Mineral waters in Slovakia — Evaluation of chemical composition stability using both historical records and the most recent data

Bodiš Dušan [a], Kordik Jozef [a], Slaninka Igor [a,*], Malík Peter [a], Liščák Pavel [a], Panák Daniel [b], Božíková Jarmila [b], Marcin Daniel [a]

[a] State Geological Institute of Dionyz Stur, Mlynská dolina 1, 817 04, Bratislava, Slovakia
[b] Ministry of Health, Limbová 2, P.O. BOX 52, 837 52, Bratislava, Slovakia

ARTICLE INFO

ABSTRACT

A methodology of temporal chemical composition stability of mineral waters is presented. Both historical chemical analyses records and modern water quality monitoring information are interpreted. Historical records can represent a precious background, but they suffer from the lack of information, short association of the analysed components and analytical methods applied; and thus can be evaluated only descriptively. Results of mineral water quality monitoring are processed by statistical methods. Selection of the proper statistical criteria was tested on time series of various sources of Slovak mineral waters. As the most suitable criteria of stability, the 1.5 IQR parameter was selected. Temporal stability of chemical composition of mineral waters is conditioned by many factors both of natural and anthropogenic origin. By help of the criteria proposed, together with limits for the dataset population, time factor and qualified approach can result into a profound estimation of chemical composition stability of mineral waters in time.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Complex geological evolution and active tectonics of the Western Carpathian explain the presence of numerous mineral waters with varying chemical composition in the Slovak Republic (Franko et al., 1975). Over the last decades, the use of mineral waters in Slovakia has been gaining in popularity. Because of their properties, the numerous mineral waters are used as drinking water (usually bottled mineral waters) as well as for balneology purposes. Natural mineral waters provide a source of essential or beneficial ions, such as fluoride, chloride, calcium, magnesium, potassium, sodium, iodine, bromine, boron, iron, manganese, zinc, selenium and silicon.

Thus, it is highly recommended that the efficient protection of mineral waters (their quality, quantity and optimal exploitation) will be within the scope of the studies in Slovakia. One of the most important elements of the mineral water protection, influencing also the criteria for their use, is the way of evaluating the stability of their chemical composition.

In accordance with European legislation (Directive 80/777/EEC) natural mineral water is defined as microbiologically wholesome water from an underground aquifer tapped via one or more natural or drilled wells. The only treatment allowed prior to bottling is to remove unstable components such as iron and sulphides and to (re)

introduce carbon dioxide. However, local standards differ per country. According to Codex Standard 108–1981 applied to all packaged natural mineral waters offered for sale as food, the natural mineral water is water clearly distinguishable from ordinary drinking water because:

- it is characterized by its content of certain mineral salts and their relative proportions and the presence of trace elements or of other constituents,
- of the stability of its composition and the stability of its discharge and its temperature, due account being taken of the cycles of minor natural fluctuations,
- it is not subjected to any treatment other than those permitted by this standard.

In practice, the above mentioned definition of mineral water means, that the composition of natural mineral waters should be inherently stable. It is recognized that some variation is inevitably occurring in all waters, but the permissible degree of the variation is usually not laid down in the national legislation. The hydrogeological and geochemical assessment should give a reasonable idea of how stable the composition of a particular mineral water source will be. To establish the chemical stability of mineral water, it is necessary to collect information over a sufficiently long period to demonstrate the extent to which the composition varies. For instance, the Scottish guidelines (Food Standards Agency Scotland, 2006) recommend an analytical regime for a number of parameters over a period of two

years. It is recommended that the variation of results should be within the following limits. For mineral content, determined as dry residue and electrical conductivity with characteristic frequency of sampling once per month, the acceptable variation is $\pm20\%$ (of mean). Similarly, for individual anions, cations, and non-ionised compounds with characteristic frequency of sampling once per 3 months, the acceptable variation is $\pm20\%$ (of mean), as well.

Temporal stability (variability) of chemical elements/compounds was examined in many environmental studies (e.g. Varsányi, 1992; Vrba, 1996; Eary et al., 2003; Steinmaus et al., 2005; Reimann and Garrett, 2005; Bagdavadze et al., 2008) in which archive data usually supported interpretation of more recent data. As part of the monitoring programmes, the stability of chemical composition of mineral waters was investigated by e.g. Muntean et al. (2006), Lujerdean et al. (2006), Barut et al. (2004). Negrel et al. (1997) measured variations in the solute concentrations of mineral waters at chosen sites. For the Thetford mineral waters, a comparison of data from different time periods was made (Raiswell and Tranter, 1982).

Representative assessment of temporal stability of chemical composition of mineral waters is closely associated with existing input dataset. Nearly six hundred years of historical records about mineral waters on the Slovak territory brings attention of water scientists to define the stability of mineral water chemical composition. Such knowledge may enable us to reach a better understanding of formation processes of mineral water chemical composition and determine their individual roles by distinguishing primary and secondary processes of their formation. The stability of chemical composition of natural mineral waters is of great importance in terms of supplier relations from the perspective of bottling companies, spas and their customers–consumers or patients. Finally, understanding of this characteristic can have a special meaning in the process of designing and development of various regulatory and legislative materials concerning mineral waters.

Issues concerning the stability of the chemical composition of mineral waters in Slovakia were studied rather rarely. Melioris and Trnovec (1995) found that the stability of mineral waters of younger Neogene and Palaeogene rock formations are less stable compared to mineral waters of Mesozoic and Palaeozoic geological units (study carried out on datasets originated in the period between 1967 and 1989). Despite the complex geological and tectonic conditions of mineral and thermal water origin in the Western Carpathians, Franko and Melioris (1999) similarly stated that majority of the mineral waters in Slovakia are stable over a time period studied. Chemical composition and its temporal stability of the Dudince healing mineral waters were studied by Hyánková and Melioris (1993). The Dudince mineral waters have an extraordinary position among the mineral waters of the Western Carpathians with Na–Ca–(Mg)–HCO$_3$–Cl–(SO$_4$) chemical type, TDS = 5–6 g l^{-1}, temperature 28 °C, content of CO$_2$ up

to 1.8 g l^{-1} and H$_2$S up to 10 mg l^{-1} (the waters are notable for the stability of their chemical composition, with an exception for gases).

The principal goals of this paper are to (1) describe the main factors affecting the mineral water stability for conditions of the Western Carpathians geological settings, (2) evaluate the criteria for temporal stability of chemical composition of selected natural mineral water resources in Slovakia (description of historical data, statistical approach of monitoring data), and (3) compare chemical composition of selected natural and bottled mineral waters found at the Slovak markets in order to improve the overall knowledge about the stability of mineral water resources and consequently to contribute to management of the mineral waters in Slovakia.

2. Methodology

2.1. Selection of mineral water sources

Evaluation of chemical composition stability of mineral waters was implemented and verified for selected famous sources of natural mineral waters or curative mineral waters in Slovakia (Fig. 1). The assessment was based on both historical data and the most recent analyses from water quality monitoring. Data were obtained by analysing of mineral waters in its natural state as well as bottled mineral water prepared for consumers in the scope of an international project coordinated by the EGS Geochemistry Working Group (Reimann et al., 2010).

The dominant role for selection of mineral water sources played their different genesis and discharge. Different conditions of mineral water formation reflect their variations in chemical types. The selected mineral water resources (Lipovce, Turčianske Teplice Spa, Budiš, Sliač Spa, Dudince Spa, Piešťany Spa) are connected with the Triassic carbonates of the Krížna or Choč nappe units.

2.2. Database and chemical analyses

Throughout the last 130 years, chemical analyses have been collected from the Lipovce mineral water spring (Salvátor). The database used in this study is a compilation of most of these historical data (7 analyses) as well as the most recent data from the monitoring. The monitoring data were used for statistical analysis and include the data set from period 1965–2009.

Data collected throughout the last 200 years (with seven historical analyses) were used for assessment of the "Červený bazén" in the Turčianske Teplice spa resort. Data collected throughout the past 175 years (with nine and six historical samples, respectively) were used for description of the Sliač – spring "Kúpeľný" and the Dudince – borehole S-3 mineral waters. In the case of the Piešťany spa resort, data collected throughout the past 150 years (six samples) were used

Fig. 1. Position of the selected mineral water sources in Slovakia.

for mineral water characterisation. The chemical composition of the Budiš mineral water is based on systematic analysis carried out since 1999 up to the present day.

Not surprisingly, the quality and representativeness of the chemical analyses vary according to the time period when they were carried out. Reproducibility of analyses evaluation concentrates mainly on major ions, where we can assume comparability with modern analyses, after recalculation of units that were used in the past. Such a presumption is allowed by applied analytical methods, in which in the past gravimetrical methods applied for large sample volumes prevailed. Trace elements are more problematic to evaluate, and in a majority of cases they were already not analysed. Problems connected to historical data interpretation were summarised by Hyánková (1989):

- Inconsistency in labelling and naming of mineral water resources. Moreover, trilingual naming of villages and changes of settlement names and names of mineral water resources represent specific problems in Slovakia over last 300 years. Mostly these facts make difficult study and processing the archive data.
- Inconsistency in applied chemical terminology (different combinations of German, Hungarian or Latin names of individual compounds).
- Common determination of some compounds resulting from used methodology limits statement of content of individual components (common statement of iron, manganese and aluminium as an oxide referred to as R_2O_3 was used at longest).
- Inconsistency in the statement of fixed CO_2, mostly referred as carbonates. At present, hydrogen carbonates are adopted because their presence in water is more realistic due to the pH values. Then, recalculation of old data can lead to different results in some cases.
- Incomplete chemical analyses in terms of the main ions limit verification of analytical error of old chemical analyses.
- Inconsistency in quantitative expression of results. In some cases, old analyses were expressed in "gran (old German unit) per 16 or 32 oz". One "gran" is equivalent of 60 mg and one "ounce" equals 30 g.

In case of new data set used in the research all the analysed were carried out by selected certified laboratories.

Chemical analyses of the bottled mineral waters (Budiš, Salvátor) were done in frame of the EGS Geochemistry expert group project "Geochemistry of bottled waters in Europe". Analyses were performed in a BGR analytical laboratory. The detailed analytical procedures are described in (Birke et al., 2010-this issue).

2.3. Statistical assessment of stability of mineral water quality

From the statistical point of view, instability of mineral water quality is caused by outlying values in the scope of certain dataset, which is retrieved from chemical analyse of the monitored mineral water resources. From the point of view of mineral water these points can be considered the most important because they may lead to changes in the chemical type of water or change in the content of the chemical element/elements in mineral water, based on which it is

recognized (notification) as the natural mineral water or healing mineral water.

The outlying values may have different grounds; they may be due to sampling error, deficiency in sample transport and analysis, simply said an error of measurement or record. Another reason may be the observation of a different nature than the other data, i.e. observation caused by other than natural conditions. This may be due to pumping of excessive water amount than is the specified exploitable amount, technical state of a borehole, the influence of a new borehole in the vicinity of the source and so forth. The last reason may be the event that we cannot explain, but the value is significantly different from the others. Such a case is rather rare in our conditions.

The most common case of outlier presence is observation of a different nature than other data. Natural conditions are close to the conditions of a permanent regime, because the mineral waters are of deeper circulation, mainly and therefore they are potentially likely to have a permanent regime. Unlike dissolved solids due to their characteristics, the nature of the parent rock and a source of instability, the least stable component of the mineral waters is the gaseous phase. In the Western Carpathians conditions the mineral waters contain mostly carbon dioxide, which as a gaseous component exhibits a greater dispersion (up to two-phase flow) and, depending on temperature and partial pressure directly affects the stability of the regime, mainly the carbonate components of the system. The impoverished conditions of exploitation (technical, exceeding exploitable amount, accident, drilling of another interacting borehole and so on) may lead to disturbance of the regime stability.

The approach to the determination of criteria for assessing the stability of the chemical composition of mineral waters, using statistical methods, is based on two basic considerations:

- The stability is characterized by the occurrence of the minimum number of outliers in the dataset time series, i.e. the task is to identify outliers.
- The trend of the time series should not exceed the established criteria for the stability of the chemical composition of mineral water, i.e. the range of concentrations over which the outlying values occur.

The testing procedures were selected on the basis of information from the search processing of the issue, as well as the experience of authors in the scope of the previous studies of similar nature (Rapant et al., 2009). In general, statistical assessment methods characterize the distribution and identify and eliminate outlying values from the original data set. Outlying values are usually considered to represent a certain degree of influence. Statistically, the values are defined as belonging to another population of observations, originating from other processes or sources, e.g. derived from contaminated component/components of a distribution (Hampel et al., 1986; Barnett and Lewis, 1994).

In general, multiple authors utilize the rule of the mean and standard deviation [mean ± 2*standard deviation] in order to express the outlying or anomalous values. However, the problem was revealed with the application of the rule mean ± 2σ, which is valid

Table 1
Chemical composition of mineral water source Lipovce–Salvátor (wells S-1 and S-2).

Year (analysed)	Na⁺ (mg l⁻¹)	K⁺ (mg l⁻¹)	Ca²⁺ (mg l⁻¹)	Mg²⁺ (mg l⁻¹)	Cl⁻ (mg l⁻¹)	SO₄²⁻ (mg l⁻¹)	HCO₃⁻ (mg l⁻¹)
1882 — S1 (prof. Balló)	22.7	1.9	46.6	28.1	6.6	6.6	83.5
1901 — S1 (prof. Balló)	20.7	2.3	48.2	28.0	6.1	5.9	85.2
1907 — S1 (prof. Balló)	20.2	2.0	47.7	29.3	5.9	5.8	86.0
1914 — S1 (Dr. Emszt)	21.5	2.0	48.0	27.8	6.4	7.2	84.1
1926 — S1 (Hochstadter)	22.1	2.5	45.3	28.0	6.1	6.0	84.8
1926 — S1 (Dr. Veselý)	19.6	2.0	48.6	28.6	6.1	6.3	87.6
1958 — S2 (IGHP. Žilina)	306[a]		401	144	95.2	126	2429
2004 — S2 (INGEO-ENVI)	220	32.5	404	147	100	130	2209

[a] Sum of (Na + K).

Table 2
Chemical composition of mineral water source Turčianske Teplice–Červený bazén.

Year (analysed)	Na$^+$ (mg l^{-1})	K$^+$ (mg l^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Cl$^-$ (mg l^{-1})	SO$_4^{2-}$ (mg l^{-1})	HCO$_3^-$ (mg l^{-1})
1807 (Wachtl)	212[a]		296	99	[b]	1047	620
1870 (Nedtvich)	38	9	347	12	4	539	638
1973 (BCHL. Piešťany)	48	10	236	53	13	460	521
1985 (Kh-PFUK. Bratislava)	45	10	250	59	3	541	527
1995 (RC. Piešťany)	60.5	9	257	65.2	12.0	555	559
2001 (INGEO. Žilina)	47	9.8	260	62.3	3.55	542	543
2004 (INGEO. Žilina)	43.5	10.2	262	62.3	3.2	514	555

[a] Sum of (Na + K).
[b] Not analysed.

only in the case of normal distribution of the assessed variables. Accounting for this fact, the rule was not tested further.

Another method is based upon the approach in which the arithmetic mean is replaced by median and standard deviation by median absolute deviation (MAD). The MAD is defined as the median of absolute deviations from the median value obtained from all data within the dataset (Tukey, 1977):

$$MAD = median \ |X_i - q_{.5}|,$$

where X_i represents each measurement and $q_{.5}$ median of all measurements in the statistical file. Median and MAD stand for statistical parameters resistant to the influence of remote and extreme values. After calculating both statistical parameters the range of values bounded by the median $\pm 2*$MAD represents the threshold for outlying values.

The most commonly used resistant measure of spread is interquartile range (IQR) (Helsel and Hirsch, 1992, 2002). It measures the range of the central 50% of the data, and is not influenced at all by 25% on either end. It is therefore the width of the non zero weight window for the trimmed mean. To determine the outlier data set the conventionally recognized 1.5 times of interquartile difference has been adopted (Tukey, 1977). The lower and upper limits of this boundary are calculated as follows:

$$Lower \ limit = Q1 - 1.5*IQR$$

$$Upper \ limit = Q3 + 1.5*IQR.$$

The further attention was focused primarily on testing the resistant methods of the distribution evaluation, i.e. median $+2*$MAD and 1.5 times the IQR. The results showed the generation of a wider range calculated by the method of 1.5 times the IQR, and therefore we recommend this method to be used for the assessment of the stability of the regime of the chemical composition of mineral waters. The main reason is the resistivity of the criterion in terms of statistics and a kind of freedom (versus the method median $+2*$MAD), which reflects the natural quality regime.

2.4. Trends

Accounting for the trend of temporal evolution of the chemical composition of mineral waters an important issue is to determine the initial (starting) value, of which the stability criteria of chemical composition of mineral water should be derived. It can be deliberated a starting point of the source quality monitoring and its derivative stability criteria over a specific period of time. The particular advantage of this approach is accounting for the extent of natural change of the regime, either cyclic or any other character. The second option is to define the initial state, which is given by the chemical analysis of sampling at a certain time and under certain conditions, for example during a hydrodynamic test, which reflects different amounts of water exploited. Afterwards, from the set of initial indicators it could be monitored from the stability criteria of chemical regime of mineral water until the following period. Uncertainty of the second procedure rests in a relatively short period of hydrodynamic testing, which may not reach a steady quality regime.

In assessing the stability of the chemical composition of mineral water plays an important role a chemical composition trends or changes in time. It is important in this respect, because it indicates a certain inhomogeneity of the hydrogeological structure and the quality regime of mineral water, even in the case in which the stability criteria for evaluated source were not exceeded; moreover it reflects the time factor. If the development trend exceeds the critical value then the causes and measures to counteract adverse developments have to be identified. Such identification of the causes of change is possible primarily by repeated sampling (however in time series the sampling does not allow go back in time) and by a thorough analysis of potential natural and secondary factors affecting the stability of the chemical composition of mineral water. Only in the case of identified natural effects a new recognition of mineral water and its reclassifying into a different chemical type is ultimate solution. Furthermore, for healing mineral waters the changes in indications from the balneology point of view is needed.

An important approach in the evaluation of qualitative regime stability of mineral water ends not only in data evaluation using

Table 3
Chemical composition of mineral water source Sliač–spring Kúpeľný.

Year (analysed)	Na$^+$ (mg l^{-1})	K$^+$ (mg l^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Cl$^-$ (mg l^{-1})	SO$_4^{2-}$ (mg l^{-1})	HCO$_3^-$ (mg l^{-1})
1834 (Wagner)	135[a]		622	127	237	1375	881
1855 (Hawch)	104[a]		643	218	4	1632	1304
1882 (Than)	56.4	36.9	640	185	4.42	1534	1158
1921 (Prokeš)	65.4	43.2	644	152	6.12	1751	744
1928 (Buchtala)	71.7	47.8	739	187	8.2	1711	646
1950 (Němejc)	57.9	32.3	699	188	4.3	1540	1316
1967 (GÚDŠ)	57	34.2	709	185	51.9	1631	1196
1972 (BCHL)	62.5	39.5	684	199	10.4	1626	1232
2005 (EL s.r.o. SNV)	65.9	36.7	698	189	6.7	1553	1200

[a] Sum of (Na + K).

Table 4
Chemical composition of mineral water source Dudince–borehole S-3.

Year (analysed)	Na^+ (mg l^{-1})	K^+ (mg l^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Cl^- (mg l^{-1})	SO_4^{2-} (mg l^{-1})	HCO_3^- (mg l^{-1})
1836 (Wehxle)	696	22	627	182	404	568	1614
1893 (Lengyel)	851	129	498	133	564	559	2965
1957 (IGHP. Žilina)	1097[a]		459	137	597	567	3216
1986 (IGHP. Žilina)	819	121	491	131	539	522	2972
1995 (INGEO. Žilina)	810	121	498	135	567	510	2953
2004 (BEL)	832	123	481	129	567	481	2953

[a] Sum of (Na + K).

statistical methods, but also the analysis of the situation from the professional point of view. An example of such assessment is the sources Budiš and Salvátor, where the dataset distribution into sequences is besides the statistical criteria underpinned also by professional hydrogeological, hydrochemical and technical reviews.

3. Results

3.1. Descriptive evaluation of selected mineral water resources

Lipovce, Salvátor. Mineral water resource represents a dug well S-2 with a depth of 4.2 m. Mineral water is genetically linked to the structure of the carbonate Mesozoic complexes and the dissolution of limestone and dolomite under active contribution of carbon dioxide is dominant in the constitution of its chemical composition. The mineral water is slightly enriched in sodium and chloride, which are captured when crossing the Flysch sediments. Ultimately, the mineral water is weakened with low mineralized water of the Quaternary sediments, consequently affecting the quality of its regime.

Execution of drilling (borehole S-2, depth 33 m) in 1953 led to alteration of chemical composition of mineral water (Table 1). Table 1 lists the chemical composition of water samples.

In the Lipovce territory, the Ca–HCO₃ or Ca–(Mg)–HCO₃ type of mineral water dominates. The mineral waters have Na^+ contents between 19.6 and 306 mg l^{-1}. Calcium, magnesium and HCO_3^- concentrations of the mineral waters range from 45.3 to 404 mg l^{-1}, 27.8 to 147 mg l^{-1} and 83.5 to 2429 mg l^{-1}, respectively. Concentrations of potassium, chlorides and sulphates are low. Water samples show a trend suggesting that dissolution of carbonates (mixture of limestone and dolomites of the Triassic carbonates of Hronicum unit) is an important process in water–rock interaction for Salvátor waters. Moreover, according to the previous studies, a mixture of young groundwater of Quaternary fluvial sediments can play a significant role on the formation of the final chemical composition of the Salvátor mineral water. Water samples also show a trend suggesting that dissolution of $CaSO_4$ is not an important process in water–rock interaction. Realization of drilling works (well S-2, depth 33 m) in 1953 caused overall change of chemical composition of mineral water (Table 1) — rapid increase of concentrations of all main cations and anions.

Turčianske teplice, Červený bazén (Red Pool) is a piscine with overflow and yield of 2,6-2,75 l s^{-1} (documented in the year 2006). From the hydrogeochemical point of view it represents a Ca–(Mg)–

HCO₃–SO₄ type. Genetically the water is bound to carbonate complexes of the Krížna and partly Choč nappes. We evaluated the stability of the chemical composition of water over the period of the years 1807–2004 (Table 2). In the first half of the 19th century a decrease of sulphates on about 500 mg l^{-1} was observed in the mineral water. A similar drop in sulphate content and at the same time in the value of total dissolved solids in other sources, genetically similar, has been reported also from other locations in the Turčianske Teplice spa resort. Up to now we are not able to explain this phenomenon. Some authors explain this difference by the use of different analytical techniques. However the reason for this may be also the dilution of mineral water by ordinary water within the hydrogeological structure, or changes in the spatial arrangement of the hydrogeological structure, as a result of geological and tectonic processes.

Sliač, Kúpeľný prameň (Healing Spring) borehole IA 58.8 m deep with overflow and yield of 4.9–5.1 l s^{-1} (documented in the year 2006). Mineral water is genetically linked to carbonates of the Krížna nappe. From the hydrogeochemical point of view the water is of Ca–HCO₃, or Ca–(Mg)–HCO₃ type. The chemical composition of water for the observed period of almost 200 years (Table 3) is less stable. In particular, the content of Ca^{2+}, Mg^{2+}, HCO_3^- and Cl^- is varying, resulting in changes in the value of the total dissolved solids and chemical type of water. According to recent knowledge of the shape and spatial extension of the hydrogeological structure and general direction of mineral water flow towards the spring we cannot explain this phenomenon yet. The cause may be assumed in the occasional temporary changes in pressure conditions in the surge area, or temporal changes of water interaction with the rock environment.

Dudince, S-3 borehole 60.6 m deep captures mineral water with overflow and yield of 4.0–5.2 l s^{-1} (documented in the year 2006). From the hydrogeochemical point of view the mineral water is of the Na–Ca–(Mg)–HCO₃–Cl–(SO₄) type. The particularity of the mineral water of "type Dudinská" rests not only in the mixed chemical type, but also in the current carbon dioxide and hydrogen sulphide enrichment and an increased content of several trace elements. Genetically, the water originates from the carbonates of the Krížna nappe and the Badenian sediments. The mineral water of the "Dudinská type" is characterized by long-term stability of chemical composition (Table 4) except the gas content. At the same time the gas-enriched waters with CO_2 and H_2S are considered to be a very rare phenomenon. The free CO_2 values show large fluctuations with max. contents of 1.8 g l^{-1} (years 1983–84).

Table 5
Chemical composition of mineral water source Piešt'any–well Trajan.

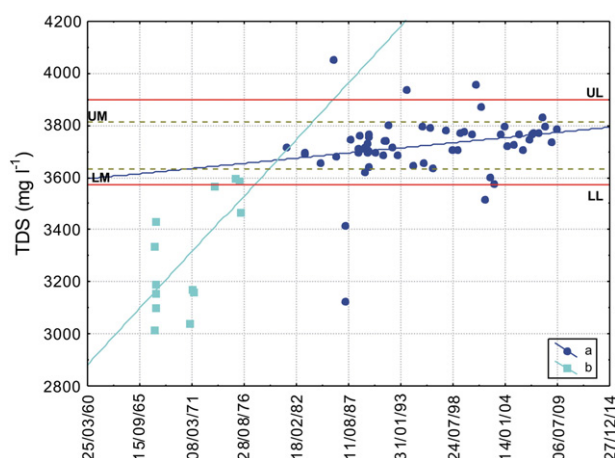| Year (analysed)	Na^+ (mg l^{-1})	K^+ (mg l^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Cl^- (mg l^{-1})	SO_4^{2-} (mg l^{-1})	HCO_3^- (mg l^{-1})
1856 (Prof. Ragsky)	108	12	228	34	97	599	290
1968 (GP. Ostrava)	80	15	214	47	109	525	262
1973 (BCHL. Piešt'any)	90	20	216	48	126	508	288
1980 (Kh-PFUK. Bratislava)	109	15	219	34	124	510	259
1990 (IGHP. Žilina)	84	15	208	47	113	533	262
2004 (BEL. Bratislava)	113	17	224	51	116	602	268

Fig. 2. Selected linear trends of TDS from boreholes S-1 and S-2 (Salvátor): a = TDS in mineral water of borehole S-2, b = TDS in mineral water of borehole S-1, UL = upper limit (75%-il + 1.5 × IQR), LL = lower limit (25%-il − 1.5 × IQR), UM = Median + 2 × MAD, and LM = Median − 2 × MAD.

The highest values of H_2S were around 10 mg l^{-1} (years 1964–65). One-shot concentration measurement provided the value of even 213 mg l^{-1} (Hyánková and Melioris, 1993). The natural healing water from the borehole S-3 sustained its stability despite the borehole yield gradually decreasing from the original 70–80 l s^{-1} (1954) to the current yield, which the max. value is limited. Moreover, during the exploitation until 1996 occurred frequent unjustified changes in yield. The originally high yield can be explained by the fact that the borehole S-3 with a max. Q = 80 l s^{-1} met a tectonic failure, which represents a preferred route of the surge of mineral water towards surface (Melioris and Trnovec, 1995).

Piešťany, well Trajan 11.2 m deep, captures the water of a Ca-SO$_4$ type. Recently, about 4.0 l s^{-1} of the water is taken from a source (documented in the year 2006) and the source is used as supplementary. The mineral water level in the well Trajan is directly hydraulically dependent on the level change in a nearby bypass channel. We evaluated the stability of water over the period of 1856–2004. During this period, the mineral water showed a stable chemical composition (Table 5).

3.2. Assessment of regime stability of mineral water quality and trend

As an example we used data from the source Salvátor in Lipovce (see the text above) for the statistical evaluation of the stability of
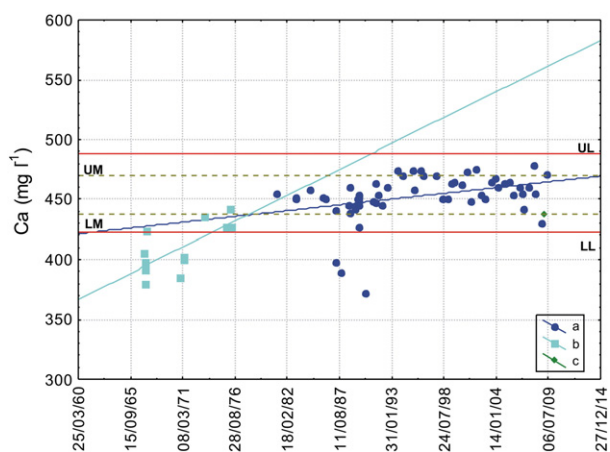

Fig. 3. Selected linear trends of calcium content from boreholes S-1 and S-2 (Salvátor): a = Ca content in mineral water of borehole S-2, b = Ca content in mineral water of borehole S-1, c = Ca content from PE bottled mineral water, UL = upper limit (75%-il + 1.5 × IQR), LL = lower limit (25%-il − 1.5 × IQR), UM = Median + 2 × MAD, LM = Median − 2 × MAD.
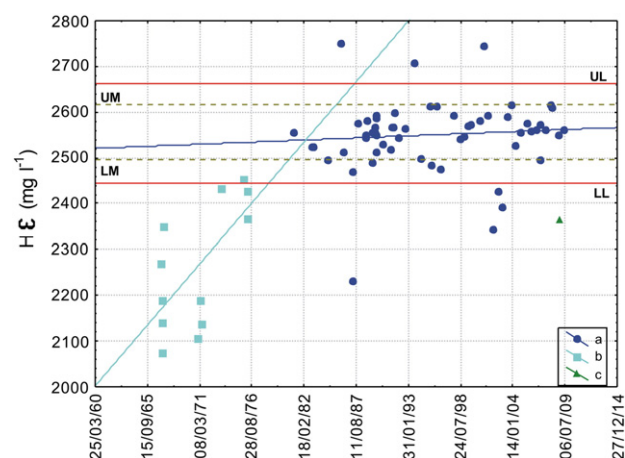

Fig. 4. Selected linear trends of content bicarbonates from boreholes S-1 and S-2 (Salvátor): a = HCO$_3^-$ content in mineral water of borehole S-2, b = HCO$_3^-$ content in mineral water of borehole S-1, c = HCO$_3^-$ content from PE bottled mineral water, UL = upper limit (75%-il + 1.5 × IQR), LL = lower limit (25%-il − 1.5 × IQR), UM = Median + 2 × MAD, LM = Median − 2 × MAD.

chemical composition and trend. It is clear from the descriptive assessment that the new borehole S-2 has detected a different chemical composition of the mineral water from the original source. The borehole S-2 captured a water of deeper circulation with a smaller contribution of water from fluvial Quaternary sediments. The dataset from 1967 until 2009 is available from the current quality monitoring, with a sampling interval of 2 samples/1 year.

The example of the TDS series assessment from both wells (Fig. 2) documents the above-stated changes. In 1976, the TDS values were significantly lower, and since putting into operation a new borehole the TDS values increased. In this case it is inevitable to select two data files and evaluate each separately. In Fig. 2 the stability criteria are evaluated for currently used borehole S-2 along with the linear trends for both wells. The outlying values were found to exceed both the UL and LL. At present we are unable to identify the causes of this situation due to the fact that there were no criteria for assessing the stability and the source was probably regarded as stable. Similar trends as the TDS have also calcium and bicarbonate contents (Figs. 3 and 4). The exception is the carbon dioxide, which virtually throughout the period of both monitoring wells shows only a small number of outliers (Fig. 5). This is because of the single source of carbon dioxide in the hydrogeological structure and it was not affected by the change in depth of the borehole S-2.
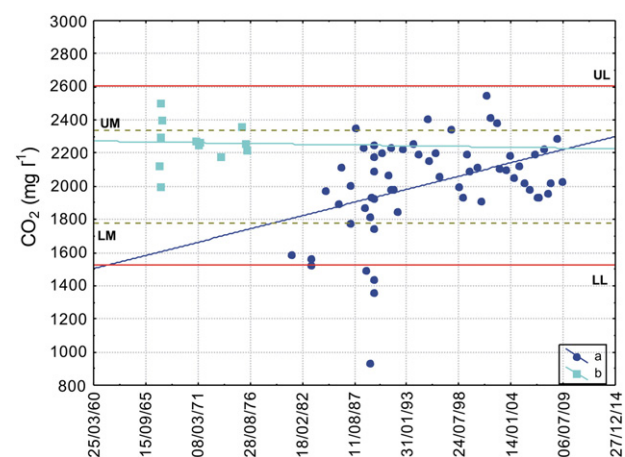

Fig. 5. Selected linear trends of carbon dioxide content from boreholes S-1 and S-2 (Salvátor): a = CO$_2$ content in mineral water of borehole S-2, b = CO$_2$ content in mineral water of borehole S-1, UL = upper limit (75%-il + 1.5 × IQR), LL = lower limit (25%-il − 1.5 × IQR), UM = Median + 2 × MAD, LM = Median − 2 × MAD.

Table 6
Descriptive statistics of selected measured and calculated parameters in mineral water Salvátor (concentrations in mg l^{-1}).

	N	Median	LM	UM	Minimum	Maximum	Q1	Q3	LL	UL
pH	58	6.4	6.60	6.20	6.00	6.75	6.29	6.50	5.98	6.82
CO_2	60	2057	2339	1775	933	2552	1931	2200	1526	2604
TDS	60	3725	3814	3635	3124	4053	3694	3775	3572	3897
Na^+	60	235	250	220	153	530	227	242	204	265
K^+	58	35.5	38.6	32.4	27.6	42.5	33.6	36.6	29.1	41.2
Ca^{2+}	60	454	470	438	372	478	447	463	422	488
Mg^{2+}	60	169	176	162	46.7	214	166	173	155	183
Cl^-	60	109	113	105	99.3	213	107	111	101	117
SO_4^{2-}	60	136	146	125	100	213	129	140	113	157
HCO_3^-	60	2557	2616	2497	2233	2752	2526	2581	2444	2664
B	36	6.44	9.06	3.82	0.76	9.96	4.29	7.30	<0.01	11.8
F^-	44	1.1	1.37	0.83	0.05	2.2	0.97	1.23	0.58	1.62

The stability values for selected components of mineral water Salvátor from the borehole S-2 is shown Table 6. We can say that these components have a stable quality regime that meets the criterion of 1.5 times the IQR. Chemical analyses of randomly selected bottled mineral water of Salvátor (Reimann et al., 2010), independent from the regular qualitative monitoring, confirm the stable regime of this source. All the analysed parameters show their values within the stability limit interval of 1.5 times IQR.

Mineral water in Budiš is formed in shallow-lying sands and sandy gravels, which constitute the environment of its secondary accumulation. The mineral water is of relatively complex genesis; we can term it as mixed. Mineral water of Na–HCO_3 type enriched in carbon dioxide are bound to the rocks of the crystalline mountains Žiar and they are mixing with Ca–SO_4 waters of the envelope Mesozoic series and in the final stage they are diluted with very low mineralized water (TDS = 0.2–0.3 g l^{-1}) of the secondary collector.

The selection of the indicators of chemical stability of natural mineral water Budiš was focused on a summary indicator — the total mineralization, bicarbonate and carbon dioxide content. In the case of natural mineral water Budiš there was evaluated irregular time series from the period 2001–2009, which included 12 chemical analyses.

As a matter of fact, and also in the case of this source, there may happen a situation when during the source exploitation the value of the total mineralization due to some reasons can exceed the calculated interval. It is also necessary to verify the reproducibility of the given criterion in the case of such changes. By simple box diagrams (Figs. 6 and 7) it is possible to document changes in mineralization, the selected cation and anion contents, but without the expected changes in the concentration of carbon dioxide.

In the samples from the period 03/04–19/10 2001 (Fig. 8) a change occurred in the chemical composition of natural mineral water. The difference in mean values of mineralization before and after the change is up to 1000 mg l^{-1} and it is expressed mainly by reducing the content of bicarbonates, calcium and sulphates.

The changes cannot be explained by the data from monitoring, because, for instance, there is no change in concentrations of CO_2. The interpretation is only possible by a more detailed analysis of the situation at the mineral water source in the observed period. At the beginning of 2001 near the source a new borehole B-6 was realized to the same depth of 55 m as of the operating B-5 source; the hydrodynamic tests proved that the B-6 affected the natural mineral water source qualitatively. Stabilization of the new steady state of the resource was registered only after approximately 30 months. Due to changes in the mineral water flow an inflow of water with a higher TDS likely occurred, while a surge of CO_2 remained unchanged within the hydrogeological structure. We assume that the main cause of changes in the stability of the chemical composition of the mineral water affiliated to this hydrogeological structure was changes in water amount withdrawals.

4. Discussion

The above examples and results show the importance of time series evaluation not only by statistical methods, but also by a detailed analysis of the situation in terms of the causal relationships conditioning of mineral water springing. Statistically speaking, the knowledge-based regime can therefore be subsequently divided into two parts in such a way that satisfies the conditions of stability of the chemical composition of natural mineral water (Table 7, Fig. 8).

For verification of the time series trend a simple linear dependence of the observed parameters on time was used. On the example of the bicarbonate content (Fig. 9) it is obvious that they show decreasing
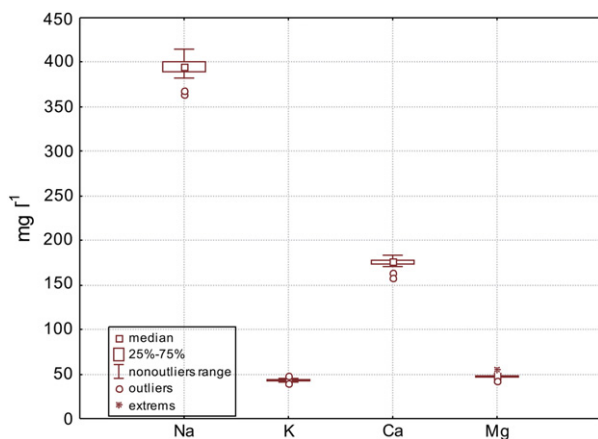

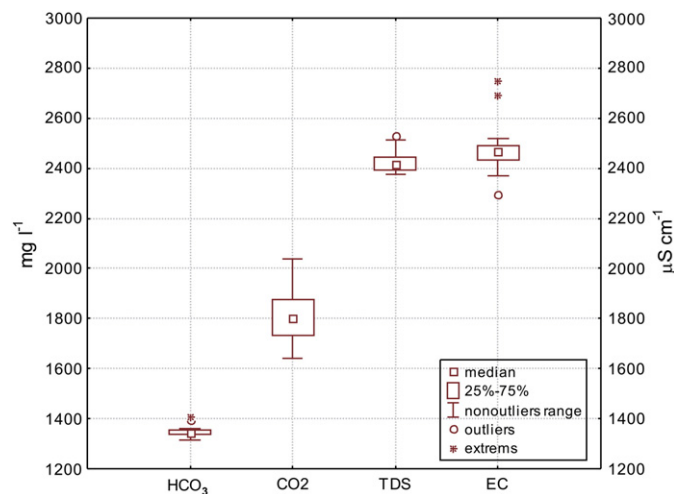**Fig. 6.** Box diagram of main ions of the mineral water Budiš.

Fig. 7. Box diagram of main anions, TDS and electric conductivity of the mineral water Budiš: EC = electrical conductivity.
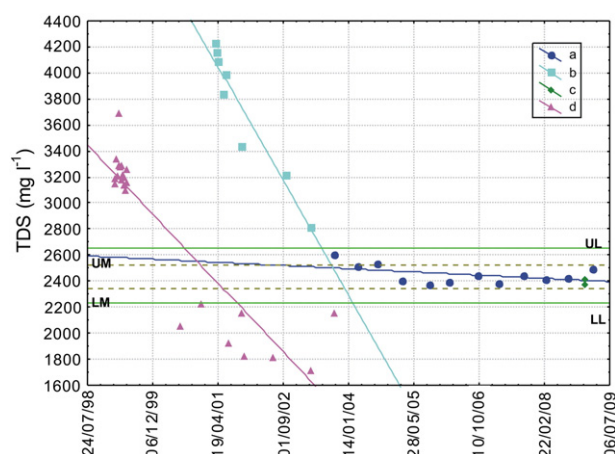
Fig. 8. Selected linear trends TDS from boreholes B-5 and B-6 (Budiš): a = TDS in mineral water of borehole B-6, before stabilization, b = TDS in mineral water of borehole B-6 after stabilization, c = TDS from PE bottled mineral water, d = TDS in mineral water of borehole B-5, UL = upper limit (75%-il + 1.5 × IQR), LL = lower limit (25%-il − 1.5 × IQR), UM = Median + 2 × MAD, LM = Median − 2 × MAD.

Fig. 9. Selected linear trends of bicarbonates content from boreholes B-5 and B-6 (Budiš): a = HCO$_3^-$ in mineral water of borehole B-6 before stabilization, b = HCO$_3^-$ in mineral water of borehole B-6 after stabilization, c = HCO$_3^-$ from PE bottled mineral water, d = HCO$_3^-$ in mineral water of borehole B-5, UL = upper limit (75%-il + 1.5 × IQR), LL = lower limit (25%-il − 1.5 × IQR), UM = Median + 2xMAD, LM = Median − 2 × MAD.

linear trend and bimodal distribution (the result of the change already referred to) and contain a large number of outliers. It follows that they don't have a stable regime that meets the calculated values because after a drop in their concentrations detected in 2001, more than half of the samples do not meet the criterion of stability calculated from the entire time series.

It should be noted that the calculated interval of 1.5 times the IQR represents a statistical confidence interval calculated from real values, which in practice means that the file contains the outlying and extreme values; this is demonstrated by the minimum and maximum values in Table 6, which exceed the interval of 1.5 times the IQR.

At low values of total dissolved solids we will get a shorter range of the 1.5 times the IQR (e.g. natural mineral water Maštinec at an average mineralization of 130 mg l^{-1} meets the stability criterion value of less than ± 19.5 mg l^{-1}). However, we have to note, that in a less active lithogeochemical environment of the water circulation usually no profound fluctuations in the content of dissolved substances occur, provided that there is no secondary interference.

In order to verify the stability criteria of natural mineral waters there were used the data from analyses of bottled waters for consumers in the scope of an international project coordinated by the EGS Geochemistry Working Group (Reimann et al., 2010). The purpose of the verification was to compare the results of water quality monitoring from the source prior to legislative authorization of the treatment and bottled water obtained directly in the market.

Results of chemical composition stability evaluation for the mineral waters Salvátor and Budiš document good fixing of their chemical composition in time, as individual analysed parameters are within the interval of 1.5 IQR. Statistical criteria are not applicable in
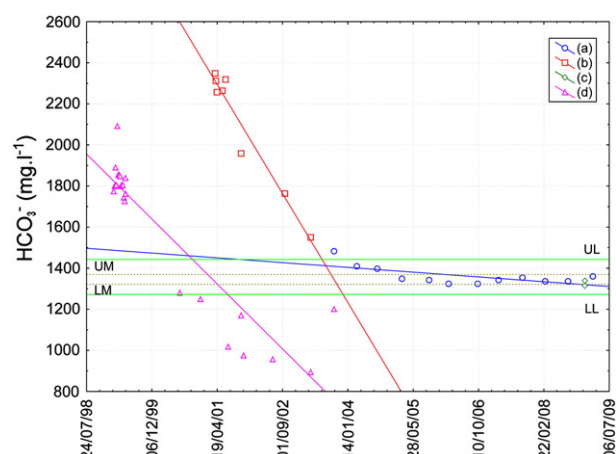
the case of trace elements in mineral waters, where more than 50% of data are bellow the detection limit.

5. Conclusion

The stability analysis of the mineral water chemical composition of selected sources was carried out from the existing results of chemical analyses of historical data and data from mineral water quality monitoring. It is obvious that the changes in the chemical composition of mineral waters may be of natural (long) and artificial origin.

From the historical observation there were detected gradual changes of chemical composition of mineral waters, whose creation processes are bound to aquifers − the structures of Mesozoic carbonates. In some cases the causes of these changes can be only assumed and for the deciphering of the regime and the chemical composition of mineral water will be important new knowledge on geological and hydrogeological conditions of these structures and the uppermost part of the geosphere. Specific components of the chemical composition of mineral waters are free gases (mainly carbon dioxide and hydrogen sulphide), even in cases where the chemical composition of dissolved solids is stable. From the historical data were also identified significant changes in the stability of the chemical composition of mineral waters due to anthropogenic activity (a result of survey work, water sampling, improper mineral water tapping, its use etc.).

Based upon the analysis of historical data it is difficult to clearly determine the initial value, of which the stability criteria of chemical composition of mineral water should be derived for the current

Table 7
Descriptive statistics of selected measured and calculated parameters in Budiš (concentrations in mg l^{-1}).

	N	Median	LM	UM	Minimum	Maximum	Q1	Q3	LL	UL
pH	12	6.21	6.35	6.07	6.05	6.49	6.14	6.33	5.86	6.6
CO$_2$	12	1815	1962	1668	1641	2040	1747	1920	1488	2178
TDS	12	2433	2526	2340	2376	2604	2398	2506	2236	2668
Na$^+$	12	395	408	383	364	438	391	409	365	435
K$^+$	12	44.0	45.9	42.1	40	48.1	43	46	38.5	50.5
Ca^{2+}	12	177	182	172	170	188	176	182	167	191
Mg^{2+}	12	47.7	49.1	46.3	41.3	54.5	46.5	48.0	44.1	50.4
Cl$^-$	12	20.9	21.6	20.3	20.6	22.3	20.8	21.3	19.9	22.1
SO$_4^{2-}$	12	366	393	339	342	414	351	378	309	419
HCO$_3^-$	12	1345	1369	1321	1324	1483	1336	1379	1272	1443
B	12	1.2	1.6	0.8	0.9	1.8	1.05	1.4	0.525	1.93
F$^-$	12	2.55	2.85	2.25	2.2	3.05	2.45	2.7	2.08	3.08

period. Similarly, due to a low number of historical data for long periods usually it is not realistic the determining of the representative criteria of the stability of these mineral waters.

The analysis and evaluation of recent data from monitoring of the mineral water quality enable to propose criteria for assessing the stability of the chemical composition of natural healing and natural mineral waters. When determining the stability criteria it is important to comply with the same frequency and sampling interval. This is a prerequisite, especially having in mind the statistical evaluation of time series in general. The number of data should not be less than 5, and should cover at least 2 to 3 years period of observation. The information about the comparative value can be provided in two forms. The first is the 1.5 times the IQR from data obtained during the hydrodynamic testing. In this case each new sample taken is compared with the criteria obtained in the scope of the hydrodynamic test.

The second one is the 1.5 times the IQR calculated from a minimum of 5 data obtained during 2 to 3 year screening. This condition is based on the recommendations for use of the smallest and largest percentile and their dependence on the number of samples (McPherson, 1990). However, not all the changes in chemical composition can be explained by the monitoring data. The example of the Budiš mineral water showed that the interpretation of variability of mineral water quality was possible only after more detailed analysis of the mineral water at its source, i.e., through a deeper analysis of the natural conditions, but also the technical parameters of source exploitation.

The proposed procedure for evaluating the stability of the chemical composition of natural healing and natural mineral waters is the first step towards clarifying and the exact expression of the criteria of the concept of "stability of the chemical composition of mineral water", which is commonly used in practice, but there is virtually no assessment of its criteria.

The suggested stability criteria of 1.5 IQR together with conditions for the number of elements in the dataset, time factor and qualified approach can result into a profound estimation of chemical composition stability of mineral waters in time. It is applicable both in bottling and balneology practice and legislative decisions. The proposed method is of perspective meaning from the point of view of mineral waters protection and should be helpful in efforts of their unique natural quality preservation for the future.

References

Barut, I.F., Erdogan, N., Basak, E., 2004. Hydrogeochemical evaluation of Western Anatolian mineral waters. Environmental Geology 45, 494–503.

Bagdavadze, L., Beon, O., Hrkal, Z., Laurendon, P., Puyoo, S., Santrucek, J., 2008. Effects of groundwater exploitation on the Borjomi mineral water reservoir in Georgia. Environmental Geology 54, 1301–1311.

Barnett, V., Lewis, T., 1994. Outliers in Statistical Data, 3 rd edition. Wiley & Sons, New York.

Birke, M., Reimann, C., Demitriadis, A., Rauch, U., Lorenz, H., Harazim, B., Glatte, W., 2010. Determination of main and trace elements in European bottled mineral water - analytical methods. Journal of Geochemical exploration 107 (3), 217–226 (this issue).

Council Directive 80/777/EEC of 15 July 1980 on the approximation of the laws of the Member States relating to the exploitation and marketing of natural mineral waters.

Eary, L.E., Runnells, D.D., Esposito, K.J., 2003. Geochemical controls on groundwater composition at the Cripple Creek Mining District, Cripple Creek, Colorado. Applied Geochemistry 18 (2003), 1–24.

Food Standards Agency Scotland, 2006. The Natural Mineral Water, Spring Water and Bottled Drinking Water (Scotland) Regulations 2006. Guidance Notes. Annex G. Food Standards Agency Scotland, p. 28.

Franko, O., Melioris, L., 1999. Condition, formation and extension of mineral and thermal waters in the Western Carpathians. Slovak Geological Magazine 5 (1–2), 93–107.

Franko, O., Gazda, S., Michalíček, M., 1975. Genesis and classification of mineral water in West Carpatians. GÚDŠ, Bratislava, p. 230. in Slovak.

Hampel, F.R., Ronchetti, E.M., Rousseeuw, P.J., Stahel, W., 1986. Robust Statistics. The Approach Based on Influence Functions. John Wiley & Sons, New York.

Helsel, D.R., Hirsch, R.M., 1992. Statistical methods in water resources. Elsevier, p. 522.

Helsel, D.R., Hirsch, R.M., 2002. Statistical methods in water resources. Techniques of Water Resources Investigations. U.S. Geological Survey, p. 522.

Hyánková, K., 1989. Data compatibility of old and recent chemical analyses of mineral waters in Slovakia. Proceedings from the IV. Balneohistorical Conference, Bojnice, Slovakia, pp. 68–87. in Slovak.

Hyánková, K., Melioris, L., 1993. The unusual chemism of mineral waters at Dudince. Geologica Carpathica 44 (2), 123–131.

Lujerdean, A., Bunea, A., Fogorosi, C., 2006. Chemical characterization of carbonated and uncarbonated mineral water from Stâna de Valle sources. Buletinul USAMV-CN 63 (2006), 223–227.

McPherson, G., 1990. Statistics in Scientific Investigation. Springer-Verlag, p. 666.

Melioris, L., Trnovec, J., 1995. Content of trace elements in mineral waters. Manuscript, Archive of KHG Bratislava (in Slovak).

Muntean, N., Muntean, E., Drugan, T., Sălăgean, M., Ghiţulescu, R., Butan, M., 2006. Chemical monitoring for a natural mineral water source located in Sâncrăieni. Journal of Agroalimentary Processes and Technologies XII (1), 145–148.

Negrel, P., Fouillac, C., Brach, M., 1997. Occurrence of mineral water springs in the stream channel of the Allier River (Massif Central, France): Chemical and Sr isotope constraints. Journal of Hydrology 203 (1–4), 143–153.

Rapant, S., Bodiš, D., Vrana, K., Cvečková, V., Kordík, J., Krčmová, K., Slaninka, I., 2009. Geochemical Atlas of Slovakia and examples of its applications to environmental problems. Environmental Geology 57 (1), 99–110.

Raiswell, R., Tranter, M., 1982. Composition and origin of Thetford mineral water. Bulletin, Geological Society of Norfolk 32, 61–70.

Reimann, C., Garrett, R.G., 2005. Geochemical background — concept and reality. Science of the Total Environment, 350. Elsevier, pp. 12–17.

Reimann, C., Birke, M., Filzmoser, P., 2010. Bottled drinking water: water contamination from bottle materials (glass, hard PET, soft PET), the influence of colour and acidification. Applied Geochemistry, 25. Elsevier, pp. 1030–1046.

Steinmaus, C.M., Yuana, Y., Smith, A.H., 2005. The temporal stability of arsenic concentrations in well water in western Nevada. Environmental Research 99, 164–168.

Tukey, J.W., 1977. Exploratory Data Analysis. Addison-Wesley, Reading, MA.

Varsányi, I., 1992. Temporal variability in groundwater chemistry in the Great Hungarian Plain during the period 1975–1989. Hydrological Sciences–Journal–des Sciences hydrologiques 37, 119–128 2, 4/1992.

Vrba, J., 1996. Thermal mineral water springs in Karlovy Vary. Environmental Geology 27 (2), 120–125.

Update

Journal of Geochemical Exploration

Erratum

Erratum to "Mineral waters in Slovakia — Evaluation of chemical composition stability using both historical records and the most recent data" [J. Geochem. Explor. 107 (2010) 382–390]

Dušan Bodiš [a], Jozef Kordik [a], Igor Slaninka [a,*], Peter Malík [a], Pavel Liščák [a], Daniel Panák [b], Jarmila Božíková [b], Daniel Marcin [a]

[a] State Geological Institute of Dionyz Stur, Mlynská dolina 1, 817 04, Bratislava, Slovakia
[b] Ministry of Health, Limbová 2, P.O. BOX 52, 837 52, Bratislava, Slovakia

The publisher regrets that in the head of the originally published article, the first- and surnames of all authors were swapped, which could lead to confusion in citations to this article.

The correct names are given in the head of this erratum.

The correct running headline for this paper is:

D. Bodiš et al./Journal of Geochemical Exploration 107 (2010) 382–390.

The correct citation to this article is:

Bodiš, D., Kordik, J., Slaninka, I., Malík, P., Liščák, P., Panák, D., Božíková, J., Marcin, D., 2010. Mineral waters in Slovakia — Evaluation of chemical composition stability using both historical records and the most recent data. Journal of Geochemical Exploration 107 (2010) 382–390.

* Corresponding author.
E-mail address: igor.slaninka@geology.sk (I. Slaninka).