Effective Ecological Half-Life of Tritium in Danube – Kinetic Approach

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***Abstract*—Determination of specific activity concentration of radioisotopes in environmental samples can be used to assess the long-term kinetics of the decline of radioisotopes. Based on the obtained activity concentrations of tritium in the Danube, the effective ecological half-life is estimated. Assuming that the Danube in Belgrade is not affected by nuclear power plants, even though it is positioned downstream of the Paks Nuclear Power Plant in Hungary, a slow decline of tritium was observed. The effective ecological half-life of tritium was also determined after correction by subtracting its components originating from cosmic radiation and the atmospheric transfer from nuclear facilities worldwide.**

***Index Terms*—tritium, surface water, effective ecological half-life.**

I. Introduction

The origin of tritium is described through three ways: the natural tritium arises in the upper atmosphere by nuclear reaction between neutrons from cosmic rays and nitrogen atoms; from the atmospheric nuclear tests, in the late 1950s and the early 1960s (during these tests, large quantities of tritium were released in the upper atmosphere), and from nuclear facilities [1,2]. Given the fact that nuclear power plants are located on river and lakes, they release tritium into the natural water recipients from where it can enters in the groundwater, which is the main source of drinking water supply [3]. On the other hand, once released into the atmosphere, the main way of tritium elimination is through precipitation and in this way it reaches surface water. After oxidation to HTO (tritiated water), tritium takes part in the hydrological cycle. From that reason, knowledge of tritium concentrations in natural waters is very important.

Tritium is β-decaying radionuclide with a half-life of 4500±8 days (12.32 y) [4,5]. Between 1936 and 2000, twenty three experimentally determined values of the tritium half-life have been reported [5].

The main characteristics of the natural temporal and spatial distribution of the tritium concentrations are: seasonal effects, ocean-continental effects and latitudinal effects. The mean tritium concentrations in surface water are 5-10 TU (TU-tritium units) [6]. TU is defined as [4]:

$$1TU = \frac{^3H}{^1H} = 10^{-18} \qquad (1)$$

Long-term monitoring studies for radioisotopes are essential for understanding hydrology of rivers and to assess impacts on river discharge. Global Network of Isotopes in Rivers (GNIR) managed by International Atomic Energy Agency (IAEA) has been available since 2007 [7].

In the literature data, there are publications related to the topic of tritium determination in Danube: in Croatia and Serbia [3], Romania [8], Austria [9], Hungary [10], Serbia [11].

This paper presents the kinetic approach of the estimation of tritium decline through determination of effective ecological half-life of tritium in Danube River, based on the obtained activity concentration of tritium in surface water samples collected in Belgrade.

II. The Method

In view of the length of the Danube River (2850 km) and the branched river basin, the Danube is the second largest river in the Europe. The course of the Danube through the Serbia is 588 km. The sampling site for the analysis of tritium activity concentrations in Danube is in Belgrade (positioned downstream of the Paks Nuclear Power Plant in Hungary).

The surface water was sampled several times a month at Belgrade and a composite monthly sample is made. The investigations were carried out during 2017-2022. Samples were taken near the coast. Sample preparation includes the method with electrolytic enrichment [12], for all samples, which were measured by liquid scintillation spectrometer Quantulus 1220. For counting efficiency determination, reference standard tritium solution ^{3}H 9031-OL-548/13 Czech Metrology Institute Type: ER X with activity 5.060 MBq on day 1.10.2013. which has traceability to the BIPM, was used, according to method ASTM D 4107-08 [13]. The counting efficiency was from 25.7 to 29.2 %. Together with the samples, background sample was also measured (tritium free water), as well as sample with known tritium concentration for enrichment factor determination. After

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electrolytic enrichment, samples were mixed with scintillation cocktails ULTIMA GOLD LLT or OptiPhase Hisafe 3 in relation 8:12 in 20 ml polyethylene vial. Measurement time for samples and the background was 18000 s.

Minimum detectable activity, *MDA*, is given with the following equation

$$MDA = \frac{2.71 + 4.65\sqrt{R_b t_b}}{60 \varepsilon V t_b Z} \qquad (2)$$

where R_b is background count rate (cps), t_b is background measuring time (s), ε is a counting efficiency, V is sample volume (l), and Z is enrichment factor.

Decreasing trend concentration of the radionuclide could be described by the first order kinetic equation [14-18]:

$$\ln C_j = -\lambda_{eff} t + \ln C_0 \qquad (3)$$

where C_j *(*^{3}*H)* is annual average activity concentration of ^{3}H in year j (Bq dm^{-3}), λ_{eff} is effective rate of decline in radioactivity concentration, t is time (year), and C_0 is ^{3}H activity at the beginning of observation.

The effective ecological half-lives were evaluated from the decrease in ^{3}H activity concentration according to the equation [14-18]:

$$T_{eff} = \frac{\ln 2}{\lambda_{eff}} \qquad (4)$$

The ecological half-life (T_{ecol}) were calculated using the following equation [18]:

$$\frac{1}{T_{ecol}} = \frac{1}{T_{eff}} - \frac{1}{T_p} \qquad (5)$$

where T_p is physical half-life of ^{3}H.

III. Main Results

Tritium activity concentrations obtained in surface water samples from Danube River, in the investigated period 2017-2022 range from 1.20 Bq dm^{-3} (January 2017) to 5.39 Bq dm^{-3} (December 2022). These results are in accordance with results from obtained for location Batina (Croatia) and Bezdan (Serbia) [3], and Belgrade (Serbia) [11].

Figure 1 presents average monthly concentrations for tritium in Danube for period 2017-2022. As can be seen from Figure 1 there is no pronounced maximum in spring and summer, as is the case with precipitation [19].

Based on the obtained tritium activity concentrations in monthly samples, effective ecological half-live of tritium was estimated assuming that the Danube in Belgrade is not affected by nuclear power plants. Figure 2 presents time changes in ^{3}H concentration in the Danube River for the period 2017-2022. For effective ecological half-life determination, annual average concentrations of tritium were used. The calculated effective ecological half-life is 7.6 y. This result is shorter than the physical half-life (12.32 y) [5].

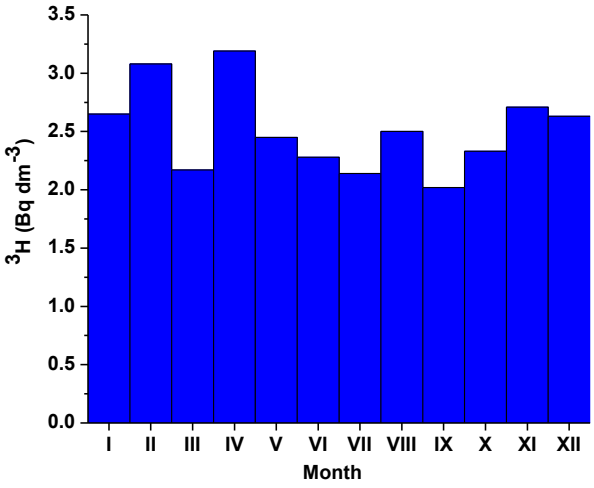

Fig. 1. Average monthly concentrations of tritium in Danube for period 2017-2022

Figure 3 presents annual average ^{3}H concentrations in surface water after correction by subtracting the natural component and the activity originating from the atmospheric transfer from nuclear facilities worldwide.

Two components were subtracted from the detected activity concentration of ^{3}H ($C_{3H,j}$): natural tritium formed in the upper layers of the atmosphere (^{14}N(n,^{3}H)^{12}C) (cosmic radiation C_{3HCR}) [14] and a trans-boundary transmission of nuclear facilities pollution (C_{3HNF}). These constant components, which were appreciated 0.48 Bq dm^{-3} [18] are subtracted from the activity concentration of ^{3}H and calculated effective ecological half-life was 6.1 y for the period 2017-2022.

The mean tritium activity calculated using the first approach (without elimination of the constant components), was 3.3 Bq dm^{-3} at the beginning of the investigated period and 2 Bq dm^{-3} at its end.

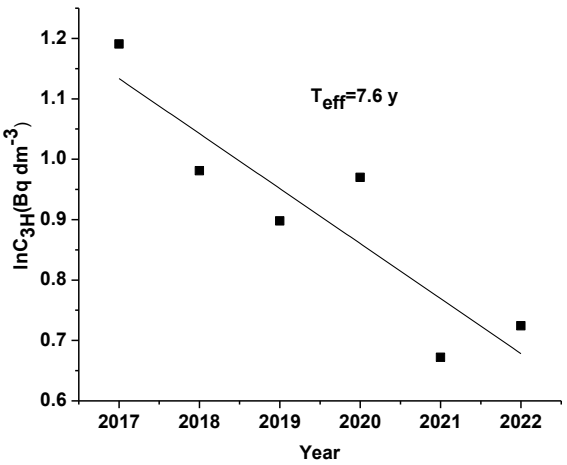

Fig. 2. Time change in ^{3}H concentration in the Danube River for the period 2017-2022

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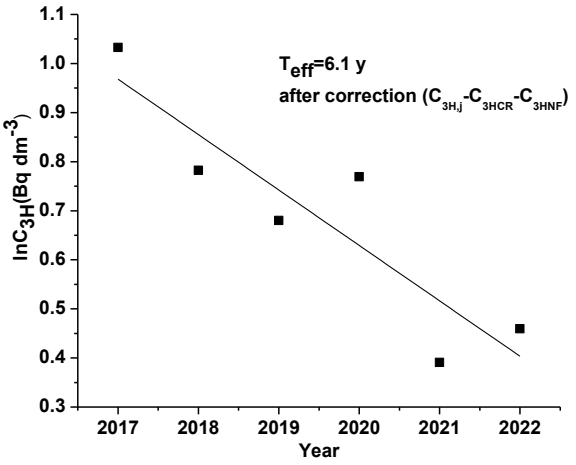

Fig. 3. Annual average ^{3}H concentrations after correction by subtracting the natural component and the activity originating from the atmospheric transfer from nuclear facilities worldwide

Calculated ecological half-life, using the equation (5), was 19.8 y.

IV. Conclusion

In the period 2017-2022 concentrations of tritium have been analyzed in surface water samples (Danube River in Belgrade). A first order kinetic equation provided a good description of the time changes of tritium activity concentrations. The estimated effective ecological half-life of ^{3}H in surface water for the observed period was 7.6 y. The analysis was done and after subtracting the components originating from the natural processes and from estimated emissions from nuclear facilities. In this case effective ecological half-life of ^{3}H was 6.1 y.

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References

[1] B. Nie, S. Fang, M. Jiang, L. Wang, M. Ni, J. Zheng, Z. Yang, F. Li, "Anthropogenic tritium: Inventory, discharge, environmental behavior and health effects" *Renewable and Sustainable Energy Reviews* 135 (2021) 110188

[2] P.A.Thomson, N.-O.A. Kwamena, M. Ilin, M. Wilk, I.D. Clark, "Levels of tritium in soils and vegetation near Canadian nuclear facilities releasing tritium to the atmosphere: implications for environmental models" *Journal of Environmental Radioactivity* 140 (2015) 105-113

[3] Ž. Grahek, B. Breznik, I. Stojković, I. Coha, J. Nikolov, N. Todorović, "Measurement of tritium in the Sava and Danube Rivers" *Journal of Environmental Radioactivity* 162-163 (2016) 56-67

[4] K. Rozanski, M. Groning, "Tritium assay in water samples using electrolytic enrichment and liquid scintillation spectrometry", in: Quantifying uncertainty in nuclear analytical measurements, IAEA-TECDOC-1401, IAEA, Vienna, (2004) 195-217.

[5] L.L. Lucas, M.P. Unterweger, "Comprehensive Review and Critical Evaluation of the Half-Life of Tritium" *Journal of Research of the National Institute of Standards and Technology* 105 (4) (2000) 541-549

[6] P. Theodorsson, "A review of low-level tritium systems and sensitivity requirements" *Applied Radiation and Isotopes* 50 (1999) 311-316

[7] N. Ogrinc, T. Kanduč, W. Stichler, P. Vreča, "Spatial and seasonal variations in δ^{18}O and δD values in the River Sava in Slovenia" *Journal of Hydrology* 359 (2008) 303-312

[8] C. Varlam, V. Patrascu, R.M. Margineanu, I. Faurescu, I. Vagner, D. Faurescu, O.G. Duliu, "Tritium activity concentration along the Western shore of the Black Sea" *Journal of Radioanalytical and Nuclear Chemistry* 298 (2013) 1679-1683

[9] F.J. Maringer "Four decades of radioecological research on the Danube River: a reliable basis for protecting the freshwater resources of central Europe of tomorrow" Japan Health Physics Society, Tokyo (Japan), IRPA-10: 10. International congress of the International Radiation Protection Association; Hiroshima (Japan); 14-19 May 2000.

[10] M. Stute, J. Deak, K. Revesz, J.K. Bohlke, E. Deseo, R. Weppering, P. Schlosser, "Tritium/^{3}He Dating of River Infiltration: An Exaple from the Danube in the Szigetkoz Area, Hungary" *Ground Water* 35(5) (1997) 905-911

[11] M.M. Janković, B.Ž. Janković, N.B. Sarap, "A new method for the determination of tritium originating in surface water: symmetrical index application" Chapter 6 in: Tritium-Advances in Research and Applications, ISBN: 978-1-53613-507-7, Nova Science Publishers, Inc. New York(2018) 213-250

[12] Tecnical Procedure Note 19, Isotope Hydrology Lab., Procedure and Technique Critique for Tritium Enricment by Electrolysis at the IAEA Laboratory, IAEA 1976.

[13] ASTM D 4107-08 Standard Test Method for Tritium in Drinking Water

[14] E. Hanslik, V. Jedinakova-Križova, D. Ivanovova, E. Kalinova, B. Sedlarova, P. Šimonek, "Observed half-lives of ^{3}H, ^{90}Sr and ^{137}Cs in hydrosphere in the Vltava River Basin (Bohemia)" *Journal of Environmental Radioactivity* 81 (2005) 307-320

[15] E. Hanslik, D. Ivanovova, E. Juranova, P. Šimonek, V. Jedinakova-Križova, "Monitoring and assessment of radionuclide discharges from Temelin Nuclear Power Plant into the Vltava River (Czech Republic)" *Journal of Environmental Radioactivity* 100 (2009) 131-138

[16] E. Hanslik, D. Ivanovova, V. Jedinakova-Križova, E. Juranova, P. Šimonek, "Concentration of radionuclides in hydrosphere affected by Temelin Nuclear Power Plant in Czech Republic" *Journal of Environmental Radioactivity* 100 (2009) 558-563

[17] E. Hanslik, D. Marešova, E. Juranova, B. Sedlarova, "Comparison of balance of tritium activity in waste water from nuclear power plants and at selected monitoring sites in the Vltava River, Elbe River and Jihlava (Dyje) River catchments in the Czech Republic" *Journal of Environmental Management* 203 (2017) 1137-1142

[18] E. Hanslik, D. Marešova, E. Juranova, B. Sedlarova, "Kinetics of ^{3}H, ^{90}Sr and ^{137}Cs content changes in hydrosphere in the Vltava River system (Czech Republic)" *Journal of Environmental Radioactivity* 188 (2018) 1-10

[19] M.M. Janković, D.J. Todorović, "Examining the Relationships Between the Activities of ^{3}H in Precipitation and ^{137}Cs in Ground-Level Air in Belgrade City Area" *Water Air and Soil Pollution* 223 (7) (2012) 4471-4483

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