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THE IMPACT OF EXPERIMENTAL PILOT FOR TRITIUM AND DEUTERIUM SEPARATION ACTIVITY ON TRITIUM LEVEL IN THE ATMOSPHERIC WATER VAPOR OF ICSI TRITIUM LABORATORY

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Abstract:

Results obtained from the monitoring of the ambient air of the ICSI Ramnicu Valcea Tritium Laboratory and the monitoring of the atmosphere around the Experimental Pilot Plant for Tritium and Deuterium Separation are used in the environmental impact evaluation of the experiments in the period 2020-2022. Even though the experiments carried out involved different tritium activity concentrations, there were no increases in the activity of tritium concentration in the analyzed samples, with numerous results of atmospheric samples being below the detection limit.

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1. INTRODUCTION

Tritium is a radioactive isotope of hydrogen, with a half-life of 4500 ± 8 days (Lucas L. L. and Unterweger M. P., 2000) and a maximum beta energy of 18.6 keV and an average of 5.7 keV. It is present naturally from the interaction between cosmic rays and the upper atmosphere constituents. Large quantities of tritium were accumulated in the atmosphere from the past thermonuclear testing. Anthropogenic tritium sources are the releases of nuclear reactors and uranium fuel reprocessing plants. Other possible sources include consumer products and medical waste.

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As an isotope of hydrogen, tritium is intimately tied to the cycle of this element in the environment. It may be found in all hydrogenated molecules and associated both with water in tissue as with the organic material of plants and animals. In the form of tritiated water [HTO] this radionuclide is extremely mobile in the environment and all biological systems, and thus quickly integrated into numerous cycles of the geo- and biosphere. In equilibrium, it does not appear to accumulate preferentially in a particular environmental or biological component. The abundance of tritium in the environment is very low compared to hydrogen or deuterium. Around 99% of the tritium produced in the upper atmosphere is oxidized to tritiated water [HTO] and dispersed into surface water (IRSN- Institute for Radiological Protection and Nuclear Safety, 2010).

Tritium activity concentration measurement in aqueous samples using the liquid scintillation method is an ISO standard method (ISO 9698:1998) since 1998. During this period this standard method had several revisions, the last version being in 2019 (ISO 9698:2019). In the last version, the ISO standard introduced the requirement to monitor the ambient air of the laboratory performing tritium measurements.

In this paper, are presented the results obtained from the monitoring of the ambient air of the ICSI Ramnicu Valcea Tritium Laboratory and the monitoring of the atmosphere around the Experimental Pilot Plant for Tritium and Deuterium Separation (PESTD) to evaluate the impact of the PESTD experiments on tritium activity concentration in the period 2020-2022. The PESTD (figure 1) is a research installation within the national nuclear energy research program. The radioactivity monitoring of environmental factors around the PESTD is ensured from the preoperative phase in accordance with the radiological safety standards (Ene et al., 2021). The PESTD can have an impact in the environment in two ways: by atmospheric release and by sewage.

Figure 1. Experimental Pilot Plant for Tritium and Deuterium Separation - PESTD (Source: www.icsi.ro)

The main experiments carried out in the period 2020-2022 within PESTD were related to the development of a Combined Electrolysis and Catalytic Exchange System (CECE) (Bornea et al., 2018). During this period, six such experiments took place. The experiments used tritiated water (HTO) or deuterated and tritiated water (DTO) with initial tritium activities between 100 and 1000 Bq/L. The maximum tritium activity concentration reached in these experiments was approximately 15 000 Bq/L. In each of the experiments, different operating parameters of the experimental installation were used. Because the isotopic exchange column was designed high enough to ensure complete decontamination of the gas produced in the electrolyser (Bornea et al., 2020), theoretically, the experiments did not affect the PESTD atmospheric releases.

2. MATERIAL AND METHODS

The sampling sites were located in the Institute of the Cryogenics and Isotopic Technologies (ICSI) and around it, about 10 km south from the Ramnicu Valcea city centre (Romania). The samples have been taken from the ICSI Ramnicu Valcea Tritium Laboratory and from the vicinity of the Experimental Pilot Plant for Tritium and Deuterium Separation (PESTD), part of the ICSI Nuclear department.

To monitor atmospheric releases of PESTD, national regulatory authorities have established 5 sampling locations (figure 2), three of them on the ICSI site and another two at 1.5 km and 9 km in the south direction, respectively. In each of these locations are placed air sampling stations (figure 3) for retaining water vapour from the air by adsorption on the molecular sieve. The air is sucked into two metal traps connected in series filled with a 13X molecular sieve. This is done with a dry vacuum pump at an adjustable flow rate of up to 1 m3/h. The 13X molecular sieve has a retention capacity of 26 grams of water per 100 g of molecular sieve, ensuring a water retention efficiency of over 99% (Bornea A. et al., 2022; Cortés et al., 2010). The sampled airflow is measured using an electronic flow meter with a volume integrator. At the end of each sampling period (one month), the two metal traps are replaced with the other two traps (whose molecular sieve has been regenerated). These are transported to the lab where the water retained in the molecular sieve is extracted and the molecular sieve is regenerated so that it can be reused. The extraction of water and the regeneration of the molecular sieve is carried out with the help of an installation composed of an oven with adjustable temperature (water extraction is done at a temperature between 100 and 150°C, and regeneration at a temperature between 250 and 350°C), a dry vacuum pump and a gas washing bottle with Drechsel type head cooled with liquid nitrogen or ice.

(a) (b)

Figure 2. Air sampling locations around PESTD, (a) the ICSI site and (b) all sampling locations (adapted from Google Earth)

According to the last version of the ISO method for tritium activity concentration measurement in aqueous samples using the liquid scintillation method in the ICSI Tritium Laboratory it was a must the establishment of a monitoring program part of the laboratory quality system, to detect any potential contamination between samples and the atmosphere due to PESTD operation. To do this, weekly we place in the lab an open vial (figure 3) in which 70 ml of blank water has been previously placed. The vial is brown glass with a diameter of 3 cm. Tritium laboratory temperature is kept constant at around 25°C, and loss of blank water during one week is around 10%.

(a) (b)

Figure 3. Air sampling station (a) and the open vial used for laboratory atmosphere monitoring (b)

After one week, the tritium activity concentration is measured, the reference value being 25 TU (1 TU = 0.11919 ± 0.00021 Bq/kg). The reference value represents the maximum tritium activity concentration recorded in water vapour of the atmosphere, during the PESTD preoperational program (Varlam et al., 2011). The tritium laboratory performed tritium measurements of aqueous samples received from different intercomparison exercises without monitoring the lab atmosphere, and the good results obtained prove the good stability of the routine procedure over more than 17 years of observations (Varlam et al., 2020). If the measured tritium activity concentration of the lab atmosphere is higher than the imposed limit, corrective measures are applied according to internal procedures.

Before the measurement and calculation of tritium activity concentration, the water samples obtained either from air monitoring stations or from laboratory atmosphere monitoring were prepared according to our preparation procedure. This involves mixing 8g of sample with 12 ml of scintillation cocktail Ultima Gold uLLT (PerkinElmer, 6013687) in antistatic polyethylene vials (PerkinElmer, 6008118) (Varlam et al., 2009) to obtain a homogenous medium. To determine the background counting rates, blank samples were prepared in the same condition as unknown samples using deuterium-depleted water with a D/(D+H) value of 7 ppm (blank water). The blank water is "tritium free" due to the production process that involves the removal of all heavy hydrogen atoms (deuterium and also tritium) from natural water (Titescu et al., 2001; Mladin et al., 2014). The measurement was done using an ultra-low level liquid scintillation spectrometers Quantulus 1220™ (figure 4). This kind of equipment has the lowest background count rates due to a passive shield (made of lead, cadmium and copper) and an active shield (based on a mineral oil scintillator) around the measurement chamber.

Figure 4. Ultra-Low Level Liquid Scintillation Spectrometers 1220 OUANTULUS

Spectra were acquired by Easy View software, where the optimal window was selected according to the highest figure of merit (FOM) values. The counting efficiency at the best FOM was determined by the internal standard method using diluted tritiated water obtained by dilution of tritiated water with a certified activity (~2.5 x 106 DPM/g, 10 mL, PerkinElmer, 6004052) and prepared in the same way as unknown and blank samples. The samples, blank and standards were stored in the spectrometer for at least one day to sufficiently decrease the interference of the chemiluminescence phenomenon, which signal overlap tritium disintegrations. Each of them was counted for 10 cycles, 50 minutes/cycle for unknown and

blank samples and respectively 10 minutes/cycle for standards. The background recorded for the optimized window was between 0.712 CPM and 0.9 CPM (counts per minute). The counting efficiency was around 27% resulting in a detection limit of around 4 TU. Calculation of tritium activity concentrations, the combined uncertainties and the detection limit was made according to chapter 8 of ISO 9698:2019.

3. RESULTS

Over the 2020-2022 period, there were performed using the PESTD facility six CECE experiments during a variable period from two weeks to three months. The experiments investigated the tritium removal process from low tritiated water/heavy water using catalytic exchange in a column of 5 m, the gaseous waste being strictly monitored (Bidica et al., 2008). Initial activity had a wide range of variation from 168 Bq/l to 8341 Bq/l of water or deuterated water. The final activity in the electrolyser varied from a few thousand to tens of thousands of Bq/l of process water, depending on the process type investigated: open circuit or closed circuit.

As we mention above around PESTD there are five air sampling stations, three of them on the ICSI site and another two at 1.5 km and 9 km, respectively. These are used to assess the environmental impact of PESTD. These records are also important for the Tritium Laboratory. If the environmental influence of PESTD is negligible, the laboratory can maintain a detection limit low enough so that the results provided are relevant given that the measured tritium activities are very small and the measurement takes place directly without electrolytic enrichment. In this context, this study aims to assess the influence of CECE experiments conducted in the period 2020-2022, because tritium activities large enough were used and they can have an influence on the laboratory atmosphere.

Figure 5 shows the evolution of tritium activity concentration recorded in S1, S2 and S3 air sampling locations, situated inside the Institute yard. The average tritium activity for the three stations from the vicinity of the PESTD was 12.6 ± 2.7 TU, with a maximum value of 19.9 ± 2.7 TU recorded in November 2021 in S2, and minimum values under the detection limit recorded in August 2021-S1, or July 2021-S3. It should be noted that the graph gaps represent values below the detection limit recorded during this study period.

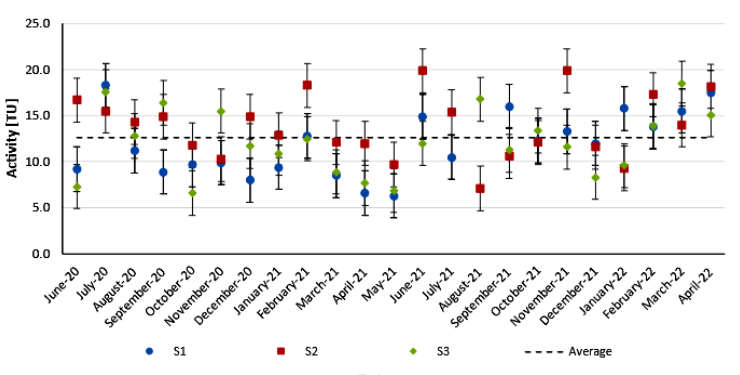

Figure 5. Tritium activity concentration recorded in S1, S2 and S3 air sampling locations in period 2020-2022

The tritium activities recorded in S4 and S5 were slightly lower, with an average value of 12.0 ± 2.6 TU. The graphic representation of tritium activity evolution in time for S4 and S5 air sampling locations is presented in figure 6. It can be seen that the maximum activity was recorded for station S4 in February 2021, respectively 25.5 ± 3.3 TU. The minimum values were under the detection limit. The same note must be made as in the previous figure, namely that the graph gaps represent values below the detection limit.

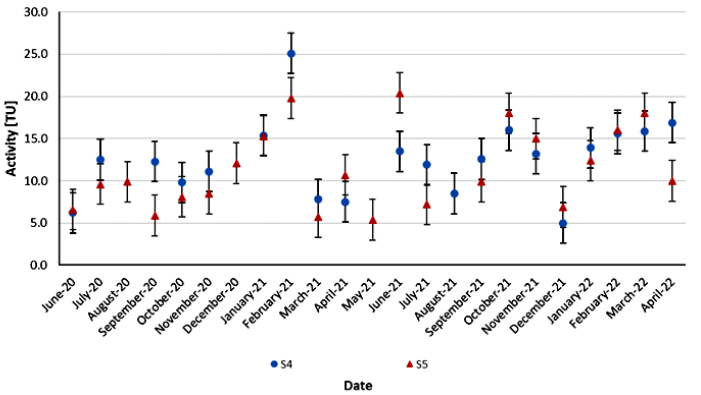

Figure 6. Tritium activity concentration recorded in S4 and S5 air sampling locations in the period 2020-2022

The means of each station established during the period of observation were: 11.8±2.6 for S1, 13.9± 2.7 for S2, 12.1± 2.6 for S3, 12.5± 2.6 for S4, and 11.4 ± 2.5 for S5. The range of tritium concentration in atmospheric water vapour of all 5 stations is very narrow, practically the same considering reported uncertainties.

Regarding the tritium activity concentration recorded in the period 2020-2022 in the Tritium laboratory atmosphere, it was generally below the detection limit in approximately 68% of the analysed samples, figure 7. For samples above the detection limit, an average of 7.1 ± 2.6 TU was recorded with a maximum of 10.5 ± 2.8 TU in July 2020, when no experiments were performed.

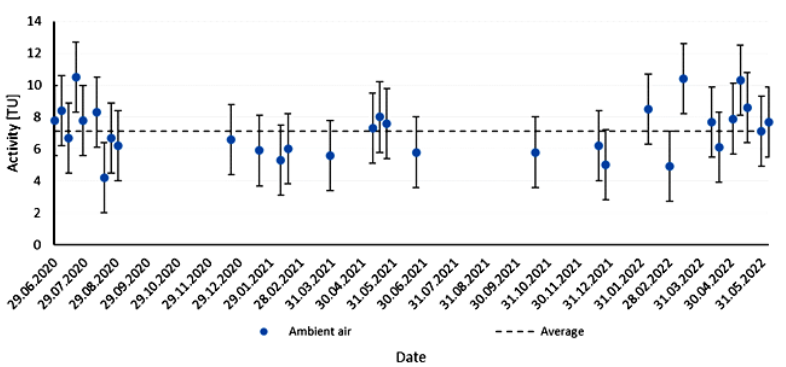

Figure 7. Tritium activity concentration recorded in the laboratory atmosphere in the period 2020-2022

The two tritium levels established in the atmospheric water vapour can only be compared qualitatively due to different types of sampling, and different periods of sampling. Lower tritium level established in the lab atmosphere is due passive exchange of depleted water with the atmosphere and exposure of only one week of the depleted water. This type of procedure was chosen to be able to apply corrective measures for samples prepared and measured during the week if atmosphere contamination appears.

During the monitored period, none of the values reached the reference value (25 TU), which reinforces the fact that the precautions taken in the experiments to limit the discharges into the atmosphere as much as possible were very efficient.

4. CONCLUSIONS AND DISCUSSION

In this study data from the quality assurance system implemented in the Tritium laboratory and the results of the radioactivity monitoring of the atmosphere around the PESTD were used in the assessment of the impact on the tritium concentration activity by the PESTD experiments in the period 2020-2022.

The mean tritium activities recorded in the samples taken with the help of the air sampling stations as well as in those sampled from the Tritium Laboratory atmosphere were similar to the average tritium concentration in the precipitation from Ramnicu Valcea (Duliu et al., 2018). Values between 15 TU and 26.7 TU were reported by Tritium Laboratory at the Archaeometry Centre of the University of Ioannina, in August 2016, (Stamoulis et al., 2017), for humidity measured after precipitation of 21 TU.

The tritium level in the laboratory atmosphere was lower than that recorded for the air sampling station. Many of the results were below the detection limit, especially for the samples taken from the laboratory due to the shorter sampling time (one week) compared to the other samples (one month).

Although the experiments carried out involved initial tritium concentrations between 168 Bq/l to 8341 Bq/l, below the exempting level for nuclear facilities as established by the Romanian National Regulations, no influence of the experiments on the tritium activity concentration in the atmosphere was evident.

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Conflict of Interest Statement: There is no conflict of interest in this article.

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