Origin and percolation times of Milandre Cave drip water determined by tritium time series and beryllium-7 data from Switzerland

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ABSTRACT

Early observations of the tritium (^{3}H) activity in precipitation from Switzerland started in 1967 in Bern and a monitoring program with improved analytical techniques was carried out between 1971 and 2009. Between 2012 and 2015, we performed tritium analyses on daily precipitation samples from north-western Switzerland to better constrain the tritium variability. We also collected waters dripping inside Milandre Cave (Jura Mountains) with a 4–6 months' resolution in order to estimate the age of the drip water, which is mandatory to interpret the high-resolution speleothem (cave carbonate deposits) records. Over the monitoring period, the mean tritium concentration in the daily precipitation samples was approximately 8.7 ± 4.7 TU with distinct seasonality showing higher values in spring and summer (from April–May to August–September). The similarity in trends with the other cosmogenic radionuclide beryllium-7 (^{7}Be) suggests that, for the study site, tritium in precipitation essentially originates from stratospheric input in spring. In winter, precipitation dynamics with increasing moisture originating from the Atlantic and diluted during transport contribute to low values close to the Atlantic background. In cave drip water, the depleted activity level of tritium indicates a relatively long percolation time from the surface to the cave of several years. A residual superimposed short tritium variability provides evidence for the occurrence of fast flowing water paths. The contribution from both components were quantified based on a two-component lumped parameter-mixing model. Finally, we show that tritium concentrations in cave drip water are linked to the moisture origin and atmospheric transport pathways.

1. Introduction

Tritium (^{3}H) is a radioactive isotope of hydrogen, naturally produced by cosmic ray spallation nucleosynthesis, i.e. the impact between a cosmic ray neutron and a nitrogen (^{14}N) nucleus in the upper atmosphere (cosmogenic radionuclide). Tritium is found at a very low concentration compared to the common stable hydrogen isotope (^{1}H) with a natural ^{3}H/^{1}H ratio of 10^{-18}, which corresponds to 1 tritium unit (TU) or a specific activity of 0.118 Bq/L of water. Approximately two thirds of the natural production occur in the stratosphere. The remaining third is produced in the troposphere (Rozanski et al., 1991). A similar distribution between stratospheric and tropospheric production applies to beryllium-7 (^{7}Be), a cosmogenic radionuclide with a half-life of 53.2 days. We therefore compare the trend of the ^{7}Be concentrations in the lower atmosphere with the tritium results. In the stratosphere the tritium content is approximately 9×10^5 TU (Fourré et al. (2018) and references therein). After its production, tritium reacts rapidly with oxygen to form tritiated water (^{1}H^{3}H^{16}O or HTO) and is integrated in the

water cycle. HTO moves to the troposphere mostly through the tropopause discontinuity at mid-latitudes (Gat et al., 2001). When it finally precipitates on the Earth's surface, it is highly diluted by five orders of magnitude due to the high absolute water content of the troposphere to reach atmospheric background levels. The HTO concentration in precipitation is typically below 20 TU in most regions except at high latitudes and especially in Antarctica (Cauquoin et al., 2015). In the 1960's, nuclear tests released large amounts of tritium in the stratosphere with values increasing to ~5000 TU (Gat et al., 2001) in precipitation. After the nuclear explosions, tritium was further distributed over the Earth through stratospheric circulations, stratosphere to troposphere transport and subsequent precipitation. Due to its half-life of 12.32 ± 0.02 years (Lucas and Unterweger, 2000) and dilution in the large oceanic reservoir (Fourré et al., 2018) tritium concentrations in the atmosphere have decreased rapidly since the mid 1960's and tritium concentration in precipitation returned closed to pre-bomb background levels of around 5 TU in central Europe (Kaufman and Libby, 1954; Rozanski et al., 1991; Gat et al., 2001). Observed values in precipitation in Europe have been

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in the range of ~5–10 TU (Cauquoin et al., 2015) for the last few decades (Kluge et al., 2010a; Rozanski et al., 1991), with supra-regional heterogeneities (Cauquoin et al., 2015) but also local differences mainly due to anthropogenic activities and local industries (FOPH, 2018; Schürch et al., 2003).

In the atmosphere and in the hydrosphere, tritium concentrations vary mainly due to atmospheric transport (Cauquoin et al., 2015) and/or regional anthropogenic sources such as nuclear facilities, chemical industries, wood-based heating systems or industries producing tritium light sources, which emit tritium leading to local contamination (Schürch et al., 2003; Rozanski et al., 1991). In Switzerland, peaks of tritium contamination in the lower atmosphere are often observed close to a few well-known industrial sites, incineration plants and watchmaking industries (Schürch et al., 2003; FOPH, 2018). Actually, one of the largest emitters of tritium in Switzerland is a plant producing tritium light sources (self-luminous panels) and is located close to Bern (FOPH, 2018). In comparison, Swiss nuclear power plants are less important emitters of tritium to the atmosphere (Schürch et al., 2003).

The Climate and Environmental Physics (CEP) division at the University of Bern continuously monitored tritium in precipitation in Switzerland (Schürch et al., 2003) from 1971 and as a contractor for the Federal Office for the Environment (FOEN) from 1992 until the end of 2009, when tritium monitoring was abandoned. This study presents five decades of tritium measurements in Switzerland for three stations located north (Basel and Bern) and south of the Alps (Locarno), from which part of the interval 1994 to 2002 was published in Schürch et al. (2003). We also provide a high-resolution record from Le Mormont MeteoSwiss station (north-western Switzerland) showing daily precipitation tritium values between 2012 and 2015. At the same time, drip water was collected in Milandre Cave (north-western Switzerland) close to Le Mormont station (Affolter et al., 2015) for tritium concentration measurements on a multi-monthly basis (Fig. 1).

In caves, tritium is used to determine the drip water age distribution, i.e. the percolation time (Kaufman et al., 2003; Kluge et al., 2010a; Jean-Baptiste et al., 2019), which is of primary importance for the correct interpretation of speleothem proxy signals, especially when attempts are being made to reconstruct past climatic conditions up to annual or seasonal time resolutions (Baker et al., 2008; Fleitmann et al., 2003). To achieve this, it is mandatory to have a solid understanding of the water transit and residence time in the karst above the cave. Tritium, with a relatively short decay time, serves as a good hydrologic tracer in hydrology for dating recently infiltrated waters or to determine the age of old and untouched underground aquifers (e.g. Corcho-Alvarado et al., 2014; Kralik et al., 2014; Sundal et al., 2019; Pärn et al., 2019). For the

Fig. 1. Location map of Switzerland. CEP stations of Basel, Bern, La Brévine and Locarno are indicated as well as Klingnau sampling site. The square indicates the location of Milandre Cave, Le Mormont and Fahy MeteoSwiss stations.

estimation of the percolation time of cave waters, we use the residual (seasonal) variability and/or shifts due to radioactive decay of tritium in precipitation and cave drip waters. For instance, it was used as a tracer in Bunker Cave in Germany (Kluge et al., 2010a), Soreq Cave in Israël (Kaufman et al., 2003), and more recently in Villars Cave in France (Jean-Baptiste et al., 2019). Here, we estimated the residence time of percolation water in Milandre Cave, which is part of a karstic system in the Jura Mountains (Switzerland) made of limestone formations characterised by dissolution processes and complex underground drainage system. In karstic areas, tritiated water from precipitation infiltrates the soil and epikarst and eventually drips into the cave through (micro-) cracks or soda straws after a percolation time in the karst vadose zone (Hartmann and Baker, 2017). A couple of dating attempts have been previously made in two different locations of Milandre cave. A weakly pronounced seasonality in the water isotopes of the drip water from the *Galerie des Fistuleuses* (translated "soda straws gallery") led to a minimum estimate of transit time of 8–10 months. Note that the uncertainty is large and the transit time could be several times this estimate. Moreover, re-measurement of these water samples challenged the occurrence of a significant seasonality (Affolter et al., 2015) and pointed towards longer transit times. Ongoing investigations based on injection of tracers in the upstream part of the cave in 2014 did not show any response in 2019. It is, however, important to mention that the long residence time applies only to the low permeability part of the karst, as the fast component of the recharge will be drained rapidly within a few days (pers. comm. Marc Luetscher, Swiss Institute for Speleology and Karst Studies, hereafter SISKA).

2. Settings and method

2.1. Site settings

Daily precipitation water samples were collected at MeteoSwiss station n° 534 Le Mormont located in the north-western Swiss Jura Mountains (Fig. 1; 47.44 N/7.04 E, altitude 540 m a.s.l.). For the last five decades, meteorological observations show a mean annual temperature of ~9 °C with a pronounced seasonality of ~17 °C in July and ~0 °C in January. Precipitation is well distributed over the year with a mean value of ~1050 mm (Affolter et al., 2015). Modern climatic conditions indicate a mid-latitude temperate area with moisture originating mostly from the Atlantic (~40%), especially during winter. The rest is shared among the Mediterranean (~23%), eastern Europe and continental (~21%) and northern Europe (16%) (Sodemann and Zubler, 2010; see also Fig. 2). The sampling site is located in a rural area surrounded by larger industrial cities at a distance of around 20–50 km. Moreover, three nuclear facilities are nearby the study site with the Swiss nuclear power plants Mühleberg located ~60 km SE and Gösgen at ~75 km E, whereas in France Fessenheim is located ~70 km NE. As previously mentioned, a well-documented source for tritium contamination in the vicinity of Bern is a microtechnology company (FOPH, 2018).

Drip water samples were collected in Milandre Cave, more exactly in the *Galerie des Fistuleuses* where the stalagmites M6 and M8 were sampled, which is located at a distance of approximately 400 m from the natural entrance (Affolter et al., 2015). Variability of the cave's temperature is low ranging between 9.5 and 10.0 °C mostly due to seasonal variations and corresponds to the mean annual air temperature outside the cave (Affolter et al., 2015, 2019). Here, the drip site potentially aggregates waters from different sources, i.e. fast (short) transit waters, perched reservoirs, etc. and thus may represent a mixed signal of different ages and correspondingly different tritium values. Nevertheless, drip rate monitoring indicates that infiltration is almost sustainable over the monitoring period (2012–2016) with only one interruption in summer 2015 which was one of the hottest and driest summer since the beginning of the measurements in 1864 (Orth et al., 2016). Because the dripping pattern in the cave is relatively similar over years with faster drip discharge of ~100 drops per hour from winter to mid-summer
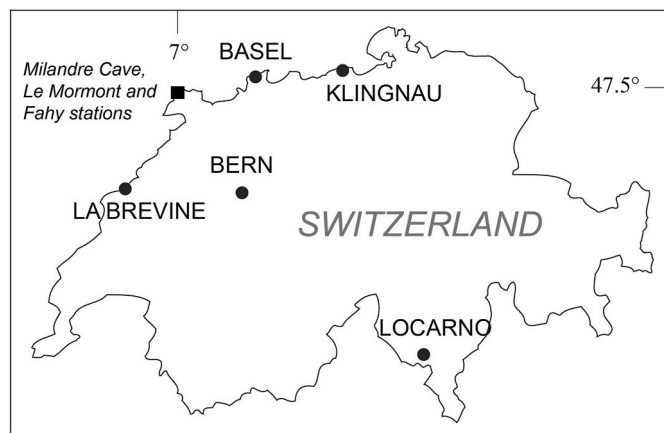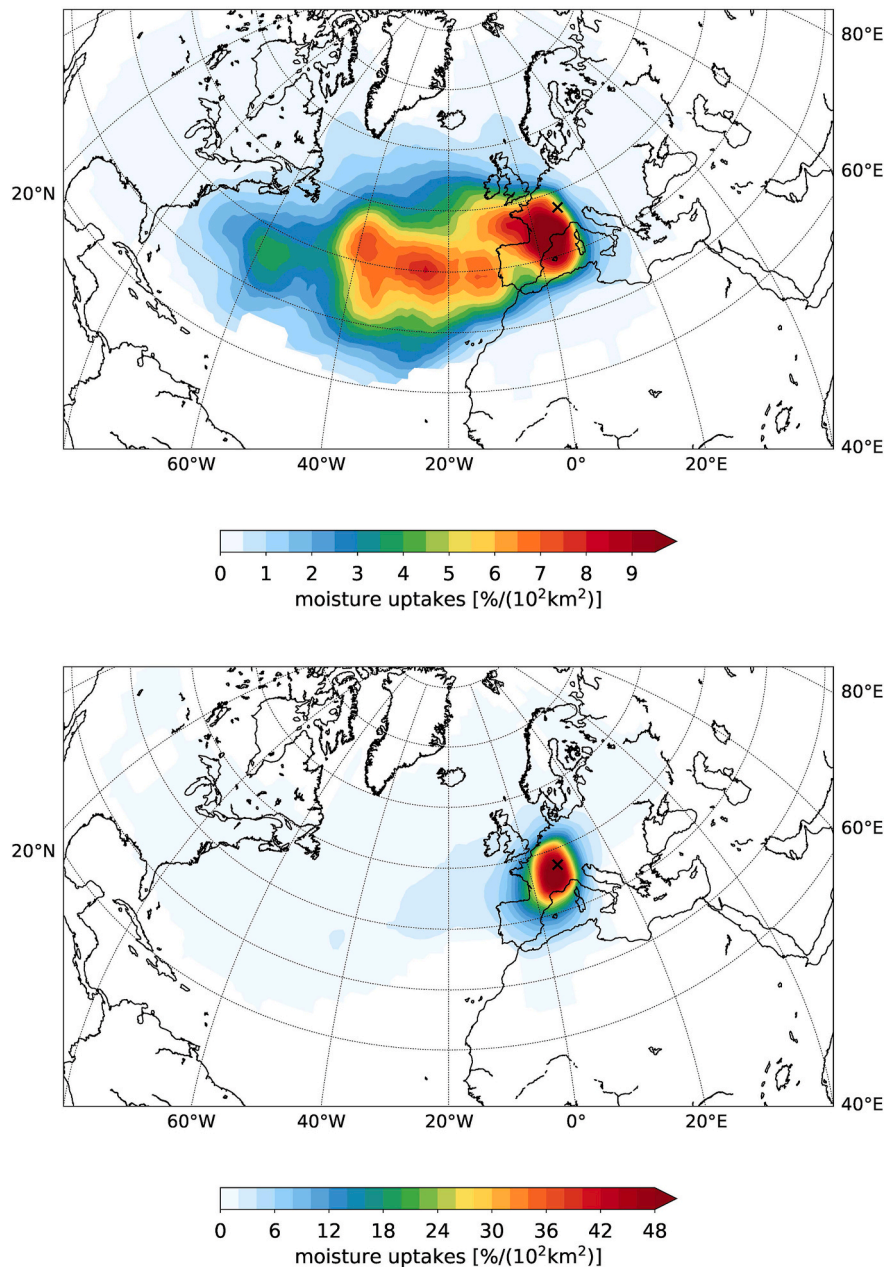
Fig. 2. Upper panel: Weighted mean moisture source area for winter months (DJF) over the three years of monitoring (2012–2015) in the Jura region. Lower panel: Idem but for summer months (JJA). The moisture sources were determined based on air parcel back-trajectories using the three-dimensional wind fields of the ERA-Interim reanalysis dataset.

compared to the ~20 drops per hour observed in autumn, we assume the hydrological paths to be constant over years with equal contributions of potential different sources. Moreover, it is unlikely that very old waters have an influence as the unsaturated karst above the cave is rather dynamic and has a quick response to heavy precipitation events. More detailed discussion about drip rate behaviour can be found elsewhere (Affolter et al., 2015).

2.2. Sampling

Precipitation water samples were collected in an open gauge every day at 8 a.m. local time between March 2012 and March 2015 at the MeteoSwiss station Le Mormont and stored in 100, 200 or 500 ml glass bottles sealed with plastic and rubber caps and deposited in a dark room. This sampling was part of a stable water isotope monitoring program

performed on precipitation and cave waters to characterize the water isotope signal transfer from the precipitation to its enclosure in speleothem fluid inclusions (Affolter et al., 2015). Subsequently, between May 2015 and May 2016, we measured the tritium concentration in every precipitation sample larger than 100 ml at the Physics institute of the University of Bern, Switzerland, which resulted in 228 measurements out of 413 precipitation events. In addition, we have collected and stored 12 samples of multi-month integrated drip water (~4–6 months) from inside Milandre Cave in 1000 ml glass vials between 2012 and 2016.

2.3. Tritium measurements and calibration

Tritium activity measurements were performed using a low-level liquid scintillation spectrometer (Aloka LSC-LBIII) that operates in the

dark and at low temperature in the underground laboratory at the University of Bern. This laboratory is located at a depth of −46 m below the surface (70 m water equivalent) in a cavern-like laboratory set in sandstone bedrock to minimize potential contamination by atmospheric tritium activity. Performance of the tritium measurements made with our Aloka LSC-LBIII was recently assessed in the frame of a certified international proficiency test and showed precise and accurate measurements (FOPH, 2018). For each measurement, 150 ml vials were filled with approximately 70 g of sample water mixed with 60 g of scintillator Ultima Gold (PerkinElmer) and shaken to homogenise the mixture. To prevent scintillator excitation by daylight that would increase the measurement time of the series, new samples were placed in the dark inside the Aloka approximately one week before the start. During measurements, the Aloka instrument counts and records the β-decay occurring in the water sample/scintillator mixtures. The deposited energy is recorded by a 10-bit Multi-Channel Analyser (MCA) with a linear energy range of 0–180 keV. For the tritium measurement only channels 25–265 are used which cover the decay energy of 18.6 keV. Per measurement series, 16 water samples and four internal standards ranging in the expected target values (0–20 TU) were used as references, loaded in the Aloka and measured over the full measurement campaign. Each sample is measured six to ten times for 100 min, which results in approximately one week per measurement series. Additionally, we ran 13 different standards (in the range from 0 to 100 TU) between October 2015 and March 2016. The count rate of each sample was repeatedly measured during several measurement intervals of 100 min. The error of the tritium concentration is then calculated by error propagation based on the standard deviation of the set of measurements and the uncertainty of the counting efficiency. On average, a tritium 1σ uncertainty of ±1.8 TU was achieved.

To calibrate our data, we applied a linear relationship between the decay count per minute and the tritium unit ($R^2 = 0.97$) based on five standard waters spanning from 1 to 6 TU where ~60% of the samples range in the interval (0–7 TU). The calibration was extended with additional standards up to 100 TU. Two corrections were applied to the measured tritium values. Firstly, a decay correction between sampling and measurement time. Secondly, premixed Ultima Gold scintillator water cocktails were shown to drift over time (Nedjadi et al., 2016). On Fig. 3, the decreasing trend is mainly caused by the degradation of the photon yield of Ultima Gold liquid scintillator as the natural decay over a year is ~0.4 TU only. This drift is relevant and significant only for the standards that were measured on a regular basis as premixed cocktail

Fig. 3. Repetitive measurements of four different water samples over the total measurement interval showing the degradation induced by the use of scintillator's liquid. Values were chosen to correspond to the natural variability range observed in precipitations.

(Fig. 3). No correction is required for the water samples as they were prepared a few days before measurements.

2.4. ^{7}Be measurements

Cosmogenic measurements of ^{7}Be were performed by the Federal Office of Public Health, Bern, Switzerland. We chose the high-volume aerosol-sampler (HVS) that is operated in Klingnau (8.2 E, 47.6 N, 318 m a.s.l.) to compare with our tritium data. Our study used the ^{7}Be concentration determination between January 2012 and January 2016. The sampling and measurement procedure in brief: HVS filters are collected weekly and compressed into 60 mm diameter and 5 mm thick discs using a hydraulic press. These discs are further processed through gamma-spectrometry analyses, where emitted gamma rays are counted for 1–2 days using a High Purity Germanium (HPGe) detector in a low background laboratory. Detailed information about the methodology and previous results can be found in a previous study (Steinmann et al., 2013).

2.5. Back-trajectory calculation and moisture source diagnostics for the Jura region

The moisture source region of precipitation in the Jura region was diagnosed by applying the algorithm described in Sodemann et al. (2008) based on air parcel back-trajectories (Wernli and Davies, 1997; Sprenger and Wernli, 2015). They started from a group of five points surrounding with $\pm0.2°$N/E the location of Milandre Cave based on a procedure similar to the one described in Aemisegger (2018). The trajectories are calculated 10 days back in time using the 3D wind fields of the 6-hourly ERA-Interim reanalyses (Dee et al., 2011) from the European Centre for Medium-Range Weather Forecasts (ECMWF). The ERA-Interim data is interpolated to a $1° \times 1°$ horizontal grid and 60 vertical levels. The back-trajectories were started every 6 h in the period 2012 to 2015 from a vertical stack of points at 12 model levels (levels 1, 3,5,7,9,11,13,15,20,25,30,35) between the surface and about 200 hPa with a spacing of 20 hPa in the lower and 150 hPa in the upper troposphere. The 6-hourly moisture uptake locations from all trajectories are gridded onto a regular $1° \times 1°$ horizontal grid. Seasonally accumulated moisture sources are obtained by weighting the moisture source fields by total surface precipitation from ERA-Interim at the trajectories' starting points and integrating over all time steps in a given accumulation period.

2.6. Method for water residence time estimation

To estimate the water residence time of the infiltrated water, a lumped parameter model (LPM) was applied. The LPM approach provides a means of characterising an integrated system response to boundary conditions where information for a physically based simulation are too scarce (Maloszewski et al., 2002; Einsiedl, 2005; Turnadge and Smerdon, 2014) and the two components approach had also already been proposed for Milandre Cave (Perrin et al., 2003). The temporal evolution of the tritium concentration c(t) in the drip water is expressed by the convolution integral (Eq. (1)):

$$c(t) = \int_0^\infty c_{in}(t - T) \cdot g(T, p_i) \cdot \exp(-\lambda T) \, dT \tag{1}$$

where c_{in} is the tritium input in precipitation, λ the decay constant and g the distribution of contributing water ages T described by model parameters p_i. The number i of model parameters depends on the complexity of the model.

The age distribution g is a priory unknown. Several studies in karstic systems revealed a double porosity characteristic with a fast-flowing compartment in conductive zones, which are coupled with a matrix porosity that contains older water. We assumed therefore a dispersion
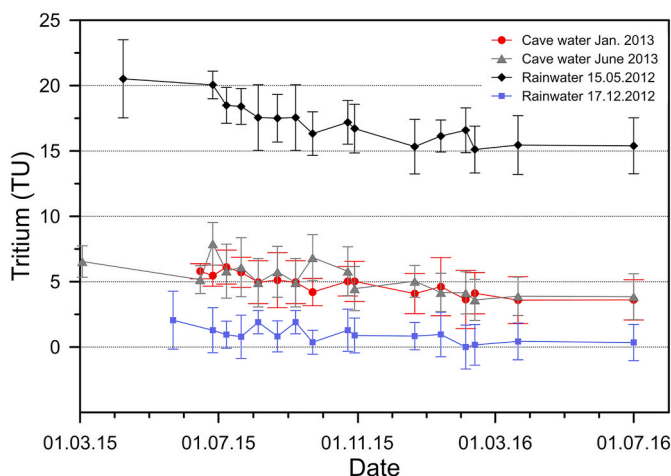
function for each flow domain that are combined in a bimodal mixing model.

$$g(T) = a \cdot DM_1(T, T_{m1}, \ d_1) + (1-a) \cdot DM_2(T, \ T_{m2}, d_2) \qquad (2)$$

with mixing proportion a of the fast-flowing component 1 and (1-a) for the slower component 2 using dispersion functions DM (Eq. (3)):

$$DM(T, T_m, d) = \frac{T_m}{\sqrt{\pi \cdot d \cdot T^3}} \cdot \exp\left(-\frac{(T - T_m)^2}{d \cdot T}\right) \qquad (3)$$

with parameters d_1, d_2 and T_{m1}, T_{m2} for dispersion and mean age respectively for both components.

3. Results and discussion

3.1. Tritium in precipitation from Switzerland

3.1.1. Long-term trend

Long-term measurements of tritium concentrations in Switzerland were performed during more than three decades at several stations (Fig. 4). On a NW-SE transect, the three stations are Basel, where the monitoring started in 1985, Bern started in 1971 and Locarno started in 1976 (Fig. 1). The monitoring of the CEP stations provided monthly mean values and was used to document the long-term decrease of the continental atmospheric load occurring since the atomic bomb testing in the 1960's (Schürch et al., 2003; FOPH, 2018). Despite the fact that the maximal intensity of the tritium concentration had already passed when the Swiss monitoring with the improved analytical techniques started,
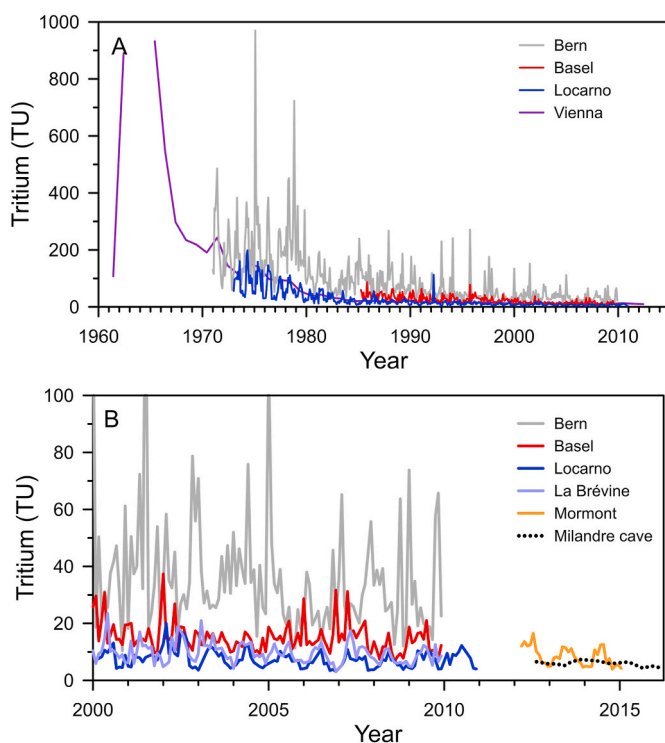

Fig. 4. (A) Long-term tritium activity curves recorded from the CEP stations for Basel (red), Bern (grey) and Locarno (blue). The GNIP station Vienna (violet) is also given for comparison (IAEA/WMO, 2019), where a maximum of 3176 TU was reached in 1963. (B) Zoom on the last two decades. In addition tritium records of La Brévine (light blue) and Le Mormont (orange) stations are given as well as corresponding multi-annual buffered drip water values (dotted black). Tritium data for stations Bern, Basel, Locarno and La Brévine are available on the WISER platform for GNIP data of the International Atomic Energy Agency (www.iaea.org). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
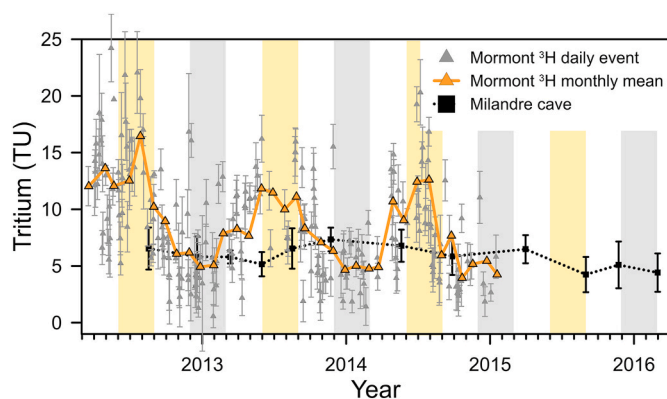
the three stations still allowed to document the atmospheric tritium concentration decrease in Switzerland between 1971 and 2009 (Fig. 4). For more recent times, it also allowed a quantification of contaminations from local industries. Over decades, the Bern record presents a typical exponential long-term trend decrease with high short-term variability due to anthropogenic release (FOPH, 2018). More specifically, the highest values of 900 TU in 1975 or 700 TU in 1978 are due to local emission from industrial activity in the vicinity of Bern (FOPH, 2018) (Fig. 4).

Locarno, in the south of the Alps, shows quite stable and low concentrations from the mid 1980's. On Fig. 4, Basel tritium concentration displays an exponential decrease of the tritium concentration. Locarno also presents this typical decreasing trend from 1976 on, although with much lower short-term variability than in Bern. Even if it covers different time periods, the seasonal variability observed in the three years' record of Le Mormont in a rural area is at the level of the long-term monitoring station of Locarno suggesting limited industrial contamination. While the Bern monitoring was stopped in 2009, Le Mormont shows lower values than Bern and Basel, which is partly expected due to decay and mixing. Local contamination centred on industrial areas leads to spatial variability in tritium concentrations from Switzerland, which deviate from natural signals (Gat et al., 2001). For the purpose of the study, we also used the record of the MeteoSwiss station La Brévine (46.59 N/6.36 E, altitude 1050 m a.s.l.) located in the Jura Mountains, where the monitoring started more recently, in 1994. This station shows a similar pattern as the less contaminated record of Locarno, which is more representative of the rural area of Milandre Cave.

The anthropogenic signals observed in Bern and Basel are unlikely to affect the signal either from Le Mormont station (i.e. Milandre Cave area) or from La Brévine station and thus will not impact groundwater age determination (see Section 3.2). Contamination documented in both cities will probably be observed only locally and emissions will not affect the Milandre Cave area, as it was documented that there is a drop of factor 10 in tritium concentrations every 10 km (IAEA, 2003). Moreover, Milandre Cave area is favourably located to the west of both cities, i.e. upwind of the main sources (Sodemann and Zubler, 2010, Fig. 2), which in addition would limit the potential influence of contamination from these industrial areas.

3.1.2. Variability of tritiated water in precipitation

Regarding precipitation from Le Mormont station, our results indicate monthly mean tritium values ranging between 5 and 15 TU with daily values spreading between 0.6 and 24.2 TU. The mean value over the three years is 8.7 ± 4.7 TU and the record shows a clear seasonality with a higher mean summer value of ~10 TU compared to winter at ~5 TU (Fig. 5). The effective infiltration weighted annual mean tritium concentration is 8.4 TU.

A comparison made between the daily tritium concentration in precipitation and the isotope data (partially published previously in Affolter et al., 2015) shows neither correlations with the local meteorological parameters (temperature, amount of precipitation or relative humidity), nor with corresponding oxygen ($\delta^{17}O$ and $\delta^{18}O$) and hydrogen (δD) isotopes of water. Based on monthly mean values, a correlation appears for tritium with $\delta^{18}O$ ($R^2 = 0.4$). At the study site, water isotopes are correlated to temperatures up to 70% on a monthly basis (Affolter et al., 2015) but tritium should not be correlated to temperature (Gat et al., 2001). Yet, we observed that the stable water isotopes (oxygen and hydrogen) and tritium show an offset of approximately one month in their seasonality. Thus, the correlation between tritium and temperature or $\delta^{18}O$ may be an artefact due to similar seasonal patterns of both isotopes resulting from different (maybe independent) reasons, i.e. the temperature for $\delta^{18}O$ and the stratospheric input for tritium. Moreover, the re-evaporation of recently precipitated water in summer – when $\delta^{18}O$ is at its maximal value – contributes to a high tritium concentration in summer as well.

Fig. 5. Tritium concentration in daily precipitation from Le Mormont station (grey triangles) as well as monthly means (orange triangles, unweighted) are shown together with cave drip water activity (black squares) for the same time interval. Shaded: summer (yellow) and winter (grey). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Furthermore, when averaging to monthly values, maximum tritium concentrations occur in late spring and summer and minimum in winter (see Section 3), which is similar to other studies (Chae and Kim, 2019). While the tritium maximum values should be centred on spring (March–May) due to the input of large amount of tritium from the stratosphere into the troposphere in spring (Gat et al., 2001; Škerlak et al., 2014), high values extend toward summer months essentially through remobilisation of winter and spring precipitation by re-evaporation on the continent, which will increase tritium concentration in later precipitation (Gat et al., 2001); see Section 4.3). An additional reason for a pronounced seasonality may be the reinforced convective activity in late spring compared to winter that can facilitate the transport of tritium from the stratosphere into the troposphere (Kralik et al., 2014).

The link with the stratospheric input is also supported by the comparison made with the cosmogenic nuclide ^{7}Be. The ^{7}Be record presented here for the interval 2012–2015 constitutes an extension of the previously published record from 1994 to 2011 in ground level air from Switzerland (Steinmann et al., 2013). As for tritium, ^{7}Be (half-life of 53.2 days) is mostly produced in the stratosphere due to cosmic rays and further transferred into the troposphere, where removal of ^{7}Be is linked to precipitation and air humidity (Kusmierczyk-Michulec et al., 2015; Steinmann et al., 2013). ^{7}Be concentration in ground-level air is clearly influenced by rain wash-out, which seems a rather constant process as rain events in Switzerland are frequent and relatively well-distributed over the year. Thus, much of the ^{7}Be input signal is preserved in the ^{7}Be concentrations measured in air-filters (Steinmann et al., 2013). We compared our record with the closest ^{7}Be station, which is the Klingnau station, located in northern Switzerland (Fig. 1). For the interval 2012 to 2015, ^{7}Be results indicate a similar behaviour as for previous observations at this station. The mean ^{7}Be concentration at Klingnau station between January 2012 and January 2016 is 3070 μBq/m^3 (with minimum and maximum values of 594 and 7453 μBq/m^3, respectively), which is lower than the mean of five Swiss stations between 1994 and 2011. Klingnau is located within the planetary boundary layer where ^{7}Be concentrations should be well-mixed (Steinmann et al., 2013) and consequently representative for the Swiss Plateau area.

Between 2012 and 2015, ^{7}Be high values were observed from March–May to July similar as during the 1994–2011 monitoring period (Steinmann et al., 2013). The study showed input of stratospheric air between March and May, increased mixing of upper tropospheric air from June to August (no stratospheric input) – potentially influenced by the alpine topography – and less exchange between the upper and lower troposphere in autumn and winter. Over the three years at Klingnau, we

calculated monthly averages of ^{7}Be concentrations that we further compared with tritium (Figs. 6 and 7). The lower ^{7}Be monthly values were observed from November to January whereas maxima are from March to July, in line with previously published data (Steinmann et al., 2013) and similar to the tritium trend (Fig. 6). As seen on Fig. 7, a similar behaviour between tritium and ^{7}Be is observed and shows a significant correlation ($R^2 = 0.42$).

In winter, the situation differs. In addition to a reduced input of stratospheric air, moisture coming from the Atlantic with low tritium levels between 1 and 5 TU may cause a dilution effect (Figs. 2 and 8) (Rozanski et al., 1991; Cauquoin et al., 2015). Over the three years of monitoring, we observed that air parcel back-trajectories clearly indicate that enhanced moisture contribution from the north Atlantic realm to winter precipitation brings more unpolluted marine moisture (Fig. 2). Fig. 8 shows the link between the Atlantic moisture source contribution and the tritium concentration of samples. It indicates that samples with low contamination directly originating from the Atlantic domain with low recycled moisture from the continent tends to have very low concentration of tritium with a minimum mean value of 4.4 TU close to the atmospheric background values of 5.1 (Rozanski et al., 1991). When the moisture source contribution consists of a larger share of continental and Mediterranean moisture sources, then the values tend to be slightly higher ~7.6 TU (Fig. 8). A moderate continental effect exists for tritium (Gat et al., 2001), as for instance observed in China (Meng and Liu, 2017) with low tritium close to the ocean, as moisture mainly originates from local ocean sources that is poor in tritium (Gat et al., 2001; Meng and Liu, 2017). This observation is corroborated with South Eastern Asian data showing that the amplitude of the seasonality depends on the contribution of the air masses with low tritium concentration above oceans (Chae and Kim, 2019). Our observations combined with the trajectory-based moisture source information show that tritium values are lower when the contribution of moisture from the Atlantic Ocean is higher, which is predominant in winter.

To sum up, as seen in Fig. 6, a similar behaviour between tritium and the other cosmogenic radionuclide ^{7}Be is observed, which is related to stratospheric input of tritium in spring (March to May). Furthermore, remobilisation of precipitation water over continental regions in summer leads to high tritium values up to July. Less exchange with the upper troposphere occurs in autumn and winter which leads to lower tritium values in precipitation. Additionally, for Switzerland, the increase of the moisture originating from the Atlantic in winter, due to intensified large-scale wind systems, will bring air (Fig. 2) carrying low concentration tritium values (see Section 4.2) especially in the winters of 2014 and 2015.

3.2. Tritium dating of drip water

3.2.1. Cave tritium

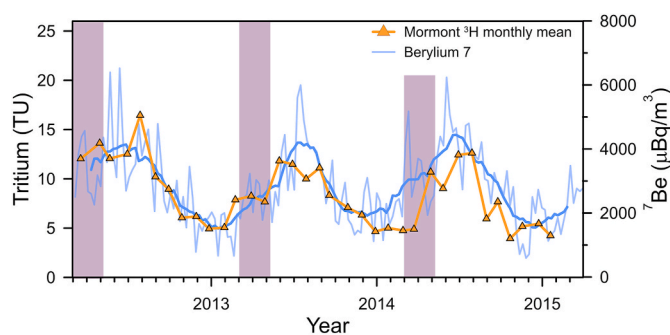The tritium concentrations in Milandre Cave drip water varies

Fig. 6. Comparison between tritium activity in precipitation and ^{7}Be concentrations measured in the atmosphere. Shaded: the high stratospheric input time in March to May (Steinmann et al., 2013).
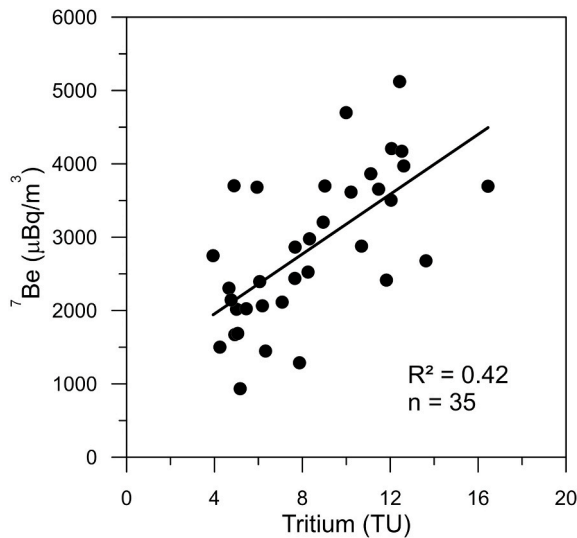
Fig. 7. Tritium activity in precipitation versus ^{7}Be in ground-level air for monthly mean values over the studied interval.
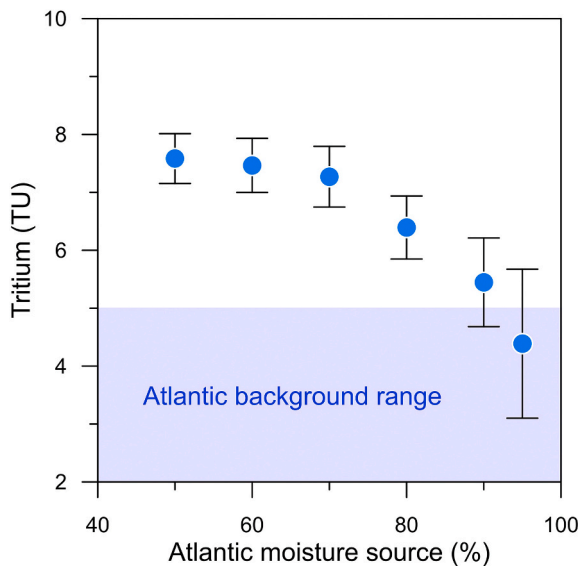

Fig. 8. Mean tritium activity for samples related to the amount of precipitation forming water vapour that originates from the North Atlantic in the period 2012 to 2015, where the Atlantic moisture source is based on back-trajectories determination corresponding to the water samples used for tritium measurements. The background level is ~1–5 TU (Cauquoin et al., 2015; Rozanski et al., 1991).

between 4.2 and 7.3 TU (mean of 6.3 ± 0.9 TU) with much lower variability than in precipitation as it integrates infiltrated precipitation waters over months or years. This fact is also supported by observations of a dampening of the variability in the hydrogen and oxygen isotope ratios measured in precipitation and cave drip water (Affolter et al., 2015). The range of tritium concentrations is similar to the one observed in Bunker Cave (located ~500 km northwards in Germany), where values range between 5.0 and 9.5 TU (Kluge et al., 2010a) and to the values determined in Villars Cave (located ~550 km westwards in France) ranging between 2.7 and 5.1 TU (Jean-Baptiste et al., 2019).

3.2.2. Estimation of the water residence time with an infiltration model

The use of tritium to date infiltrated waters has become challenging as the effect of the bomb enrichment in the atmosphere has now

disappeared. Thanks to a small tritium enrichment in precipitation in Germany between 2003 and 2008, Kluge et al. (2010a) succeeded in estimating a water residence time of 2–4 years above Bunker Cave. Similarly, in Villars Cave, France, transit times of 7 and 11 years were concluded for two different locations in the cave. For Milandre Cave, we followed a similar approach as Jean-Baptiste et al. (2019) and used the tritium seasonality in precipitation and an infiltration model (see Section 2.6). For the cave location, no precipitation input function is available for the time period before 2012. Data from the next station La Brévine (46.59 N/6.36 E, altitude 1050 m a.s.l.) covers the years 1994–2009, which leaves a data gap for the years 2009–2012. Therefore, a synthetic input function was reconstructed in the following way: First, the La Brévine precipitation data (from year 2000) were fitted with a sine function (Eq. (4); Jean-Baptiste et al., 2019) with the parameters given in Table 1:

$$y(t) = y_0 \cdot \exp(-B \cdot t) + A \cdot \sin\left(\pi \cdot \frac{(t - t_c)}{w}\right) \tag{4}$$

which describes a sine function with exponentially decreasing baseline (first term with parameters y_0 and B), amplitude A, period w and phase shift t_c. All five function parameters from Eq. (4) were left free for fitting the precipitation data of La Brévine. Second, a constant offset of +1 TU was applied in order to adjust to the level of local precipitation data of Fahy, a MeteoSwiss station next to Le Mormont station. The shift is justified by the different geographical locations of Fahy compared to Basel and La Brévine stations. The resulting input function is shown in Fig. 9.

Curves c(t) were calculated with this input function and the convolution integral output. Dispersion parameters d_1 and d_2 of the two main components were fixed and pre-set according to empirical literature values of 10 and 30 days for components 1 and 2 respectively (Gelhar et al., 1992).

Proportion a of young water and mean ages (T_{m1}, and T_{m2}) of the two components in the binary mixing were estimated by adjusting the model output to the measured data by a least square fit procedure. In accordance to previous studies (see above) dominates the old water fraction. Young water components originating from a fast flow path contribute not more than 40% and likely less than 10%. In Fig. 10 output curves for a-values between 0 and 0.4 are plotted. It turns out that the variability of the output is mainly controlled by the proportion of the young components. The age T_{m1} of the young component is constrained by the phase shift between the peaks in the precipitation data and the cave data and results in an estimate of ~180 days or less. The age of the old component controls the location of the baseline of the output curve. A comparison with the cave data and applying the exponential decay law ($T_{1/2}$ is 12.32 years) indicates an age of 2000–2400 days, which corresponds to 5.5–6.6 years. This new estimation agrees with the current observation made by Marc Luetscher (pers. comm., SISKA) based on tracer injection in 2014 in the upstream part of the cave without any tracer response at dripping sites in December 2019. Moreover, a previous tracer attempt made in the upstream part, indicates a response after more than 7 years. Assuming that the 80 m of karst column above the dripping site, a transit time of ~6 years leads to a mean transfer rate of ~37 mm day^{-1}. Such a

Table 1
Parameters for the sine function used to reconstruct data in La Brévine for the missing interval.

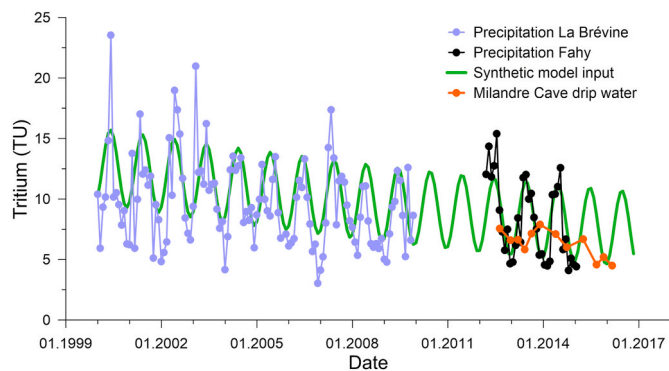| Parameters	Values
y0	11.25392 ± 0.54701
xc	55.90468 ± 13.40902
w	183.37506 ± 1.21616
A	3.01038 ± 0.36915
B	0.0000864463 ± 2.52352 E−5
Reduced chi-square	7.77043
R² (COD)	0.41633
Corr. R²	0.39585

Fig. 9. Tritium data in precipitation and cave drip water. The synthetic input curve for precipitation was obtained by fitting the sine function to the data of La Brévine with a subsequent offset of 1 TU to synchronise it with the activity level at the cave location. Values for Fahy are effective infiltration weighted monthly means. Multi-annual scale low frequency variations of tritium in precipitation (Fourré et al., 2018) have not been considered here and would not affect the concluded model parameters.
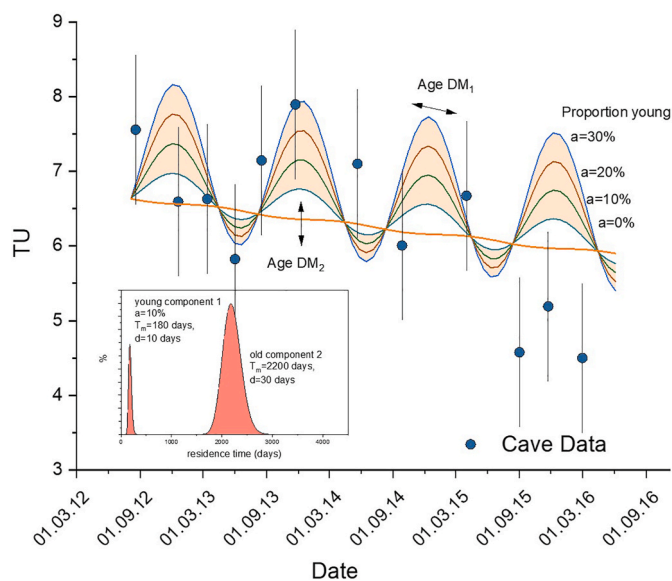

Fig. 10. Output curves for the binary mixing model for different proportions of a fast-flowing component. Variability of the old component is very small because of dispersive dampening (a = 0% curve). Inset: Concluded age distribution of the drip water.

residence time implies a strong smoothing of the seasonal and annual tritium isotope signal found in precipitation, as it was already suggested for the stable isotope (Affolter et al., 2015).

4. Conclusion

The CEP stations monitored the tritium concentrations in precipitation since the early seventies. The long-term record documents a decreasing tritium trend in the atmosphere occurring since nuclear bomb tests. It also indicates that tritium values in precipitation are at the atmospheric background level at approximately 5–6 TU. Between 2013 and 2015, seasonal tritium concentrations are higher in spring-summer and lower in winter. In spring, higher values mostly depend on stratosphere – troposphere exchange, which is supported by a synchronous and similar pattern to the cosmogenic nuclide [7]Be. In winter, due to intensified large-scale wind systems, more precipitation with moisture sources from the Atlantic realm leads to an input of unpolluted moisture

source from the ocean with values close to the atmospheric background. Locally and mainly around industrial areas, significant peaks occur due to anthropogenic tritium release. Furthermore, the residence time of the water dripping in the *Galerie des Fistuleuses* in Milandre Cave is estimated to be ~6 years. In order to better constrain the water age, additional methods could be used as for instance the combination of the ^{3}H – ^{3}He method (Kluge et al., 2010b) or with the use of conventional hydrologic tracers. Finally, a few characteristics of the relation between atmospheric transport pathways and tritium concentrations were established in a qualitative way. Future investigations on the links between historical tritium levels and large-scale transport could provide additional information to the stable water isotope records.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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