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# Determination of Tritium Concentration in Mlaka Creek

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**The main purpose of this paper was to determine tritium concentration in surface water samples, using liquid scintillation counting. Surface water samples were collected from the Mlaka creek on three different locations near PC „Nuclear Facilities of Serbia“. The importance of tritium monitoring around nuclear reactors and nuclear waste storages is due to prevention of possible internal exposure through ingestion of drinking waters with elevated levels of tritium from existing water supply in their nearby. Tritium concentrations that have been measured during the period from 2017 to 2022 ranged from less than 2 Bq/L to 103 Bq/L.**

*Key words*: **tritium, scintilation counting, surface water samples.**

## Introduction

TRITIUM (from Ancient Greek τρίτος (trítos) 'third') is a rare, radioactive naturally occurring isotope of hydrogen with a half-life of 12.32 ± 0.02 years (approximately 4500 ± 8 days). It was discovered in 1934 by the physicists Ernest Rutherford, M.L. Oliphant and Paul Harteck. Tritium decays to 3He, realizing a beta particle which has a maximum energy of 18.6 keV [1]. Tritium decays to $^{3}$He, realising: (1) natural production in the upper atmosphere, as a result of the interaction of cosmic-ray particles with nitrogen molecules in the air, (2) nuclear weapons testing, and (3) operation of nuclear reactors and other fields. The production of artificial tritium has increased as nuclear weapons testing which included high-yield thermonuclear reactions started to grow. The total amount of tritium estimated to have been found in the atmosphere from 1945 to 1980 due to nuclear weapons testing was 186 000 PBq [2]. The quantity of tritium in the atmosphere due to weapons testing achieved maximum in 1963 and is decreasing ever since [2].

Also, in addition to these origins of artificial tritium, a significant contribution to its amount in the environment is tritium made in nuclear power plants, which greatly raised the accumulation of tritium in the atmosphere. Large accidental release of tritium from tritium production facilities happened in the Lawrence Livermore Laboratory (1970) and Savannah River Plant (1974–1984), both situated in the United States [2]. The measured activity has been reduced over time, achieving a maximum of 18 PBq in the early 1970s and dropped below 0.3 PBq during 1984. Monitoring has shown that in the environment elemental tritium gradually converted to tritium oxide [2]. The Chernobyl accident in 1986, and also the accident that happened in Fukushima nuclear power plant in 2011 has raised levels of tritium in the environment significantly [2]. Since tritium can replace hydrogen in chemical compounds which are essential for life, therefore it is very mobile within the physical and biological environment. The potential radiotoxicity of tritium besides heterogeneous dose distribution within tissues and cells includes also the transmutation and isotopic effects. Laboratory studies which included use of animals, have demonstrated that tritium, as a source of radiation, can adversely affect on the embryo or fetus, and can cause carcinogenic, heritable and reproductive effects and cell death. The doses absorbed due to tritium intake cannot be measured directly, therefore they have to be assessed indirectly (by assessment of tritium concentrations in urine) or based on environmental monitoring. The largest annual doses received by the world population from tritium in fallout happened as a result of the large number of nuclear weapon testing during the period from the end of 1950s to the beginning of 1960s, when in 1962 it reached the peak global average annual effective dose of 7.2 μSv. All this led to signing of The Limited Test Ban Treaty in 1963 [2]. However, North Korea had a series of six weapon testing conducted during 2006-2017 [3].

Starting from 1998, the upper limit for tritium in water has been 100 Bq/L, according to the European Commission Directive 98/83/EC [4]. This limit presents a screening value, providing an indication of the possible presence of other, potentially more harmful, artificial radionuclides discharged into the environment. Most EU member states have transposed the 1998 EU directive into a national law, regulation or standard, and most have followed this recommendation of using the 100 Bq/L value for tritium only as a screening value. Republic of Serbia also established this recommendation in form of the Rulebook on radionuclide

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content limits in drinking water, food, animal feed, medicines, items of general use, construction materials and other goods that are put into trade [5].

Environmental radiation monitoring, which includes tritium determination, is mandatory in the vicinity of the PC "Nuclear Facilities of Serbia" (PC NFS) according to the Rulebook on Radioactivity Monitoring [6]. Consequently, monitoring at the location of PC NFS is carried out by two authorized organizations: Institute of Nuclear Science Vinca, Radiation and Environmental Protection Department and University of Novi Sad, Faculty of Sciences, Department of Physics, Laboratory for radioactivity and dose measurements. Monitoring is essential due to existing of two research nuclear reactors and radioactive waste storage facilities which are the responsibility of PC NFS. The two reactors are out of use (one is permanently and the other is temporarily shut–down). Moreover, in the view of the existence of nuclear power plants in the vicinity of the Republic of Serbia (Krsko on the Sava River) and number of nuclear power plants on the Danube and of possible malicious nuclear weapons testing, it is necessary to monitor radioactivity in water, especially tritium. Systematic environmental monitoring of tritium began in 1976, through sampling and measurements of surface waters and precipitation [7].

Liquid scintillation counting was the method chosen for assessment of tritium concentrations in surface water samples taken from the Mlaka creek at three specific locations along its course through the PC NFS site. Liquid scintillation counting was used due to the fact that the values of tritium in the Danube and Sava River were low – 1 to 2 Bq/L and 0.3 to 1 Bq/L, respectively [8].

## Experimental procedure

*Equipment*

Environmental monitoring of tritium in surface waters was conducted using the spectrometry system Quantulus 1220 manufactured by Perkin Elmer in Finland, which contains low background liquid scintillation system. This spectrometry system is constructed especially for measurement of very low concentrations of beta and alpha radiation in the environment. This instrument has its own background reduction system around the vial chamber, which consists of both active and passive shields. The passive shield is made of lead, copper and cadmium and the active shield is using a mineral oil scintillator that is necessary to remove natural background fluctuations. Two pulse analysis circuits are incorporated in the system: pulse shape analysis (PSA) and pulse amplitude comparator (PAC). There is also a delayed coincidence circuit (DCOS) inside the Quantulus, which is useful for the correction of chemiluminescence. The instrument is equipped with two multichannel analyzers (MCAs), which have a role to record the spectra and to act as active shield. As the level of quenching can notably influence the counting efficiency, therefore the assessment of the total activity of the sample should be evaluated first, due to the loss of scintillations,.

## Sample treatment and measurement

Three locations along the Mlaka creek were chosen and monthly samples from these locations were analyzed. The Mlaka creek flows along the nuclear facilities site and confluence of the Bolečica stream, which ends at the Danube River. The Mlaka creek is 5 km long with an average water flow of only 10 l $s^{-1}$. The sampling points were situated near the discharge from the research reactor RA. The first sampling point is chosen to represent the Mlaka creek before any influence of the nuclear facilities, the second is in the middle of the site and the third one is at the end of PC NFS site, representing the potential influence of PC NFS (Fig.1).

All samples were prepared according to validated method, in accordance with ASTM D4107[9] and validated method, which is based on the Procedure and Technique Critique for Tritium Enrichment by Electrolysis at the IAEA Laboratory [10]. The two analytic methods used to estimate the level of tritium in the Mlaka creek are both accredited according to the SRPS ISO/IEC 17025:2017 standard [11].

Laboratory for radioactivity and dose measurements used validated method for surface water in which the samples were first distilled. Middle fraction of the distillate is collected for tritium analysis. Before the analysis, 8 ml of the distillate is mixed with 12 ml of scintillation cocktail UltimaGold. In order to prevent other radionuclides from distilling over with tritium, the alkaline treatment of the samples with sodium hydroxide was used. Also, treatment with potassium permanganat was used to oxidize organics in the samples which could cause quenching. Deep well water was used to represent a background sample. Background and standard samples were prepared in the same way as the samples. To avoid the occurrence of luminescence, the samples were kept in a dark place for minimum 6 hours prior to measuring. Minimal detectable activity (MDA) value achieved using this method is 2.1 Bq/L.

Radiation and Environmental Protection Department performed determination of tritium by a validated method for surface water samples in which samples were first distilled in order to remove any impurities, and then concentrated by electrolytic enrichment, to increase concentration. The parameters that define the process of electrolysis are calculated: separation factor, enrichment parameter and enrichment factor. The next step was distillation in order to remove sodium peroxide used in the previous steps. Middle fraction of the distillate is collected for tritium analysis. Before the analysis, 8 ml of the distillate is mixed with 12 ml of scintillation cocktail UltimaGold. To avoid the occurrence of luminescence the samples were kept in a dark place for minimum 6 hours prior to measuring. The polyethylene vials turned out to be better than glass and teflon, which have a higher level of background radiation in tritium window, so the 20 ml polyethylene vials were used. MDA value accomplished using this method is 0.1 Bq/L.


**Figure 1.** Sampling locations

## Results and discusion

Tritium concentrations obtained measuring different water samples from three sampling points on the PC NFS site during 2017-2022 are discussed in this paper. These measurements were a part of mandatory environmental radiation monitoring, carried out by two authorized

organizations: Institute of Nuclear Science Vinca, Radiation and Environmental Protection Department and University of Novi Sad, Faculty of Sciences, Department of Physics, Laboratory for radioactivity and dose measurements.

In the previous measurements, the optimal counting window for tritium was established to be between 1st and 250th channel. To obtain sufficient MDA, total counting time for samples and background was set to 5 hours.

In Figures 2 - 4 monthly values of tritium in surface water samples, the Mlaka creek, during 2017-2022 at three sampling points are shown.

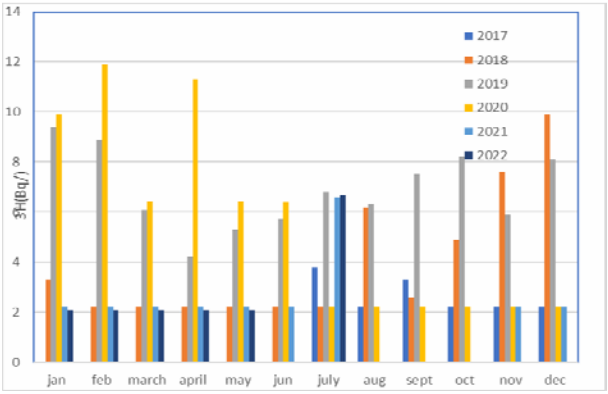


**Figure 2**. Monthly tritium concentrations for period 2017-2022 at the sampling point 1

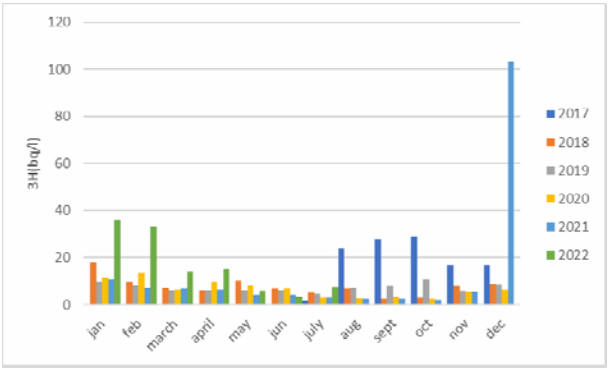


**Figure 3.** Monthly tritium concentrations for period 2017-2022 at the sampling point 2

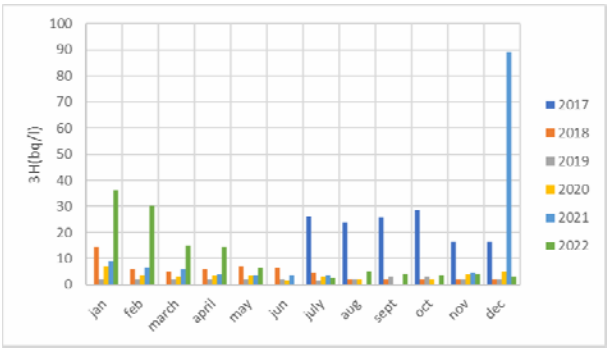


**Figure 4.** Monthly tritium concentrations for period 2017-2022 at the sampling point 3

Tritium concentrations in the Mlaka creek ranged from less than 2 Bq/L to 103 Bq/L (December 2021). Presented values of tritium concentration obtained by measuring the samples from the first sampling point at the Mlaka creek (without the nuclear facilities influence) were from less than 2.1 Bq/L value to 11.9 Bq/L. Other two sampling points had $^3$H concentrations larger for some periods. All presented results are in accordance with annual tritium concentrations mentioned in [7] and [12]. The maximal tritium concentration of 133.8 Bq/L has been measured in January 1993. Fig.5 represents concentration values of tritium in the Mlaka creek for the period 1990 - July 2009 [12], where variations of its concentration through the years are shown.

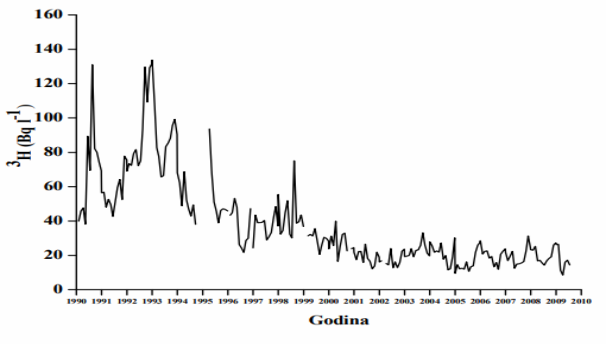


**Figure 5.** Concentration values of tritium in the Mlaka creek for the period 1990 - July 2009 [12]

In Tables 1, 2 and 3 minimal, maximal and average values of tritium in surface water samples, the Mlaka creek, during 2017-2022 at three sampling points are shown.

**Table 1.** Maximal, minimal and average tritium concentrations in surface water samples at the sampling point 1

| Year | Maximal $^3$H activity concentration [Bq/L] | Minimal $^3$H activity concentration [Bq/L] | Average $^3$H activity concentration [Bq/L] |
|---|---|---|---|
| 2017 | 3.8 | <2.1 | 2.6 |
| 2018 | 9.9 | <2.1 | 4.0 |
| 2019 | 9.4 | 4.2 | 6.9 |
| 2020 | 11.9 | <2.2 | 5.5 |
| 2021 | 6.6 | <2.2 | 2.7 |
| 2022 | 6.68 | <2.1 | 2.9 |

**Table 2.** Maximal, minimal and average tritium concentrations in surface water samples at the sampling point 2

| Year | Maximal $^3$H activity concentration [Bq/L] | Minimal $^3$H activity concentration [Bq/L] | Average $^3$H activity concentration [Bq/L] |
|---|---|---|---|
| 2017 | 29 | 1.8 | 19.3 |
| 2018 | 18 | 2.3 | 7.6 |
| 2019 | 10.6 | 4.67 | 7.3 |
| 2020 | 13.3 | 2.4 | 6.6 |
| 2021 | 103 | <2.2 | 13.1 |
| 2022 | 36.2 | 3.4 | 16.4 |

**Table 3.** Maximal, minimal and average tritium concentrations in surface water samples at the sampling point 3

| Year | Maximal $^3$H activity concentration [Bq/L] | Minimal $^3$H activity concentration [Bq/L] | Average $^3$H activity concentration [Bq/L] |
|---|---|---|---|
| 2017 | 28.6 | 16.5 | 22.9 |
| 2018 | 14.5 | <2.2 | 5.0 |
| 2019 | 3.0 | 1.6 | 2.2 |
| 2020 | 6.9 | 1.8 | 3.5 |
| 2021 | 89 | 3.8 | 14.5 |
| 2022 | 36.2 | 2.7 | 11.4 |

As we can see the tables above, minimum, maximum and average tritium concentration values in surface water samples obtained in the years that have been observed are in accordance with the values from previous years. Maximum value obtained in December 2021 by the Laboratory for radioactivity and dose measurements was confirmed by PC NFS laboratory, which measured 110 Bq/L.

In Fig.6 monthly values of tritium in surface water samples, the Mlaka creek, during December 2021 - July 2022

at the sampling point 2 are shown. It is shown that concentration values have been decreasing.

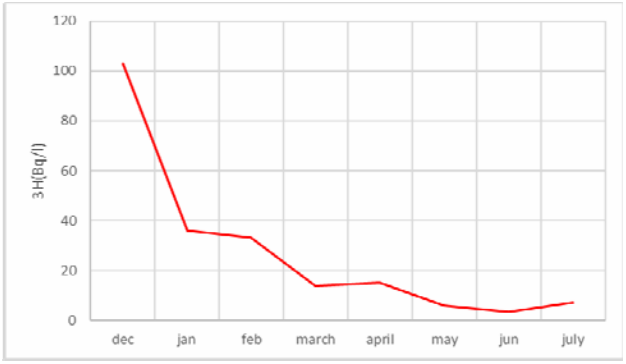


**Figure 6.** Concentration values of tritium in the Mlaka creek for the period December 2021 - July 2022

## Conclusion

All gained results for tritium activity measurements in the surface water samples from the Mlaka creek, gathered at PC NFS site, during 2017-2022 are shown in this paper. Tritium concentrations are from less than 2 Bq/L to 103 Bq/L for the surface water samples at PC NFS site. After measurements in December 2021 that showed that the concentration value had peaked for the observed period, further measurements determined that the concentration values have been declining since then.

Considering the stated concentrations, it is important to regularly monitor tritium levels in surface waters in order to identify the possible rise of environmental tritium regarding the possible influence on drinking water supplies and life cycle generally.

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# Određivanje koncentracije tricijuma u potoku Mlaka

**Glavni cilj ovog rada bio je da se utvrdi koncentracija tricijuma u uzorcima površinske vode. Korišćena metoda bila je tečna scintilaciona spektrometrija. Uzorci površinske vode uzeti su iz potoka Mlaka na tri različite lokacije u blizini JP „Nuklearni objekti Srbije“. Značaj monitoringa tricijuma oko nuklearnih reaktora i skladišta nuklearnog otpada je sprečavanje unutrašnjeg izlaganja unošenjenjem vode za piće sa povišenim nivoom tricijuma iz postojećih izvora vodosnabdevanja u njihovoj blizini. Koncentracije tricijuma koje su izmerene u periodu od 2017. do 2022. godine kretale su se od manje od 2 Bq/L do 103 Bq/L.**

*Ključne reči:* **tricijum, scintilaciona spektrometrija, uzorci površinske vode.**