Isoscape of precipitation amount-weighted annual mean tritium (^{3}H) activity from 1976 to 2017 for the Adriatic-Pannonian region - AP^{3}H_v1 database

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Abstract. Tritium (^{3}H) as a constituent of the water molecule is an important natural tracer in hydrological sciences. The anthropogenic tritium introduced into the atmosphere became unintentionally an excellent tracer of processes on the time scale of up to 100 years. A prerequisite for tritium applications is to know the distribution of tritium activity in precipitation. Here we present 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 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 to 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 its 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 was still prevailing 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 of technogenic tritium from these backgrounds. The gridded tritium isoscape is available in NetCDF-4 at doi: 10.1594/PANGAEA.896938 (Kern et al., 2019).

Keywords: precipitation, Hungary, Slovenia, geospatial tritium model, tritium isoscape

1. Introduction

Tritium (^{3}H) is a radioactive isotope of hydrogen (Alvarez and Cornog, 1939) with a half-life of 12.32 years (4,500 ± 8 days, (Lucas and Unterweger, 2000)). Natural tritium is formed mainly by spallation reactions of protons and neutrons of primary and secondary cosmic radiation with atmospheric nuclei, mainly by the interaction of fast neutrons with atmospheric nitrogen (Lal and Peters, 1967). Tritium emission by thermonuclear tests between the 1950s and 1980 enormously exceeded the natural production (Araguas-Araguas et al., 1996; Palcsu et al., 2018). Since that time, tritium emission to the atmosphere from anthropogenic sources (e.g. nuclear industry, medical applications, luminizing industry) corresponds to ~10% of the natural production and influences ^{3}H content in precipitation mainly at local to regional scales (Araguas-Araguas et al., 1996). Starting from the 1980s, the technogenic tritium became the prevailing anthropogenic atmospheric tritium input signal over the bomb tritium in Central Europe (Hebert, 1990).

Tritium is introduced into the hydrological cycle following oxidation to tritiated water (^{3}H^{1}HO). Tritium is an excellent tracer for determining time scales for the mixing and flow of waters, and is ideal for studying processes that occur on a time scale of less than 100 years (Kendall and McDonnell, 2012). It proved to be a powerful tool in various applications in hydrological researches (Jasechko, 2019) such as estimating mean residence time for surface water and groundwater (Michel, 1992; Stewart and Morgenstern, 2016; Zuber et al., 2001); dating cave drip waters (Kluge et al., 2010); understanding water circulation/mixing in geothermal (Ansari et al., 2017; Chatterjee et al., 2019) or permafrost settings (Gibson et al., 2016) and many other fields (Eyrolle et al., 2018).

A prerequisite for such applications is either a measured or modelled reference of precipitation tritium activity (Stewart and Morgenstern, 2016). Long-term measurements for precipitation tritium activity are worldwide rare, and even the longest time series are usually intermitted by gaps. In the absence of on-site measurements, either remote monitoring data have to be used as references (Huang and Pang, 2010; Thatcher et al., 1961), or estimations are required. There are several methods to reconstruct precipitation tritium time series for geographical locations (Li et al., 2019). The prediction of the first global model for tritium distribution in precipitation from 1960 to 1986 (Doney et al., 1992) was improved and provided a higher accuracy estimate for precipitation ^{3}H variations (Zhang et al., 2011) extending up to 2005 called, 'Modified global model of tritium in precipitation (MGMTP)'. Unfortunately, the key parameters of MGMTP only available as isoline maps (Zhang et al., 2011), from which the model's coefficients can be extracted with high uncertainty in a manual way, which leads them to be ambiguous. In addition, the quality of the estimated precipitation tritium activity values by MGMTP after1990 become quite poor (Zhang et al., 2011); for instance in the studied region it produced uninterpretable, negative values (Sect. 4). The most recent global model for precipitation tritium activity covering the period 1955-2010 (Jasechko and Taylor, 2015), used inverse distance weighting for interpolation and its output is available in gridded format. However, this is based only on precipitation

^{3}H activity concentration records of the stations of the Global Network of Isotopes in Precipitation (Rozanski et al., 1991) and it does not represent the most recent decade.

Although, global models are available, due to the differences in tritium activities around the globe, it is beneficial to define local precipitation ^{3}H input curves (Stewart and Morgenstern, 2016). In the northern part of the Balkan region, for instance, it was shown that ^{3}H content in precipitation deviated considerably after 1980 from the Vienna record (Miljević et al., 1992) which is popularly used as remote reference station in hydrological modeling/calculations in the Adriatic-Pannonian region. The quality of such curves is vital for the reliability of a hydrological model outputs when employed as input signal/data in hydrological modeling/calculations (Koeniger et al., 2008; Miljević et al., 1992). Indeed, it has recently been found that the (in)accuracy of the used precipitation tritium time series is the key uncertainty factor for groundwater recharge estimations (Li et al., 2019).

Measurements of precipitation tritium activity in the Adriatic-Pannonian region began in Vienna Hohe Warte in 1961, which is the longest continuously operating station in the world, and in Central Europe (IAEA, 2019). Additional stations started operation in the past ~50 years with frequent interruption in data collection (Araguas-Araguas et al., 1996; Krajcar Bronić et al., 1998; Rozanski et al., 1991; Vreča et al., 2008). The demand in long-term precipitation ^{3}H reference time-series in various hydrological/hydrogeological applications across the Adriatic-Pannonian region called forth the use of remote stations (e.g. Gessert et al. (2019); Kanduč et al. (2014); Kanduč et al. (2012)) and/or motivated the derivation of case specific "composite" tritium reference curves, e.g. (Kern et al., 2009); Krajcar Bronić et al. (1992); Ozyurt et al. (2014); Szucs et al. (2015). Derivation of these ad hoc "composite" ^{3}H reference curves usually applied different imputation methods to the 'gappy' time series and/or employed different interpolation techniques. Differences in the absolute values due to methodological differences might seem marginal if the peak concentration of the mid-1960s is used as a time-marker, however if data is used as input in tritium mass balance models in the post-bomb period differences become highly important (Li et al., 2019).

The aim of this study was to create a spatially continuous gridded database for tritium (isoscape) in precipitation across the Adriatic-Pannonian Realm for the decades around the turn of the 21st century with a special focus on the post-2010 which is not covered by the existing global models.

2. Materials and Methods

2.1. Used ^{3}H and precipitation data

An initial dataset was collected with 8450 monthly precipitation tritium activity values from 46 stations covering the period from Jan 1961 to Dec 2017 obtained from GNIP (IAEA, 2019), ANIP (Umweltbundesamt, 2019), SLONIP (SLONIP, 2020; Vreča and Malenšek, 2016), and published data (Fórizs et al., 2020; Krajcar Bronić et al., 2020; Mandić et al., 2008; Palcsu et al., 2018). Until 1973 tritium activity data was only available from Austria. Monitoring of isotopes in precipitation on a larger scale in the region began in the mid-1970s in Belgrade (RS), Zagreb (HR) and Budapest (HU) as well. Following the initiation of these measurements becomes the network suitable - specifically from 1976 - for the spatiotemporal analysis of the largescale variability of precipitation tritium activity in the region. To maximize the spatiotemporal density of the data set not only the Adriatic-Pannonian region, but the bordering areas were included in the analyses as well. The availability of ^{3}H data varied in the investigated period. The relatively abundance of data increased in the early 1980s, early 2000s and from around 2010 onward (Fig. 1a). Between 2003 and 2005, the number of stations dropped (<9, Fig. 1a) due to a halt in the data collection of the Austrian stations. This was the lowest number of active stations in the investigated period. For the purpose of further calculations, the geographical coordinates of the stations were converted from latitude and longitude (EPSG: 4326, WGS84 projection) to metric coordinate system (EPSG:3857, WGS 84 / Pseudo-Mercator projection), since interpolation (variography see Sect. 2.3) has to be done on a metric scale. To be able to derive amount weighted annual tritium activity averages, monthly precipitation amounts were used from the GPCC's (1.0° × 1.0°) Full Data Monthly Product Version 2018 (Schneider et al., 2018).

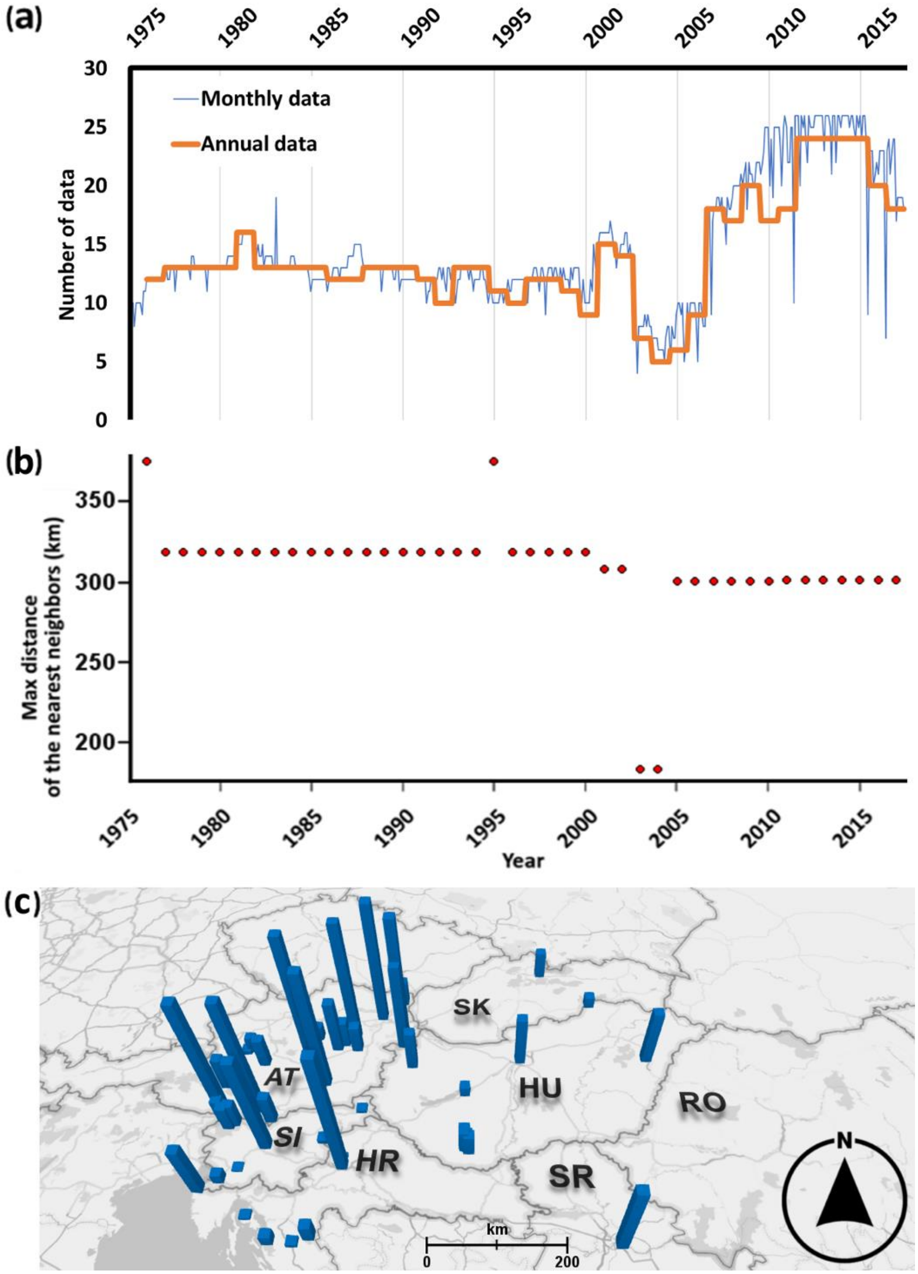

Figure 1 Temporal and spatial characteristics of the dataset. Number of data from precipitation stations producing measurements of ^{3}H (1975-2017) **(a)** The thick orange line represents the number of stations applicable for computing precipitation amount weighted annual averages later used in the interpolation (1976-2017). **(b)** The largest distance between the neighboring active stations of the studied ^{3}H network in each year for 1976-2017. **(c)** Spatial distribution of the monitoring sites, where the height of the blue columns is proportional to the number of monthly data available between 1976 and 2017 at a given station; max = 479 data at Podersdorf Austria. The country codes follow the ISO-3166-1 ALPHA-2. The basemap was taken from Bing maps, HERE Technologies 2019; accessed on 27.09.2019.

2.2. Data preprocessing

A sequential univariate outlier detection procedure (Ben-Gal, 2005) was applied to the data to find possible outlying values, which deviate to a high extent from the other observations (Barnett and Lewis, 1974; Hawkins, 1980). During the procedure, the time series of the stations were pairwise compared for each year. The approach is similar to the relative homogeneity test applied to meteorological data, in which e.g. a candidate station's time series is compared to its neighboring stations'; e.g. (Alexandersson, 1986; Lindau and Venema, 2019; Sugahara et al., 2012).

To avoid comparing a station with all the others from the network, including distant ones recording different environmental conditions (e.g. Alpine region vs. Great Hungarian Plain), the comparison was done only within a given search radius. The network was screened for each station's distance to its nearest neighbor for each year. Then out of all the years, the most frequently occurring largest nearest neighbor (~320 km) was chosen (Fig. 1b) to serve as the search radius for the sequential univariate outlier detection. There were only two years when a station – specifically Belgrade - did not have a pair to compare it with due to its relatively isolated location from the others in the network (Fig. 1c).

Pairwise differences of ^{3}H data in monthly steps were calculated for each station with its neighbors within the ~320 km search radius. These pairwise differences were then averaged per month and the values belonging to the same calendar year were handled together. Due to the decrease in atmospheric concentration in tritium (Palcsu et al., 2018; Rozanski et al., 1991), the difference values were not comparable between the years, so the outliers were identified annually. The monthly average difference values were annually standardized.

It was found that the standardized mean differences were mostly within the ±1 interval (89%) suggesting the usually small difference between neighboring records. In rare occasions (n = 11 occurrences; 0.15%) the difference value was outside the ±7 interval. These deviations were considered as threshold, determining the set of possibly erroneous data (outlier (Ben-Gal, 2005)), which were investigated one-by-one, if possible, by consulting the data providers. Only two monthly values were left out from further calculations both much higher than measured ones compared to their surroundings.

Annual amount-weighted means were only calculated if at least 85% of the fallen precipitation was analyzed for ^{3}H, these years are herein referred to as "complete-year". If more than 15% of the fallen precipitation was not analyzed for ^{3}H, the year in question will be referred to as an "incomplete-year". This required completeness is stricter criterion than the GNIP protocol (70%; (IAEA, 1992). These amount-weighted annual averages served as the input values for deriving the isoscapes with variography. An additional checking was performed on the amount weighted annual means using h-scattergrams (Bohling, 2005) which did not find any outliers that have been introduced by the weighting procedure confirming that the dataset satisfies certain prerequisites of kriging.

A robust hemispheric-scale pattern is a poleward increasing trend of precipitation ^{3}H (Rozanski et al., 1991). Regression analysis between geographical latitude (using the metric coordinates in EPSG: 3857) and amount weighted-annual precipitation ^{3}H activity concentration mostly yielded insignificant linear relationships or contradictory to what was expected (i.e. poleward decreasing values e.g. 1987). The limited latitudinal extent of the study area (5°) might explain the failure to detect the expected relationship. However, due to the lack of a clear spatial trend statistical trend removal was not conducted on the amount-weighted annual mean ^{3}H activities instead they were used for regional isoscape modeling.

2.3. Derivation of precipitation amount-weighted annual mean tritium activity isoscapes

Semivariograms (Webster and Oliver, 2008) were used as the weighting function in kriging (Cressie, 1990) to explore the spatial variance of precipitation amount-weighted annual mean ^{3}H activity for the stations of the Adriatic-Pannonian region. The empirical semivariogram may be calculated using the Matheron algorithm (Matheron, 1965), where $\gamma(h)$ is the semivariogram and $Z(x)$ and $Z(x+h)$ are the values of a parameter sampled at a planar distance $|h|$ from each other

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \tag{1}$$

$N(h)$ is the number of lag-h differences, i.e. $n\times(n$-1)/2 and n corresponds to the number of sampling locations at a distance h. The most important properties of the semivariogram are the nugget, quantifying the variance at the sampling location (including information regarding the error of the sampling), the sill that is, the level at which the variogram stabilizes, which is the sum of the nugget (c_0) and the reduced sill (c), and the range (a), which is the distance within which the samples have an influence on each other and beyond which they are uncorrelated (Chilès and Delfiner, 2012). If the semivariogram does not have a rising part and the points of the empirical semivariogram align parallel to the abscissa, a nugget-type variogram is obtained. In this case, the sampling frequency is insufficient to estimate the sampling range using variography (Hatvani et al., 2017).

For geostatistical modeling (e.g. kriging), theoretical semivariograms have to be used to approximate the empirical ones (Cressie, 1990). Gaussian semivariograms were obtained with a maximum lag distance of 400 km and 11 uniform bins (steps) in order to achieve the most balanced number of station pairs per bin in the analysis. The effective (or even called practical) range (a_e), which is the distance within which the samples have an influence on each other and beyond which they are uncorrelated (Chilès and Delfiner, 2012) were determined and used to evaluate the spatial representativity of the network. In the case of Gaussian semivariograms $a_e = \sqrt{3} \times a$)(Wackernagel, 2003). The reported ranges in the study area are planar distances in km; conversion to geodetic distance in the region: $d_{planar} \times 0.678 \approx d_{geodetic}$.

Semivariograms applicable for interpolation were obtained from years 1977, 1982, 1983, 2001, 2010, and from 2012 to 2015 which, unsurprisingly, belonged to the periods with a relatively higher abundance of data (Fig. 1a). Common characteristics of the variograms from these years (further on used as the *reference years)* were that (i) the number of stations behind the variograms from these years varied between 13 and 24 and (ii) the variograms had at least 11 pairs in the first 3 bins without any empty ones. This seemed a minimum requirement in the present database to derive theoretical variograms suitable for kriging.

The years with a reduced number of available stations (Fig. 1a) produced semivariograms not applicable for kriging (for technical explanation see Appendix 1), because the data were sporadically spread in space and/or none of the stations provided continuous measurements in time. Both types of data gaps can be classified as missing at random (MAR) (Little and Rubin, 2002). Because most modern data-imputation-methods start by assuming the missing data is MAR, imputation tools could have been applied in years with insufficient data density for proper interpolation. However, in every case, no method can provide an 'automatic' solution to the problem of missing data, and any approach must be used with caution considering the context of the problem (Kenward and Carpenter, 2007); for instance, the accuracy of the imputed value will not be optimal and the spatial correlation and intra-variable relationships will be corrupted (Barnett and Deutsch, 2015).

Thus, in these – so called - "intermediate" years, the semivariogram of the reference years having the most overlap with regard to its station distribution, was used as the weight for kriging. To do so, it was investigated for each intermediate year, how many sites are commonly active in its temporally neighboring reference year. The following requirements were also considered:

- the maximum number of sites active in a given intermediate year which are not active in the reference year can be 3
- if the difference in the number of active stations between an intermediate year and the "neighboring" two reference years is the same, then the semivariogram of the reference year with the greater number of active stations was used rendering that variogram more robust,
- and the one closest to the intermediate year in time.

Finally, 46 stations were considered for further evaluation out of which 41 stations were used for tritium isoscape derivation. The amount weighted annual tritium activities from these 41 stations were used to derive the gridded (1 × 1 km) annual precipitation ^{3}H isoscapes across Slovenia and Hungary for 1976-2017, called the AP^{3}H_v1 database, using ordinary point kriging with the assigned variograms derived as discussed above. Note here, that the grid resolution was chosen based on practical consideration, it does not aim to imply that there are such fine km-scale differences, yet help the users to delineate smaller outcrops of e.g. watershed areas more accurately.

For out-of-sample verification two stations were withheld from Hungary and Slovenia each: Nick (HU; active: 1990-2004) and Zgornja Radovna (SI; active: 2010-2017) to validate that the interpolated product is useful and -in a sense- justifies the application of kriging in the region. Two additional stations recorded precipitation ^{3}H for multiple, but exclusively 'incomplete-years': Jósvafő (HU; active: 1988-1996) and Malinska (HR; active: 2000-2001) that were not applicable for variography, yet were used to further test the performance of the geospatial model of precipitation ^{3}H and the critical limit of ratio of annual precipitation amount with missing ^{3}H data. Lastly, an additional short record from Siófok (HU; active: 2013-2016) was also excluded from the spatial model to compare it with the interpolated data; see Sect. 4.

All computations were performed with Golden Software Surfer 15, ArcGIS 10, GS+ 10 and R (R Core Team, 2019) using the script in Supplement. For certain visualizations of the results, Gimp 2.8 and MS Excel 365 were used.

Table 1: Sampling sites with basic geographical information used in the study arranged alphabetically by country codes (ISO-3166-1 ALPHA-2) and station names. The number of monthly precipitation ^{3}H activity concentration data between 1976 and 2017 used in this study is indicated as well as the number of monthly data available in the Global Network of Isotopes in Precipitation in the same period (column title GNIP). The stations below the dashed line were used for model performance testing; for details see Sect. 4.

Country	Station	Latitude	Longitude	Elevation	No. of data (1976-2017)	GNIP
AT	Apetlon	47.741	16.831	119	321	
AT	Bad Aussee	47.600	13.783	640	15	
AT	Eisenkappl	46.489	14.584	550	106	
AT	Gloggnitz	47.675	15.943	440	96	
AT	Gößl	47.640	13.901	710	59	
AT	Graz Universität	47.078	15.450	366	447	321
AT	Gutenstein	47.875	15.886	475	447	
AT	Karlgraben	47.678	15.560	775	193	
AT	Klagenfurt	46.643	14.320	447	445	318
AT	Lackenhof	47.870	15.142	882	51	
AT	Nasswald	47.764	15.688	774	95	
AT	Planneralm	47.403	14.200	1605	106	
AT	Podersdorf	47.855	16.835	120	467	
AT	St. Peter im Katschtal	47.027	13.596	1220	121	
AT	Villacher Alpe	46.603	13.672	2164	451	334
AT	Wien Hohe Warte	48.249	16.356	203	444	421
AT	Wildalpen	47.664	14.978	610	447	
AT	Zistersdorf	48.544	16.750	201	88	
HR	Plitvice	44.881	15.619	580	65	27
HR	Puntijarka	45.908	15.968	988	9	
HR	Tonkovića	44.790	15.368	432	13	
HR	Zagreb[1]	45.817	15.983	157	473	325
HR	Zavižan	44.815	14.976	1594	39	38
HU	B	46.070	18.111	177	104	
HU	Boda	46.087	18.047	233	135	

HU	Budapest	47.464	19.073	101	287	181
HU	Debrecen	47.475	21.494	110	202	
HU	Het	46.125	18.047	165	136	
HU	II	46.100	18.093	332	79	
HU	V	46.122	18.092	330	60	
HU	Z	46.037	18.125	117	137	
RS	Belgrade	44.783	20.533	243	283	283
SI	Kozina	45.604	13.932	486	35	35
SI	Kredarica	46.379	13.849	2514	91	
SI	Ljubljana[2]	46.095	14.597	282	371	291
SI	Murska Sobota	46.652	16.191	186	11	
SI	Portorož	45.467	13.617	2	196	70
SI	Postojna	45.766	14.198	533	5	
SI	Rateče	46.497	13.713	864	88	
SI	Sv. Urban	46.184	15.591	283	16	
SK	Liptovský Mikuláš	49.098	19.590	570	96	96
HR	Malinska	45.121	14.526	1	10	10
HU	Jósvafő	48.484	20.551	211	39	
HU	Nick	47.385	17.036	139	142	
HU	Siófok	46.911	18.041	108	39	
SI	Zgornja Radovna	46.428	13.943	750	89	

1: In the investigated period two stations were conducting measurements in Zagreb in a non-overlapping way (Krajcar Bronić et al., 2020)

2: In the investigated period three stations were conducting measurements in Ljubljana in a non-overlapping way (Vreča et al., 2014; Vreča et al., 2008)

3. Tritium isoscapes from 1976 to 2017

The obtained regional gridded precipitation amount-weighted annual mean ^{3}H activity time series for the Adriatic-Pannonian region (AP^{3}H_v1 database) capture the well-known decrease in precipitation ^{3}H activity (e.g. Fig. 2).

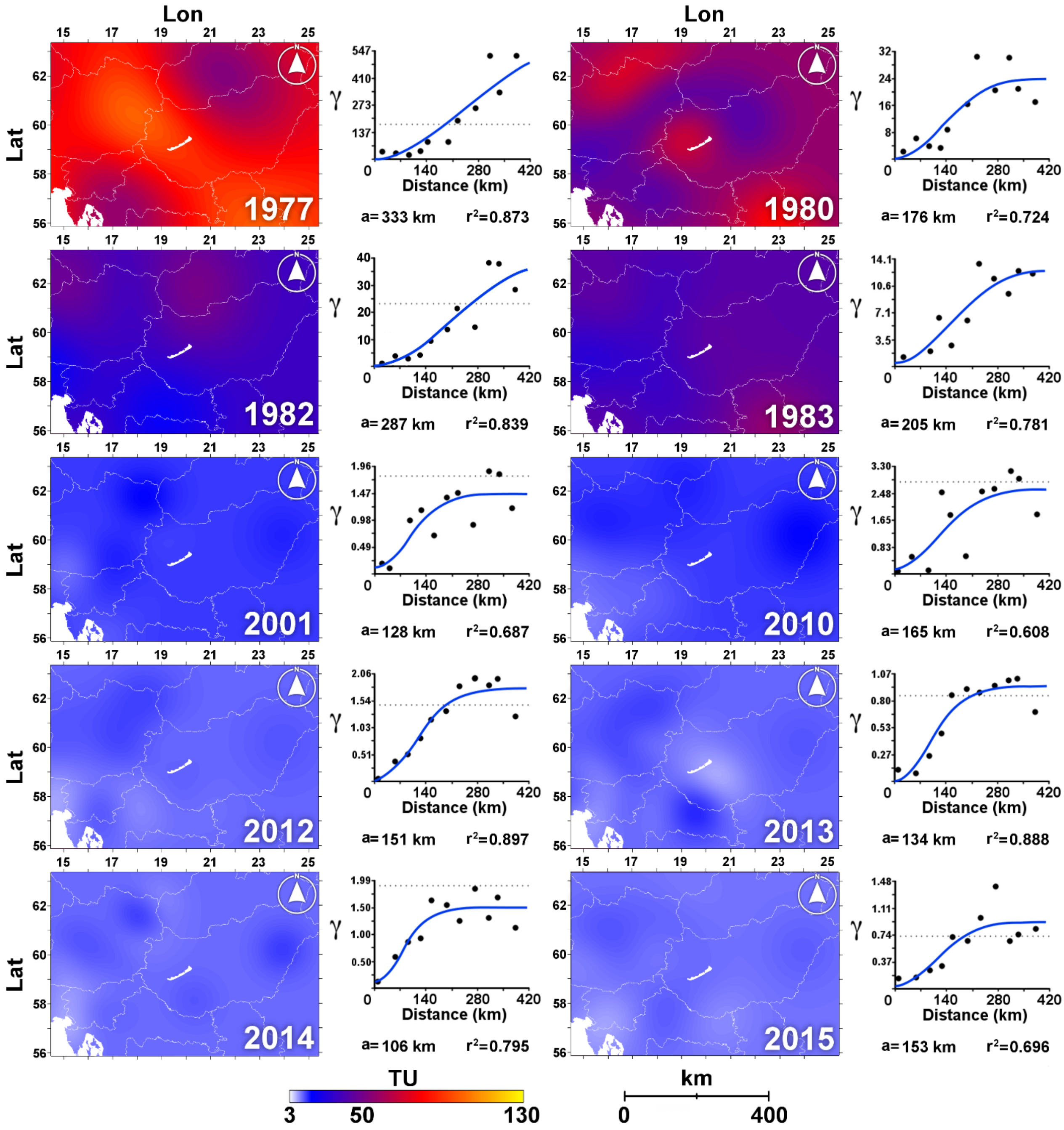

Figure 2 Isoscapes of amount-weighted annual mean ^{3}H activity (TU) in precipitation and semivariograms for the reference years in the Adriatic-Pannonian Region. The Adriatic Sea and Lake Balaton are marked in white. Isoscape grid resolution: 1 × 1 km. The figures on the right side of the isoscapes show the empirical (black dots) and theoretical semivariograms (blue line) used for kriging along with the obtained ranges (a planar distances in km) and the fit (r^2) of the theoretical semivariograms. The dotted horizontal line indicates the average variance.

Besides this most striking long-term temporal pattern prevailing in the whole region seen from the isoscapes subregional differences in precipitation ^{3}H activity within the region is also reconstructed. Although no significant relationship was documented between latitude and/or continentality, still increasing precipitation ^{3}H activity was observable inland with the lowest values documented along the Slovenian and northern Croatian coast in all years (see e.g. 1982, 2010, 2014; Fig. 2). This pattern can be related to the generally observed lower activity at maritime coastal stations due to the higher contribution of primary marine evaporation practically free from ^{3}H (Eastoe et al., 2012; Rozanski et al., 1991; Tadros et al., 2014; Vreča et al., 2006) and higher contribution of recycled modern meteoric water over the continent. For instance, moisture originating from continental Europe and the Atlantic Ocean was found to be distinct regarding tritium concentrations (8.8 TU and ~0 TU, respectively) (Juhlke et al., 2020).

Two of the longest records from Slovenia (Ljubljana) and Hungary (Budapest) illustrate the performance of the estimations and their potential in mitigating lack of data. Budapest and Ljubljana ^{3}H records – 'complete-years' were used both in the variograms of the "anchor years" and in the interpolation - were compared to the interpolated product's time series of the nearest grid cell (Fig. 3). In the 'complete-years', when the measured values were used in interpolation, there is an expected perfect match between the measured and modelled values. It becomes clear that the estimated records are more than capable in filling the gaps of the measured time series, when there were no measurements (e.g. Ljubljana: 1985 and 1996; Fig. 3b). and usually provide a higher mean annual precipitation ^{3}H in the case of 'incomplete-years'. The magnitude of differences between the measured and modeled data in the 'incomplete-years' varied between ~16.5 and 1 TU for Budapest and Ljubljana, with a general tendency of obtaining higher differences with a higher ratio of precipitation not represented by tritium measurements.

The distinctive interannual fluctuation of amount-weighted annual mean ^{3}H activity at Budapest and Ljubljana (Fig. 3) also indicate that the AP^{3}H database produced differing sub-regional variability over the modelled time. In the whole investigated period (1976-2017) the coefficient of variation of the annual differences between the precipitation ^{3}H values of the 'complete-years' in Budapest and Ljubljana was 62%, calling for the need for spatially representative estimates, such as the ones presented from the AP^{3}H database. In the period when both stations were parallel active (1981-2003, excluding the 'incomplete-years') the precipitation ^{3}H activity in Budapest was higher by 5.5 TU than in Ljubljana on average, and this difference is quite well reflected by the AP^{3}H data which were 4.57 TU higher at Budapest on average. Besides these overall differences, distinct interannual variability can be observed at the Ljubljana and Budapest stations. For example, the maxima of the modelled precipitation ^{3}H activity occurred in 1976 at the Ljubljana- and in 1978 at the Budapest station, and a minor peak seen in 1988 at Budapest (Fig. 3a) was without a counterpart in the Ljubljana records (Fig. 3b).

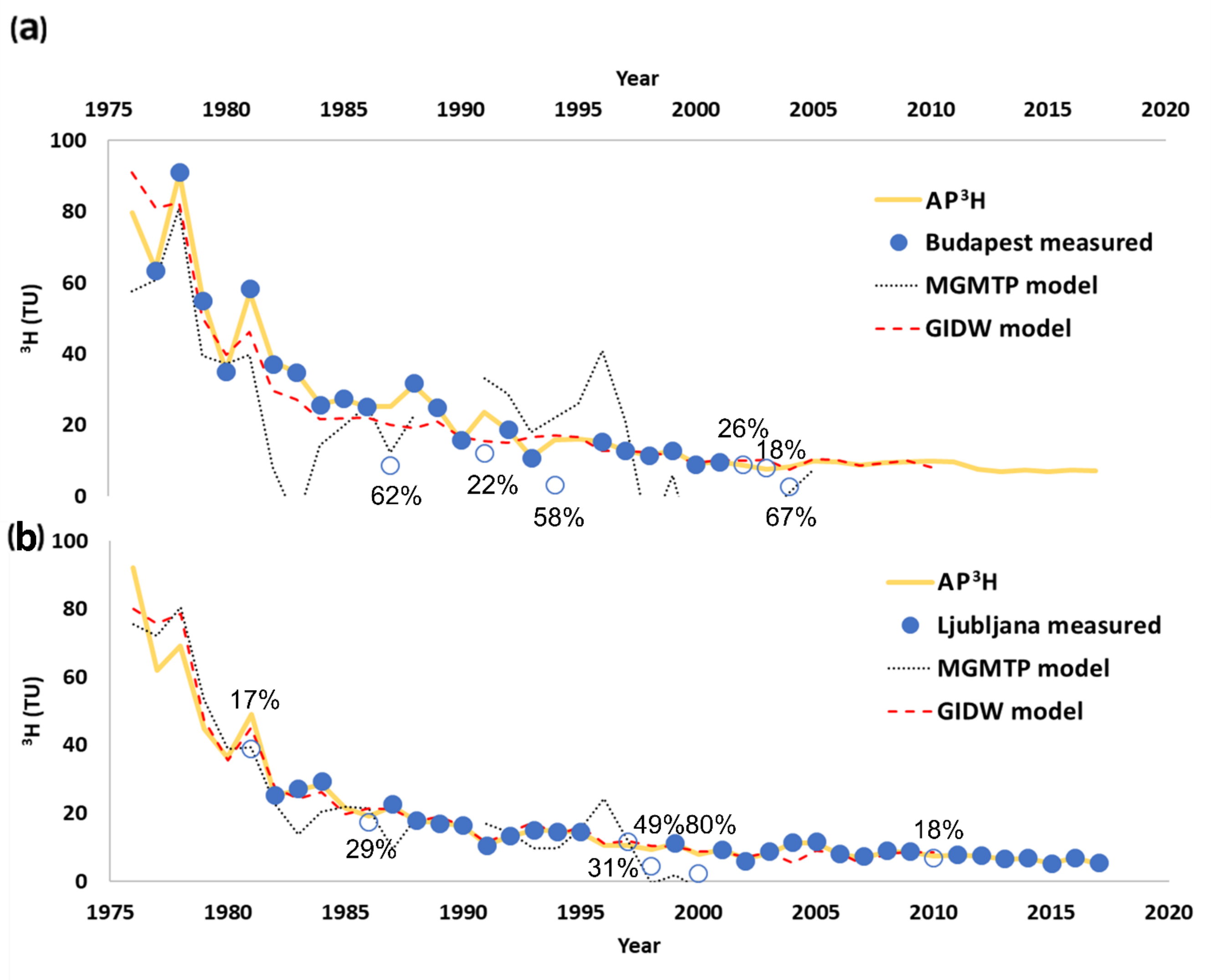

Figure 3 Measured and estimated ^{3}H values at **(a)** Budapest, Hungary and **(b)** Ljubljana, Slovenia between 1976 and 2017. The black dotted lines indicate the estimations of the 'modified global model of tritium in precipitation' (MGMTP; (Zhang et al., 2011)) and the red dashed ones indicate the Global inverse distance weighted model (GIDW; (Jasechko and Taylor, 2015)). Note here that uninterpretable negative estimates of MGMTP were not shown. The empty circles indicate an 'incomplete-year' in which the given ^{3}H value was not used for interpolation in the AP^{3}H database and the percentages next to these symbols indicate the ratio of fallen precipitation not analyzed for ^{3}H in a given year.

The estimated effective range show a decrease in the spatial autocorrelation of tritium activity concentration of precipitation from the 1970s to the 2010s: ~440 km in the 1970s, ~425 km in the 1980s, to ~360 km and 235 km in the 2000s and 2010s respectively (Fig. 4). This period (1970-2010) was characterized by the removal of bomb-tritium from the atmosphere (Araguas-Araguas et al., 1996; Palcsu et al., 2018). The overwhelming activity of bomb-produced ^{3}H was several orders of magnitude higher than the natural background (Rozanski et al., 1991), and largely masked the smaller-scale natural variability. During recent decades the tritium activity in precipitation has declined globally and regionally, approaching the natural pre-bomb levels indicating that the bomb-tritium is now barely present in modern precipitation. Since, in the Adriatic Pannonian region, the ^{3}H activity in precipitation approached natural levels by the 2000s (Krajcar Bronić et al., 2020; Palcsu et al., 2018; Vreča et al., 2008), it can be expected that the ~200-300 km range obtained for the 2010s reflects the range of similarity of natural ^{3}H variability in the study area (SE Europe and E Central Europe).

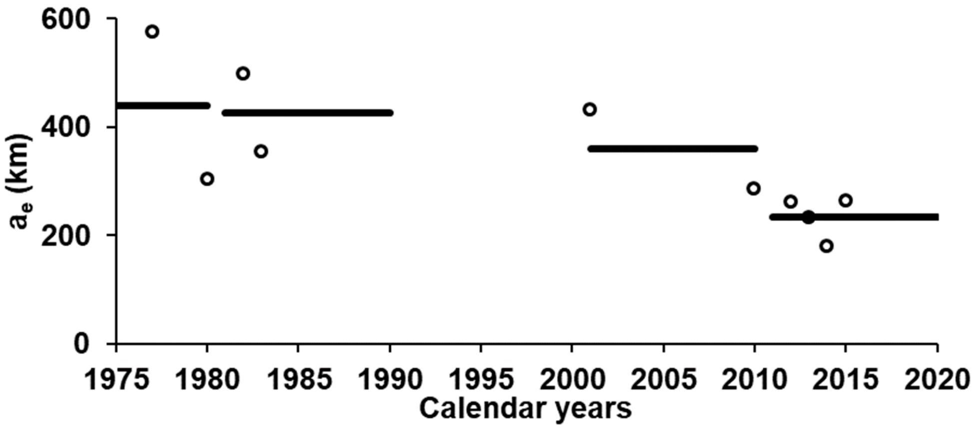

Figure 4 Effective ranges (a_e) of the semivariograms used for kriging. Annual ranges are indicated by empty circles, and the decadal averages by horizontal black lines.

4. Verification of goodness of interpolation

The performance of the AP^{3}H database replicating measured precipitation ^{3}H activity was tested via out-of-sample verification. The actual amount-weighed annual mean precipitation ^{3}H activity time series at a Hungarian (Nick, Fig. 5a) and a Slovenian (Zgornja Radovna, Fig. 5b) station were compared to the AP^{3}H data of the grid cell closest to the specific stations. The annual mean precipitation ^{3}H activity estimates from the AP^{3}H database nicely fitted to the amount-weighed annual mean precipitation ^{3}H activity data for both independent records even if a small portion (<8%) was not represented with measured ^{3}H in the experimental data (Fig. 5a,b). The agreement between the independent mean annual precipitation ^{3}H record and the AP^{3}H estimates is superb for Zgornja Radovna where the difference between modeled and actual values ranged from 1 to 6% (mean: 3.2%). The difference between modeled and actual values in ‘complete-years’ for Nick ranged from 0 to 31% (mean: 8.3%). The relatively larger mean error for the Nick record is due to an overestimation of the model values in 1994 (Fig. 5a); however, the model data fit to the rest of the measured ones as good as seen for Zgornja Radovna. The pattern observed for the ‘incomplete-years’ strengthens previous impressions that (i) modeled mean annual precipitation ^{3}H is higher than the mean calculated from just a few monthly measurements and (ii) there is a tendency of obtaining higher differences with a higher ratio of precipitation not represented by tritium measurements. The comparison between the modeled and actual values for the stations recorded precipitation ^{3}H for multiple, but exclusively 'incomplete-years', further strengthens these impressions.

Station records from Nick and Zgornja Radovna were not used in the interpolation to derive the AP^{3}H database, yet perfectly match the actual values when ^{3}H activity concentration was measured for the total volume of annual precipitation. This excellent agreement supports the assumption that the AP^{3}H database provides similarly accurate estimates as at other stations for the 'incomplete-years', as well. If so, then differences between the AP^{3}H data and the mean precipitation ^{3}H activity estimates accompanied with certain portion of precipitation amount lacking ^{3}H activity can represent a weighting bias due to the fragmented observation record. Comparing the differences between the estimated mean precipitation ^{3}H activity values from these fragmented records and the AP^{3}H estimates to the percentage of precipitation amount lacking ^{3}H activity data in the so called 'incomplete-years' for Zgornja Radovna, Nick, Jósvafő, and Malinska reveled the relation between these characteristics (Fig. 5e). If ^{3}H activity was lacking for less than 15% of the annual precipitation total the difference between the calculated mean precipitation ^{3}H activity values and the AP^{3}H estimates is practically negligible (Fig. 5e). The difference between modeled and calculated mean precipitation ^{3}H considerably increased (> 6 TU) if the proportion of the precipitation lacking ^{3}H activity was between 15% and 30% of the annual precipitation total (Fig. 5e). According to the GNIP protocol the required completeness is 70% of the precipitation total for calculating amount-weighted mean isotopic values for a certain period (IAEA, 1992). Above results (Fig. 5e) confirm that 30% missing data is indeed a critical limit because if exceeded, each calculated mean precipitation ^{3}H activity value of these scanty annual datasets showed great deviation from the modeled values. However, occasionally, a precipitation deficit over 15%, yet under 30%, causes a noticeable difference (Fig. 5e) suggesting that fewer than 30% missing data may be advisable for the calculation of a representative amount-weighted isotopic means. In addition, these reinforcing the decision made in the present study to only include values for which more than 85% fallen precipitation was analyzed for ^{3}H.

Although at Nick and Zgornja Radovna –as seen above– the AP^{3}H database provides a realistic estimation (Fig. 5a,b) one may ask why are the calculated annual mean precipitation ^{3}H activity values are systematically higher at Siófok (mean difference in the 'complete-years': 1.52 TU) than AP^{3}H data (Fig. 5d). It could be explained by the closeness of the largest shallow lake in Central Europe, Lake Balaton (Hatvani et al., 2020). The mean residence time in the largest basin of the lake, Siófok Basin, was estimated to be between two and six years in the 1990s (Istvánovics et al., 2002), which presumably in the same range in the 2010s as well. Keeping in mind the gradual decrease of ^{3}H in meteoric waters (in the region e.g. Fig. 4), the local evaporation from this 'aged' reservoir can provide an isotopically detectable contribution to the atmospheric moisture which can be transferred to the falling rain droplets via molecular exchange mechanisms (Bolin, 1959), resulting in higher tritium activity values at the Siófok station than the ones from the AP^{3}H database(Fig. 5d). This is a simple example illustrating the potential of this new regional annual mean precipitation ^{3}H activity database (AP^{3}H_v1) in hydrological applications.

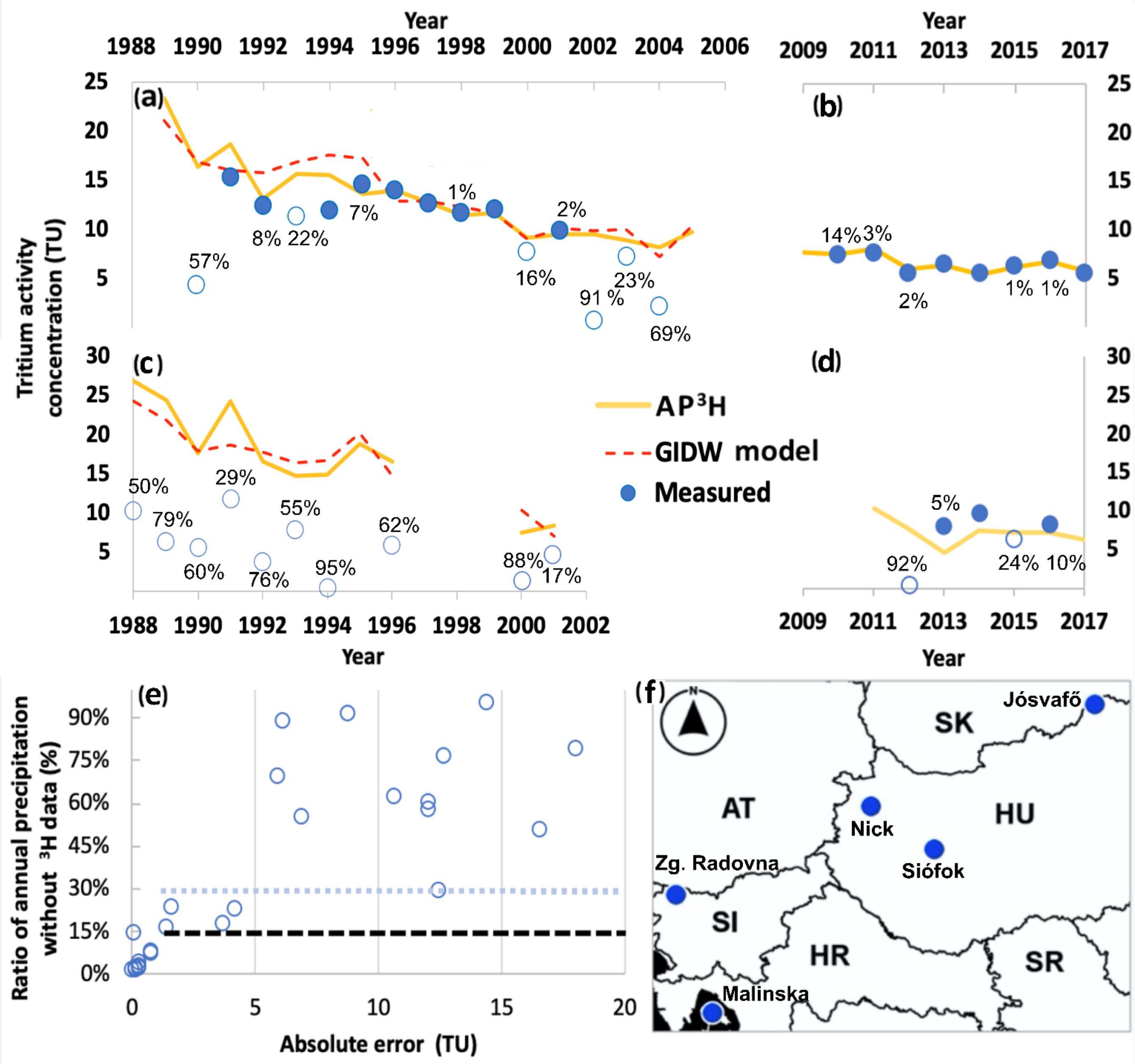

Figure 5 Amount-weighted annual mean ^{3}H activity concentration in precipitation measured at **(a)** Nick (1990-2004; HU), **(b)** Zgornja Radovna (2010-2017; SI) **(c)** Jósvafő (HU; 1988-1996) and Malinska (2000-2001; Krk Island; HR), and **(d)** Siófok (2009-2017; HU) stations along with the corresponding AP^{3}H esitmates. The percentages next to the symbols of the measured values indicate the ratio of fallen precipitation not analyzed for ^{3}H in a given year, if it was >0%. The red dashed line in panels **(a)** and **(c)** show the corresponding values of Global inverse distance weighted model (GIDW; (Jasechko and Taylor, 2015)). **(e)** Cross plot showing the relation between absolute error of estimated precipitation ^{3}H activity by the AP^{3}H and the percentage of precipitation without ^{3}H measurement at Nick, Zgornja Radovna, Jósvafő, and Malinska. Thick dashed line mark the limit of completeness (15%) applied in this study, while gray dotted line marks the limit

of completeness (30%) according to the GNIP protocol (IAEA, 1992). **(f)** The map shows the location of the five sites used for evaluation of the performance of the AP^{3}H database.

5. Comparison between global and regional modelled annual mean ^{3}H activity concentrations in precipitation across the Adriatic-Pannonian Region

The presented AP^{3}H_v1 database of tritium activity was compared with the spatially corresponding output of both currently available global precipitation tritium isoscapes: the Modified global model of tritium in precipitation (MGMTP (Zhang et al., 2011)) and the Global inverse distance weighted model (GIDW) at Budapest (Fig. 3a) and Ljubljana (Fig. 3b). Between 1975 and 1980 the estimates from the AP^{3}H database and the MGMTP are very similar and resemble the actual weighted annual mean precipitation ^{3}H at Budapest. However, only at Ljubljana is the MGMTP capable of steadily reproducing the actual measurements until the late-1990. Afterwards, it indicates solely negative values, which are uninterpretable, just as most of the MGMTP predicted values at Budapest after 1980. In the meanwhile, the AP^{3}H database provided much more accurate and reliable results (Fig. 3) as discussed above. Note here, that the weak estimation of the MGMTP can be attributed to the difficulties in reading the precipitation tritium activity values from the only available output (isoline map) of the model and the undocumented factors of the model in given years.

The GIDW (Jasechko and Taylor, 2015) model was capable of reproducing the measured precipitation tritium values much more accurately at all locations than the MGMTP (Fig. 3). Nevertheless, the GIDW model produced a striking overestimation at the beginning of the modelled period, for example, in 1977, when the measured values at Budapest were overestimated by >20 TU (Fig. 3a). On the contrary, the GIDW model underestimated the actual values from 1981 to 1991, except for one year (Fig. 3a).

The skills of the AP^{3}H database and the GIDW model could only be compared at Nick station because the record of Zgornja Radovna starts in the terminal year of the GIDW model's coverage. In the first 'complete-year' of the Nick record the GIDW estimation is closer to the actual measurements compared to the AP^{3}H estimations, however from 1992 to 1994 the GIDW estimations show much higher (mean error: 4.6 TU) annual mean ^{3}H activity compared to the values calculated from the monthly measurements. In the meanwhile the difference with the AP^{3}H estimations is smaller (mean error: 2.2 TU). Interannual variations of the estimated precipitation ^{3}H activity from the GIDW and the AP^{3}H database are in agreement at Jósvafő and the models are largely in agreement regarding the absolute values and the decreasing trend, too.

However, the MGMTP had practically no success in estimating the actual measured values. For instance, in both 2000 and 2001 the MGMTP produced negative - thus meaningless - values at Malinska, when direct measurements were available, while the present database provided more reliable estimates (Fig. 5c).

Taken all together, the AP^{3}H_v1 database gave better regional estimates, than either of the global models. This may be because i) the AP^{3}H database is based on more local station-data for the study area compared to the global models relying only on the GNIP records (Table 1) and ii) the improved performance of the database obviously benefitted from incorporating the spatial correlation structure of precipitation tritium activity into the presented geostatistical prediction.

6. Possibility of applications (outlook, conclusions)

Continuous long-term records of tritium in precipitation are scarcely available worldwide, thus estimations or modelling are necessary to exploit its potential in hydrological researches. In order to decrease the uncertainty of tritium activity in the hydrological models, the application of regional ^{3}H models have to be increased, since these are more capable of producing accurate estimations than global ones (Stewart and Morgenstern, 2016).

Instead of using remote station data or ad hoc composite curves, site specific time-series retrieved from the presented AP^{3}H_v1 database of precipitation amount-weighted annual mean ^{3}H isoscapes should be used. These isoscapes (Kern et al., 2019) can serve as a reference dataset for studies on infiltration dynamics, water transport through various compartments of the hydrological cycle, mixing processes, run-off modelling; e.g. to estimate mean residence time in surface waters and groundwater (Kanduč et al., 2014; Ozyurt et al., 2014; Szucs et al., 2015). As a specific type of hydrogeological application, the Regional model of ^{3}H time-series will serve as a benchmark in estimating the mean infiltration age of dripwater (Kluge et al., 2010) which can provide an additional tool for ongoing cave monitoring studies from the region (e.g. Czuppon et al. (2018); Czuppon et al. (2013); Fehér et al. (2016); Surić et al. (2010)) in a spatiotemporally accurate way.

The higher precipitation ^{3}H activity observed at a lakeshore station (Fig. 5c) likely reflects moisture recycling from the aged lake surface water via evaporation to the local precipitation. The observed deviation highlights the potential of the database to reveal sub-regional anomalous local sources in the hydrological cycle. As a special case the post-2010 isoscapes can serve as benchmarks for background tritium activity for the region, helping to determine local increases of technogenic tritium from these backgrounds.

The AP^{3}H database was able to provide better estimates than either of the currently available global models for the study area. Its values seem capable of reproducing the actual annual mean precipitation ^{3}H activity than from the fragmented ^{3}H data representing fewer than 85% of the annual sum of precipitation. Prior to 1975 we encourage the use of the GIDW model's estimations (Jasechko and Taylor, 2015) as a reference for studies dealing with precipitation tritium activity. The Regional model and the GIDW model should be spliced together at 1975 and can be used together in the need of a semi-centennial precipitation tritium activity dataset.

7. Data format and availability

The final product (AP3H_v1.nc), the spatially continuous annual (1976-2017) 1×1 km grids of precipitation amount-weighted annual mean tritium activity for the Adriatic-Pannonian Region is provided in a netCDF-4 (net-work common data form) format available at PANGAEA (https://doi.pangaea.de/10.1594/PANGAEA.896938) (Kern et al., 2019), compiled using the EPSG 3857 projection. For a solely visual inspection of the annual grids Panoply (https://www.giss.nasa.gov/tools/panoply/) is recommended. An `R`-script written to be able to browse the dataset and convert the projection to EPGS 4326 is provided in the supplement. This publication describes AP^{3}H_v1 database. As the database is updated with corrected or extended new data the new versions will be indexed with incrementing integers.

8. Author contribution

ZK designed the experiments. PV, MŠ, TK, LP, MS, GyC and IKB contributed data. IGH and DE developed the model code and performed the analyses. ZK, IGH, PV and DE prepared the manuscript with contributions from TK, MŠ, IF, and BK. The authors applied the FLAE approach for the sequence of authors. See https://doi.org/10.1371/journal.pbio.0050018 for further details. All authors took part in the manuscript preparation, and revision.

9. Competing interests:

The authors declare that they have no conflict of interest.

10. Acknowledgements

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References

Alexandersson, H.: A homogeneity test applied to precipitation data, Journal of Climatology, 6, 661-675, doi: doi:10.1002/joc.3370060607, 1986.

Alvarez, L. W. and Cornog, R.: Helium and Hydrogen of Mass 3, Physical Review, 56, 613-613, doi: 10.1103/PhysRev.56.613, 1939.

Ansari, M. A., Sinha, U. K., Deodhar, A., Mendhekar, G. N., Kumar, M., Patbhaje, S. D., and Dash, A.: Evaluation of groundwater tritium content and mixing behavior of Tatapani geothermal systems, Chhattisgarh, India, Journal of Radioanalytical and Nuclear Chemistry, 313, 617-623, doi: 10.1007/s10967-017-5377-9, 2017.

Araguas-Araguas, L., Danesi, P., Froehlich, K., and Rozanski, K.: Global monitoring of the isotopic composition of precipitation, Journal of Radioanalytical and Nuclear Chemistry, 205, 189-200, doi: 10.1007/BF02039404, 1996.

Barnett, R. M. and Deutsch, C. V.: Multivariate Imputation of Unequally Sampled Geological Variables, Mathematical Geosciences, 47, 791-817, doi: 10.1007/s11004-014-9580-8, 2015.

Barnett, V. and Lewis, T.: Outliers in Statistical Data, John Wiley and Sons, Chichester, 1974.

Ben-Gal, I.: Outlier Detection. In: Data Mining and Knowledge Discovery Handbook, Maimon, O. and Rokach, L. (Eds.), Springer US, Boston, MA, 2005.

Bohling, G.: Introduction to geostatistics and variogram analysis, Kansas geological survey, 1, 1-20, 2005.

Bolin, B.: On the use of tritium as a tracer for water in nature, International Meteorological Inst., Stockholm, 1959.

Chatterjee, S., Gusyev, M. A., Sinha, U. K., Mohokar, H. V., and Dash, A.: Understanding water circulation with tritium tracer in the Tural-Rajwadi geothermal area, India, Applied Geochemistry, 109, 104373, doi: https://doi.org/10.1016/j.apgeochem.2019.104373, 2019.

Chilès, J.-P. and Delfiner, P.: Geostatistics, Wiley, Canada, 2012.

Cressie, N.: The origins of kriging, Math Geol, 22, 239-252, doi: 10.1007/BF00889887, 1990.

Czuppon, G., Demény, A., Leél-Őssy, S., Óvari, M., Molnár, M., Stieber, J., Kiss, K., Kármán, K., Surányi, G., and Haszpra, L.: Cave monitoring in the Béke and Baradla caves (Northeastern Hungary): implications for the conditions for the formation cave carbonates, International Journal of Speleology, 47, 13-28, 2018.

Czuppon, G., Kern, Z., Kármán, K., Németh, S., John, S., Haszpra, L., Kohán, B., Kiss, K., Siklósy, Z., and Polacsek, Z.: Spatial and temporal variations of dD and d18O values of cave drip waters: implicationsfor paleoclimate signal in stalagmite, Central European Geology 56, 274-276, doi: 10.1556/CEuGeol.56.2013.2-3.1, 2013.

Doney, S. C., Glover, D. M., and Jenkins, W. J.: A model function of the global bomb tritium distribution in precipitation, 1960–1986, Journal of Geophysical Research: Oceans, 97, 5481-5492, doi: 10.1029/92jc00015, 1992.

Eastoe, C. J., Watts, C. J., Ploughe, M., and Wright, W. E.: Future Use of Tritium in Mapping Pre-Bomb Groundwater Volumes, Groundwater, 50, 87-93, doi: 10.1111/j.1745-6584.2011.00806.x, 2012.

Eyrolle, F., Ducros, L., Le Dizès, S., Beaugelin-Seiller, K., Charmasson, S., Boyer, P., and Cossonnet, C.: An updated review on tritium in the environment, Journal of Environmental Radioactivity, 181, 128-137, doi: https://doi.org/10.1016/j.jenvrad.2017.11.001, 2018.

Fehér, K., Kovács, J., Márkus, L., Borbás, E., Tanos, P., and Hatvani, I. G.: Analysis of drip water in an urban karst cave beneath the Hungarian capital (Budapest), Acta Carsologica, 45, 213-231, 2016.

Fórizs, I., Kern, Z., Csicsák, J., and Csurgó, G.: Monthly data of stable isotopic composition (δ^{18}O, δ^{2}H) and tritium activity in precipitation from 2004 to 2017 in the Mecsek Hills, Hungary, Data in Brief, in review, 2020.

Gessert, A., Straková, V., Palcsu, L., Koltai, G., Braun, M., Heim, E., and Czébely, A.: Differences in temporal changes of selected water quality parameters on Jasovská Planina Plateau (Slovak Karst, Slovakia), GEOGRAPHIA CASSOVIENSIS XIII, 1, 5-20, 2019.

Gibson, J. J., Birks, S. J., and Yi, Y.: Higher tritium concentrations measured in permafrost thaw lakes in northern Alberta, Hydrological Processes, 30, 245-249, doi: 10.1002/hyp.10599, 2016.

Hatvani, I. G., de Barros, V. D., Tanos, P., Kovács, J., Székely Kovács, I., and Clement, A.: Spatiotemporal changes and drivers of trophic status over three decades in the largest shallow lake in Central Europe, Lake Balaton, Ecological Engineering, 151, 105861, doi: https://doi.org/10.1016/j.ecoleng.2020.105861, 2020.

Hatvani, I. G., Leuenberger, M., Kohán, B., and Kern, Z.: Geostatistical analysis and isoscape of ice core derived water stable isotope records in an Antarctic macro region, Polar Science, 13, 23-32, doi: https://doi.org/10.1016/j.polar.2017.04.001, 2017.

Hawkins, D. M.: Identification of Outliers, Springer Netherlands, Dordrecht, 1980.

Hebert, D.: Technogenic Tritium in Central European Precipitations, Isotopenpraxis Isotopes in Environmental and Health Studies, 26, 592-595, doi: 10.1080/10256019008622441, 1990.

Huang, T. and Pang, Z.: Changes in groundwater induced by water diversion in the Lower Tarim River, Xinjiang Uygur, NW China: Evidence from environmental isotopes and water chemistry, Journal of Hydrology, 387, 188-201, doi: https://doi.org/10.1016/j.jhydrol.2010.04.007, 2010.

IAEA: Global Network of Isotopes in Precipitation. The GNIP Database, Http://Www.Isohis.Iaea.Org, last access: 12.11.2019, 2019.

IAEA: Statistical treatment of data on environmental isotopes in precipitation, International Atomic Energy Agency, Vienna, 1992.

Istvánovics, V., Somlyódy, L., and Clement, A.: Cyanobacteria-mediated internal eutrophication in shallow Lake Balaton after load reduction, Water Research, 36, 3314-3322, doi: https://doi.org/10.1016/S0043-1354(02)00036-2, 2002.

Jasechko, S.: Global Isotope Hydrogeology―Review, Reviews of Geophysics, 57, 835-965, doi: 10.1029/2018rg000627, 2019.

Jasechko, S. and Taylor, R. G.: Intensive rainfall recharges tropical groundwaters, Environmental Research Letters, 10, 124015, doi: 10.1088/1748-9326/10/12/124015, 2015.

Juhlke, T. R., Sültenfuß, J., Trachte, K., Huneau, F., Garel, E., Santoni, S., Barth, J. A. C., and van Geldern, R.: Tritium as a hydrological tracer in Mediterranean precipitation events, Atmos. Chem. Phys., 20, 3555-3568, doi: 10.5194/acp-20-3555-2020, 2020.

Kanduč, T., Grassa, F., McIntosh, J., Stibilj, V., Ulrich-Supovec, M., Supovec, I., and Jamnikar, S.: A geochemical and stable isotope investigation of groundwater/surface-water interactions in the Velenje Basin, Slovenia, Hydrogeol J, 22, 971-984, doi: 10.1007/s10040-014-1103-7, 2014.

Kanduč, T., Mori, N., Kocman, D., Stibilj, V., and Grassa, F.: Hydrogeochemistry of Alpine springs from North Slovenia: Insights from stable isotopes, Chemical Geology, 300-301, 40-54, doi: https://doi.org/10.1016/j.chemgeo.2012.01.012, 2012.

Kendall, C. and McDonnell, J. J.: Isotope tracers in catchment hydrology, Elsevier, Amsterdam, The Netherlands, 2012.

Kenward, M. G. and Carpenter, J.: Multiple imputation: current perspectives, Statistical Methods in Medical Research, 16, 199-218, doi: 10.1177/0962280206075304, 2007.

Kern, Z., Hatvani, I. G., Erdélyi, D., Mona, T., and Vreca, P.: Isoscape of precipitation weighted annual mean tritium activities across the Adriatic-Pannonian Region (1976-2017); AP3H_v1 database, PANGAEA, https://doi.pangaea.de/10.1594/PANGAEA.896938, 2019.

Kern, Z., Molnár, M., Svingor, É., Perşoiu, A., and Nagy, B.: High-resolution, well-preserved tritium record in the ice of Bortig Ice Cave, Bihor Mountains, Romania, The Holocene, 19, 729-736, doi: 10.1177/0959683609105296, 2009.

Kluge, T., Riechelmann, D. F. C., Wieser, M., Spötl, C., Sültenfuß, J., Schröder-Ritzrau, A., Niggemann, S., and Aeschbach-Hertig, W.: Dating cave drip water by tritium, Journal of Hydrology, 394, 396-406, doi: https://doi.org/10.1016/j.jhydrol.2010.09.015, 2010.

Koeniger, P., Schwientek, M., Uhlenbrook, S., Leibundgut, C., and Krause, W. J.: Tritium balance in macro-scale river basins analysed through distributed hydrological modelling, Hydrological Processes, 22, 567-576, doi: 10.1002/hyp.6634, 2008.

Krajcar Bronić, I., Barešić, J., Borković, D., Sironić, A., Mikelić, I. L., and Vreča, P.: Long-Term Isotope Records of Precipitation in Zagreb, Croatia, Water, 12, 226, 2020.

Krajcar Bronić, I., Horvatinčić, N., and Obelić, B.: Two decades of environmental isotope records in Croatia: Reconstruction of the past and prediction of future levels, Radiocarbon, 40, 399-416, 1998.

Krajcar Bronić, I., Horvatinčić, N., Srdoč, D., and Obelić, B.: Tritium concentration in the atmosphere over NW Yugoslavia. In: Rare nuclear processes, Proceedings of the 14th Europhysics Conference on Nuclear Physics, Povinec, P. (Ed.), Worlds Scientific, 1992.

Lal, D. and Peters, B.: Cosmic Ray Produced Radioactivity on the Earth. In: Kosmische Strahlung II / Cosmic Rays II, Sitte, K. (Ed.), Springer Berlin Heidelberg, Berlin, Heidelberg, 1967.

Li, Z., Jasechko, S., and Si, B.: Uncertainties in tritium mass balance models for groundwater recharge estimation, Journal of Hydrology, 571, 150-158, doi: https://doi.org/10.1016/j.jhydrol.2019.01.030, 2019.

Lindau, R. and Venema, V.: A new method to study inhomogeneities in climate records: Brownian motion or random deviations?, International Journal of Climatology, 39, 4769-4783, doi: 10.1002/joc.6105, 2019.

Little, R. J. and Rubin, D. B.: Statistical analysis with missing data. John Wiley & Sons, New York, 2002.

Lucas, L. L. and Unterweger, M. P.: Comprehensive Review and Critical Evaluation of the Half-Life of Tritium, J Res Natl Inst Stand Technol, 105, 541-549, doi: 10.6028/jres.105.043, 2000.

Mandić, M., Bojić, D., Roller-Lutz, Z., Lutz, H. O., and Bronić, I. K.: Note on the spring region of Gacka River (Croatia), Isotopes in Environmental and Health Studies, 44, 201-208, doi: 10.1080/10256010802066364, 2008.

Matheron, G.: Les Variables régionalisées et leur estimation: une application de la théorie des fonctions aléatoires aux sciences de la nature, Masson et Cie Luisant-Chartres, impr. Durand, Paris, 1965.

Michel, R. L.: Residence times in river basins as determined by analysis of long-term tritium records, Journal of Hydrology, 130, 367-378, doi: https://doi.org/10.1016/0022-1694(92)90117-E, 1992.

Miljević, N., Boreli-Zdravković, D., Golobočanin, D., Janković, M., Ogrinc, N., Holko, L., and Solomon, D.: Surface water–groundwater relationship in the velika morava catchment, Serbia. In: Isotopic Age and Composition of Streamflow as Indicators of Groundwater Sustainability, IAEA, Vienna, 1992.

Ozyurt, N. N., Lutz, H. O., Hunjak, T., Mance, D., and Roller-Lutz, Z.: Characterization of the Gacka River basin karst aquifer (Croatia): Hydrochemistry, stable isotopes and tritium-based mean residence times, Science of The Total Environment, 487, 245-254, doi: https://doi.org/10.1016/j.scitotenv.2014.04.018, 2014.

Palcsu, L., Morgenstern, U., Sültenfuss, J., Koltai, G., László, E., Temovski, M., Major, Z., Nagy, J. T., Papp, L., Varlam, C., Faurescu, I., Túri, M., Rinyu, L., Czuppon, G., Bottyán, E., and Jull, A. J. T.: Modulation of Cosmogenic Tritium in Meteoric Precipitation by the 11-year Cycle of Solar Magnetic Field Activity, Scientific Reports, 8, 12813, doi: 10.1038/s41598-018-31208-9, 2018.

R Core Team: R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, 2019.

Rozanski, K., Gonfiantini, R., and Araguas-Araguas, L.: Tritium in the global atmosphere: Distribution patterns and recent trends, Journal of Physics G: Nuclear and Particle Physics, 17, S523, 1991.

Schneider, U., Becker, A., Finger, P., Meyer-Christoffer, A., and Ziese, M.: GPCC Full Data Monthly Product Version 2018 at 1.0°: Monthly Land-Surface Precipitation from Rain-Gauges built on GTS-based and Historical Data. Federal Ministry of Transport and Digital Infrastructure, Germany, Deutscher Wetterdienst, 2018.

SLONIP: Slovenian Network of Isotopes in Precipitation. The SLONIP Database, https://slonip.ijs.si/, last access: 01.05.2020, 2020.

Stewart, M. K. and Morgenstern, U.: Importance of tritium-based transit times in hydrological systems, Wiley Interdisciplinary Reviews: Water, 3, 145-154, doi: 10.1002/wat2.1134, 2016.

Sugahara, S., da Rocha, R. P., Ynoue, R. Y., and da Silveira, R. B.: Homogeneity assessment of a station climate series (1933–2005) in the Metropolitan Area of São Paulo: instruments change and urbanization effects, Theor Appl Climatol, 107, 361-374, doi: 10.1007/s00704-011-0485-x, 2012.

Surić, M., Roller-Lutz, Z., Mandić, M., Bronić, I. K., and Juračić, M.: Modern C, O, and H isotope composition of speleothem and dripwater from Modrič Cave, eastern Adriatic coast (Croatia), International Journal of Speleology, 39, 91-97, 2010.

Szucs, P., Kompar, L., Palcsu, L., and Deak, J.: Estimation of the groundwater replenishment change at a Hungarian recharge area, Carpathian Journal of Earth and Environmental Sciences, 10, 227-236, 2015.

Tadros, C. V., Hughes, C. E., Crawford, J., Hollins, S. E., and Chisari, R.: Tritium in Australian precipitation: A 50 year record, Journal of Hydrology, 513, 262-273, doi: https://doi.org/10.1016/j.jhydrol.2014.03.031, 2014.

Thatcher, L., Rubin, M., and Brown, G. F.: Dating Desert Ground Water, Science, 134, 105-106, doi: 10.1126/science.134.3472.105, 1961.

Umweltbundesamt, H. O. F., Bundesministerium für Land-und Forstwirtschaft, U. u. W. B. (Ed.), https://wasser.umweltbundesamt.at/h2odb/fivestep/abfrageQdPublic.xhtml, last access: 01.05.2020, 2019.

Vreča, P., Bronić, I. K., Horvatinčić, N., and Barešić, J.: Isotopic characteristics of precipitation in Slovenia and Croatia: Comparison of continental and maritime stations, Journal of Hydrology, 330, 457-469, doi: https://doi.org/10.1016/j.jhydrol.2006.04.005, 2006.

Vreča, P., Bronić, I. K., Leis, A., and Demšar, M.: Isotopic composition of precipitation at the station Ljubljana (Reaktor), Slovenia–period 2007–2010, Geologija, 57, 217-230, 2014.

Vreča, P., Krajcar Bronić, I., Leis, A., and Brenčić, M.: Isotopic composition of precipitation in Ljubljana (Slovenia), Geologija, 51, 169, 2008.

Vreča, P. and Malenšek, N.: Slovenian Network of Isotopes in Precipitation (SLONIP) - a review of activities in the period 1981-2015, Geologija, 59, 67-84, doi: 10.5474/geologija.2016.004, 2016.

Wackernagel, H.: Multivariate Geostatistics, Springer-Verlag Berlin Heidelberg, 2003.

Webster, R. and Oliver, M. A.: Geostatistics for Environmental Scientists, John Wiley & Sons, Ltd, 2008.

Zhang, Y., Ye, S., and Wu, J.: A modified global model for predicting the tritium distribution in precipitation, 1960–2005, Hydrological Processes, 25, 2379-2392, doi: 10.1002/hyp.8001, 2011.

Zuber, A., Michalczyk, Z., and Maloszewski, P.: Great tritium ages explain the occurrence of good-quality groundwater in a phreatic aquifer of an urban area, Lublin, Poland, Hydrogeol J, 9, 451-460, doi: 10.1007/s100400100149, 2001.