The Spread of Tritium in the Ecosystem of the Yenisei River

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Abstract: - The potential sources of tritium in the Yenisei river ecosystem are the global environment pollution and the operation of the Mining and Chemical Combine (MCC), Rosatom State Corporation. The background tritium content of zoobenthos, bottom sediments, some commercial fish species, and the most widely spread aquatic plant species was determined for the first time. The MCC operation affected the tritium content in the nearest impact zone, and significant excess of the tritium content in aquatic plants over the background level was revealed.
Key-Words: - tritium, Yenisei River, accumulation, transformation, freshwater ecosystem

1 Introduction

Tritium (^3H) in the natural environment is derived from natural or anthropogenic sources and can be used to estimate human radiation exposure around nuclear fuel reprocessing facilities.

Elevated concentrations of ^3H in the environment are generally associated with its production at nuclear facilities and exposure of local populations can be of public concern. The concentration of cosmogenic ^3H in natural waters is estimated to be 0.1 BqL^{-1} [1, 2].

There are numerous anthropogenic sources of ^3H. These ^3H sources include fallout from nuclear weapons testing; nuclear reactors; nuclear fuel reprocessing plants; heavy water production facilities; commercial production of radionuclides for radiopharmaceuticals; luminous paint manufacturing; production of illumination lighting; airport runway lights; luminous dials, gauges and wrist watches; and others [3, 4]. Nonetheless, commercial applications for ^3H accounts for only a small fraction of ^3H use worldwide. Rather, the primary use of ^3H has been to boost the yield of both fission and thermonuclear (or fusion) weapons, thereby increasing the efficiency of explosive nuclear devices [5].

In the Krasnoyarsk Region, the major source-term of radioactive environmental contamination has long been the operation of the state-operated «Mining and Chemical Combine» (MCC) facility located in the town Zheleznogorsk, Siberia (Russia). These operations are located on the so-called “right bank” (eastern bank) of the Yenisei River, approximately 50 km north (down-stream) of the city Krasnoyarsk. Discharges of ^3H into the Yenisei River are almost entirely in the form of HTO. The MCC produced weapons-grade plutonium for many years, and as a result, there are considerable quantities of radioactive wastes, which are currently dispositioned in storage facilities and open ponds located within the MCC facilities. However, the great majority of wastes produced by the facility have been injected into the deep aquifers of the nearby “Severny” testing site, located 12 km north of the MCC radiochemical plant [6, 7], situated at the confluence of the Yenisei and the Bolshaya Tela Rivers (Fig. 1).

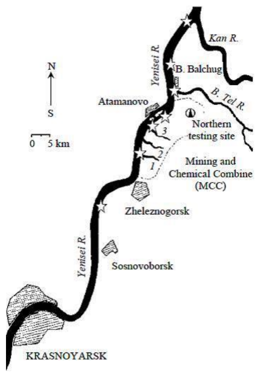

Fig. 1. Schematic map of the main investigation area near the Mining and Chemical Combine. (*1*) Shumikha river, (*2*) technological brook no. 2, and (*3*) Ploskii brook; the dashed line denotes the border of the sanitary-protection zone, and asterisks denote the sampling points.

Analysis of the existing literature on the radiochemical composition of the surface waters of the Yenisei River suggests several potential sources of the ^3H input to the system [8, 9]: Liquid discharges associated with nuclear weapons testing;

- Aerosol emissions of MCC;

- Reactor-derived cooling-water system discharges;
- Liquid wastes resulting from radiochemical production facilities;
- Liquid discharge migration from MCC operations;
- Migration of ^{3}H via groundwater from the discharges to the Severny landfill.

Thus, there are six potential sources of the ^{3}H inflow into the Yenisei River. To our knowledge, no other riverine system in the world has been observed to have so many sources of ^{3}H contamination. Therefore, the Yenisei River system provides a unique opportunity to examine the environmental radiochemical pathways of various ^{3}H migration source-terms to a riverine environmental ecosystem [8, 9].

2 Sampling sites

The Yenisei River, which represents a nominal boundary between East and West Siberia, is one of the largest riverine systems in the world, coursing a greater distance than the Mississippi (3734 km) in the United States. The annual watershed yield (624 km^3) of the Yenisei River is the greatest of Russia, with an average water discharge to its estuary of 19800 m^3s^{-1}, and a maximal flux of up to 1.9 x 10^5 m^3s^{-1}. The surface area (2580 thousand km^2) of the Yenisei River basin is the second largest in Russia (second only to the River Ob) and is the seventh largest in the world.

2.1. Water

Samples were collected in the upper layer of the river flow (0–10 cm) into 2,0 l plastic containers. The studied samples were collected along the right river bank at a distance of 40–60 m from the bank edge. Controls were collected at a distance of 500 m from the left bank edge, in the main navigation channel with the highest flow velocity and depth.

2.2. Sediment Sampling and Treatment

Using cylindrical coring tubes 150/100 cm in length and 13.5/11 cm in inner diameter, respectively, relatively undisturbed sediment cores were obtained by hand as visualised by an attached underwater camera. Suction and friction ensured the core retention during the sediment collection until the bottom of the coring tube could be sealed by a second lid. The sediment cores were completely filled up with water and the lids were kept closed during the transportation to reduce possible water motion/disturbances [10]. (Tolhurst et al., 2000).

2.3 Zoobenthos

All the samples were collected using a standard Ekman dredge. Zoobenthos samples were sieved through a 200-micron mesh sieve onboard a ship. Meiobenthos samples were extracted from the third Ekman dredge sample and immediately frozen to be later sieved in the laboratory. In the total content of the zooplankton community 40 species and organism groups were found, among them *Cladocera* - 19, *Copepoda* - 5, *Rotatoria* – 16. After sampling the zoobenthos was carefully washed. The tritium content in each of the three groups was evaluated separately.

2.4. Aquatic Plants

To determine the tritium content in plants use was made of the most common aquatic plants of the river Yenisei: *Elodea canadensis* Michx., *Potamogeton L.* Submerged plants are those in which the biggest part remains beneath the water surface.

2.5. Fish

Reproductive species *Thymallus thymallus, Coregonus lavaretus pidschian, Acipenser ruthenus, Coregonus tugun* were caught in the whole studied area of the Yenisei River in 2010-2018. The fish bodies were weighted. Soft tissues were separated and placed into a stripping flask and mixed with toluene.

2.6. Method of Estimating Tritium in Sediments and Biological Samples

To estimate the total tritium in the samples it was necessary to eliminate all liquid from the samples.

Weights of about 50 g dry weight of aquatic plants (determination of OBT) or 100 g wet weight (determination of total tritium) of aquatic plants or fish were taken from the previously prepared sample. This weight was placed into a round-bottomed flask, where it was mixed with toluene chosen for stripping the azeotropic mixture. The mixture obtained was kept in a corked flask for 12 h. Then, the flask was placed into a flask heater. A special device was put onto the flask neck to strip the azeotropic mixture and separate aqueous and organic phases. This device was designed by the author, L.G. Bondareva.

Stripping was performed at t ~70°C for 4 hours. After the separation the aqueous phase was either immediately mixed with a scintillation cocktail and prepared for the measurements or, when necessary, purified from organic impurities by distilling it with $KMnO_4$ [11] until a transparent and colorless liquid was obtained. Then, an aliquot of the solution was mixed with the cocktail and prepared for the measurements.

After distillation, an aliquot was mixed with the liquid scintillation cocktail and counted with a liquid scintillation spectrometer. Standards and background samples were prepared and counted with each group of samples. The tritium activity concentration in the sample was determined from and measurements [12]:

$$c = [(R-R_0)/\varepsilon \cdot V] \cdot e^{\lambda \Delta t} \quad (1)$$

where:

c is the tritium activity concentration of the sample, ($Bq \cdot L^{-1}$),

R is the counting rate of the sample in counts per second,

R_0 is the counting rate of the blank in counts per second,

ε is the counting efficiency,

V is the volume of the sample in the counting vial in L, is the decay constant of tritium in reciprocal years ($\lambda = 0.05576$)

Δt is the interval between sampling and counting in years.

2.7. Method of measuring the tritium activity

The method described below is intended for measuring the volumetric activity of tritium in liquid samples by liquid-scintillation spectrometry (LSS) using a scintillation cocktail where the sample under study is dissolved.

Standard tritiated water, with a certified value of 0.1 $Bq \cdot L^{-1}$, was used as a reference for each type of the sample measured. The samples, backgrounds, and ^3H references were stored in the system for at least one day to sufficiently decrease chemiluminescence, which interferes with ^3H measurement. All vials were then counted using a Quantulus Model 1220 liquid scintillation counter (200 min $sample^{-1}$, cycle – 7 times, total measuring time per sample – 1400 min, measuring region – 0.0-18.6 keV, corrected appropriately using a quench indicating parameter (i.e., transformed Spectral Index of External standard, tSIE) [12].

The background determined for the tritium free water samples prepared ranged between 0.926 CPM and 1.002 CPM and the counting efficiency, using the internal standard method [13], was between 25.37% and 26.10% for the maximum figure of merit.

3. Results and Discussion

3.1. Tritium in the Water of the Yenisei River

Fig. 2 presents the results of the ^3H measurements in the Yenisei River samples, collected in 2001-2018, across the entire area under study (80-1760 km downstream from Krasnoyarsk) (n = 587). The ^3H content in the Yenisei River water in the background areas (the city of Krasnoyarsk – «0 km» and village Yesaulovo – «46 km») upstream from MCC did not exceed ~4$Bq \cdot L^{-1}$ at any time during the period of investigations presented here.

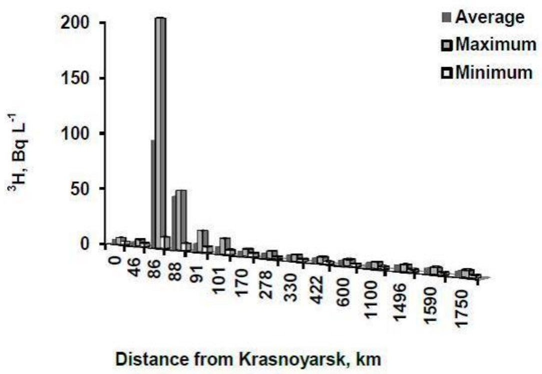

Fig. 2. Results of ^3H determination in the Yenisei River water (samplings in 2001-2018, spring-autumn low-water period).

It was found that after the third reactor shutdown (2010), the ^3H content was within the concentration range established previously for river systems of the Russian Federation, i.e., ~5 $Bq \cdot L^{-1}$ [7]. It was further observed that downstream from the MCC discharges (beginning from 15 km downstream), the ^3H content in the main stream of the Yenisei River also did not exceed ~6 $Bq \cdot L^{-1}$ (2011-2016), which is in agreement with the results obtained earlier by us [8, 9] and others [7].

The tritium content estimated in the water of the River Yenisei is significantly lower than the tritium content in the water reservoirs located around Russian nuclear stations (for example, the Ural region). In spite of this, the obtained evidence is necessary for preparing the Environmental Passport of the Krasnoyarsk Region as well as for predicting the state of the Yenisei River ecosystem after the MCC nuclear reactor shutdown.

3.2. Tritium in the Sediments of the Yenisei River

The bottom sediments were sampled and analyzed during the period of the operation of the MCC nuclear reactor (Table 1).

Table 1. Water content (%) and tritium content (Bq kg^{-1}) in the bottom sediment samples. The 0-10 cm layers (n = 10)

Site	2005-2010		2011-2015	
	Water, %	^3H, $Bq \cdot kg^{-1}$	Water, %	^3H, $Bq \cdot kg^{-1}$
village Yesaulovo	37 ± 2	1.5 ± 0.4	38 ± 2	1.3 ± 0.4
village Atamanovo	36 ± 2	8 ± 3	38 ± 2	4 ± 1
village Bolshoy Balchug	42 ± 2	6 ± 2	41 ± 1	1.6 ± 0.8

The results obtained indicate that the bottom sediments sampled in the areas of the village Atamanovo and Bolshoy Balchug (Fig. 1) contain ^3H at levels near the background. This indicates that ^3H is weakly retained by the bottom sediments and is quickly exchanged with the riverine water.

3.3. Tritium in Plants, Zoobenthos, and Fish Muscle

The ^3H content in zooplankton and aquatic plants was assessed during the operation of the nuclear reactor (2009-2010) and after its shutdown (2011-2015). The results obtained through these studies reveal that the ^3H content in the plant and zoobenthos mass for the background area of the Yenisei River (Yesaulovo, Fig. 1) varies from 2 to 3 Bq·kg^{-1}.

In spite of the morphological differences of the plants under study their tritium content is approximately the same. This is also true for the plants sampled in the control area (village Yesaulovo), and for those sampled in the impact area of MCC (village Atamanovo, Fig. 1) as well as for the plants downstream where the tritium content decreases due to the significant dilution by the river flow (Fig. 2). The obtained values can show that the plants develop under the same conditions. The tritium content in the zoobenthos species under study is comparable with the tritium content in the aqueous plants.

Taking into account that in the studied areas the middle biomass of zoobenthos in the studied littoral areas of the River Yenisei amounts to about 6 g·m^{-2}, an assumption can be made on a relatively low content of tritium in the bottom layer of the water flow and, consequently, in the bottom sediments of the River Yenisei (Table 1). This fact can also confirm that tritium enters the water plants with the water flow of the upper and middle (insignificantly) part of the river.

Investigations were also carried out with the common species of commercial fish caught in areas with different levels of ^3H impact due to the MCC discharges: i.e., the upstream background (40 km); in the vicinity of operations (0–15 km); and at a considerable distance from the MCC discharges (1760 km downstream).

Here, the ^3H content amounted to ~17 Bq·kg^{-1} of the wet weight.

The species-specific level of tritium accumulation in fish bodies considerably depends on the diet composition. The common species of commercial fish are representative of nonpredatory fish, consuming mainly zoobenthos and insects, but large-size individuals can also consume fish and small mammals [14]. The common species of commercial fish is staple food for the residents of small villages downstream of Krasnoyarsk. According to the results obtained, it can be concluded that the ^3H content in the fish muscle did not depend on the species, food type, or fishing area. This was due to the fact that the specimens of all the studied fish species are of a similar trophic level and the main source of the ^3H intake is water and food. This concerns the results obtained only for the ecosystem of the River Yenisei, because the results for other freshwater ecosystems can be very different.

4 Conclusion

The baseline determination of the ^3H content in water, sediments, zooplankton, submerged plants and fish in an ecosystem comprising a region of the Yenisei River near the Mining and Chemical Combine nuclear facility was carried out. In the present study we did not investigate the impact of possible sources of tritium on the ecosystem of the Yenisei River. The measurements of the ^3H content in particular sample types in this region of the Yenisei River water demonstrated that:

- The observed ^3H concentrations in the open-water main-channel environment of the Yenisei River were 4-6 Bq·L^{-1}, to be taken as the background values of the tritium content for the water of the Yenisei River, especially after the last MCC nuclear reactor shutdown in 2010.
- The ^3H concentration in the bottom sediment of the Yenisei River after 2010 did not exceed the value of ~4 Bq·kg^{-1}, which was obtained for the bottom sediments taken near the MCC discharge area. Approximately 1.5 Bq·kg^{-1} was taken to be the background value.
- The ^3H concentration in the aquatic plants growing nearest to the impact area of MCC (6-8 Bq·kg^{-1}) considerably exceeded the background values determined for the upstream site (village Yesaulovo, 2-3 Bq·kg^{-1}), which is the control site in our investigations of the tritium behavior in the Yenisei River ecosystem.
- The ^3H concentration in some species of commercial fish was not influenced by the fishing area, the ^3H concentration being 12-20 Bq·kg^{-1} of wet weight.

So, these results obtained after the last nuclear reactor shutdown (in 2010) suggest that ^3H due to the Rosatom MCC operation does not result in a significant impact on the Yenisei River ecosystem under study.

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