VI. RADIATION ECOLOGY

DISTRIBUTION OF TRITIUM IN SURFACE WATER AND PRECIPITATION IN RILA MOUNTAIN, BULGARIA

Elena Geleva, Dimitar Tonev, Hristo Protohristov, Svetoslav Dimitrov, Vladimir Bashev, Stefan Genchev, Anguel Demerdjiev

Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 72, Tsarigradsko chaussee Blvd., 1784 Sofia, Bulgaria

Abstract. A study of the tritium content of surface water from three Rila lakes – Moussala lake, Aleko lake and Ice lake, and precipitation at Moussala mount has been performed by means of high precision nuclear and radiochemical methods. The measurements are part of a long-term environmental monitoring program developed and maintained by the Institute for Nuclear Research and Nuclear Energy, Bulgaria Academy of Science. The results for lake water and precipitation samples collected at Moussala part of Rila over the period 2012–2017 were found to range from < 1.20 to 2.77 $Bq.L^{-1}$ and from 2.14 to 4.12 $Bq.L^{-1}$ respectively. The content of ^{3}H in all samples is below the recommended level of 100 $Bq.L^{-1}$
The obtained new results are used to assess the radiation status of the investigated water sources and can be used for evaluation of possible future changes and trends.

Keywords: ^{3}H, surface water, precipitation, Rila mountain

INTRODUCTION

Tritium (^{3}H) is the heaviest isotope of hydrogen with atomic mass A=3. ^{3}H is a radioactive low-energy beta emitter (E_{β} max = 18.6 keV) with a half live equal to 12.43 (± 0.02) years. It decays to helium-3 (^{3}He) by emitting a low-energy beta particle (electron) and a neutrino with an average energy of 5.7 keV and a maximum energy of 18.6 keV (Fig. 1a, b).

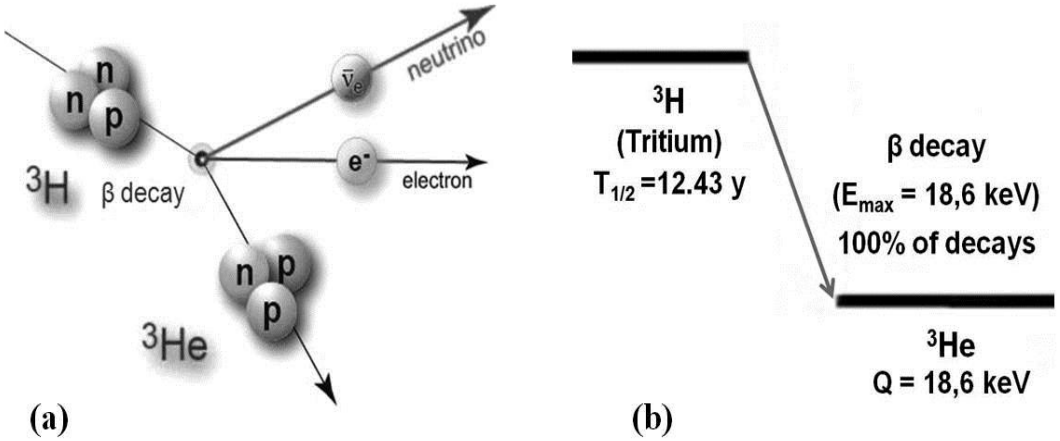

Fig.1. a) Disintegration of tritium (^{3}H) in helium-3 (^{3}He); b) in the process only electrons (E_{max} = 18.619 keV), emitted from the ^{3}H nucleus can be detected. The total energy of the radioactive decay is statistically distributed between the electron and the neutrino, the latter one not detected in the LS spectrometer.

Tritium occurs in nature, originating from natural and anthropogenic sources. It is produced naturally from interactions of cosmic rays with ^{14}N and ^{16}O atoms in the upper atmosphere, and in small amounts in the earth crust from the neutron capture reaction of ^{6}Li in rocks containing uranium [1, 2, 3, 4]. Natural atmospheric ^{3}H values are in the range of 0.24-1.18 $Bq.L^{-1}$, depending on geographical location and weather phenomenon [1]. The ^{3}H environmental level increased in the period from 1945 to 1963 as a result of nuclear weapon tests [1, 3]. Approximately 600 kg of the radionuclide was

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released into the atmosphere, which resulted in a significant increase in its content in the global precipitation [2]. The maximum concentration of ^{3}H activity, being 6000 TU (550 $Bq.L^{-1}$), was recorded in 1963 in precipitation on the Northern Hemisphere. 1 TU is equal to one tritium atom per 1018 hydrogen atoms, corresponding to 0.11919 $Bq.L^{-1}$ for water at standard temperature and pressure [2]. After the ban of atmospheric nuclear tests in 1963, its concentration in precipitation 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 [5].

In addition, ^{3}H is released into the atmosphere from weapons manufacturing, operation of heavy water nuclear power plants, and reprocessing of nuclear fuel [3, 6].

The tritium shows slight differences in its chemical and physical characteristics in comparison with hydrogen and exchange very easily with hydrogen or water molecules, and is distributed everywhere in the environment [2, 7]. ^{3}H can reach surface water by variety of pathways: directly through precipitation and molecular exchange with the atmospheric hydrogen and indirectly from run-off or by influx of streams from groundwater. Practically, all the continental deposition of ^{3}H occurs by precipitation. In case of local releases of ^{3}H to the atmosphere, its dry deposition on the ground surface can occur [4].

In the last decades ^{3}H has been used as an environmental tracer for solving some hydrological problems. It is a part of the water molecule (HTO) and being used as an ideal tracer in understanding the hydrological processes. Additionally, it is being used in tracing the pathway of water in complex hydrological systems. Its isotopic concentration is not undergoing any changes by chemical reaction in the aquifer except decay and minor fractionation during phase changes [2]. Tritium as natural tracer has been used by many researchers in studying the hydrological characteristics of water resources such as lakes Van and Nemrut (Eastern Turkey) [8], Laurentian Great Lakes (Lake Superior, Lake Huron, Lake Erie and Lake Ontario) and Georgian Bay [1], etc. Some lakes in Bulgaria, as Rila lakes, are also objects of special interest for their ^{3}H content. In order to obtain complete data from analyses of ^{3}H concentration in water it is necessary to know its level in precipitation of the area where the activity has been measured.

The objective of this study is to measure contemporary ^{3}H levels in three Rila lakes (Moussala lake, Aleko lake and Ice lake) surface water and precipitation and to assess their spatial distribution. The measurements are part of a long-term radiological environmental monitoring program developed and performed by the Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences.

MATERIAL AND METHODS

Study area. The area under investigation is situated in the Moussala Eastern part of Rila mountain. Rila is the highest mountain on the Balkan peninsula and the biggest water source in Bulgaria. It is the main supply for pure drinking water for the Bulgarian capital Sofia, part of north Greece and part of Turkey. In the mountain there are situated about 200 lakes – 120 of them are permanent from the Ice Earth period. The Mussala lakes are 7 and all are situated in the Moussala part of Rila at altitude ranging from 2389 to 2715 m. Ice lake is the highest and the deepest lake – altitude 2709 m, depth -16.4 m. Its water flows in the Mussala lake (alt. 2577 m) and Aleko lake (alt. 2545 m) [9].

Sampling. The samples are collected during the 2012 –2017 period from Moussala lake, Aleko lake and Ice lake and from precipitation on Moussala mount (alt. 2925.4 m). Water samples were collected using 1 l polyethylene bottles washed with distilled water. For collection of rain water, special large polyethylene bottles were used. After collection, the samples were transported to the laboratory as soon as possible.

The geographical distribution of localities, from where water samples have been investigated is shown in Fig. 2.

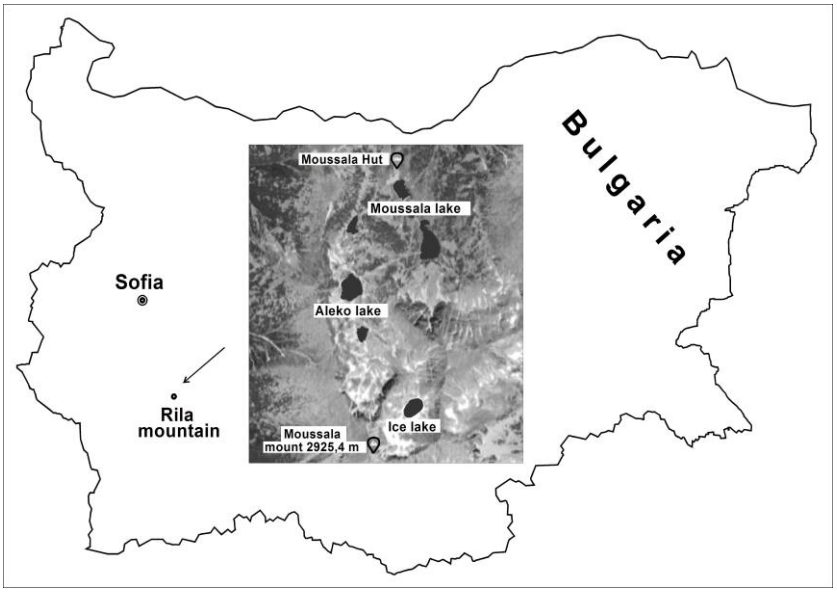

Fig. 2. Geographical distribution of glacial lakes, from where water samples have been investigated

Analytical procedures. Samples were distilled to a volume of 100 ml as a pretreatment step to remove the impurities and reduce quenching, to prevent any interference, which might adulterate the results. The distillation was performed by adding 0.5 g of sodium hydroxide (NaOH) and 0.1 g of potassium permanganate (K_2MnO_4) to a 100 ml aliquot of the sample in a 250 ml distillation flask. The first 10 ml of distillate is discarded. An aliquot of 10 ml from the second fraction of the distillate was transferred in a polyethylene vial, mixed to 10 ml of scintillation cocktail (PACKARD ULTIMA GOLD LLT) at a sample pH value ranging from 5 to 7. To prevent luminescence in the vial that contains the sample, it is recommended to store the sample for a minimum of 1 h in the dark before it is measured [3, 7, 9].

Instrumentation. ^{3}H is a radioactive isotope that emits low energy beta particles with a maximum energy of 18.6 keV. Its activity was measured by means of a liquid scintillation (LS) spectrometer PACKARD TRI-CARB 2770 TR/SL [10].

The detector signals are processed in a multi-channel analyser (MCA) that separates tritium signals in the sample from those produced by chemiluminescence in two different spectra.

The calibration was performed automatically with the use of the unquenched ^{3}H and ^{14}C calibration standards and background standard [10]. The quenched spectrum of ^{3}H is shown in Fig. 3. In our measurements the energy window for tritium was fixed to 0–4.5 keV.

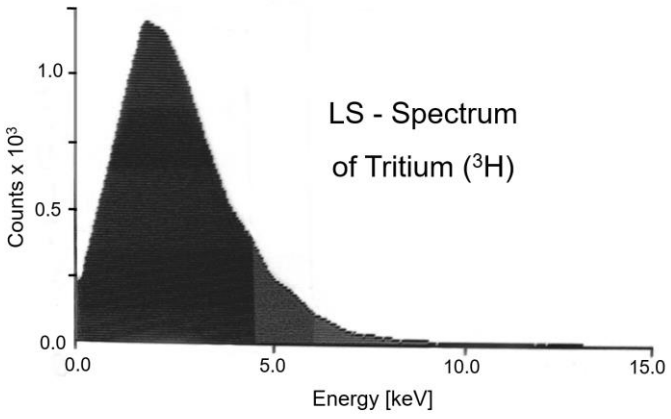

Fig.3. Liquid scintillation spectrum of the $^{3}H \rightarrow {}^{3}He$ decay, measured in the LS spectrometer.

The activity of tritium (^{3}H) is calculated from the peak area of the quenched spectrum. In order to determine the counting window for ^{3}H measurements, we collected spectra of ^{3}H and background and the window was set to maximize E^2/B (Figure-of-Merit). The term Figure of Merit (FOM), expressed as a function of efficiency (E) and background (B), is currently the most widely used parameter to assess counter sensitivity and performance. For our measurements, the energy window for ^{3}H was fixed to 0-4.5 keV. Quenching is quantified with transformed Spectral Index of the External Standard (tSIE), which is used to determine the counting efficiency of the system with appropriate calibration curves (Fig. 4). The transformed Spectral Index of the External Standard (tSIE) is calculated from the Compton spectrum induced in the scintillation cocktail by an external ^{133}Ba gamma source.

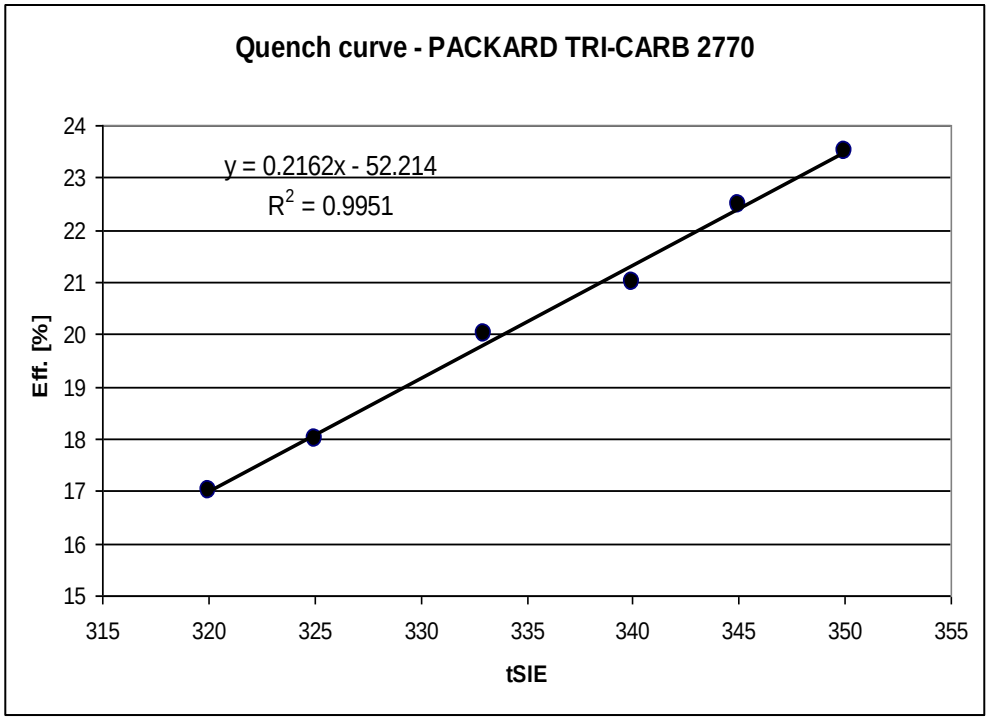

Fig. 4. Quench curve for ^{3}H using tSIE as quench indicator

The counting efficiency was evaluated with tritiated water standards (Amersham) and oscillates around 23 %. The background samples are prepared using 10 ml of liquid scintillation cocktail mixed with 10 ml of the reference water with very low ^{3}H concentration.

RESULTS AND DISCUSSION

The main source of tritium (^{3}H) contamination is the wet and dry deposition and diffusion from stratospheric and tropospheric air [4]. Atmospheric precipitation can deposit this radionuclide in surface water. The ^{3}H containing water deposited on the ground can infiltrate in soil and internal layers. The extent of this infiltration depends on such factors as the type and permeability of the soil, water content, organic matter, etc. Therefore, the ^{3}H levels are different in various soils and sites. In order to study the ^{3}H distribution monitoring of its activity in surface water from different lakes – Moussala lake, Aleko lake and Ice lake and precipitation between 2012-2017 has been carried out. Due to its location the three lakes are not affected by the presence of anthropogenic sources.

The results of the ^{3}H content in surface lake water are presented in Fig. 5.

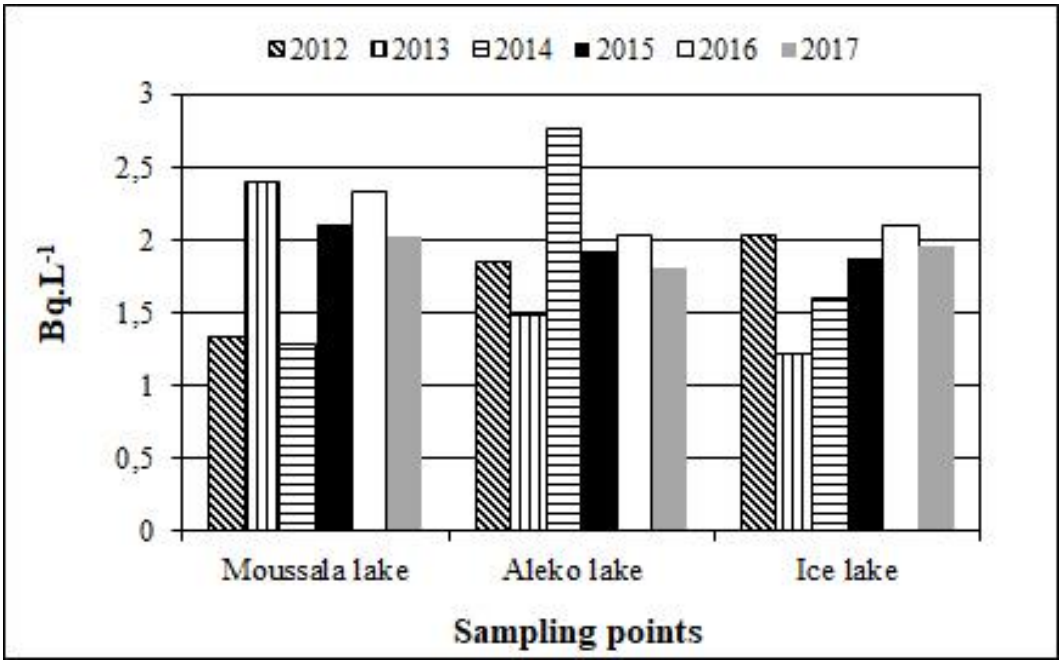

Fig. 5. Tritium activity concentration in surface water from Moussala lake, Aleko lake and Ice lake

In Table 1 some statistical results obtained for the studied surface water and precipitation are presented.

As can be seen from Fig. 5 and Table 1, the activity concentration of ^{3}H in the surface water samples collected from the lakes during the last six years varied from < 1.20 $Bq.L^{-1}$ to 2.77 $Bq.L^{-1}$. The minimum of < 1.20 $Bq.L^{-1}$ was registered in 2013 (Ice lake) and the maximum of 2.77 $Bq.L^{-1}$ in 2014 (Aleko lake). Activity concentration values of ^{3}H published earlier [9] for the same water sources in Rila mountain are similar to the results obtained here. The results are slightly lower than those obtained for the 2009–2011 period (1.22–3.20 Bq.L-1). The mean values for surface water for the whole period from 2012 to 2017 are very close – 1.91 $Bq.L^{-1}$ for Moussala lake, 1.98 $Bq.L^{-1}$ for Aleko lake, and 1.80 $Bq.L^{-1}$ for Ice lake. The content of ^{3}H in all samples is below the recommended level of 100 $Bq.L^{-1}$ [11].

Table 1. Statistical results for ^{3}H content [$Bq.L^{-1}$] for the studied surface water and precipitation

Parameter	^{3}H [$Bq.L^{-1}$]		
	Min	Max	Mean
Moussala lake	1.28	2.39	1.91
Aleko lake	1.49	2.77	1.98
Ice lake	< 1.20	2.10	1.80
Precipitation	2.14	4.12	3.03

The results obtained in this study are in agreement with other investigations. Dove et al. [1] reported mean values for ^{3}H between 0.67 $Bq.L^{-1}$ and 3.70 $Bq.L^{-1}$ in surface water from Great lakes, Canada. An activity concentration of ^{3}H of up to 3.58 Bq.Lhas been determined in water samples from of Lake Nemrut in Eastern Turkey [8].

Fig. 6 represents the values obtained for precipitation in the 2012–2017 period and shows that all data vary within a narrow range of 2.14-4.12 $Bq.L^{-1}$ and there are no extreme values.

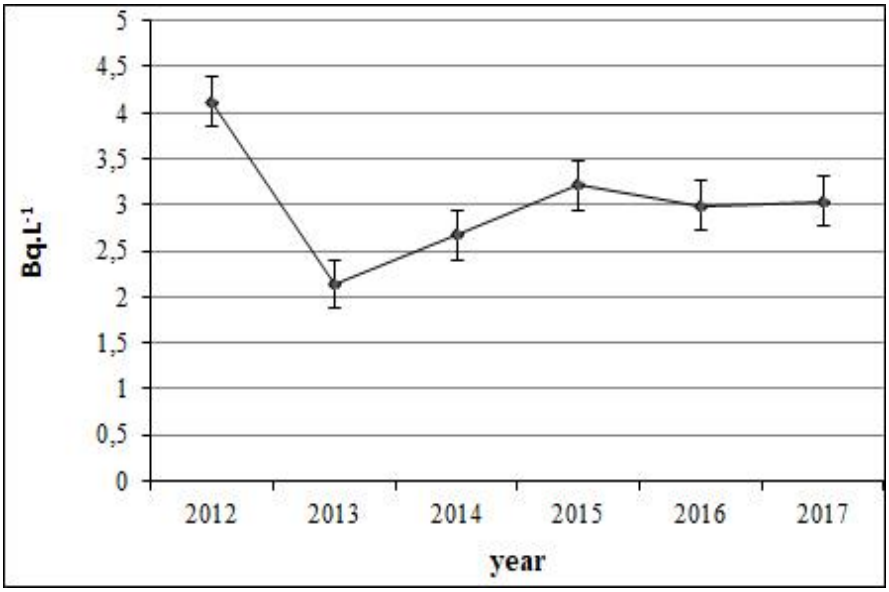

Fig. 6. Tritium (^{3}H) activity concentration in precipitation at Moussala mount

These results are similar to the results obtained during the 2009-2011 period [9] – from 1.61 to 3.31 Bq.L^{-1}. Tritium (^{3}H) shows higher concentrations in precipitation in comparison with the data for surface water. The tritium distribution in precipitation depends on latitude, proximity to the sea and distances from artificial sources or thermonuclear test zones, place where cloud was generated and ^{3}H concentration in migration pathway of clouds [12]. The values do not differ significantly from the data reported for other countries [4, 12, 13].

The results obtained in this study are within the normal levels for this geographical region and do not exceed the limits set by the national the legislation [11].

CONCLUSIONS

Investigations of ^{3}H activity concentration of surface water in three Rila lakes (Moussala lake, Aleko lake and Ice lake) and precipitation at Moussala mount were carried out.

On the base of these results, we conclude that, the tritium concentration in surface lake water, which ranges between MDA (1.20 Bq.L^{-1}) and 2.77 Bq.L^{-1}, and precipitation (between 1.66 and 4.12 Bq/l) at Mousala area in Rila mountain is low. The activity concentration of tritium measured in this study is below the recommended level of 100 Bq.L^{-1} The presented measured data and results can be used in further studies of glacial lake in Bulgaria and in the Balkan region, as well as in global climate change investigations.

New investigations of high-altitude water sources are planned, and novel, more precise methods will be applied in the Analytical Laboratory of the National Cyclotron Centre at INRNE [14].

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REFERENCES

[1] Dove A., S. Backus, K. King-Sharp, Tritium in Laurentian Great Lakes surface waters, Journal of Great Lakes Research, Vol. 47, 2021, 1458-1463.

[2] Ansari Md., H. Mohokar, A. Deodhar, N. Jacob, U. Sinha, Distribution of environmental tritium in rivers, groundwater, mine water and precipitation in Goa, India, Journal of Environmental Radioactivity, Vol. 189, 2018, 120-126.

[3] Palomo M., A. Penalver, C. Aguilar, F. Borrull, Tritium Activity Levels in Environmental Water Samples from Different Origins, Applied Radiation and Isotopes, Vol. 65, 2007, 1048-1056.

[4] Radwan I., Z. Pietrzak-Flis, Tritium in Surface Water, Tap Water and in Precipitation in Poland during the 1994-1999 period, Journal of

Radioanalytical and Nuclear Chemistry, No 1, Vol. 247, 2001, 71-77.

[5] Corina S., R. Margineanu, N. Mocanu, Anthropogenic Tritium in Some Ecosystems in South-Eastern, Romania; A Continuous Effort for Education and Public Awareness, Proc. of the 3rd International Conference – Water resources and wetlands, Tulcea, Romania, 8-10 September, 2014, 286-295.

[6] Madruga M., M. Sequeira, A. Gomes, Determination of Tritium in Waters by Liquid Scintillation Counting, Advances in Liquid Scintillation Spectrometry, 2009, 353–359.

[7] Geleva E., A. Damianova, M. Iovtchev, Data on Tritium Activity in Mineral Waters, Comptes rendus de l'Academie bulgare des Sciences, No 1, Vol. 67, 2014, 35-42.

[8] Sheng, I., H. Ming, Evidence for tritium production in the Earth's interior, Chinese Science Bulletin, No 4, Vol. 53, 208, 540-547.

[9] Geleva E., A. Damianova, Tracing of Tritium Activity in Precipitation and Lake Water in Rila Mountain, Bulgaria, Journal of Balkan Ecology, No 4, Vol. 14, 2011, 431-436.

[10] Packard. Tri-Carb Liquid Scintillation Analyzer Model 2770 TR Series Reference Manual. – Meriden, CT 06450, 1995, 534.

[11] Ordinance No 9 on the Quality of Water Intended for Drinking and Domestic Purposes, SG 30 of 2001. Ministry of Environment and Waters (MEW).

[12] Nakasone S., A. Ishimine, Y. Ishizu, Y. Shiroma, M. Tanaka, N. Akata, H. Kakiuchi, T. Sanada, M. Furukawa, Recent Tritium Concentration of Monthly Precipitation in Japan, Radiation Protection Dosimetry, No. 3-4, Vol. 184, 2019, 334-337.

[13] Technical Reports Series No. 371, Environmental Isotope data No. 10: World Survey of Isotope Concentration in Precipitation (19881991), IAEA, Vienna, 1994.

[14] Tonev D., N. Goutev, L. S. Georgiev (2016) Cyclotron laboratory of the Institute of Nuclear Research and Nuclear Energy, J. Phys. Conf. Ser., 724 (UNSP 012049).

Assist. Prof. Dr Elena Geleva
Prof. Dr Dimitar Tonev
Assos. Prof. Dr Hristo Protohristov
Svetoslav Dimitrov
Vladimir Bashev
Stefan Genchev
Anguel Demerdjiev

Institute for Nuclear Research and Nuclear Energy,
Bulgarian Academy of Sciences
72, Tsarigradsko Shosse
Sofia 1784, Bulgaria
e-mails: elenag@inrne.bas.bg
dimitar.tonev@inrne.bas.bg
proto@inrne.bas.bg
svtod@abv.bg
v_bashev@abv.bg
sgg@phys.bas.bg
a.demerdzhiev@gmail.com