RESEARCH ON WATER INTERCONNECTIONS WITHIN THE ŠAR MOUNTAINS AQUATORIUM BY RADIOACTIVE HYDROGEN ISOTOPE TRITIUM

by

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The waters of two lakes and two streams that dominate in the Šar Mountains aquatorium were analyzed. The tritium profile of soil was also recorded. All samples were taken at approximately the same time, together with samples of precipitation. During the period of taking samples, the ambient temperature conditions were taken into account for ten days around the time of sampling. Monitoring of the seasonal maximum with taking into account the obtained tritium soil profile and the temperature on and around the day of sampling unambiguously showed that all tested water in the Šar Mountains aquatorium is of atmospheric origin and as such unsuitable for any major transformation for commercial purposes.

Key words: tritium, tritiated water, water tracing, Šar Mountains aquatorium

INTRODUCTION

Water supply for the needs of the population, industry and agriculture is one of the most pressing issues of today's civilization. This problem is particularly relevant to the idea of obtaining energy from the so-called renewable energy sources (RES), which include mini-hydropower plants. There is reasonable doubt about the idea related to an increase in RES as it has been shown that often more energy is invested in their construction (mostly of non-renewable origin) than can be obtained during their operation life. Also, RES, especially mini-hydropower plants, disrupt the ecological balance of the environment in which they are built. For this reason, it is necessary to have the basic data *i*. *e*. the energy potential of the aquatorium where the construction of a mini-hydro power plant is planned. This means, among other things, quantitative (percentage) knowledge of the atmospheric water, surface water, and groundwater participation in the amount of water intended for the operation of mini-hydropower plants. For this purpose, commonly used are the artificial tracers (paints) that are inserted into the water and based on their concentration the water connection (relationship) in the observed aquatorium is estimated [1, 2]. However, such tracers are not guided by the same hydrodynamic laws as water which leads to the measurement uncertainty type B of the procedure itself.

In the world, as well as in Serbia, the method of tritium concentration measurement in hydrological studies has been present since the sixties and together with the same method with deuterium are considered to be the most accurate [3-5].

This paper aimed at investigating the connection of atmospheric, surface and groundwater using tritium which, as a natural component of water (HTO), is subject to the same hydrodynamic laws as tritium-free water components (H_2O). By now no such tests have been carried out for the Šar Mountains aquatorium (southern Serbia) as it was assumed that the water resources of the mountain are purely of atmospheric origin. Such an assumption is logically justified as the Serbian province of Kosovo is extremely water-poor, so the existence of lakes and streams at an altitude of about 2000 m can hardly be attributed to some underground water springs. However, this issue became relevant after the beginning of the construction of mini-hydropower plants in the Šar Mountains aquatorium with unproven claims that a part of the aquatorium waters was of underground origin. In addition to the research of water interconnection within the Šar Mountains aquatorium by a radioactive hydrogen isotope tritium, chemical and biological analysis were carried out in parallel.

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TRITIUM IN NATURE

The level of interest in tritium has changed over time since its discovery (1939) to the present. Its initial high interest subsequently decreased as it was considered a *fairly benign isotope* [6, 7]. However, tritium *benignities* is being checked in water metabolism nowadays [8], and the use of tritium in hydrology has become a standard method [9].

Tritium (or super heavy hydrogen) is a radioactive isotope of hydrogen of 0.0002 % abundance. Abundance of tritium in natural hydrogen is changing due to human activities so that this percentage should be understood conditionally [6]. Tritium is produced by nuclear reactions and the most important are [10-12]

$$D + D = T + H + 4\ \text{MeV} \quad (1)$$

$$^{6}\text{Li} + n = {}^{4}\text{He} + T + 4.69\ \text{MeV} \quad (2)$$

$$^{10}\text{B} + n = {}^{9}\text{Be} + T + 0.2\ \text{MeV} \quad (3)$$

$$^{11}\text{B} + n = {}^{9}\text{Be} + T + 9.6\ \text{MeV} \quad (4)$$

$$^{14}\text{N} + n = {}^{12}\text{C} + T + 4.5\ \text{MeV} \quad (5)$$

$$^{14}\text{N} + n = {}^{33}\text{He} + T + 11.5\ \text{MeV} \quad (6)$$

$$^{9}\text{Be} + n = {}^{8}\text{Be} + T + 5.53\ \text{MeV} \quad (7)$$

$$D + n = T + \gamma \quad (8)$$

The artificial tritium was obtained for the first time by reaction (1). Reactions (5) and (6) are associated with the formation of tritium in the upper layers of the atmosphere under the influence of fast neutrons of cosmic radiation. Nuclear power plants, especially heavy-water reactors, are the most important permanent producer of tritium. In reactors, tritium is formed as a fission fragment in 0.01 % yield by reactions (7) and (8) which take place in the active zone. Over 70 % of the tritium thus produced remains at the site of formation, and the rest goes into the natural environment which continuously (in correlation with the development of nuclear power) increases the concentration of tritium in nature [13]. Based on this presentation, it can be concluded that the total amount of tritium in nature can be divided by origin into natural and artificial. The most important natural sources of tritium are the upper layers of the atmosphere wherein, under the action of high-energy neutrons of cosmic radiation, reactions (5) and (6) take place. Fast neutrons of cosmic radiation also produce tritium causing the decay of heavy elements in the Earth's crust. The yield of these reactions is less than the total amount of natural tritium indicating that cosmic radiation and interactions in the oceans create some additional tritium [14-16]. Artificial sources of tritium are thermonuclear explosions and nuclear power plants. Since 1953, thermonuclear explosions have been responsible for the insertion of large amounts of tritium in nature, tab. 1 [17]. Tritium is usually measured in tritium units where 1 TU is defined as the ratio of 1 tritium atom to 10^{18} hydrogen atoms, approximately equal to 0.118 BqL^{-1}.

Table 1. Tritium concentration before thermonuclear explosions and at the contemporary level. The TU unit is defined as the ratio of one tritium atom to 10^{18} hydrogen atoms

	Tritium concentration [TU]	
	Before 1953	Present situation
Oceans	0.54	10
Rivers	2.5-6	300
Precipitation	10	100-200

Application of tritium in hydrology

The most common form of tritium in nature is HTO (called tritiated water). The molecules of tritiated water enter the hydrological cycle within which (except for phase transitions) they behave identically to ordinary water molecules. At phase transitions HTO behaves like other heavier components of water *i. e.* with a lower vapor pressure (at 15 °C the vapor pressure of the tritiated water is 10 % lower than in H_2O). The concentration of HTO, in all phases of the hydrological cycle, is also affected by the average age of the tritiated water molecules due to tritium losses from the system by radioactive decay. Properties of tritium, as well as the properties of the tritiated water, enable the use of tritium in hydrology, which consists of testing: groundwater restoration, infiltration of precipitation into the soil, surface water and groundwater communication and determination of groundwater age [18, 19].

The so-called *excess water* [2] is negative from April to August, and positive from August to April with high values in the winter period [20]. Change of the tritium concentration in precipitation seasonal minimum corresponds to the negative part of the *excess water*. It can be concluded that isotopic fluctuation, which reflects the mechanism of renewal, is a correlation of several magnitudes, making it difficult to unambiguously conclude its monitoring [21-23]. For the Balkan geographical position, low average annual temperatures can be considered to lead to an increase in *excess water* in winter and that the change in tritium concentration in the restoration waters follows the tritium concentration in precipitation (since most of the precipitation is in winter when renewal is minimal) [24].

The initial application of tritium for hydrological purposes was as an artificial tracer for studying the penetration of precipitation water through the soil [25, 26]. At the same time, high concentrations of tritium were injected into the water at the infiltration sites and the further process was monitored by time. More recently, natural tritium has been used for this purpose.

Specifically, by recording the so-called tritium profile for the composition of the observed soil, we can determine the infiltration rate through the soil, by infiltration mechanism and a fraction of precipitation which in the longer period performs renewal of water [27, 28].

For the last thirty years, tritium has been used to determine the connection between groundwater and surface water. In general, in one hydrological system, the movement of water, and therefore tritium, can be shown according to the scheme in the fig. 1 [7, 8, 24].

The equilibrium equation for each area of the scheme in fig. 1 is [27, 28]

$$Q_i T_i \quad Q_o T_o \tag{1}$$

where Q_i and Q_o are the input and output components, and T_i and T_o are the corresponding tritium concentrations. The application of this equation is simple, namely, the measurement of tritium concentration in each component of Q_i and the knowledge of one of the components makes it possible to determine the other component.

A very important feature of groundwater is its age. The age of some groundwater means the time elapsed since its entry into the underground. The basic method of determining the age of groundwater using radioactive isotopes is to record the change in radioactivity of the water over time. It should be noted that due to the heterogeneity of underground systems, it is not possible to use the exponential decay law since its application would require a strictly isolated system. For this reason, the exponential model is used with the following classification: 1– tritium content between 3 TU and 10 TU indicates that the groundwater is over 40 years old; 2- tritium content greater than 20 TU means that it is of more recent origin [29]. Of course, there are more precise divisions as well as completely different divisions for thermal waters. It should be noted that tritium is not the only isotope that can be used to determine the age of groundwater. The tritium field of application is for waters younger than 30 years. In systems containing water of different ages, carbon ^{14}C and silicon ^{32}Si are used in addition to tritium to determine the proportions of the various components [29].

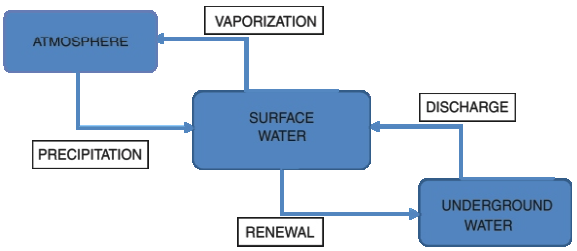

Figure 1. Flow diagram of water and tritium in the hydrological system

EXPERIMENT

Experimental determination of tritium activity took place in the following stages: sample taking, sample preparation for enrichment, sample enrichment, preparation of the enriched sample for measurement, and measuring tritium activity in the sample.

When sampling, care must be taken to ensure that the sample is a true representative of the analyzed water. Care should also be taken that after sampling the sample must not be in contact with atmospheric moisture. Therefore, the samples are sent immediately after taking in one-liter, filled to the top and well closed, polyethylene bottles for further processing. To determine the waters connection in the Šar Mountains aquatorium, fig. 2, samples were taken from 1 – Jažinačko Lake (fig. 3), 2 – Štrbačko Lake (fig. 4), 3 – Durlov Creek (fig. 5), and 4 – Berevački Creek (fig. 6). Sampling was performed five times in one calendar year (2018). The samples thus obtained are marked chronologically by a month of sampling: 1 – January, 2 – April, 3 – July, 4 – September, and 5 – December. At the same time with the mentioned samples, precipitation samples (rain or snow) were also taken.

To measure the tritium activity all of the standard methods used in the measurement of ionizing radiation can be implemented and using a gas counter, nuclear emulsion, as the detector. The main problem of measuring tritium activity using the standard methods is that tritium emits low-energy beta particles so it must be introduced directly into the detector active

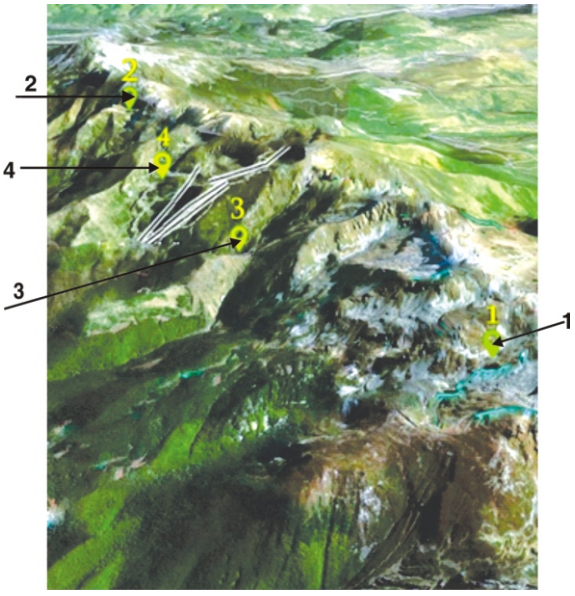

Figure 2. Šar Mountains aquatorium: *1 – Jažinačko Lake, 2 – Štrbačko Lake, 3 – Durlov Creek, 4 – Berevački Creek*

Figure 3. Jažinačko Lake

Figure 4. Štrbačko Lake

zone (into the working volume of the counter, into the liquid scintillator, or the ionization chamber). In most cases, the tritium activity of natural waters is measured by a scintillation counter. The liquid phase scintillator

Figure 5. Durlov Creek

Figure 6. Berevački Creek

can be used to determine the water activity of more than 40 TU from a sample of about 10 ml of water, without any preliminary preparations and with standard measuring equipment. This is quite satisfactory for the detection of tritium inserted as a tracer, but for natural tritium with an average concentration up to 20

TU, such a procedure is not sufficiently precise so sample enrichment is necessary.

Sample enrichment is the most important part of the process for determining the apparent tritium concentration. Typically, enrichment is performed by a factor of 10 to 100. All methods that are normally used for isotopic enrichment can be applied (distillation, chromatography, diffusion, electrolysis, and centrifugation).

Electrolysis is the most commonly used enrichment method (and was also used in this research). Electrolysis enrichment is based on the abandonment of hydrogen in the gas phase from a solution after the electrolysis of water. The rate of hydrogen evolution far exceeds that of deuterium and tritium. Therefore, the separation factor is greater for tritium than for deuterium and for deuterium greater than for hydrogen. As a result of this phenomenon, the concentration of tritium in the electrolyte residue increases progressively during electrolysis. The combined measurement uncertainty of the total measurement of tritium activity was less than 10 % [30-32].

RESULTS AND DISCUSSION

In figs. 7-10 the measured tritium content is shown in the precipitation and in Jažinačko Lake, Štrbačko Lake, Durlov Creeks, Berevački Creeks, respectively.

From figs. 7-10, it can be concluded that all the waters of the observed aquatorium are of atmospheric origin. The noticeable differences between fig. 7-10 are a consequence of the ratio of the precipitation volumes of water to water in lakes or torrents. These figures also show a decrease in the concentration of tritium in the winter months. In the winter months, when precipitation is the highest, there is a previously explained decrease in tritium concentration. The same effect, in a slightly milder form, is felt during the summer months as water tests were carried out at high altitudes, which reduced the tritium concentration in precipitation. Unlike flowing water, lake water is the water of older origin, which is reflected by its slower

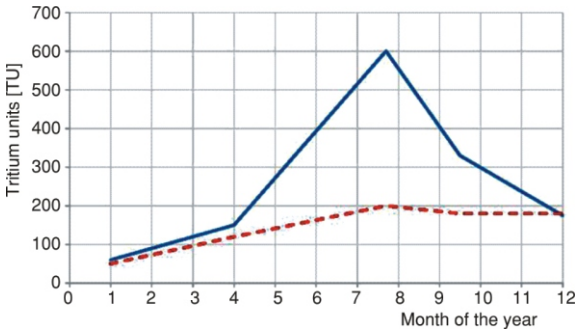

Figure 7. The content of tritium at the site Jažinačko Lake; *full line – precipitation, dashed line – lake water*

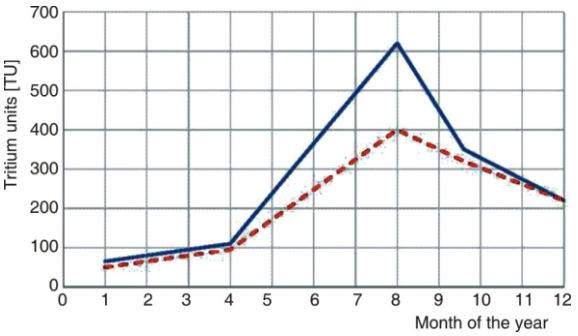

Figure 8. The content of tritium at the site Štrbačko Lake; *full line – precipitation, dashed line – lake water*

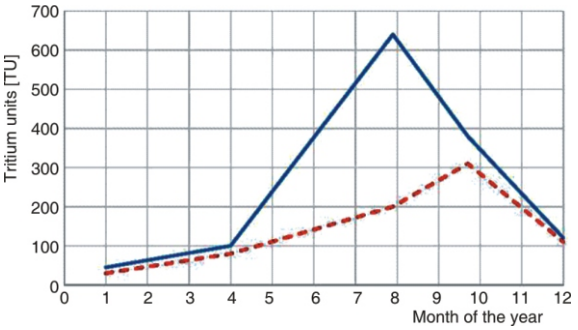

Figure 9. The content of tritium in precipitation and in Durlov Creek; *full line – precipitation; dashed line – lake water*

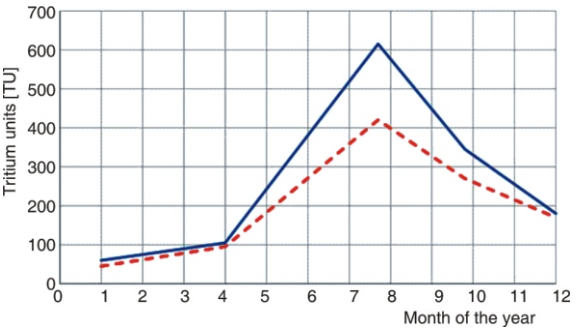

Figure 10. The content of tritium in precipitation and in Berevački Creek; *full line – precipitation; dashed line – lake water*

monitoring of the seasonal (summer) maximum in precipitation waters. The difference that can be observed between the ratio of tritium concentration in precipitation water and water from Durlov and Berevački Creeks is due to the configuration of the terrain. Precipitation water into the Durlov Creek, for much of its course, flows to the stream through the ground (which can be noticed when examining the tritium soil profile and the profile completely agrees with the observed delay of tritium concentration in stream water and precipitation water). During the examination, it was not possible to detect the existence of any larger basin with groundwater unrelated to precipitation.

CONCLUSION

An analysis of the tritium concentration in the waters of Štrbačko Lake, Jažinačko Lake, Durlov Creek, and Berevački Creek (which form the backbone of the aquatorium of the observed part of the Šar Mountains) clearly shows that all the waters of this aquatorium are of atmospheric origin. Some differences in the temporal positioning of the seasonal maximum are due to the aging of the waters in the lakes and the different morphological composition of the soil, which causes different tritium profiles (which were also recorded during the experiment, but for reasons of rationality they are not shown in this paper). From the above it can be concluded that the waters in the Šar Mountains aquatorium should not be commercialized because they are unpredictable as an energy source, and their commercialization could produce changes in the eco and biosystems of the mountain.

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AUTHORS' CONTRIBUTIONS

The experiments were carried out by all the authors. Also, all authors analyzed results and participated in the preparation of the final version of the manuscript.

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ИСПИТИВАЊЕ МЕЂУСОБНЕ ПОВЕЗАНОСТИ ВОДА АКВАТОРИЈУМА ШАР-ПЛАНИНЕ ТРИЦИЈУМОМ, РАДИОАКТИВНИМ ИЗОТОПОМ ВОДОНИКА

У раду је приказано испитивање порекла и повезаности вода акваторијума Шар-планине. Анализиране су воде језера и два потока који доминирају овим акваторијумом. Такође су извршена и снимања трицијумског профила земљишта од интереса. Узимани су (по могућности) истовремени узорци падавина у испитиваном рејону. Приликом узимања узорака водило се рачуна о температурским условима амбијента десетак дана око тренутка узимања узорака. Праћење сезонског максимума, уз узимање у обзир добијеног трицијумског профила земљишта и температуре на дан узимања (и око њега), недвосмислено је показало да је сва вода акваторијума испитиваног дела Шар-планине атмосферског порекла и као таква непогодна за било каква већа преобликовања у комерцијалне сврхе.

Кључне речи: трицијум, трицирана вода, трасирање вода, акваторијум Шар планина