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Estimation of the solar-induced natural variability of the tritium concentration of precipitation in the Northern and Southern Hemisphere

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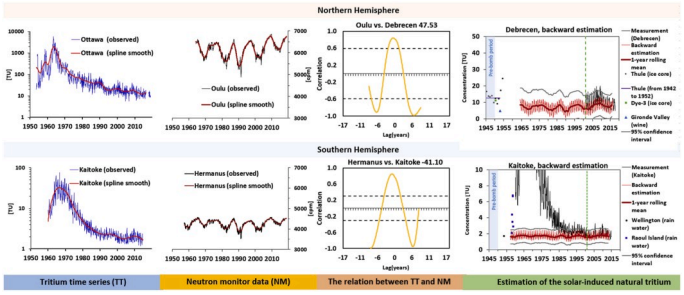
HIGHLIGHTS

- Classification of technogenic tritium-rich and poor stations.
- The technogenic tritium-poor stations time-series had a natural seasonal behavior.
- Estimation of the solar-induced natural tritium time-series by neutron monitor data.
- The neutron flux is a good predictor of natural tritium levels in the atmosphere.

GRAPHICAL ABSTRACT



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ABSTRACT

Tritium has been long recognized as a useful tracer for the study of atmospheric transport, ocean circulation, and the global water cycle. In addition, the application of tritium measurements in various fields has grown significantly in the last few decades. Since 1963, the atmospheric test-ban treaty, bomb tritium concentrations in precipitation have significantly declined. Therefore, in the last two decades, global tritium concentration of precipitation (including anthropogenic and natural sources) has almost reached a steady-state level. The aim of this study is to estimate the temporal variation of the natural tritium concentration of precipitation during the past decades. To do this, we use a backward predicting time-series model that exploits the correlation between precipitation tritium concentration and the secondary neutron flux in the atmosphere. The measured tritium time series of 21 Northern and two Southern Hemispheric stations are used, while neutron monitor (NM) data, which are widely compared to the production rate of cosmogenic isotopes in the atmosphere, is used as an external variable for the model. Backward predicting SARIMAX statistical models are fit on the period 2001–2018 and provide estimates of the natural precipitation tritium levels for the bomb peak period 1960–2000. Evaluation of backward estimations on the 1990–2000 test period yields RMSE measures between 0.5 and 4.6 TU for four of the 23 investigated stations, pointing out locations where the neutron flux is a good predictor of the precipitation tritium concentration.

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1. Introduction

Tritium is a radioisotope of hydrogen with a half-life of 12.32 years (4500 ± 8 days) (Janovics et al., 2014; Lucas and Unterweger, 2000) and is found in nature as a part of the water molecule and organically-bound tritium (OBT). Tritium is produced naturally in the upper atmosphere by the interaction between secondary nuclear particles of cosmogenic origin, mainly neutrons, and protons with nitrogen and oxygen nuclei (Craig and Lal, 1960; Masarik and Beer, 2009). The secondary neutrons mainly produce cosmogenic isotopes, such as ^{14}C and ^{3}H, at energies greater than 1 MeV. Theoretical studies have calculated a natural tritium production rate of ~2500 atoms·m^{-2} s^{-1} (Craig and Lal, 1961; Masarik and Beer, 1999). Two-thirds of the cosmogenic tritium is produced in the stratosphere and one third in the troposphere. The formed tritium reacts with stratospheric oxygen and hydroxide ions in the form of $T^{+} + OH^{-} \rightarrow$ HTO and the tritiated water (HTO) enters the global water cycle (Rozanski et al., 1991).

The steady-state natural tritium content of stratospheric HTO vapor is estimated to be 3.8 kg. The tritium concentration of stratospheric water vapor is 5–9 × 10^5 tritium unit (TU, one tritium unit corresponds to 1 ^{3}H per 10^{18} hydrogen atoms). This is several orders of magnitude greater than the tritium content of the troposphere in both vapor and precipitation. This surplus is due to the high production rate and the low water content in the stratosphere (Ehhalt and Rohrer, 2009, 2002). From the large stratospheric reservoir, the natural tritium enters the troposphere through mixing at the tropopause. The tritium transport is moderate in the stratosphere-troposphere interaction, which has seasonal variability: it can be seen indirectly in the tritium of the precipitation (Zahn et al., 1998). The effects that influence the ambient level of tritium in precipitation are the various physical processes of the hydrological cycle, precipitation amount, dilution, the latitudinal effect of the neutron flux and the continental effect (Araguas et al., 1996; Rozanski et al., 1991). In addition, the variation of tritium concentration in precipitation can be influenced by several atmospheric processes such as cloud formation, convective and stratiform precipitation fractions (Aggarwal et al., 2016), atmospheric circulation, origin and transport of water vapor, change of moisture source region, evaporation, stratosphere-troposphere interaction, seasonality and prevailing weather systems (Momoshima et al., 2008; Tadros et al., 2014; Visser et al., 2018). The effect of solar activity has been proven by a previous study to have a significant influence on the long-term change of tritium concentration (Palcsu et al., 2018).

The level of global tritium of precipitation is the result of both natural and anthropogenic sources. A large part of the anthropogenic tritium was generated by atmospheric hydrogen bomb experiments. It is believed that more than 2000 nuclear weapon experiments were conducted during the cold war. As a result, in 1961, the tritium concentration measured in the precipitation in the mid-latitudes in the Northern Hemisphere exceeded 3000 TU. Approximately 520–550 kg of anthropogenic tritium from nuclear tests was injected into the atmosphere during the 1950–1960s (Michel, 1976). Since the Soviet–American Partial Test-Ban Treaty in October 1963, which banned nuclear tests in the atmosphere and under water, global tritium levels of precipitation have been steadily decreasing due to radioactive decay and dilution into the hydrosphere and atmosphere (Cauquoin et al., 2015; Jasechko, 2019). However, emissions from anthropogenic sources are continuing in the local environment of nuclear facilities (power stations, radioactive waste depositories, reprocessing plants), but their amount is much smaller than the results of nuclear weapons experiments (Köllő et al., 2011; Fiévet et al., 2013).

Recent studies have focused on bomb tritium time-series reconstruction based on long-term observation, in particular at Ottawa, Vienna, Tokyo, Thonon-les-Bains (Ducros et al., 2018; Gusyev et al., 2019; Michel et al., 2018). There are several commonly-used methods for reconstructing bomb tritium time series in precipitation, including a double reference curve developed between 1960 and 1986 (Celle-Jeanton et al., 2002; Michel et al., 2018; Morgenstern et al., 2010; Zhai et al., 2013). In addition to statistical models, bomb tritium concentrations in water vapor and precipitation were estimated using numerical methods. These have been able to study the spatial and temporal variability of natural and bomb tritium in water vapor and precipitation, as simulated by an Atmospheric General Circulation Model and its comparison with observations. However, the effect of the temporal variations of solar modulation was not taken into account in the model, which is an important parameter for a more accurate isotope modeling of natural tritium (Cauquoin et al., 2016, 2015).

The aim of our study is to identify the solar-induced natural variability of the tritium concentrations in the Northern and Southern Hemispheres in the past, which can be used as an important input parameter for atmospheric and hydrological modeling. Our backward estimation method exploits the relationship between the global tritium time series and the neutron flux, which has already been presented in our previous study (Palcsu et al., 2018).

2. Methods

2.1. Selection of tritium time series

The backward-estimating model was based on monthly precipitation tritium-concentration data measured at Northern and Southern Hemispheric monitoring sites. There were important considerations when selecting the sites: 1) a long-term continuous record of tritium concentration of precipitation is available; 2) error in analytical measurement should not exceed 2.0 TU; 3) the tritium concentration of precipitation is close to the natural level, which is known from some earlier studies (Begemann and Libby, 1957; Craig and Lal, 1961, 1960; Kaufman and Libby, 1954; von Buttlar and Libby, 1955).

The levels of tritium concentration in precipitation have returned close to the pre-bomb range in most parts of the world. This has already occurred for the first time in the tropics, in the Southern Hemisphere and lastly in the Northern Hemisphere (Araguas et al., 1996). However, the near-equilibrium concentration consists of two main components of natural and anthropogenic sources. Assuming that natural tritium concentration is dominant in the time series, its seasonal variability follows the same rule. That is, most of the natural tritium concentration of precipitation is supplied from the stratosphere. In addition, time-series in which anthropogenic sources dominate do not strictly follow seasonal variability i.e., irregularities can be observed. These irregularities are the result of anthropogenic sources. Anthropogenic tritium emissions in the Northern Hemisphere persist at many locations, which can be characterized by random fluctuations due to ground-level releases of technogenic tritium (including nuclear power plant and factory emission). Based on the above definitions, we can distinguish technogenic tritium-rich and poor stations. The ratio and the correlation of the tritium time series between pairs of stations are used as an indicator of the strength of the long-term cosmogenic production fluctuations as the cause of variability.

Several stations have local or regional anthropogenic tritium contamination that obscures the solar-induced natural variability of the tritium concentrations in the last two decades. Only a few of the IAEA GNIP stations have long and continuous time series, such as Ottawa (Fig. 1.) and Hong Kong, but these precipitation time series are loaded with significant anthropogenic tritium contamination caused by CANDU reactors (Harms et al., 2016; Michel et al., 2018). Moreover, Vienna (Austria), which has tritium measurements in precipitation from 1961 to 2012, is suspected to have regional contamination by nuclear power plants located in neighboring countries (Rank et al., 2012). Further European GNIP stations can be affected by local and regional anthropogenic sources such as Cuxhaven (Fig. 1.). The precipitation of this latter station is influenced by the moisture evaporated from the North Sea, which contains an artificial emission from the Le Hague reprocessing plant (Fiévet et al., 2013).

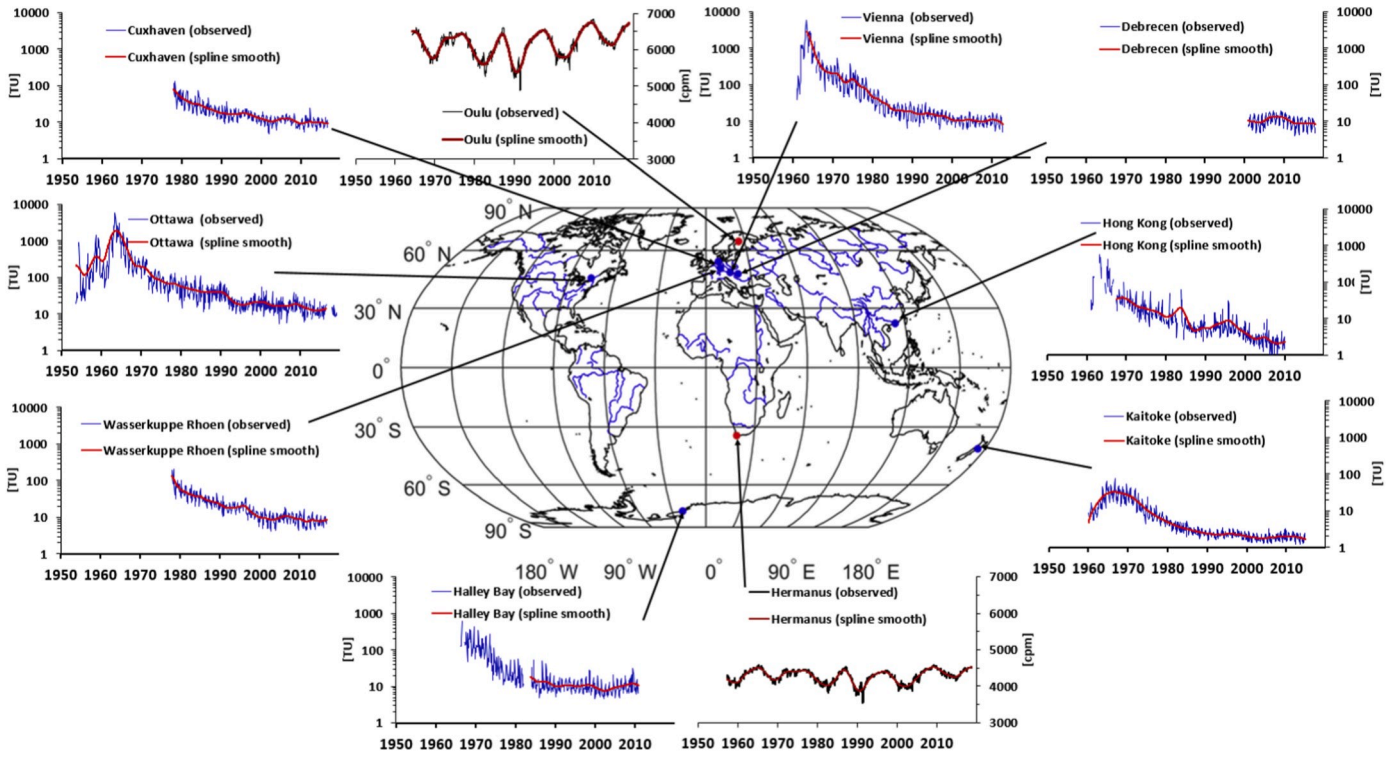

Fig. 1. The tritium time series and neutron monitor data in the Northern and Southern Hemisphere.

Stations in the Southern Hemisphere such as Kaitoke and Halley Bay are free of local tritium contamination (Morgenstern and Taylor, 2009). The selected data are embedded in the Global Network for Isotopes in Precipitation (GNIP), which is a joint program of the International Atomic Energy Agency (IAEA) and the World Meteorological Organisation (WMO). The GNIP and ANIP (Kralik et al., 2003) databases are available online (https://nucleus.iaea.org/wiser/index.aspx).

In this study, we examined tritium time series from 23 stations (Table 1.) and those were selected where a linear predictive time series model could be constructed with significant relationship with the external variable neutron flux (model details in section 2.2). These were 6 of the 23 stations: Debrecen, Wasserkuppe Rhoen, Weil, Zagreb, Halley Bay, and Kaitoke. Two long neutron-monitor data sets were used as external predictors, using the criteria that all neutron monitors that we use in this study must have been running since the bomb peak without large gaps in the data. The neutron monitors that we have selected are listed in Table 1.: Oulu (Finland) neutron monitor station has continuous time series in the Northern Hemisphere and Hermanus (South-Africa) neutron monitor station also has long-term observations in the Southern Hemisphere.

2.2. Statistical methods

The goal of the study was to backwards estimate the solar-induced natural variability of the tritium concentrations through their correlation with the neutron flux. To achieve this, a statistical time series model was constructed to represent the solar-induced behavior (correlation with neutron flux) as well as the annual seasonality and the natural variability due to other reasons. The time series model was fitted onto the nearly steady-state post-2001 part of the time series and then estimated backwards to estimate natural (hypothetical) tritium levels between 1964 and 2000 (Northern Hemisphere) and 1957–2000 (Southern Hemisphere). Prior to the model definition, a cross-correlation analysis was performed on a spline-smoothed, yearly time series on four stations to confirm the significant relationship between tritium concentrations and the neutron flux. An exponential trend, representing the long-term draining of atmospheric tritium reservoir, was fit on the post-1980 part of the time series (Münch et al., 2016). The trend took the form:

$$^3H = c + e^{-At+b}$$

where t is the number of months since January 1980.

The detrended time series was reversed to enable backward estimation of time series. Twelve-month differencing was applied to eliminate annual seasonality, i.e. the difference compared to the same month in the previous year was estimated with the regression model. A linear regression model was built between the 1-year differences of the detrended and reversed tritium time series; and the neutron flux. The residuals of the linear regression were tested to follow a stationary time series. A 12-lag augmented Dickey-Fuller (ADF) test was used to reject non-stationarity at 95% confidence level. If rejected, the detrended and reversed tritium time series were considered as a Seasonal Autoregressive Integrated Moving Average model with an external variable (Duan et al., 2016; Soebiyanto et al., 2010; Taşpinar, 2015). A SARIMAX (2,0,0,0,1,1,12,X) model was used to estimate the tth element of the time series Y_t:

$$Y_t = \alpha_1 Y_{t\pm1} + \alpha_2 Y_{t\pm2} + \delta_1 \varepsilon_{t\pm12} + \varepsilon_t$$

where two autoregressive, one seasonal moving average and a noise term were considered, respectively. The noise term ε_t was assumed to be a sample from a normal distribution with zero mean. Note that time lag was expressed with a $\pm$ sign, where $+$ refers to the model constructed for backward prediction on a reversed time series, while $-$ refers to the forward predictive model (t is the number of months since January 1980). The autoregressive model requires stationarity that could be enhanced by taking the seasonal differences of the original time series, i.e. differences from the same month of the previous year:

$$Y_t = M_t - M_{t\pm12}$$

The lag of 12 represents the monthly time series with annual seasonality. M_t is the time series of the residuals of a linear regression between the detrended tritium time series and the X_t external variable:

Table 1
Summary of tritium concentrations in precipitation (GNIP and local tritium study in Hungary) stations and neutron monitor records from Neutron Monitor stations.

Location name	Latitude	Longitude	Altitude, m a. s.l.	Number of data	Calculated trend parameters *A,b,c [TU]*	Period of ^{3}H or neutron record	Reference
Berlin (Germany)	52.46	13.40	8	452	0.010, 3.8, 7.9	1978–2016 (tritium)	IAEA/WMO (2019)
Braunschweig (Germany)	52.29	10.44	81	462	0.012, 3.7, 8.8	1978–2016 (tritium)	IAEA/WMO (2019)
Cuxhaven (Germany)	53.87	8.70	5	489	0.011, 3.6, 10.1	1978–2018 (tritium)	Schmidt et al. (2020)
Debrecen (Hungary)	47.47	21.49	110	192	0.012, 3.0, 10.0	2001–2017 (tritium)	This study
Garmisch Partenkirchen (Germany)	47.48	11.06	719	465	0.008, 3.9, 7.1	1978–2016 (tritium)	IAEA/WMO (2019)
Groningen (Netherlands)	53.23	6.55	1	466	0.012, 3.2, 9.7	1970–2010 (tritium)	IAEA/WMO (2019)
Hohensaas (Germany)	50.31	11.87	565	405	0.009, 3.7, 7.5	1983–2016 (tritium)	IAEA/WMO (2019)
Hong Kong (China)	22.31	114.16	66	492	0.008, 2.4, 2.6	1961–2010	IAEA/WMO (2019)
Karlsruhe (Germany)	49.03	8.36	112	477	0.010, 4.2, 7.4	1977–2016 (tritium)	IAEA/WMO (2019)
Koblenz (Germany)	50.33	7.6	85	501	0.011, 4.1, 8.7	1975–2016 (tritium)	IAEA/WMO (2019)
Konstanz (Germany)	47.67	9.19	443	467	0.006, 3.9, 5.5	1978–2016 (tritium)	IAEA/WMO (2019)
Krakow (Poland)	50.06	19.84	205	490	0.015, 3.6, 9.7	1975–2016 (tritium)	IAEA/WMO (2019)
Ottawa (Canada)	45.32	−75.67	114	754	0.007, 3.9, 10.6	1953–2019 (tritium)	IAEA/WMO (2019)
Regensburg (Germany)	49.04	12.10	365	467	0.012, 3.9, 9.7	1978–2016 (tritium)	IAEA/WMO (2019)
Thonon-Les-Bains (France)	46.37	6.47	385	571	0.006, 3.5, 4.2	1963–2012 (tritium)	IAEA/WMO (2019)
Tokyo (Japan)	35.68	139.77	4	672	0.014, 4.6, 3.0	1960–2015 (tritium)	Gusyev et al. (2019)
Valentina (Ireland)	51.93	−10.25	9	605	0.010, 2.6, 3.9	1958–2009 (tritium)	IAEA/WMO (2019)
Vienna (Austria)	48.24	16.35	198	676	0.012, 3.5, 9.6	1961–2018 (tritium)	ANIP (2019), (Kralik et al., 2003)
Wasserkuppe Rhoen (Germany)	50.49	9.94	921		0.009, 3.9, 7.0	1978–2018 (tritium)	Stumpp et al. (2014)
Weil (Germany)	47.59	7.59	249	343	0.007, 4.4, 4.0	1988–2016 (tritium)	IAEA/WMO (2019)
Zagreb (Croatia)	45.81	15.98	157	508	0.010, 3.4, 7.5	1976–2018 (tritium)	Bronić et al. (2020)
Halley Bay (Antarctica)	−75.58	−20.56	30	504	0.015, 2.3, 9.6	1965–2010 (tritium)	IAEA/WMO (2019)
Kaitoke (New Zealand)	−41.10	175.17	200	660	0.014, 1.1, 1.9	1960–2014 (tritium)	Morgenstern and Taylor (2009)
Oulu (Finland)	65.05	25.47	15	648	–	1964–2018 (neutron)	Usoskin (2017)
Hermanus (South-Africa)	−34.43	19.23	26	780	–	1957–2018 (neutron)	Moraal and Stoker (2010)

$$M_t = C_t - \beta X_t$$

where C_t is the detrended tritium concentration measurement and X_t is the neutron flux. Regression parameters $\alpha_1, \alpha_2, \delta_1$ and β were fitted on the post-2001 part of the detrended and seasonally differenced time series with maximum likelihood estimation. Therefore, the total number of fitted parameters was 4 on each of the detrended time series plus 3 for the exponential trend. The model was implemented using the Python StatsModels library (Seabold and Perktold, 2010).

3. Results

3.1. The ratio of tritium concentrations of precipitation

The role of natural and anthropogenic sources in the tritium concentration of a given station was assessed by investigating the ratio and correlation of time series, where common behavior is attributable to large-scale natural (solar-driven) reasons, while differences are due to local and anthropogenic effects.

The tritium content in precipitation of the Ottawa station was very similar to that of Vienna, as shown by the strong Pearson correlation (r = 0.99, n = 51, n – number of an elements based on yearly data). This similarity is due to the geographical and climatic characteristics of these two locations. However, there are significant differences in the tritium concentration covering longer and shorter periods. During the years 1971–78, the tritium concentration was higher in Vienna, while since 1980, this trend has reversed. Fig. 2 shows the ratios of annual tritium time series, which is derived from arithmetic averages of monthly tritium values. In the time series, we have searched for patterns that closely follow long-term natural changes, such as solar activity, in order to distinguish tritium rich and poor stations. At the Ottawa station, the surplus of tritium concentration is clearly visible compared to that of Vienna in 1980–2012. However, there is no significant decreasing trend which is due to local and regional emissions from the heavy water reactors operating in Canada. In addition, the regional tritium contamination of Vienna is caused by nuclear power plants located in neighboring countries and factories (Rank et al., 2012).

The ratio of Vienna/Cuxhaven tritium concentrations is characterized by stagnation, although minor changes can be observed in the time series (Fig. 2.). Comparing the tritium values of coastal (Cuxhaven) and continental (Vienna) stations, there is no significant difference, which is confirmed by the correlation coefficient of yearly time series (r = 0.95, n = 35). Although tritium concentration dilution is a typical process at coastal stations due to the huge water surface, it can be characterized by similar tritium values as Vienna, which suggests the growing relative importance of the contamination in the region. The sources of this contamination are French nuclear facilities bordering the English Channel (Fiévet et al., 2013; Tappin and Millward, 2015).

The Wasserkuppe Rhoen/Cuxhaven ratio has been steadily decreasing since 1980, which suggests the growing relative importance of the natural tritium source in Wasserkuppe Rhoen. This is also confirmed by the fact that the seasonal variability is regular, and the effect of solar activity can be revealed.

The tritium content in the precipitation of the Debrecen station has been different to that of Cuxhaven, as shown by the weak correlation of yearly time series (r = 0.13, n = 17). Debrecen station has a continental location, thus the continental effect prevails, which can be seen in the tritium concentration as well. In addition, seasonal and long-term changes are regular, which means that the tritium time series represents natural changes. This is supported by the fact that the station environment is free from local contamination (Köllő et al., 2011).

Regular and irregular changes were identified in the tritium time series. The regular changes indicate a dominance of the tritium of natural origin in the time series of Debrecen and Wasserkuppe Rhoen, ie. they follow long-term changes. In contrast, irregular changes are observed in time series rich in anthropogenic tritium and local/regional tritium contamination, which is typical in the cases of Ottawa, Vienna, and Cuxhaven.

3.2. Relationship between neutron flux and tritium concentration of the precipitation

In an earlier study, we presented for the first time, the relationship between tritium in precipitation and neutron monitor count rate (Palcsu et al., 2018). This relationship could be confirmed using the time series of two more stations, Halley Bay and Wasserkuppe Rhoen.

Spline-smoothed time series of tritium concentration of precipitation from four stations were applied for cross-correlation analysis (Fig. 3.). Cross-correlation coefficients are strong for all stations, above the 95% significance level. This shows that the neutron monitor count rate is the leading factor in the variation of tritium concentration. Cross-correlation significance has been calculated by the Ebisuzaki method because the high degree of autocorrelation in the spline smoothed series requires non-parametric methods of the significance estimate (Ebisuzaki, 1997). The relationship between the two variables confirms the use of neutron monitor data as an external variable to estimate the solar-induced tritium of precipitation.

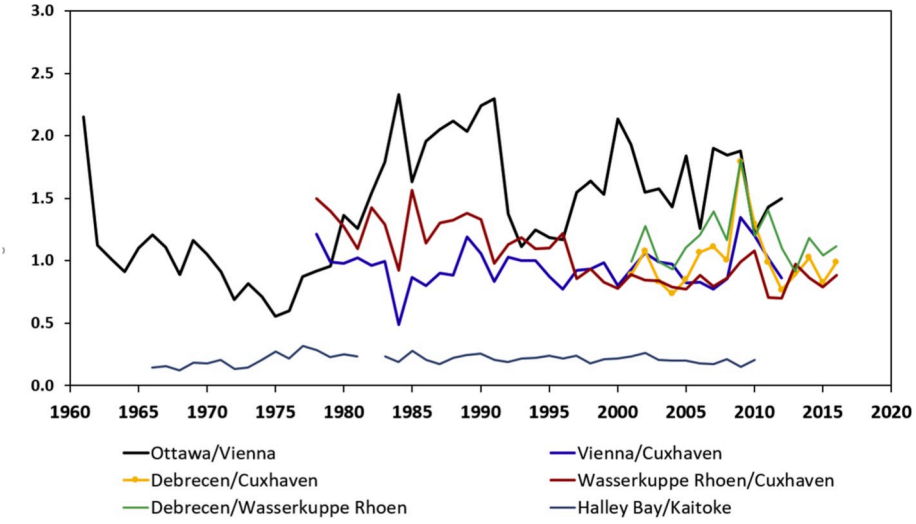

Fig. 2. The ratios of the long-term trends of tritium concentration of precipitation (ratios after calculating the annual averages).

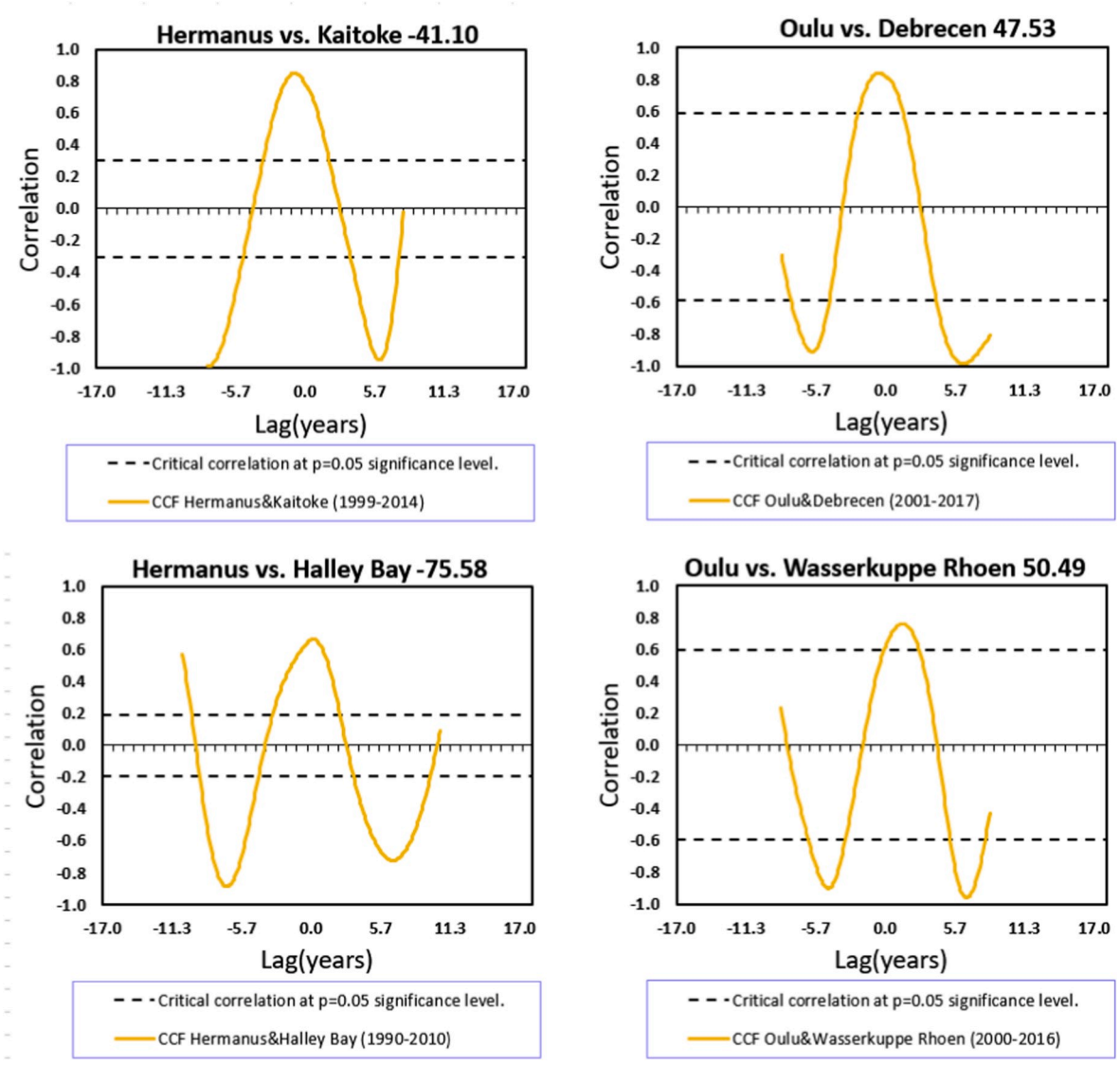

Fig. 3. Cross-correlation between neutron flux and tritium concentration of precipitation in the Northern (Debrecen, Wasserkuppe Rhoen) and Southern Hemisphere (Kaitoke, Halley Bay). The black dashed lines denote a critical correlation at p = 0.05 significance level calculated by the Ebisuzaki method.

3.3. Time series model

The relationship between the surface neutron flux and the precipitation tritium concentration was exploited to build a backward predictive SARIMAX statistical model to estimate natural tritium levels in the precipitation in the past decades. The obtained trends had exponents *A* around -*0.*01 month^{-1}, the concentrations are now close to equilibrium after the rapid decay in the second half of the 20th century (Table 1). After fitting the SARIMAX model on each of the time series presented in Table 1, we selected stations where the relationship with the external variable (neutron flux) remained significant besides the internal (autoregressive and seasonal moving average) terms and the residuals of the linear regression were rejected to be non-stationary by the ADF test at 12 lags and 95% significance level (Table 2). These stations were Debrecen, Wasserkuppe Rhoen, Weil, Zagreb, Halley Bay and Kaitoke. As the model was fitted on a detrended time series, its primary result is the time series of the natural solar-induced anomaly around the underlying trend. In Figs. 4–5. a constant background value was added to

Table 2
SARIMAX(2,0,0,0,1,1,12,X) model parameters for backward tritium concentration estimation fitted on the reversed post-2001 time series. RMSE is the root mean squared error between the estimate and the detrended 1990–2000 ^{3}H time series. Parameter superscripts *, ** and *** depict significance at the 95%, 99% and 99.9% level, respectively.

Station	α_1	α_2	δ_1	β	post-2001 mean [TU]	RMSE of estimate 1990–2000 [TU]
Debrecen	0.32 ± 0.07***	0.18 ± 0.07**	−0.77 ± 0.06***	0.004 ± 0.001**	10.4	n.a.
Wasserkuppe Rhoen	0.33 ± 0.07***	0.05 ± 0.07	−1.0 ± 0.3**	0.0025 ± 0.0007***	9.0	4.6
Weil	0.46 ± 0.08***	−0.10 ± 0.08	−0.86 ± 0.08***	0.0020 ± 0.00095*	9.9	9.0
Zagreb	0.31 ± 0.06***	0.10 ± 0.06	−1.0 ± 0.2***	0.0019 ± 0.0009*	8.2	9.1
Hally Bay	0.33 ± 0.09***	−0.09 ± 0.09	−0.8 ± 0.1***	0.007 ± 0.003**	9.7	3.9
Kaitoke	−0.01 ± 0.09	0.19 ± 0.07*	−1.0 ± 3.2	0.0005 ± 0.0002**	1.9	0.5

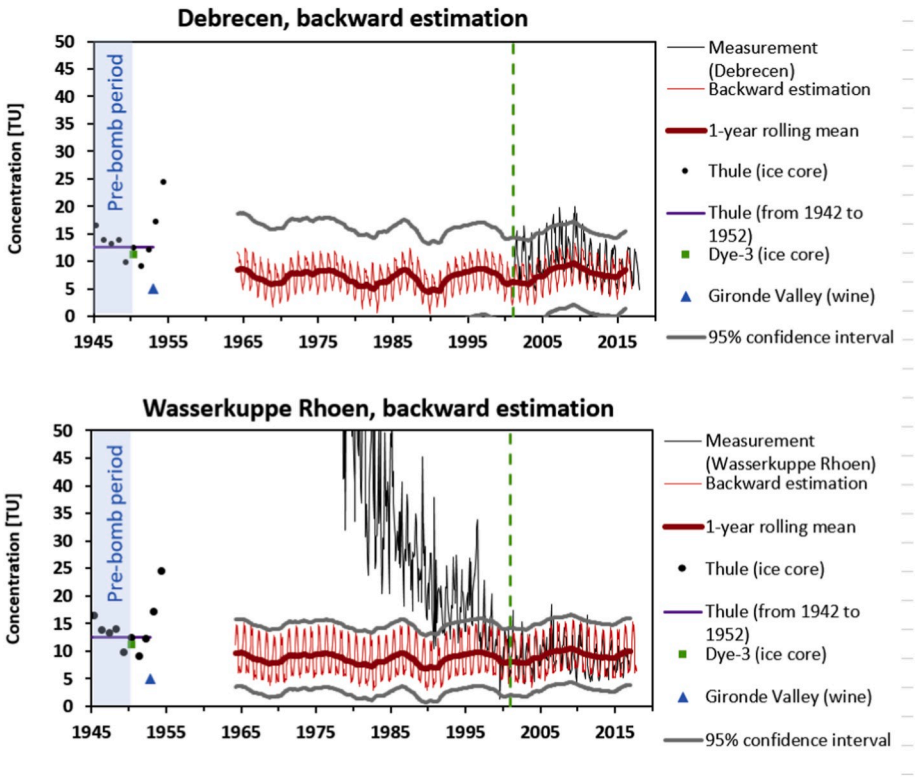

Fig. 4. Northern Hemispheric backward estimation of tritium concentration using a *SARIMAX(2,0,0,0,1,1,12,X)* model with the neutron flux from Oulu being the external variable X. The models were fit on the detrended post-2001 part on the time series (green line) and assume a constant background level that equals the last 11-year mean of the measurements. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

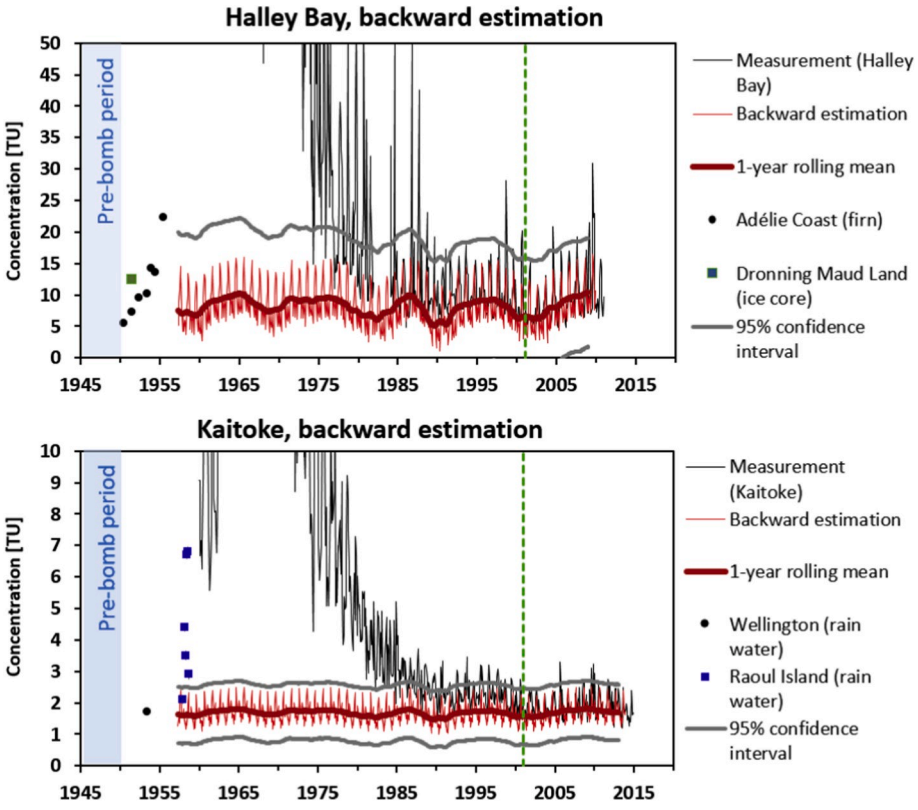

Fig. 5. Southern Hemispheric backward estimation of tritium concentration using a *SARIMAX(2,0,0,0,1,1,12,X)* model with the neutron flux from Hermanus being the external variable X. The models were fit on the detrended post-2001 part on the time series (green line) and assume a constant background level that equals the last 11-year mean of the measurements. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the model results; defined as the mean concentration of the last solar cycle period (11 years) in the measured time series. To assess model error, the root mean square error (RMSE) was calculated between model results and the detrended 1990–2000 time series.

The model is also suitable for forward predictions. In this application, the 1990–2009 period was used for model fitting and results were evaluated on the post-2010 time series (Table 3). The SARIMAX time series model was fitted on all stations presented in Table 1. Among these, Debrecen, Wasserkuppe Rhoen, Weil, Halley Bay, and Kaitoke showed a significant relationship with the neutron flux, similarly with the backward estimating period. Meanwhile, Karlsruhe and Koblenz were found to have a significant relationship with the neutron flux when fitting the time series model on the 1991–2009 period, while Zagreb was found to not have this relationship.

The SARIMAX model estimates show the cyclic behavior of precipitation tritium concentrations caused by solar cycles, which could not be measured due to the large anthropogenic pollution in the second half of the 20th century. Meanwhile, the seasonal part of the model captures the annual variability. Due to the large noise caused by other natural and anthropogenic factors, the confidence intervals are wide, reaching 50–100% of the expected value. The 1990–2000 root mean square error between the detrended time series and the predicted anomaly was found to be at around 50% of the mean absolute values, with worse performance for two stations (Weil and Zagreb) and better performance for Kaitoke (Fig. 6.). With these uncertainties, the backward predicted time-series are proposed as estimates of the natural precipitation tritium concentration in the past at stations where the neutron flux is a good predictor of the tritium level.

3.4. Comparison of estimated and measured data

Here, we compare the estimated and measured tritium in precipitation at four sites representative of each hemisphere: Debrecen, Wasserkuppe Rhoen (Northern Hemisphere) and Kaitoke, Halley Bay (Southern Hemisphere). Tritium values from the pre-bomb period represent the natural level, which is supposed to be free from anthropogenic sources. Therefore, for comparing measured concentrations with the background level added to the predicted anomalies in the statistical model, we used the pre-bomb measurements from water, firn, wine and glacier samples from previous studies (Begemann, 1958; Fourré et al., 2006; Fourré et al., 2018; Taylor, 1966).

The background tritium level for Kaitoke was further compared with the measured tritium concentrations of Wellington, New Zealand (41°S, 275°E). The estimate shown in Fig. 5 Predicts an average concentration of about 1.76 TU for solar-induced tritium content of fallout rainwater at Kaitoke. It is clear that the reconstructed time series of Kaitoke is a match to that of the nearby Wellington (Kaitoke estimated 1.76 ± 0.4 TU in 1957 (Fig. 5.) and Wellington measured from 1.7 ± 0.2 TU concentration of the precipitation in 1953/54) (Taylor, 1966; von Buttlar and Libby, 1955). In addition, the results were compared with the Raoul Island (29°S, 178°W) tritium data (Fig. 5.), the first data point (2.1 ± 0.2TU) of which closely matches the estimated value. The tritium concentration of the samples from summer in 1958 is higher than the estimated value because it probably contained some fallout from the Hardtack Pacific test series of 1958 (Taylor, 1966).

For comparison between our background tritium value at Halley Bay and the pre-bomb levels, two measured tritium content values in ice cores from Antarctica were available from earlier studies (Oerter et al., 1999; Ravoire et al., 1970). The first such station in Dronning Maud Land/DML07 (76°S, 8°W), which is relatively close to Halley Bay, but it is not representative of the coastal area. The natural tritium value 12.5 ± 7.5 TU from the station is higher than the estimated values for Halley Bay, which can be explained by the continental effect. While the second station, Adélie Coast (66°S, 140°W), is located on the other side of the continent, its geographical and climatic characteristics are similar to those of Halley Bay. This similarity can be seen in the agreement between the estimated (9.2 ± 0.5 TU) and the measured (7.5 ± 2.5 TU) tritium content, which supports the model's background estimation.

Estimates for the Northern Hemisphere represent the inland of the European continent, which we compared with observations from Greenland stations and France, which are free of anthropogenic sources, and thus well represent the pre-bomb period. For the Debrecen station, the estimated tritium level (10.9) is lower than that observed at Thule (12.6 ± 0.5 TU) (Begemann, 1958). This could also be caused by the fact that Thule (77° N, 140° W) is closer to the North Pole than Debrecen, which is more favorable for the production of cosmogenic tritium, which is known as the latitude effect. The latitude effect can be observed for Dye-3 (65° N, 44° W), so that the concentration of tritium is higher (11.1 ± 0.5) than that of Debrecen and lower than that of Thule.

In addition, the Debrecen estimates were compared with tritium values from wine samples. The estimated value (10.9) in Debrecen is higher than the tritium concentration (4.9 ± 0.5 TU) of wine from the Gironde Valley (France, 45° N, 0.6° W) (Libby, 1955). This can be explained by the fact that the wine region is closer to the open water surface, which facilitates the dilution of tritium, while in Debrecen the continental effect is dominant. This effect is also seen in the Wasserkuppe Rhoen, as it has a higher tritium concentration (8.5 TU) than the Gironde valley (4.9 ± 0.5 TU).

Overall, the estimates are matched or close to the observed values in both the northern and southern hemispheres. The variability of the solar-induced tritium estimated by the SARIMAX model remains in the range of a given background value during backward estimation. Note that this comparison does not validate the anomalies predicted by the statistical model, only shows that the concentrations are now close the natural levels and the model estimates with the applied background levels are in the range of pre-bomb levels. It is an encouraging result that we can process using reconstructed ice core tritium time series.

4. Conclusion

The tritium concentration of precipitation is an important input parameter for atmospheric and hydrological modeling, and additionally provides fundamental information for surface hydrology assessment. This paper analyzes the tritium time series of precipitation from Northern and Southern Hemispheric stations. These environments contain natural and artificial sources of tritium, which were categorized

Table 3
SARIMAX(2,0,0,0,1,1,12,X) model parameters for forward tritium concentration estimation fitted on the 1990–2009 time series. RMSE is the root mean squared error between the estimate and the detrended post-2010 ^{3}H time series. Parameter superscripts *, ** and *** depict significance at the 95%, 99% and 99.9% level, respectively.

Station	α_1	α_2	δ_1	β	*post-2010 mean [TU]*	*RMSE of post-2010 estimate [TU]*
Debrecen	0.2 ± 0.1*	0.1 ± 0.1	−0.8 ± 0.1***	0.004 ± 0.001***	9.3	3.1
Karlsruhe	0.44 ± 0.06***	0.09 ± 0.06	−0.91 ± 0.08***	0.004 ± 0.002**	8.3	7.5
Koblenz	0.35 ± 0.05***	0.10 ± 0.06	−0.80 ± 0.06***	0.002 ± 0.001*	8.8	6.2
Wasserkuppe Rhoen	0.30 ± 0.06***	0.14 ± 0.07*	−0.87 ± 0.08***	0.003 ± 0.001***	8.4	7.2
Weil	0.32 ± 0.04***	−0.01 ± 0.05	−1.0 ± 0.8	0.003 ± 0.001*	8.7	12.3
Hally Bay	0.33 ± 0.05***	−0.11 ± 0.05*	−0.84 ± 0.06***	0.005 ± 0.001**	9.7	3.0
Kaitoke	0.09 ± 0.07	0.05 ± 0.07	−0.88 ± 0.07***	0.0005 ± 0.0001***	1.9	0.5

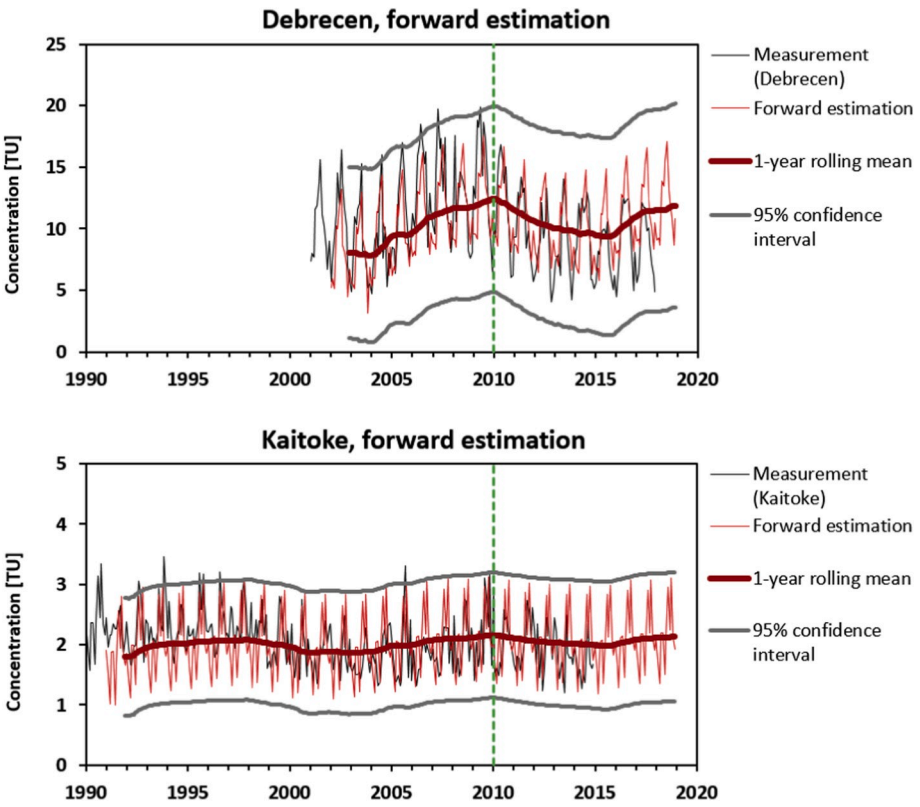

Fig. 6. Northern and Southern Hemispheric forward estimation of tritium concentration using a *SARIMAX (2,0,0,0,1,1,12,X)* model with the neutron flux from Oulu and Hermanus being the external variable X. The models were fit on the detrended 1990–2009 part on the time series (green line) and assume a constant background level that equals the post-2010 mean tritium concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

as rich and poor in technogenic tritium. The technogenic tritium-rich stations showed a weak correlation with the neutron monitor data because they were loaded with local and regional contamination. The technogenic tritium-poor stations had a natural seasonal pattern, the variation of tritium followed well the change in neutron flux count rate. The temporal variability of tritium in the Northern and Southern Hemispheres at technogenic tritium-poor stations is well determined by the temporal variations of solar modulation.

The relationship between neutron flux and tritium time series were exploited to reconstruct the seasonal and long-term variability of past solar-induced tritium time series by SARIMAX model. The statistical method provides a backward estimate of the natural tritium level without using the information on the bomb peak and its atmospheric decay. However, the method is only applicable at locations where local tritium sources are weak and therefore the neutron flux is a good predictor of precipitation tritium levels. On the 1990–2000 test period, RMSE between 0.5 and 4.6 TU were found between the statistical model and the detrended measurement for 4 of the 23 stations, although the model was applicable for two more stations with larger errors. The SARIMAX model can be used to suggest which stations are dominated by local pollution and which are the stations where the natural variability of tritium is significant in precipitation. The constructed statistical model was also shown to be applicable for forward prediction of monthly tritium time series.

The backward estimated tritium values remained within the expected range at the applied background concentration. However, further validation should be possible by more measurement data from glacier and wine samples. The reconstructed results can be used for research on the stratosphere-troposphere interaction, water cycle and related studies in surrounding areas.

Data availability

The data used in this study are all freely accessible from existing sources. The neutron monitor data can be found on the Neutron Monitor Database website (http://nmdb.eu), and Oulu neutron monitor data (http://cosmicrays.oulu.fi/), while data from the Hermanus neutron monitor can be accessed freely from North-West University's webpage (http://natural-ciences.nwu.ac.za/neutron-monitor-data). The presented model results are freely available from the authors upon request.

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.

CRediT authorship contribution statement

Elemér László: Conceptualization, Methodology, Software, Data curation, Writing - original draft, Writing - review & editing. **László Palcsu:** Data curation, Writing - review & editing. **Ádám Leelőssy:** Conceptualization, Methodology, Software, Visualization, Software, Validation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.atmosenv.2020.117605.

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