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ISOTOPES OF OXYGEN-18 AND DEUTERIUM IN PRECIPITATION IN SLOVAKIA

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The article synthesizes available information on isotopic composition of precipitation in Slovakia (the Western Carpathians). Monthly $\delta^{18}O$ data from eleven stations and period 1988–1997 were used to investigate correlations among the stations, altitude, air temperature and precipitation amount effects. The mean annual altitude and air temperature gradients of $\delta^{18}O$ in precipitation were 0.21‰/100 m and 0.36‰/1°C, respectively. Maps of spatial distribution of mean annual $\delta^{18}O$ in precipitation based on both gradients were constructed. The two maps do not significantly differ for the majority of Slovakia. δ^2H data were available for only three stations. Local meteoric water line derived for the station with the longest data series ($\delta^2H = 7.86\delta^{18}O + 6.99$) was close to the Global Meteoric Water line. Its parameters in periods 1991–1993 and 1991–2008 did not change. The study indicates that a more detailed monitoring of isotopic composition of precipitation in mountains should be carried out in the future. The highest station exhibited very small seasonal variability of $\delta^{18}O$ in precipitation compared to other Slovak stations. The second highest mountain station had significantly higher deuterium excess than the neighboring stations located in the valley. In some analyses the data from the nearest stations situated abroad (Vienna, Krakow) were used.

KEY WORDS: Isotopes of Oxygen-18 and Deuterium in Precipitation, $\delta^{18}O$, Altitude and Air Temperature Gradients, Local Meteoric Water Line, Western Carpathians.

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Príspevok syntetizuje dostupné údaje o izotopickom zložení zrážok na území Slovenska (Západné Karpaty). Hodnotí koreláciu hodnôt $\delta^{18}O$ v kumulatívnych mesačných zrážkach z rokov 1988–1997 medzi jednotlivými stanicami, vplyv nadmorskej výšky, teploty vzduchu a úhrnu zrážok. Priemerný ročný výškový gradient $\delta^{18}O$ v zrážkach je 0,21‰/100 m, priemerný ročný teplotný gradient $\delta^{18}O$ v zrážkach je 0,36‰/1°C. Oba gradienty boli použité na vytvorenie mapy priestorového rozdelenia $\delta^{18}O$ v zrážkach na území Slovenska. Mapa vytvorená pomocou výškového gradientu $\delta^{18}O$ v zrážkach sa pre väčšinu územia Slovenska významne nelíši od mapy vytvorenej pomocou teplotného gradientu. Hodnoty δ^2H v zrážkach boli k dispozícii len pre tri stanice na Slovensku. Pre stanicu s najdlhším radom údajov (1991–2008) bola určená lokálna meteorická čiara ($\delta^2H = 7.86\delta^{18}O + 6.99$), ktorej priebeh je blízky globálnej meteorickej čiare. Parametre lokálnej meteorickej čiary sa počas skúmaného obdobia nezmenili. Merané mesačné údaje poukazujú na potrebu podrobnejšieho monitoringu izotopického zloženia zrážok v horách. Najvyššie ležiaca stanica mala v porovnaní s ostatnými stanicami veľmi malú sezónnu variabilitu $\delta^{18}O$ v zrážkach. Druhá najvyššie položená stanica mala podstatne vyšší exces deutéria, ako susedné stanice ležiace v kotlinovej polohe. Pri niektorých analýzach boli údaje zo Slovenska porovnávané s najbližšie ležiacimi zahraničnými stanicami (Viedeň, Krakov).

KĽÚČOVÉ SLOVÁ: izotopy kyslíka-18 a deutéria v zrážkach, $\delta^{18}O$, výškový a teplotný gradient, lokálna meteorická čiara, Západné Karpaty.

Introduction

Stable water isotopes are used in hydrology and hydrogeology to trace the movement of water in hydrological cycle since the 1960's (e.g. *Zimmerman* et al., 1967; *Fontes* and *Gonfiantini*, 1967; *Dinçer*, 1968; *Gat* et al., 1969; *Dinçer* et al., 1970). In research, their main applications address the separation of hydrograph components and estimation of mean transit time of water in a catchment or aquifer. Such applications generally need more sampling effort or longer data series. However, there are also practical applications where a small number of samples can help to identify the origin of water, e.g. groundwater recharged from a lake, altitude of recharge area or contribution of river water to a production well (a number of examples are given e.g. by *Clark* and *Fritz*, 1997). Such applications usually require certain background information on isotopic composition of precipitation which is the basic input into the hydrological cycle of a catchment or an aquifer. This background information is represented by the local meteoric water line (LMWL), altitude or air temperature gradients of isotopic composition of precipitation. Basic knowledge on the dependence of isotopic composition of precipitation on climatic factors, altitude and latitude was gained already in the 1950's (*Gourcy* et al., 2005). A valuable source of isotopic data at the global scale is the IAEA-WMO Global Network of Isotopes in Precipitation GNIP (e.g. *Gourcy* et al., 2005). Analyses of the global distribution of stable water isotopes in precipitation based on the GNIP data were published in a number of works (e.g. *Dansgaard*, 1964; *Yurtsever* and *Gat*, 1981; *Rozanski* et al., 1993, *Gat* et al., 2001). A comprehensive review of the topic is given by *Ingraham* (1998). Yet, the new articles on isotopic composition of precipitation in various regions of the world based on local data appear regularly (e.g. IAEA, 2005; *Argiriou* and *Lykoudis*, 2006; *Yamanaka* et al., 2007).

Stable water isotopes have been monitored in Slovakia for hydrogeological and hydrological applications since the mid-1980's (e.g. *Kantor* et al., 1985; *Holko* 1995; *Malík* et al., 1996, *Michalko*, 1999; *Holko* et al., 2011). With exception of a few stations, collected precipitation samples were mostly analysed for δ^{18}O. The data were partially analysed by *Holko* et al. (1995) and *Bošková* (2004). Nevertheless, a synthesis of the data facilitating wider utilization of stable water isotopes in practical applications has not yet been done. The objective of this article is to fill this gap by synthesizing the existing long-term monthly data on stable water isotopes in precipitation in Slovakia. Specific objectives include:

- examination of the links among precipitation stations situated at different locations in Slovakia,
- investigation of altitude and air temperature gradients of isotopic composition of precipitation and correlation of isotopic composition of precipitation and precipitation amount in Slovakia,
- determination of the local meteoric water line, its comparison with the lines derived for the nearby GNIP stations at Krakow and Vienna, dependence of the LMWL on the time period used in its construction,
- construction of the map of spatial distribution of mean annual δ^{18}O in precipitation in Slovakia.

The article supplements similar evaluations elaborated in various worldwide studies for both global and regional datasets. Since the studied territory is situated in the Western Capathians, the results are applicable to this part of central Europe. The map of spatial distribution of δ^{18}O precipitation for Slovakia represents a new outcome which was not available at finer resolution for this region until now. Another new aspect of the article is the examination of monthly altitude gradients of isotopic composition of precipitation.

Data

Monthly precipitation, air temperature, and isotopic composition of monthly precipitation at eleven stations in Slovakia are used in the analyses. Data from the nearest GNIP stations situated outside Slovakia (Krakow, Poland and Vienna, Austria) were used as well (Fig. 1).

Slovakia is situated in the Western Carpathians, the north-western part of the Carpathian arch. The landscape of the country is mostly mountainous and the highest peaks of the Carpathians are situated in Slovakia. Yet, lowlands defined as areas with altitude below 300 m a.s.l. cover about 41% of the country. About 8.5% of Slovakia is situated above 900 m a.s.l. Spatial and altitudinal distribution of precipitation stations used in this study attempts to cover all altitudinal zones. The stations are situated at altitudes between 104–2008 m a.s.l. Most of the data cover the period from 1988 to 1997, but some stations had shorter or longer data series (Tab. 1). All stations except Priemstav and Červenec are standard or professional meteorological stations of Slovak Hydrometeorological Institute. Standard stations are operated by an observer who visits a station three times per day. Professional stations have permanent staff. Precipitation depth at both standard and professional meteorological stations is

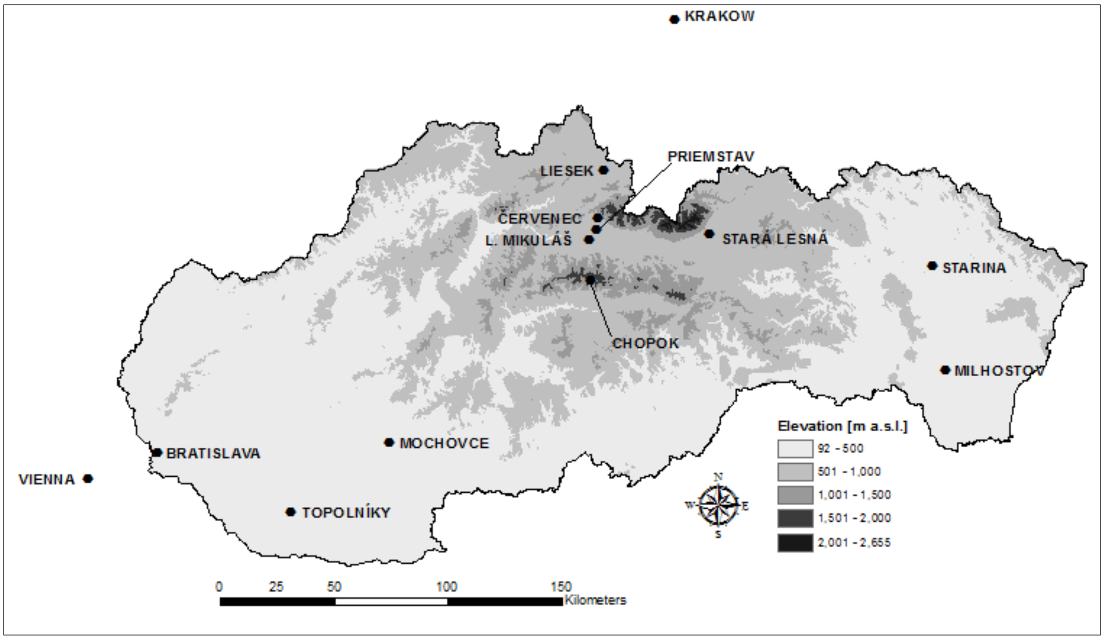

Fig. 1. Digital elevation model of Slovakia and location of precipitation stations used in this study; a more detailed information is given in Tab. 1.

measured daily. Standard gauge of the Czechoslovak meteorological service (orifice area 500 cm^2, height 1 m above surface) is used to measure precipitation and collect the samples. The gauge uses a funnel and inner container in summer to prevent evaporation. Precipitation at stations Priemstav and Červenec is measured once per week.

Composite samples of monthly precipitation measured at the stations were analysed for $\delta^{18}O$. Only three stations in Slovakia had additional data on $\delta^{2}H$ (Tab. 1). Thus, most analyses presented in this article were only focused on $\delta^{18}O$. Isotopic composition of precipitation was analysed by mass spectrometers either at the International Atomic energy Agency (IAEA) or in Slovakia (Tab. 1). Typical analytical uncertainties for $\delta^{18}O$ and $\delta^{2}H$ were below 0.1‰ V-SMOW and 1‰ V-SMOW, respectively.

Methodology

The correlations of $\delta^{18}O$ in monthly precipitation, monthly air temperatures and precipitation amounts at different stations were examined by correlation matrices. Simple linear (least squares) regressions were used to examine the relationships of isotopic composition of precipitation with other variables such as altitude or air temperature. Predictive power of calculated models was described by coefficients of correlation or determination.

Regression equations determining the relationships of $\delta^{18}O$ in precipitation with air temperature and precipitation amount in individual stations were calculated for monthly and annual data.

Mean monthly values of $\delta^{18}O$ in precipitation were calculated to investigate the seasonal variability at different stations. Correlations of mean annual values of $\delta^{18}O$ in precipitation with air temperature, and precipitation amount were examined. Altitude gradients of $\delta^{18}O$ in precipitation were evaluated for mean annual and mean monthly data. Maps of the mean annual values of $\delta^{18}O$ in precipitation in Slovakia were constructed using two approaches. Both approaches make use of the digital elevation model of Slovakia with resolution of 100 m. The first approach is based on the altitudinal gradient of $\delta^{18}O$ in precipitation. The second approach is based on the air temperature gradient of $\delta^{18}O$ in precipitation. The map of the mean annual temperature employed in the second approach was based on the altitudinal gradient of mean annual air temperature. The differences between the maps of spatial distribution of mean annual $\delta^{18}O$ in precipitation in Slovakia constructed by means of the two approaches were also calculated.

All of the above calculations were performed with data from the period 1988–1997. One station (Liptovský Mikuláš) and the two nearest GNIP stations situated outside of Slovakia (Vienna, Krakow) have longer data series. The time series plot

T a b l e 1. Altitudes of precipitation stations [m a.s.l.], sampling periods, isotopes available for the study and the laboratory where the isotopic analysis was performed

Station	Altitude	Sampling period	Isotopes	Lab
Milhostov	104	1988–1997	^{18}O	GÚDŠ*
Topoľníky	118	1988–1997	^{18}O	GÚDŠ
Vienna	203	1988–2008	^{18}O, ^{2}H	IAEA
Krakow	205	1988–2008	^{18}O, ^{2}H	IAEA
Mochovce	206	1988–1997	^{18}O	GÚDŠ
Bratislava	286	1988–1996	^{18}O	GÚDŠ
Starina	345	1994–1997	^{18}O	GÚDŠ
L. Mikuláš	570	1991–2008	^{18}O, ^{2}H	IAEA
Liesek	692	1988–1997	^{18}O	GÚDŠ
Stará Lesná	721	1988–1997	^{18}O	GÚDŠ
Priemstav	750	1991–1993	^{18}O, ^{2}H	GÚDŠ
Červenec	1500	1991–1993, 2005–2008	^{18}O, ^{2}H	IAEA
Chopok	2008	1988–1997	^{18}O	GÚDŠ

*GÚDŠ stands for the laboratory of Geological Institute of Dionýz Štúr in Bratislava.

of both $\delta^{18}O$ and $\delta^{2}H$ data in stations Liptovský Mikuláš, Vienna and Krakow from period 1991––2008 were used to examine the possible trend in the isotopic composition of precipitation over the last 20 years.

Stable isotopes of oxygen and hydrogen in natural waters (e.g. precipitation, rivers, groundwaters) are correlated. *Craig* (1961) described the correlation by the equation $\delta^{2}H = 8\ \delta^{18}O + 10$. This relationship later called Global Meteoric Water Line (GMWL) is a very useful tool to trace waters which originated from precipitation or identify waters which underwent evaporation. Isotopic composition of precipitation in different areas of the world usually slightly differs from the global meteoric water line, following the so-called local meteoric water line. Local meteoric water lines were constructed and compared for three stations in northern Slovakia for which both $\delta^{18}O$ and $\delta^{2}H$ analyses were available. The stations were close to each other. The distance between them is just a few kilometers. Two of the stations have data for only three years. One station (Liptovský Mikuláš) has data until 2008. The local meteoric water line for this station is compared to the lines constructed for Vienna and Krakow. Changes of parameters of the LMWLs between periods 1991–1993 and 1993–2008 were also investigated.

Availability of $\delta^{18}O$ and $\delta^{2}H$ data allows calculation of the deuterium excess d ($d = \delta^{2}H\text{-}8\ \delta^{18}O$) which is useful in identification of the vapour source regions, re-evaporation of falling rainfall drops or moisture recycling (e.g. *Yamanaka* et al., 2007; *Liu* et al., 2008; *Froehlich* et al., 2008). We calculated the deuterium excess for three Slovak stations, compared it with those at the stations Vienna and Krakow and investigated its seasonal and spatial variations.

Results

Correlations of isotopic composition of precipitation at individual stations, temperature and altitude gradients

The best correlations of monthly data (air temperature, precipitation amount, $\delta^{18}O$) among all stations were found for monthly air temperatures (the correlation coefficients ranged from 0.951 to 0.998). Correlation of precipitation amounts was worse (mean correlation coefficient 0.613). Correlations of $\delta^{18}O$ in precipitation among individual stations were relatively high (mean value 0.731). $\delta^{18}O$ in precipitation at Liptovský Mikuláš which has the longest record in Slovakia is well correlated not only with the nearby stations (e.g. Liesek; correlation coefficient 0.916) but also with the distant stations (e.g. Mochovce; correlation coefficient 0.841). The worst correlation coefficients for station Liptovský Mikuláš vary around 0.74. Fig. 2 provides an idea on the scatter of values measured at Liesek and Chopok plotted against the values measured at Liptovský Mikuláš. It shows that although the correlation coefficient of $\delta^{18}O$ in precipitation is relatively high (0.811 for Chopok), there may be a systematic difference between the two adjacent stations. The differences were higher for isotopically lighter, i.e. winter precipitation.

The correlation matrix analysis reveals that stations with shorter records (e.g. Starina) tend to be highly correlated with all stations.

Mean monthly values of $\delta^{18}O$ in precipitation at different precipitation stations were highly correlated. The mean correlation coefficient was 0.903. Nevertheless, comparison of seasonal distribution of $\delta^{18}O$ in precipitation at different stations reveals several patterns (Fig. 3). Generally, the isotopically lightest precipitation falls in February and the heaviest in July. However, the February minimum was not particularly pronounced at some stations (Bratislava, Vienna, Starina). Smaller autumn increases occur in some stations in September (Topoľníky) or October (Liptovský Mikuláš, Liesek, Starina). An unusually small seasonal variability of $\delta^{18}O$ in precipitation was observed at the highest station of Chopok (Fig. 3).

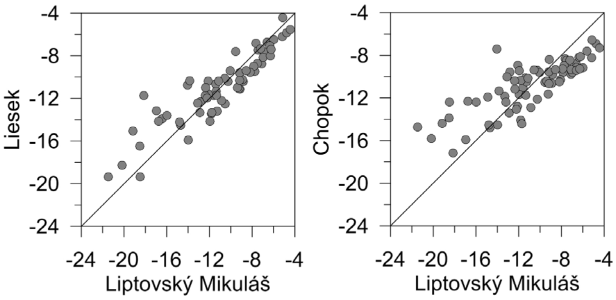

Fig. 2. Correlations of monthly values of $\delta^{18}O$ [‰] in precipitation between stations Liptovský Mikuláš-Liesek (correlation coefficient 0.906) and Liptovský Mikuláš-Chopok (correlation coefficient 0.811); all three stations are relatively close to each other (cf. Fig. 1).

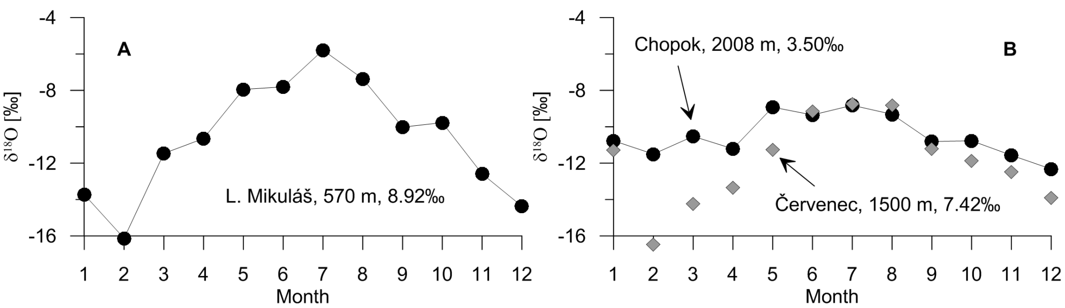

Fig. 3. Seasonal variability of $\delta^{18}O$ in precipitation in Slovakia; the numbers next to the station name represent the altitude of the station and the annual range of $\delta^{18}O$ in precipitation, respectively; A – a typical variability for Slovakia with winter minimum, summer maximum and small secondary autumn maximum; B – an unusual seasonal course with very small seasonal variability observed at the highest station of Chopok; for comparison also data from the second highest station of Červenec situated across the valley from Chopok are shown.

$\delta^{18}O$ in precipitation is typically correlated with air temperature and in some regions of the world (e.g. tropics) it is also correlated with precipitation amounts (e.g. *Gat* et al., 2001). Knowledge of these effects for individual stations is useful in filling-in missing isotopic data series at a particular station. In Slovakia, monthly $\delta^{18}O$ in precipitation was mostly well correlated with the air temperature measured at the same station. Except for one station (Chopok), coefficients of determination (R^2) were about 0.5 (Tab. 2, Fig. 4). $\delta^{18}O$ in precipitation was not correlated with precipitation amount (the highest R^2 is only 0.17).

Correlations of mean annual values of $\delta^{18}O$ in precipitation with air temperature (T), precipitation amount (P) and altitude can be used to estimate the isotopic composition of precipitation in the studied region. Knowledge of local isotopic composition of precipitation is useful in practical applications, e.g. in estimation of recharge areas of springs. The correlations for the Slovak stations are shown in Fig. 5. When the data from the station of Chopok was not considered, the correlations with mean annual air temperature and altitude were high. Linear regressions with air temperature and altitude explain about 73% and 80% of the variability, respectively (Fig. 5). Altitude gradient of $\delta^{18}O$ in precipitation in Slovakia for mean annual values was 0.21‰/100 m of altitude (standard deviations of the slope and intercept of the regression line were 0.16 and 1.59, respectively). The air temperature gradient of $\delta^{18}O$ in precipitation was 0.36‰/1°C (standard deviations of the slope and intercept of the regression line were 0.18 and 1.84, respectively). Addition of data from the closest GNIP stations situated outside Slovakia (Krakow, Vienna) slightly decreased the altitude gradient to 0.19‰/100 m and the air temperature gradient to 0.31‰/1°C. The correlation of $\delta^{18}O$ with precipitation amount was not very strong.

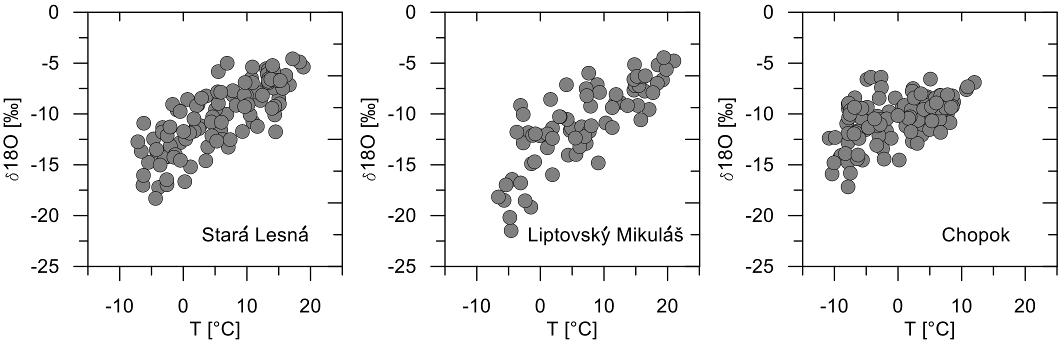

Fig. 4. Relationships of monthly air temperature and $\delta^{18}O$ in precipitation at selected stations.

T a b l e 2. Slopes and intercepts of linear regressions between monthly air temperature and $\delta^{18}O$ in precipitation in Slovakia and nearby GNIP stations in the period 1988–1997; the regression equation has the form $\delta^{18}O$ = Slope * Air temperature + intercept; R^2 is the coefficient of determination, N is the number of points (pairs) used in the regression analysis (maximum is 120); ST_{slp} and ST_{int} are standard deviations of slope and intercept, respectively.

Station	Slope	ST_{slp}	Intercept	ST_{int}	R^2	N
Milhostov	0.28	0.06	–11.78	0.61	0.548	115
Topoľníky	0.32	0.06	–12.36	0.62	0.556	115
Mochovce	0.28	0.06	–11.85	0.61	0.553	114
Bratislava	0.31	0.07	–11.93	0.71	0.458	99
Starina	0.26	0.10	–11.45	1.02	0.530	46
L. Mikuláš	0.41	0.07	–13.62	0.80	0.639	77
Liesek	0.31	0.07	–12.34	0.74	0.551	99
Stará Lesná	0.35	0.06	–11.45	0.66	0.530	108
Priemstav	0.30	0.10	–11.50	1.07	0.628	36
Červenec	0.31	0.12	–12.89	1.50	0.493	36
Chopok	0.19	0.08	–10.36	0.87	0.261	113
Vienna	0.38	0.06	–13.70	0.63	0.580	118
Krakow	0.31	0.06	–12.40	0.63	0.553	120

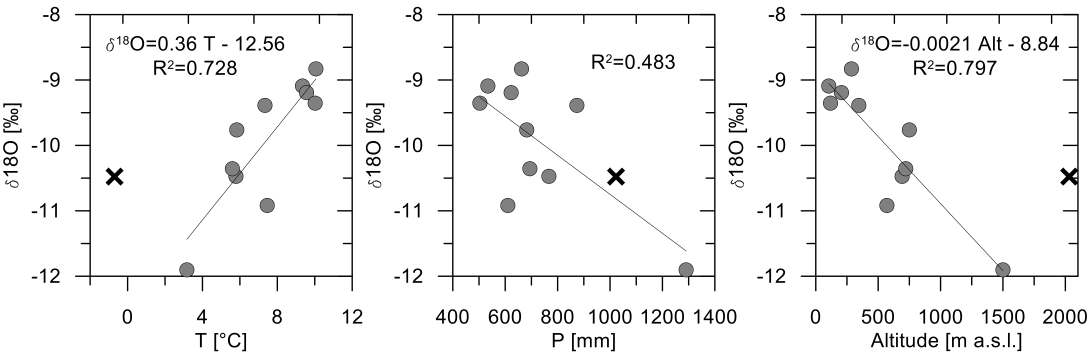

Fig. 5. Relationships of mean annual $\delta^{18}O$ in precipitation with air temperature (*T*), precipitation amount (*P*) and altitude for the Slovak stations; R^2 is coefficient of determination; regression equations in the left and right panels were calculated without the data from station Chopok indicated by the cross.

Altitude gradients of $\delta^{18}O$ in precipitation varied during the year (Tab. 3). Gradients in the warm period of the year were slightly smaller than in the colder period. Very small altitude gradients were calculated for January, August and December (Fig. 6). Data from the station Chopok were not used in calculation of the gradients presented in Tab. 3. Their consideration would improve correlations in summer months (June to September), but it would not change the calculated altitude gradients. In other words, unlike in winter, the isotopic composition of precipitation at station Chopok in summer months better corresponds to that in other Slovak stations. Use of mean monthly data from the nearest

GNIP stations outside Slovakia (Vienna, Krakow) negligibly decreased the altitude gradients in individual months (by 0.01–0.03 ‰/100 m of altitude). We can thus assume that the gradients calculated with data from only Slovak stations are valid for the whole territory of Slovakia (the Western Carpathians).

Data series plots of monthly data of $\delta^{18}O$ and δ^2H in precipitation at stations Liptovský Mikuláš, Krakow and Vienna did not reveal any significant trends in isotopic composition of precipitation in period 1991–2008.

T a b l e 3. Monthly altitude gradients of $\delta^{18}O$ in precipitation [‰/100 m of altitude], data from Slovak stations without Chopok and period 1988–1997, *0 means that either gradient or R^2 is below 0.01.

Month	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Gradient	0*	–0.31	–0.33	–0.26	–0.32	–0.15	–0.21	0*	–0.26	–0.27	–0.15	0*
R^2	0*	0.64	0.86	0.64	0.81	0.67	0.75	0.22	0.59	0.89	0.36	0.30

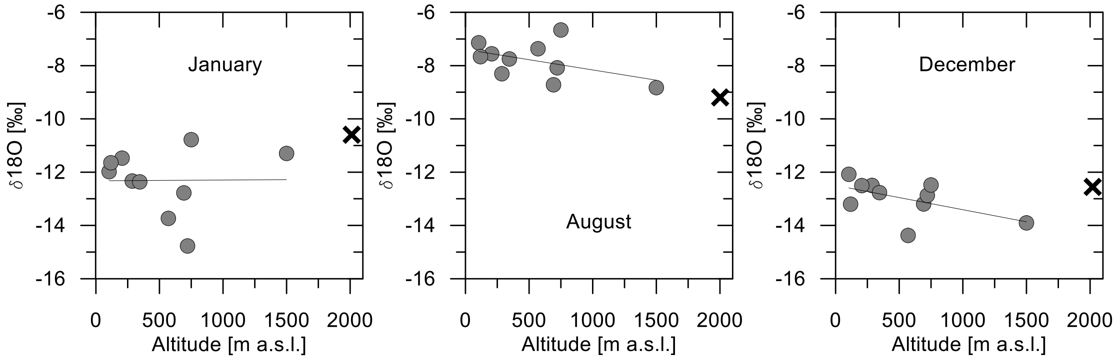

Fig. 6. Relationships of mean monthly $\delta^{18}O$ in precipitation with altitude in months with negligible altitude gradients; the data from station Chopok which were not used in calculation of the gradients are marked with the cross.

Map of mean annual $\delta^{18}O$ in precipitation in Slovakia

The map based on the altitude gradient given in Fig. 5 is shown in Fig. 7. The differences between that map and the map based on the air temperature gradient are shown in Fig. 8. In the majority of Slovakia the differences between the two maps did not exceed the analytical precision of $\delta^{18}O$ analyses, i.e. 0.1‰. For the highest mountains the map based on altitudinal gradient of $\delta^{18}O$ provided lower (more negative) values of $\delta^{18}O$ in precipitation than the map based on the air temperature gradient, while for the lowlands and hilly areas of Slovakia it was vice versa.

Local meteoric water lines, deuterium excess

The local meteoric water line (LMWL) for the station Liptovský Mikuláš, i.e. the only Slovak station with the long data series, is shown in Fig. 9. Parameters of the LMWL for this station did not differ much from the Global Meteoric Water Line (Tab. 4). The parameters practically did not change in the two periods analysed (1991–1993, 1991––2008). Tab. 3 also shows that the slopes of the LMWLs in the Slovak stations which were all situated in the same catchment (Liptovský Mikuláš, Priemstav, Červenec) increased with altitude. Slopes and intercepts of the LMWL for station Červenec in periods 1991–1993, 1991–2008 were significantly different. It was probably caused by the relocation of the rain gauge, which remained at the same altitude, but moved to a different location.

Deuterium excess at the mountain station Červenec (1500 m a.s.l.) was significantly higher than at the nearby valley station Liptovský Mikuláš (570 m a.s.l., 11 km from Červenec). Seasonal variability of the deuterium excess at the two stations seems to change slightly since the 1990' (Fig. 10). Maxima in the mountains (Červenec) in period 1991–1993 often occurred in summer (July-September) while in the valley they mostly occurred in September. Maxima in period 1991–2008 in both mountains and the valley are shifted to autumn (October and November). Fig. 10 also shows seasonal variability of deuterium excess in Vienna and Krakow.

Existence an altitude gradient of deuterium excess for some stations was already reported earlier by *Holko* (1995).

Discussion

Climate in Slovakia is on the transition between the oceanic and continental. Despite the occasional influence of precipitation coming from the south, most of the precipitation typically comes from the west. Relatively high correlation of $\delta^{18}O$ in monthly precipitation in different parts of Slovakia confirms that precipitation at the monthly time scale generally comes from the same source.

We do not have any explanation for the small seasonal variability of $\delta^{18}O$ in precipitation at the highest station Chopok (Fig. 3). All nearby stations have much higher seasonal variability. The weather systems producing precipitation at Chopok were the same as in the nearby stations, e.g. Liptovský Mikuláš. Thus, the small seasonal variability of $\delta^{18}O$ in precipitation at Chopok should be rather attributed to specific site conditions. Precipitation at

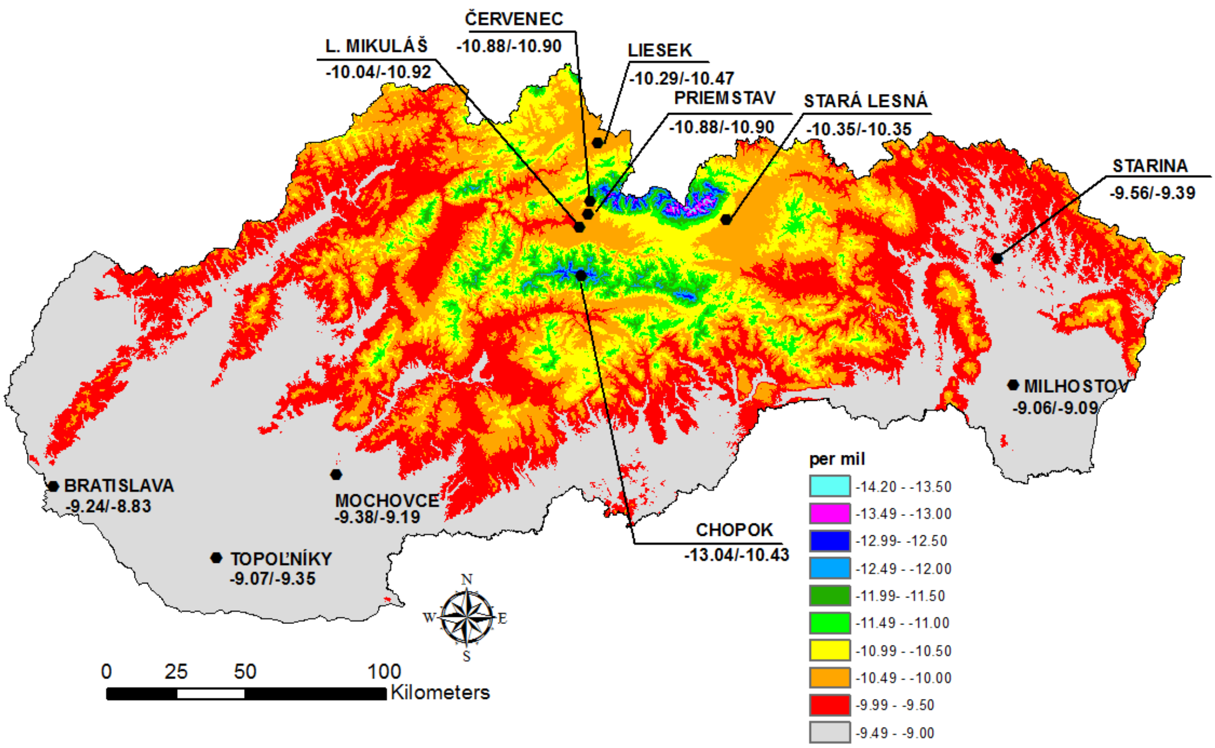

Fig. 7. Map of spatial distribution of mean annual $\delta^{18}O$ in precipitation in Slovakia based on the altitude gradient (cf. the equation in Fig. 5); the first number under the name of a station represents the value [in ‰] extracted from the map, the second number is the measured value.

Chopok was isotopically very heavy in the autumn and winter months. The station was located near the summit of the Chopok mountain, thus exposed to high winds. Precipitation measurement errors caused by the wind are especially pronounced in winter. Accumulation of snow blown uphill from the lower altitudes is apparent at Chopok during the winter months. However, we assume that this process does not fully account for isotopically heavier autumn and winter precipitation at Chopok. The fact that the gauge was often situated in clouds may be of higher importance. Isotopic exchange between the water and vapour continuously takes place in the cloud (*Jouzel* and *Merlivat*, 1984). This may have caused a difference in isotopic composition of precipitation between the site that was cloudy during precipitation events and the nearby sites that were situated under the clouds.

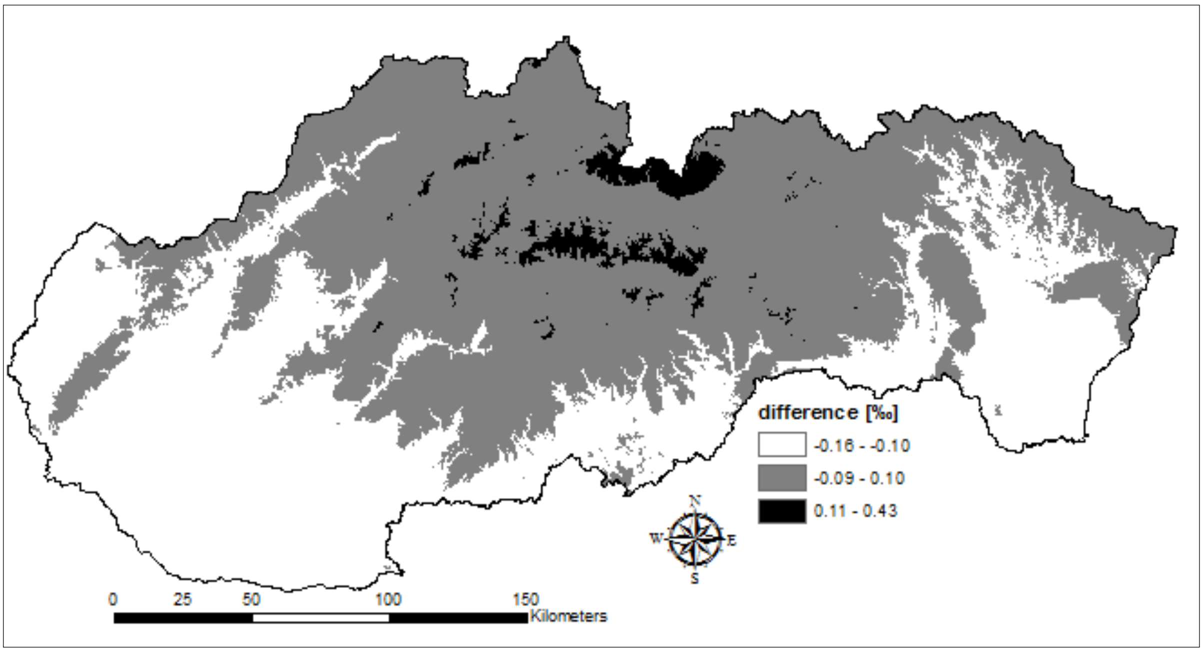

Fig. 8. Difference of the maps of $\delta^{18}O$ in annual precipitation based on the temperature and altitude gradients, respectively.

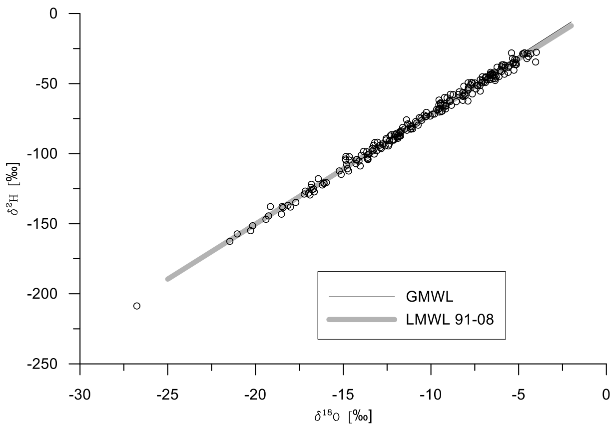

Fig. 9. Isotopic composition of precipitation and LMWL for station Liptovský Mikuláš based on monthly data from period 1991–2008 and the comparison with the Global Meteoric Water Line (GMWL).

Air temperature gradient of $\delta^{18}O$ in precipitation calculated for the Slovak stations (0.36‰/1°C) was slightly smaller than the global values 0.53‰/1°C, 0.69‰/1°C and 0.58‰/1°C calculated by *Gourcy* et al. (2005), *Dansgard* (1964) and *Rozanski* et al. (1993), respectively. It may be caused by the fact that the average global values were calculated for a much larger number of stations with mean annual air temperature ranging between 0 and 20°C. The Slovak data represent generally the same climate and mean annual air temperature varied in a much smaller range (approximately between 3 and 9°C).

The altitude gradient of $\delta^{18}O$ in precipitation calculated for Slovakia (0.21‰/100 m) was similar to that found elsewhere in Europe, e.g. 0.26––0.37‰/100 m in Croatia and Slovenia, 0.18––0.19‰/100 m in Italy or 0.25‰/100 m in Austria (*IAEA*, 2005). Observed altitude gradients in different studies from other parts of the world vary between 0.1 and 0.6 ‰/100 m (*Gat* et al., 2001).

The altidude gradient of $\delta^{18}O$ in precipitation calculated by *Holko* (1995) using just two stations (Liptovský Mikuláš and Červenec) and the period 1991–1993 was smaller (0.14‰/100 m) than the above mentioned gradient calculated in this study for the entire of Slovakia. It was caused by the occurrence of negative gradients in winter months. However, the summer altitude gradient (July––September) in the same area based on data from 6 raingauges situated at altitudes 750–1900 m a.s.l. reached the value of –0.28‰/100 m (*Holko*, 1995). That value better corresponds to the altitude gradients calculated in this article for the entire Slovakia (Tab. 3). Altitude gradient of $\delta^{18}O$ calculated by *Malík* et al. (1996) for groundwaters of karst springs in a neighboring mountain range of northern Slovakia was 0.1 ‰/100 m.

Negligible gradient of $\delta^{18}O$ in precipitation found in this study for January (Fig. 6) was also caused by the fact that the highest (mountain) station used in the analysis (Červenec) had isotopically heavier January precipitation than most of other stations situated at lower altitudes. Fig. 6 indicates a small decrease of $\delta^{18}O$ in precipitation with altitude in August and December (0.08 and 0.09‰/100 m of altitude, respectively). However, the coefficients of determinations are very small.

T a b l e 4. Slopes and intercepts of local meteoric water lines calculated for all stations where both $\delta^{18}O$ and $\delta^{2}H$ data were available and two different time periods.

	Altitude	Local Meteoric Water Line	
	[m a s l]	Slope	Intercept
1991–1993			
L. Mikuláš	570	7.88	7.906
Priemstav	570	8.03	8.196
Červenec	1500	8.33	16.685
Vienna	203	7.54	3.139
Krakow	205	7.67	5.202
1991–2008			
L. Mikuláš	570	7.86	6.985
Červenec	1500	7.83	10.62
Vienna	203	7.64	2.640
Krakow	205	7.71	5.674

The map of mean annual $\delta^{18}O$ in precipitation in Slovakia (Fig. 7) compared very well with the measured values at stations Červenec, Stará Lesná and Milhostov. The differences for other four stations were within ±0.2‰ (Liesek, Starina, Mochovce, Topoľníky). Higher differences were found for stations Bratislava and Priemstav that had heavier precipitation than the neighboring stations located at similar altitude. The $\delta^{18}O$ value extracted from the map for station Liptovský Mikuláš was significantly heavier than the measured value. It was already mentioned that Chopok had very heavy precipitation compared to other stations and considering its altitude. Therefore, the regression equation which did not use the data from Chopok provided a significantly different estimated value. Comparison of measured values with the values extracted from the map showed that the map generally provided a good estimate of mean annual values of $\delta^{18}O$ in precipitation in Slovakia. However, the small scale differences in isotopic composition of precipitation were not well characterized by the equation derived for the entire country. Since we had data from only 10 stations situated in Slovakia, it was not meaningful to use more sophisticated interpolation methods such as the geostatistics. Furthermore, the data showed that altitude and air temperature were good descriptors of mean annual values of $\delta^{18}O$ in precipitation. We thus believe that altitude and air temperature gradients of $\delta^{18}O$ in precipitation were the only appropriate approaches under given conditions. The map provides a new, more detailed information for this part of central Europe that was not available until now.

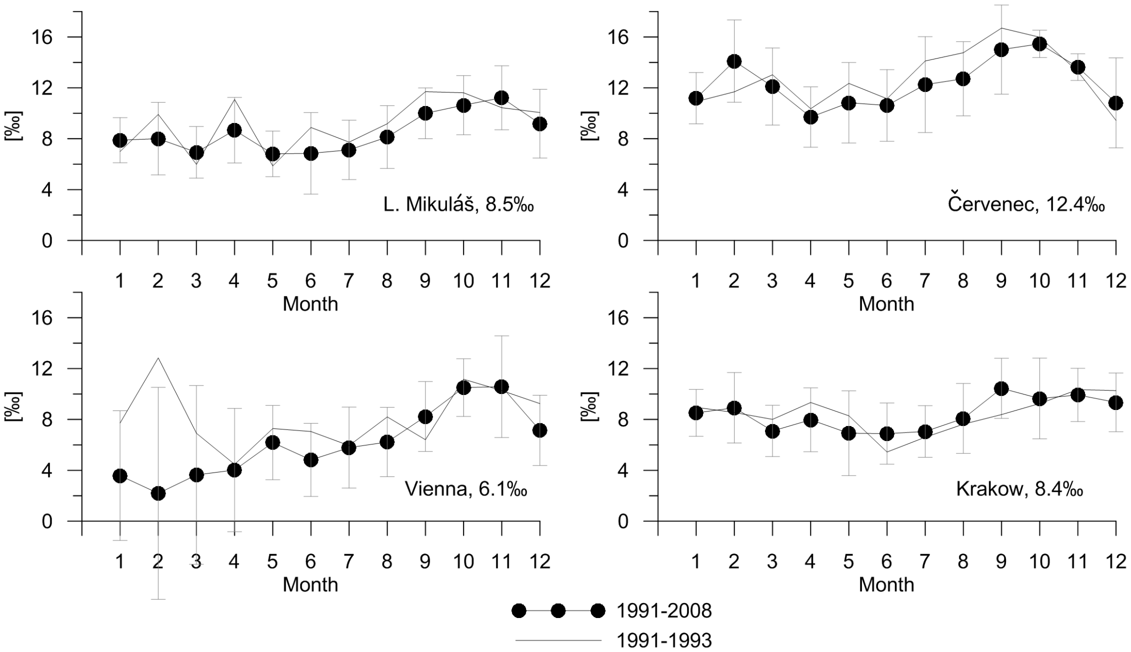

Fig. 10. Seasonal variations of deuterium excess in precipitation in periods 1991–1993 and 1991–2008; the error bars indicate standard deviations for individual months in the period 1991–2008, the mean for the period 1991–2008 is given next to the station name.

Local meteoric water lines for stations Liptovský Mikuláš, Vienna and Krakow calculated for two periods 1991–1993 and 1991–2008 did not indicate any influence of a changed climate. Similar findings were reported by *Gourcy* et al. (2005) who calculated decadal changes of the Global Meteoric Water Line on the basis of data from 31 GNIP stations and period 1961–2000.

Significantly different values of deuterium excess were found for two neighboring stations of Liptovský Mikuláš (large river valley) and Červenec (mountains). In Europe, precipitation with higher deuterium excess (14‰) often comes from the western part of the Mediterranean (*IAEA*, 2005). *Rank* and *Papesch* (2005) report on significant differences in seasonal variability in deuterium excess in the Austrian Alps. They attribute the differences rather to local conditions than to different origin of air masses. *Froehlich* et al. (2008) calculated that the long-term sub-cloud evaporation (that generally decreases deuterium excess) represents less than 1% of precipitation in the Austrian Alps. Calculated contribution from recycling of continental moisture (that generally increases deuterium excess) was 2.5–3% of the local precipitation at two mountain stations. It is not probable that precipitation at Liptovský Mikuláš and Červenec come from air masses of different origin. We assume that similarly to the Alps, local conditions are responsible for a significant difference in deuterium excess at the two stations. One of the reasons may be the influence of water vapour from two larger water reservoirs situated relatively close to the station (Liptovská Mara, Oravská priehrada).

Conclusions

The paper provides a synthesis of all available data on isotopic composition of precipitation in Slovakia. It supplements existing international studies by the knowledge from the Western Carpathians. Presented results, e.g. altitude and temperature gradients of $\delta^{18}O$ in precipitation, seasonal variability of the gradients and the map of mean annual $\delta^{18}O$ in precipitation promote the use of stable isotopes in the region, e.g. in hydrogeological surveys. A more detailed map of spatial distribution of $\delta^{18}O$ in annual precipitation in the studied part of the central Europe could be useful also in larger-scale water balance studies (e.g. *Szilagyi* and *Kovacs*, 2011). Future monitoring of isotopic composition of precipitation in the Western Carpathians should provide more data on $\delta^{2}H$. More attention should be paid to monitoring of isotopic composition of precipitation in the mountains, because the existing data from the mountain stations show some unexpected features such as small seasonal variability of isotopic composition of precipitation or high deuterium excess.

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REFERENCES

ARGIRIOU A. A., LYKOUDIS S., 2006: Isotopic composition of precipitation in Greece. J. Hydrol., 327, 486–495.

BOŠKOVÁ K., 2004: Distribution of oxygen isotopes in precipitation in Slovakia. In Slovak, Bachelor thesis, Faculty of Natural Sciences, Comenius University Bratislava, 58 p.

CLARK I. D., FRITZ P., 1997: Environmental Isotopes in Hydrogeology. Lewis, Baton-Rouge, 328 p.

CRAIG H., 1961: Isotope variations in meteoric waters. Science, 133, 1702–1703.

DANSGAARD W., 1964: Stable isotopes in precipitation. Tellus, 16, 438–468.

DINÇER T., 1968: The Use of Oxygen 18 and Deuterium Concentrations in the Water Balance of Lakes. Water Resour. Res., *4*, 6, 1289–1305.

DINÇER T., PAYNE B. R., FLORKOWSKI T., MARTINEC J., TONGIORGI E., 1970: Snowmelt Runoff from Measurements of Tritium and Oxygen-18. Water Resour. Res., *6*, 1, 110–124.

FONTES J.-CH., GONFIANTINI R., 1967 : Comportement isotopique au cours de l'evaporation de deux bassins Sahariens. Earth and Planetary Science Letters, 3, 258–266.

FROEHLICH K., KRALIK M., PAPESCH W., RANK D., SCHEIFINGER H., STICHLER W., 2008: Deuterium excess in precipitation of Alpine regions-moisture recycling. Isotopes Environ. Health Stud., *44*, 1, 61–70.

GAT J. R., MAZOR E., TZUR Y., 1969: The stable isotope composition of mineral waters in the Jordan rift velley, Israel. J. Hydrol., 7, 334–352.

GAT J. R., MOOK W. G. MEIJER A. J., 2001: Atmospheric water. Environmental isotopes in the hydrological cycle – Principles and applications, Vol. *2*. (W.G. Mook (Ed.) IHP-V, Technical Document N. 39, UNESCO, Paris, 113 p.

GOURCY L. L., GROENING M., AGGARWAL P. K., 2005: Stable oxygen and hydrogen isotopes. Isotopes in the Water Cycle (P. K. Aggarwal, J.R. Gat, F.O. Froehlich, Eds.) Springer, Dordrecht, Chapter 4, 39–52.

HOLKO L., 1995: Stable environmental isotopes of ^{18}O and ^{2}H in hydrological research of mountainous catchment. J. Hydrol. Hydromech., *43*, 4-5 249–274.

HOLKO L., KOSTKA Z., ŠANDA M., 2011: Assessment of Frequency and Areal extent of Overland Flow Generation in a Forested Mountain Catchment. Soil &Water Research, *6*, 1, 43–53.

IAEA, 2005: Isotopic composition of precipitation in the Mediterranean basin in relation to air circulation patterns and climate. IAEA-TECDOC-1453, IAEA, Vienna, 2005.

INGRAHAM N. L., 1998: Isotopic variations in precipitation. Isotope Tracers in Catchment Hydrology. (Kendall C., McDonnel J. F., Eds) Elsevier, Amsterdam, Chapter 3, 87–118.

JOUZEL J., MERLIVAT L., 1984: Deuterium and Oxygen 18 in Precipitation: Modeling of the Isotopic effects During Snow formation. J. Geoph. Res., 89, D7, 11749–11757.

KANTOR J., GARAJ M., RYBÁR, M. et al., 1985: Isotopic characteristics of waters of different genetic types. (In Slovak.) State Geological Institute, rep. no. R-52-547-202-03, 17 p.

LIU Z., TIAN L, YAO T., YU W., 2008: Seasonal deuterium excess in Nagqu precipitation: influence of moisture transport and recycling in the middle of Tibetian Plateau. Environmental Geology, *55*, 7, 1501–1506, DOI: 10.1007/s00254-007-1100-4.

MALÍK P., MICHALKO J., MANSELL S.J., FENDEKOVÁ, M., 1996: Stable isotopes in karstic groundwaters of Veľká Fatra mountains, Slovakia. In Proc. of Int. Symp. on Isotopes in Water Resources Management, IAEA, Vienna, 191–192.

MICHALKO J., 1999: Stable isotopes of hydrogen, oxygen and sulphur in the waters of Slovakia. Slovak Geological Magazine, Vol. *5*, 1-2, Geological Survey of Slovak Republic, Dionýz Štúr Publishers, Bratislava, 63–68.

RANK D., PAPESCH W., 2005: Isotopic composition of precipitation in Austria in relation to air circulation patterns and climate. In: Isotopic composition of precipitation in the Mediterranean basin in relation to air circulation patterns and climate, IAEA-TECDOC-1453, IAEA, Vienna, 19–36.

ROZANSKI K., ARAGUÁS-ARAGUÁS L., GONFIANTINI R., 1993: Isotopic Patterns in Modern Global precipitation. Climate Change in Continental Isotopic Records (Swart P. K., Lohmann K. L., McKenzie J., Savin S., Eds.) Geophysical Monograph 78, American Geophysical Union, Washington, DC, 1–37.

SZILAGYI J., KOVACS A., 2011: A calibration free evapotranspiration mapping technique for spatially-distributed regional-scale hydrologic modelling. J. Hydrol. Hydromech., *59*, 2, 118–130.

YAMANAKA T., TSUJIMURA M., OYUNBAATAR D., DAVAA G., 2007: Isotopic variation of precipitation over eastern Mongolia and its implication for the atmospheric water cycle. J. Hydrol., 333, 21–34.

YURTSEVER Y., GAT J. R., 1981: Atmospheric waters. Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle. (Gat J. R., Gonfiantini R., Eds.) Technical Reports Series 210, IAEA, Vienna, 103–142.

ZIMMERMANN U., MÜNNICH O., ROETHER W., 1967: Downward Movement of Soil Moisture Traced by Means of Hydrogen Isotopes. In: Isotope Techniques in the Hydrologic Cycle (G.E. Stout,, Ed.), Geophysical Monograph no. 11, Washington, D.C., 28–36.

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