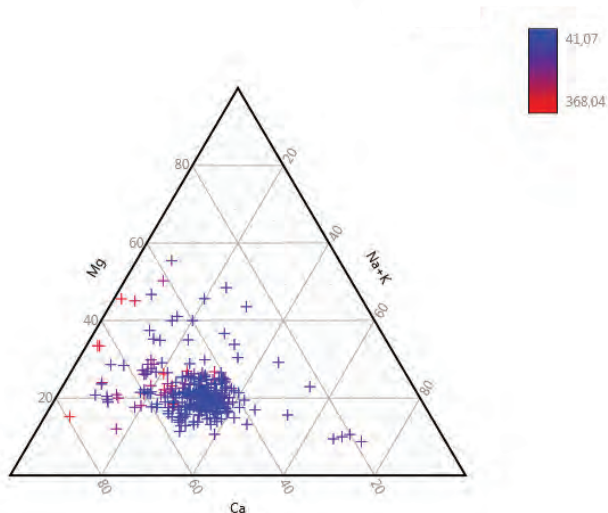


Fig. 5.6 Cationic composition of the surface water of the group B.

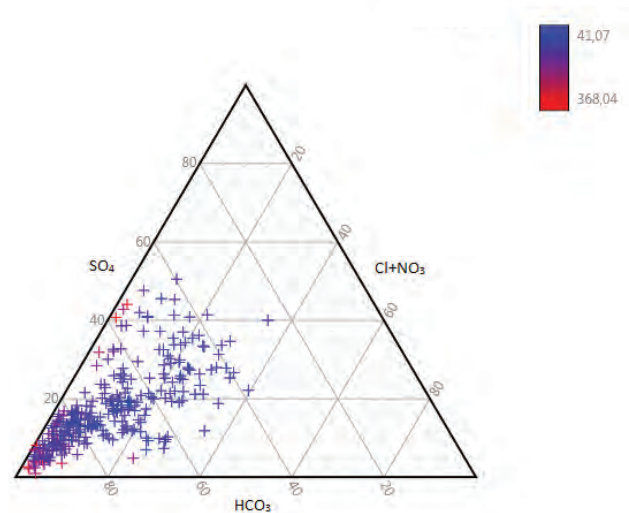


Fig. 5.7 Anionic composition of the surface water of the group B.

Tab. 5.6 The descriptive statistical parameters of the B group surface water.

	Average	Median	Minimum	Maximum	Lower quartile	Upper quartile	St. deviation
pH	7.7	7.7	3.5	9.4	7.4	8.0	0.5
Na	5.11	4.60	0.60	31.50	3.16	6.22	3.01
K	2.10	1.90	0.05	10.19	1.21	2.66	1.26
Ca	20.71	17.23	3.35	103.81	12.42	23.82	12.92
Mg	5.87	4.79	1.30	64.16	3.16	6.98	4.59
Fe	0.196	0.069	0.004	4.242	0.028	0.230	0.341
Mn	0.031	0.008	0.001	1.644	0.003	0.026	0.100
NH <sub>4</sub>	0.09	0.03	0.03	1.78	0.03	0.08	0.14
F	0.08	0.05	0.05	1.63	0.05	0.08	0.09
Cl	2.3	2.3	0.5	4.4	1.5	3.2	1.0
SO <sub>4</sub>	25.4	19.9	2.2	309.0	12.8	30.8	24.7
NO <sub>3</sub>	4.6	3.6	0.5	40.4	1.5	7.0	4.1
HCO <sub>3</sub>	71.62	57.97	3.66	341.09	36.60	97.65	49.17
SiO <sub>2</sub>	30.51	30.73	2.62	137.00	21.80	39.49	14.75
Ca + Mg (mmol·l <sup>-1</sup> )	0.76	0.62	0.21	3.39	0.44	0.87	0.47
TDS	143.77	123.41	41.07	368.40	92.27	170.39	75.61

Note: Values besides pH are stated in mg·l<sup>-1</sup>.

In the case of surface water of the B group, the final factor structure is represented by four factors (Table 5.7). The first factor expresses the high saturation of pH, calcium, magnesium, and bicarbonate. It represents own conditions of a bicarbonate equilibrium in surface water. It is the dominant system, even though the carbonates in the rock environments are absent and calcite, dolomite and aragonite are according to thermodynamic model unsaturated mineral phases. Thus, the source of the individual members of the carbonate equilibrium are other minerals, mainly plagioclase, pyroxene, etc., as well as the carbon dioxide.

In the second factor there is dominating the positive saturation of sodium, potassium, and silica (expressed

as SiO<sub>2</sub>). It can be assumed that this factor reflects the hydrolytic degradation of silicates. The third factor represents the high saturation of iron and manganese, which enhances their presence in surface water of the B category. The fourth factor represents the sulphate saturation, which enters this environment through the oxidative degradation of the sulphides.

In terms of the interaction water-mineral, amorphous aluminium hydroxide in this system represents prevalently unsaturated mineral phase, eventually the mineral phase in equilibrium (Fig. 5.8). By contrast, the gibbsite and kaolinite are in the whole pH range of the values the oversaturated and from the water they will probable precipitate in the form of colloidal parts.

Tab. 5.7 Factor matrix - surface water of the group A.

	Factor 1	Factor 2	Factor 3	Factor 4
pH	<b>0.737</b>	-0.046	-0.154	-0.210
Na	0.072	<b>0.748</b>	0.041	0.461
K	0.010	<b>0.738</b>	0.479	-0.045
Ca	<b>0.701</b>	0.128	0.029	0.568
Mg	<b>0.754</b>	-0.019	0.022	0.430
Fe	-0.112	0.065	<b>0.798</b>	-0.022
Mn	0.076	-0.024	<b>0.782</b>	0.130
NH <sub>4</sub>	0.022	0.129	0.699	-0.002
F	0.155	0.315	0.015	0.181
Cl	0.067	0.080	0.240	0.591
SO <sub>4</sub>	0.139	-0.041	-0.159	<b>0.847</b>
NO <sub>3</sub>	-0.169	-0.546	0.079	0.033
HCO <sub>3</sub>	<b>0.846</b>	0.297	0.163	0.224
SiO <sub>2</sub>	-0.240	<b>0.816</b>	0.149	-0.171

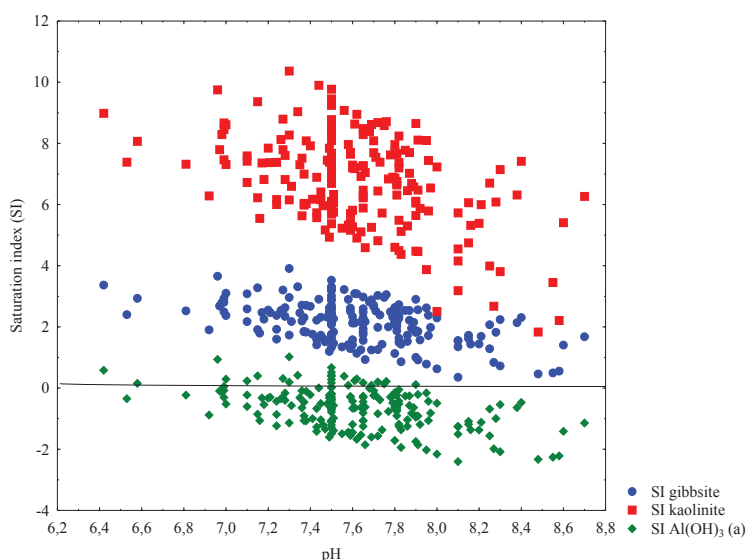


Fig. 5.8 Saturation index of selected mineral phases.

Hematite, goethite, amorphous ferric hydroxide are oversaturated in this group of surface water (Fig. 5.9). The amorphous silica is an undersaturated mineral phase, but silica is prevalingly oversaturated, eventually it is in equilibrium.

The above data indicate that the surface water of the B group, similarly as A group, in terms of genetic classification, is silicogene. Its characteristic feature is represented by the ratio of different ions, higher values of total mineralisation and the highest SiO<sub>2</sub> content among all groups of surface waters.

### Surface water of the group C

The environment of the surface water generation of this group is built mostly of pelitic sediments. They have specific characteristics, both in terms of permeability, as well as the creation of a complex system of interaction water-mineral phases. The pelitic sediments have variable amounts of carbonate cement and, therefore, their chemical composition to some extent corresponds to that in the surface water of D group. The cationic representation in the surface water of C group has an interesting distribution (Fig. 5.10), which can be simply divided into two areas. The first is characterized by higher values of the total dissolved solids and prevalence of calcium and magnesium ions. The second area is represented by a larger pro-

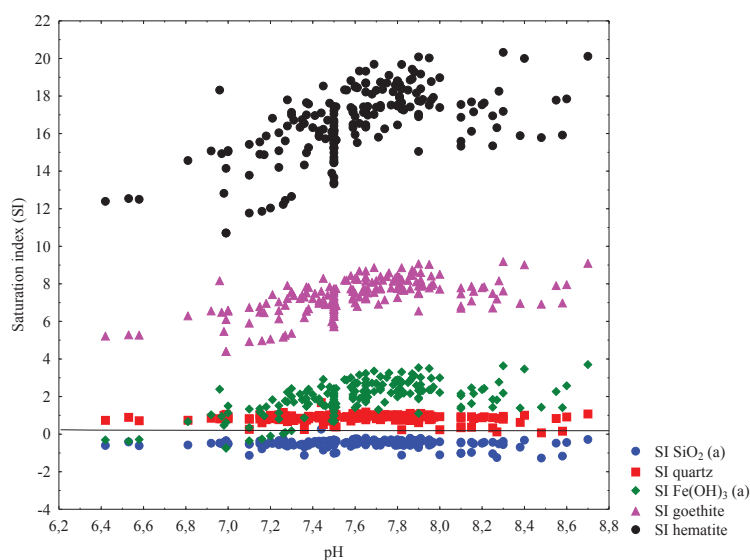


Fig. 5.9 Saturation index of selected mineral phases.

portion of the sum of sodium and potassium. It can be said that the first area probably represents the rock environment with a higher content of calcareous cement in sediments. The second area is obviously characterized by a smaller proportion of calcareous cement and the water formation is more influenced by the ion exchange reaction. In anionic composition of the surface water of the C group the

bicarbonates are dominating, next there follow sulphates and a sum of chlorides with nitrates (Fig. 5.11). Water with a characteristic bicarbonate content manifests the highest TDS. It means that distinct Ca(Mg)–HCO<sub>3</sub> chemical types have the highest total dissolved solids, which is in compliance with above stated part with dominant representation of calcium and magnesium.

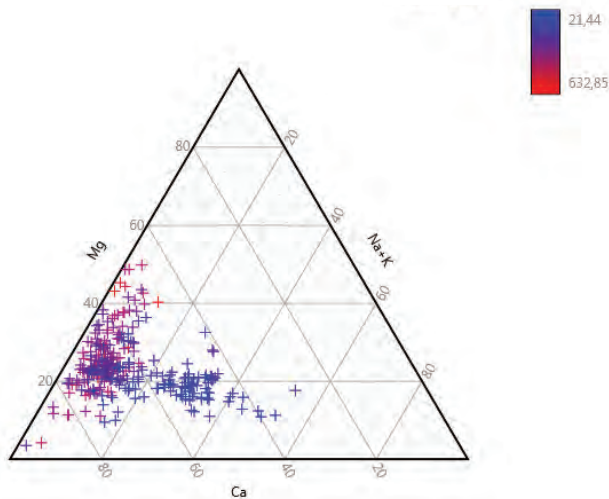


Fig. 5.10 Cationic composition of the surface water of the group C.

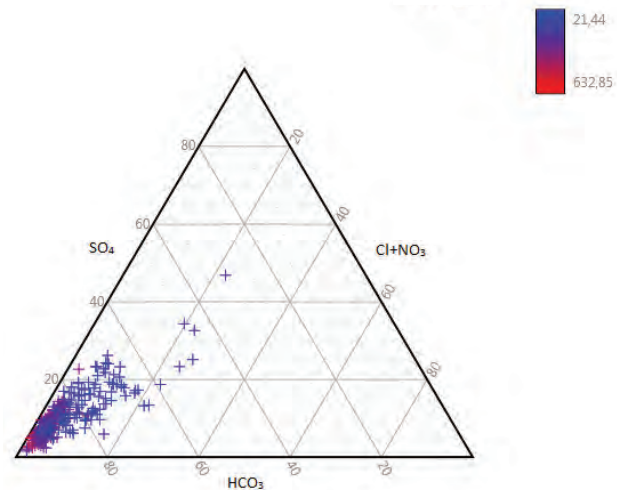


Fig. 5.11 Anionic composition of the surface water of the group C.

Tab. 5.8 The descriptive statistical parameters of the surface water of the group C.

	Average	Median	Minimum	Maximum	Lower quartile	Upper quartile	St. deviation
pH	8.0	8.1	6.2	9.5	7.8	8.3	0.4
Na	4.45	4.10	0.40	24.70	2.80	5.53	2.65
K	1.59	1.30	0.10	8.80	0.80	2.00	1.20
Ca	53.70	56.50	3.52	142.68	26.67	76.34	28.95
Mg	13.46	11.67	0.59	49.13	6.18	17.91	9.39
Sr	0.220	0.180	0.020	0.830	0.100	0.310	0.149
Fe	0.176	0.077	0.004	3.518	0.034	0.180	0.316
Mn	0.028	0.010	0.001	1.770	0.005	0.027	0.082
NH <sub>4</sub>	0.12	0.03	0.03	2.52	0.03	0.13	0.23
F	0.12	0.10	0.05	0.88	0.05	0.13	0.10
Cl	3.4	3.0	0.5	7.2	1.9	4.8	1.8
SO <sub>4</sub>	29.8	27.2	4.0	193.2	16.7	38.9	18.2
NO <sub>3</sub>	4.5	3.4	0.5	33.9	1.6	5.7	4.3
PO <sub>4</sub>	0.07	0.02	0.02	0.77	0.02	0.08	0.11
HCO <sub>3</sub>	193.42	201.30	4.27	454.45	90.30	281.76	109.06
SiO <sub>2</sub>	11.44	7.91	0.35	84.10	6.12	12.70	9.95
Ca + Mg (mmol.l <sup>-1</sup> )	1.89	1.97	0.11	4.24	0.93	2.76	1.03
TDS	306.94	320.56	21.44	632.85	163.29	443.09	158.20

Note: Values besides pH are stated in mg.l<sup>-1</sup>.

The statistical characteristics of the chemical composition of the surface water of C group are documented in Table 5.8. The chemical composition is similar to the surface water of the group D, but it has a higher mean value of TDS, different ratios of the main cations and higher content of  $\text{SiO}_2$ . This similarity results from the high variability of the rock environment of both selected groups of the surface water. This is documented e.g. by large differences in minimum and maximum total dissolved solids (Table 5.8).

The resulting factor structure of the surface water of C group includes three factors (Table 5.9). The first represents a high positive saturation by calcium, magnesium and bicarbonates. This factor represents dissolution of the carbonate cement, as well as varying amounts of carbonates in these sediments. The resulting product of interactions represent significant  $\text{Ca}(\text{Mg})\text{-HCO}_3$  types of surface water. The second factor is represented by the high saturation of sodium and potassium. Presumably, that is a reflection of the ongoing processes of ion exchange, where from the sorption complex of the clay minerals Na and K enter into a solution. The last factor with a strong representation of

iron and manganese indicates the source of these elements in the form of scattered minerals in sediments.

Tab. 5.9 Factor matrix - surface water of the group C.

	Factor 1	Factor 2	Factor 3
pH	0.552	-0.023	-0.157
Na	0.094	<b>0.861</b>	0.047
K	0.135	<b>0.774</b>	0.119
Ca	<b>0.931</b>	0.022	0.001
Mg	<b>0.844</b>	0.009	-0.085
Fe	-0.071	0.025	<b>0.872</b>
Mn	-0.063	0.042	<b>0.841</b>
$\text{NH}_4$	0.015	0.161	0.466
Cl	0.500	0.546	0.212
$\text{SO}_4$	0.675	0.268	-0.134
$\text{NO}_3$	0.452	0.024	0.143
$\text{HCO}_3$	0.927	0.009	-0.010
$\text{SiO}_2$	-0.414	0.614	0.090

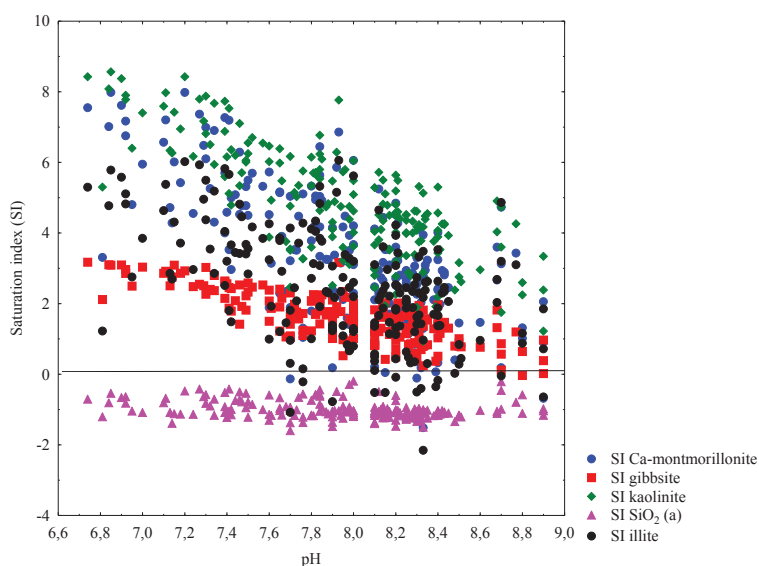


Fig. 5.12 Saturation index of selected mineral phases.

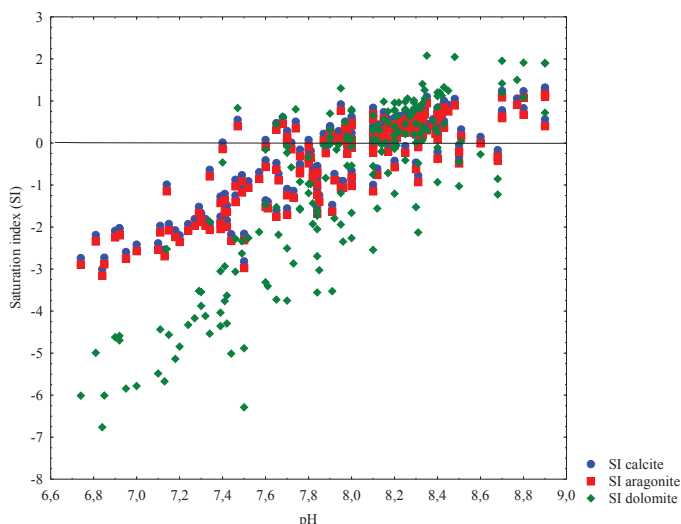


Fig. 5.13 Saturation index of selected mineral phases.

Regarding the saturation index of carbonate mineral phases versus pH measurements (Fig. 5.12) it is interesting that part of the water is saturated with calcite, dolomite and aragonite. This concerns the surface water in the environment of sediments with calcareous cement, resp. presence of carbonate minerals. Because their permeation is buffered by the rainwater of acid character, into surface water there is deliberated Ca, Mg and  $\text{HCO}_3$ . Obviously, the oversaturation of carbonate mineral phases increases with increasing pH value (Fig. 5.12).

The only plausible phase from the clay minerals, which is oversaturated in the whole interval of pH values, is a kaolinite. The calculated saturation indexes of Ca-montmorillonite and illite (Fig. 5.13) indicate that with increasing pH value they are lower, or in some cases they are in equilibrium with the water. Gibbsite typically is the first mineral phase, which is oversaturated in the process of silicate weathering. This is also in respect to this surface water. Insufficiently saturated mineral phase in this group is represented by amorphous  $\text{SiO}_2$ .

From the above assessment, there can be concluded that in surface waters bound predominantly to pelitic sediments the chemical composition is partially formed by the water interaction with carbonatic minerals, ion exchange processes and oxidative degradation of pyrite. In terms of genetic classification of the water, there can be said that it is of carbonatogene-hydrosilicatogene type.

#### Surface water of the group D

It represents a selected group of surface water bound to the catchment areas, formed pre-viously by the siliciclastic rock environment.

Regarding to the cationic representation (Fig. 5.14), this water has the supreme Ca content (60 – 80%), Mg (pre-vaillingly 20 – 40%) and Na + K sum up to 20%. In their anionic composition (Fig. 5.15) the bicarbonates fully prevail (more than 80 %), next there follow sulphates and a sum of Cl and NO<sub>3</sub>. The highest values of total dissolved solids exhibits a water with predominant representation of bicarbonates and increased content of sulphates.

The general chemical composition of the D group surface water is documented in Table 5.10. The TDS of the water varies in a wide diapason, 23 – 521 mg·l<sup>-1</sup>. It is mainly due to a high variability of the rock environment in the catchment area. It consists of relatively inactive lithogeochemical composition from sandstone to gravels, characterized by a varying degree of calcium content. Therefore, in an environment of sandstones the values

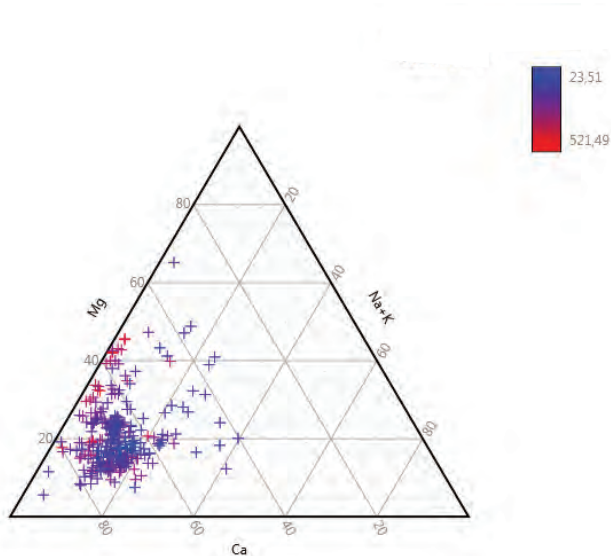


Fig. 5.14 Cationic composition of the surface water of the group D.

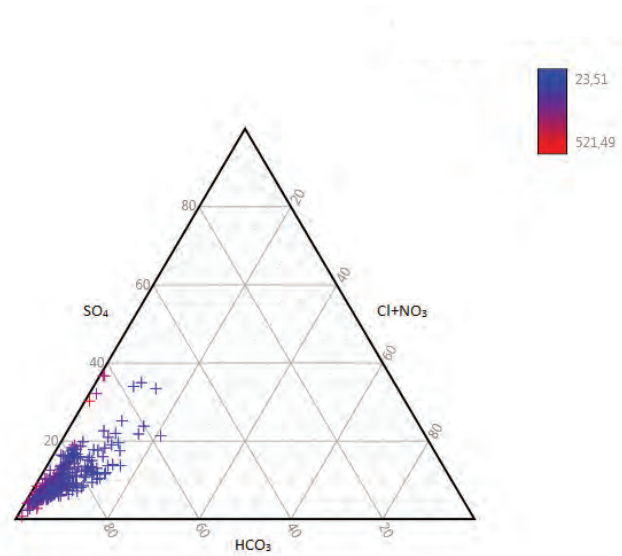


Fig. 5.15 Anionic composition of the surface water of the group D.

Tab. 5.10. The descriptive statistical parameters of the surface water of the group D.

	Average	Median	Minimum	Maximum	Lower quartile	Upper quartile	St. deviation
pH	8.1	8.1	4.6	9.4	7.9	8.3	0.4
Na	4.85	4.35	0.19	16.90	2.70	6.57	2.91
K	1.38	1.20	0.05	5.51	0.88	1.70	0.79
Ca	47.25	46.33	2.98	179.56	30.46	62.91	21.55
Mg	8.86	7.04	0.32	36.48	4.65	11.22	6.12
Sr	0.282	0.251	0.018	0.990	0.111	0.384	0.205
Fe	0.119	0.043	0.004	6.309	0.020	0.101	0.355
Mn	0.021	0.007	0.001	3.010	0.003	0.015	0.107
NH <sub>4</sub>	0.08	0.03	0.03	0.84	0.03	0.08	0.10
F	0.09	0.05	0.05	1.02	0.05	0.10	0.10
Cl	2.3	2.1	0.5	4.4	1.6	2.9	0.9
SO <sub>4</sub>	26.6	23.7	2.5	160.7	19.1	30.4	15.2
NO <sub>3</sub>	3.6	2.8	0.5	22.3	1.8	4.7	2.7
PO <sub>4</sub>	0.04	0.02	0.02	1.07	0.02	0.04	0.07
HCO <sub>3</sub>	158.75	154.99	9.76	372.21	99.46	215.39	74.81
SiO <sub>2</sub>	7.42	6.98	0.40	29.30	5.69	8.36	3.13
Ca + Mg (mmol.l <sup>-1</sup> )	1.54	1.47	0.10	4.78	0.99	2.05	0.71
TDS	254.90	249.07	23.51	521.49	166.35	342.72	110.64

Note: Values besides pH are stated in mg.l<sup>-1</sup>.

of mineralisation are the lowest and in sandy and gravel sediments the highest. From the hydrogeochemical viewpoint there runs probably the most intense infiltration, resp. the draining effect of the surface flow, depending on the season and rainfall. On the water of surface flows the greatest impact has an infiltration, or drainage effect, which the most intensively changes the chemical composition of the water flow. In many cases, its composition corresponds to that of the groundwater. Stated wide range of TDS values, of course, causes a high variability in other components, most in the case of calcium, bicarbonates and sulphates.

Interrelations between different selected components are documented by resulting factor structure (Table 5.11). The first factor is characterized by a high saturation of calcium, magnesium, and bicarbonate. It can be explained by the process of carbonates dissolution, which is probably the most significant process of formation of this group of surface water. The second factor represents a saturation of sodium and potassium and apparently is a common source of these cations. Regarding the environment of this water formation, it can be supposed that it will be a product of the hydrolytic decomposition of silicates. Third factor, being represented by the iron and manganese saturation, is characteristic for virtually all selected groups of surface water. It results from the geological conditions of the Western Carpathians, where almost all lithochemical types involve the above elements. The significant is that in the groundwater they are in a dissolved form owing the creation of local reducing conditions in the aquifer and in the surface stream there occurs the oxidation by atmospheric oxygen. The fourth factor has a high negative saturation of nitrates, which demonstrates that they are involved to a minimum degree in the chemical composition of the surface water. With this consideration we should bear in mind that the

Tab. 5.11 Factor matrix - surface water of the group D.

	Factor 1	Factor 2	Factor 3	Factor 4
pH	0.408	0.023	-0.042	-0.112
Na	0.215	<b>0.786</b>	0.040	0.323
K	0.157	<b>0.833</b>	0.067	0.156
Ca	<b>0.871</b>	0.292	-0.011	0.111
Mg	<b>0.839</b>	-0.109	0.009	-0.141
Fe	-0.066	-0.014	<b>0.815</b>	0.090
Mn	-0.041	0.001	<b>0.810</b>	0.016
NH <sub>4</sub>	0.107	0.220	0.330	-0.169
Cl	0.468	0.652	0.090	-0.122
SO <sub>4</sub>	0.624	0.214	0.000	-0.112
NO <sub>3</sub>	0.174	-0.090	-0.007	<b>-0.852</b>
HCO <sub>3</sub>	<b>0.891</b>	0.202	0.045	0.136
SiO <sub>2</sub>	-0.103	0.652	-0.018	-0.379

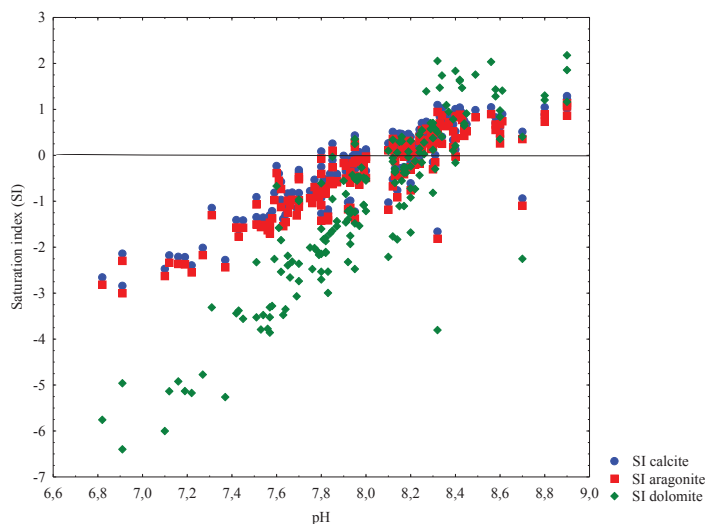


Fig. 5.16 Saturation index of selected mineral phases.

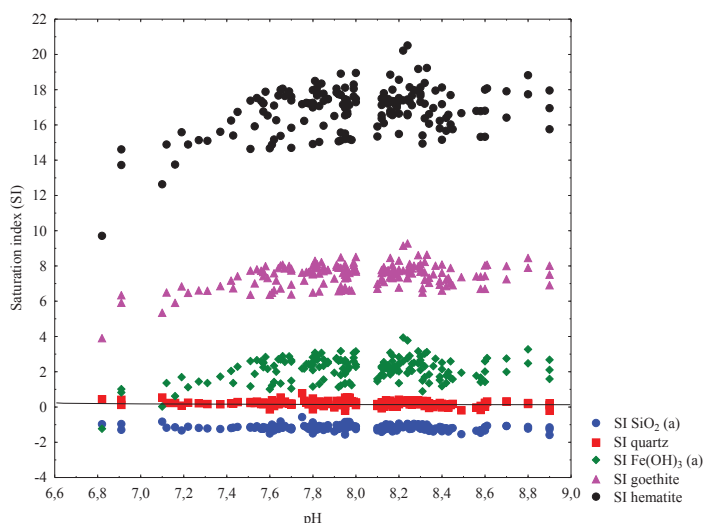


Fig. 5.17 Saturation index of selected mineral phases.

selection was done by the way to exclude the input of anthropogenically polluted water.

The thermodynamic analysis supplements the results of the factor matrix. In the case of the carbonate balance, calcite, aragonite and dolomite in the solution are oversaturated at a pH values higher than 8 (Fig. 5.16). Undersaturation of other samples of the surface water may be due to the higher pressure of carbon dioxide and the lack of carbonate minerals in the environment of their origin.

Concerning the iron mineral phases, the amorphous ferric hydroxide as well as goethite and hematite are oversaturated in the solution (Fig. 5.17). By contrast, all surface waters are undersaturated by amorphous SiO<sub>2</sub>, and in respect to the quartz they are in equilibrium.

From the genetic point of view, the surface water of the D category bound to siliciclastic geological environment can be described as carbonatogene-silicatogene. The main mineralising processes, producing its chemical composition, encompass the dissolution of carbonates and hydrolytic decomposition of silicate minerals.



### Surface water of the group E

The surface water of this group is bound to the catchment areas made up mainly of carbonate rocks. It is also reflected in its chemical composition, which is different from that of the other groups of surface water. In its cationic composition (Fig. 5.18), the calcium is the most abundant and magnesium represents the second main ion. The sum of Na and K is represented only minimally, it is the lowest of all distinguished groups of surface water. The ratio of Mg/Ca has an average value of 0.49, with a minimum value of 0.03 and the maximum 2.43. This ratio depends on the representation of limestone and dolomite in the catchment area. When the value of this ratio is about 0.5, the environment contains approximately the same proportion of limestone and dolomite, at 0.75 and more limestones prevail and a ratio 0.3 and less is typical for the environment of dolomites. Fig. 5.30 demonstrates that any small increase in the sum Na and K causes the decrease in the total dissolved solids of surface water of the E group. It is probably caused by a certain proportion of the clayey limestones in the rock environment, which in interaction with water deliberate the sodium and potassium ions into solution, while the Ca and Mg content in comparison with

limestones is lower. In anionic composition there dominate the bicarbonates, the second most represented anions are sulphates (Fig. 5.19). The source of sulphates in the surface water represent the gypsum in the rock environment of the basin.

The chemical composition of surface water is documented in Table 5.12. The greatest variability of cations has a calcium content, which is probably related to the time of the contact with the groundwater, temperature and partial pressure of CO<sub>2</sub> in the water of surface flow, as well as to the mineral composition in the rock environment. Similar relation is manifested at minimum and maximum values of pH and bicarbonates. The lowest concentration of SiO<sub>2</sub> from all classes of the surface water is related mainly to its low content in the rock environment of carbonate sediments. Significantly different, and the highest is the hardness value of the water, expressed as the sum of Ca and Mg. Similarly, within the selected catchment areas according to prevailing lithochemical types there can be stated that in the environment of carbonates the surface water has the highest mean values of total dissolved solids. Environment with a predominance of carbonate rocks also represent rocks with the highest buffer capacity in relation to acid precipitation.

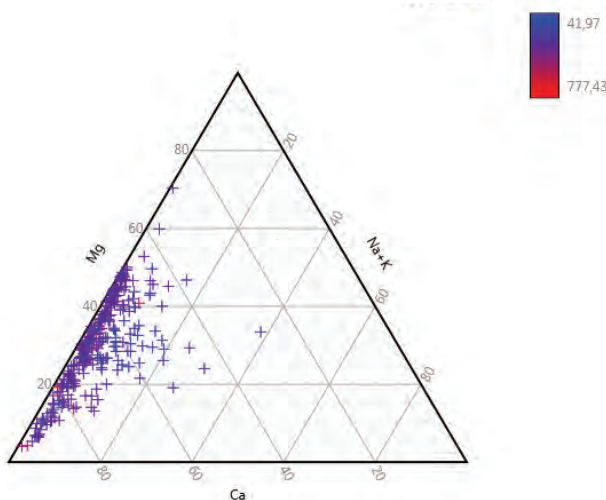


Fig. 5.18 Cationic composition of the surface water of the group E.

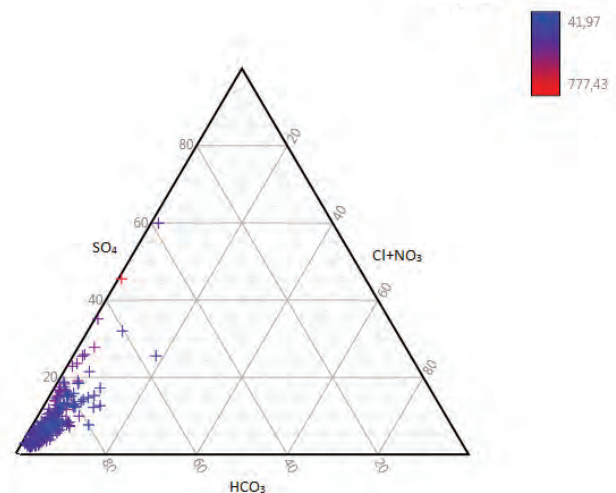


Fig. 5.19 Anionic composition of the surface water of the group E.

The resulting factor structure of the surface water of the E group contains three factors (Table 5.13). The first is represented by a high saturation of calcium, magnesium and bicarbonate. It can be explained by the interaction of water-carbonates, representing the main mineralisation process in this water group. The second factor represents the high saturation of sodium and potassium. A common source of these elements in the surface water can be a hydrolytic decomposition of silicate minerals, present mainly in sandy limestones. It must be emphasized that regarding the small presence of these rocks, these processes in carbonate environments are not dominant.

For this group of surface water in terms of the thermodynamic analysis, the most significant is the relation

between the balance of the carbonate mineral phases, pH and gypsum (Fig. 5.20). Gypsum represents a mineral phase undersaturated in the water, which follows from the above stated characteristics of the water forming environment. By contrast, calcite, aragonite and dolomite at a particular pH range higher than 8.2 occur in equilibrium with these minerals, resp. they are oversaturated. This equilibrium state was found at a simple majority of surface waters, allocated to the group E. It is interesting that despite the lowest silica concentration in all distinguished groups of surface water, it is detected in equilibrium in the whole range of pH values (Fig. 5.21). At Ca-montmorillonite and illite there can be stated that in the mild acid to neutral environments they are oversaturated in solution (Fig. 5.21).

In slightly alkaline environment their stability is divided to undersaturated part (obviously from the environment of pure limestones and dolomites) and oversaturated part.

Overall, we can state that the surface water is formed in parts of the catchment areas, built mainly by carbonates, by the dissolution of limestones and dolomites, less of

gypsum. From a genetic point of view, this water can be regarded as carbonatogene and to a much lesser extent as sulphatogene. Less significant process, forming the chemical composition of this group of surface water, is a hydrolytic decomposition of silicate minerals.

Tab. 5.12 The descriptive statistical parameters of the surface water of the group E.

	Average	Median	Minimum	Maximum	Lower quartile	Upper quartile	St. deviation
pH	8.2	8.3	6.7	9.0	8.0	8.4	0.3
Na	1.69	1.20	0.10	9.96	0.70	2.11	1.50
K	0.76	0.60	0.05	11.00	0.32	0.90	0.82
Ca	58.03	58.06	4.41	174.79	44.60	71.33	23.50
Mg	15.62	14.20	1.84	46.50	8.76	21.60	8.70
Sr	0.225	0.120	0.010	3.380	0.057	0.250	0.340
Fe	0.061	0.025	0.004	1.348	0.011	0.055	0.112
Mn	0.009	0.003	0.001	0.260	0.003	0.006	0.023
NH <sub>4</sub>	0.06	0.03	0.03	1.40	0.03	0.05	0.10
F	0.11	0.05	0.05	0.79	0.05	0.11	0.12
Cl	2.4	2.0	0.5	7.1	1.4	3.0	1.5
SO <sub>4</sub>	30.6	24.8	3.9	326.8	16.7	36.8	25.3
NO <sub>3</sub>	5.4	4.6	0.5	27.5	2.3	7.3	4.1
PO <sub>4</sub>	0.04	0.02	0.02	2.50	0.02	0.03	0.12
HCO <sub>3</sub>	205.63	208.68	18.31	397.00	161.70	250.17	77.24
SiO <sub>2</sub>	5.43	4.93	0.15	24.76	3.12	6.62	3.49
Ca + Mg (mmol.l <sup>-1</sup> )	2.09	2.13	0.24	5.41	1.70	2.53	0.75
TDS	323.23	325.54	41.97	777.43	255.91	391.89	113.99

Note: Values besides pH are stated in mg.l<sup>-1</sup>.

Tab. 5.13 Factor matrix – surface water of the group E .

	Factor 1	Factor 2	Factor 3
pH	0.340	-0.287	-0.243
Na	0.008	<b>0.789</b>	0.342
K	0.047	<b>0.756</b>	-0.039
Ca	<b>0.817</b>	0.190	-0.016
Mg	<b>0.715</b>	-0.170	0.058
Fe	0.093	0.044	<b>0.790</b>
Mn	0.113	0.233	<b>0.753</b>
Cl	0.455	0.653	0.060
SO <sub>4</sub>	0.492	0.131	0.196
NO <sub>3</sub>	0.299	0.460	-0.359
HCO <sub>3</sub>	<b>0.886</b>	0.061	-0.018
SiO <sub>2</sub>	-0.188	0.682	0.293

## 5.5 Isotopic composition of oxygen and deuterium in the surface water

The water in surface flows in Slovakia is a product of precipitation, as evidenced by its isotopic composition. It originates directly from the precipitation, as well as from the groundwater. The share of the groundwater, having different than the meteoric origin, is negligibly small in the surface flows of Western Carpathians. On the territory of Slovakia there are known several groundwater sources of marine origin, bitter brines resources associated with the oil and gas occurrences, as well as the sources with a ratio of the groundwater originating during the complicated conditions in buried flysch units. Though, they have a minimum yield and have virtually no impact on the composition of surface water flows.

Under standard conditions, the isotopic composition of the natural water molecule retains its principal characteristics even in different environments. It means that the surface water flows should reflect the distribution of isotopes in precipitations, as well as derived groundwater, which

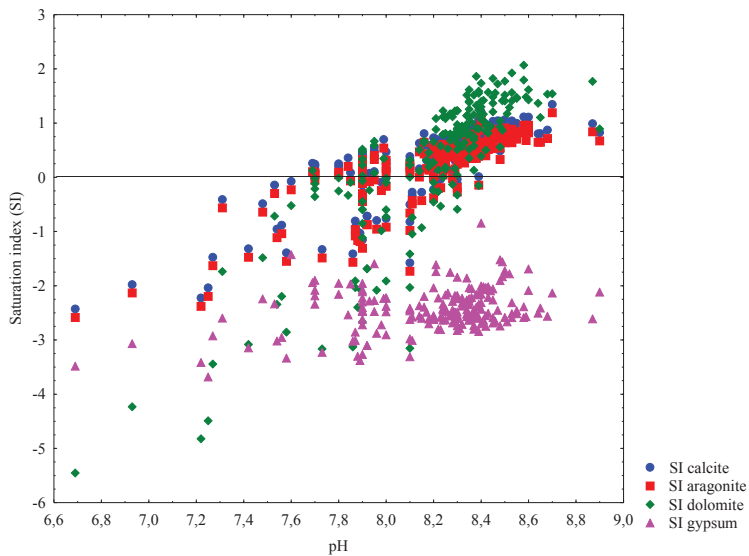


Fig. 5.20 Saturation index of selected mineral phases.

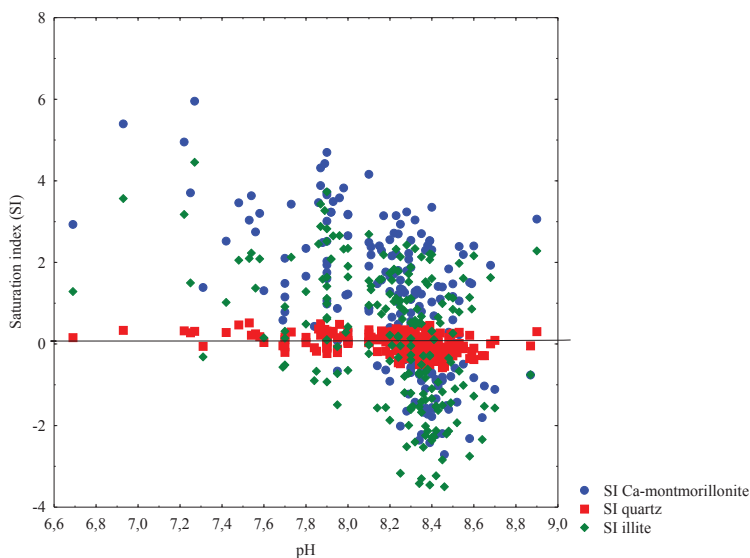


Fig. 5.21 Saturation index of selected mineral phases.

could take part in formation of surface water. The distribution of oxygen and hydrogen isotopes in precipitations depends mainly on the temperature, and thus the altitude in which precipitations fall, resp. it depends on the altitude of the relevant hydrogeological structure catchment and in our conditions also on the year season. The representation of lighter isotopes of both elements with decreasing temperature correspondingly increases, water is isotopically lighter, depleted, and the  $\delta$  values are more negative.

Isotopic composition of 55 water samples of the main water flows (sampling date 5.–10. 8. 2013) has a relatively large spread,  $\delta^{18}\text{O}$  from  $-6.84$  to  $-12.09$  ‰,  $\delta^2\text{H}$  from  $-47.6$  to  $-87.7$  ‰. Average values ( $\delta^{18}\text{O} = -9.90$  ‰ and  $\delta^2\text{H} = -71.7$  ‰) converge to average  $\delta$  values from precipitations in Slovak territory. Water in all documented water flows is unambiguously of the meteoric origin. It is evidenced by the position of the projection points of the samples in the vicinity of the global meteoric water line (GMWL) in Fig. 5.22. In some rivers, especially in southern Slovakia (Bodva, Bodrog, Ipeľ, Nitra and Slaná rivers) and in the

Morava River the water is apparently influenced by evaporation. These rivers in warm climates are mostly slowly flowing; they are influenced also by the surface reservoirs in which the water circulation is slower, and the water surface is larger. In order to assess whether it is not only a local rainfall line, a sufficient knowledge of the isotopic composition of local precipitation is not yet available.

Among the “autochthonous” streams, the Biela voda and Belá streams, dewatering the Vysoké Tatry Mts., have the highest proportions of the light isotopes. The presence of the light isotopes in the water of the Biely Váh, Dunajec and Poprad rivers is assumed. The increased representation of the light isotopes in the Váh River in the Kolárovo town is a consequence of the water of the Danube provenance entering into the Váh River through the Malý Dunaj water flow, eventually by a disguised transfer owing to groundwater infiltration from the Danube River. Isotopically the lightest water is proven in the Danube River in Bratislava, which corresponds to its Alpine origin. The distinct increase in the proportion of heavy isotopes in the Danube water in Komárno and Štúrovo towns is obviously a consequence of the increased share of the Váh and Hron rivers water in the sample (it was taken from the left bank), where apparently the water of flowing stream apparently modifies the strong Danube flow.

The specific isotopic composition was found in the water of Rudava and Malina flows. These left-side tributaries of the Morava River have up-to-now the highest documented presence of hydrogen and oxygen heavy isotopes, while the evaporation can be excluded. Both streams drain the western, windward slopes of the Malé Karpaty Mts. Despite no data about

the distribution of isotopes in the precipitations in this area are available, their specific isotopic composition can be assumed. Such indications are in the higher representation of the oxygen and hydrogen heavy isotopes in the water of Vlára and Kysuca water flows.

## 5.6 Conclusions

The final part of the *Geochemical Atlas of Slovakia* is devoted to results of hydrogeochemical mapping of the surface water, being obtained in the frame of the project 04 08 *Geochemical Atlas of the Slovak Republic, part 7 – Surface Waters*. This project was solved in SGIDŠ within the years 2008–2014. The input data consisted of 10,960 samples of surface water, representing a sampling density one sample per 4.5 km<sup>2</sup>. The sampling was not done in regular network, but it was modified to the density of river net in Slovakia. In the Atlas the following elements/compounds/indicators are evaluated: TDS, pH, Li, Na, K, NH<sub>4</sub>, Mg, Ca, Sr, Mn, Fe, F, Cl, NO<sub>3</sub>, SO<sub>4</sub>, PO<sub>4</sub>, HCO<sub>3</sub>, Sb, As, Ba, Al, Cr, Cd, Cu, Pb, Se, Zn, SiO<sub>2</sub> and COD<sub>Mn</sub>.

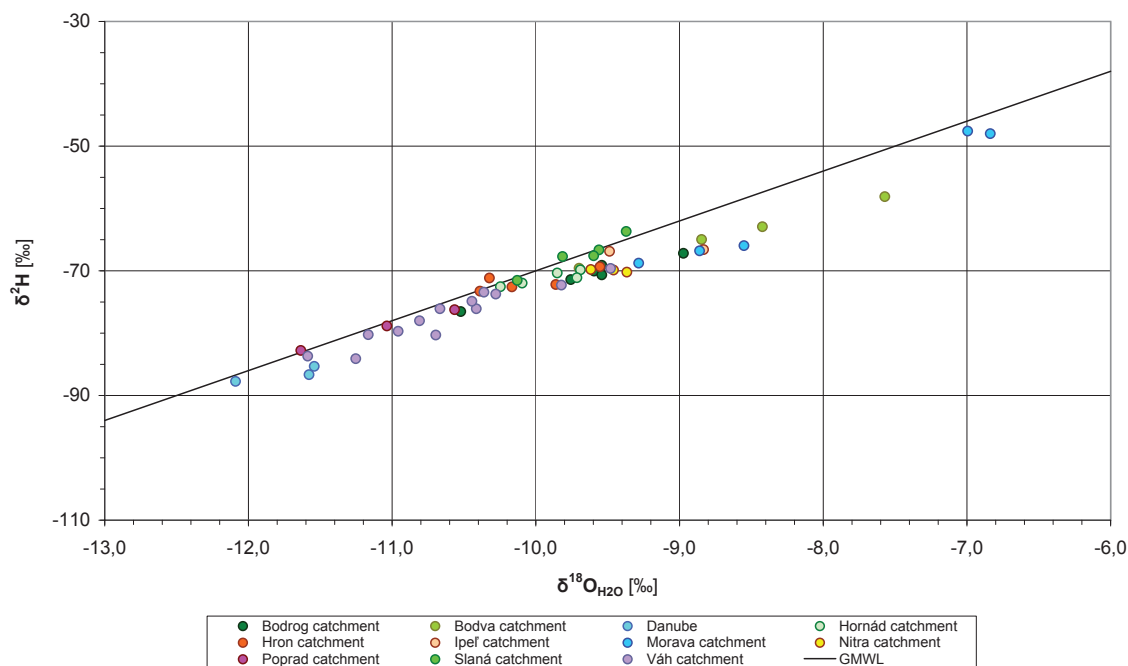


Fig. 5.22 Contents of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in Slovak rivers according to catchment areas.

The Geochemical Atlas of Surface Waters is focused mainly on clarification and interpretation of the distribution of elements/compounds/indicators in maps at a scale 1:1,000,000. For the first time in conditions of Slovakia, the genesis of elements/compounds in such important medium like the surface water was assessed.

The results of the geochemical mapping allowed to carry out hydrogeochemical assessment of the surface water. According to selected end members of the chemical composition of the surface water there were characterized the main chemical types of the water by means of ternary diagrams, statistical methods and thermodynamic analysis. Concerning the chemical composition, the surface water is characterized by the prevalence of  $\text{Ca-HCO}_3$  compound. In cationic composition there prevails the calcium content and in variable representation in individual lithotypes present in the source environment there alternate the magnesium and calcium. In anionic composition there dominate the bicarbonates and the second most frequent compound represent sulphates. In individual groups in the varying proportions there is represented  $\text{SiO}_2$ .

According to the conceptual model the formation of the chemical composition of the surface water is very complex mechanism. Moreover, the surface flow is an open, dynamic system that is affected by a large number of factors. A simplified approach is based on the initial water - atmospheric precipitation (solid and liquid), which represents primary input for the formation of surface and groundwater. In this system it is clear that in the natural conditions of Slovakia the most important factor is the interaction of water - rock - gas. Therefore, the resulting chemical composition of surface water is the most dependent on the composition of the ground, altitude and climatic period. The chemical composition of surface water quickly reacts to climatic period (spring snow melt, torrential rainfall, etc.), which leads to significant changes in water quality.

In simple substantiation, surface water was divided into five groups, named A, B, C, D and E, which are characterized by petrography and geochemistry of catchment areas:

- A) Acid almosilicate rocks and siliciclastic sediments, as well as their metamorphic rock equivalents
- B) Basic and intermediary rocks
- C) Dominantly pelitic sediments
- D) Dominantly siliciclastic rocks
- E) Carbonate rocks

According to these groups the surface water was characterized hydrogeochemically in detail.

As an integral part of the atlas, also a comprehensive evaluation of the isotopic composition of the surface water is presented for the first time in the nation-wide Slovak scale. The isotopic composition of oxygen and deuterium, characterizing the water molecule, clearly points to their meteoric origin.

The formation of chemical composition of the surface water represents a complicated geochemical and biological system, where the most significant role in the Slovak conditions is played by the water-rock interaction and anthropogenic influence. The hydrobiological processes, influencing the chemical composition of the surface water, are not treated in this paper.

All data and interpretations constitute a basis for further evaluations especially of environmental and hydrological character. They are also important in terms of improving the status of natural waters in Slovakia. The results of the Geochemical Atlas of Surface Waters in connection with the results of monitoring of surface water quality, reflecting the temporal factor, represent a unique tool to fill the noble goal to improve water conditions in Slovakia and the whole continent.

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