Final report of SNN118205

Spatial distribution of water isotopes in precipitation in Europe – with special focus on the transect from the Adriatic Coast to the Pannonian Plain

CONTRIBUTION TO A COMMON HUNGARIAN-SLOVENIAN ISOTOPE DATABASE

One of the primary goals of the project was to contribute new data to the establishment of a Slovenian-Hungarian isotope database. Project partners were eager to achieve this goal, both through newly collected data and by facilitating the publication of data from an industrial monitoring that was not yet available to the scientific community.

1) Precipitation samples have been collected and their stable oxygen and hydrogen isotope composition were analyzed at four stations (Kékestető, Farkasfa, Siófok, Budapest-Lőrinc) throughout the entire project period in Hungary. The original plan was to extend the then-current network for precipitation stable isotope monitoring in NE Hungary by acquiring and installing an automatic evaporation-proof rainfall collector. However, the manufacturer who provided the quotation for the proposal "disappeared". We tried to produce the evaporation-proof rainwater sampler relying on the support of our own institutional workshop, but our technical equipment did not prove satisfactory. Hence, the idea of the automatic evaporation-proof rain collector in NE Hungary was rejected and precipitation sampling has been launched with traditional manual collectors, by the help of two volunteer of the Hungarian Meteorological Service observers, at two sites (Tornyospálca, Rakamaz) in NE Hungary from January 2017 to avoid further delays. This change, however, can be viewed as an improvement from a scientific point of view compared to the original plan because the national precipitation stable isotope monitoring network has been expanded by not only one, as was planned, but with two stations. In addition, the budget balance provided an opportunity to involve another volunteer observer for the project's extension period collecting precipitation samples at two more sites (Üröm, Szántód) from January 2020. *The monthly water stable isotope compositions for 2016-2018 period is freely available as supplementary table* [*https://www.mdpi.com/2073-4441/12/6/1797/s1*](https://www.mdpi.com/2073-4441/12/6/1797/s1) .

2) We acquired a permission to evaluate and publish the precipitation isotope data collected since 2004 in the Mecsek region (South Hungary) in the framework of the geological research programme of the Boda Claystone Formation within the site selection of a planned high activity radioactive waste repository. *The quality checked tritium activity concentration and stable isotope compositions of monthly precipitation samples from the Mecsek region are freely available in tabulated form* [*https://doi.org/10.1016/j.dib.2020.106206*](https://doi.org/10.1016/j.dib.2020.106206) .

GEOSTATISTICAL EVALUATION OF THE DISTRIBUTION PATTERNS OF ISOTOPES IN PRECIPITATION OVER DIFFERENT EUROPEAN CLIMATE REGIONS AND OROGRAPHIC COMPLEXITY

1) Iberian Peninsula

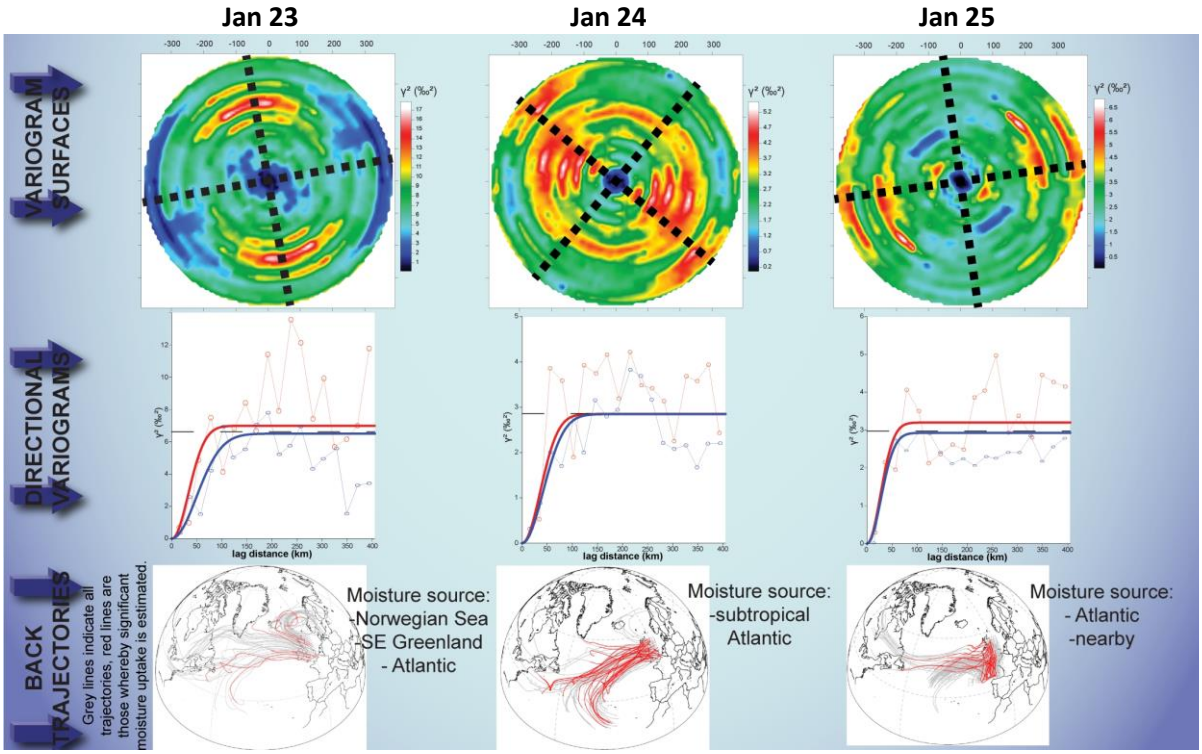
The spatial variation of oxygen and hydrogen stable isotope composition (δ^2H and $\delta^{18}O$) and d-excess of precipitation was explored across the Iberian Peninsula for October 2002–September 2003 with 24 monitoring stations of the Global Network of Isotopes in Precipitation (GNIP), and for October 2004–June 2006, in which 13 GNIP stations were merged with 21 monitoring stations from a regional network in NW Iberia. Spatial autocorrelation structure of monthly and amount weighted seasonal/annual mean δ^2H and $\delta^{18}O$ values was modelled, and two isoscapes were derived for stable oxygen and hydrogen isotopes in precipitation with regression kriging. Only using the GNIP sampling network, no spatial autocorrelation structure of $\delta^{18}O$ could have been determined due to the scarcity of the network. However, in the case of the merged GNIP and NW dataset, an exemplary empirical semivariogram with two sills, corresponding to ~100 km and ~450 km spatial range was determined. The larger range probably refers to the spatially variable moisture contribution of the western, Atlantic-dominated, and eastern, Mediterranean-dominated domain of the Iberian Peninsula. Isoscapes of stable oxygen and hydrogen isotope composition of precipitation for the Iberian region have been determined and compared to the regional subset of the latest version of the global reference dataset. The estimation error of the presented Iberian precipitation isoscapes, both for oxygen and hydrogen, is smaller than the ones that were reported for the regional subset of the most widely used global model, suggesting that the current regional model provides a higher predictive power. *An MSc student won First Prize at the Competition of National Scientific Student Council in 2019 and successfully defended his Master thesis from the study. The main results have been published* *https://doi.org/10.3390/w12020481*

2) Baltic Artesian Basin

Although Baltic Artesian Basin (BAB) is an important palaeogroundwater reservoir of Europe little has been known about the spatial variability of δ^2H and $\delta^{18}O$ values in modern precipitation input across the region. State-of-art geostatistical approach were employed to an extensive dataset of water stable isotopes of shallow groundwater to model the isotopic composition of shallow groundwater in the BAB with high spatial resolution. Clear discrepancies have been observed when the isotopic composition of precipitation and shallow groundwater were compared in the area. The isotopic composition of shallow groundwater was mostly biased towards isotopically depleted wintertime precipitation. We proposed that the formation of shallow groundwater in the BAB area could be largely affected by variations in soil structure and land cover. Despite the difference between isotope composition of precipitation and shallow groundwater, the shallow groundwater isoscape for the BAB can be used as input in isotope-based hydrogeological models and the presented methodology can be adopted in other regions, where monitoring observed precipitation (GNIP or national network) is sparse, but shallow groundwater isotope data is available. *The results have been published* *https://doi.org/10.1016/j.jhydrol.2016.09.004*

3) British Isles

Daily precipitation water samples were collected from ~70 sites over the British Isles on the 23rd, 24th, and 25th January 2012 as part of a pilot study for the British Isotopes in Rainfall Project. Spatial correlation structure of daily precipitation stable oxygen isotope composition has been explored by variogram analysis similarly as above. The relatively copious number of stations allowed the derivation of meaningful directional semivariograms and semivariogram surfaces.



Estimates for the range of spatial variance (~70-100km) of daily $\delta^{18}O$ correspond fairly well to the width of warm and cold frontal rainbands. The spatially very scattered moisture sources could induce larger variance in $\delta^{18}O$ values along the rainbelt than the Rayleigh distillation during the rainout process for 23 Jan. In contrast, the more convective processes accompanied with a cold front on 25 Jan presumably caused a more effective moisture removal which means larger isotopic changes due to the Rayleigh distillation. In other words, in this case the isotopic variations induced by the Rayleigh distillation oppressed the variability due to moisture source differences. The more complex weather situation (a warm and an occluded front were in the study region) of 24 Jan could explain the different spatial variance found. A message for isotope mapping efforts can be that if the spatial correlation structure is different for each individual rain events then isotropic variance structure can be expected when multiple events are integrated, e.g. annual or multiannual scales. *These results have been presented at international conferences e.g. EGU General Assembly 2017 and European Society of Isotope Research 2017. The final paper is under preparation.*

TRITIUM (^3H) IN PRECIPITATION IN THE ADRIATIC–PANNONIAN FROM 1976 TO 2017, THE AP^{3}H_V1 DATABASE

Tritium (^3H) as a constituent of the water molecule is an important natural tracer in hydrological sciences. The anthropogenic tritium introduced into the atmosphere unintentionally became an excellent tracer of processes on a time scale of up to 100 years. A prerequisite for tritium applications is to know the distribution of tritium activity in precipitation. We created a database of isoscapes derived from 41 stations for amount-weighted annual mean tritium activity in precipitation for the period 1976 to 2017 on spatially continuous interpolated 1×1 km grids for the Adriatic–Pannonian region (called the AP^{3}H_v1 database), with a special focus on post-2010 years, which are not represented by existing global models. Five stations were used for out-of-sample evaluation of the model performance, independently confirming its capability of reproducing the spatiotemporal tritium variability in the region. The AP^{3}H database is capable of providing reliable spatiotemporal input for hydrogeological application at any place within Slovenia, Hungary, and their surroundings. Results also

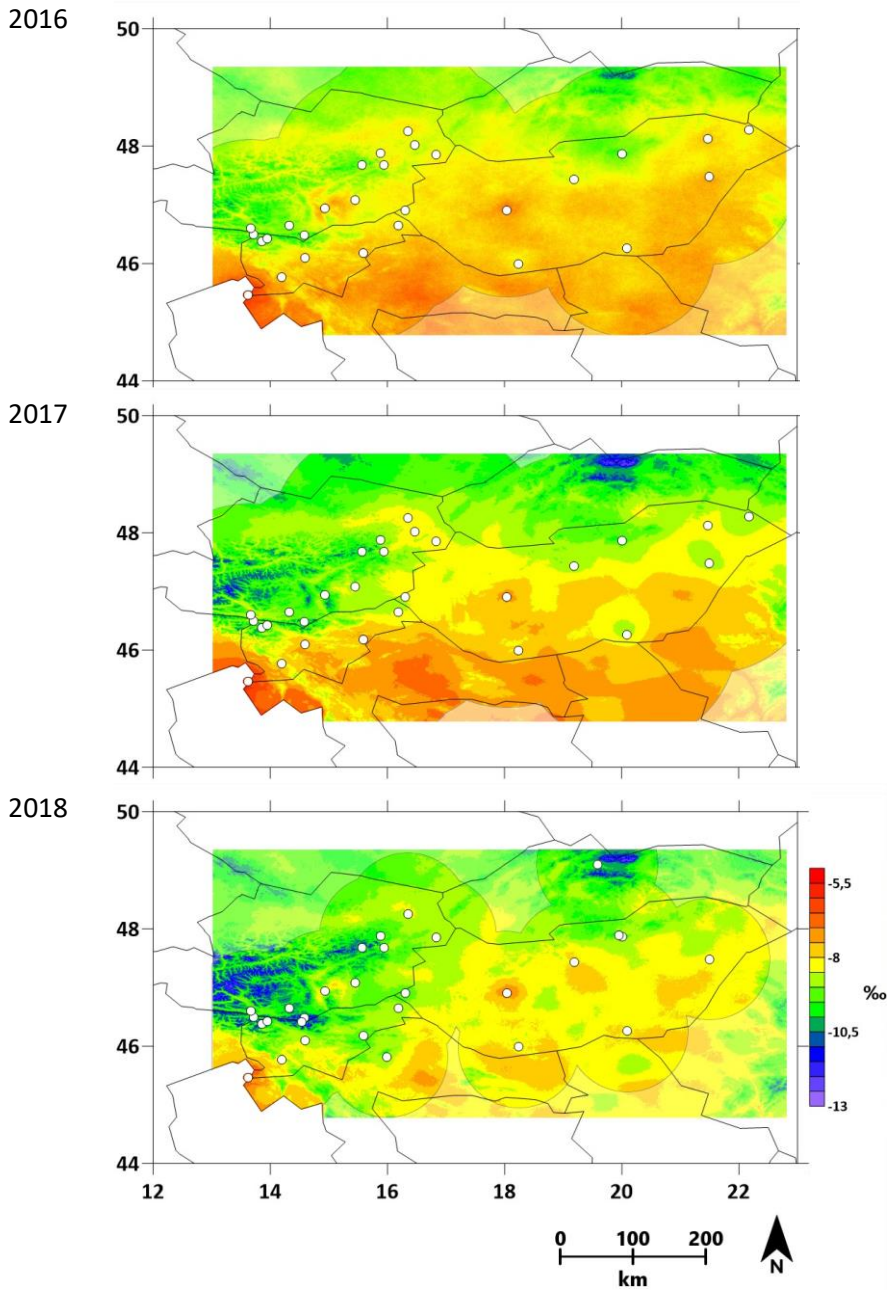
show a decrease in the average spatial representativity of the stations regarding tritium activity in precipitation from ~440 km in 1970s, when bomb tritium still prevailed in precipitation, to ~235 km in the 2010s. The post-2010 isoscapes can serve as benchmarks for background tritium activity for the region, helping to determine potential future local increases in technogenic tritium from these backgrounds. *The gridded tritium isoscape is available in NetCDF-4 at https://doi.org/10.1594/PANGAEA.896938 and the data description paper has been also published https://doi.org/10.5194/essd-12-2061-2020*

ISOTOPIC 'ALTITUDE' AND 'CONTINENTAL' EFFECTS IN MODERN PRECIPITATION ACROSS THE ADRIATIC–PANNONIAN REGION

Stable isotope composition of monthly precipitation fallen between January 2016 and December 2018 was studied for selected stations situated along an elevation transect and a continental transect in order to assess the isotopic 'altitude' and 'continental' effects in modern precipitation across the Adriatic–Pannonian region. Isotopic characteristics argue that the main driver of the apparent vertical depletion of precipitation in heavy stable isotopes is different in summer (raindrop evaporation) and winter (condensation), although, there is no significant difference in the resulting 'altitude' effect. Specifically, an 'altitude' effect of −1.2‰/km for $\delta^{18}O$ and −7.9‰/km for $\delta^{2}H$ can be used in modern precipitation across the Adriatic–Pannonian region. Isotopic characteristics of monthly precipitation showed seasonally different patterns and suggest different isotope hydrometeorological regimes along the continental transect. While no significant decrease was found in $\delta^{18}O$ data moving inland from the Adriatic from May to August of the year, a clear decreasing trend was found in precipitation fallen during the colder season of the year (October to March) up to a break at ~400 km inland from the Adriatic coast. The estimated mean isotopic 'continental' effect for the colder season precipitation is −2.4‰/100 km in $\delta^{18}O$ and −20‰/100 km in $\delta^{2}H$. A prevailing influence of the Mediterranean moisture in the colder season is detected up to this breakpoint, while the break in the $\delta^{18}O$ data probably reflects the mixture of moisture sources with different isotopic characteristics. A sharp drop in the d-excess (>3‰) at the break in precipitation $\delta^{18}O$ trend likely indicates a sudden switch from the Mediterranean moisture domain to additional (mainly Atlantic) influence, while a gradual change in the d-excess values might suggest a gradual increase of the non-Mediterranean moisture contribution along the transect. *The results have been published https://doi.org/10.3390/w12061797*

TEMPORAL AND SPATIAL DISTRIBUTION OF WATER ISOTOPES IN PRECIPITATION OVER SLOVENIA AND HUNGARY

The spatial variability of precipitation $\delta^{18}O$ values was evaluated across the Adriatic -Pannonian transect based on monthly records collected from 2016 to 2018, at 8 locations in Slovenia, 5 in Hungary, complemented with records from Croatia, Austria and Slovakia to improve the spatial density of the assessed network. The large-scale spatial trend was removed from the amount-weighted annual average $\delta^{18}O$ records using multivariate regression analysis, employed latitude and elevation as the independent variables (r^2≈54%). The residual variance was modelled with a Gaussian semivariogram (spatial representativity ~105 km) highlighting yet unrepresented (S Hungary), and well covered areas (Slovenian – Austrian border). The seasonal-, annual- and multiannual precipitation $\delta^{18}O$ isoscapes derived with residual kriging. The map series below illustrates annual precipitation $\delta^{18}O$ isoscapes for 2016, 2017, and 2018.



The results have been presented at international conferences such as 5th international Slovenian Geological Congress, Synergy International Conferences - Engineering, Agriculture and Green Industry Innovation. The final paper is under preparation.

STABLE OXYGEN AND HYDROGEN ISOTOPES IN PRECIPITATION COMPARISON BETWEEN AN ISOTOPE-INCORPORATED AGCM SIMULATION AND MEASURED DATA FOR EUROPE

The IsoGSM is an isotope-incorporated atmospheric general circulation model. IsoGSM simulations are available from 1979. We examined the reliability of the model, using the data of nearly 60 European stations of the GNIP as a reference data set. The model performance was tested on daily-, monthly-, seasonal-, and annual timescales. On the daily scale, the correlations ranged from r=0.36 to r=0.79, regressions' slopes (GNIP vs. IsoGSM) ranged from 0.26 to 0.91 for $\delta^{18}O$ (in case of $\delta^{2}H$:0.32 < r < 0.79, slope from 0.33 to 0.89). On the monthly scale, the correlations ranged from r=0.22 to r=0.99, regressions' slope ranged from 0.12 to 1.27 for $\delta^{18}O$ (in case of $\delta^{2}H$ r from -0.12 to 0.91, slope from 0.18 to 0.99). The model results accurately reflected the actual observed precipitation stable isotope

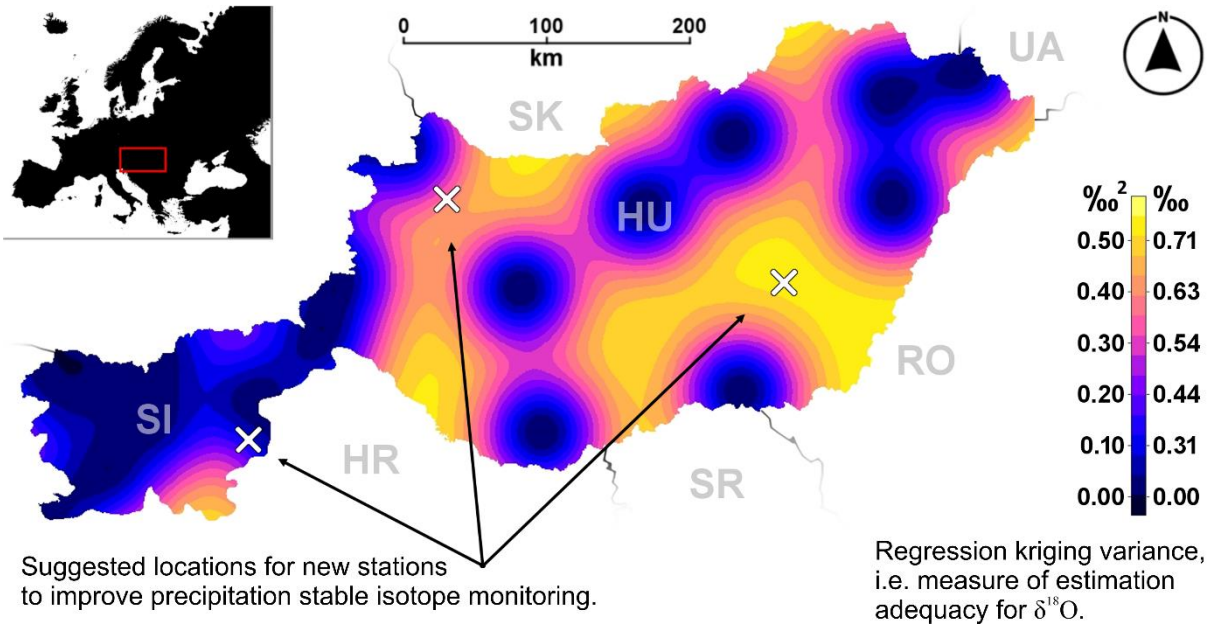
composition in continental areas regardless of the chosen temporal scale. The IsoGSM is contracted applying a constant $\delta^{18}O=\delta^{2}H=0‰$ parameterization for surface seawater, which can explain the much-reduced variance in the simulated precipitation stable isotope values at coastal locations. The regression slope of monthly $\delta^{18}O$ of 11 coastal GNIP stations ranged from 0.12 to 0.45. As general feature of all global models, IsoGSM also has a smooth topography producing insufficiently depleted compositions from model precipitation for high elevation GNIP stations. A constant bias correction using the elevation difference between the model surface and a high resolution continental elevation model significantly improved the correspondence with the GNIP records referring to mountainous localities of the reference data set. *The results were presented at the European Meteorological Society Annual Meeting 2018 (Mona et al., 2018).*

APPLICATION OF WRF SIMULATIONS TO IMPROVE OUR UNDERSTANDING OF STABLE ISOTOPE COMPOSITION OF PRECIPITATION

The WRF (Weather Research Forecast) model and the RIP (Read/Interpolate/Plot) trajectory calculations were utilized to establish relationship between the isotopic composition of the precipitation and the state of atmosphere during the route of air parcels to the sampling site. Thus the interpretation of isotopic measurements are also aided by the state of the atmosphere during the route of air parcels arriving at the measurement sites. WRF simulations are run over most of Europe for four days in order to allow ample time to precipitation formation and advection in the model. The RIP program is used in backward trajectory setting. Trajectories are started at the measurement sites at 23 different heights from surface to near the tropopause. For these analysis 18 events were chosen from period between 2013 and 2014 based on the amount of precipitation, season and source of precipitation - e.g. cyclonic (Atlantic or Mediterranean) or local. Initial results showed that cases when the continental evapotranspiration is more significant, the isotopic compositions of the samples are situated further from the global meteoric water line than in cases of e.g. precipitation resulting from Mediterranean cyclones. Also, all cases show a relation to the temperature along trajectories to $\delta^{18}O$ ratio. *The results were presented at the European Meteorological Society Annual Meeting 2017 (Breuer et al., 2017).*

EVALUATING THE SPATIAL ORGANIZATION OF THE NATIONAL NETWORKS FOR WATER ISOTOPE MONITORING IN PRECIPITATION HUNGARY AND SLOVENIA

The representativity of the currently operating (at least, as of 2018) precipitation stable isotope monitoring stations across Slovenia (n=8) and Hungary (n=9) was evaluated on the basis of amount-weighted annual averages with the aim of revealing any redundantly (i.e. over-) represented or un(der)represented areas. In the case of the latter, optimal locations for additional sites were suggested in Slovenia (n=1) and Hungary (n=2). The evaluation of the monitoring network was performed taking into consideration those stations operating in Slovenia and Hungary, as well as closely situated ones operating in neighboring countries. The evaluation was carried out in nine different combinations, using spatial simulated annealing, with regression kriging variance as a quality measure. The results showed that (i) there are over- and un(der)represented areas in the network, an issue requiring remedial action, (ii) the mutual information exchange of the precipitation stable isotope monitoring networks of Slovenia and Hungary increases the precision of precipitation $\delta^{18}O$ estimation by ~0.3‰ in a 15-30 km wide zone near the borders, and (iii) by an even greater degree in the neighboring countries' stations.



The current research maybe termed pioneering in the matter of the detailed geostatistical assessment of spatial representativity of a precipitation stable isotope monitoring network, and as such, can serve as an example for future studies aiming for the spatial optimization of other regional precipitation stable isotope monitoring networks. *The composed study is in the stage of second round of review at the journal of Environment International.*

Finally, precipitation stable isotope data and knowledge gathered in the project were contributed to additional studies e.g. Demény et al., 2019, Fórizs et al., 2019 which can be considered as partly related to the current project.

FURTHER ACTIVITIES

Project participants conveyed special sessions at international conferences and guest edited two special issues related to the topic of the project. These activities helped the professional dissemination of some results related to the project:

The Slovenian and the Hungarian PIs engaged as co-conveners in the organization of a session at the **EGU General Assembly 2017** (**Stable isotopes in the atmosphere - from vapor to precipitation, link:** http://meetingorganizer.copernicus.org/EGU2017/session/22726) tightly related to the topic of the project. Project participants contributed an oral and two poster presentations to this session.

A special session was devoted to "**Isotopes in precipitation across Europe**" *at the* XIVth Workshop of the European Society for Isotope Research (ESIR) - ESIR 2017. The workshop was hosted by the National Research and Development Institute for Cryogenics and Isotopic Technologies – ICSI Rm. Vâlcea, at Băile Govora (Romania) between 25 and 29 June, 2017. Four project members (2 Hungarian, 2 Slovenian) were attended at the meeting and contributed an oral and three poster presentations to this special session. Details can be found in the abstract book: http://www.icsi.ro/esir2017/files/book_of_abstracts.pdf

Guest editing Special issues

Two senior participants of the Hungarian Team served as guest editor in the special issue on the topic of 'Isotope Geochemistry of Meteoric Waters' at the journal of Geosciences (web page:

http://www.mdpi.com/journal/geosciences/special_issues/meteoric_waters). The SI includes a contribution from the Team which is related to the topic of the project and attracted two additional contributions on precipitation water isotopes.

PIs of the Slovenian and the Hungarian Teams served as guest editor in the special issue on the topic of 'Use of Water Stable Isotopes in Hydrological Process' at the journal of Water (web page: https://www.mdpi.com/journal/water/special_issues/Isotopes_Hydrological_Process). The SI includes two contributions from the Team which is related to the topic of the project and attracted five additional contributions on precipitation water isotopes. Final meeting communicating the most important results and introducing the produced datasets have been organized at the grant holder institutes. A normal workshop was held at the Jozef Stefan Institute at 9th December 2019, while, due to the travel restrictions that came into effect on March 12th, the event has been organized as a hybrid event (the speakers were present in person for the audience was provided with an online opportunity to get involved) at the Institute of Geological and Geochemical Research at 16.03.2020.