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Solar activity cycles recorded in long-term data on tritium activity concentration in precipitation at Zagreb, Croatia

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ABSTRACT

It has been expected that the solar cycle may have an influence on the production rate of cosmogenic tritium. However, prevailing anthropogenic bomb tritium in precipitation in the second half of the 20th century prevented such studies. We analyzed long-term data (1976–2020) of tritium activity concentration in precipitation at Zagreb, Croatia, by various statistical methods looking for the solar cycle periodicity. Frequency and Wavelet analyses were performed on the whole data set, while sinusoidal fitting was performed on data since 1996, when bomb tritium is negligible. All methods resulted in two distinct periods. The shorter 1-year period corresponds to the annual variation of tritium in precipitation typical for the Northern Hemisphere stations. The longer period of 10.21 yr, ≈11 yr and 12.17 yr was obtained by frequency analysis, wavelet analysis and sinusoidal fitting, respectively. These values are close to the solar cycle with 11 yr period on the average (ranging from 9 yr to 13.6 yr). Additionally, we compared the maxima in the smoothed monthly sunspot number in the 23rd and 24th solar cycles and the minima in tritium activity concentration in precipitation. A delay of about 30 months between them was observed and plausibly explained by the residence time of cosmogenic tritium in the stratosphere before entering the troposphere.

1. Introduction

Radioactive isotope of hydrogen, tritium (^{3}H), with the half-life of 12.32 years (4500 ± 8 days) (Lucas and Unterweger, 2000), is of both cosmogenic and anthropogenic origin. Natural cosmogenic tritium is produced in the atmosphere from the interaction of cosmic radiation with atmospheric nitrogen. Most of the naturally produced tritium (99% of a global natural inventory of 3.6 kg of tritium) oxidizes to water, becoming a constituent of the water molecule, $^1H^3HO$, and enters the natural water cycle. The average natural tritium activity concentration in environmental waters prior to nuclear testing has been estimated to range from 0.12 to 0.9 Bq l^{-1} (1–8 TU) with the highest concentrations occurring in mid-continental areas (Mook, 2000).

The natural levels of tritium in the environment have been disturbed by the anthropogenic production of tritium. The anthropogenic tritium can be divided into the "bomb-produced" tritium and technogenic tritium. The bomb-produced tritium has been a consequence of a series of thermonuclear atmospheric testing of fusion weapons between 1952 and 1963. The highest activity concentration of tritium of about 6000 TU (700 Bq l^{-1}) was observed in 1963 in precipitation at the continental stations of the Northern Hemisphere (IAEA/WMO, 2017; Mook, 2000; Nikolov et al., 2018) and it is known as the „bomb-peak". After the ban/cessation (Nuclear Test Ban Treaty in 1963) of atmospheric thermonuclear tests, tritium activity concentrations began to decline gradually due to the relatively short half-life of tritium and exchange between the compartments of the hydrological cycle, mostly due to dilution of tritiated precipitation in ocean waters. The bomb-peak tritium has been globally distributed thus labeling precipitation and other types of water bodies in the hydrological cycle (Michel, 2005). The value of tritium as a transient tracer for studying hydrologic processes was quickly recognized and for the past five decades of the 20th century, tritium has been widely used to obtain time scales for various processes in oceanographic and hydrologic systems (Michel, 2005).

The thermonuclear "bomb peak" is barely present in modern precipitation and tritium contents in precipitation have generally decreased to near background levels. The scientific value of tritium in precipitation for hydrological applications is no more as high as in the second half of the 20th century (IAEA, 2017) due to almost constant mean annual values.

Technogenic tritium should be also mentioned as a source of local or regional tritium activity above the new natural level. Technogenic tritium is produced in various industries, such as nuclear power plants,

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nuclear reactors, future fusion reactors, fuel reprocessing plants, and is present in various commercial products (Nikolov et al., 2018).

Tritium activity concentration in precipitation has been monitored since 1952. International Atomic Energy Agency (IAEA) and World Meteorological Organization (WMO) established in 1961 a program of worldwide monitoring isotopic composition of monthly precipitation called GNIP (IAEA/WMO, 2017). The worldwide database of tritium activity concentration, and also stable isotope composition of precipitation, is available through the WISER – Water Isotope System for data analysis, visualization and Electronic Retrieval database (IAEA, 2017). The objective of the GNIP program was and still remains a systematic collection of data on the isotopic composition of precipitation across the globe to determine temporal and spatial variations of isotopes in precipitation.

Prevailing anthropogenic bomb tritium in precipitation before 1996 prevented studies on whether the natural production of (cosmogenic) tritium was influenced by variations in solar activities. Recently, it was shown that some long-term tritium activity data showed modulation of cosmogenic tritium in meteoric precipitation by the 11-year cycle of solar activity (Palcsu et al., 2018). Our aim in this paper is to look at the Zagreb long-term tritium-in-precipitation data and to look if the solar cycle periodicity can be detected.

2. Methods

Monitoring of tritium activity concentration in monthly precipitation at Zagreb (Croatia, 15.98 E, 45.81 N, Fig. 1.) has been continuously performed since 1976 (Krajcar Bronić et al., 1998, 2020). The data are included in the Global Network of Isotopes in Precipitation (GNIP) and available through WISER until 2003 (IAEA/WMO, 2017).

Details on the experimental method of tritium activity concentration measurement, including changes and improvements in measurement techniques since 1976, have been described in (Krajcar Bronić et al., 2020). Currently, the liquid scintillation counting (LSC Quantulus 1220) with electrolytic enrichment of water with tritium is applied (Stojković et al., 2018).

Tritium activity concentrations are here expressed in „tritium units“, TU, which is a widely used unit in atmospheric and hydrologic studies (IAEA, 2017). One tritium unit (TU) is defined as one tritium atom per 10^{18} atoms of hydrogen, equivalent to 0.118 Bq l^{-1}.

Our long-term data were evaluated by applying frequency analysis (FA), wavelet analysis (WA), and sinusoidal curve fitting (SF). To perform FA for our unevenly spaced discrete data, we used the Lomb periodogram (Horne and Baliunas, 1986). For the further evaluation of the frequency spectrum in the time dimension, the Wavelet method was used. In order to encompass unevenly spaced data the algorithm used is based on the Weighted Wavelet z-transform (Foster, 1996). Wavelet representation gives time-frequency dependence which can further support the Lomb periodogram data. The drawback is the loss of the frequency resolution. Sinusoidal regression was then used on data where the “bomb-peak” influence is negligible, i.e., to data since 1996, to find dominant frequencies. The algorithm assumes the sinusoids with unknown amplitudes and phases and is based on a least-squares criterion and singular value decomposition. The chi-squared value is a measure of fitting error. Past 4.05 software was used (Hammer et al., 2001).

3. Results

3.1. Tritium activity concentration in precipitation

The complete set of tritium activity concentrations (A) in monthly precipitation in Zagreb, for the period 1976–2020 is presented in Fig. 2. Data for 2019–2020 are added to the dataset available in (Krajcar Bronić et al., 2020). Note the gap in 1994 due to local contamination with the technogenic tritium in the nearby department close to the sampling site. As a consequence of local contamination, a new location for precipitation sampling has been used since 1995.

The tritium pattern (Fig. 2) is typical of continental stations of the Northern Hemisphere, Seasonal variations were superposed to the basic decreasing trend of mean annual values until approximately 1996. The maximal ^{3}H activity concentration at station Zagreb is observed between May–July, mostly in June. A secondary maximum (Rozanski et al., 1991) is also observed occasionally in January and/or February. Since 1996 no significant decrease has been observed, although average values for the recent periods indicate a slight decrease. The average value for the whole period 1996–2020 is 8.7 ± 3.9 TU, for 2007–2020 8.3 + 3.6 TU, and for 2012–2020 7.8 ± 3.3 TU. Seasonal variations remained observable, with winter activities close to the natural prebomb ^{3}H levels (≤5 TU), and summer values rarely above 20 TU.

3.2. Frequency analysis

Results of frequency analysis (FA) based on the data from 1976 to 2020 are shown in Fig. 3. The strongest peak, well above the significance level $p = 0.01$, is obtained at the frequency $f = 0.08326$ month^{-1}, which corresponds to the period of 12.01 months. This is expected since the tritium activity concentration exhibits strong annual seasonality (Fig. 2.). There is another peak in the frequency distribution that is above the significance level of $p = 0.05$ at the frequency $f = 0.00816$ month^{-1}, corresponding to the period of 122.55 months or 10.21 years.

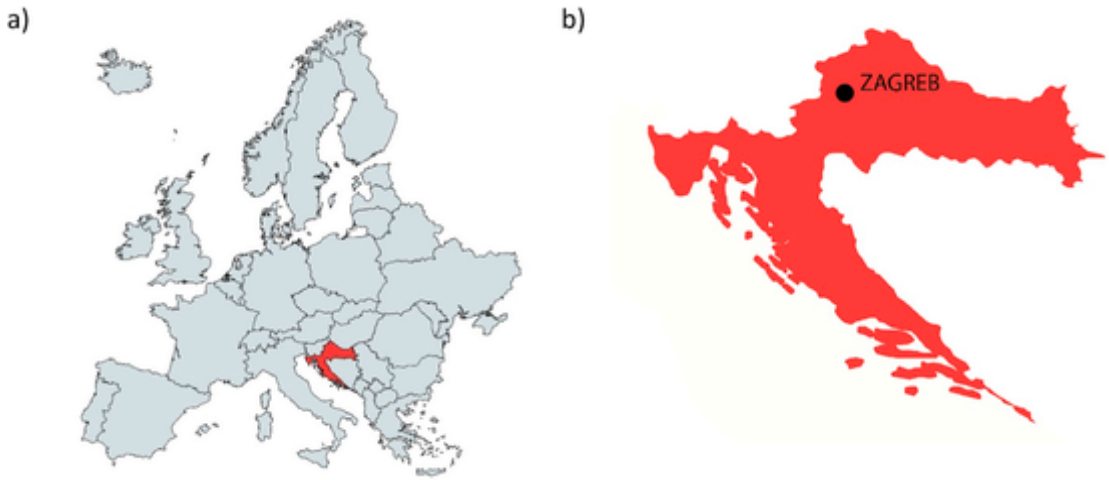

Fig. 1. a) Map of Europe with Croatia highlighted in red. B) Map of Croatia with the position of the capital city Zagreb.

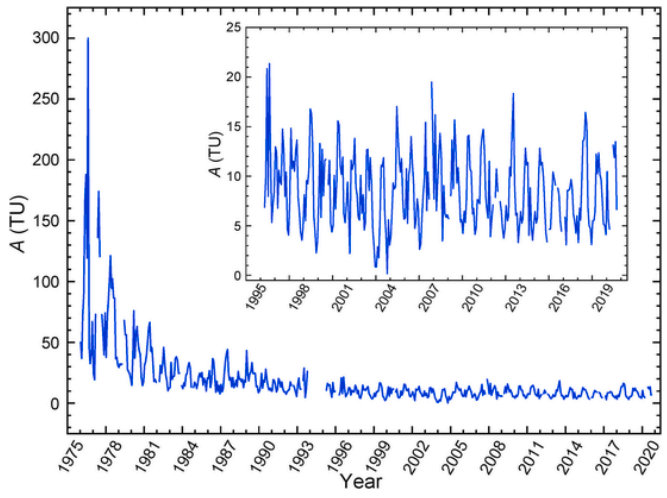

Fig. 2. The complete set of tritium activity concentration data in monthly precipitation in Zagreb, for the period 1976–2020. Insert: data for 1996–2020.

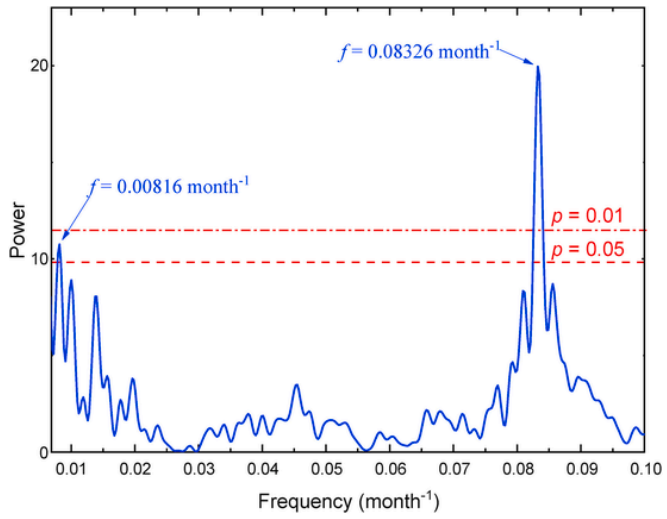

Fig. 3. Frequency – Power spectrum for precipitation data in Zagreb from 1976 to 2020. Significance levels p of 0.01 and 0.05 are also shown.

3.3. Wavelet analysis

Results of the Wavelet analysis (WA) on the same data set as FA are shown in Fig. 4. Two important features are pronounced. Strong frequency signal around $f \approx 0.085$ month^{-1}, which corresponds to a period of one year (≈12 months) appearing from 1976 to 2020 with a few empty areas in it. Those areas are consequences of missing data in that range. Other pronounced frequencies are in the lower range corresponding to the period ≈11 years.

3.4. Sinusoidal fitting

The measured data from the period 1996 to 2020 were fitted to the three most dominant sinusoidal functions (Fig. 5a)

$$y_1 = 3.417 \cdot \cos\left(\frac{2\pi}{12}m\right) - 2.165 \quad (1a)$$

$$y_2 = 1.138 \cdot \cos\left(\frac{2\pi}{5.976}m\right) + 0.9848 \quad (1b)$$

$$y_3 = 0.9848 \cdot \cos\left(\frac{2\pi}{146.1}m\right) - 0.9848 \quad (1c)$$

where m is a number of months starting from January 1996. The period of 12 months (eq. (1a)) is simply explained by the seasonal annual variations. The period of ≈6 months (eq. (1b)) is a consequence of a smaller, so-called secondary maximum, observed occasionally in January and/or February. The sinusoidal curve (1c) with the longest period of 146.1 months, has maxima in 1997 and 2009 and minima in October 2003 and November 2015 (Fig. 5a).

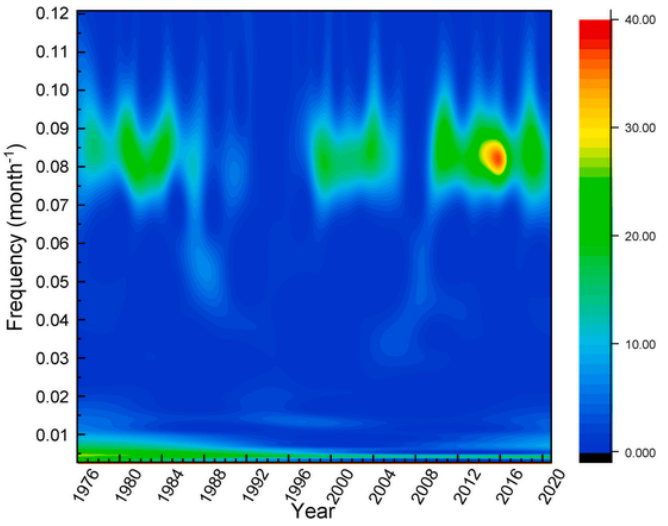

Fig. 4. The wavelet analysis showing two distinct periods corresponding to one year and ≈11 years. Missing data are clearly seen as empty areas in the spectrum.

4. Discussion

All three statistical methods of analysis of long-term data of tritium activity in precipitation at Zagreb, Croatia, resulted in two distinct periods. The shorter period of 1 year corresponds to seasonal variations of tritium in precipitation, typical for the continental stations of the Northern Hemisphere. The longer period of 122.5 months or 10.21 yr (FA), ≈11 years (WA) and 146.1 months or 12.17 yr (SF) is very close to the solar activity cycle period. Frequency analysis gave information of the peaks in frequency distribution and its significance levels. The Wavelet analysis shows a continuity of frequency distribution over the period 1976–2020, except for the short period with missing data. In addition, the SF gave positions of the curve maxima/minima.

Solar cycle periods available for 24 solar cycles since 1755 (SILSO, 2021) range from 9 years to 13 years and 7 months (13.58 yr), with an average of 11.0 ± 1.1 yr. The 23rd cycle lasted from August 1996 (minimum) to December 2008, i.e., 12 years and 4 months, while the 24th cycle ended in December 2019, having duration of exactly 11 years (Fig. 5b). A mean monthly number of sun spots ("SILSO | World Data Center for the production, preservation and dissemination of the international sunspot number," n.d.) is shown in Fig. 5b, where the blue line presents smoothing achieved with a Savitzky-Golay filter (Press and Teukolsky, 1990) which used polynomial order method 4 points of window 5 parameters.

The 12.17 yr SF curve, described in equation (1c), can now be compared to the monthly sunspots number (SILSO, 2021) (Fig. 5.). Maxima in the sunspot number, based on the smoothed curve (Fig. 5b, vertical black lines) are observed in March 2001 in the 23rd solar cycle and in July 2013 in the 24th solar cycle. The minima in the tritium activity concentration, based on the sinusoidal curve 1c, are observed in October 2003 and November 2005, respectively, and are shown as vertical black lines in Fig. 5a. Therefore, a delay of 31 months and 28 months in 23rd and 24th cycle, respectively, of the lowest tritium activity concentration compared to the maximum in sunspot number is observed. The plausible explanation of the delay may be the life cycle of tritium in the atmosphere: it is produced in nuclear reactions in the stratosphere and then it enters the troposphere by temporary mixing between the stratos-

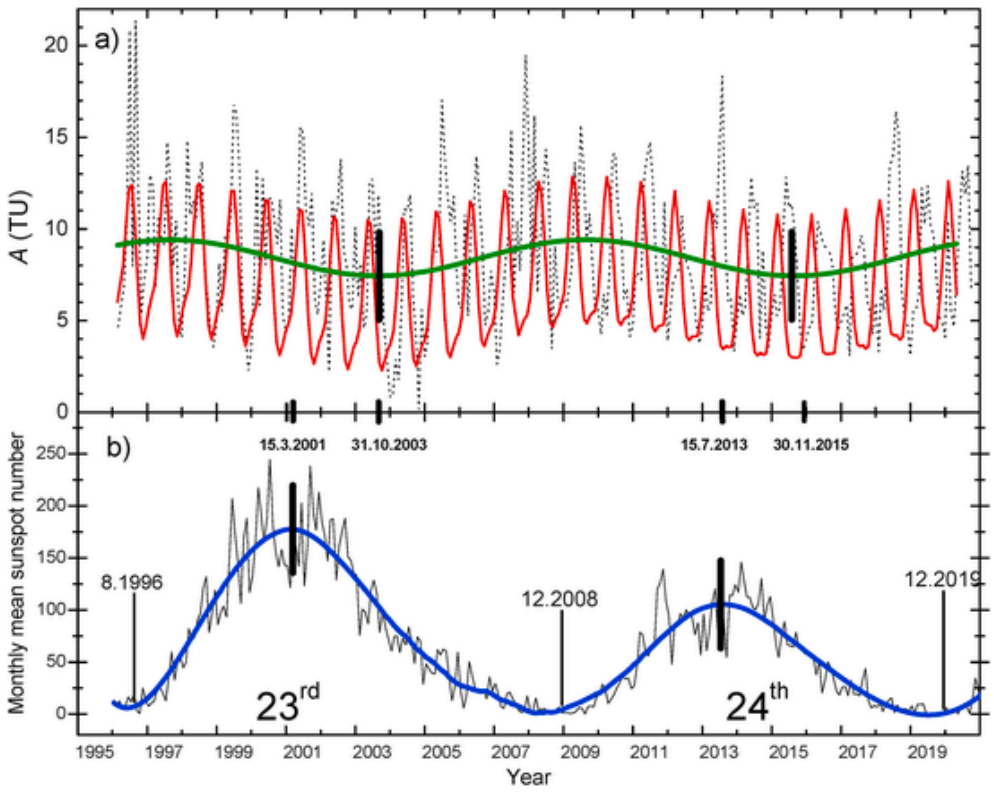

Fig. 5. a) Tritium activity concentrations in monthly precipitation in Zagreb, for the period 1996–2020 (dotted line) fitted by sinusoidal functions, eq. (1). Red line presents summed sinusoids (1a), (1b) and (1c). Green line presents the sinusoid (1c) with a period of 146.1 months. b) Monthly number of the sunspots (SILSO, 2021). The smoothed blue line is achieved with the Savitzky-Golay filter (Press and Teukolsky, 1990). The 23rd and 24th solar cycle and the months of the minima are also marked.

phere and troposphere at high latitudes in early spring. The atmospheric mixing that occurs in early springs suggests a delay of at least several months to a year of the appearance of tritium in the meteoric water. Taking into account the estimated residence time of tritiated water in the stratosphere of a few years (Mook, 2001), a delay of about 30 months is a reasonable delay. Previously, Palcsu et al. (2018) found that local maxima in ^{3}H activity concentration in precipitation at several stations with a long enough data record appeared to coincide with the maxima in neutron count rate, i.e., minima in the sunspot numbers. They found a periodicity in ^{3}H activity concentration variations of 12.4 ± 1.8 years and concluded that it is in good agreement with the 11-year solar cycle.

5. Conclusion

Strong evidence of the variations in tritium activity concentration in precipitation at Zagreb, Croatia, with the 10–12 yr period is obtained by the statistical analysis of the long-term data. For the solar cycle representation, we took the mean monthly sunspot number. Frequency analysis and Wavelet analysis gave information about the two significant periods in the distribution of ^{3}H activity concentration in precipitation at Zagreb. The most significant period of 1 year describes the annual variation typical for the Northern hemisphere stations, and the second period of 10.2 yr in the frequency spectrum (≈11 yr by Wavelet analysis) may be related to a solar cycle. Wavelet analysis confirmed the periodicity being constant over the complete period, except for the short periods with missing data. These findings support evidence of solar influence on meteoric tritium. Sinusoidal fit to the data after 1996, when bomb-tritium is no longer observed in precipitation, resulted in the periodicity of 146.1 months (12.17 years) confirming the period close to that of the solar cycle. We observed a delay of about 30 months between the maxima in the sunspot number and the minima in ^{3}H activity concentration in precipitation due to residence time of tritium in the stratosphere. This striking feature has been reported here for the first time. Our finding points to the importance of further exploration of this effect, both temporaly in precipitation in Zagreb in the 25th solar cycle, and spatialy to study possible latitude effect on tritium in precipitation, since it is known that the strongest exchange stratosphere-to-troposphere occurs between 30 and 60° N latitude each spring, causing a leakage of stratospheric water vapor into the troposphere. Further observations may additionally help in studying the rate of exchange between the stratosphere and the troposphere and in determining the residence time of cosmogenic tritium in the stratosphere.

Continuation of regular monitoring of tritium in environmental water bodies is therefore recommended in spite of the fact that tritium is no more very useful in hydrological applications. However, contribution to the atmospheric science is foreseen, especially when data for several solar cycles will be available from more sampling sites. For studies of natural production and relation with the solar cycle, local effects (technogenic ^{3}H) should be minimized or absent. Local technogenic tritium sources include nuclear power plants, other nuclear facilities that use tritiated material, and also future fusion facilities/power plants. Monitoring of tritium activity in the environment will therefore be of constant importance in the future from point of view of both scientific studies and applied environmental protection.

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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References

Foster, G., 1996. Wavelets for period analysis of unevenly sampled time series. Astron. J. 112, 1709–1729. https://doi.org/10.1086/118137.

Hammer, Ø., Harper, D.A.T., Ryan, P.D., 2001. Past: paleontological statistics software package for education and data analysis. Palaeontol. Electron. 4, 4.

Horne, J.H., Baliunas, S.L., 1986. A prescription for period analysis of unevenly sampled time-series. Astrophys. J. 302, 757–763. https://doi.org/10.1086/164037.

IAEA/WMO Global Network of isotopes in precipitation. The GNIP database [WWW Document]. URL http://www.iaea.org/water 2017

IAEA WISER water isotope system for data analysis, visualization and electronic retrieval URL https://nucleus.iaea.org/wiser/ 2017

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

Krajcar Bronić, I., Barešić, J., Borković, D., Sironić, A., Mikelić, I.L., Vreča, P., 2020. Long-term isotope records of precipitation in Zagreb, Croatia. Water 12, 226. https://doi.org/10.3390/w12010226.

Lucas, L.L., Unterweger, M.P., 2000. Comprehensive review and critical evaluation of the half-life of tritium. J. Res. Natl. Inst. Stand. Technol. 105, 541.

Michel, R., 2005. Tritium in the hydrologic cycle. In: Isotopes in the Water Cycle. Springer, pp. 53–66.

Mook, W.G., 2020. Environmental isotopes in the hydrological cycle. In: Principles and Applications, Volumes I, IV and V. IAEA, Vienna.

Nikolov, J., Krajcar Bronić, I., Todorović, N., Stojković, I., Barešić, J., Petrović-Pantić, T., 2018. Tritium in water—hydrology and health implications. In: Janković, M.M. (Ed.), Tritium—Advances in Research and Applications. NOVA Science Publishers, New York, NY, USA, pp. 157–213.

Palcsu, L., Morgenstern, U., Sültenfuss, J., Koltai, G., László, E., Temovski, M., Major, Z., Nagy, J.T., Papp, L., Varlam, C., 2018. Modulation of cosmogenic tritium in meteoric precipitation by the 11-year cycle of solar magnetic field activity. Sci. Rep. 8, 12813. https://doi.org/10.3390/w12010226.

Press, W.H., Teukolsky, S.A., 1990. Savitzky-golay smoothing filters. Comput. Phys. 4, 669. https://doi.org/10.1063/1.4822961.

Rozanski, K., Gonfiantini, R., Araguas-Araguas, L., 1991. Tritium in the global atmosphere: distribution patterns and recent trends. J. Phys. G Nucl. Part. Phys. 17, 523–536. https://doi.org/10.1088/0954-3899/17/S/053.

SILSO World Data Center for the production, preservation and dissemination of the international sunspot number [WWW Document], URL http://www.sidc.be/silso/home 2021 s1 April 2021

Stojković, I., Todorović, N., Nikolov, J., Krajcar Bronić, I., Barešić, J., Kozmidis Luburić, U., 2018. Methodology of tritium determination in aqueous samples by Liquid Scintillation Counting techniques. In: Janković, M.M. (Ed.), Tritium—Advances in Research and Applications. NOVA Science Publishers, New York, NY, USA, pp. 99–156.