

STABLE ISOTOPES OF OXYGEN AND HYDROGEN IN THE TAP WATER IN THE JALOVECKÝ CREEK VALLEY IN HYDROLOGICAL YEARS 2018–2020

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We present the results of probably the first monitoring of isotopic composition of tap waters in Slovakia. The isotopic composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$) of the tap water in two municipalities in the Jalovecký Creek catchment in northern Slovakia documented their different sources. The tap water in the Liptovský Mikuláš town (part Ondrašová) is on average isotopically similar to the Váh River water while the tap water in the Jalovec village is similar to the Jalovecký Creek. The temporal variability of the isotopic composition of both tap waters shows the contribution of the isotopically lighter snowmelt water. The consistently high electrical conductivity of the tap water in Jalovec suggests that the water comes from the Mesozoic rocks. The ground water in the alluvium of the Jalovecký Creek sampled in a borehole in Jalovec was isotopically similar to local tap water in summer and isotopically heavier in other seasons. The streamflow mean transit times were about a half of those of the tap waters and the borehole ground water (about 2 years versus about 1 year, respectively).

KEY WORDS: stable isotopes of oxygen and hydrogen, tap water, mountain catchment, mean transit time

Introduction

Isotopes are atoms of the same element that differ in the number of neutrons in the nucleus. Because neutrons have a weight, the atoms containing more neutrons are heavier than the ones with less neutrons. Hydrogen and oxygen as the elements building the water molecule have three isotopes each, i. e. the ^1H , ^2H , ^3H (radioactive) and the ^{16}O , ^{17}O , ^{18}O , respectively. The lighter isotopes are much more abundant than the heavier ones. Excluding the radioactive isotope of ^3H (tritium, the isotope of hydrogen that has two neutrons in the nucleus), the natural waters are mixtures of nine combinations of the oxygen and hydrogen isotopes. Three of them are the most significant for hydrology – the most abundant $^1\text{H}_2^{16}\text{O}$, $^1\text{H}_2^{18}\text{O}$ (abundance 310 ppm) and $^2\text{H}_2^{16}\text{O}$ (abundance 1990 ppm); e.g. Hoefs (1987). If unaffected by the geothermal processes, the isotopic composition of waters on the Earth changes only during the phase changes (evaporation, condensation) and by mixing of different waters. During water evaporation, lighter isotopes move to the vapour more easily than the heavier ones. Because this process is significantly affected by temperature, the water vapour in summer (or at low latitudes) contains more heavy isotopes than in winter (at high latitudes). During precipitation formation in clouds (condensation), heavier isotopes move to a condensate more easily than the lighter ones. Therefore, precipitation at the sea or in coastal areas (the first condensate) is

isotopically heavier than that falling at a greater distance from the sea (ocean). Thus, evaporation and condensation create typical isotopic signatures of water that help trace the origin and movement of water in the hydrological cycle. A more detailed information about the concepts is provided e.g. in Kendall and McDonnell (1998) and Aggarwal et al. (2005). The concentrations of hydrogen and oxygen isotopes in water samples (*sample*) are expressed relatively as the δ -values (in ‰), representing the ratios of the heavy to light isotopes related to the same ratios in the international standard (*st*), e.g. in the case of oxygen:

$$\delta^{18}\text{O}_{\text{sample}} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{st}}}{(^{18}\text{O}/^{16}\text{O})_{\text{st}}} \quad (1)$$

Plots of $\delta^2\text{H}$ against $\delta^{18}\text{O}$ (the dual isotope plots) are useful in identifying waters of different origin. The $\delta^2\text{H}$ - $\delta^{18}\text{O}$ relationship in precipitation (the input into the hydrological cycle of a catchment) determines the meteoric water line (Craig, 1961) along which usually most water samples plot. Groups of samples plotted at different positions represent waters of different origin (the reasons of different origin may not be explained solely by the isotopes). A number of examples can be found e.g. in Clark and Fritz (1997). Another application of the stable isotopes of hydrogen and oxygen in water utilizes the seasonal variability in the isotopic

composition of precipitation (input) and runoff or ground water (output). Damping or time shift of the $\delta^2\text{H}$ or $\delta^{18}\text{O}$ in runoff with respect to precipitation allow calculation of the streamflow mean transit/residence time characterizing the time the water spent in a catchment (Zuber et al., 1986; McGuire and McDonnell, 2006; Kirchner, 2016a; 2016b). The third large group of the application of isotopes (perhaps the largest one) uses the two-component mixing model (Pinder and Jones, 1969) to calculate the components of catchment runoff hydrographs, ground water recharge, etc. (e.g. Stichler et al., 1986; Jasechko et al., 2014; Klaus and McDonnell, 2013; Kirchner, 2019).

Monitoring of the isotopic composition of tap water that has been increasingly reported for over a decade, can help in the management of water supply. Bowen et al. (2007) conducted a national-level monitoring of the tap water in the USA. While the intra-annual ranges of tap water isotopic composition were mostly relatively small (i. e. $< 10\%$ for $\delta^2\text{H}$), the spatial variation was very large and similar to that of the isotopic composition of precipitation. Landwehr et al. (2014) concluded that the seasonal differences in the isotopic composition of tap waters in the USA were significant at many places. Zhao et al. (2017) constructed the TapWater Line for China. Good et al. (2014) identified probable situations of the nonlocal water use in the western U.S. by comparisons of the isotopic composition of tap waters and potential water resources within hydrological basins. The bi-annual series of samples from the Salt Lake Valley, USA (spring and autumn 2013 and 2014) allowed clustering of urban tap water into four groups (Jameel and Bowen, 2015). Jameel et al. (2016), using an extended data set (2013–2015) from the same area, found that mean tap water had a lower ^2H and ^{18}O concentrations than local precipitation, highlighting the importance of nearby montane winter precipitation as source water for the region. They identified a significant correlation between the water source and demographic parameters including population and income. A multi-year drought in California in 2012–2015 resulted in an increased need to understand the linkages between urban centers, water transport and usage and the impacts of climate change on water resources. Tipple et al. (2017) used stable isotopes of oxygen and hydrogen to improve the understanding of the complex water transport systems and varying municipality-scale management decisions in the San Francisco Bay Area. The isotopic composition of the tap water was consistent with the snowmelt from the Sierra Nevada Mountains, local precipitation, ground water and partially evaporated reservoir sources. They also estimated that about 6.6% of water in one reservoir system evaporated in 2015. Du et al. (2019) used samples of the tap water, precipitation and surface water in the urban area of Lanzhou, China, to construct the Local Tap Water Line and concluded that the isotopic composition of the tap water collected from one single sampling site can be considered as a representative for tap water isotopes in the area with a single tap water source. The tap water was isotopically different from local precipitation, but it was similar to that of the surface

water. They concluded that the isotopic composition of tap water in Lanzhou can be used as a representative of isotopes in the surface water. De Wet et al. (2020) used the seasonal variation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in tap water in South Africa to identify two tap water worlds – the municipalities that are supplied by seasonally invariant sources that have long residence periods, such as ground water, and those supplied by sources that vary seasonally in a manner consistent with evapo-concentration, such as surface water. Such a division of water sources allows for an efficient identification of municipalities that are dependent on highly variable or depleted surface water resources, which are more likely to be vulnerable to climate and demographic changes. Distributions of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the tap water in France was recently analysed by Daux et al. (2021) to provide isoscapes useful in archaeology, forensics and evaluate whether the modelled data can be used as surrogates for the measured ones. The isotopic composition of the tap water reflected the effects of altitude and distance from the coast with small variations along the year.

To the best of our knowledge, the isotopic composition of tap waters in Slovakia has not yet been monitored and analysed. This article presents the results of a small study carried out in the foreland part of the Jalovecký Creek catchment, located in the Liptovská dolina valley in northern Slovakia. The temporal variability of $\delta^{18}\text{O}$, $\delta^2\text{H}$ in the tap water at two sites based on a frequent sampling is compared with the isotopic composition of local precipitation, streams and ground water. The objectives of our work were to elucidate the origin of the tap waters and the ground water, investigate the temporal variability of their isotopic composition and estimate the mean transit times.

Material and methods

The tap water samples were collected once per week in hydrological years 2018–2020 at two sites. The first one is located in the Liptovský Mikuláš town (Ondrašová, elevation 570 m a.s.l.), the second one in the Jalovec village (696 m a.s.l.). The sampling started in November 2017 and June 2018, respectively. The tap water was allowed to flow for a few minutes before the sample was collected. Water temperature and electrical conductivity (EC) were measured by the handheld meter WTW. The tap water in Liptovský Mikuláš comes from several sources that include ground water from the Váh River alluvium and surface water of the Demänovka Creek from the Low Tatra Mountains. The tap water in Jalovec is supplied by the local spring from the Mesozoic rocks of the Western Tatra Mountains. Ground water samples were collected in Jalovec (at the same site as the tap water samples) from a borehole drilled in the alluvium of the Jalovecký Creek. The depth of the pump was 15 m and the samples were collected after at least of 10 minutes of pumping. Ground water temperature and conductivity were measured as well.

Isotopic composition of precipitation has been sampled at meteorological station in Liptovský Mikuláš (570 m a.s.l.). Monthly composite samples have been collected

at the site for the isotopic analyses since November 1990 and the station is included in the WMO-IAEA network GNIP (Global Network of Isotopes in Precipitation). The isotopic composition of local streams has been sampled at three sites. Weekly samples have been collected from the Jalovecký Creek in Liptovský Mikuláš (570 m a.s.l.; catchment area to the sampling site is about 45 km²). Monthly samples have been collected from the Jalovecký Creek also at the outlet of the mountain part of the catchment (820 m a.s.l., catchment area 22.2 km²). Monthly samples have been collected also from the Váh River in Liptovský Mikuláš (catchment area about 1100 km²). Water temperature and conductivity were measured during the sampling by the WTW device.

Isotopic composition of water samples ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were measured at the Institute of Hydrology of the Slovak Academy of Sciences by the off-axis integrated cavity output laser spectroscopy (Picarro L2130-i). Each sample was analysed at least two times with seven injections per vial (Holko, 2015). The results were referenced against the internal laboratory standards calibrated against the primary reference materials and reported as per mil (‰) relative to the Vienna Standard Mean Ocean Water. Typical precision, expressed as the 1-year variance of an internal control standard, was better than $\pm 0.1\text{‰}$ and $\pm 1.0\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively.

The differences in the isotopic composition, EC and water temperature were evaluated by the simple statistics, comparison of boxplots, dual plots of $\delta^2\text{H}$ against $\delta^{18}\text{O}$, and plots of temporal variability. An estimate of the mean transit time was done for the tap waters, ground water in the borehole and for the streams. Minima and maxima of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were used to provide the amplitude (one half of the difference between the minimum and maximum) and the mean transit time (MTT) was calculated according to formula:

$$\tau_r = \frac{\sqrt{\frac{1}{f^2} - 1}}{2\pi} \quad (2)$$

where

τ_r – MTT in years,

f – ratio of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ amplitudes in the output (the tap water, the borehole and the streams, respectively) to the amplitude in precipitation (e.g. Herrmann and Stichler, 1981).

The MTT calculated by either isotope was expressed in month. The calculation assumes that the amplitude in precipitation measured in Liptovský Mikuláš was the same as the amplitude in the infiltration zones of all waters and that the tap water was not formed by mixing of water from several different sources (e. g. the alluvium and a spring).

Results and discussion

The basic statistical characteristics of $\delta^{18}\text{O}$, $\delta^2\text{H}$, deute-

rium excess (calculated as $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$), water temperature and electrical conductivity are given in Table 1. A significant difference in the mean isotopic composition of the tap waters in Liptovský Mikuláš and Jalovec confirms different water sources. The tap water in Liptovský Mikuláš is isotopically similar to the Váh River water while the tap water in Jalovec is isotopically significantly lighter (considering the analytical error) and similar to the Jalovecký Creek. The average isotopic composition of the Jalovecký Creek does not change much between the outlet of the mountain part of the catchment and the outlet of the entire catchment while the water temperature of the creek increases downstream with the altitude gradient of $0.6^\circ\text{C}/100\text{ m}$. For the comparison, the mean annual air temperatures (1988–2018) at 570 m a. s. l., 750 m a. s. l. and 1500 m a. s. l. (the mean elevation of the mountain part of the Jalovecký Creek catchment) are 7.3°C , 6.5°C and 3.0°C , respectively. The EC of the tap water in Jalovec is much higher than in Liptovský Mikuláš. We do not have the information about the tap water treatment before the supply, but the consistently greater electrical conductivity could be related to different origin of the tap waters (the Mesozoic spring for Jalovec and river alluvium for Liptovský Mikuláš, respectively).

The plot of the isotopic composition of all samples against the local meteoric water line (Fig. 1) allows a more detailed analysis of the links among the tap waters, streams and ground water in the borehole. The meteoric water line represents the precipitation falling in Liptovský Mikuláš, i. e. at a lower elevation than the elevation where the sampled waters infiltrate. A clear difference in the isotopic composition of the tap water in Liptovský Mikuláš and the similarity of the isotopic composition of the Jalovecký Creek at the outlet of the mountains and of the entire catchment (Liptovský Mikuláš) are documented by Figs. 1a and 1b, respectively. While many ground water samples collected in the borehole are different from the Jalovecký Creek water (slightly greater concentrations of heavy isotopes indicated partial contribution of local precipitation in addition to the isotopically lighter water sources), Fig. 1c shows that part of the tap water in Jalovec is isotopically identical with the ground water in the borehole. The temporal variability of isotopic composition of the samples (Fig. 2) reveals that the tap water and ground water in Jalovec are isotopically different in winter and spring (approximately between January and June). The faster decrease in the concentrations of heavy isotopes in the ground water sampled in the borehole during the snowmelt period compared to that of the tap water suggests a greater dynamics of the ground water turnover. On the other hand, the influence of the snowmelt water in the borehole is visible for a longer time than in the tap waters. A smaller decrease in $\delta^{18}\text{O}$ found in the tap water in Jalovec in spring 2020 (that is similar to the analytical accuracy) could suggest longer transit time compared to the tap water sampled in Liptovský Mikuláš. However, the data series from Jalovec are not complete in springs 2018 and 2019. The occurrence of the isotopically lighter

Table 1. Statistical characteristics of the isotopic composition, water temperature and electrical conductivity of the samples; Stdev is the standard deviation, Cv is the coefficient of variation [%]; MTT is the mean transit time [months] calculated from the oxygen and deuterium, respectively

Samples	Characteristic	Average	Min	Max	Stdev	Cv abs	MTT
L. Mikuláš precipitation	$\delta^{18}\text{O}$ [‰]	-9.7	-16.9	-4.4	3.4	35.1	-
L. Mikuláš tap		-10.5	-11.1	-10.1	0.2	1.9	24/30
Jalovec tap		-11.2	-11.5	-10.6	0.2	1.8	26/37
Jalovec borehole		-10.8	-11.2	-10.3	0.2	1.9	26/30
Jalovecký Creek mountains		-11.3	-12.4	-10.7	0.3	2.7	14/17
Jalovecký Creek L. Mikuláš		-11.1	-12.1	-9.8	0.3	2.7	10/12
Váh River L. Mikuláš		-10.6	-11.4	-9.8	0.4	3.8	15/17
L. Mikuláš prec.	$\delta^2\text{H}$ [‰]	-69	-128	-32	27	39.1	-
L. Mikuláš tap		-71	-74	-68	1	1.4	-
Jalovec tap		-77	-79	-74	1	1.3	-
Jalovec borehole		-74	-77	-71	1	1.4	-
Jalovecký Creek Mountains		-76	-84	-73	2	2.6	-
Jalovecký Creek L. Mikuláš		-75	-82	-67	2	2.7	-
Váh River L. Mikuláš		-72	-77	-66	3	4.2	-
L. Mikuláš prec.	d-excess [‰]	8.8	2	14.7	2.8	31.8	-
L. Mikuláš tap		13.7	11.9	14.9	0.5	3.6	-
Jalovec tap		13	11	13.6	0.5	3.8	-
Jalovec borehole		12.4	9.5	13.8	0.8	6.5	-
Jalovecký Creek Mountains		14.2	11.9	14.9	0.6	4.2	-
Jalovecký Creek L. Mikuláš		13.4	11	14.6	0.7	5.2	-
Váh River L. Mikuláš		12.9	11.3	14	0.6	4.7	-
L. Mikuláš tap	Water temperature	11.1	4.3	17.6	4.0	36.0	-
Jalovec tap	[°C]	11.6	3.7	16.9	4.1	35.3	-
Jalovec borehole		9.3	6.2	13.8	1.5	16.1	-
Jalovecký Creek Mountains		5.7	0	12.3	3.9	68.4	-
Jalovecký Creek L. Mikuláš		7.3	0	19.8	4.9	67.1	-
Váh River L. Mikuláš		8.2	0.4	17.7	5.3	64.6	-
L. Mikuláš tap	Water conductivity	209	111	465	44.8	21.4	-
Jalovec tap	[$\mu\text{S cm}^{-1}$]	403	376	419	11	2.7	-
Jalovec borehole		136	84	194	24	17.6	-
Jalovecký Creek Mountains		43	31	53	5	11.6	-
Jalovecký Creek L. Mikuláš		139	61	306	52	37.4	-
Váh River L. Mikuláš		240	130	376	60	25.0	-

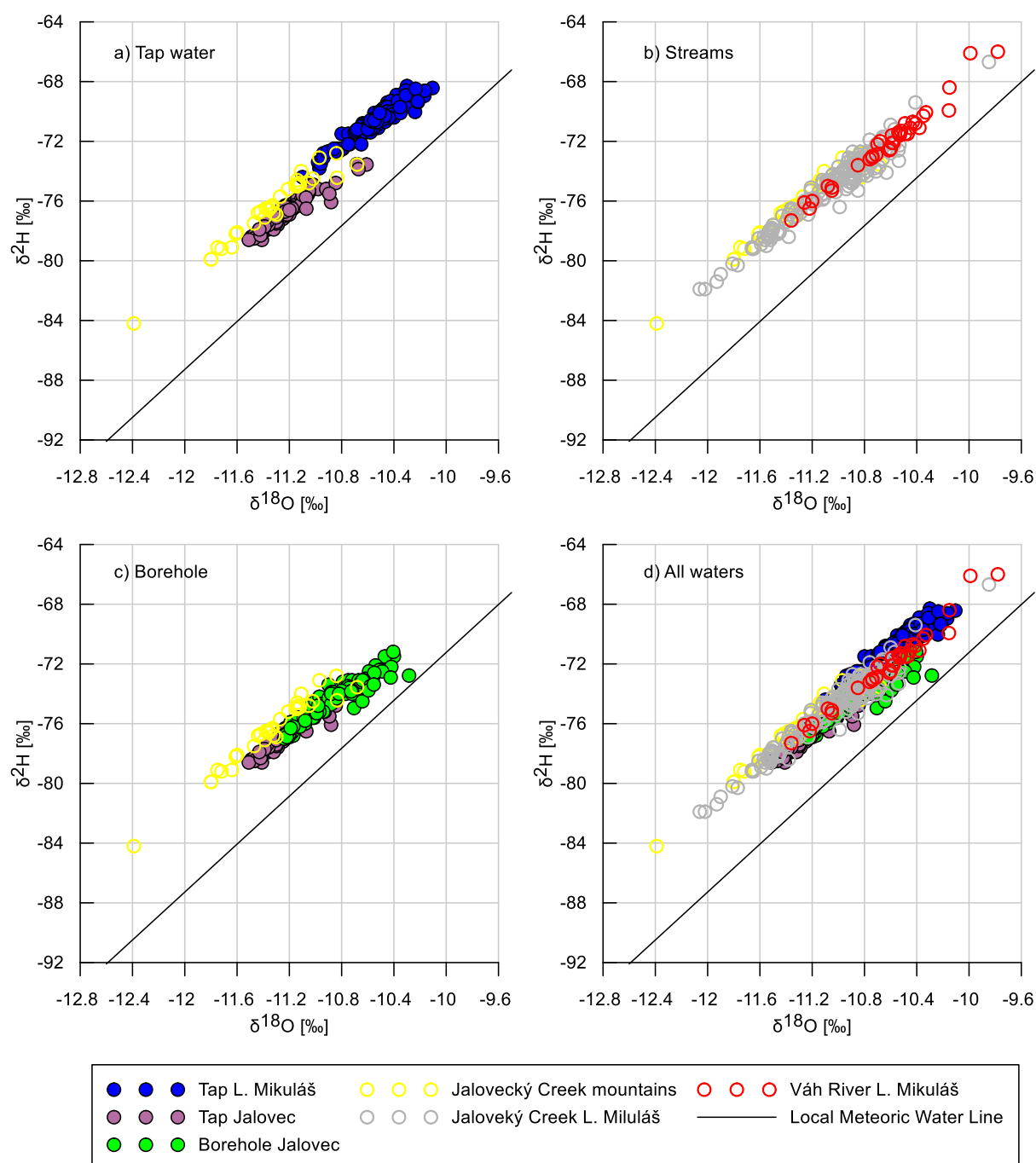


Fig. 1. The dual isotope plots for the sampled waters; a) different water sources of the tap waters, b) similarity in the isotopic composition of the Jalovecký Creek at the outlet of the mountains and at the entire catchment, c) partially overlapping isotopic composition of the borehole water and tap water in Jalovec, d) isotopic composition of all samples of the tap waters, stream waters and the borehole; the isotopic composition of the Jalovecký Creek mountains is shown in all panels to allow a better intercomparison of waters among the panels; the Local Meteoric Water line ($\delta^2\text{H}=8.02\delta^{18}\text{O}+9.0$) was constructed for the monthly composite data from precipitation station in Liptovský Mikuláš collected between November 2018 and October 2020 (hydrological years 2018–2020).

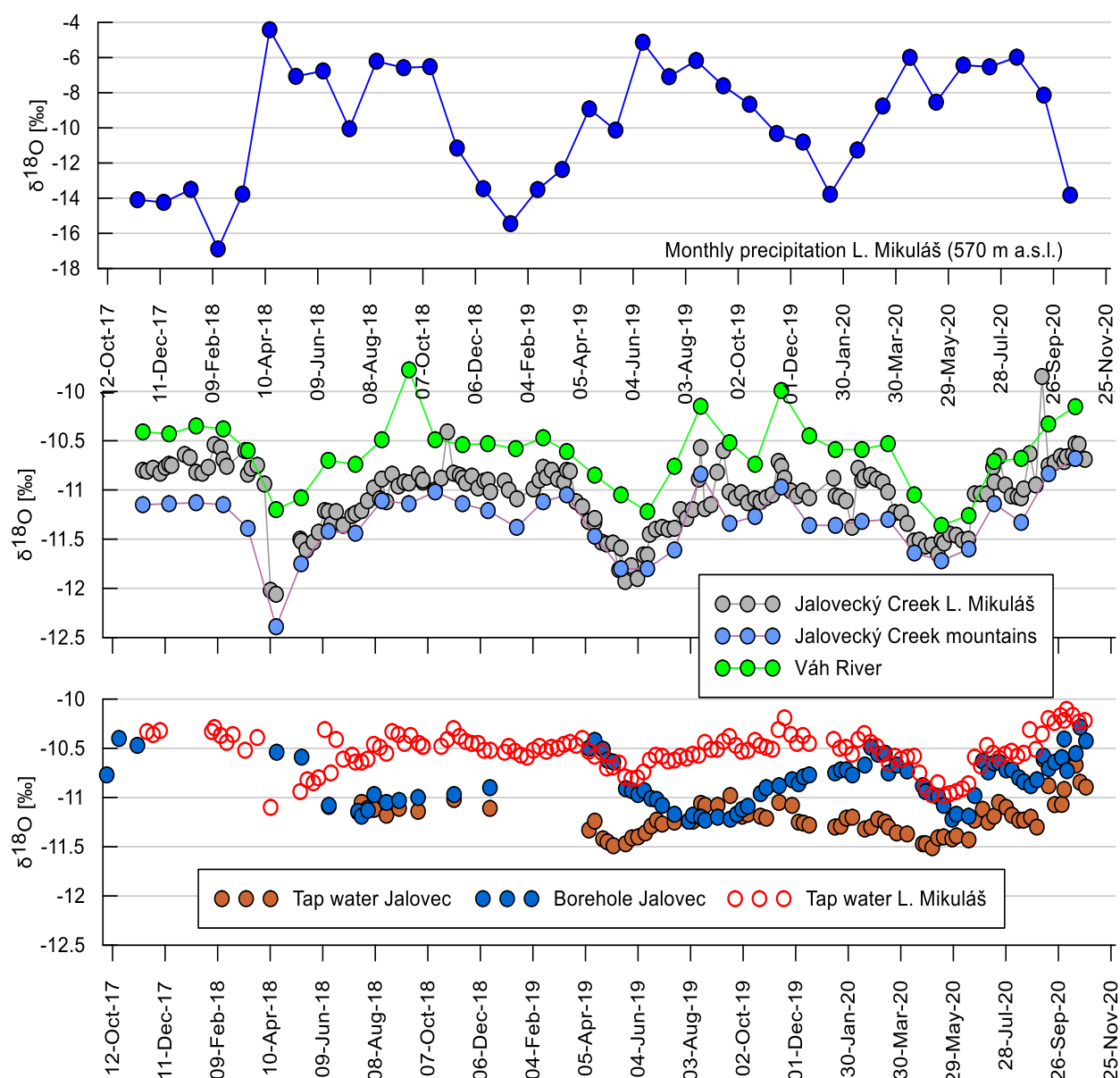


Fig. 2. Temporal variability of the isotopic composition of the samples between November 2017 and October 2020; note that the vertical axis in the uppermost panel has a different scale.

snowmelt water in the borehole is postponed compared to the Jalovecký Creek by about two months in springs 2018 and 2019, but only by two weeks in spring 2020 (Fig. 2). We cannot explain such a different behaviour among different years.

Interesting supplementary information is provided by the electrical conductivity and water temperature (Fig. 3). The EC shows a significant decrease during the snowmelt period, a small increase in the summer and the highest increase in winter before the beginning of

the snowmelt in the Jalovecký Creek in Liptovský Mikuláš and in the Váh River.

The highest values occur in winter periods when the streamflow is presumably contributed by water from the longer storage (ground water). The EC variability in the Jalovecký Creek at the outlet of the mountains is much smaller (Table 1). Small temporal variability in EC was found also in the tap water in Jalovec (Fig. 3). The EC variability in the tap water in Liptovský Mikuláš was much higher and similar to that in the Jalovecký Creek

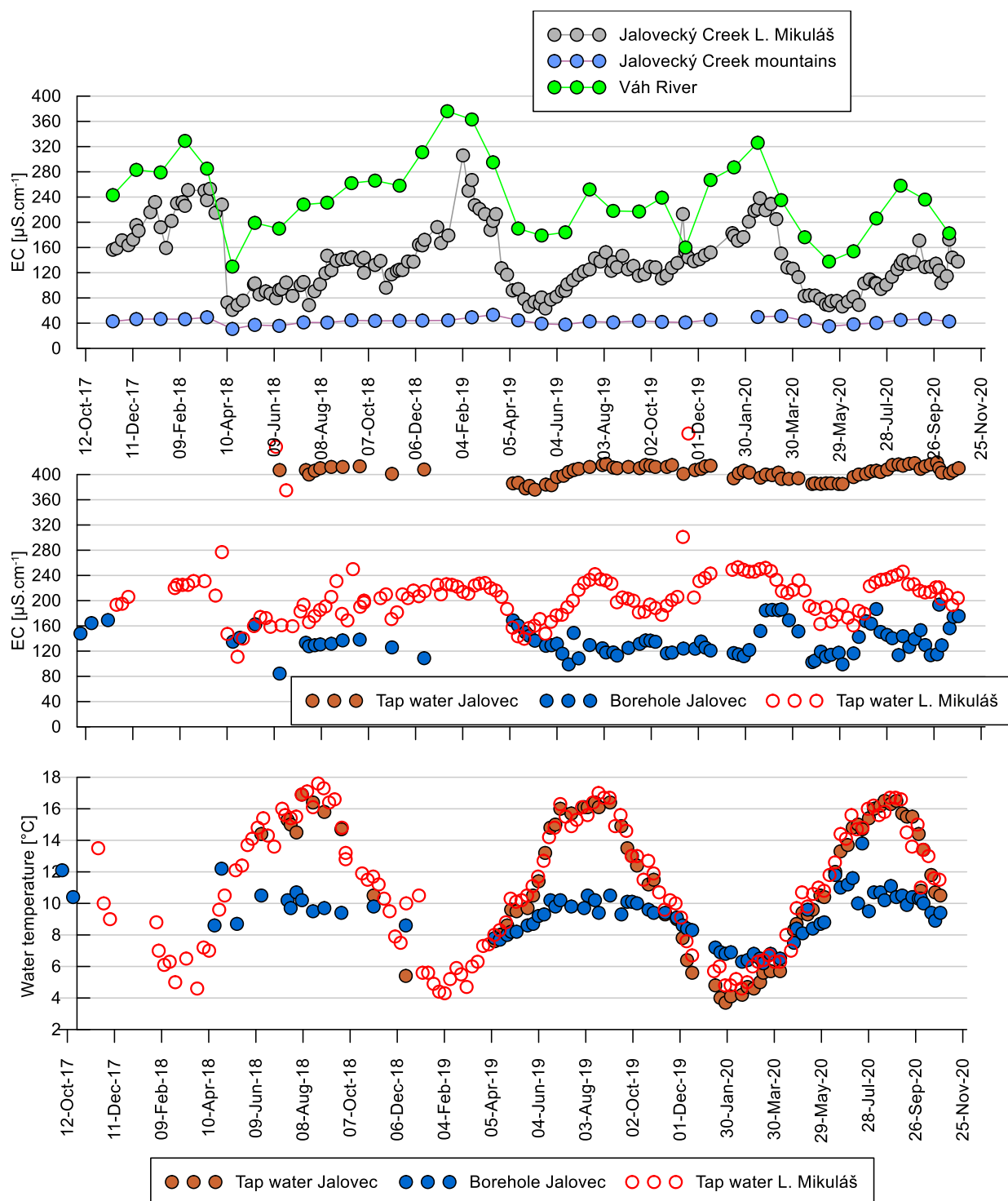


Fig. 3. Temporal variability of the electrical conductivity (EC) and water temperature between November 2017 and October 2020.

in Liptovský Mikuláš. Ground water in the borehole had a more stable EC in 2018 and 2019 (with winter maxima), but the EC time course became similar to that in the Jalovecký Creek in Liptovský Mikuláš since spring 2020.

Although there are gaps in the borehole data until April 2019, we can currently not explain why was the EC time course different in 2019 and 2020. The tap water temperature variability in Jalovec and Liptovský Mikuláš was similar while the ground water temperature had a much smaller amplitude (Fig. 3).

The mean transit times of the tap waters (assuming that the tap water did not originate by mixing of water from several different sources) and the ground water in the borehole are longer than those of the streams (about 2 years versus about 1 year). The differences in the MTT estimated from $\delta^{18}\text{O}$ and from $\delta^2\text{H}$ are quite great for the tap waters (particularly for Jalovec) while they are relatively similar for the streams (Table 1).

Conclusion

The results of our small study indicate that a more systematic monitoring of the isotopic composition of tap water at a larger area could provide a useful information also in Slovakia. While the basic relationships can be elucidated from the monthly data, the weekly sampling provides a more detailed information, especially about the influence of the snowmelt water.

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