

ANTHROPOGENIC TRITIUM IN SOME ECOSYSTEMS IN SOUTH-EASTERN ROMANIA; A CONTINUOUS EFFORT FOR EDUCATION AND PUBLIC AWARENESS

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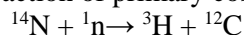
ABSTRACT

In Romania, since the commissioning of the Nuclear Power Plant (NPP) at Cernavoda (U1 & U2), tritium is constantly measured in the environment, both on-site and in vicinities (from an area with 30 km around NPP). Having both cosmogenic and anthropogenic origin, this is the way to make the difference between the tritium radioactivity produced in atmosphere and as a result of human activities. Current surveillance activity for the presence of tritium in environment is provided by a dedicated laboratory of the nuclear power plant in Cernavoda. The fate of anthropogenic tritium in the environment is also one of the topics of interest for a research group at Horia Hulubei National R&D Institute for Physics and Nuclear Engineering (IFIN-HH) which, along the time, has undertaken a series of studies on the temporal evolution of tritium released in the environment by the nuclear activities, on its distribution and accumulation in different compartments of terrestrial and aquatic ecosystems. In this respect, the present work shows the results of a five years study regarding the concentration levels of tritium measured in biotope (soil, surface and well water) and biota (spontaneous and cultivated vegetation, fish) samples, collected periodically in areas of influence and beyond them.

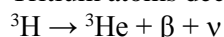
Keywords: Tritium, South-Eastern Romania, aquatic / terrestrial ecosystems, biotope, biota.

1 INTRODUCTION

Tritium (^3H , T) is the radioactive isotope of hydrogen with atomic mass 3 and half-life of 12.43 years ($3.866 \cdot 10^8\text{s}$) which is formed in higher layers of the atmosphere by interaction of thermal neutrons, products of interaction of primary cosmic radiation, to atoms of atmospheric nitrogen:



Tritium atoms decay according to the reaction:



The reaction energy is 18 keV, distributed between electron and antineutrino.

Concentration of tritium activity is commonly expressed by so called tritium units (TU), where one tritium unit represents the ratio of one atom of ^3H to 10^{18} atoms of ^1H , corresponding to the concentration of activity:

$$1 \text{ TU} = 7.2 \text{ disintegration/min/L water} = 0.118 \text{ Bq/dm}^3; 10 \text{ TU} = 1.18 \text{ Bq/dm}^3$$

An important part of tritium present in the atmosphere and in the hydrosphere is of anthropogenic origin, formed by a series of thermonuclear explosions in the atmosphere since 1952. The maximum concentration of ^3H activity, being 6000 TU (550 Bq/dm^3), was recorded in 1963 in precipitation on the Northern Hemisphere. After the ban of atmospheric nuclear tests in 1964, tritium activity started to decrease due to its relatively short half-life. Today, in the atmosphere it is less than 10 TU and is approaching the natural level of the first half of the last century (1967; König and Winter 1977).

Main characteristics of the natural temporal and spatial distribution of ^3H activity concentration are seasonal effect, ocean-continental effect and latitudinal effect.

Due to these characteristics, tritium became one of the most important natural tracers and has an important role in hydrological, geological, ecological, climatological and meteorological investigations.

A more and more notable proportion of anthropogenic tritium in the atmosphere is a result of its production in nuclear reactors and experimental fusion reactors, as well as its presence in various consumer products. Anthropogenic tritium changes the spatial distribution of ^3H in the atmosphere on a local and/or regional level.

Measurement of concentration of tritium activity in natural waters (precipitation, surface or ground waters) and environment can be used as a very successful tool in hydrology and related sciences. Relating to the concentration of tritium activity, waters can be divided into two groups: to those containing only natural tritium, that were not in contact with the atmosphere after thermonuclear tests and those labeled by artificially produced tritium. In this way it is possible to follow the path of precipitation and its flow into underground aquifers and to measure age or the mean residence time of water in the underground under the supposition that the initial activity of tritium is known and that there exists no mixing with older or recent water (Obelic 2005).

Today, measurement of tritium activity in environmental samples belongs mainly to the category of low-activity measurements. Therefore a very sensitive technique such as radiometric method is needed. Most often gas proportional counters or liquid scintillation counters are used. Due to the low energy and the low range of β -particles emitted by tritium decay, the sample should be mixed with the detector. Very low concentration (below 1 TU) of tritium activity should be determined by using of electrolytic enrichment of the sample prior to the measurement in a counter.

Radiometric methods are sensitive ways for the determination of tritium due to its short half-life (12.43 years), and therefore its high specific radioactivity (value of 3.6×10^{14} Bq g⁻¹). Tritium decays by pure beta particle emission with low energy (i.e. $E_{\max} = 18.6$ keV), it is therefore favorably measured by liquid scintillation counting (LSC), a detection limit of 50 mBq (1×10^{-16} g) was reported for the determination of tritium in nuclear waste with low-level LSC for 500 min counting time (Hou 2005). In LSC, the sample is normally prepared in a small volume of liquid (<10 mL), which is mixed with a scintillator cocktail for counting. The tritium concentration in environmental samples is normally very low (<1 mBq mL⁻¹), the LSC is not sensitive enough for the direct measurement, an electrolytic method is therefore often applied to enrich tritium from water (Taylor 1981), the enrichment factor of 30÷100 can easily be obtained for 100÷500mL of water. For the determination of tritium in solid samples, a combustion method is used to convert tritium to tritiated water (HTO), which subsequently is measured by LSC (Hou 2005; Taylor 1981; Pointurier et.al., 2004).

Accelerator Mass Spectrometry, (AMS), is also a sensitive method for the determination of tritium, a detection limit of 1 mBq (or 10^{-13} to 10^{-15} for $^3\text{H}/^1\text{H}$ ratio) has been reported (Chiarappa-Zucca & colab., 2002). The primary benefit of this method is the analysis of small samples (2 mg hydrogen), which is very suitable for the analysis of very small or biological samples. In this method, the tritium is first released from the sample and converted to hydrogen gas which is then absorbed on metal (i.e. Ti), and then measured by AMS. For this reason the sample preparation for AMS is more complicated comparing to LSC. Combining with the less availability of AMS facility, the application of AMS for the determination of tritium is very limited.

In the routine analysis, LSC is still the most often used method for tritium determination in environmental and radioactive waste samples (Hou and Roos 2008).

2 EXPERIMENTAL METHODS

The difficulties in the collection of water samples for tritium analysis arise in connection with ground-water samples, oceanic precipitation and water vapour. Collection of surface water samples including also ocean water present no significant problems (1967). Tests conducted by the IAEA have shown the magnitude of possible vapour transfer of tritium through polyethylene storage containers. As a maximum transfer factor in an atmosphere saturated with water vapour having a very high tritium concentration (2×10^6 TU), the increase of tritium in the sample was of approximately 1.5 TU per year per 100 TU of ambient atmospheric tritium. Observations of routine analytical data indicate that the change of tritium concentration in environmental conditions, in completely filled bottles is considerably less.

Variations of the tritium concentration in air humidity correlate with the variations of the tritium concentration in the tissue water of plants; the tritium concentration level in the tissue water of plants is close to the tritium concentration in air humidity (König and Winter 1977).

The amount of collected sample should be 2÷3 times the amount needed for one analysis. Only one species of plants or fish should be used for one analysis per sample. Samples are put into plastic bags firmly closed, weighed immediately after collection and stored in a refrigerator. Freshly caught fish (not-clean) is sorted by species, packed in plastic bags, transported in ice boxes and shock frosted in the laboratory until further treatment. The values are reported as Bq/dm³ water tissue or Bq/kg wet weight.

For soil sampling, cylindrical tubes of steel of different lengths are used for typical depths of 5, 10, 15, 20 cm. For undisturbed grassland usually one takes 5 cm of soil and in agriculturally used areas 15÷20 cm, depending on the depth of plowing. The typical diameter of the corer is about 10 cm. The samples are deposited in plastic bags in order to avoid the moisture loss (Schüttelkopf 1990).

In laboratory, the water samples are distilled under normal pressure and the product is directly mixed with liquid scintillation cocktail (OIDIRM-LRPM, PL-LRPM-02 Internal procedure, 2014; SR ISO 9698:1998).

For determining of tritium content in water free tissues (in plants and fish) or soil pores (in disturbed and undisturbed soil samples) we applied the azeotropic extraction by toluene to extract the tissue water.

Azeotropic distillation allows obtaining the distilled product within a short period, whereas the vacuum distillation process takes more time (OIDIRM-LRPM, PL-LRPM-03, 2014).

Vacuum distillation gives two products, a distillate and dry biological matter (for plant and fish tissues), enabling to determine organically bound tritium (OBT) which is not possible with the azeotropic method. For the samples with higher tritium content in free water tissues (TFWT) it is interesting to determine and compare tritium in the tissue water with tritium bound organically. Normally, the ratio OBT/TFWT is greater than one which means that the tritium deposited in the organic part (mainly by biochemical reactions) still remains long after the tritium concentration in the water free tissues depleted. This depletion is due to the changes in the tritium concentration in the air and water. It was found that the amounts of tritium in water obtained from the dried mass by incineration (total combustion using a Sample Oxidizer M307, as example) is lower than that in fresh tissue/sample and clearly higher than that in tissue water. With the ratio of tritium concentration in tritiated water (HTO) from organic material to tritium concentration of tissue water, distinct differences were found between different chemical species.

For expressing the radioactive concentration in tritium per unit mass (Bq/kg), a part of soil sample is dried in an oven (at 105÷110°C) until the sample weight becomes constant. For fish and plants, parts of the samples are cut up and dried at 110°C until the sample weight becomes constant. In this way, the percent of humidity has to be determined. The Romanian legislation does not provide specific requirements for mass concentrations of tritium in soil, plant and fish, the only given limit is 100 Bq/dm³ for drinking water (LAW No. 301 of November 27, 2015).

3 RESULTS AND DISCUSSION

The five years investigation, from 2011 to 2015 was deployed in the South-Eastern part of Romania in both agricultural and wetlands or rural and urban areas, as one can see on the maps below (Figure 1 and 2).

In both cases of IFIN-HH (Figure 1) and the CNE (Figure 2) we searched several sampling points to emphasize some particular aspects related to each nuclear facility in part.

For IFIN-HH, selected points were chosen so as to emphasize:

- Tritium concentration variation with distance from IFIN-HH
- The influence of urban areas on gaseous effluents ex. Bucharest town
- Influence vicinity of watercourses (Arges, Danube) or lakes on biotope or biota in rural areas
- The dynamic development in the Bucharest – Ilfov region which requires constant reassessment of "zero" areas available as needed to evaluate previous cases.

For the CNE Cernavoda, specific factors that determined the choice of sampling sites were dictated by:

- Determining the influence of nuclear power plant activities on more remote areas East of Cernavoda, but different from the seaside area (where there is an additional influence of the Black Sea)
- Establish the impact of the plant on some areas apparently isolated, beyond the 30 km of permanent supervision of CNE, placed either plateau Dobrogea, away from sources of large water areas or in high areas of Dobrogea Plateau and near the Great Lakes of N, NE
- Establish a point "zero" affordable sampling sites for Dobrogea area.

In water samples, tritium was determined as HTO by simple distillation procedure. In plant and fish tissues the azeotropic process was used for determining TFWT. Total combustion process on Sample Oxidizer M307 was used to determine the OBT and total tritium content. The results are expressed in Bq/dm³ unit because the only value of radioactive concentration in tritium presented in legislation is for drinking water.

The measurements were performed by liquid scintillation counting (LSC) technique using Tricarb 1600TR, Tricarb 2910TR and Quantulus 1220 Ultra Low Level Counting System. The Minimum Detectable Activity, (MDA), was 1.18 Bq/dm³ (i.e.

~ 10 TU) on Quantulus 1220 being the expected value for unenriched water samples; no electrolytic enrichment was used.

The measured values being 8 to 10 times lower than upper acceptable limit for tritium in drinking water, (i.e. 100 Bq/dm³), in Tables 1 and 2 we present only averages for the five years interval, the difference between minimal and maximal values being within 15% for similar sampling conditions.



Figure 1. Sampling points over 5 km around IFIN-HH



Figure 2. Sampling points over 30 km East from Cernavoda NPP

Table 1. Tritium radioactive concentration around IFIN-HH in Bq/dm³; average values (2011 – 2015)

	Bucharest; Sixth District; South-West Area	Bucharest; South-East Area; Popesti- Leordeni Lake	Calnisteia Lake	Buturugeni Lake	50 km South from Bucharest; Curcani rural area
Surface water	N.D.	MDA	N.D.	4.3	N.D.
Well water	N.D.	N.D.	N.D.	N.D.	4.0
Grass from undisturbed soil	5.2	N.D.	20.0	4.5	2.3
Grass from disturbed soils	3.6	N.D.	N.D.	N.D.	N.D.
Leaves	14.6	N.D.	N.D.	5.0	N.D.
Pine needles	2.3	N.D.	N.D.	N.D.	N.D.
Nut leaves	N.D.	N.D.	N.D.	N.D.	3.8
Green nuts	N.D.	N.D.	N.D.	N.D.	2.7
Vine leaves	4.2	N.D.	N.D.	N.D.	2.5

	Bucharest; Sixth District; South-West Area	Bucharest; South-East Area; Popesti- Leordeni Lake	Calniste Lake	Buturugeni Lake	50 km South from Bucharest; Curcani rural area
Grapes	3.0	N.D.	N.D.	N.D.	5.0
Raspberry leaves	N.D.	N.D.	N.D.	N.D.	5.2
Raspberry fruit	N.D.	N.D.	N.D.	N.D.	2.1
Algae	N.D.	N.D.	N.D.	4.2	N.D.
Fish	N.D.	6.0	9.1	3.0	N.D.
Undisturbed soil; 0-5 cm depth	N.D.	N.D.	9.3	5.1	5.4
Disturbed soil; 0- 20 cm depth; mean value	N.D.	N.D.	N.D.	N.D.	4.1

N.D. = Not Determined

MDA = Minimum Detectable Activity; 1.18 Bq/dm³ on Quantulus 1220 Liquid Scintillation Analyzer

Table 2. Tritium radioactive concentration in Eastern Dobrogea in Bq/dm³; average values (2011 – 2015)

	40 km from Cernavoda; Ciocarla rural area	Techirghiol Lake	Mangalia urban area; 2 Mai rural area	Gura Dobrogei protected area	Sinoe Lake; Histria ancient city	Constanta urban area; Corbu rural area
Surface water	N.D.	6.5	3.9 (Mangalia Lake)	N.D.	MDA	N.D.
Well water	2.2	N.D.	3.0 (thermal spring Mangalia)	N.D.	N.D.	MDA (Corbu)
Grass from undisturbed soils	8.7	N.D.	MDA (2 Mai)	14.4	7.4; 3.8 on the beach	14.50
Grass from disturbed soils	N.D.	N.D.	N.D.	N.D.	N.D.	4.1 (Corbu)
Leaves	4.0	N.D.	3.6 (2 Mai)	N.D.	N.D.	N.D.
Pine needles	N.D.	N.D.	N.D.	17.2; 18.2 in pine buds	N.D.	MDA
Nut leaves	MDA	N.D.	6.1 (2 Mai)	N.D.	N.D.	3.9 (Corbu)
Green nuts	4.0	N.D.	MDA	N.D.	N.D.	5.3 (Corbu)
Vine leaves	25.6	N.D.	4.4 (2 Mai)	N.D.	N.D.	6.7 (Corbu)
Grapes	7.6	N.D.	N.D.	N.D.	N.D.	MDA; 8.7 (Corbu)
Algae	N.D.	N.D.	N.D.	N.D.	7.0	N.D.

N.D. = Not Determined

MDA = Minimum Detectable Activity; 1.18 Bq/dm³ on Quantulus 1220 Liquid Scintillation Analyzer

As we can see, the major factors that influence increasing local and regional values for some points are the proximity to the nuclear objective, the vicinity of large water areas such as Danube River or lakes from N and NE Dobrogea, the dominant wind direction and a higher altitude, major obstacles such as large cities lowering the tritium activity concentration in environment.

In most cases, the tritium distribution as HTO in environment compartments is as predicted: higher in undisturbed soil and plants that belong to, or in waxy leaves which prevent water loss through sweat.

In some cases, however unexpected values appear due to a complex contribution of all factors outlined above affecting tritium accumulation. Despite this, the overall tritium concentration seems to depend mainly on the distance from the nuclear objective and the large water accumulation in the immediate vicinity of the sampling point or a combination of the two factors.

4 CONCLUSIONS

Radioactive concentration of tritium as HTO in different ecosystem compartments for areas over 5 km from nuclear objectives was determined. The values are at least 8 to 10 times lower than upper limit of normal concentration in drinking water (i.e. 100 Bq/dm³ according to Romanian laws) within the expected interval for continental waters with no contamination / minor contamination from anthropogenic tritium (2 ÷ 18 Bq/dm³) (Feldt 1990). In many cases the values are lower than MDA (i.e. 1.18 Bq/dm³ determined with Quantulus 1220). Higher or unexpected values have been found in the places nearest to nuclear facilities, near large volume of water areas like rivers and lakes and, if the dominant wind direction coincide with the moment of radioactive releases, in the atmosphere.

For IFIN-HH we can conclude that a reference “zero” point near Magurele (on the East / South-East part of Bucharest) can be considered.

For Cernavoda NPP, samples taken from the Eastern part of Constanta may be a good solution, but more investigation is needed.

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