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ENVIRONMENTAL TRITIUM AND ITS MEASUREMENT CHALLENGES USING LIQUID SCINTILLATION COUNTING

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Abstract:

Tritium, the radioactive isotope of hydrogen, is one of the most versatile radionuclides due to its role as a tracer of hydrogen and carbon structures. The liquid scintillation counting method is the preferred tritium measurement method especially in the case of numerous samples as radioactivity monitoring programs. The changes that appeared in the liquid scintillation spectrometers market and in the liquid scintillation cocktail formula demand adaptation of the laboratory routine procedure. Tritium level in the environmental water samples of 2022 is presented in the paper. The low level around 2 Bq/L imposes the necessity of tritium enrichment. Each of the above problems is extensively presented in this work together with some conclusions.

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1. INTRODUCTION

Tritium (^{3}H or T), an isotope of hydrogen, is typically found in nature as a part of the tritiated water molecule (HTO). T is formed naturally within the atmosphere as a result of the interaction of the fast neutrons produced by the galactic cosmic rays in the upper terrestrial atmosphere with nitrogen nuclei [Young P., Foster D., 1972], at an average annual rate of about 3.5 kg [Masarik J., Beer J., 2009]. Tritium behaves like stable hydrogen and is usually found attached to molecules replacing hydrogen. Tritium is constantly produced both by natural processes (the interaction of cosmic rays with the atmosphere) and by human-made processes.

Concentration levels of tritium in the environment not influenced by nuclear activities range from 1-4 Bq/L of water for the continental environment to 0.1 or 0.2 Bq/L in the marine environment [https://en.irsn.fr/en/research/publications-documentation/radionuclides-sheets/ environment/pages/

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tritium-environment.aspx, 2023]. The level of 1-2 Bq/L can be found in water vapor of the atmosphere or in biological matrices. Its environmental levels are used in various ways; to verify and improve the atmospheric circulation models [Duliu, O.G., et all., 2018], to study the water interaction with the atmosphere and biosphere [Bin Feng and Wei-Hai Zhuo, 2022], and to provide an isotopic baseline for authentication of food and drinks [Neary M.P. at all., 1997].

The tritium of most of the samples is usually prepared in its aqueous form, whether it is gaseous form, liquid form, or assimilated in living organisms as tissue-free water tritium and organically bound tritium [UNESCEAR, 2016]. There are different types of tritium measurements, but for environmental tritium level only two, He-3 ingrowth (mass spectrometry of rare gases) and tritium enrichment followed by liquid scintillation counting (LSC), [Varlam C., et all., 2009]. LSC is the preferred method in the case of a large number of samples (radioactivity monitoring program, precipitation, drinking water, underground water) due to the reasonably necessary time to provide the results.

The paper presents the tritium level in the environmental water established by the ICSI Tritium Laboratory during the mo nitoring program of the Experimental Pilot Plant for Tritium and Deuterium Separation (PESTD) for 2022, along with the challenges faced from the point of view of tritium measurement and possible solutions to them.

2. PESTD ENVIRONMENTAL MONITORING PROGRAM

ICSI Rm. Valcea is a Romanian research unit aimed at supporting nuclear energy through research, development, and innovation activities. ICSI Ramnicu Valcea operates a nuclear installation, namely "Experimental Pilot for Separation of Tritium and Deuterium" (PESTD), a semi-industrial installation designed for the detritiation of heavy water moderator of CANDU reactors. Even if PESTD's operation involves tritiated water below the exemption level approved by Romanian legislation it's a necessity to have an environmental monitoring program.

The Institute is situated on an industrial estate. The industrial water supply is provided by surface water, Olt River, which is the only source in the area. There were established five sampling locations three reference locations and two control locations. Various types of samples are measured as part of the monitoring program, such as atmospheric release, precipitation, surface water, drinking water, wastewater, vegetation, and foodstuff. More than 250 samples/year are environmental water due to the fact that they are individual precipitation and weekly samples from wastewater and from three locations of surface water; upstream of the industrial estate, mixing chamber of the Water Treatment Station, and downstream of the industrial estate.

Considering numerous samples of the tritium monitoring program, the most efficient method applied in our laboratory was the direct liquid scintillation counting method. The used equipment were Quantulus 1220 liquid scintillation spectrometers and the analytical method followed the steps recommended by the ISO standardized method [ISO 9698:2019] 8 ml of distillate was mixed with 12 ml of scintillation cocktail UltimaGold uLLT in polyethylene vials, counting time being 500 min/samples. Tritium standards were diluted tritiated water provided by PerkinElmer, with a certified activity of 43193.3 ± 1295.8 Bq/g (reference date August 2020). Tritium-free water (blank water) was deuterium-depleted water with a D/(D+H) value of 15 ppm. The counting efficiency at the best factor of merit was between 24.81 % and 25.25 %, and the background between 0.632 ± 0.014 CPM (Counts Per Minutes) and 0.763 ± 0.017 CPM, following on a minimum detectable activity around 0.4 Bq/L (confidence level of 95%, k = 2). The uncertainty due to the statistical nature of radioactive decay and background radiation was reported at 1σ.

Tritium levels in the environmental water did not exceed an average of 2 Bq/L over the year 2022. The precipitation composite monthly sample, figure 1, recorded higher values during the summer month, but its average of 12.1 +/- 2.5 TU (1 Tritium Unit = 1 tritium atom to 10^{18} hydrogen atoms) is part of the general trend.

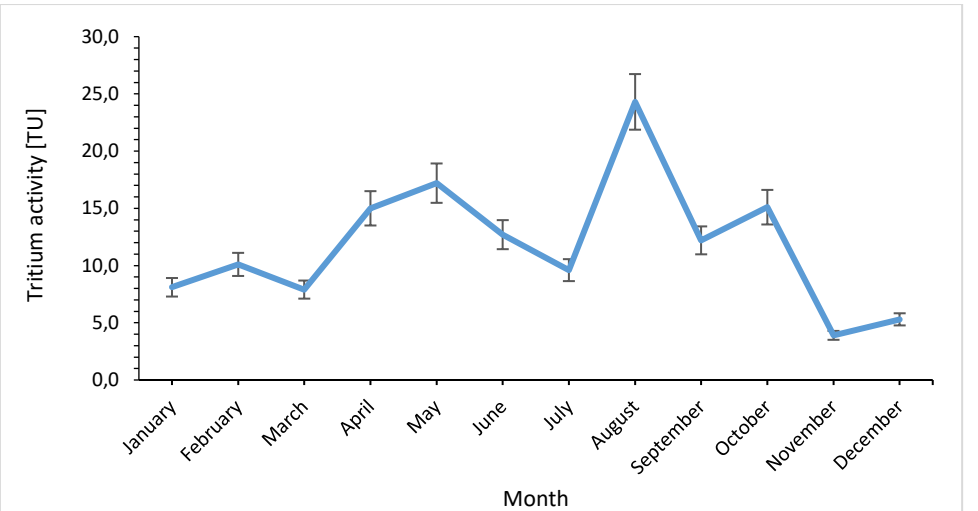

Figure 1. Tritium level of composite monthly precipitation during the year 2022

The monthly average of the three sampling locations of the Olt River was around 1 Bq/L (1TU = 0.11919 +/- 0.00021 Bq/kg [Rozansky K., Gröning M., 2004]), figure 2, with slightly higher values downstream of the industrial estate.

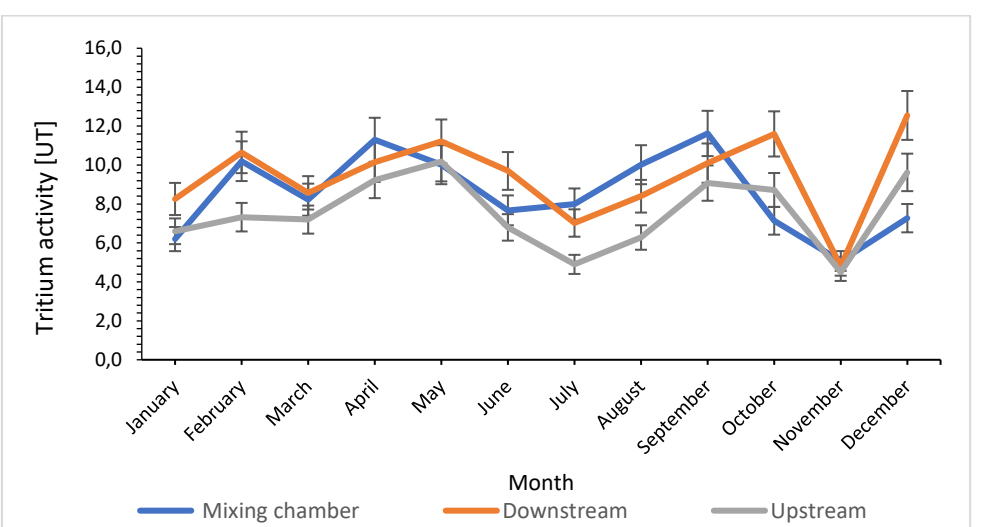

Figure 2. Tritium level in monthly average of the three sampling locations of Olt River.

Comparing tritium level established in precipitation and surface water one can definitely identified the influence of the underground water in Olt River, despite the direct measurement of samples, without tritium enrichment. The routine procedure applied, the liquid scintillation cocktail, and the used equipment provide accurate results despite the environmental tritium level which is near the limit of detection.

3. MEASUREMENT CHALLENGES

The present challenges are affecting both liquid scintillation cocktails and liquid scintillation spectrometers. The availability of liquid scintillation cocktails will be adversely affected by the change in EU regulations preventing the use of Nonylphenol Ethoxylates (NPEs) [Official Journal of the European Union, Commission Regulation (EU) 2017/999].

Their price will be higher to include the necessary authorizations, but even so, the NPE's production will be limited due to lower market demand.

Our routine procedure of tritium measurement in the environment uses a liquid scintillation spectrometer Quantulus 1220. In order to fulfill the quality assurance exigencies, Tritium Laboratory participated in numerous intercomparison exercises, figure 3. The good results obtained over the years, confirm not only the routine procedure applied in the laboratory but also the operating parameters of the used equipment, even if one of the Quantulus 1220 spectrometers is in operation since 1998.

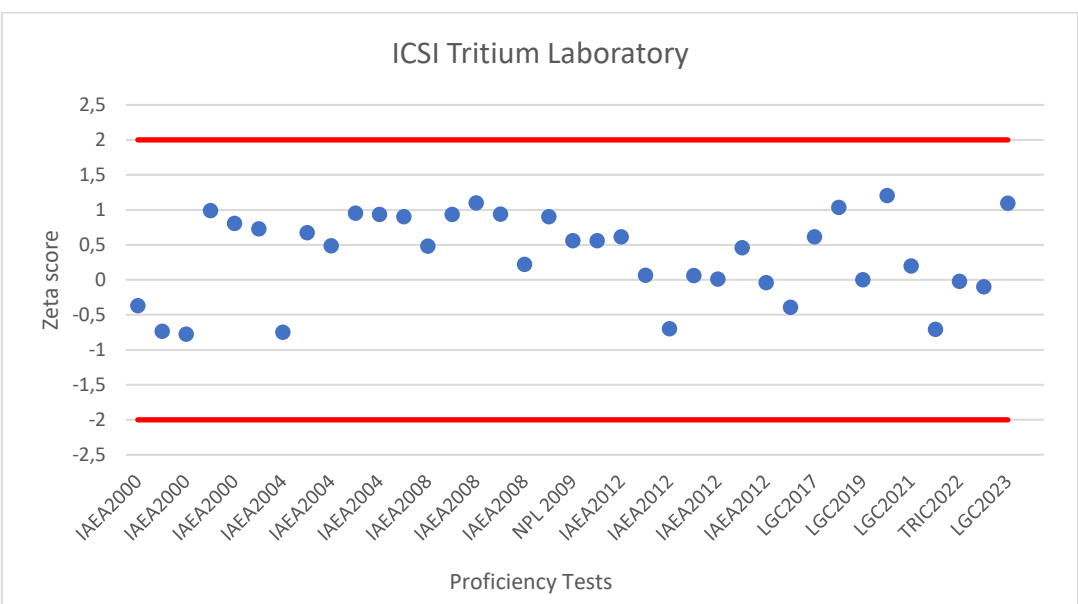

Figure 3. Zeta score obtained for different intercomparison exercises using Quantulus 1220 liquid scintillation spectrometer

Despite the very good performances of this liquid scintillation spectrometer of environmental radioactivity monitoring, it is no longer available on the market, and its provider decided that this type of spectrometer has reached the end of its serviceable lifecycle. The environmental radioactivity monitoring laboratories need to consider a new generation of liquid scintillation spectrometers available on the market, ALOKA LB7 spectrometer [Yoon Y., Yongcheol K., 2020] or Quantulus GCT 6220 [Edler R.H.W., 2017]. The other type of liquid scintillation spectrometer with a higher limit of detection is Hydex 300SL or Tri-Carb series from Perkin Elmer. In these conditions, the need of tritium enrichment procedure is a must for environmental studies. The enrichment of ^{3}H is usually accomplished using alkaline electrolytic cells with Ni/Ni or mild-steel electrodes, a procedure developed in the early 1960s [Taylor C.B., 1981]. There are several drawbacks to the alkaline electrolyze procedure. Operational disadvantages include labor-intensive procedures for maintenance, careful gravimetric requirements, cleaning and drying of enrichment cell apparatus, as well as the use and disposal of noxious chemicals for the

electrolysis and/or neutralization (e.g. Na_2O_2, CO_2, $PbCl_2$). In general, the alkaline electrolytic procedure remains cumbersome and labor intensive, hampering widespread implementation of ^3H low-level measurements in routine laboratory practice.

An alternative that is easier to use instead of the alkaline electrolytic cells is H_2O electrolyzers based on solid polymer electrolyte membranes (PEMs). It is usually used in hydrogen fuel cells [Carmo M., et all., 2013], and it has very good thermal and chemical stability, mechanical strength, and proton conductivities. The PEM has the same behavior as Natrium peroxide added in alkaline electrolysis cells but without any chemicals dissolved in the water sample. Using the same procedure as alkaline electrolysis, positively charged ions migrating to the cathode receive electrons from the external electric power circuit to form hydrogen gas, and the given electrons to the anode by the oxygen molecules, complete the circuit. Intensive studies on PEM cells used for ^3H enrichment of environmental water samples were published by Muranaka and Shima [Muranaka, T., et all., 2005; Muranaka T., Shima N., 2008] and later commercialized as the single-sample, Tripure® Tritium Condensation Apparatus (www.permelec.co.jp; not available outside Japan). Wassenaar et al. proposed in 2017 [Wassenaar L., et all., 2018] an open-access tritium enrichment PEM system, whose components (anode and cathode of PEM produced by De Nora Permelec LTD.) are not available outside Japan. There are still questions about the sample memory effect and robustness of the cell constant k among and between enrichment cells.

4. CONCLUSIONS

The environmental tritium level is usually low, and due to this characteristic, some type of liquid scintillation spectrometers used are dedicated to low-level measurement and they are able to detect approximately 1 Bq/L of tritium in water without electrolytic enrichment.

Legislation and equipment provider market changes impose new type of routine procedures established in the laboratories.

The tritium environmental measurements need to consider a new generation of liquid scintillation spectrometers available on the market. The ALOKA LB7 spectrometer, with its 0.3 Bq/L limits of detection for tritium, seems to be appropriate for the environmental application. Another option is the Quantulus GCT 6220 spectrometer, which uses a special technique of energy-dependent correction of the background, lowering the limit of detection, and making it useful for environmental studies.

More or less tritium enrichment procedure starts to be a must for tritium environmental measurements, otherwise, a large number of reported results will be less than the limit of detection.

The routine practice of numerous laboratories and their experience recommend the alkaline electrolytic enrichment procedure.

The tritium enrichment using PEM seems to be a tempting alternative due to the simplified applied procedure, but the lack of essential parts of the installation on the European market requires the investigation of alternative possibilities.

Despite all the present challenges of the tritium environmental measurement, this radionuclide remains one of the important transient tracers used in hydrological studies, or in environmental studies.

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