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Tritium Behavior from Vine to Wine

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Abstract: The hydrogen radioactive isotope, tritium, not only reflects seasonal variation in precipitation but also variations on a local level. To use this radioisotope in authentication and geographical indication procedures, the tritium levels in vines, grapes, and wine were measured in two forms: (1) tissue-free water tritium (TFWT), measured in the free water of the plant or the aqueous phase of the wine; (2) organically bound tritium (OBT), measured in the organic part of the plant or wine (as ethanol). This paper presents the tritium behavior in vines from May to October and in the wine produced from harvested grapes for both tritium forms (TFWT and OBT) in connection with environmental tritium concentrations in air and precipitations during the 2019–2023 vegetation periods near the Râmnicu Vâlcea city. If the tritium of tissue-free water was influenced by precipitation and air humidity during the harvest period, the organically bound tritium recorded a maximum level with a delay of 1–2 months compared with tritium's seasonal variation in precipitation and air. The tritium values of early mean in precipitation and ethanol from wine were approximately an average value of 11 TU for all 5 years of observations.

Keywords: tritium in environment; liquid scintillation counting; tritium fractions in food and wine; authentication using radioisotopes

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Citation: Vagner, I.; Varlam, C.; Faurescu, I.; Faurescu, D.; Bogdan, D. Tritium Behavior from Vine to Wine. *Appl. Sci.* **2024**, *14*, 5478. https://doi.org/10.3390/app14135478

Academic Editor: Alessandro Genovese

Received: 21 May 2024
Revised: 18 June 2024
Accepted: 19 June 2024
Published: 24 June 2024

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1. Introduction

Currently, consumers are seeking natural foods and beverages in the market, with their prices incorporating not only the hard work required to obtain them but also the destruction-related dangers faced to achieve an eco-friendly harvest. Higher prices have increased the potential for the use of less expensive synthetic compounds, and the mislabeling of geographical locations has started to become another common way of committing fraud in the industry. Wine, with its worldwide market, is frequently subject to fraud in the wine market in general or collector fraud at the top of the wine market. A bottle of wine from a private collector obtained the price of GBP 105,000 at an auction at Christie's in London in 1985, and numerous historical and contemporary examples of consumption fraud can be found [1]. Special attention has been given to wine. In the EU, several adopted proposals have been applied both to the geographical indication [2] and the methods of analysis [3]. To ensure the correct labeling of the product and to deter the fraudulent use of synthetic compounds, analytical methods incorporating both stable isotopes and radioactive isotopes have been developed.

Isotopic ratios are official methods used in the EU since the 1990s for food and beverage authentication, not only in wine, due to their versatility in characterizing the climatic conditions, soil, location, and geology of the soil from which the food ingredients were provided. Nitrogen isotopes are related to agricultural practices. Sulfur isotopes are affected by geology, distance from the sea, or anthropogenic influences, and hydrogen, oxygen, and carbon isotopes are influenced by climatic conditions with geographical variability [4]. If the $^{13}C/^{12}C$ ratios in the CO_2 of the atmosphere are strongly modified by plant photosynthesis, the radioactive isotope of carbon, radiocarbon, has a small seasonal cycle, which is partly due to the seasonal input of ^{14}C-enriched stratospheric air into the troposphere and partly

to the seasonal contributions from biogenic and anthropogenic CO_2 fluxes [5]. The ^{14}C isotope was used to date old wine [6], with the procedure on the increased amount of atmospheric radiocarbon due to nuclear tests of the 1950–1963 period, which regularly decays each year. Unfortunately, it was necessary to obtain measurements of the amount of atmospheric radiocarbon since that period, and the ^{14}C atmospheric concentration was not a routine measurement in the 1950s. Apart from the lack of information, several factors affect the dating procedure, and only for very old wines does the method have some relevance. Alternative methods were investigated for young wines, with one of the promising methods being the concentration of pinotin A (a reaction product of maldivin 3-O-β-D-glucoside and 4-vinylcatechol in Pinotage wine), which seems to be connected to the age of red wine [7]. Another application of radiocarbon is to certify that certain alcoholic beverages are of agricultural or fossil origin. This method assumes that plant growth involves the rapid uptake of primarily atmospheric carbon, and during the manufacturing process, no other phenomenon or carbon fossil source interfered. Radiocarbon atmospheric content has been published for different locations [8,9], and even in locations where these data were missing, the raw material of the constituent ingredients could be used as reference data to certify the agricultural origin [10,11].

H and O isotopic data have been linked to their behavior in the water-feeding organic matter of food, so the seasonal variability of temperature and precipitation has specific isotopic fingerprints of the region from which ingredients are provided. The radioactive isotope of hydrogen, tritium, is produced in the upper part of the atmosphere through cosmic rays, mostly present as part of water molecules (HTO) from water vapor or precipitation. There is a seasonal difference in the northern hemisphere caused by the interaction of the stratosphere and troposphere, with its level of precipitation being affected by several parameters such as altitude, distance from the ocean coast, or anthropogenic activities. Tritiated water makes up a part of biological organisms as tissue-free water tritium (TFWT). Considering plants, the water content makes up approximately 80–90% of the fresh mass, but this percentage depends on the species and their stage of development [12]. Tritium from a plant water pool can be labeled in organic matter as organically bound tritium (OBT) through metabolic processes, with the main process being photosynthesis. The nature of the chemical bonds of tritium defines the type of organic tritium, labile or not. Non-exchangeable OBT is tritium bound to carbon atoms, unlike exchangeable OBT, which is bound to sulfur, nitrogen, or oxygen atoms [13]. Exchangeable organic tritium is in equilibrium with the plant's water pool, and its turnover rate is the same as TFWT, influenced by the surrounding atmosphere and soil water [14]. At any rate, this labile organic tritium can be folded into biological macromolecules and can exchange very slowly due to its isolation from cellular water, with this behavior causing a long debate with the aim of defining organically bound tritium [15,16]. If the plant's water pool rapidly reaches equilibrium with atmospheric moisture, TFWT reflects the tritium level of the environment when the sample was taken. This is not the case for organically bound tritium because it integrates the environmental tritium level of the growing period, which is why OBT is used for retrospective measures and is an important indicator of radioactivity monitoring programs near nuclear facilities. Assuming that the organically bound tritium level is related to the environment and, by consequence, to the location, we investigated its behavior in vines during the growing season in grapes and in wine to find a connection between its level and location.

A tritium analysis of wines is usually carried out to reconstruct the actual precipitation tritium level in the past [17]. The principal isotope tools to authenticate the wine plant extracts are radiocarbon level, $^{13}C/^{12}C$ ratios, and $^{2}H/^{1}H$ ratios. Few published studies have investigated tritium concentration in natural and synthetic products or orange oils from different locations [18,19]. In the case of wines, it has been confirmed that wine tritium data reflect not only the long-term trend or the seasonal variation in precipitation but also the local tritium level.

To use its level in the authentication and geographical indication procedures of vine, it is necessary to understand tritium behavior from vine to wine. This paper presents the tritium concentrations in vine components (leaves, branches, grapes) from June to November and in the wine produced from harvested grapes for both tritium forms (TFWT and total OBT) in connection with environmental tritium concentration in air and precipitations, during the 2019–2023 vegetation periods, near Râmnicu Vâlcea city. To correlate the influence of meteorological conditions with tritium behavior in vines to grapes and wine, the following monthly parameters were recorded: temperature, air humidity, amount of precipitation, tritium level in the atmospheric vapor, and precipitation.

2. Materials and Methods

2.1. Samples and Sampling Procedures

The vine samples were collected in a location from our institute during vegetation periods, starting from 2019 until 2023, from June to November. It started in June when the grapes were formed, and they were harvested in October for the wine, but the harvest was also done in November for the leaves and the grapes left in the vineyard.

The precipitation samples were collected monthly, according to IAEA recommendations [20], from 2019 to 2023 using a Palmex rainwater collector [21]. The atmospheric parameters were recorded daily by Davis Vantage Pro2 weather station, the reported values being the monthly average provided by the station.

For the tritium in air measurement, air humidity was trapped for one month, using an air pump with a flow rate of 4.80 L h^{-1} in molecular sieve type 13X. At the end of each month, the water trapped was extracted by heating the molecular sieve and trapping the water in a cold trap.

Soil samples were collected once a year, from the surface to 20 cm deep, and this kind of sampling was considered relevant for the collected sample types.

The ripe grape samples were collected each year in October, were prepared for TFWT and OBT analysis, and the same batch was used for the preparation of the wine, using natural fermentation of the grape juice, using a glass bottle hermetically closed in a dried place, for approximatively two months, until the opaque juice becomes clear.

2.2. Preparation Procedures

Each monthly precipitation was distilled according to ISO recommendations [22]: 250 mL of sample was distilled with 0.1 g of $KMnO_4$ and 0.1 g of Na_2O_2 (both analytical grade, supplied by Merck, Darmstadt, Germany), discarding the first 75 mL and collecting approximately 100 mL for preparation and measurement using liquid scintillation counting method.

Soil and vegetation samples were prepared for TFWT analysis by azeotropic distillation with toluene [23] using a Heidolph LABOROTA 4002 distillation installation (Heidolph, Schwabach, Germany). The ratio of sample: toluene (expressed as g:mL) was 1:5 for soil and 1:3 for vegetation samples. The first 50 mL of the water-toluene mixture was discarded, and the next 150 mL of this mixture was collected. The water was separated in a separation funnel and analyzed using the liquid scintillation counting method. The vegetation materials were dried in an oven at 60 °C for OBT analysis. The total OBT analysis requires a more elaborate procedure: 20 g of dried vegetable material was subsequently used in a Parr bomb type 1121 (Parr Instrument Company, Moline, IL, USA) at an O_2 pressure of 17 bars to obtain the combustion water, which was purified before OBT analysis. Purification of the combustion water was carried out using chemical treatment with Na_2O_2 and $KMnO_4$, followed by lyophilization. The water obtained after purification was checked to have a pH between 5.5 and 7 and conductivity under 50 μS cm^{-1} to be compatible with the type of scintillation cocktail used in our routine procedure for low-level measurements [24].

The wine samples obtained after the natural fermentation of the grape juice were fractionally distilled using an automatic distillation control system (ADCS) with Cadiot columns. The aqueous fraction resulting from fractional distillation (free water from wine)

was purified by applying chemical treatment ($KMnO_4$ and Na_2O_2) and lyophilization before liquid scintillation counting (LSC) for tritium analysis as TFWT. The ethanol samples from the fractional distillation of wines were combusted using the above-mentioned Parr bomb. A purification method similar to that of combusted water from vegetation was applied before tritium measurement from wine's ethanol using LSC.

2.3. Tritium Measurement Procedure and Correlation Coefficient

All tritium measurements were performed by a low-background liquid scintillation spectrometer Quantulus 1220™ (PerkinElmer, Waltham, MA, USA), using a low-background liquid scintillation cocktail (Ultima Gold uLLT, PerkinElmer, Waltham, MA, USA). Thus, 8 g of water sample (distilled water from precipitation, extracted water from air, soil, and vegetable material, or purified combustion water) was mixed with 12 g of scintillation cocktail mentioned above in 20 mL polyethylene vials. Samples, background, and tritium standards (Tritiated water provided by PerkinElmer; reference standard NIST SRM 4927E [25] with a certified tritium activity of 2,632,100 dpm/g $\pm$ 3.208%, reference date 12 June 2017) were counted for 500 min (50 min/cycle, 10 cycles/sample) with a counting efficiency between 26.6% and 28.5% at the best figure of merit. In the same experimental conditions, the background varied between 0.675 $\pm$ 0.016 and 0.798 $\pm$ 0.016 CPM (counts per minute), following a minimum detectable activity of about 0.5 Bq/L, evaluated according to ISO 9698:2019 (ISO, Switzerland) [22]. The uncertainty due to the statistical nature of radioactive decay and background radiation was reported at 1σ. Tritium-free water used as background was a deuterium-depleted water produced in our institute, with a deuterium concentration below 15 ppm [26]. To better visualize tritium variation during the observation period, the results were reported in tritium units (1 TU is equivalent to one tritium atom to 10^{18} hydrogen atoms). One TU corresponds to 0.119 Bq/kg of water using the following numerical constants: Avogadro constant, 6.0221×10^{23} mol^{-1}; molar mass of water, 0.018 kg mol^{-1}; tritium half-life 4500 days; tritium decay constant 1.54×10^{-4} $days^{-1}$.

The Pearson's correlation coefficient between the tritium concentration values recorded for precipitation and atmospheric water vapor and monthly atmospheric parameters (amount of precipitation, temperature, and air humidity) was calculated using the formula:

$$r = \frac{1}{n} \frac{\sum\limits_{i} (x_i - \overline{x})(y_i - \overline{y})}{\sqrt{\frac{1}{n}\sum (x_i - \overline{x})^2}\sqrt{\frac{1}{n}\sum (y_i - \overline{y})^2}}$$

where x_i is the monthly tritium concentration, and y_i is the monthly atmospheric parameter. This coefficient ranges from +1 to −1, with +1 indicating a positive correlation, −1 indicating a negative correlation, and 0 indicating no correlation.

3. Results and Discussion

The National Institute for Cryogenic and Isotopic Technologies is located on an industrial estate in the Sub-Carpathian hills, about 10 km far from Râmnicu Vâlcea city and about 200 m above sea level. The Carpathian Mountains and Sub-Carpathian hills constrain air mass circulation along the Olt River valley, causing a decrease in temperature from south to north and an increase in precipitation with the altitude. The temperature average of this location is 10.4 °C, and the precipitation average is 698.5 mm, values established by multiannual observations (2001–2010 period) from the meteorological station of Râmnicu Vâlcea city [27].

The monthly amount of precipitation varied between 4.6 mm in February 2019 and 166.4 mm in September 2022, Figure 1. The years 2019, 2020, and 2021 were dry years with annual amounts of precipitation lower than the characteristic value of 698.5 mm in this location: 616.6 mm in 2019, 601.2 mm in 2020, and 634.2 mm in 2021. The last two years were rainy years, with 758 mm in 2022 and 815.8 mm in 2023.

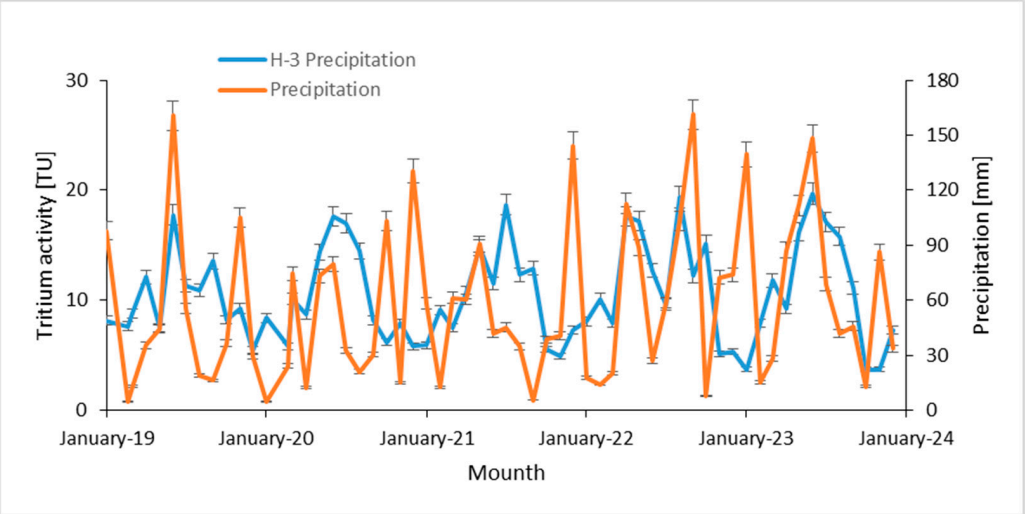


Figure 1. Tritium activity in precipitation and precipitation amounts during the 2019–2023 period.

The tritium activity concentration varied between around 4 TU during the cold months and a maximum of 22 TU during the warm months. The stratosphere is the main repository of tritium produced by cosmic rays in interaction with atmospheric nitrogen. During the late spring and summer of each year, the warming of the land masses causes instability in the troposphere. This break-up leads to a mixing of stratospheric air in the troposphere, increasing tritium activity concentration of precipitation. The Pearson coefficient between tritium activity concentrations and precipitation amounts is low, around 0.2, but its value increases for a long period of observations (15 years) to 0.87, proving that the months with maximum values of precipitation are the months with maximum tritium activity concentration, a location characteristic's [28].

The monthly recorded temperature from 2019 to 2023 varied between 0.3 °C, usually in January, and 24.6 °C in July, Figure 2. The annual means were higher than that established by National Meteorological Administration: 12.3 °C in 2019, 11.6 °C in 2020, 11.5 °C in 2021, 11.8 °C in 2022, and 12.3 °C in 2023. The behavior of tritium concentration in precipitation during this period is typical of continental temperate climate [29], with major seasonal differences caused by the interaction of the stratosphere and troposphere during late spring and summer. The Pearson coefficient between tritium activity concentrations and temperature values of the observation period is around 0.7, indicating a positive correlation.

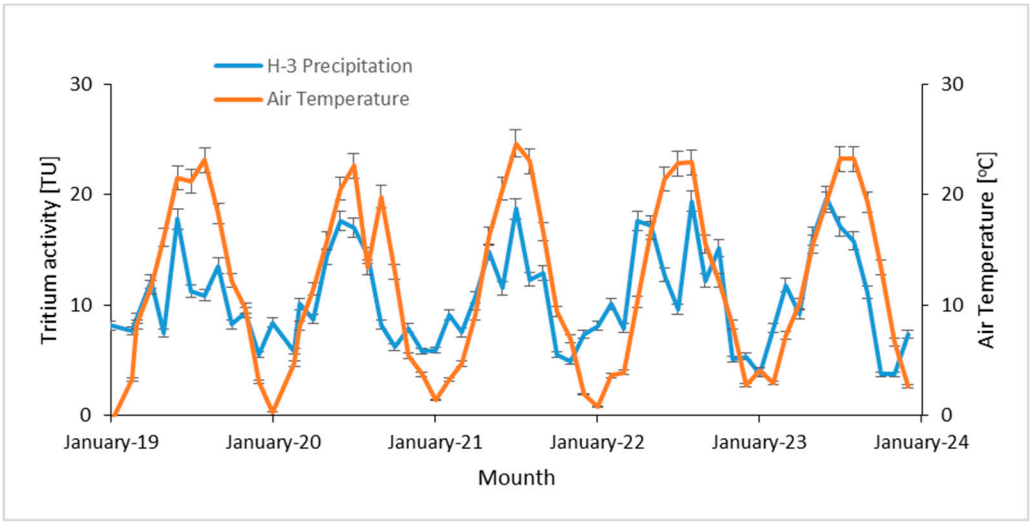


Figure 2. Tritium activity in precipitation and air temperature during the 2019–2023 period.

The monthly air relative humidity recorded specific values for dry years and rainy years, Figure 3.

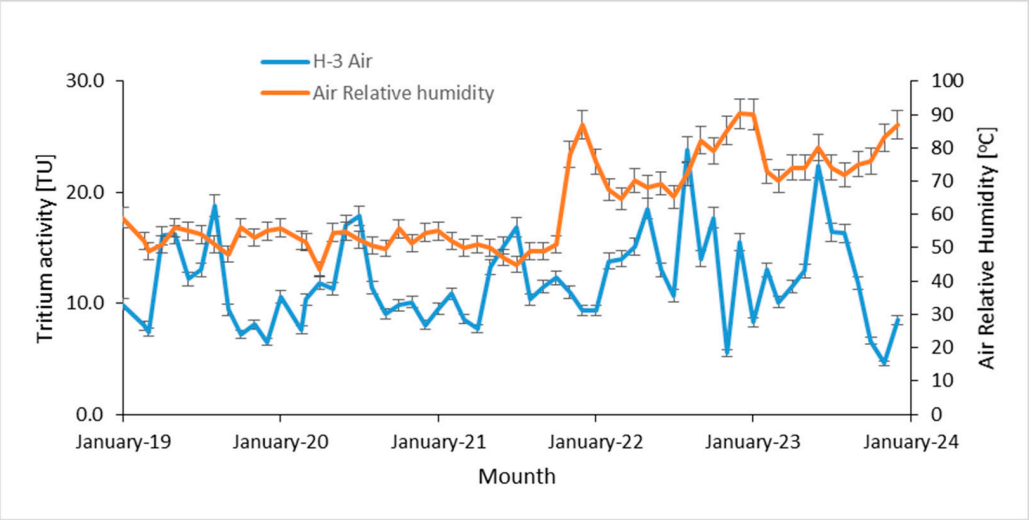


Figure 3. Tritium activity concentration in air and relative humidity during 2019–2023.

Its values varied between 43.4% (April 2020) and 59% (January 2019) during 2019–2021, when the annual precipitation was below 635 mm, with at least 9% lower than the precipitation characteristic of this location. Another interval was recorded for the rainy years, between 64.8% (March 2022) and 90.2% (December 2022), when the annual precipitation exceeded by 8.5% the amount of 2022, and 16.8% in 2023 the amount of 698.5 mm established for this location. Tritium activity concentration in air varied between 4.6 +/− 1.4 TU (November 2023) and 23.8 +/− 2.4 TU (August 2022), following the same behavior as precipitation, with higher values during the late spring and early summer and lower values during the cold month. The Pearson coefficient established was around 0.07, demonstrating no correlation between air relative humidity and tritium activity concentration in air. The water soil measured during the period of observation did not exceed 12 TU.

Connecting all the above parameters and observing the behavior of tissue-free water tritium (TFWT) from the vine during the growing season, Figure 4, one can conclude that the recorded values are in equilibrium with the environment and follow tritium concentration in precipitation.

The absorption of H_2O (thus HTO) vapor by the aerial parts of the plants (mainly the leaves) is a diffusion phenomenon through small pores (stomata) and is controlled mostly by climatic conditions (temperature, relative humidity, precipitation) and plant physiology. The level of TFWT can be considered a mixture of tritium level in atmospheric water vapor incorporated by diffusion and tritium level in precipitation diluted in soil and incorporated by the roots plant. Without identifying a predictable behavior, the tritium activity concentration of TFWT varied between 6.3 +/− 1.6 TU in November (2021) and around 19 TU in July–August, its level being influenced if the precipitation occurred before the time of sampling. Maximum tritium activity was recorded in August for the dry years and in June for the rainy years.

The tritium level of OBT during the growing season of 2019, Figure 5, starts with around 10 TU in leaves, branches, and grapes in June, and it increases to around 15 TU in September for branches and grapes, and around 17 TU for leaves in October. The grapes used to obtain vine in October had a value of 13.3 +/− 1.8 TU, and the tritium activity concentration of ethanol of wine had a value of 11.7 +/− 1.7 TU, near the annual mean of precipitation, 10.9 +/− 1.5 TU.

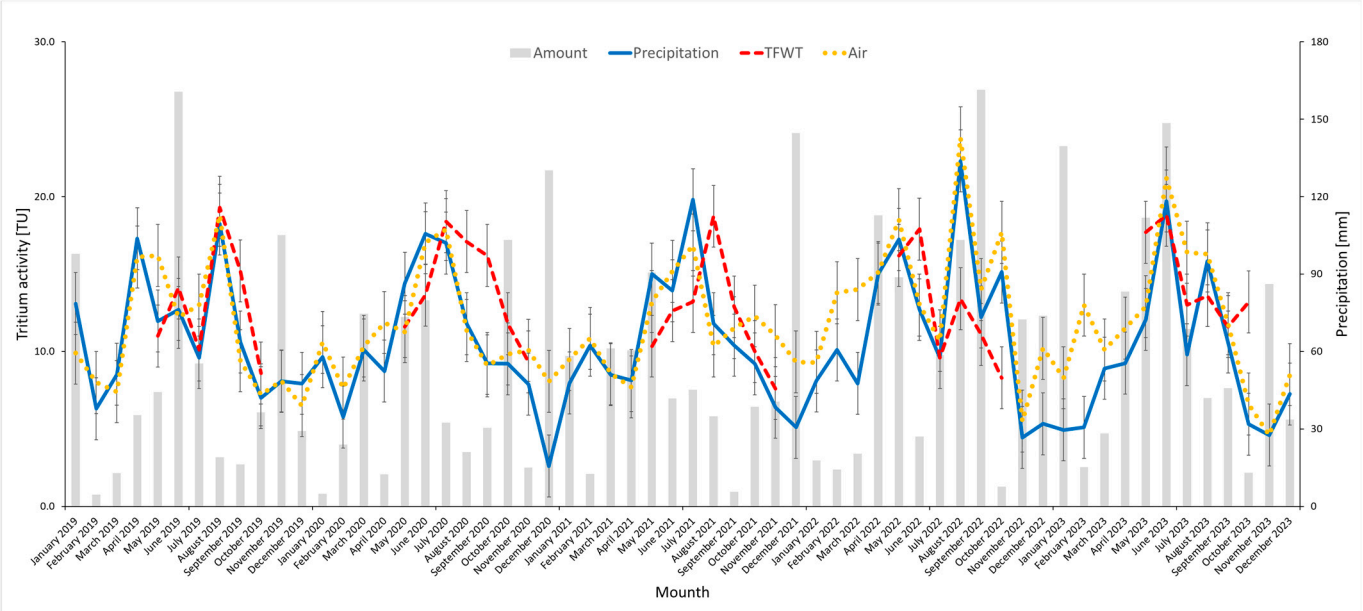


Figure 4. Tritium activity concentration in TFWT of the vine during the growing seasons compared with tritium in the environment during 2019–2023.

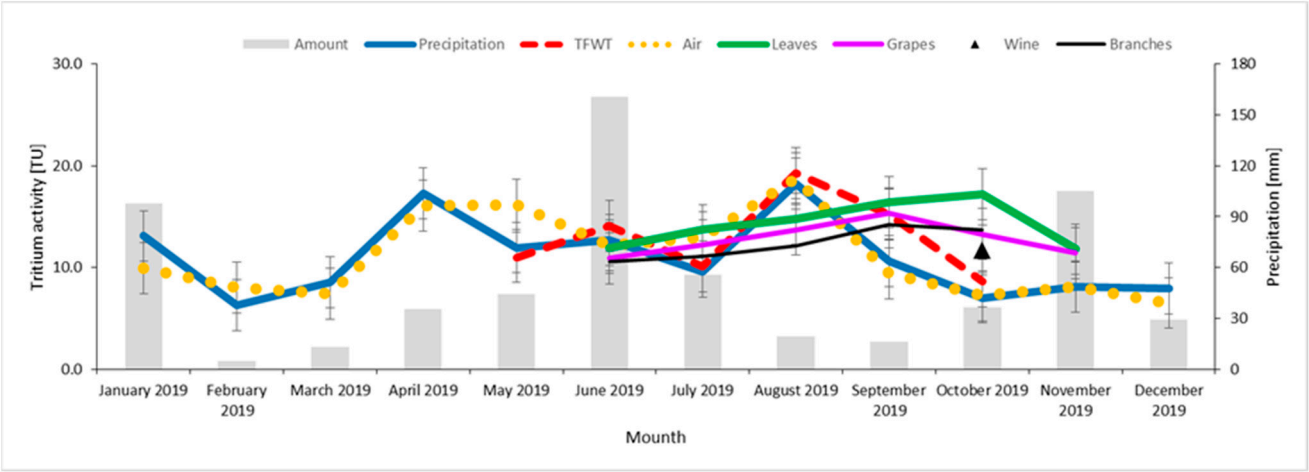


Figure 5. Tritium activity evolution during the growing season of 2019 in vine leaves, vine branches, grapes, and wine.

The same behavior can be observed during the growing season of 2020, Figure 6, with values around 11 TU in the early stage of development, June, and maximum values around 20 TU in September for all observed components of the vine.

The grapes of October had a value of 17.5 +/− 2 TU, and the tritium activity of wine ethanol had a value of 14.1 +/− 1.9 TU, slightly higher than the annual mean of precipitation, which was 10.6 +/− 1.5 TU.

The last year with a precipitation deficit was 2021, during the growing season recording May–October, an amount in precipitation of 257 mm, one of the lowest precipitation amounts recorded for the 6-month growing period. The tritium level of OBT of vine components started in June below 10 TU, and it increased to a maximum of around 17 TU in October, with a value of ethanol wine of 14.8 +/− 1.9 TU, Figure 7.

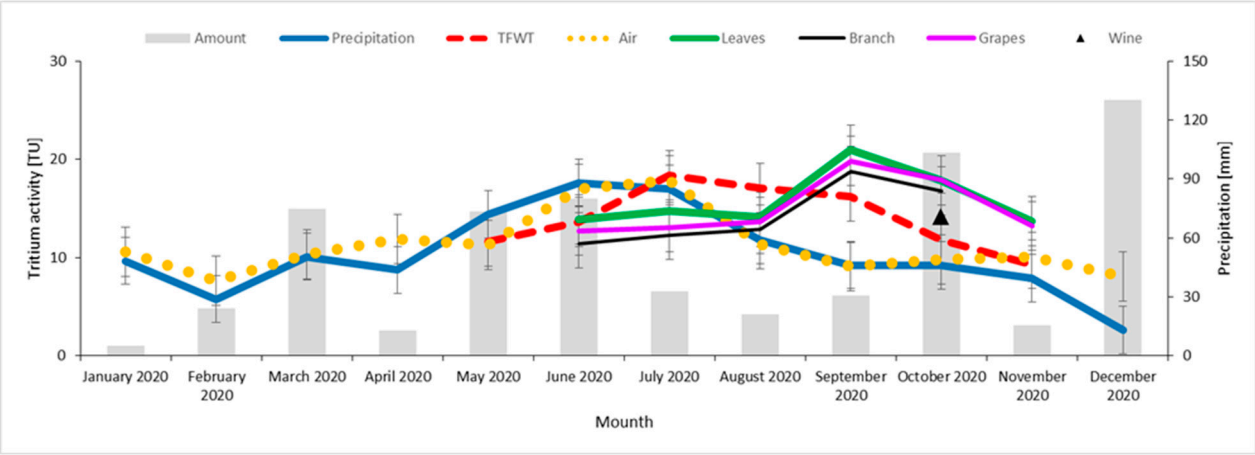


Figure 6. Tritium activity evolution during the growing season of 2020 in vine leaves, vine branches, grapes, and wine.

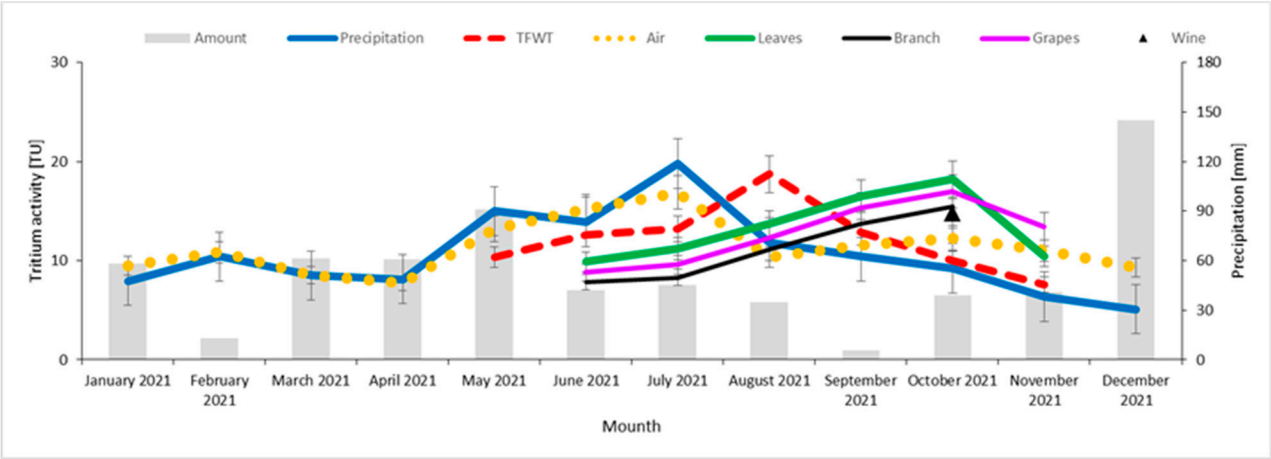


Figure 7. Tritium activity evolution during the growing season of 2021 in vine leaves, vine branches, grapes, and wine.

The year 2022 was the year with an 8% surplus of precipitation above the normal precipitation of this location during the growing season May–October, recording 446.6 mm, Figure 8, considerably higher than the amount of precipitation from the previous year.

The OBT tritium level of vine parts started in June at around 10 TU, and it increased to a maximum of around 15 TU in September. The OBT tritium level in the grape of October was 12.8 +/− 1.7 TU, and the OBT tritium level in wine ethanol was practically the same, taking into account measurement uncertainty, 11.5 +/− 1.6 TU. The annual mean precipitation was 11.4 +/− 1.6 TU.

The last year of observations was 2023, another year with a surplus in precipitation of 16.8% above the normal amount of precipitation of this location. The amount of precipitation during the period May–October was 429.8 mm, lower than the previous year. The same behavior of OBT tritium level is recorded in Figure 9, around 9 TU in June for all vine parts, and a maximum in September, around 17 TU.

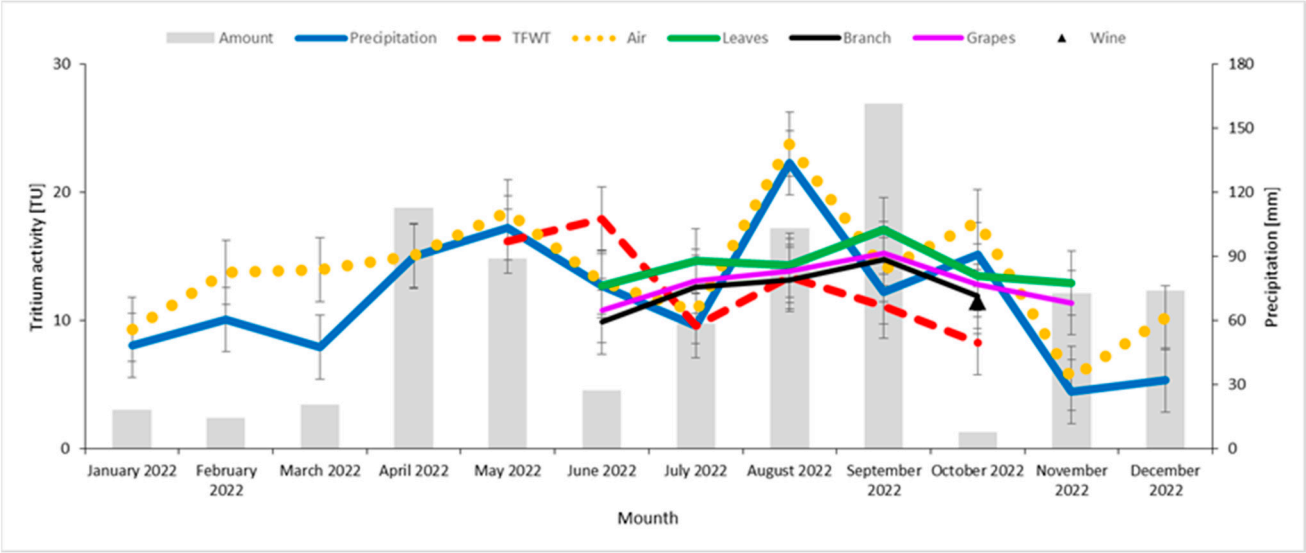


Figure 8. Tritium activity evolution during the growing season of 2022 in vine leaves, vine branches, grapes, and wine.

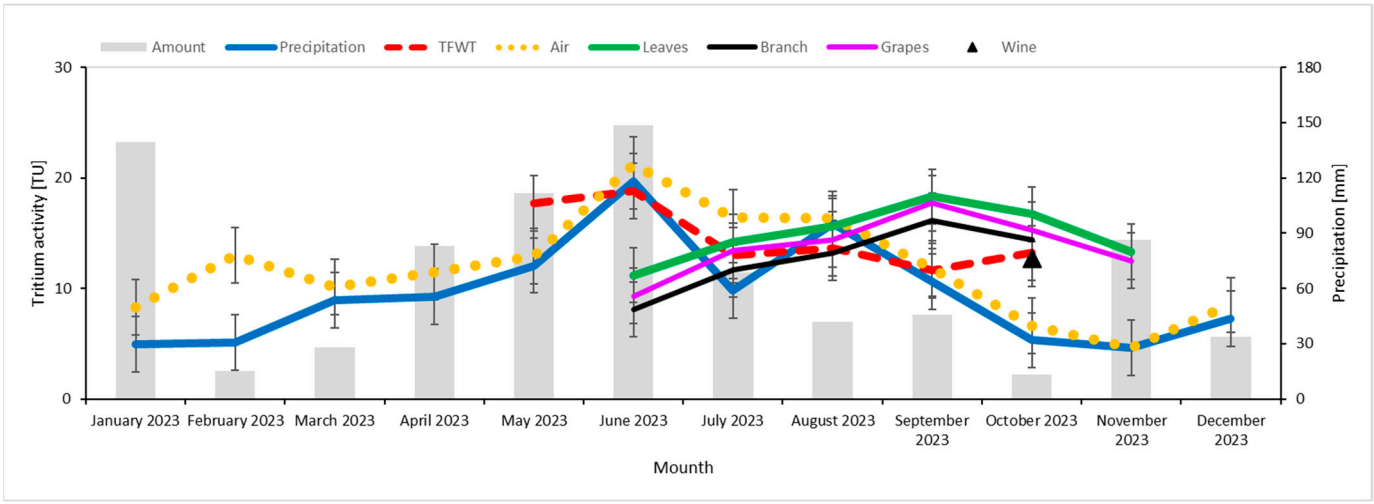


Figure 9. Tritium activity evolution during the growing season of 2023 in vine leaves, vine branches, grapes, and wine.

The OBT tritium level in the grape of October was 15.3 +/− 2 TU, and the OBT tritium level in wine ethanol was 12.7 +/− 1.6 TU. The annual precipitation mean of 2023 was 10.5 +/− 1.5 TU.

The activity of tritium varies according to the types of matrices. According to IRSN data [30], the ranges of activities of free tritium (HTO) and organically bound tritium (OBT) measured in fruit, in areas not influenced by nuclear activities are between 8 and 150 TU, both for HTO and OBT. The recorded values for TFWT and OBT for vine and wine agree with the literature.

A general view of tritium activity from ethanol wine, compared with the tritium level of the average precipitation of each studied year, is presented in Figure 10. As can be seen, all tritium values, precipitation and ethanol from wine—are around an average value of 11 TU. According to the IAEA network "Isotopes in Precipitations" [31], the temporal evolution of tritium concentration in precipitations around the continental Nordic Hemisphere was influenced by the nuclear tests, with tritium concentrations increasing by up to three orders of magnitude between the early and late 1960s. In 2008, the measured

activities varied between 8 and 35 TU in rainwater, but the reference value quoted for northern hemisphere rainwater is 5 TU in the winter and double in the summer [31]. The recorded tritium level of precipitation over the 5 years of observation was 10.6 +/− 1.5 TU, the typical value for the inland Europe. The recorded tritium level of wine ethanol over the 5 years of observation was 12.9 +/− 1.6 TU, close to that of the precipitation if taking into account the measurement uncertainty.

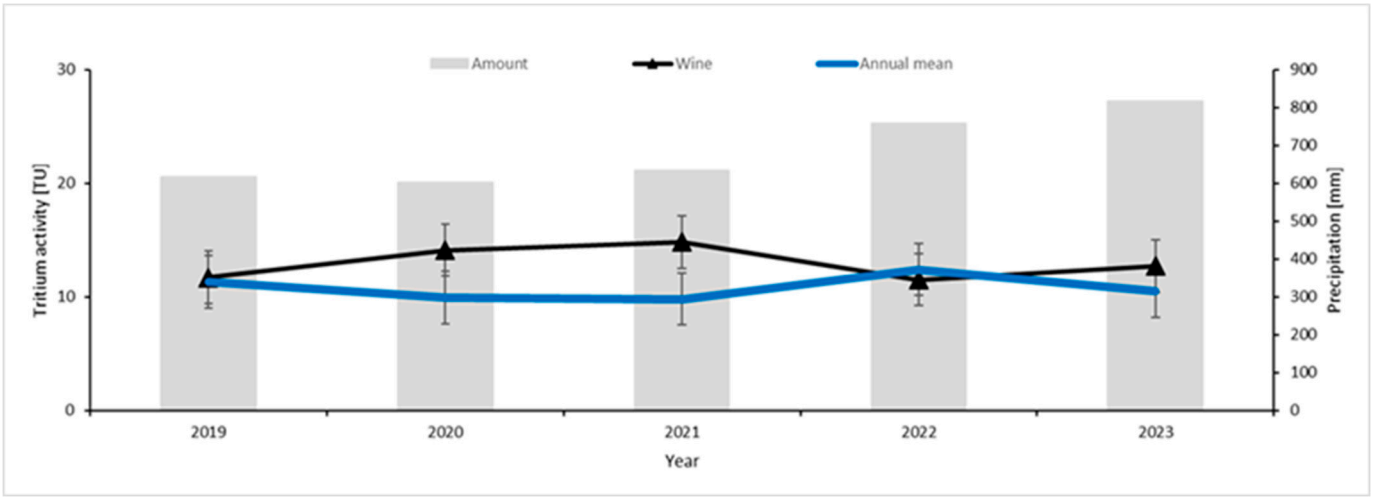


Figure 10. Tritium activity in annual precipitation mean and wine ethanol.

4. Conclusions

Tritium concentration can be used to determine the authenticity of natural products, such as wine, relying on the data of the ambient tritium levels in the region where the vine was grown.

The origin of natural wine can be determined if an adequate estimation of the tritium from all environmental compartments is realized. Therefore, the vegetation stage of the studied plant, the vine, correlated with the tritium activity from the environment (rain, air, and free water of plants), may influence the OBT activity levels in the studied samples and implicitly on the wine resulting from the ripped grapes.

The study of tritium activity in the vine (branches, leaves, and grapes), in its different forms—TFWT and total OBT—during the vegetation period in the above-mentioned location near ICSI showed only the normal variation specific for this area. The variation of TFWT followed the precipitation and air seasonal variations, but the OBT showed slightly different behavior.

The vegetation stage of the vine correlated with the HTO (rain, air, and free water), which influenced the OBT level in the samples. A general tendency is observed for the recorded OBT activity to follow with a delay of 1–2 months, depending on the stage of vegetation and the level of tritium from precipitation and the air. This trend can be explained by the fact that the biological half-life for OBT in plants is longer than that of TFWT, although part of the total OBT analyzed is Ex-OBT, which has the same behavior as TFWT. Thus, the maximum activity of OBT is recorded more or less in autumn for all plant organs and wine, an important factor being the amount of precipitation received by plants.

Considering all five years of measurements, one can observe higher values of OBT tritium levels in leaves and lower values in branches (without considering the measurement uncertainty) due to the overall mechanism of tritium transfer from the environment to plants summarized as the HTO uptake. The foliar uptake of tritium from the atmosphere influenced the tritium level in leaves, and the root uptake of tritium from the soil influenced the tritium level in branches. Another interesting behavior is the decreasing values of OBT tritium levels for leaves and grapes in November, a constant decrease over all five years, proving the influence of exchangeable organic tritium lost by the drying leaves and grapes.

The origin of a natural product can only be determined if a fair estimate of the environmental tritium levels can be ascertained corresponding to a particular botanical, as one can see for the vine and the wine.

The years with a deficit in precipitation determined slightly higher values of tritium in ripped grapes and wine. This is due to the enrichment process occurring in nature that can increase tritium content in precipitation and atmospheric vapor for short or long periods. If such processes occur during the growing season, they will most likely be reflected in the OBT of the vine. In the absence of more detailed information concerning the environmental tritium level and the fractionation of tritium by meteoric and transpiration process, the useful tools to be used together with tritium level are stable isotopes of oxygen, hydrogen, and carbon [32].

If the tritium values from OBT can be successfully used for the reconstruction of the tritium level in the precipitation, its use for authentication and geographical indication is much more difficult. Long periods of observation are required, but the real challenge is to obtain a useful limit of detection and a reduction of counting error by enrichment of a small volume of water [19], especially presently when legislation and equipment providers market demand changes in the routine procedure of the laboratories [33]. Despite high tritium measurement uncertainty compared with stable isotope measurements [34], a study of the relationship of $^{18}O‰$ between tritium activity and $D‰$ in wine from geographical locations is in development.

Author Contributions: Conceptualization, C.V. and I.V.; methodology, I.V. and I.F.; software, I.F. and C.V.; validation, D.B. and D.F.; formal analysis, I.V., D.B. and D.F.; investigation, C.V. and I.V.; resources, I.F.; data curation, D.F.; writing—original draft preparation, C.V.; writing—review and editing, C.V. and I.V.; visualization, I.F.; supervision, C.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: This work was prepared in connection with the work done for the monitoring program of the Experimental Pilot Plant for Tritium and Deuterium Separation—PESTD from ICSI Râmnicu Vâlcea, project PN 23 15 03 03, and project PN 23 15 03 01, part of National Core Program ICSI—LAB2FIELD and Project for Financing Excellence in R&D 19PFE/2021, supported by the Romanian Ministry of Research, Innovation and Digitization.

Conflicts of Interest: The authors declare no conflicts of interest.

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