A. O. KOVALEVSKY INSTITUTE OF BIOLOGY OF THE SOUTHERN SEAS OF RAS
ZOOLOGICAL INSTITUTE OF RAS

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FOREWORD

The Readings "Radiochemoecology: Progress and Prospects", dedicated to the 90th anniversary of Academician Gennady Grigorievich Polikarpov (1929–2012), were held at A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS (Sevastopol) on 14–16 August 2019.

Being a student of Professor N. V. Timofeev-Ressovsky and a follower of Academician V. I. Vernadsky, G. G. Polikarpov developed their teachings on the role of living and inert matter in the biosphere in relation to marine problems and created new sciences: marine radioecology and chemoecology.

He headed radiation and chemical biology department at the Institute of Biology of the Southern Seas. For the first time in the USSR, he organized a second-class radioisotope laboratory and founded a world-famous scientific school on marine radiochemoecology. Research by G. G. Polikarpov and his school made it possible to adequately respond to the problem of probability of radioactive waste burying in the hydrogen sulfide zone of the Black Sea, to study its radioecological response to the Chernobyl nuclear disaster, to develop new radiotracer methods for studying oceanographic processes, and to substantiate biogeochemical criteria for standardizing anthropogenic pressure on marine ecosystems.

This issue of the journal includes materials recommended for publication by Readings program committee.

Marine Biological Journal Editor-in-Chief,
IBSS Supervisor,
Academician of RAS, D. Sc., Prof.
Egorov V. N.

ПРЕДИСЛОВИЕ

С 14 по 16 августа 2019 г. в Федеральном исследовательском центре «Институт биологии южных морей имени А. О. Ковалевского РАН» (г. Севастополь) проходили чтения «Радиохемоэкология: успехи и перспективы», посвящённые 90-летию со дня рождения академика Геннадия Григорьевича Поликарпова (1929–2012).

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SCIENTIFIC COMMUNICATIONS

UDC 547.211(262.5)

TRANSFER OF FREE METHANE BY GAS BUBBLE STREAMS FROM ANAEROBIC TO AEROBIC WATERS OF THE BLACK SEA*

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"Breath of earth" in the form of methane gas bubble streams from a seabed (methane seeps, bubble emanations) is a planetary phenomenon that was noticed only at the end of the XX century. The study of this phenomenon, being an important link in processes of lithosphere, hydrosphere, atmosphere, and biosphere interaction, is relevant to date. In this work, methane fluxes were determined in the known area of intense methane occurrences of biogenic nature, geographically tied to Dnieper River paleochannel in the northwest of the Black Sea. Bubbling (free) methane flux from anaerobic to aerobic waters in the active methane seeps area of Dnieper River paleochannel in the depth range of 140–725 m is estimated averagely as $1.2 \cdot 10^3$ $m^3 \cdot km^{-2} \cdot year^{-1}$ (STP), or 2.8 % of bubbling methane emitted from a seabed. The value of the investigated flux was 4.2 % of the specific flux of bubbling methane to a water column on shelf depths (less than 140 m) in the same area. Methane flux estimate, obtained in this work, seems to be a significant environmental factor in conditions of strong stratification of Black Sea waters, where methane transfer by gas bubble streams is the main mechanism for introducing deep-water methane into biogeochemical cycles and carbon transformation processes of Black Sea aerobic zone.

Keywords: Black Sea, gas bubble streams, aerobic waters, anaerobic waters, methane fluxes

Methane studies in A. O. Kovalevsky Institute of Biology of the Southern Seas (hereinafter IBSS) began after the discovery of methane gas bubble streams in Black Sea hydrogen sulfide zone made by a team of researchers led by G. G. Polikarpov and V. N. Egorov in 1989 [4].

Later, Black Sea water area served as a testing ground for numerous interdisciplinary international studies related to the phenomenon of gas bubble streams. IBSS employees contributed to many works in priority research areas, including bubbling methane fluxes study.

It has been found that gas bubble stream discharge into the Black Sea is manifested in areas with different geomorphological characteristics: in paleochannels of the Danube, Dnieper – Kalanchak, Don – Kuban rivers; in the alluvial fan of Transcaucasian rivers; on the western continental slope with an adjacent shelf; and on the northwestern shelf [2]. The overwhelming number of methane seeps examined is classified as cold ones, *i. e.* seeps of biogenic origin [3]. Over 98 % of gas bubble streams were located

*The materials of the article were presented at the Readings in memory of Academican G. G. Polikarpov "Radiochemoecology: Progress and Prospects" (Sevastopol, IBSS, 2019).

above the boundary of gas hydrates stability zone (725 m for the Black Sea), which indicates the barrier effect of gas hydrates in bottom sediments. In Black Sea deep-water area, gas bubble streams are mainly associated with areas of active development of mud volcanism and diapirism. At the same time, gas bubble streams can reach sea surface only in Black Sea shallow water areas (in coastal areas; on the shelf; and at the top edge of continental slope at a depth of not more than 262 m) due to a high dissolution rate of methane, contained in bubbles [2].

The total content and vertical distribution of methane in Black Sea waters is generally considered to remain quasi-stationary, at least over a 30-year observation period, with a stable balance between methane discharge and consumption [7].

Previously, a direct calculation of rate and volume of bubbling methane discharge into Black Sea anoxic water column was carried out at IBSS in ten already studied and promising areas of active methane occurrences from three types of methane gas bubble streams existing in the Black Sea: methane seeps at anoxic depths down to 725 m; gas bubble streams, induced by a vertical heat flux, in gas hydrates stability zone; and mud volcanoes [1]. It has been found that among the considered sources of methane gas bubble streams, the largest contribution to Black Sea waters is made by methane seeps at anoxic depths down to 725 m. Contribution of other sources is orders of magnitude less. Moreover, the estimate of total emission of bubbling methane obtained is at least 2.5 times lower than corresponding estimates determined by biogeochemical methods. This work was aimed at obtaining the maximum estimate of bubbling methane discharge into Black Sea waters; therefore, some features of gas exchange of bubble flares with water, surrounding them, were not taken into account. In particular, the distributed flux of dissolved methane along gas flares in a water column was not considered. It was assumed that all bubbling methane from a seabed at depths of more than 140 m completely enters Black Sea anoxic waters in the dissolved form. In fact, some methane bubbles, emitted from a seabed, can cross the boundary between anaerobic and aerobic waters, when rising, and even reach sea surface, emitting free methane directly into the atmosphere.

The aim of this work is to study the significance of directed transfer of free methane by gas flares from anaerobic to aerobic waters.

MATERIAL AND METHODS

The study focuses on Dnieper River paleochannel area (Fig. 1) characterized as one of the most active areas of methane occurrences. This is the part of an extensive alluvial fan accumulating huge masses of organic material from the entire northwestern part of the Black Sea with adjacent rivers [6].

In this region, 902 seeps were recorded on a shelf area of 41.2 km^2 (sector A), and 1,295 seeps were recorded on a continental slope in the anoxic zone (sector B) over an area of 345 km^2 [5].

For each of the seeps detected, data on bubbling methane emission flux from a seabed Φ_0 ($L \cdot min^{-1}$ under normal conditions: standard temperature and pressure, STP) was obtained, as well as free methane fluxes into the atmosphere [5]. Summary of the data obtained in Dnieper River paleochannel area is given in Table 1.

As seen from Table 1, the isobath of 140 m was chosen as a boundary between sectors A and B, which approximately corresponds to the middle of a boundary layer between aerobic and anaerobic zones. Mainly, seeps, located below the upper boundary of pycnocline (140 m) and above the upper boundary of gas hydrates stability zone (725 m), emit bubbling methane into the anoxic water

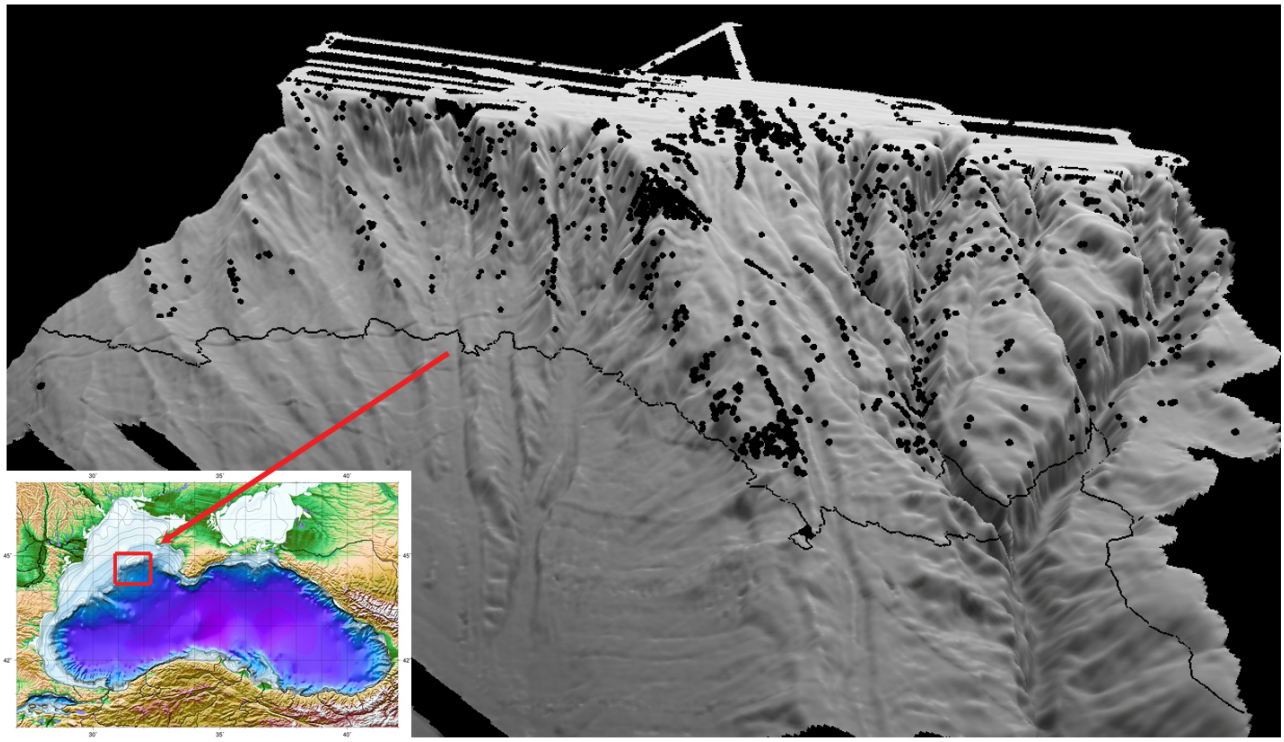

Fig. 1. Gas bubble streams (●) on a bathymetric map of a seabed in Dnieper River paleochannel area. The line is drawn along the isobath of 725 m. The inset shows location of Dnieper River paleochannel on the map of the Black Sea

Table 1. Parameters of bubbling methane emission in Dnieper River paleochannel area

Parameter	Sector A: depths 60–140 m	Sector B: depths 140–725 m
Acoustic coverage, km^2	41	346
Seeps number	902	1295
Total initial methane flux Φ_0, $\cdot 10^6$ $m^3 \cdot year^{-1}$ (STP)	1.2	15.6
Spatial density of methane emission flux Φ_p, $\cdot 10^3$ $m^3 \cdot km^{-2} \cdot year^{-1}$ (STP)	29.5	45.1
Total methane flux into the atmosphere Φ_a, $\cdot 10^5$ $m^3 \cdot year^{-1}$ (STP)	3.1	0.1

column of the Black Sea. Gas bubble streams of the oxic zone emit a significant part of free methane into the atmosphere, while methane, dissolved as gas bubbles rise, is more likely to migrate to sea surface than overcome the density gradient in pycnocline layer and penetrate the anaerobic zone with a higher concentration of dissolved methane.

To assess the evolution of methane concentration in gas bubble streams of seeps in the anaerobic zone when moving away from gas emission source, we used the approach described earlier in [5]. It involves using the model of gas exchange between methane seeps bubbles and seawater, surrounding them. This model is based on a system of differential equations that take into account, inter alia, the effect of van der Waals forces on gas exchange between bubbles and a water column; the adsorption of surfactants, contained in water, by bubbles; and the appearance of the Marangoni effect reducing gas bubbles rising speed and weakening mass transfer of substances through shells of these bubbles.

Initial sizes of methane bubbles of gas bubble streams were determined using statistical data obtained by measuring bubbles target strength. Size range was divided into size classes with a step of 2 mm, and frequency of occurrence of each class in the sample was determined. Initial methane fluxes of gas bubbles, *i. e.* vertically directed flux of methane contained in the rising bubble at the moment it emerges from a seabed, Φ_0 were determined by volume and rise rate of bubble at the moment it emerges from a seabed. Then, bubble model was run for each size class.

The following parameters were recorded at the model output: time t, sec; bubble rise depth h, m; bubble diameter d, mm; gas content in a bubble m, μmol. The depth of methane seep was 140 m and deeper. It was assumed that gas composition of bubbles includes highly and sparingly soluble gases (CH_4, N_2, He, and Ar). Initial methane content, *i. e.* at the moment a bubble emerges from a seabed, was set at no less than 99 %, the same as in [5].

Model calculation was stopped either when a bubble reached sea surface or when its diameter decreased to 0.001 mm, which was interpreted as a complete dissolution of gas contained in the bubble. For each size class of bubbles according to modeling data, vertical profiles of methane content m(h) and dissolved methane flux into a water column $f_w(h)$ were calculated:

$$f_w(h) = \bar{v}_h \frac{m(h+\Delta h) - m(h)}{\Delta h}\,, \tag{1}$$

where $\bar{v}_h$ is average bubble rise rate in a sector (h + Δh, h).

Methane content in average bubble of gas flare M(h) and methane flux into a water column $F_w(h)$ from a seabed to the horizon of 140 m were determined by summing over size classes of bubbles with weights proportional to their frequency distribution.

The use of $F_w(h)$ profiles made it possible to estimate integral methane fluxes from local gas bubble seeps into a water column in the range from localization depth of methane seep to the horizon of 140 m Φ_{140+}:

$$\Phi_{140+} = \int_{H_0}^{140} F_w(h) \cdot dh\,. \tag{2}$$

The obtained graph of Φ_{140+}/Φ_0 ratio depending on localization depth of methane seep emission (Fig. 2) was approximated by a simple function:

$$Y = 100\left(1 - e^{(150.0-X)\cdot 37^{-1}}\right), \tag{3}$$

where X is depth, m.

Formula (3) allowed estimating Φ_{140+} values for each of 1,295 methane seeps from Table 1 according to previously determined values of their initial flux:

$$\Phi_{140+} = Y \cdot \Phi_0\,. \tag{4}$$

Then, flux of methane, transferred by rising bubbles of methane seeps outside Black Sea anaerobic zone, was estimated by the ratio as follows:

$$\Phi_{140-} = \Phi_0 - \Phi_{140+}\,. \tag{5}$$

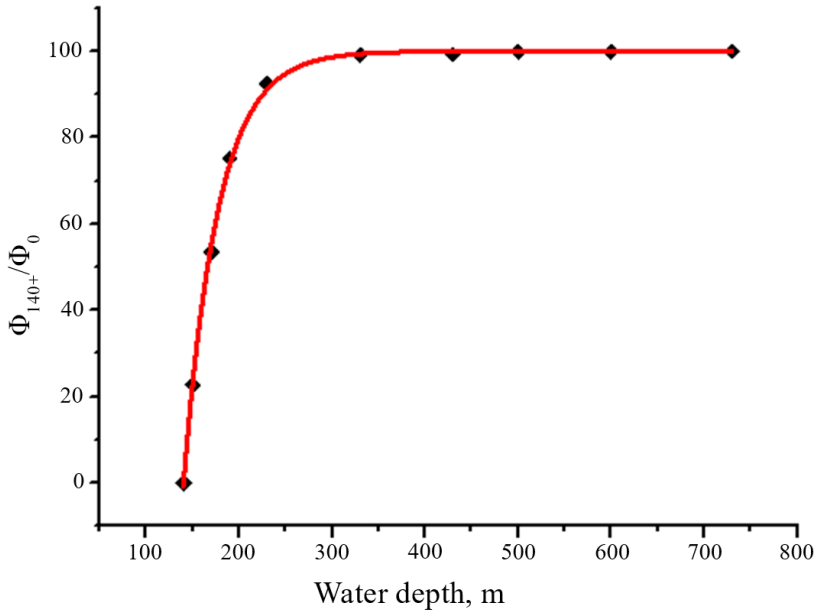

Fig. 2. Dependence of Φ_{140+}/Φ_0 ratio value on localization depth of methane seep emission (♦). Red line is an approximating curve

RESULTS AND DISCUSSION

Fig. 3A presents a histogram of frequency of occurrence of gas bubble streams, transferring free methane by rising bubbles above the horizon of 140 m, in Dnieper River paleochannel area.

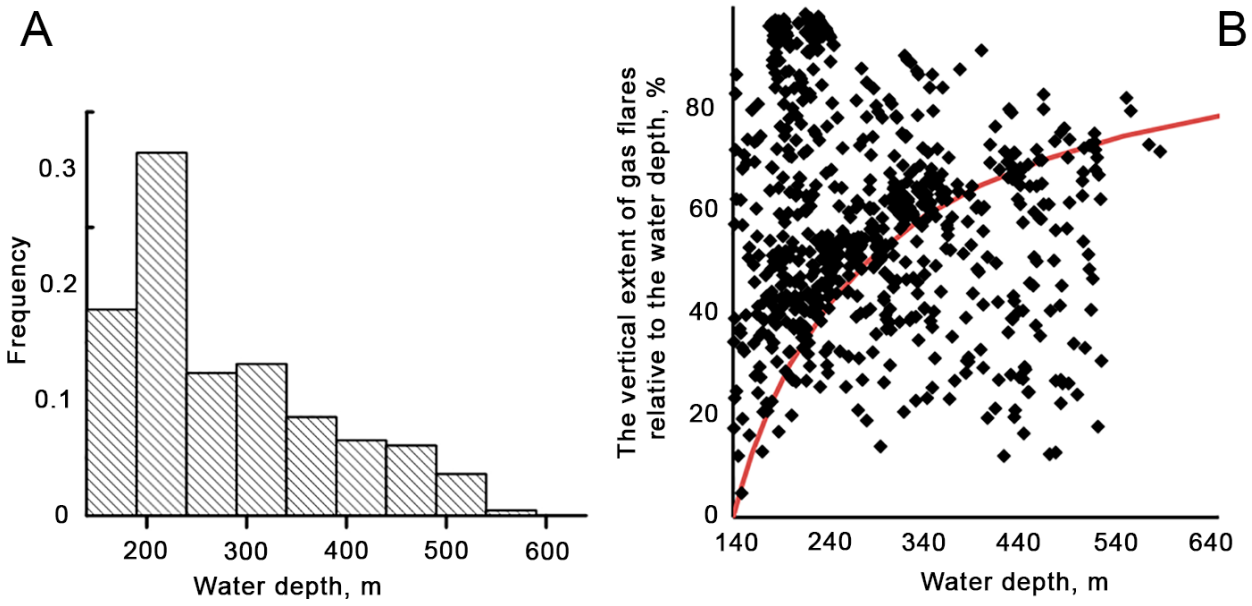

Fig. 3. A – histogram of frequency of occurrence in Dnieper River paleochannel area of gas bubble streams, transferring free methane above the horizon of 140 m; B – vertical extent of gas flares relative to water depth (♦) and graph of relative heights of hypothetical flares, reaching strictly the horizon of 140 m [(D – 140)/D × 100], where D is water depth (red line)

As shown in Fig. 3A, free methane transfer from the anaerobic zone is provided in Dnieper River paleochannel area both by seeps, emitting methane into the atmosphere (localized above a depth of 262 m), and seeps, located much deeper (up to 590 m). The validity of this statement is confirmed by Fig. 3B, showing data on the height of gas flares at sites of gas bubble emissions from a seabed in Dnieper River paleochannel area. The data are stored in IBSS marine research database, containing, inter alia, electronic echograms of seeps, as well as heights of registered gas flares throughout the Black Sea [2]. For clarity, the curve of the function [(D – 140)/D × 100] is plotted in Fig. 3B. This allows comparing flares rising above the horizon of 140 m (all dots on Fig. 3B above the red line) with flares not reaching this horizon (all dots below the red line). It is quite obviously seen from Fig. 3B that a significant number of seeps, located on a seabed in a depth range of 140–600 m, form gas flares of height being sufficient to transfer free methane outside the anoxic zone. It is interesting that this factor had not been previously investigated. Meanwhile, the total estimate of methane flux from all seeps outside the anoxic zone, calculated by formula (5) (Table 1, sector B), was 824 L·min^{-1}, or 4.3·10^5 m^3·year^{-1} (approximately 2.8 % of the initial flux). At the same time, emission of free methane into the atmosphere from seeps in this area is only 0.1·10^5 m^3·year^{-1} (2.3 % of the emission of bubbling methane to the aerobic zone in sector B).

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ПЕРЕНОС СВОБОДНОГО МЕТАНА СТРУЙНЫМИ ГАЗОВЫДЕЛЕНИЯМИ ИЗ АНАЭРОБНЫХ В АЭРОБНЫЕ ВОДЫ ЧЁРНОГО МОРЯ*

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«Дыхание недр» в форме метановых струйных газовыделений из морского дна (метановые сипы, или пузырьковые эманации) — явление планетарного масштаба, на которое обратили внимание лишь в конце XX столетия. Изучение этого явления как важного звена процессов взаимодействия литосферы, гидросферы, атмосферы и биосферы не потеряло своей актуальности до настоящего времени. В данной работе определены потоки метана в известном районе интенсивных метанопроявлений биогенной природы, географически привязанных к палеоруслу р. Днепр в северо-западной части Чёрного моря. Впервые оценено, что поток струйного (свободного) метана из анаэробных в аэробные воды на участке активных метановых газовыделений в районе палеоруслa р. Днепр в диапазоне глубин 140–725 м составляет (в среднем по участку) $1{,}2 \cdot 10^3$ $м^3 \cdot км^{-2} \cdot год^{-1}$ (STP), или 2,8 % от выделившегося из дна струйного метана. Величина исследованного потока — 4,2 % от удельного потока струйного метана в водный столб на шельфовом участке (глубúны менее 140 м) в этом же районе. Полученная в работе оценка потока метана — значимый экологический фактор в условиях стратификации вод Чёрного моря, где перенос метана струйными газовыделениями является основным механизмом внесения глубоководного метана в биогеохимические циклы и процессы трансформации углерода аэробной зоны Чёрного моря.

Ключевые слова: Чёрное море, струйные газовыделения, аэробные воды, анаэробные воды, потоки метана

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BAROMEMBRANE METHOD FOR ANALYSIS OF ULTRA-LOW CONCENTRATIONS OF RADIONUCLIDES IN WATER SAMPLES*

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This paper demonstrates the use of the baromembrane method for measuring ultra-low concentrations of radionuclides in water of freshwater reservoirs. The relevance is due to the need to determine radionuclides introduction into water cooling ponds used by enterprises of nuclear fuel cycle. Radionuclides of natural and technogenic origin, not associated with enterprise discharge, are always present in water cooling ponds, forming a natural or technogenic altered background. Its presence often makes it difficult to identify contribution of enterprise's discharge to water activity, since routine monitoring methods are characterized by a very high detection limit for radionuclides. Traditional methods for determining background radionuclides concentrations require sampling of at least 500 L of water, followed by their evaporation to get a dry residue. This procedure takes at least 5 days. It is possible to reduce time and energy spent on vaporizing hundreds of liters of water by pre-concentrating radionuclides in a smaller sample volume with the baromembrane method. To demonstrate this method, a portable installation with osmotic membranes was used being characterized with initial productivity of 6.0 $L \cdot min^{-1}$. The osmotic membranes separate source water sample into two components: demineralized permeate and concentrate, containing radioactive substances. This method allows preliminary concentration of water samples from 500 to 20 L in 10–15 hours with minimal losses of radionuclides (time period depends on water mineralization level). The method is universal; it can be used for concentration of dissolved salts of any heavy metals and other organic compounds. It allows preparation of water countable samples in much shorter time that traditional method (evaporation).

Keywords: baromembrane method, reverse osmosis, radionuclides, volumetric activity, nuclear power plant

During nuclear facilities operation, one of the ways in which radioactive substances enter the environment is liquid discharge into surface water bodies. Radionuclides activity monitoring in water of impact cooling ponds allows confirming the safety of nuclear facility, as well as the compliance with the requirements for the levels of radiation exposure to the environment and population [11]. The environment around any nuclear facility contains radionuclides of natural and technogenic origin, forming a technogenic altered background [5]. As a result, technogenic radionuclides are found in water supply and sewage systems of nuclear facilities, the source of which is global fallout due to nuclear weapon tests, Chernobyl and Fukushima Daiichi disasters, etc.

*The materials of the article were presented at the Readings in memory of Academican G. G. Polikarpov "Radiochemoecology: Progress and Prospects" (Sevastopol, IBSS, 2019).

According to the International Atomic Energy Agency recommendations, values of background levels should be subtracted from measurement results to determine dose loads on population only due to practical activities [11]. Analysis of available information shows the need to take into account radionuclides background activity in water bodies used by nuclear power plants (hereinafter NPP) [10]. The International Atomic Energy Agency considers 31 radionuclides to be among the most important ones from the point of view of the impact on the environment from NPP discharge [12]. Meanwhile, national requirements of the Russian Federation indicate the need for state regulation of 81 radionuclides in liquid discharge [4].

Taking into account radionuclides background content, it is possible to determine the activity introduced into water body from NPP operation. To determine radionuclides background content in water bodies, the one has to use instruments and methods providing measurements of ultra-low concentrations of radionuclides. The data of state monitoring system on technogenic radionuclides content in atmospheric fallout and precipitation, snow cover, freshwater, and seawater on the territory of the Russian Federation indicates the need to concentrate radionuclides in countable samples to reliably determine their activity [5]. The existing highly efficient methods of radionuclides sorption based on sulfides, dioxides, and cyanides of various metals are selective and cannot be universal [6 ; 13].

Routine control methods do not allow to reliably determine concentration of radionuclides of various metals in NPP discharge due to small source sample volume. Current regulation assumes evaporation of 10–20 L of initial water and analysis of dry residue. This method does not allow to reliably determine additional contribution of radionuclides with existing contamination. Moreover, concentration by evaporation of 500 L and bigger volume is rather laborious and energy-consuming.

In this paper, the approach is proposed, that allows concentrating water samples from natural sources for further radiometric and spectrometric analyses. To determine ultra-low concentrations of radionuclides in water, the method involving baromembrane technologies was chosen. They were developed in the mid-1960s and have been successfully used to purify liquid radioactive waste [1 ; 2 ; 7 ; 8].

The method can also be used to prepare water samples of large volume with a high salt content, such as seawater. Meanwhile, when implementing mobile sampling equipment, it is necessary to use membranes with a larger filtration area and an electric motor of higher capacity: this will help to effectively separate permeate from concentrated high-salt solution. To confirm the possibility of using the baromembrane method for preliminary concentration of radionuclides without activity loss, it is necessary to carry out a number of experiments with freshwater samples of different mineralization levels. The method is validated by continuous monitoring of parameters reflecting an increase in mineralization in concentrate and minimal loss of salts in permeate. To verify the method, the one has to simultaneously take equal water volumes from the same water body sector for subsequent parallel measurements of volumetric activity by traditional method (evaporation) and the developed baromembrane method of preliminary concentration.

The aim of this work is to demonstrate the possibility of using the baromembrane method to determine low values of volumetric activity of radioactive substances in water cooling ponds of Russian NPPs.

MATERIAL AND METHODS

The baromembrane method of preliminary concentration of water samples is based on sedimentation of impurities on osmotic membranes. When an overpressure is created on the membranes, suspended particles and dissolved salts are sequentially removed from a certain water volume by reverse osmosis, and this allows obtaining a concentrated salt solution. When passing through the semi-permeable membrane, source water is separated into two fluxes: pure water (permeate) and solution with contaminants (concentrate). In this case, permeate passes through the membrane, while dissolved substances do not (membrane efficiency is not less than 99.0 %) (Fig. 1).

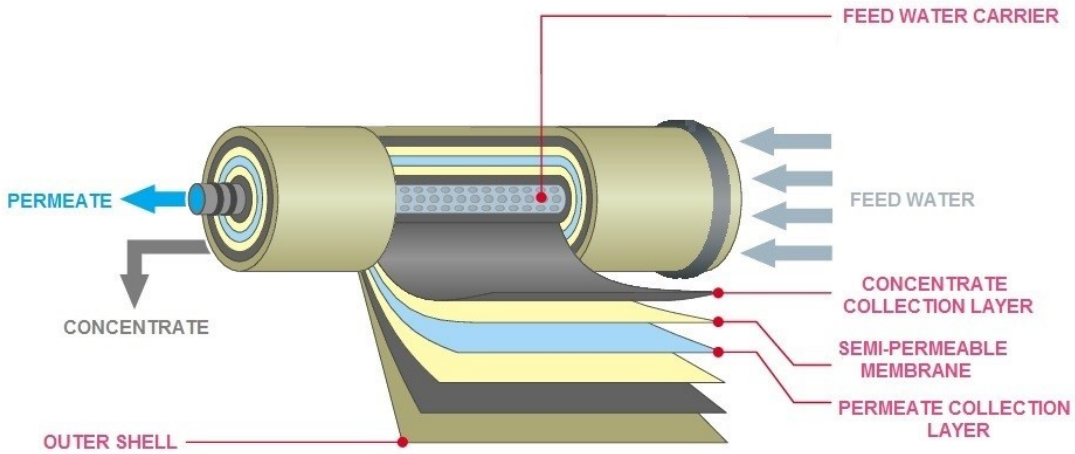

Fig. 1. Operating principle of an osmotic membrane

Functional scheme of an experimental installation for validation and verification of the method of preliminary concentration of water samples of impact reservoirs is presented in Fig. 2.

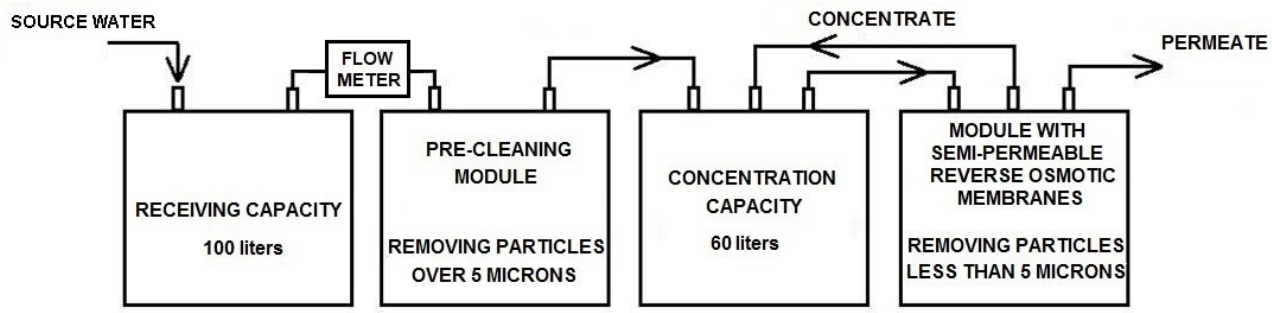

Fig. 2. Functional scheme of an installation for concentrating water samples

The installation consists of separate tanks and two separate blocks (Fig. 3): block 1 is pre-cleaning module; block 2 is module of two reverse osmotic membranes. This makes transportation and placing of the installation more convenient.

Fig. 3. View of portable installation modules for concentrating water samples

The pre-cleaning module is equipped with a cold water meter with a measurement error of no more than 2 %. It ensures control of source volume of water supplied for concentration.

The module of two osmotic membranes is equipped with two manometers and two flow meters: to monitor operating parameters of each osmotic membrane. Filmtec XLE-2521 osmotic membranes (DOW, USA) are used for experiments with freshwater samples.

A natural water sample analyzed is poured into receiving tank. Through an integral water meter, the water enters the pre-cleaning module. There, suspended particles and insoluble impurities larger than 5 μm are removed from the source water on a mechanical cleaning cartridge made of foamed polypropylene. After that, the water enters the next storage tank, where closed-loop water concentration occurs. The water from this tank is supplied under pressure up to 10 bar to a module with the osmotic membranes. There, dissolved salts and suspended particles with a size of less than 5 μm are removed.

When operating the baromembrane method, three parameters are of great importance: membrane area, selectivity, and hydraulic efficiency [3].

Hydraulic efficiency of a baromembrane installation characterizes the degree of effective use of water. It is defined as a ratio of permeate consumption to source water consumption. Hydraulic efficiency is calculated by formula:

$$\eta = \frac{Q_{\text{fil}}}{Q_{\text{fd}}} \cdot 100\% , \qquad (1)$$

where Q_{fil} and Q_{fd} indicate flows of filtrate and source water, respectively, $L \cdot h^{-1}$.

The average hydraulic efficiency of the installation used is 30 %. This coefficient can change during water sample concentration due to an increase in poorly soluble salts content in concentrate and in boundary layer above membrane surface. During water processing by this method, predominant transfer of H_2O

molecules through the membrane occurs, and this leads to concentration polarization and to an increase in salts concentration in boundary layer. It is in the boundary layer that active formation of crystals of sparingly soluble salts with their subsequent sedimentation on the membrane is observed.

The ability of a baromembrane installation with a specific type of membrane to demineralize source water for various separated substances is called selectivity. It is calculated by formula:

$$S_{\text{y}} = \frac{q_{\text{fd}} - q_{\text{fil}}}{q_{\text{fd}}} \cdot 100\% \,, \tag{2}$$

where q_{fd} and q_{fil} indicate amounts of dissolved salts in source water and filtrate, respectively, $mg \cdot L^{-1}$.

In practice, specific conductivity of water χ ($\mu S \cdot cm^{-1}$) is measured, which is proportional to q. Selectivity value for the installation used is in the range from 37 to 94 % with an average of 70 %.

Another important parameter for osmotic membranes is salt impermeability characterizing the amount of salts that have passed through the membrane. It is calculated by formula:

$$SP = \frac{C_{\text{fil}}}{C_{\text{fd}}} \cdot 100\% \,, \tag{3}$$

where C_{fil} and C_{fd} indicate salt concentration in filtrate and source water, respectively, $mg \cdot L^{-1}$.

Salt impermeability value for the installation used is in the range from 6 to 63 % with an average of 30 %.

The volume of permeate obtained from a membrane surface unit per time unit at constant pressure is called specific productivity ($L \cdot m^{-2} \cdot h^{-1}$). It is calculated by formula:

$$J = \frac{Q_{\text{fil}}}{S_{\text{mem}}} \,, \tag{4}$$

where Q_{fil} is permeate consumption, $L \cdot h^{-1}$;

S_{mem} is membrane filtration area, m^2.

The use of membranes with a filtration area of 1.1 m^2 in the osmotic installation made it possible to achieve specific productivity values in the range of 48–70 $L \cdot m^{-2} \cdot h^{-1}$ at pressure up to 10 bar.

Water purified from impurities (permeate) is drained, and remaining concentrate is fed back to the osmotic membranes. That is the way how source water is concentrated by salt composition.

After concentrating the volume of source water required, it is necessary to clean the module using acid and alkaline solutions recommended by installation manufacturer. This is needed to remove settled impurities of organic and inorganic origin from the osmotic membranes.

After the concentration, the concentrate (salt residue from source water) and the rinsing liquid (solution with suspended salt particles, which sedimented on the osmotic membranes during the process) are transferred to a laboratory.

The subsequent laboratory evaporation allows obtaining dry residue from the concentrate and the rinsing liquid. By gamma-spectrometry, the main radionuclides, which may be present in discharge (Cs-137, Co-60, Mn-54, etc.), were determined on the installation with a detector made of ultrapure germanium. Beta-emitting radionuclide Sr-90 was analyzed radiometrically after radiochemical isolation, using monoisooctyl methyl ester of phosphonic acid.

To verify the method of preparing countable samples using the osmotic membranes, we compared it with traditional method (evaporation). For this purpose, water from Beloyarsk Reservoir was sampled (the volume of each sample was of 500 L).

In each dry residue, absolute activity of countable sample was determined. It is calculated by formula:

$$A = \frac{(I_{cs} - I_{bg}) \cdot m_{dr}}{\eta \cdot \varepsilon \cdot m_{cs}}, \quad (5)$$

where I_{cs} is count rate at total absorption peak, imp·sec^{-1};
I_{bg} is background count rate in a channel range of radionuclide studied, imp·sec^{-1};
m_{dr} is mass of ash obtained by evaporation of liquid, g;
η is quantum yield of an energy line, from which sample activity is calculated;
ε is registration efficiency for the energy line analyzed;
m_{cs} is mass of the sample analyzed on a spectrometer, g.

Uncertainty of activity was evaluated by formula:

$$U(A) = \sqrt{\begin{array}{c}(\frac{\delta A}{\delta I_{cs}})^2 \cdot \Delta I_{cs}^2 + (\frac{\delta A}{\delta I_{bg}})^2 \cdot \Delta I_{bg}^2 + (\frac{\delta A}{\delta m_{dr}})^2 \cdot \Delta m_{dr}^2 + \\ +(\frac{\delta A}{\delta m_{cs}})^2 \cdot \Delta m_{cs}^2 + (\frac{\delta A}{\delta \eta})^2 \cdot \Delta \eta^2 + (\frac{\delta A}{\delta \varepsilon})^2 \cdot \Delta \varepsilon^2\end{array}}, \quad (6)$$

where ΔI_{cs} is uncertainty of count rate at total absorption peak, imp·sec^{-1};
ΔI_{bg} is uncertainty of background count rate in a channel range of radionuclide studied, imp·sec^{-1};
Δm_{dr} is uncertainty of mass of ash obtained by evaporation of liquid, g;
Δm_{cs} is uncertainty of mass of the sample analyzed on a spectrometer, g;
$\Delta \eta$ is uncertainty of quantum yield of an energy line, from which sample activity is calculated;
$\Delta \varepsilon$ is uncertainty of registration efficiency for the energy line analyzed.

Expanded uncertainty of measurement was calculated by formula:

$$U = 2 \cdot U(A). \quad (7)$$

To confirm metrologically substantiated results of the assessment of specific activity in countable samples, we carried out gamma-spectrometric analysis of dry residues of the concentrate and the rinsing liquid in different laboratories: at the Institute of Industrial Ecology of UB RAS (hereinafter IIE) and at the Biophysical Station of the Institute of Plant and Animal Ecology of UB RAS (hereinafter IPAE).

RESULTS

Validation of the baromembrane method and evaluation of osmotic membranes efficiency were carried out during the analysis of concentrations of stable chemical elements, radioactive isotopes of which in the discharge can form 99 % of effective dose loads on population. The content of elements studied in water samples was determined by atomic absorption spectroscopy and mass spectrometry (Table 1).

Table 1. Results of analysis of various chemical elements concentration when using osmotic membranes

Element	u	Source water, mg·L^{-1}	Concentrate, 1st cycle, mg·L^{-1}	Concentrate, 3rd cycle, mg·L^{-1}	Concentrate, 5th cycle, mg·L^{-1}	Concentrate, 10th cycle, mg·L^{-1}
Na	23	84.9	118	278	431	2853
K	39	4.8	6.3	13.1	18.1	123
Ca	40	75.5	81.0	189	224	335
Sr	88	0.67	0.98	2.36	3.19	10.3
Mn	55	1.80	2.77	3.94	6.63	185
Co	59	< 0.1	0.14	0.22	0.62	3.57
Element	u	Source water, μg·L^{-1}	Concentrate, 1st cycle, μg·L^{-1}	Concentrate, 3rd cycle, μg·L^{-1}	Concentrate, 5th cycle, μg·L^{-1}	Concentrate, 10th cycle, μg·L^{-1}
Ni	59	< 2.0	4.51	9.91	12.7	63.8
Cs	133	< 0.05	< 0.05	< 0.05	0.078	0.094

The results presented in Table 1 demonstrate an exponential increase in concentrations of the elements analyzed, which proves the possibility of using this method for preliminary concentration. Exponential value in the experiment is specific for each element. The maximum values were determined for Co, Mn, and Ni: 1.08; 1.01; and 0.93, respectively. The minimum exponential value was obtained for Ca: 0.40. Exponential values for Na, Cs, K, and Sr were as follows: 0.83; 0.77; 0.75; and 0.66, respectively.

Verification of the baromembrane method for preliminary concentration of radionuclides in freshwater samples was carried out on samples of water cooling pond of the Beloyarsk NPP. Four 500-L water samples were taken in one place at one time period.

Countable samples No. 1 and 2 were obtained by evaporation of two samples to dry residue; countable samples No. 3 and 4 – by preliminary concentration of two other samples by the baromembrane method. Source volume of each sample taken (500 L) was transferred to a concentrated solution with a volume of 30 times less. Source water salinity (193 mg·L^{-1}) was increased in each concentrate to 5.8 g·L^{-1}. Mineralization level was determined by a conductometer in terms of NaCl salts content. The concentrates obtained were also evaporated to dry residue. The total preparation time for two countable samples when using the baromembrane method was five days. Evaporation of 500 L of source water to prepare two countable samples required two weeks.

Determination of radionuclides content in all countable samples was carried out on two different gamma-ray spectrometers with a detector made of ultrapure germanium having efficiency of 15 % (IPAE laboratory) and 40 % (IIE laboratory). The results of interlaboratory comparison of gamma-emitting radionuclides activity demonstrate a clear presence of Cs-137 in the Beloyarsk Reservoir with the values of volumetric activity in the range of 1.4–3.1 mBq·L^{-1} (Table 2).

The results of interlaboratory comparison demonstrate a good convergence of volumetric activities of radionuclides. The absence of a significant difference in the results of two methods for preparing water countable samples allows concluding that the baromembrane method is applicable for determining ultra-low concentrations of radionuclides. The results obtained demonstrate the absence of activity losses on osmotic membrane elements.

Table 2. Results of interlaboratory comparison of gamma-emitting radionuclides in dry residue samples

Sample number	Cs-137, $\cdot 10^{-3}$ Bq·L^{-1}		K-40, $\cdot 10^{-1}$ Bq·L^{-1}	
	IIE	IPAE	IIE	IPAE
1	3.1 ± 0.9	1.6 ± 0.4	3.2 ± 0.7	2.5 ± 0.1
2	2.6 ± 0.8	1.8 ± 0.4	2.8 ± 0.6	2.4 ± 0.1
3	1.9 ± 0.7	2.8 ± 0.8	1.9 ± 0.5	3.6 ± 0.2
4	1.4 ± 0.7	1.9 ± 0.8	1.6 ± 0.4	3.3 ± 0.1

Note: ± indicates extended measurement uncertainty. Samples No. 1 and 2 were prepared by evaporation; No. 3 and 4 – using an installation with osmotic membranes.

DISCUSSION

Experiments on validation and verification of the baromembrane method for concentrating radionuclides in freshwater samples made it possible to increase the number of research objects. In addition to the Beloyarsk Reservoir, four water cooling ponds of Russian NPPs (Balakovo, Kursk, Rostov, and Novovoronezh) were selected to investigate background concentrations of radioactive substances in water.

Sampling was carried out at various water outlets, which allowed suggesting what radionuclides could be present in Russian NPPs discharge and making a list. Table 3 contains information about sampling locations and salinity values of water samples analyzed. The differences in salinity of concentrated water and concentration coefficients for each of water outlets at Russian NPPs analyzed can be caused by various factors: NPP location region; operation mode of water cooling pond; and water exchange rate in it. According to project documentation, Russian NPPs have discharge both in closed water cooling ponds and in rivers.

Table 3. Results of analysis of various chemical elements concentrations when using osmotic membranes

NPP	Water outlet	Result of concentration		
		Salinity of source water, mg·L^{-1}	Salinity of concentrated water, g·L^{-1}	Concentration coefficient by sample volume
Balakovo	Inlet channel	980	13.8	36.8
Kursk	Inlet channel	568	27.7	34.9
	Outlet channel	659	22.8	33.9
	Seym River	345	4.2	43.1
	Domestic sewage	212	3.1	20.8
Rostov	Domestic sewage	690	13.5	34.9
	PPU 1, 2 outlet channel	277	8.2	43.8
	PPU 3, 4 outlet channel	900	12.0	31.1
Novovoronezh	PPU 1, 2 outlet channel	246	3.1	27.7
	Fisheries outlet channel	253	3.8	37.6
	PPU 3, 4 inlet channel	253	3.9	38.6
	PPU 5 outlet channel	362	4.1	23.7
	Filter fields outlet	300	4.1	19.1

Note: PPU is power plant unit.

The results of the experiments show as follows: the baromembrane method makes it possible to concentrate radionuclides in water samples repeatedly (up to 30–40-fold), and source sample volume can be reduced from 1000 to 30 L. Concentration parameters obtained are limited by membrane filtration area, technical characteristics of electric motor, and types of connector units in a mobile installation.

Concentration coefficient can be influenced by osmotic membrane area, source water salinity (it should not exceed 1.5–2 $g \cdot L^{-1}$), and organic compounds presence.

Analysis of dry residues of gamma-emitting radionuclides from water samples of Russian NPPs shows mainly presence of Cs-137, Mn-54, and Co-60. Among beta-emitting radionuclides, Sr-90 was analyzed (Table 4).

Table 4. Results of analysis of dry residues of gamma-emitting radionuclides from water samples of Russian nuclear power plants

NPP	Water outlet	Volumetric activity of radionuclide in water, $\cdot 10^{-3}$ $Bq \cdot L^{-1}$			
		Cs-137	Sr-90	Mn-54	Co-60
Balakovo	Inlet channel	1.48 ± 0.67	3.25 ± 1.33		
Kursk	Inlet channel				
	Outlet channel				
	Seym River				
	Domestic sewage	11.8 ± 1.28		1.64 ± 0.47	13.9 ± 0.92
Rostov	Domestic sewage		15,4 ± 7,08		
	PPU 1, 2 outlet channel				
	PPU 3, 4 outlet channel				
Novovoronezh	PPU 1, 2 outlet channel		37.7 ± 22.0		
	Fisheries outlet channel		31.9 ±19.3		
	PPU 3, 4 inlet channel		24.0 ± 13.8		
	PPU 5 outlet channel		22.5 ± 13.4		
	Filter fields outlet	15.1 ± 6.20	26.0 ± 15.6	2.49 ± 1.01	11.5 ± 4.80

Note: PPU is power plant unit.

Gamma-spectrometric analysis of dry residue after evaporation of 30 L of concentrate, remaining from source sample, allows determination of Cs-137 at the level of $5.0 \cdot 10^{-4}$ $Bq \cdot L^{-1}$. As a result of the research, it was shown that water activity of water outlets of Russian NPPs is mainly due to Cs-137 and more mobile radionuclide Sr-90 [9]. Changes in technological processes during NPP operation can form a wider range of radionuclides in discharge; therefore, Mn-54 and Co-60 might be occasionally detected in the samples.

Conclusion. The possibility of using the baromembrane method for determining ultra-low concentrations of dissolved salts of radioactive substances was demonstrated. To conduct field experiments, a special mobile installation was developed and constructed; it provides multiple concentrating of water samples up to 500 L within a day. Its hydraulic efficiency is 30 %; average selectivity is 70 %; average salt impermeability is 30 %. Specific productivity values are in the range from 48 to 70 $L \cdot m^{-2} \cdot h^{-1}$.

The method was validated by analyzing concentrations of stable chemical elements. From cycle to cycle, the exponential increase in concentration of each element analyzed was shown. The exponential value was specific for each element. In a row from higher to lower value, the elements are arranged as follows: Co > Mn > Ni > Na > Cs > K > Sr > Ca.

The method was verified by evaporation of water of equal volume (traditional method). A sufficient convergence of the values of volumetric activity of Cs-137 was demonstrated in the samples obtained by the baromembrane method of concentration and by evaporation.

Analysis of water samples for presence of radioactive substances in water outlets of Russian NPPs made it possible to establish the main regularities affecting concentration process by the baromembrane method. During the experiments, the average value of concentration coefficient of source volume of water was determined, which is (33 ± 8). This value is comparable with theoretical calculations obtained during installation constructing in a technical design proposed.

The method allows concentrating radionuclides with the osmotic membrane 30–40-fold. Source sample volume can be reduced from 1000 to 30 L. Dry residue analysis, with evaporation of remaining 30 L of sample, allows to determine Cs-137 at the level of $5.0 \cdot 10^{-4}$ Bq·L^{-1}, Co – $6.0 \cdot 10^{-4}$ Bq·L^{-1}, Mn-54 – $6.8 \cdot 10^{-4}$ Bq·L^{-1}, and Sr-90 – $9.0 \cdot 10^{-5}$ Bq·L^{-1}.

The method developed made it possible to reliably determine concentration of dissolved salts of the main radionuclides in the ranges as follows: for Cs-137 – from $1.48 \cdot 10^{-3}$ to $15.1 \cdot 10^{-3}$ Bq·L^{-1}, for Sr-90 – from $3.25 \cdot 10^{-3}$ to $37.7 \cdot 10^{-3}$ Bq·L^{-1}. Mn-54 and Co-60 can also be occasionally detected in water samples from water outlets of Russian NPPs.

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БАРОМЕМБРАННЫЙ МЕТОД ПОДГОТОВКИ СЧЁТНЫХ ОБРАЗЦОВ ВОДЫ ДЛЯ ИЗМЕРЕНИЯ УЛЬТРАНИЗКИХ КОНЦЕНТРАЦИЙ РАДИОНУКЛИДОВ*

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В работе показана возможность применения баромембранного метода для измерения ультранизких концентраций радионуклидов в воде пресноводных водоёмов. Актуальность задачи обусловлена необходимостью определения привноса радионуклидов в водные объекты, используемые предприятиями ядерно-топливного цикла. Радионуклиды естественного и техногенного происхождения, не связанные со сбросами предприятия, всегда присутствуют в таких водных объектах, формируя естественный или техногенно изменённый радиационный фон. Его наличие часто затрудняет идентификацию вклада сбросов предприятия в активность воды, так как штатные методы мониторинга характеризуются очень высоким порогом обнаружения радионуклидов. Традиционные способы определения фоновых концентраций радионуклидов требуют отбора минимум 500 л воды с последующим её выпариванием до образования сухого остатка, а на такую процедуру необходимо не менее пяти рабочих дней. Сократить затраты времени и энергии на выпаривание сотен литров воды можно путём предварительного концентрирования радионуклидов в меньшем объёме пробы баромембранным методом.

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Для его демонстрации применяли мобильную установку с осмотическими мембранами. Её начальная производительность составляет 6,0 л·мин$^{-1}$. Осмотические мембраны позволяют разделить исходную пробу из водоёма на два компонента — деминерализованный пермеат и содержащий радиоактивные вещества концентрат. В зависимости от степени минерализации воды исследуемой пробы, установка позволяет проводить за 10–15 ч предварительное концентрирование 500 л до образца объёмом 20 л с минимальными потерями радионуклидов. Этот подход универсален и может быть применён для концентрирования растворённых солей любых тяжёлых металлов и прочих органических соединений. Он позволяет готовить счётные образцы водных проб в гораздо меньшие сроки, чем традиционный метод упаривания.

Ключевые слова: баромембранный метод, обратный осмос, радионуклиды, объёмная активность, атомная электростанция

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MOLECULAR BASES OF THE EFFECT OF LOW DOSES OF RADIATION*

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By definition, low doses are minimum doses of a damaging agent, in particular radiation, causing a recorded biological effect. The problem of exposure to low doses of radiation is being discussed in scientific literature for decades, but there is still no generally accepted conclusion concerning the existence of some features of the effect of low doses in contrast to that of acute exposure. This is due to the fact as follows: if being fixed, these effects have a weak expression and can be easily criticized. The second important aspect of this problem is that biological effects are mainly described phenomenologically in literature, without deciphering their molecular causes. In recent years, a number of articles appeared in which the authors, when studying exposure to low doses of DNA-tropic agents, show that postreplication repair (in particular, its error-free branch) plays a key role in these effects. In the laboratory of eukaryotic genetics of Petersburg Nuclear Physics Institute named by B. P. Konstantinov, it was possible to isolate unique yeast mutants with a disrupted branch of error-free postreplication repair. A study of the processes of eliminating DNA damage with minimal deviations of their number from a spontaneous level made it possible to explain at the molecular level the differences in cell response to low doses from acute exposure.

Keywords: low doses, yeast, postreplication repair, tolerance

Cellular genome functions under the constant influence of exogenous and endogenous factors causing DNA damage. It is estimated that in one cell cycle, eukaryotic cells must repair more than 10,000 DNA damage, arising from the effects of endogenous sources only, such as reactive oxygen species, endogenous alkylating agents, and single and double DNA breaks resulting from replication forks collapse. DNA damage number also increases as a result of impact of external factors: chemical mutagens, as well as ultraviolet and ionizing radiation. Unrepaired genetic damage leads to mutations, genetic instability, cancer, and cell death.

DNA damage repair is divided into a number of independent or partially overlapping pathways: nucleotide excision repair (NER); base excision repair (BER); DNA mismatch repair (MMR); postreplication repair (PRR); nonhomologous end joining (NHEJ); and homologous recombination (HR).

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Significant progress has been made in the study of biochemical mechanisms of the main repair pathways, including direct, excisional, recombination, and mismatch. To a lesser extent, this progress affected postreplication repair (hereinafter PRR). This repair type is often included in the system of cell tolerance to DNA damage since DNA damage is not removed but is bypassed in replication process using PRR mechanisms. Such a bypass is not always error-free and is the main source of mutagenesis.

Under normal conditions and under the effect of low doses of mutagens, the key way to combat DNA damage in bacterial and eukaryotic cells is systems of DNA damage tolerance [2 ; 7 ; 8 ; 11 ; 12].

DNA damage tolerance (hereinafter DDT) has historically been called postreplication repair due to the observation that UV treatment of budding yeast cells caused single-stranded gaps in replicating DNA [11]. PRR substrate is replication forks, stopped at DNA damage. UV-induced pyrimidine dimers, causing single-stranded gaps in DNA, were often preserved after “repair”; this indicates that PRR simply bypasses the damage rather than repairs it [3 ; 6].

In all eukaryotic organisms, two different DDT pathways operate: error-prone and error-free ones [10]. In yeast, PRR can also follow two different pathways. The first one is error-prone pathway (translesion synthesis, hereinafter TLS); it involves protein polymerase zeta complex (encoded by *Rev1*, *Rev3*, and *Rev7* genes) and polymerase eta (encoded by *Rad30* gene). These polymerases are conservative in everyone from yeast to human [4]. TLS is controlled by *Rad6*/*Rad18* complex coordinating gap filling by PCNA monoubiquitination. In the second DDT pathway (error-free) one strand (newly synthesized) serves as a matrix for replication of another strand (blocked) [2 ; 12]. The choice between these DDT pathways has serious consequences for genome stability.

The error-free PRR branch, often called recombination one, plays a dominant role in tolerance, since two repair types have a common D-loop formation stage. In the study of relationship between mutagenesis, repair, chromatin dynamics, and cellular cycle, the greatest progress has been made on the example of a unicellular eukaryotic organism: budding yeast *Saccharomyces cerevisiae*. Experiments with yeast have shown that error-free mechanisms are the main PRR pathways under both low and high replication stress [2 ; 7 ; 8 ; 11 ; 12], although the pathway of synthesis through damage (TLS) may also be effective under little number of DNA damage [8].

In response to DNA damage, cells use a net of signal carriers related both to cell cycle passing (the checkpoint) and to repair implementation. It has been noted as follows: in yeast, zero mutants by the checkpoint are surplus in TLS, but partially defective in gap filling [10]. It is still not clear how do these effects relate to the role of the replication checkpoint in maintaining the stability of stopped replication forks or in regulating factors, providing tolerance [5]. In any case, the checkpoint machine obviously modulates cell response to DNA damage.

Earlier, for the first time in the world, using direct screening, yeast mutants, characterized by increased induced mutagenesis and practically unchanged sensitivity to mutagens lethal action, were isolated by us, as well as spontaneous mutators [1 ; 9]. Epistatic analysis of these mutants showed that they belong to three groups; mutants of *HSM3* epistatic group belong to the error-free PRR branch. Further study of these mutants (with the most pronounced mutator phenotype) showed that the products of these genes are related to control of polymerases involved in gap filling in DNA. Replacement of accurate replicative polymerases with inaccurate polymerase Polη often occurs in mutant cells, and this significantly increases mutation rate. The study of molecular mechanisms of biological action of ultra-small number of DNA damage is very convenient if using methods of accounting for spontaneous mutagenesis in yeast (Table 1).

Table 1. Spontaneous mutagenesis in repair mutants

Strain	Mutation frequency per generation, $\cdot 10^{-7}$ (replicative)	Mutation frequency per generation, $\cdot 10^{-7}$ (reparative)
Wild type	3.2 ± 0.3	3.2 ± 0.6
rad1	10 ± 1.4	28 ± 4.0
rad2	2.4 ± 0.5	18 ± 3.9
rad14	3.3 ± 0.2	31 ± 3.5
pol3	80.2 ± 7.2	75 ± 4.5

Table 1 shows our results for measuring mutation rate by two methods. The first one is Lea – Coulson method. It measures mutation rate in cells, growing under the most favorable conditions. The generation lasts for less than 2 hours. During this time, the number of spontaneous DNA damages in cells is minimal, and most of the mutagenesis is a consequence of replication errors. The second one is method of ordered seeding; it has been developed in the Leningrad State University. This method is simpler and more convenient in execution, but, as we have shown, it is applicable only for strains with an undamaged repair system. This method differs from the previous one: cell cycle is artificially stretched many times (it lasts for several days). In this case, a significant number of spontaneous damages accumulate in DNA, which are effectively removed in cells with normally functioning repair. In cells with disrupted repair system, some of these damages remain and get into the replication fork.

As it can be seen from the Table 1, wild type cells show the same mutation rate in both tests. In polymerase mutant, where all the increased mutagenesis is defined by errors of damaged polymerase, two tests also give identical mutation rate. At the same time, all repair mutants show a significantly higher mutation rate in the Leningrad Test (see Table 1).

The data in Fig. 1 are a good illustration of the effects of low doses of spontaneous damage. This figure shows the effect of adaptive mutagenesis, controlled by *HSM3* gene we have discovered. In the upper row, there are dishes with antibiotic, sown with wild type cells. Colonies of antibiotic-resistant mutants can be seen, which grew after 3 days (dish on the left) and after 15 days (the same dish on the right). Dishes of the lower row were sown with *hsm3* mutant cells. It is noticeable that in the upper row, the difference in colonies number after 3 and 15 days is little. In the lower row, this difference reaches 2 orders of magnitude.

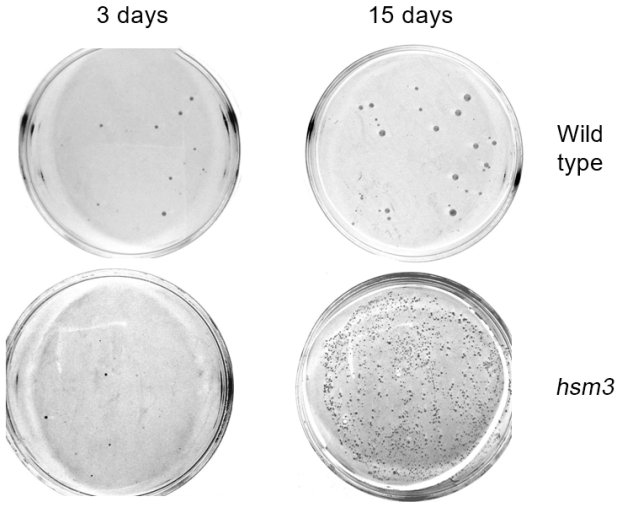

Fig. 1. Adaptive response of *hsm3* mutant with a disrupted error-free branch of postreplication repair

A very subtle tool for assessing the effect of a little number of DNA damage on cell survival is the measurement of spontaneous death of mutant cells along certain repair pathways. For example, disabling of recombination repair blocks DNA repair from double-strand breaks, which rarely occur in normally growing yeast cells (less than 1 break per generation). Nevertheless, we can see a significant increase in the proportion of dead cells in population with blocked recombination repair: wild type – (3.6 ± 1.2) %; *rad52* mutant – (10.1 ± 3.2) %.

Low doses of DNA damage do not activate the checkpoint induced by DNA damage. The checkpoint may not be essential for survival under these conditions [5]. Therefore, in cells with blocked nucleotide excision repair after low-dose irradiation, almost all UV-induced damages get into the replication fork and are exposed to PRR. In our experiments, nucleotide excision repair mutants were used for studying the characteristics of this PRR type. We injected into *rad2* mutant an additional *hsm3* mutation, disrupting the main pathway of the error-free repair branch. As it can be seen from Fig. 2, the double mutant showed significantly higher UV-resistance than the single *rad2* and very high induced mutagenesis. Thus, disabling of error-free repair branch directs DNA damage to an erroneous repair pathway being less cytotoxic.

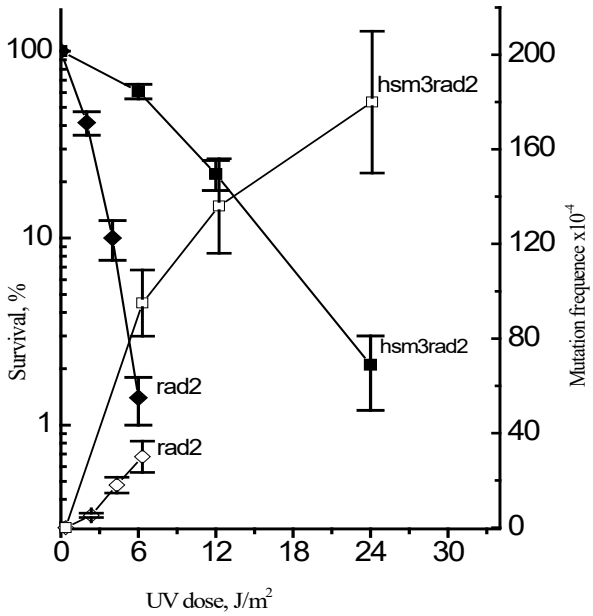

Fig. 2. Effect of blocking the error-free branch of postreplication repair

Japanese scientists have obtained interesting data on the effect of low doses of UV rays on yeast cells [7]. They showed (Fig. 3) that *rad14* mutant, which blocks nucleotide excision repair, grows under conditions of chronic irradiation at about the same rate as wild type cells, while cells of *rad18* mutant (the one that blocks PRR) show high sensitivity to this impact. At the same time, according to our studies, behavior of *rad14* and *rad18* mutants in the experiment with usual dose commitments (acute irradiation) has a completely different character (Fig. 4). In this case, *rad14* mutant is much more sensitive than *rad18*. There are two main reasons for this paradoxical difference. Firstly, with a little number of DNA damage, the checkpoint is not activated; as a consequence, there is no induction of repair systems being under control of the checkpoint. Secondly, at low doses, most of the resulting DNA damage avoids the action of non-activated repair systems due to difficulties in detecting them and gets into the replication fork. Replication forks, stopped at DNA damage, are PRR substrate.

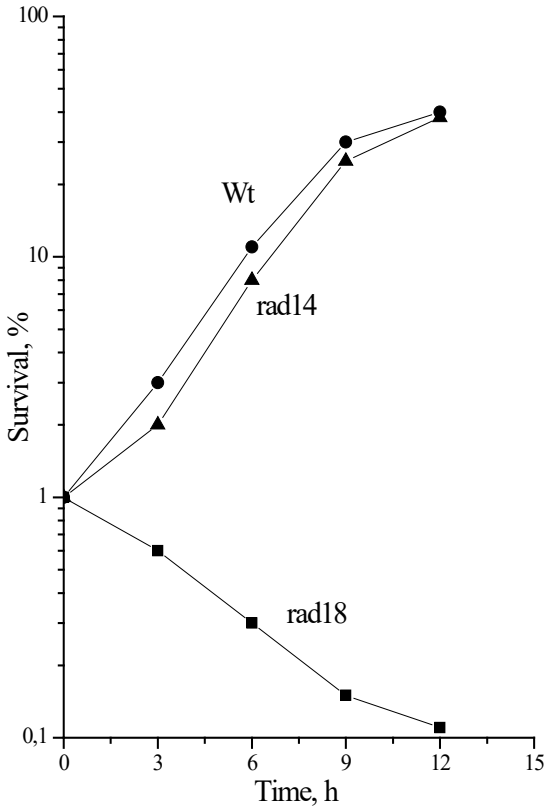

Fig. 3. Dependence of yeast strains survival on exposure to chronic UV with a low dose rate

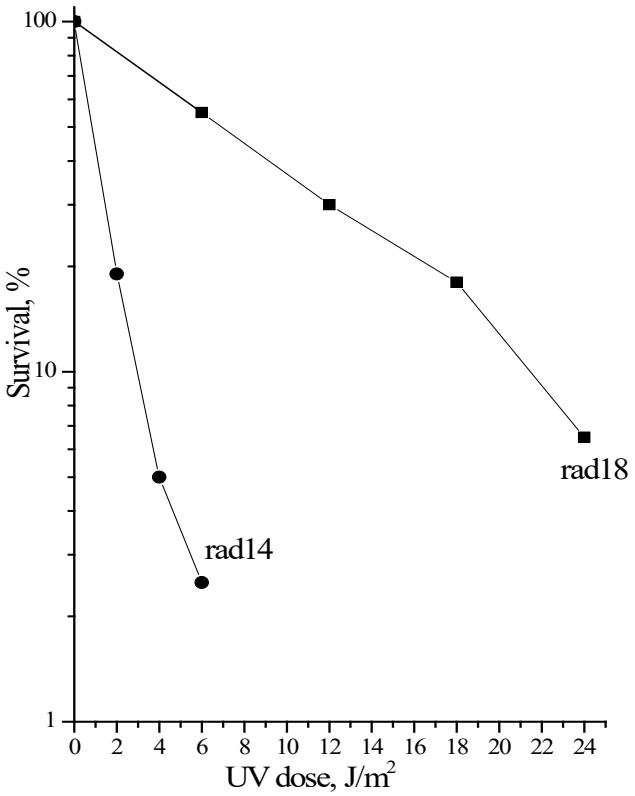

Fig. 4. Survival of *rad18* and *rad14* mutants in an acute experiment

The checkpoint activation has a threshold character and occurs when a certain number of single-stranded DNA accumulates, arising during damage repair. Thus, when a threshold level of DNA damage is exceeded as a result of induction, the efficiency of repair systems increases dramatically, and that allows the cells to get rid of the overwhelming number of DNA damage and to reduce the load on postreplication repair. It follows that the efficiency of DNA damage repair, not reaching a threshold level, will be much lower than in case of its exceeding, and the biological significance of the former will be higher than that of the latter.

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МОЛЕКУЛЯРНЫЕ ОСНОВЫ ЭФФЕКТА МАЛЫХ ДОЗ РАДИАЦИИ*

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По определению, малые дозы — это минимальные дозы повреждающего агента, в частности радиации, вызывающие регистрируемый биологический эффект. Проблема воздействия малых доз радиации обсуждается в научной литературе в течение десятилетий, но прийти к общему выводу о наличии каких-то особенностей их воздействия, в отличие от таковых острого облучения, не удаётся. Это связано с тем, что эффекты, если они фиксируются, имеют слабое выражение и легко могут быть подвергнуты критике. Другой важный аспект проблемы — то, что биологические эффекты в основном описаны в научной литературе феноменологически, без расшифровки их молекулярных причин. В последние годы появился ряд статей, в которых авторы, изучая действие малых доз ДНК-тропных агентов, показывают, что ключевую роль в этих эффектах играет пострепликативная репарация, в частности её безошибочная ветвь. В лаборатории генетики эукариот Петербургского института ядерной физики имени Б. П. Константинова удалось выделить уникальных мутантов дрожжей с нарушенной ветвью безошибочной пострепликативной репарации. Исследование процессов ликвидации повреждений ДНК при минимальных отклонениях их количества от спонтанного уровня позволило на молекулярном уровне объяснить различия в клеточном ответе на малые дозы от острого облучения.

Ключевые слова: малые дозы, дрожжи, пострепликативная репарация, толерантность

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COMPREHENSIVE RADIOECOLOGICAL MONITORING OF FRESHWATER ECOSYSTEMS IN THE VICINITY OF ROOPPUR NPP (PEOPLE'S REPUBLIC OF BANGLADESH)*

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The paper presents experience of developing and maintaining a system of radioecological monitoring of freshwater ecosystems in the vicinity of Rooppur Nuclear Power Plant (Bangladesh). Components of freshwater ecosystems in the zone of NPP impact are both very informative for determining the environmental state and very important for conducting economic activities. Therefore, the issue of assessing and predicting quality of freshwater ecosystems in the vicinity of NPP is relevant for ensuring radiation and environmental safety. During the studies, we developed a detailed monitoring program; selected observation points for the state of surface water and groundwater at different distances from Rooppur NPP; determined monitoring objects (water, bottom sediments, higher aquatic vegetation, and fish), list of parameters to be studied, observation regulation, methods, and regulatory and technical support. Among the indicators controlled we considered the following ones: physicochemical properties of water and bottom sediments; radionuclide content of components of freshwater ecosystems including natural (^{40}K, ^{226}Ra, and ^{232}Th) and technogenic (^{90}Sr, ^{137}Cs, and ^{3}H) radionuclides; and content of 19 heavy metals, as well as chemical pollutants. Monitoring studies were conducted in 2014–2017, considering climatic peculiarities of the region at different periods of the year. Radionuclides in environmental objects were determined by spectrometry and radiochemistry; heavy metals – by atomic absorption and plasma emission analysis methods. It was established that higher aquatic vegetation in the Padma River is found not in all seasons. In December, it was almost absent. The maximum species diversity was registered in June. Differences between surface water and groundwater in the vicinity of Rooppur NPP were distinguished for several physical and chemical characteristics. Values of drinking water total mineralization and hardness were higher than that of surface water by 2–3 times. This is due to Padma River water composition, the basis of which is meltwater and rainwater. Organic pollutants content in surface water and groundwater was below detection limits or at minimum ones (benzopyrene – less than 0.01 μg·L^{-1}; phenols – 1.3–3.5 μg·L^{-1}; and petroleum products – 0.01–0.043 mg·L^{-1}). Activity concentration of ^{137}Cs in Padma River water did not exceed 0.18 Bq·L^{-1} (with a mean of 0.07 Bq·L^{-1}) during the observation period. The content of ^{90}Sr was 0.02–0.12 Bq·L^{-1}, and the concentration of ^{3}H varied in the range of 0.8–2.1 Bq·L^{-1}. Mean specific activity of ^{90}Sr in bottom sediments was 0.5–1.8 Bq·kg^{-1}, and ^{137}Cs – 0.8–2.1 Bq·kg^{-1}. Specific activity of ^{3}H in bottom sediments was less than 3 Bq·kg^{-1}, except for 3 samples in 2017 (12–30 Bq·kg^{-1}), which was most likely due to a local pollution. Specific activity of ^{90}Sr in higher aquatic vegetation

*The materials of the article were presented at the Readings in memory of Academican G. G. Polikarpov "Radiochemoecology: Progress and Prospects" (Sevastopol, IBSS, 2019).

was 0.4–3.9 Bq·kg^{-1}, and ^{137}Cs – 0.4–1.0 Bq·kg^{-1}. In drinking water, activity concentrations of radionuclides were as follows: ^{137}Cs – 0.03–0.27 Bq·L^{-1}; ^{90}Sr – 0.01–0.16 Bq·L^{-1}; ^{3}H – 0.4–1.2 Bq·L^{-1}. Specific activity of ^{90}Sr in fish was 0.02–1.6 Bq·kg^{-1}.The content of ^{137}Cs in fish was 0.26–0.3 Bq·kg^{-1}. Analysis of monitoring data on heavy metal levels in components of freshwater ecosystems in the vicinity of Rooppur NPP showed that for a number of elements their increased concentrations were recorded, most of which belong to monsoon season. In Padma River surface water, a repeating increase in As, Cd, Mn, and Al concentrations was noted, and in bottom sediments – an increase in As, Cd, Ni, Co, and Zn content, which was associated with anthropogenic impact and increasing runoff of pollutants during monsoon rains. Repeatedly increased As and Mn concentrations were noted in drinking water of Rooppur NPP 30-km zone. In separate samples, there was an increase in Fe and Al content. This might be due to both natural peculiarities of the region (relatively high As content in aquifers) and the state of water supply systems. Obtained results and developed network of radioecological monitoring of freshwater ecosystems would make it possible to register a change in the situation and to identify impact of Rooppur NPP operation on human population and the environment.

Keywords: Bangladesh, Rooppur NPP, water resources, freshwater ecosystems, Padma River, drinking water, radioecological monitoring, radionuclides, heavy metals, chemical pollution

Based on the agreement signed between the Russian Federation and the People's Republic of Bangladesh in 2011, Rosatom State Corporation began in 2017 the construction of Rooppur Nuclear Power Plant (hereinafter NPP) with two VVER-1200 power units. NPP project is being implemented within the framework of the Bangladesh Nuclear Power Action Plan in accordance with recommendations and under the control of the International Atomic Energy Agency [24]. Rooppur NPP site is located on the northern bank of the Padma River (Ganges), 20 km east of the city of Pabna, 160 km northwest of Dhaka (Bangladesh capital), and 300 km along Padma and Meghna rivers to Bay of Bengal in the Indian Ocean. The Padma is one of the deepest and longest rivers in Southern Asia. River basin area is 1060 thousand km^2. Average amount of water carried by the river into the Bay of Bengal is estimated at 12 thousand m^3 per sec. All this indicates the importance of Padma's impact on the ecology of the Bay of Bengal and the Indian Ocean in general.

Radioactivity poses a potential hazard to humans and biota, including freshwater and marine organisms, when using nuclear power. It is possible to assess and minimize potential negative NPP impact on living organisms only on the basis of regular observations of the environment in the vicinity of NPP: by developing a system of radioecological monitoring. Such system is aimed to a greater extent at ensuring the radiation safety of humans and biota, *i. e.* has two components: sanitary, related with health protection of facility personnel and population, and environmental ones. Meanwhile, other types of hazard (chemical pollution, heat generation, electromagnetic radiation, noise level, etc.) are also subjects to control.

NPP life cycle lasts for more than 50 years from construction to decommissioning. That is why the development of radioecological monitoring system at NPP starts at the stage of designing: when preparing documents on investment justification and environmental impact assessment within the framework of engineering and ecological surveys [1 ; 2 ; 30]. Radiation and environmental monitoring prior to NPP construction makes it possible to assess the state of all ecosystems, as well as dose commitments on humans and biota at background level (so-called zero level). This stage is of great importance since it creates an informational basis for further analysis of NPP impact on the environment and humans during facility construction and operation. When assessing such an impact, it is necessary to take into account technogenic pollution of the environment from operating industrial enterprises in the vicinity of NPP during its construction. Composition and number of radionuclides, entering terrestrial and freshwater ecosystems from NPP due to its emissions and discharges, are strictly regulated; however, these contaminants

can eventually enter a human body through food chains and direct contact with the environment. Thus, knowledge of the ways of spreading both technogenic and natural radionuclides is important for ensuring population radiation safety [34].

Being a densely populated country (1.2 thousand people per km^2), Bangladesh strongly depends on existence of water resources, their regional and seasonal availability, and quality of surface water and groundwater. These factors are greatly impacted by monsoon climate peculiarities and country's physiography. The eastern part of Bangladesh receives about 3 thousand mm of precipitation annually, while the western part receives only half of this amount. About 80 % of precipitation occurs in 5 rainy months during monsoon. A large volume of water (about 70 %) is used by population for irrigation. Besides agriculture, water is used in household and municipal water supply, industry, fishing, and shipping. Water use in the country largely depends on groundwater reserves (irrigation area is 7.5 million hectares, and 65–70 % of it is provided by groundwater). Dhaka Water Supply and Sewerage Authority produces 2.1 million liters of water per day for 12.5 million citizens of Bangladesh's capital, with 87.7 % of water volume provided by groundwater and the remainder – by surface water. Bangladesh groundwater system is threatened by the presence of natural arsenic in water of several regions, salinization of shallow aquifers in coastal zones, and decrease in groundwater levels due to irrational water abstraction [30].

Water regime in Padma River basin, being the main source of cooling for reactors of Rooppur NPP under construction, is not the same during the rainy season and outside it. For example, in Farakka River basin, average annual flow rate of the Padma River is 12.1 thousand m^3 per sec, and flow volume is 382.1 thousand m^3. From June to October, average flow rate is 24.5 thousand m^3 per sec, and from January to May – only 2.2 thousand m^3 per sec. Of total annual flow volume, 80 % occur on monsoon period [35]. The studies of various authors of fish catch dynamics in middle and lower flows of the Padma River differ in the data; this is due to ichthyofauna migration being associated, in particular, with river water regime. Components of freshwater ecosystems in Rooppur NPP area are both one of the most informative for determining environmental state and one of the most important for conducting economic activity. Therefore, the problem of assessing and predicting their quality is urgent. So, radiation and environmental monitoring of freshwater ecosystems is an obligatory element of a complex assessment of NPP impact on the environment.

The aim of this work is to present the experience in developing and maintaining a system of radiation and environmental monitoring of freshwater ecosystems in the vicinity of Rooppur NPP (People's Republic of Bangladesh).

MATERIAL AND METHODS

At the first stage of research, a detailed program of radiation and environmental monitoring of freshwater ecosystems in Rooppur NPP impact zone was developed in accordance with the requirements [1 ; 2]. The basis of this program is complexity of observations, consistency of their timing with characteristic hydrological and hydrobiological phases, and determination of indicators of water quality, composition of bottom sediments, and hydrobiocenosis state, as well as ensuring necessary accuracy and reproducibility of the results. Observation points for surface water and groundwater state were selected taking into account the results of the reconnaissance survey of water ecosystems in Rooppur NPP area (2014) and the analysis of stock data on physical, geographical, and morphometric characteristics of water bodies, on radionuclides and heavy metals contamination of surface water, bottom sediments, and water organisms, and on sanitary and hygienic indicators of drinking water quality.

The object of surface water study was Padma River area and other watercourses within 30-km zone of Rooppur NPP impact. These water bodies were considered as reference ones, *i. e.* the most affected by a possible negative NPP impact. To determine radionuclides and heavy metals content in components of freshwater ecosystems, a network of sampling points for water, bottom sediments, higher aquatic vegetation, and ichthyofauna was established. Sampling points included observation sites located within a radius of 30 km from Rooppur NPP. The allocated territory was conditionally divided into three zones with varying degrees of spatial provision. Most often, observation sites were set up in the area with a radius of 5 km from the NPP. Fewer observation sites were chosen in the area with a radius up to 10 km, taking into account existing anthropogenic sources of pollutants. Background sites (for the NPP) were set up along the edges of 30-km zone. The samples of components of freshwater ecosystems taken above Rooppur NPP characterize conditional background state of the water body. Samples taken in the lower sites make it possible to evaluate nature and degree of changes in river water composition under the impact of NPP runoff and wastewater. Sampling points were located taking into account coastline geomorphology at a distance of 3–5 m from both banks and on the midstream with geographic reference of the terrain coordinates. Taking into account the changes in river bed during the year (due to different hydrological regime) and in time, the sampling points were subject to some adjustment. Sampling points of bottom sediments, higher aquatic vegetation, and surface water coincided so that we had an opportunity to comprehensively compare the content of pollutant studied in components of freshwater ecosystems.

Thus, 11 sites were installed on the Padma River, from which components of freshwater ecosystems were sampled: site I – 25.5 km northwest of NPP platform (background values fixing); II – 11 km northwest above the platform; III – 5.5 km northwest above the platform; IV – 3 km northwest above the platform; V – 2.2 km west above the platform; VI – 0.5 km west of the platform; VII – 4.5 km south-southeast below the platform; VIII – 10 km south-southeast below the platform; IX – 14.5 km southeast below the platform; X – 20.5 km southeast below the platform; and site XI – 26.5 km southeast below the platform (Fig. 1).

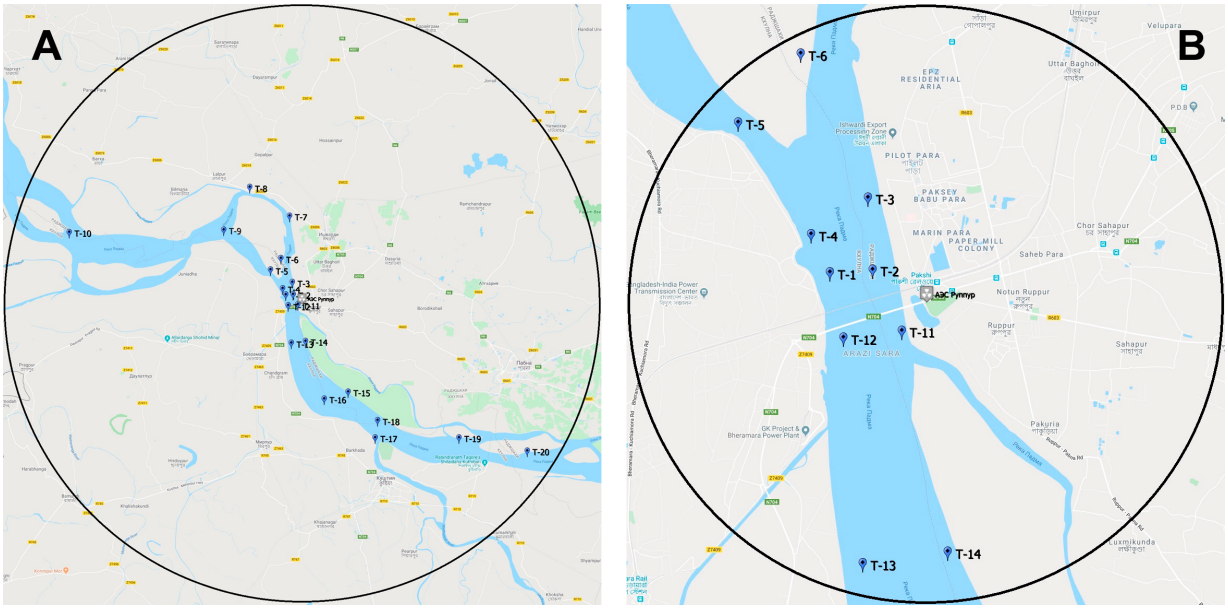

Fig. 1. Schematic map of radioecological monitoring network of freshwater ecosystems in the vicinity of Rooppur NPP: A – 30-km zone; B – 5-km zone (T indicates control point)

Water was sampled using a Niskin bottle. The suspension was separated using a device with filters for particles larger than 0.5 μm. Suspended matter and filtrate samples were analyzed separately. Volume of water samples for the analysis of gamma-radiation radionuclides and tritium, as well as for radiochemical analyses of radionuclides and heavy metals, was determined by the applied methods of sample preparation and measurements. Bottom sediments sampling was carried out with a benthic box corer DCh-0.025; weight of one sample (air-dry weight) was not less than 0.3 kg. Ichthyofauna and higher aquatic vegetation samples were taken with species description. Air-dry weight of higher aquatic vegetation samples was at least 0.2 kg, and that of ichthyofauna was 0.5–3.0 kg (wet weight). Samples of groundwater, used by local population for drinking and household needs, were taken in settlements of 30-km zone of Rooppur NPP impact at various distances and directions from the power plant from water columns, bore-holes, water pipes, and wells (Fig. 2).

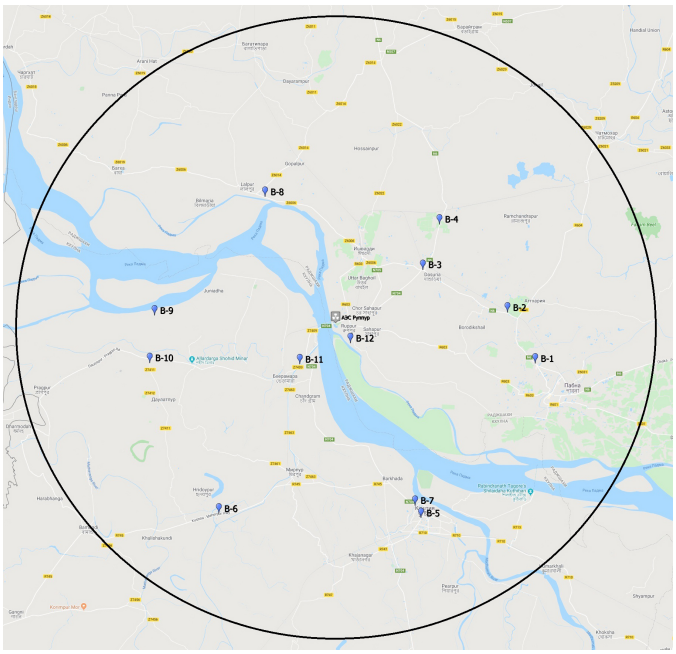

Fig. 2. Schematic map of radioecological monitoring network of groundwater (drinking water) in the vicinity of Rooppur NPP

Significant seasonal differences in climatic characteristics (monsoon rains from May to September; dry period from December to March) notably affect the regime of freshwater ecosystems in the vicinity of Rooppur NPP. Thus, during monsoons, Padma River water level rises 6–8 m, and in winter it drops to a minimum. Therefore, sampling of components of freshwater ecosystems in Rooppur NPP area was carried out in different periods of the year: August (2014), April (2015), December (2016), and June (2017). If the depth at water sampling point on the Padma River was more than 5 m, surface and bottom water samples were taken (Table 1).

Higher aquatic vegetation was detected not in every sampling period. Thus, it was virtually absent in December. The maximum species diversity was recorded in June. Ichthyofauna samples were taken only in 2016–2017 due to the fact that in the early years of the development of radioecological monitoring network in Rooppur NPP area, the emphasis in research was placed on assessing population diets with food obtained from terrestrial (agricultural) ecosystems.

Table 1. Number of samples of components of freshwater ecosystems taken in the vicinity of Rooppur NPP in 2014–2017

Component of freshwater ecosystem	Sampling period			
	21–28 August 2014	03–09 April 2015	02–07 December 2016	04–09 June 2017
Padma River surface water	22	20	20	23
Padma River bottom sediments	20	20	20	20
Padma River higher aquatic vegetation	3	4	1	19
Padma River fish	–	–	6	14
Groundwater (drinking water)	3	–	6	3

Sampling of components of freshwater ecosystems, their preparation for measurements, and measurements themselves were carried out following the developed regulations (Table 2) according to the certified methods in the accredited laboratories of Russian Institute of Radiology and Agroecology: for radionuclides – in the radiation control testing laboratory (accreditation certificate RA.RU.21AD81); for heavy metals and physical and chemical indicators – in the testing laboratory (accreditation certificate RA.RU.513078).

Table 2. Regulations of radioecological monitoring of freshwater ecosystems in the vicinity of Rooppur NPP

Component of freshwater ecosystem	Sampling frequency	Pollutants detected		
		Radionuclides	Heavy metals	Organic substances
Surface water, groundwater	Every season (4 times a year)	^{40}K, ^{226}Ra, ^{232}Th, ^{3}H, ^{90}Sr, ^{137}Cs	As, Hg, Cd, Ni, Co, Sr, Zn, Cu, Cr, Mn, Fe, Al	benzopyrene, phenols, petroleum products, organochlorine pesticides, polychlorinated biphenyls
Bottom sediments	Once a year		As, Hg, Cd, Ni, Co, Zn, Cu, Cr, Mn, Pb, Fe, Al	–
Higher aquatic vegetation	Once a year	^{3}H, ^{90}Sr, ^{137}Cs	As, Hg, Cd, Ni, Co, Zn, Cu, Cr, Mn, Pb, Fe, Al, Sr, Se, Mo, Sb, V, Li, Cs	
Fish	Once a year			

To assess radionuclide content in environmental objects, we used: low-background gamma spectrometer with a DKDK-100V detector; spectrometric alpha- and beta-radiometer Quantulus 1220; alpha- and beta- liquid scintillation counter Tri-Carb 4810TR; gamma-radiation energy spectrometer GAMMA-1P for two measuring paths with semiconductor detectors made of ultrapure germanium (EG&G ORTEC, USA); multichannel analyzer Desktop InSpector 1270 based on a semiconductor detector made of ultrapure germanium (Canberra Industries, Inc., USA); and gamma-radiation energy spectrometer Accuspec with a semiconductor detector made of ultrapure germanium based on an integral cryostat (Canberra Industries, Inc., USA). The relative measurement error of radionuclide activity was 6–35 % depending on the instrument and method used.

Heavy metals in environmental objects were determined by atomic absorption and plasma emission analysis methods. An axial atomic emission spectrometer (optical) with samples atomization in inductively coupled plasma Liberty II (Varian, Australia – USA) and a KVANT.Z.ETA-1 spectrometer with GRG-3 attachment were used for measurements. To prepare samples for measurement, both dry and wet ashing methods were used with a microwave system MARS-5 (CEM, USA).

Organic pollutants were determined by fluorometric method on a Fluorat-02 liquid analyzer according to methods, standards, and environmental regulations as follows: benzopyrene – ISO 28540-2011; phenols – PND F 14.1:2:4.182-02 (2010 edition); and petroleum products – PND F 14.1:2:4.128-98 (2012 edition).

Quality assessment of components of freshwater ecosystems was carried out by comparing measurement results with the data of regulations in the field of radiation and environmental safety, as well as with clarke content of toxicants or with regional background being established according to literature data.

RESULTS AND DISCUSSION

During surface water and groundwater sampling in the vicinity of Rooppur NPP, physical and chemical indicators were determined by a multiparameter water quality assessment instrument U-52 (Table 3).

Table 3. Physical and chemical indicators of surface water and groundwater in the vicinity of Rooppur NPP at sampling time (numerator is the mean; denominator is min.–max.)

Indicator	Sampling period			
	August 2014	April 2015	December 2016	June 2017
Surface water				
Temperature, °C	27.9 / 27.0–29.0	28.8 / 27.9–30.1	24.2 / 23.4–24.8	29.8 / 29.0–31.0
Hydrogen indicator (pH)	7.5 / 7.2–8.2	8.5 / 7.2–9.5	8.1 / 7.4–8.5	8.1 / 7.8–8.5
Redox potential, mV	No data	148.8 / 63.0–247.0	158.1 / 111.0–237.0	No data
Electrical conductivity, $\mu S \cdot cm^{-1}$	0.37 / 0.31–0.40	0.31 / 0.26–0.43	0.31 / 0.30–0.34	0.30 / 0.28–0.31
Turbidity, FTU	335.5 / 279.6–426.9	92.7 / 14.8–294.8	92.6 / 66.0–143.0	No data
Dissolved oxygen, $mg \cdot L^{-1}$	No data	13.0 / 6.4–13.8	11.1 / 7.1–12.5	12.0 / 11.1–13.4
Suspended matter, $mg \cdot L^{-1}$	No data	31.1 / 5.0–80.0	42.5 / 0.4–109.0	13.1 / 2.2–77.4
Total mineralization (dry residue), $mg \cdot L^{-1}$	131.0 / 112.0–150.0	177.9 / 158.0–249.0	195.3 / 11.4–395.0	160.9 / 108.0–198.0
Total hardness, $mmol \cdot L^{-1}$	4.1 / 3.4–5.0	5.2 / 4.4–7.4	5.5 / 5.0–5.8	4.0 / 3.8–4.4
Groundwater (drinking water)				
Hydrogen indicator (pH)	7.1 / 6.9–7.2	No sampling	7.3 / 7.1–7.9	7.2 / 6.9–7.4
Suspended matter, $mg \cdot L^{-1}$	62.7 / 33.3–92.0		No data	32.4 / 5.8–78.2
Total mineralization (dry residue), $mg \cdot L^{-1}$	396.0 / 337.0–454.0		382.3 / 175.0–498.0	375.5 / 258.0–466.0
Total hardness, $mmol \cdot L^{-1}$	12.63 / 7.8–15.3		17.8 / 14.8–18.9	10.8 / 8.1–13.9

The average water temperature in the Padma River varied from April to August within +28…+30 °C. It was minimal in December: +24 °C. Hydrogen indicator (pH) of surface water was on average 7.5–8.5. Redox potential of Padma River water was 149–158 mV. Specific electrical conductivity of water samples was at the level of 0.30–0.37 μS·cm^{-1}. Average turbidity of the Padma River during the low rainfall period was 92–93 FTU; it increased up to 335 FTU during monsoon period (August) due to high soil runoff into the river with rainwater. Dissolved oxygen content in surface water varied within 11–13 mg·L^{-1}. Suspended matter in water samples was in the range of 13–43 mg·L^{-1}, and total mineralization (dry residue) was 130–195 mg·L^{-1}. Total water hardness of the Padma River varied from 4.0 to 5.5 mmol·L^{-1}.

Hydrogen indicator (pH) of groundwater was slightly lower than that of surface water: 7.1–7.3. Amount of suspended matter in groundwater was higher than that in surface water. It averaged 32–63 mg·L^{-1}, which was most likely due to the state of water supply system in the vicinity under study. Total mineralization in groundwater varied within 375–395 mg·L^{-1}, and total hardness – within 11–18 mmol·L^{-1}, being 2–3 times higher than similar characteristics of surface water. This is due to the composition of Padma River surface water, the basis of which is meltwater and rainwater.

In water samples studied in the vicinity of Rooppur NPP, organic pollutants content was quite low. In 2014–2017, benzopyrene in water samples from the observation area was less than 0.01 μg·L^{-1}. Phenols concentration varied in the range of 1.3–3.5 μg·L^{-1}, and that of petroleum products was 0.01–0.043 mg·L^{-1}. Organochlorine pesticides and polychlorinated biphenyls content in water samples was below detection limits.

When analyzing cation-anion composition of bottom sediments, it was noted that the samples did not contain carbonate ion, which is determined in water extract at pH = 8.4. In the results obtained, the maximum pH value was 8.2 (with a mean of 7.8). Therefore, only the bicarbonate ion was determined (Table 4).

Table 4. Cation-anion composition of bottom sediments of the Padma River (numerator is the mean; denominator is min.–max.)

Cations, mL-eq per 100 g		Anions, mL-eq per 100 g	
Ca^+	9.7 / 0.7–43.3	Cl^-	1.0 / 0.5–2.1
Mg^+	3.6 / 0.3–14.9	NO^{3-}	3.2 / 1.3–4.4
Na^+	1.1 / 0.1–2.9	Bicarbonate ion	0.4 / 0.04–0.6
K^+	0.4 / 0.02–2.5	F^-, μg per kg	7.4 / 5.8–9.7
NH_4^+	0.02 / 0.01–0.04	I^-, μg per kg	25.9 / 5–71

Granulometric composition of bottom sediments in different years of monitoring was quite stable and was characterized by: sand – 77.9 % (with a wide variability within 7.7–97.1 %); dust – 19.0 % (with a spread of values within 2.9–71.0 %); and clay – 3.1% (data range of 0.1–27.1 %). Very low ammonium content in bottom sediments was due to both absence of organic matter and minimum content of clay minerals. Ability of bottom sediments to fix ammonium is manifested in the presence of clay

with a three-layer crystal lattice, especially vermiculite. Nitrates are not included in poorly soluble compounds composition and are not absorbed by negatively charged colloids of bottom sediments. Since the samples of light granulometric composition of bottom sediments analyzed were very poor in organic matter, nitrate content was also very low.

During field researches in 2014–2017, species composition of water and coastal flora in Rooppur NPP 30-km zone, including the Padma River and water bodies outside its impact, was determined. A total of 79 taxa were identified; this was not much, given the potential diversity of regional flora [17]. Macrophytes were represented by 5 species from 3 families of macroscopic algae, 1 species of fern, and 73 species of vascular plants from 63 genera and 35 families. For aquatic and coastal flora, the following families were leading in terms of taxa number: Poaceae (13 taxa), Leguminosae (5), Polygonaceae (5), Cyperaceae (4), Potamogetonaceae (4), and Asteraceae (3). In the families Amaranthaceae, Araceae, Hydrocharitaceae, Lemnaceae, Najadaceae, Pontederiaceae, Rubiaceae, Scrophulariaceae, Typhaceae, and Verbenaceae, two species were found in each; in the rest – one in each. A similar set of leading families is generally characteristic of riverside and waterlogged habitats in the region [23]. In the spectrum of life forms of aquatic and coastal flora, herbaceous annuals and perennials are absolutely dominant (51 and 43 %, respectively). Shares of the rest life forms were in the range of 1–3 %. This ratio is natural, given instability of river water regime, regular erosion of coastal zone, and high anthropogenic load on Padma River freshwater ecosystem [21]. Annuals, completing their life cycle prior to monsoon period, and rhizome perennials get the advantage here. Zones of different distance from NPP do not differ much in terms of vegetation cover characteristics since they have practically identical ecological habitat conditions characterized by severe coastline erosion, which greatly limits the set of species and communities. When planning monitoring for assessing the state of aquatic and coastal vegetation of the Padma River, it should be taken into account that spring and summer are the most appropriate periods for research: for the most complete identification of species and coenotic diversity.

Radionuclides inflow into surface water prior to the start of NPP operation occurs due to precipitation. Radioactive substances, entering water bodies, are rapidly redistributed and usually accumulated in bottom sediments, benthos, aquatic flora, and ichthyofauna. Analysis of natural and technogenic radionuclide content in components of freshwater ecosystem of the Padma River showed that it was quite low and corresponded in general to the global radiation background both before NPP construction (2014–2015) and after its start (2016–2017). The volumetric activity in Padma River water of the main radiologically significant ^{137}Cs during the entire observation period did not exceed 0.18 Bq·L^{-1} (with a mean of 0.07 Bq·L^{-1}) (Table 5). The content of ^{90}Sr in surface water was on average at the level of 0.02–0.12 Bq·L^{-1}.

Tritium (^{3}H) is one of the most mobile radionuclides being found mainly in water; therefore, under natural conditions, it can be transported by water flow over long distances. According to the research data of 2014–2017, values of the volumetric activity of tritium in Padma River water in the observation area of Rooppur NPP were in the range of 0.8–2.1 Bq·L^{-1}. The global ^{3}H natural background in water is taken to be (2.2 ± 0.7) Bq·L^{-1}; the technogenic background – 5 Bq·L^{-1}. Thus, tritium content in surface water near Rooppur NPP is in the range below the global average value; ^{3}H content is 3 orders of magnitude lower than intervention level (7600 Bq·L^{-1} according to Radiation Safety Standards NRB-99/2009). Similar picture was observed for ^{90}Sr and ^{137}Cs. According to NRB-99/2009, intervention levels for the content of these technogenic radionuclides in water

Table 5. Radionuclide content in components of freshwater ecosystem of the Padma River in the vicinity of Rooppur NPP, Bq·kg^{-1} (Bq·L^{-1}) (numerator is the mean; denominator is min.–max.)

Sampling period	^{40}K	^{226}Ra	^{232}Th	^{90}Sr	^{137}Cs	^{3}H
Surface water						
2014	< 1.5	< 0.5	< 0.5	0.12 / 0.01–0.39	0.07 / 0.02–0.18	1.03 / 0.8–1.29
2015	< 1.1	< 0.4	< 0.4	0.03 / 0.01–0.05	< 0.05	1.15 / 0.77–2.05
2016	1.05 / 0.48–1.77	0.16 / 0.1–0.31	0.18 / 0.1–0.3	0.06 / 0.01–0.21	< 0.07	< 3
2017	2.54 / 1.19–6.99	< 0.2	< 0.4	0.02 / 0.01–0.04	0.07 / 0.03–0.11	< 3
Bottom sediments						
2014	735 / 570–820	48.5 / 42–51	59.5 / 44–71	1.79 / 1.5–2.19	2.1 / 0.5–4.2	< 3
2015	582 / 369–721	47.1 / 14.9–121	71.2 / 34.5–136	0.96 / 0.36–1.98	1.46 / 0.6–3.2	< 3
2016	494 / 340–710	43.2 / 21.4–82	66.8 / 24.7–137	1.54 / 0.09–3.53	0.75 / 0.25–1.4	< 3
2017	569 / 350–852	61.4 / 24.8–122	96.6 / 21.5–211	0.45 / 0.2–0.99	1.26 / 0.5–2.83	20.3 / 12.2–30.8
Higher aquatic vegetation						
2014	No data	No data	No data	3.19 / 2.51–3.54	2.23 / 1.8–2.6	< 3
2015	621 / 253–1090	21.9 / 19.2–24.6	49.9 / 31.5–68.3	1.58 / 0.91–2.18	1.1	< 3
2016	134.5	< 1.2	< 1.4	9.7	< 0.3	< 3
2017	742.6 / 347–1431	21.8 / 8.7–41.7	38.3 / 17.1–70.3	1.91 / 0.38–3.89	0.73 / 0.4–1.0	< 3

are as follows: ^{90}Sr – 4.9 Bq·L^{-1}; ^{137}Cs – 11 Bq·L^{-1}. The monitoring results showed that the volumetric activity of technogenic radionuclides in water of Padma River area studied is 40 times lower than intervention level for ^{90}Sr and 60 times – for ^{137}Cs. In the work [29] on the determination of radioactivity levels on Rooppur NPP site and in its vicinity, carried out by Bangladesh Atomic Energy Commission specialists in 2009, the results of measuring the content of natural radionuclides ^{238}U, ^{232}Th, and ^{40}K in water samples were presented. Their volumetric activities varied in the range of 0.11–0.21 Bq·L^{-1} for ^{238}U; 0.13–0.30 Bq·L^{-1} – for ^{232}Th; and 0.30–0.47 Bq·L^{-1} – for ^{40}K. Our research (2014–2017) showed the absence of significant changes in background content of natural radionuclides in Padma River water (Table 5).

The analysis of the results of measurements of natural radionuclide content in bottom sediments samples of the Padma River in the vicinity of Rooppur NPP showed that during the entire observation period (2014–2017) no increased level of their specific activity was detected. The maximum values were

as follows: ^{40}K – 852 Bq·kg^{-1}; ^{226}Ra – 122 Bq·kg^{-1}; and ^{232}Th – 211 Bq·kg^{-1} (Table 5). Technogenic radionuclide content was also not high. Mean specific activity of ^{90}Sr in bottom sediments samples varied in the range of 0.5–1.8 Bq·kg^{-1}, and ^{137}Cs – 0.8–2.1 Bq·kg^{-1}. Specific activity of tritium in bottom sediments samples was less than 3 Bq·kg^{-1}, except for three samples (T-8, T-9, and T-10) taken upstream of the Padma River from Rooppur NPP at a distance of 15–20 km in 2017. These three samples showed increased tritium values: 12–30 Bq·kg^{-1}. They were taken in shallow water areas. Most likely in this area in January – May 2017, pollutants, containing this radionuclide in small concentrations, were discharged, and they have settled in bottom sediments. Since no increased tritium concentrations were detected in bottom sediments samples in December 2016, a possible discharge occurred in 2017 before June. Tritium concentrations identified in bottom sediments are not abnormally high. At the same time, this fact requires additional study to determine a possible pollution source. No research of radionuclide content in sediments of the Padma River in Rooppur NPP construction area has previously been carried out, but in 2016 a work on natural radionuclide content in sediments of the Brahmaputra River, which is similar to the Padma River in location and size, was published [26]. According to these studies, mean ^{232}Th and ^{40}K content in bottom sediments was (113 ± 5) and (1002 ± 43) Bq·kg^{-1} of dry weight, respectively; these values are comparable with our results obtained. The content of natural and technogenic radionuclides in aquatic vegetation is extremely low. According to the most representative sample of 2017 including 19 samples, specific activity of ^{90}Sr in aquatic vegetation varied within 0.4–3.9 Bq·kg^{-1}, and ^{137}Cs – within 0.4–1.0 Bq·kg^{-1} of wet weight.

When assessing the state of freshwater ecosystems from the point of view of radiation safety, it is important to analyze radionuclide content in components of population diet (drinking water and fish) from NPP area and to compare the data obtained with international and Russian standards governing annual enter of radioactive substances into a human body. Thus, in drinking water, the volumetric activity of standardized radionuclides varied in the ranges as follows: ^{137}Cs – 0.03–0.27 Bq·L^{-1} (40 times less than intervention level according to NRB-99/2009); ^{90}Sr – 0.01–0.16 Bq·L^{-1} (30 times less); ^{3}H – 0.4–1.2 Bq·L^{-1} (more than 6 thousand times less than intervention level) (Table 6).

For ^{226}Ra and ^{232}Th, the difference with intervention levels according to NRB-99/2009 was 2–3 times. Studies on radionuclide content in drinking water in the vicinity of Rooppur NPP were carried out in 1998 [14]. In Kushtia and Rajshahi area at that time, ^{232}Th content in drinking water was at the level of 0.25–0.27 Bq·L^{-1}, and ^{40}K – 7.95–8.52 Bq·L^{-1}. The results obtained during the radioecological monitoring (2014–2017) for ^{232}Th correlate well with the data of that work, and for ^{40}K they are a little bit lower.

In 2016–2017, fish from the Padma River in the vicinity of Rooppur NPP was sampled to assess radionuclide content. In 2017, the sample was quite representative: 14 samples of different species. The standardization of human radiation safety when eating fish is provided by both international and Russian regulations for the most radiologically significant radionuclides: ^{90}Sr and ^{137}Cs (Table 6). During the observation period, specific activity of ^{90}Sr in fish varied from 0.02 to 1.6 Bq·kg^{-1}, which is more than 60 times lower than in Russian and international standards. The content of ^{137}Cs was in the range of 0.26–0.3 Bq·kg^{-1}, which is more than 400 times lower than in Russian standards and more than 3 thousand times – in international ones. In general, it can be concluded that radionuclide content in drinking water and fish in the vicinity of Rooppur NPP does not exceed the values specified by requirements of international and Russian sanitary and hygienic standards for these types of population diet.

Table 6. Radionuclide content in drinking water and fish in the vicinity of Rooppur NPP, Bq·kg^{-1} (Bq·L^{-1}) (numerator is the mean; denominator is min.–max.)

Sampling period	^{40}K	^{226}Ra	^{232}Th	^{90}Sr	^{137}Cs	^{3}H
Groundwater (drinking water)						
2014	< 1.3	< 0.2	< 0.11	0.07 / 0.02–0.16	0.05 / 0.03–0.08	0.92 / 0.42–1.18
2016	0.9 / 0.6–1.1	0.28 / 0.11–0.71	0.24 / 0.2–0.33	0.03 / 0.01–0.07	0.27	< 3
2017	1.02	< 0.2	< 0.11	0.042 / 0.041–0.043	0.05 / 0.03–0.06	< 3
Standard[1]	–	0.49	0.60	4.9	11	7600
Fish						
2016	110 / 103–120	< 1.2	< 1.2	0.6 / 0.03–1.55	< 0.4	–
2017	95 / 78–124	< 1.4	< 2.4	0.13 / 0.02–0.24	0.28 / 0.26–0.30	–
Standard[2]	–	–	–	100	1000	–
Standard[3]	–	–	–	100*	130*	–

Note:
[1] SanPiN 2.6.1.2523-09 Radiation Safety Standards (NRB-99/2009);
[2] Codex Alimentarius. General Standard for Contaminants and Toxins in Food and Feed;
[3] SanPiN 2.3.2.1078-01 Hygiene Requirements for Safety and Nutritional Value of Food Products (as amended on 06.07.2011);
* excluding dried fish.

The second direction of monitoring studies was the assessment of heavy metals content in components of freshwater ecosystems in the vicinity of Rooppur NPP. Analysis of the data of 4-year observations of water pollution levels in the Padma River showed that for some heavy metals there are increased concentrations in different seasons of the year, and most of them are confined to August (2014) being monsoon period. Thus, arsenic belonging to the I hazard class enters surface water naturally from rocks and sediments as a result of related biogeochemical and hydrological processes, some of which are currently impacted by human activities [16]. This process intensifies during monsoon season. The limit of As content in water, recommended by the World Health Organization (hereinafter WHO) [18], the US Environmental Protection Agency [4], and Russian regulations, is 10 μg·L^{-1}. Taking into account WHO recommendations and Russian threshold limit values (hereinafter TLV), it can be concluded that an excess of standards for As in Padma River water occurred only in 2014. In other periods, arsenic content in surface water was at the level of 0.9–3.6 μg·L^{-1} (with a mean of 2.6). Mercury was not measured in 2014. In other years, Hg concentration in Padma River water was much lower than specified by Russian standards (Table 7).

The maximum permissible level of cadmium (the II hazard class) in drinking water, established by WHO, is 3 μg·L^{-1} [18]; Russian TLV is 1 μg·L^{-1}. Monitoring results showed that only in 2014 there was an excess of WHO permissible level and Russian TLV by 3–9 times in water for Cd (as in case with As). According to [10], cadmium content in water samples was very low (≤ 1 μg·L^{-1}, trace concentration), which is close to the results of our studies in other periods of the year. These Cd levels are considered safe for irrigation [32]. Similar low cadmium concentrations were registered in water samples from other Bangladesh rivers: Buriganga, Turag, and Shitalakshya [7 ; 19].

Table 7. Heavy metals gross content in surface water of the Padma River in the vicinity of Rooppur NPP, $\mu g \cdot L^{-1}$ (numerator is the mean; denominator is min.–max.)

Element	Sampling period				TLV*	TLV**
	2014	2015	2016	2017		
The I hazard class						
As	59.0 / 10.04–170.11	0.96 / 0.42–2.53	2.19 / 1.27–3.84	3.58 / 2.93–5.56	10	–
Hg	–	$5.9 \cdot 10^{-3}$ / $3.7 \cdot 10^{-3}$–$1.5 \cdot 10^{-2}$	$1.03 \cdot 10^{-2}$ / $6 \cdot 10^{-3}$–$2.3 \cdot 10^{-2}$	$9.35 \cdot 10^{-4}$ / $1.1 \cdot 10^{-5}$–$2.8 \cdot 10^{-3}$	0.5	–
The II hazard class						
Cd	8.97 / 0.1–34.7	0.08 / 0.001–0.21	0.08 / 0.01–0.18	0.6 / 0.2–1.2	1	–
Ni	5.84 / 1.29–8.97	1.67 / 0.19–6.47	4.05 / 1.26–8.23	19.5 / 7.2–42.4	20	10
Co	3.6 / 3.0–4.2	0.2 / 0.1–0.5	2.6 / 1.6–3.9	1.5 / 0.3–2.8	100	–
Sr	103.8 / 71.0–165.0	48.3 / 9.3–67.0	135.5 / 102.2–154.6	–	7000	–
The III hazard class						
Zn	15.7 / 10.3–18.8	0.9 / 0.1–3.7	17.4 / 6.0–75.9	8.9 / 4.5–15.5	1000	10
Cu	6.5 / 1.1–13.4	0.4 / 0.06–1.25	3.3 / 1.4–7.9	7.7 / 2.7–18.5	1000	1
Cr	2.6 / 1.0–4.8	0.5 / 0.04–0.97	2.8 / 1.6–9.1	3.97 / 1.0–7.4	50	20
Mn	180.2 / 16.0–386.7	1.7 / 0.1–12.4	51.9 / 27.9–84.9	22.8 / 7.4–97.9	100	10
Fe	102.0 / 11.3–280.9	27.2 / 0.99–250.1	223.3 / 119.1–831.4	198.7 / 95.1–355.1	300	100
Al	151.8 / 113.3–382.3	28.9 / 0.2–244.4	252.4 / 52.0–595.2	211.1 / 128.9–358.9	200	–

Note:
* GN 2.1.5.1315-03 Threshold Limit Values (TLV) of Chemicals in the Water of Water Bodies of Domestic, Drinking, and Cultural-Domestic Water Use: Hygiene Standards;
** Water Quality Standards for Water Bodies of Fishery Importance, Including Standards for Threshold Limit Values (TLV) of Harmful Substances in the Waters of Water Bodies of Fishery Value. Approved on 13.12.2016 by order No. 552 of the Ministry of Agriculture of the Russian Federation.

Mean content of nickel (the II hazard class) in Padma River water for 4 years of monitoring varied within 1.7–19.5 $\mu g \cdot L^{-1}$, and this does not exceed TLV for domestic, drinking, and cultural-domestic water use (Table 7). In 2017, Ni values in water were higher than Russian standards for fishery water use, but they were safe if using water for irrigation, according to the Food and Agriculture Organization of the United Nations (hereinafter FAO) recommendations (200 $\mu g \cdot L^{-1}$) [32]. Other studies in Bangladesh show that nickel concentration in water samples from the Buriganga River varies from 7.2 to 10.3 $\mu g \cdot L^{-1}$ [7], which corresponds to levels, determined during monitoring in the vicinity of Rooppur NPP. In [19], heavy metals were studied in Karatoa River waters, and it was noted that Ni concentration was in the range of 9.3–66.0 $\mu g \cdot L^{-1}$, which was slightly higher than the values obtained for Padma River area. For cobalt and strontium also belonging to the II hazard class, no excess of standards in Padma River water was detected over the entire observation period.

Zinc content (the III hazard class) in Padma River water was minimal (0.94 μg·L^{-1}) in 2015 being significantly lower than values of other years (Table 7). However, maximum Zn concentrations recorded in the samples were much lower than the permissible level for irrigation (2000 μg·L^{-1}) [37] and Russian standards (1000 μg·L^{-1}). The results of studies on the Turag River presented in [10] show that water samples contained zinc in the range of 60–300 μg·L^{-1} (with a mean of 100 μg·L^{-1}). Zn concentration in Buriganga River water samples [27] varied within 220–260 μg·L^{-1}. These values are higher than monitoring data in the Padma River in the vicinity of Rooppur NPP. In [20], Balu River waters were studied, and zinc content varied from 8.39 to 76.86 μg·L^{-1}, which is comparable with our results.

The maximum copper concentration in Padma River waters averaged 7.7 μg·L^{-1} in 2017 (Table 7). According to other studies, Cu content in Turag River water samples varied from ≤ 1 to 90 μg·L^{-1} (with a mean of 46 μg·L^{-1}) [10]. As noted in [12], copper concentration in the samples from the same river varied within 10–70 μg·L^{-1} being higher than the results obtained during the monitoring of Rooppur NPP area. Cu content in Dhalesvari River water samples ranged from 98.4 to 188.1 μg·L^{-1} [6], which was also higher than in Padma River water.

Chromium content in Padma River water samples was quite stable over 4 years of monitoring (Table 7). Only in April 2015, a slight decrease in Cr concentration was noted, possibly due to peculiarities of river hydrological regime since in this period of the year water level there is much lower than during monsoon. Studies by other authors [10] show that chromium content in the waters of Bangladesh rivers exceeded the permissible levels and ranged from 0.23 to 0.47 mg·L^{-1} (with a mean of 0.32). Such Cr levels exceed TLV by an order of magnitude. Chromium pollution of river water was probably due to runoff from leather and textile enterprises. Similar results are presented in [7 ; 19]: among the content of heavy metals in water samples from urban rivers Buriganga, Turag, and Shitalakshya, the highest concentrations were that of Cr.

Manganese concentration in Padma River waters varied from 0.1 to 386.7 μg·L^{-1} during 4 years of monitoring (Table 7). In 2014, mean content of this heavy metal (180 μg·L^{-1}) was higher than in other years of observation (1.7–51.9 μg·L^{-1}), which was most likely associated with monsoon period. The maximum permissible level of Mn concentration in drinking water, established by WHO, is 500 μg·L^{-1}, and by Bangladesh Centre for Advanced Studies – 100 μg·L^{-1} [18 ; 37]. In all years of this study, except for 2014, manganese levels in Padma River water were several times lower than those recommended by WHO and Bangladesh Centre for Advanced Studies. According to [28], in 2010 in the vicinity of Mohanpur, Mn content in surface water varied from 0.9 to 2.86 μg·L^{-1}, which is on average an order of magnitude lower than monitoring results of 2014–2017. In [10], manganese concentration in river water was registered at the level of 350–920 μg·L^{-1} (mean value was 530 μg·L^{-1}). Probably, Mn appeared in polluted river waters from discharges by chemical and textile enterprises. These values exceed the permissible levels of manganese content when using water for irrigation (200 μg·L^{-1} according to the recommendations [32]). Mn concentrations registered in [20] in most of Balu River water samples (28.3–730.8 μg·L^{-1}) were comparable with the data of this study. It is shown in [39] that manganese content in Karatoa River water samples varied from trace concentrations to 320 μg·L^{-1}; this corresponds to the level of values obtained by us for surface water in the vicinity of Rooppur NPP.

Iron content in Padma River waters according to monitoring data of 2014–2017 (Table 7) averaged 0.03–0.2 mg·L^{-1} (with a maximum of 0.8 mg·L^{-1}) and did not exceed TLV for domestic, drinking, and cultural-domestic use (0.3 mg·L^{-1}). However, Fe concentration in water was higher

than TLV values for fishery use (0.1 mg·L^{-1}), except for 2015. It is shown in [10] that iron content in water samples from some Bangladesh rivers varied from 0.8 to 14.8 mg·L^{-1} (with a mean of 4.6 mg·L^{-1}). In a number of samples from this study, Fe concentration was above the acceptable limit (5.00 mg·L^{-1}) [37]. Iron contamination of river water might result from discharges by pharmaceutical, leather, and textile enterprises. In was noted in the study [5] that Fe content in Turag River water was in the range of 0.78–6.33 mg·L^{-1}, which was much higher than monitoring results of 2014–2017 of Padma River water.

Analysis of the data on aluminum content in Padma River water for the entire observation period showed that almost half of the samples are characterized with an excess of Al concentration in comparison with TLV (Table 7). The highest value reached 595 μg·L^{-1}, which is 3 times higher than TLV. Sources of aluminum intake into river system were also discharges by numerous industrial enterprises neglecting the environmental safety of production technologies.

Due to the absence of regulations governing TLV of heavy metals in bottom sediments, the method of comparing the values obtained with the officially established TLV of chemicals in soil was used (Hygiene Standards GN 2.1.7.2041-06 and GN 2.1.7.2511-09). Content of all heavy metals in bottom sediments in 2014 turned out to be higher than the values registered in other years of monitoring, which is most likely associated with a large soil runoff into the Padma River during monsoon period (Table 8).

Table 8. Heavy metals gross content in bottom sediments of the Padma River in the vicinity of Rooppur NPP, mg·kg^{-1} (dry weight) (numerator is the mean; denominator is min.–max.)

Element	Sampling period				TLV*	APC**
	2014	2015	2016	2017		
As	73.3 / 46.2–91.6	1.2 / 0.9–1.7	0.5 / 0.2–1.1	3.3 / 2.2–6.0	2.0	2.0
Hg	$1.24\cdot10^{-2}$ / $6.3\cdot10^{-3}$–$2.1\cdot10^{-2}$	$8.24\cdot10^{-3}$ / $4.4\cdot10^{-3}$–$1.2\cdot10^{-2}$	$7.4\cdot10^{-3}$ / $3.2\cdot10^{-3}$–$1.3\cdot10^{-2}$	$5.99\cdot10^{-3}$ / $7\cdot10^{-4}$–$1.8\cdot10^{-2}$	2.1	–
Cd	2.7 / 1.7–3.3	1.3 / 0.6–2.5	0.22 / 0.04–0.9	0.21 / 0.02–1.6	–	0.5
Ni	29.4 / 24.2–34.0	17.1 / 5.3–35.1	10.7 / 4.4–32.4	17.8 / 5.6–39.0	–	20.0
Co	20.6 / 15.7–23.3	3.9 / 1.7–6.9	8.8 / 4.8–16.4	8.9 / 4.1–15.9	–	–
Zn	73.3 / 45.1–88.8	21.2 / 7.8–52.3	77.3 / 20.7–190.0	200.7 / 27.2–582.8	–	55.0
Cu	23.4 / 17.8–27.1	9.5 / 1.5–20.2	6.9 / 2.4–29.3	6.1 / 0.7–19.0	–	33.0
Cr	–	9.8 / 3.8–18.3	25.4 / 16.2–55.3	23.9 / 11.5–51.8	–	–
Mn	602.5 / 505.0–701.0	411.7 / 140.0–935.0	388.9 / 150.0–902.0	406.2 / 163.0–928.0	1500	–

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Element	Sampling period				TLV*	APC**
	2014	2015	2016	2017		
Pb	25.4 21.5–28.4	3.6 0.3–7.5	17.3 12.8–22.6	16.4 11.4–48.5	32.0	32.0
Fe	$3.2 \cdot 10^4$ $2.6 \cdot 10^4$–$3.5 \cdot 10^4$	$1.7 \cdot 10^4$ $7.2 \cdot 10^3$–$3.5 \cdot 10^4$	$1.8 \cdot 10^4$ $1.0 \cdot 10^4$–$3.5 \cdot 10^4$	$2.0 \cdot 10^4$ $1.0 \cdot 10^4$–$3.7 \cdot 10^4$	–	–
Al	$4.8 \cdot 10^4$ $3.7 \cdot 10^4$–$6.6 \cdot 10^4$	$9.9 \cdot 10^3$ $3.2 \cdot 10^3$–$2.1 \cdot 10^4$	$3.8 \cdot 10^4$ $3.1 \cdot 10^4$–$5.4 \cdot 10^4$	$4.3 \cdot 10^4$ $3.3 \cdot 10^4$–$6.3 \cdot 10^4$	–	–

Note:
* GN 2.1.7.2041-06 Threshold Limit Values (TLV) of Chemicals in the Soil: Hygiene Standards;
** GN 2.1.7.2511-09 Approximate Permissible Concentrations (APC) of Chemicals in the Soil: Hygiene Standards.

For example, mean As concentrations in 2014 exceeded its TLV in the soil by more than 35 times and correlated with the data on its content in Padma River surface water. High As concentration in bottom sediments may also be associated with anthropogenic activity: operating of enterprises producing arsenic-containing fertilizers and pesticides [8]; wood processing using copper arsenate [33]; leather production [13].

Mean Cd concentration in bottom sediments in 2014 and 2015 was 2.7 and 1.3 mg·kg^{-1}, respectively, exceeding approximate permissible concentration (hereinafter APC) by 1.5–2.5 times. In subsequent years, it declined to acceptable levels.

The results obtained when determining lead concentration in bottom sediments (3.6–25.4 mg·kg^{-1}) were lower than the data presented in [9], where mean Pb content during summer and winter periods was 38.33 and 49.04 mg·kg^{-1}, respectively. High lead concentrations in bottom sediments could be associated with the impact of point-source and nonpoint-source pollution near the area under study: use of leaded gasoline and oil; industrial wastewater; and operating of steel plants and enterprises producing chemicals, electronics, cables, oils, tires, and cement [38].

Zn content in bottom sediments in all years, except for 2015, also exceeded APC.

Heavy metals content in higher aquatic vegetation of the Padma River varied in different years of monitoring (Table 9). In December 2016, relatively low concentrations were noted, which could be explained by the season of significant slowdown in plants vegetative activity.

Table 9. Heavy metals content in higher aquatic vegetation of the Padma River in the vicinity of Rooppur NPP, mg·kg^{-1} (dry weight) (numerator is the mean; denominator is min.–max.)

Element	Sampling period			
	2014	2015	2016	2017
As	1.6 1.1–2.1	1.8 0.5–2.7	0.04	0.9 0.1–2.6
Hg	$1.1 \cdot 10^{-2}$ $9.1 \cdot 10^{-3}$–$1.2 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$ $9.6 \cdot 10^{-3}$–$1.8 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$5.9 \cdot 10^{-4}$ $2 \cdot 10^{-4}$–$2 \cdot 10^{-3}$
Cd	0.2 0.2–0.3	0.8 0.1–1.2	0.02	0.2 0.01–0.4

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Element	Sampling period			
	2014	2015	2016	2017
Ni	3.3 1.2–7.2	8.2 0.7–12.3	0.13	4.2 0.2–16.7
Co	0.4 0.2–0.8	1.1 0.1–1.8	0.04	1.3 0.04–7.0
Zn	16.3 13.2–19.9	15.3 10.5–22.9	9.7	10.6 1.9–33.1
Cu	17.1 15.6–18.5	11.2 0.96–19.3	0.7	5.1 1.2–12.4
Cr	2.2 1.3–3.8	4.7 0.7–6.2	1.3	2.5 0.6–10.3
Mn	171.7 122.0–200.0	954.5 213.0–1492.0	42.6	259.5 15.8–770.0
Pb	1.8 1.4–2.1	1.8 0.1–3.1	0.7	2.1 0.01–15.3
Fe	1153.7 391–2523	6194 210–9026	1209	2999.3 163–15010
Al	1668.3 457.0–3547.0	7210.5 185.0–11458.0	48.1	1862.7 36.5–9918
Sr	40.3 34.5–49.3	54.2 3.6–95.1	3.2	55.6 8.8–102
Se	2.6 1.8–4.0	13.8 2.6–22.2	1.58	22.1 2.3–61.0
Mo	1.1 0.8–1.5	0.9 0.7–1.2	0.14	1.2 0.1–3.5
Sb	0.4 0.2–0.5	–	0.11	1.5 0.2–7.4
V	1.5 0.8–2.6	7.6 0.2–10.7	0.19	4.1 0.1–21.4
Li	–	6.7 0.2–10.1	0.16	2.6 0.2–15.2
Cs	–	0.31 0.03–0.5	0.52	0.5 0.2–1.9

In [28], As concentration in groundwater varied from 2.08 to 3.16 $\mu g \cdot L^{-1}$ at different sampling sites, which corresponds to our monitoring data of 2016–2017.

It was pointed out in [36] that Cd levels (the II hazard class) in groundwater in a number of Bangladesh regions vary from 6 to 13 $\mu g \cdot L^{-1}$, *i. e.* exceed the limits established by Bangladesh, WHO, and USA standards (5, 3, and 5 $\mu g \cdot L^{-1}$, respectively). Values of cadmium concentrations in drinking water of Rooppur NPP 30-km zone, obtained during the monitoring, do not exceed international standards; however, in some samples, Cd content was higher than Russian TLV (Table 10).

Table 10. Heavy metals gross content in drinking water of the Padma River in the vicinity of Rooppur NPP, μg·L^{-1} (numerator is the mean; denominator is min.–max.)

Element	Sampling period			TLV*
	2014	2016	2017	
The I hazard class				
As	80.5 / 14.2–136.6	3.5 / 0.96–8.1	4.4 / 0.5–13.3	10
Hg	–	$9.7\cdot10^{-3}$ / $5\cdot10^{-3}$–$1.3\cdot10^{-2}$	$1.2\cdot10^{-2}$ / $1.9\cdot10^{-3}$–$3.02\cdot10^{-2}$	0.5
The II hazard class				
Cd	0.2 / 0.1–0.4	0.1 / 0.02–0.3	0.8 / 0.2–1.5	1
Ni	1.01	1.74 / 0.3–3.8	14.7 / 11.3–18.7	20
Co	< 3	0.74 / 0.4–1.2	1.95 / 0.9–2.7	100
Sr	197.7 / 39.0–355.0	338.1 / 294.9–383.4	–	7000
The III hazard class				
Zn	< 30	8.9 / 3.7–23.8	10.3 / 4.0–16.5	1000
Cu	< 1	2.02 / 0.1–9.0	2.9 / 1.1–6.2	1000
Cr	2.1 / 1.8–2.4	0.96 / 0.64–1.43	2.8 / 2.3–3.5	50
Mn	225.5 / 52.1–398.9	484.9 / 197.8–1036.3	492.3 / 374.5–579.7	100
Fe	35.9 / 3.2–68.6	251.1 / 63.7–594.9	136.9 / 23.9–291.7	300
Al	50.6 / 5.8–95.4	190.3 / 73.9–336.8	120.6 / 85.3–147.0	200

Note:
* GN 2.1.5.1315-03 Threshold Limit Values (TLV) of Chemicals in the Water of Water Bodies of Domestic, Drinking, and Cultural-Domestic Water Use: Hygiene Standards.

Manganese concentration (the III hazard class) in groundwater of Rooppur NPP area during the entire observation period varied from 52 to 1036 μg·L^{-1}. The maximum permissible level of Mn content in drinking water is 0.1 μg·L^{-1} (according to Bangladesh, Russian, and WHO standards [18 ; 37]). Consequently, in all drinking water samples of 2016–2017, manganese concentration exceeded the upper limit established by international and Russian standards. Studies carried out in [28] showed that Mn content in groundwater in the Mohanpur region was in the range of 0.72–3.66 μg·L^{-1} (mean of 1.83 μg·L^{-1}), which was significantly lower than in Rooppur NPP 30-km zone. Exceeding standards for manganese was most likely associated with the poor condition of the water supply system of artesian wells in NPP construction area.

Concentrations of other heavy metals did not significantly exceed international and national standards.

Heavy metals content in fish of the Padma River, recorded during monitoring in 2016–2017, was lower than Russian TLV (Table 11) and partially comparable with the results of studies on the Buriganga River [25].

Table 11. Heavy metals content in fish of the Padma River in the vicinity of Rooppur NPP, mg·kg^{-1} (numerator is the mean; denominator is min.–max.)

Element	Sampling period	
	2016	2017
As (1.0*)	0.011 / 0.005–0.02	0.012 / 0.001–0.03
Hg (0.3)	0.011 / 0.004–0.019	$6.98 \cdot 10^{-3}$ / $6 \cdot 10^{-5}$–$1.99 \cdot 10^{-2}$
Cd (0.2)	0.011 / 0.003–0.032	0.02 / 0.002–0.075
Pb (1.0)	0.3 / 0.15–0.55	0.22 / 0.03–0.6
Ni	0.94 / 0.4–1.6	0.7 / 0.2–1.3
Co	0.03 / 0.01–0.07	0.04 / 0.006–0.11
Zn	7.71 / 3.77–10.7	7.3 / 4.4–16.2
Cu	1.42 / 0.16–3.12	1.2 / 0.03–4.5
Cr	1.6 / 0.8–2.2	0.4 / 0.1–0.6
Mn	0.5 / 0.12–1.02	0.4 / 0.07–1.03
Fe	8.8 / 2.9–13.1	14.1 / 7.5–28.3
Al	4.8 / 3.6–5.9	3.6 / 1.6–8.7
Sr	1.3 / 0.7–1.9	2.4 / 0.7–4.7
Se	1.13 / 0.12–2.24	1.96 / 0.8–3.5
Mo	0.15 / 0.08–0.35	0.4 / 0.13–1.01
Sb	0.6 / 0.2–1.3	0.9 / 0.23–2.23
V	0.15 / 0.05–0.3	0.26 / 0.06–0.5
Li	0.03 / 0.006–0.12	0.008 / 0.002–0.018
Cs	0.11 / 0.01–0.24	0.1 / 0.02–0.4

Note:
* SanPiN 2.3.2.1078-01 Hygiene Requirements for Safety and Nutritional Value of Food Products (as amended on 06.07.2011).

In this work, Cr, Mn, Ni, Cu, Zn, and Pb content in some samples exceeded TLV in fish recommended by FAO/WHO. Results of monitoring in Rooppur NPP area showed that in some fish samples Mn concentration was slightly higher than FAO standard [31], and Sb concentration in several samples exceeded FAO/WHO recommendations [15]. These metals do not pose a carcinogenic hazard, but their combined effects can negatively affect human health.

Conclusion. Based on radiation and environmental monitoring of freshwater ecosystems in Rooppur NPP 30-km zone (2014–2017), it can be concluded that the ecological situation in this area is generally favorable. It is determined by both the climatic peculiarities of the region and anthropogenic impact.

It is shown that organic pollutants content in surface water and groundwater is below detection limits or at minimum ones (benzopyrene – less than 0.01 $\mu g \cdot L^{-1}$; phenols – 1.3–3.5 $\mu g \cdot L^{-1}$; and petroleum products – 0.01–0.043 $mg \cdot L^{-1}$). The volumetric activity of ^{137}Cs in Padma River waters during the entire observation period did not exceed 0.18 $Bq \cdot L^{-1}$ (with a mean of 0.07 $Bq \cdot L^{-1}$). The content of ^{90}Sr was in the range of 0.02–0.12 $Bq \cdot L^{-1}$, and that of ^{3}H – in the range of 0.8–2.1 $Bq \cdot L^{-1}$. Mean specific activity of ^{90}Sr in bottom sediments varied from 0.5 to 1.8 $Bq \cdot kg^{-1}$, and ^{137}Cs – from 0.8 to 2.1 $Bq \cdot kg^{-1}$. Specific activity of ^{3}H in bottom sediments was less than 3 $Bq \cdot kg^{-1}$, except for three samples in 2017 (12–30 $Bq \cdot kg^{-1}$), which is most likely due to a local pollution. Specific activity of ^{90}Sr in higher aquatic vegetation was at the level of 0.4–3.9 $Bq \cdot kg^{-1}$, and ^{137}Cs – of 0.4–1.0 $Bq \cdot kg^{-1}$. In drinking water, the volumetric activity of standardized radionuclides varied in the ranges as follows: ^{137}Cs – 0.03–0.27 $Bq \cdot L^{-1}$; ^{90}Sr – 0.01–0.16 $Bq \cdot L^{-1}$; ^{3}H – 0.4–1.2 $Bq \cdot L^{-1}$. Specific activity of ^{90}Sr in fish varied from 0.02 to 1.6 $Bq \cdot kg^{-1}$. The content of ^{137}Cs in fish was in the range of 0.26–0.3 $Bq \cdot kg^{-1}$.

The situation in the area studied on pollution of freshwater ecosystems with heavy metals is somewhat worse, which is caused by the discharge of toxicants by industrial enterprises. As content in Padma River water is at the level of 0.9–3.6 (with a mean of 2.6 $\mu g \cdot L^{-1}$). Ni concentration varies within 1.7–19.5 $\mu g \cdot L^{-1}$. The maximum Cu content in Padma River waters during the observation period reached 7.7 $\mu g \cdot L^{-1}$. Mn concentration varied in the range of 1.7–51.9 $\mu g \cdot L^{-1}$. Fe content in surface water averaged 0.03–0.2 $mg \cdot L^{-1}$ (with a maximum of 0.8 $mg \cdot L^{-1}$). Analysis of the data on Al content in Padma River water showed that in almost half of the samples, its concentration was higher than threshold limit value, and the highest value reached 595 $\mu g \cdot L^{-1}$, which exceeds TLV by 3 times. Mean As concentration in bottom sediments exceeded its TLV in soil by more than 35 times and correlated with the data on its content in Padma River surface water. Mean Cd concentration in bottom sediments was 1.3–2.7 $mg \cdot kg^{-1}$, which exceeded soil approximate permissible concentrations by 1.5–2.5 times. Pb content in bottom sediments was 3.6–25.4 $mg \cdot kg^{-1}$. During some years of monitoring, an excess in As content in drinking water in the vicinity of Rooppur NPP was registered. Mn concentration in groundwater of this area during the entire observation period varied from 52 to 1036 $\mu g \cdot L^{-1}$. In all drinking water samples of 2016–2017, Mn content exceeded the upper limit established by international and Russian standards.

Monitoring network established will make it possible to register changes in the situation in the zone of Rooppur NPP impact, as well as to identify the impact of power plant operation on the environment, including the Bay of Bengal in the Indian Ocean. The results obtained during the radioecological studies of components of freshwater ecosystems will make it possible to estimate dose commitments on humans and hydrobionts due to technogenic-altered background in the region.

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КОМПЛЕКСНЫЙ РАДИАЦИОННО-ЭКОЛОГИЧЕСКИЙ МОНИТОРИНГ ВОДНЫХ ЭКОСИСТЕМ В РЕГИОНЕ РАЗМЕЩЕНИЯ АЭС «РУППУР» (НАРОДНАЯ РЕСПУБЛИКА БАНГЛАДЕШ)*

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Представлен опыт создания и ведения системы радиационно-экологического мониторинга водных экосистем в регионе АЭС «Руппур» (Бангладеш). Компоненты водных экосистем в зоне влияния АЭС являются как наиболее информативными для определения состояния окружающей среды, так и важными с точки зрения ведения хозяйственной деятельности. Именно поэтому оценка и прогнозирование качества водных экосистем в районе АЭС — актуальная проблема для обеспечения радиационной и экологической безопасности. Разработана детализированная программа мониторинга; выбраны пункты наблюдения за состоянием поверхностных и подземных вод на разном расстоянии от АЭС «Руппур»; определены объекты мониторинга (вода, донные отложения, высшая водная растительность, рыба), перечень исследуемых параметров, регламент наблюдений, а также методы и нормативно-техническое обеспечение. В числе контролируемых показателей рассмотрены: физико-химические характеристики воды и донных отложений; радионуклидный состав компонентов водных экосистем, включающий природные (^{40}K, ^{226}Ra, ^{232}Th) и техногенные (^{90}Sr, ^{137}Cs, ^{3}H) радионуклиды; содержание 19 тяжёлых металлов, а также химических загрязнителей. Мониторинговые исследования проведены в 2014–2017 гг. на фоновом уровне и на этапе строительства АЭС «Руппур» с учётом климатических особенностей региона в различные периоды года. Радионуклиды в объектах окружающей среды определены методами спектрометрии и радиохимии, тяжёлые металлы — атомно-абсорбционным и плазменно-эмиссионным методами анализа. Установлено, что высшая водная растительность в реке Падма (Ганг) встречается не во все сезоны. В декабре она фактически отсутствует; максимальное видовое разнообразие отмечено в июне. Выделены различия между поверхностными и подземными водами в регионе АЭС «Руппур» по ряду физико-химических характеристик. Показатели общей минерализации и жёсткости в питьевой воде выше, чем в поверхностной, в 2–3 раза, что обусловлено составом вод р. Падма, основа которых — талые воды ледников гор и дождевая вода. Содержание в поверхностных и подземных водах органических загрязнителей ниже или на уровне порога их обнаружения приборами (бензпирен — менее 0,01 мкг·л$^{-1}$; фенолы — 1,3–3,5 мкг·л$^{-1}$; нефтепродукты — 0,01–0,043 мг·л$^{-1}$). Объёмная активность в водах р. Падма ^{137}Cs за весь период наблюдений не превышала 0,18 Бк·л$^{-1}$ при среднем значении 0,07 Бк·л$^{-1}$. Содержание ^{90}Sr было в диапазоне 0,02–0,12 Бк·л$^{-1}$, а ^{3}H — в пределах 0,8–2,1 Бк·л$^{-1}$. Средняя удельная активность ^{90}Sr в донных отложениях варьировала в диапазоне 0,5–1,8 Бк·кг$^{-1}$, а ^{137}Cs — 0,8–2,1 Бк·кг$^{-1}$. Удельная активность ^{3}H в донных отложениях составляла менее 3 Бк·кг$^{-1}$, за исключением трёх проб в 2017 г. (12–30 Бк·кг$^{-1}$), что обусловлено, по всей видимости, локальным загрязнением. Удельная активность ^{90}Sr в высшей водной растительности была на уровне 0,4–3,9 Бк·кг$^{-1}$, а ^{137}Cs — 0,4–1,0 Бк·кг$^{-1}$. В питьевой воде объёмная активность нормируемых радионуклидов колебалась в следующих диапазонах: ^{137}Cs — 0,03–0,27 Бк·л$^{-1}$, что в 40 раз ниже уровня вмешательства по НРБ-99/2009; ^{90}Sr — 0,01–0,16 Бк·л$^{-1}$ (в 30 раз ниже норматива); ^{3}H — 0,4–1,2 Бк·л$^{-1}$ (более чем в 6 тыс. раз ниже уровня вмешательства). Удельная активность ^{90}Sr в рыбе варьировалась в диапазоне 0,02–1,6 Бк·кг$^{-1}$, что в 60 раз ниже российских и международных стандартов. Содержание ^{137}Cs

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в рыбе было в пределах 0,26–0,3 Бк·кг$^{-1}$, что в 400 раз ниже российских нормативов и более чем в 3 тыс. раз — международных. Анализ данных наблюдений за уровнями загрязнения тяжёлыми металлами компонентов водных экосистем в регионе АЭС «Руппур» показал, что по ряду элементов зарегистрированы их повышенные концентрации, бóльшая часть которых относится к сезону муссонов. Так, в поверхностных водах р. Падма отмечено периодическое увеличение содержания As, Cd, Mn, Al, а в донных отложениях — As, Cd, Ni, Co, Zn, что связано с антропогенным влиянием и с усиленным стоком загрязняющих веществ в период муссонных дождей. В питьевой воде 30-километровой зоны АЭС «Руппур» зафиксированы периодические повышенные концентрации As и Mn, а в отдельных пробах — Fe и Al, что может быть обусловлено как природными особенностями региона (относительно высокое содержание As в водоносных горизонтах), так и состоянием систем водоснабжения. Заложенная сеть радиационно-экологического мониторинга водных экосистем позволяет регистрировать изменение ситуации в регионе размещения АЭС «Руппур» и выявлять влияние работы атомной электростанции на человека и окружающую среду.

Ключевые слова: Бангладеш, АЭС «Руппур», водные ресурсы, пресноводные экосистемы, река Падма, питьевая вода, радиоэкологический мониторинг, радионуклиды, тяжёлые металлы, химическое загрязнение

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^{137}CS CONCENTRATION IN SURFACE WATERS OF FAR EASTERN SEAS: RESULTS OF EXPEDITIONARY RESEARCH IN 2018*

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Based on the results of expeditionary research carried out during the 82nd cruise of the RV "Akademik M. A. Lavrentyev" (01.06.2018–20.07.2018), the assessment of current levels of concentration activity of technogenic radionuclide ^{137}Cs in surface waters of Far Eastern seas is given. The studies were carried out in the northwestern part of the Sea of Japan, the southern part of the Sea of Okhotsk, the coastal waters of the Pacific Ocean near the Kamchatka Peninsula, and the western part of the Bering Sea. Activity of ^{137}Cs in seawater samples was determined by sorption method using two series-connected adsorbers with subsequent measurement of ^{137}Cs content *via* its gamma-emitting daughter radionuclide ^{137m}Ba. Sorption efficiency was assessed by the difference in activity on the first and second adsorbers. A comparative analysis of contamination levels of water areas studied was made. It was revealed that ^{137}Cs volumetric activity in surface water of the Sea of Japan varied from (2.9 ± 0.1) to (5.1 ± 0.3) Bq·m^{-3}, in the Sea of Okhotsk – from (1.8 ± 0.1) to (2.3 ± 0.1) Bq·m^{-3}, and in the Bering Sea – from (1.7 ± 0.1) to (3.1 ± 0.1) Bq·m^{-3}. The maximum ^{137}Cs concentrations were registered in the Sea of Japan, which might be due to its isolation from other water areas and presence of secondary sources of radionuclide intake. In general, contamination of adjacent water areas is insignificant, and fluctuations in concentrations occur within technogenic isotopes global background in the marginal seas of the Pacific Ocean.

Keywords: ^{137}Cs, concentration, seawater, Far Eastern seas

Currently, one of the key markers radioactive contamination of biosphere, including aquatic ecosystems, is long-lived radionuclide ^{137}Cs with a half-life being 30.17 years [10 ; 14]. The main sources of intake of technogenic radionuclides, including ^{137}Cs, into the northern part of the Pacific Ocean and its marginal seas were global fallout after testing nuclear weapon in open environments in the 1950–1960s, as well as the accident at the Chernobyl Nuclear Power Plant (hereinafter NPP) in 1986. According to researchers, ^{137}Cs fallout over the water area of the northern part of the Pacific Ocean as a result of nuclear tests amounted to about 104 PBq [10 ; 13].

In the XXI century, Far Eastern seas were exposed to radioactive contamination after the accident at the Fukushima Daiichi NPP. The disaster occurred on 11.03.2011; it was caused by a magnitude 9.0

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earthquake and an enormous tsunami. As a result, electricity supply at the Fukushima Daiichi NPP, located on the eastern coast of Japan (Honshu Island), was interrupted. Power units were damaged, and this led to a release into the atmosphere of such radioactive products as ^{137}Cs, ^{134}Cs, and ^{131}I. They were transported over long distances by air masses, namely eastward to the Pacific Ocean since westerly winds were prevailing in disaster zone. In addition, seawater was used to cool the damaged reactors, and then it was discharged into adjacent sea area [5]. This resulted in contamination of Pacific Ocean waters with technogenic radionuclides. According to various estimates, from 4 to 41 PBq of radioactive cesium entered marine environment due to accidental discharge [12 ; 15 ; 21]. For comparison, we present data on ^{137}Cs intake into the World Ocean as a result of other nuclear events: global fallout – 600 PBq; Sellafield radiological releases – 39 PBq; and Chernobyl fallout – 18 PBq [13]. The scale of the disaster in terms of ^{137}Cs release because of the accident at the Fukushima Daiichi NPP is comparable to that caused by the accident at the Chernobyl NPP.

The change in technogenic isotopes concentration in waters of Far Eastern seas, contaminated by the Fukushima Daiichi NPP discharge, is the result of hydrodynamic processes: transport by currents and water exchange [5 ; 18]. Pacific currents, washing Honshu Island coast, transport water masses northward and eastward to the open ocean, thereby preventing the transport of accidental radionuclides to Far Eastern seas [14]. In this regard, radioactive discharge after the disaster had little impact on the radioecological situation in Far Eastern seas, in particular in coastal waters of Russia; this was confirmed by numerous studies [1 ; 4 ; 6]. Meanwhile, ^{134}Cs was detected in 2017 in surface water and in water up to 200 m of the western subarctic part of the Pacific Ocean; this means that cesium radioisotopes continue entering the region [19]. Potential sources of ^{137}Cs intake into marine environment of Far Eastern seas are disposals of nuclear fleet reactors in the bays of the Sea of Japan and in Kamchatka coastal area [7 ; 8].

Thus, the radioecological situation in Far Eastern seas is still of great concern. The risk of technogenic isotopes intake into marine environment from the sources listed above requires regular monitoring. The aim of this study is to assess current concentrations of technogenic radionuclide ^{137}Cs in surface waters of Far Eastern seas and make a comparative analysis of contamination levels of these water areas.

MATERIAL AND METHODS

The material for the study was taken during the 82nd cruise of the RV “Akademik M. A. Lavrentyev” (01.06.2018–20.07.2018) in the northwestern part of the Sea of Japan, the southern part of the Sea of Okhotsk, the coastal waters of the Pacific Ocean near the Kamchatka Peninsula, and the western part of the Bering Sea (Fig. 1). To analyze the content of technogenic radionuclide ^{137}Cs, surface water samples were taken using RV flow system.

The samples were taken as follows: 3 seawater samples in the Sea of Japan; 3 samples in the Sea of Okhotsk; 3 samples in the coastal area of the Pacific Ocean near the Kamchatka Peninsula; and 5 samples in the Bering Sea.

Activity concentration of ^{137}Cs in seawater samples (100 L) was determined by sorption method using two series-connected adsorbers with subsequent measurement of ^{137}Cs content *via* its gamma-emitting daughter radionuclide ^{137m}Ba [20]. Water sample taken was first filtered through a polypropylene filter with a nominal pore size of 0.5 μm to remove suspended matter. Then, the filtrate was passed through plastic 10-mL adsorbers filled with a loose sorbent. This inorganic composite sorbent is a thin film of mixed nickel-potassium ferrocyanide, obtained by a chemical method

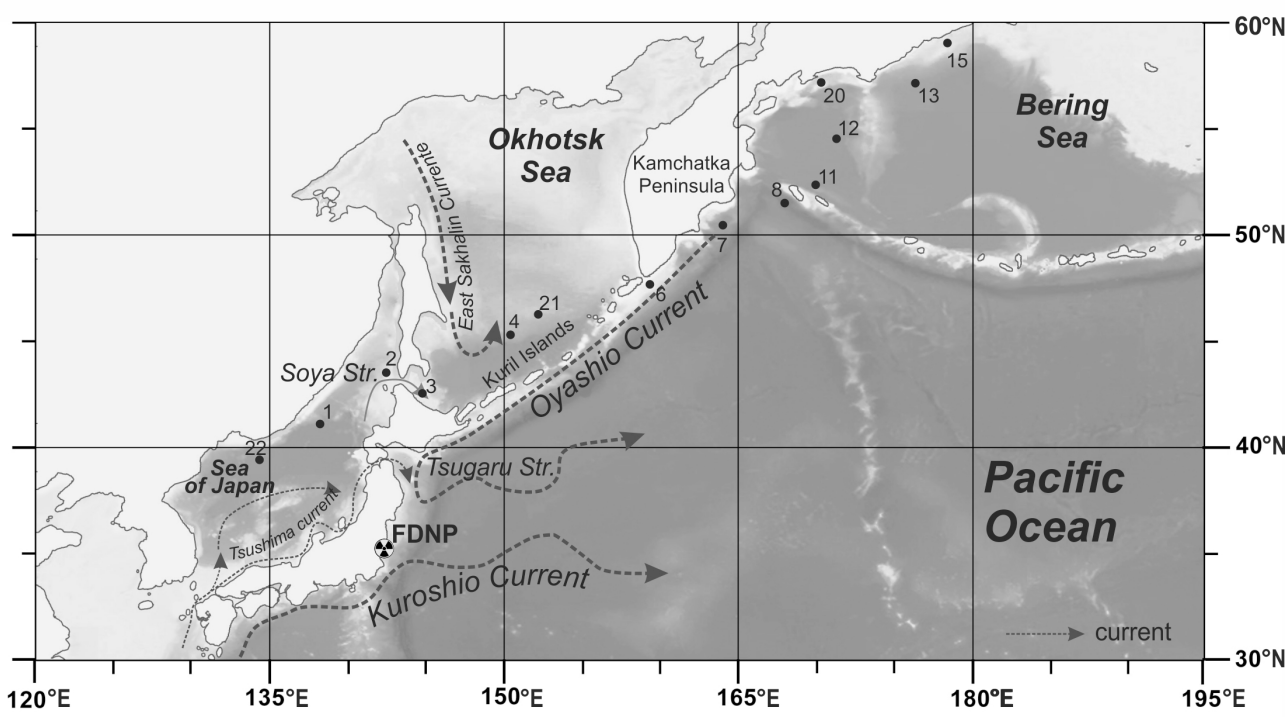

Fig. 1. Station map of the 82nd cruise of the RV "Akademik M. A. Lavrentyev"

from water solutions on a carrier, being delignified wood flour. The approximate composition of the film is $K_{1.33}Ni_{1.33}[Fe(CN)_4]$; the grade is NPF-C [2]. Sorbent mass in one absorber is 2.5 g; sorbent height in a column is 7 cm; column diameter is 1.5 cm. The water filtered was passed through the adsorbers using a peristaltic pump (Elpan 372.C, Poland) at a rate of 0.07 L·min^{-1}, at which extraction efficiency of ^{137}Cs ranged 46–94 %. To reduce sorbents volume, they were burned in a muffle furnace at a temperature of +400 °C; sorbent mass after ashing was about 0.8 g. Then, the sorbent ashed was placed into bottles for gamma-spectrometric measurements. Content of ^{137}Cs in the samples was determined using a 1282-CompuGamma counter (LKB Wallac, Finland) with a counting geometry close to 4π (well type detector), taking into account radioactive background and detection efficiency of ^{137}Cs radiation. Sorption efficiency was assessed by the difference in activity on the first and second adsorbers. Then, ^{137}Cs activity concentration (Bq·m^{-3}) in the water sample was calculated [20].

RESULTS

The results of determining ^{137}Cs content in surface water of areas studied are presented in Table 1.

Table 1. Sampling stations and ^{137}Cs concentration in seawater based on the results of the 82nd cruise of the RV "Akademik M. A. Lavrentyev"

Station number	Water area	Coordinates	Date	Depth, m	^{137}Cs concentration, Bq·m^{-3}
1	The Sea of Japan	43°34′15.6″N, 136°03′21.6″E	03.06.2018	3288	3.9 ± 0.2
2	The Sea of Japan	45°33′40.8″N, 140°20′47.4″E	04.06.2018	446	5.1 ± 0.3

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Station number	Water area	Coordinates	Date	Depth, m	^{137}Cs concentration, Bq·m^{-3}
3	The Sea of Okhotsk	45°50′27″N, 143°10′42.6″E	04.06.2018	102	2.1 ± 0.1
4	The Sea of Okhotsk	48°03′45.6″N, 149°07′10.2″E	05.06.2018	2820	2.3 ± 0.1
6	The Pacific Ocean	50°19′23.4″N, 157°02′11.4″E	07.06.2018	431	2.7 ± 0.1
7	The Pacific Ocean	53°08′22.2″N, 161°27′45.6″E	08.06.2018	3720	3.4 ± 0.2
8	The Pacific Ocean	55°20′35.4″N, 165°54′25.8″E	09.06.2018	40	2.9 ± 0.1
11	The Bering Sea	55°21′27.6″N, 167°16′08″E	18.06.2018	1226	2.3 ± 0.1
12	The Bering Sea	58°18′40.8″N, 169°50′25.8″E	22.06.2018	1586	2.2 ± 0.1
13	The Bering Sea	60°49′31.8″N, 174°24′31.2″E	23.06.2018	729	3.1 ± 0.1
15	The Bering Sea	62°01′06″N, 175°20′33″E	26.06.2018	30	1.7 ± 0.1
20	The Bering Sea	60°23′59.4″N, 167°30′08″E	07.07.2018	20	2.0 ± 0.1
21	The Sea of Okhotsk	49°09′46.2″N, 151°40′47.4″E	11.07.2018	1527	1.8 ± 0.1
22	The Sea of Japan	42°43′06″N, 132°17′49.8″E	15.07.2018	70	2.9 ± 0.2

DISCUSSION

Concentration of ^{137}Cs at the stations under study in the Sea of Japan ranged from (2.9 ± 0.1) to (5.1 ± 0.3) Bq·m^{-3} (Table 1).

The Sea of Japan is separated from other Pacific seas and the Pacific Ocean by the Japanese Archipelago [3]. Water exchange with adjacent areas occurs through the straits as follows: Korea, Tsugaru, Sōya, and Nevelskoy [3]. The currents passing through the Tsugaru Strait, connecting the Sea of Japan with the Pacific Ocean, are directed mainly from west to east; this prevented accidental discharge from the Fukushima Daiichi NPP into the Sea of Japan.

On the other hand, in the first months after the Fukushima Daiichi NPP disaster, the short-lived radionuclide ^{134}Cs with a half-life being 2.06 years was detected in Sea of Japan surface waters; it entered seawater with precipitation immediately after the accident [14 ; 17]. Radioactive cesium content can increase, especially in the coastal area, due to its intake into marine environment with precipitation and from Sea of Japan catchment area.

Peculiarities of water exchange and the isolation of the Sea of Japan from adjacent seas and oceans can also contribute to technogenic radionuclides accumulation in water [3]. During our studies, the maximum activity concentration of ^{137}Cs [(5.1 ± 0.3) Bq·m^{-3}] was recorded in the northeastern part of the Sea of Japan (see Table 1) in the area of the shallow-water Sōya Strait (station No. 2). The data obtained

are consistent with the results of the expedition carried out in April – May 2011: ^{137}Cs activity concentration in the coastal area of the Sea of Japan was estimated at 1.5–2.0 Bq·m^{-3} [1 ; 4]. In 2014, ^{137}Cs activity concentration in coastal and central areas of the Sea of Japan was 4.2 and 5.0 Bq·m^{-3}, respectively [1]. According to the studies carried out in 2018, ^{137}Cs activity concentration values in the northwestern part of the Sea of Japan ranged from (2.1 ± 0.4) to (7.8 ± 1.1) Bq·m^{-3} [22]. In addition, a relatively high ^{137}Cs content was recorded in coastal water area adjacent to the Chazhma Bay [(46.0 ± 3.4) Bq·m^{-3}], which is associated with consequences of an explosion on the nuclear-powered submarine K-431 in 1985 [22]. Thus, after the Fukushima Daiichi NPP disaster, ^{137}Cs activity concentration doubled by 2014 and actually did not change by 2018. This may indicate stabilization of the processes of radionuclides intake into the water body. The levels of ^{137}Cs concentration in water are determined by such factors as secondary radionuclides intake from the continental runoff, desorption from bottom sediments, and transport by currents [9].

The Sea of Okhotsk is separated from the Pacific Ocean by the Kuril Islands and is connected with the Sea of Japan through the Sōya Strait and the Strait of Tartary [3]. In 2009, ^{137}Cs concentrations in Sōya Strait area ranged 1.0–1.6 Bq·m^{-3}; in June 2011, the level of radioactive cesium in the area increased to 3.4 Bq·m^{-3} [17]. In 2018, ^{137}Cs activity concentration in Sea of Okhotsk waters to the north of the Sōya Strait along the Kuril Chain decreased to the range from (1.8 ± 0.1) to (2.3 ± 0.1) Bq·m^{-3} (Table 1). The maximum was observed at station No. 3 directly at the Sōya Strait outlet.

This strait is indicative in assessing water masses transport between adjacent water areas [17]. It was determined that through the Sōya Strait, despite its shallowness, water masses with a higher ^{137}Cs content are transported. In turn, water masses with a lower ^{137}Cs content enter this area with East Sakhalin Current waters, and due to this its concentration at the boundary of two seas decreases. Our research confirms this conclusion. It is worth noting that ^{137}Cs activity concentration estimates, obtained in 2018 by another group of researchers, in the southern part of the Sea of Okhotsk were from (1.2 ± 0.5) to (38.3 ± 3.5) Bq·m^{-3} [22]. The authors explain the presence of relatively high values of ^{137}Cs content in surface waters of this area by the consequences of the accident at the Fukushima Daiichi NPP, but this fact obviously needs further, more detailed studies.

In the Pacific Ocean at stations No. 6, 7, and 8, ^{137}Cs concentration was registered in the range from (2.7 ± 0.1) to (3.4 ± 0.2) Bq·m^{-3} (Table 1). In 2000, the level of ^{137}Cs concentration in the northern part of the Pacific Ocean and its adjacent seas was about 1.0–2.0 Bq·m^{-3} [11 ; 23] (according to other estimates, it was 1.7–2.8 Bq·m^{-3} [16]). In 2011, ^{137}Cs activity concentration in surface water along the Kuril Chain in the Pacific Ocean was in the range from 1.4 to 3.6 Bq·m^{-3} [4]. Thus, the levels of radiocesium contamination in water areas studied are comparable to those in adjacent water areas.

The results of the studies in 2018 [22] show that the values of ^{137}Cs activity concentration in surface waters near the Kamchatka Peninsula were in the range from (3.2 ± 0.8) to (12.2 ± 2.4) Bq·m^{-3}. In the Bering Sea, the average ^{137}Cs concentration in coastal waters was (1.85 ± 0.1) Bq·m^{-3} (stations No. 15 and 20); in open water areas – (2.7 ± 0.1) Bq·m^{-3}. At the Bering Sea – Pacific Ocean boundary, ^{137}Cs concentrations registered were as follows: (2.3 ± 0.1) and (2.9 ± 0.1) Bq·m^{-3} (stations No. 8 and 11, respectively) (Table 1). These data are consistent with the results obtained in this area by another group of researchers: from (2.8 ± 0.4) to (6.3 ± 1.5) Bq·m^{-3} [22]. Before the Fukushima Daiichi NPP disaster, similar ^{137}Cs concentrations were registered in the Bering Sea: 1.0–2.0 Bq·m^{-3} [11]. Currents, transporting the accidental discharge of the Fukushima Daiichi NPP, do not enter Bering Sea water area (Fig. 1).

Thus, it has been established that the levels of ^{137}Cs concentration in surface waters of the Sea of Japan are higher (on average, 1.65 times) than those in the Sea of Okhotsk and the Bering Sea. Comparison between the data on contamination level in 2018 and the data before and after the Fukushima Daiichi NPP disaster reveals as follows: in the Sea of Japan, being isolated from other water areas, ^{137}Cs activity concentration in surface waters increases. The increase in concentrations seems to be due not only to hydrological peculiarities of the water area but also to isotope intake into the sea with continental waters. Comparison of the results of our study with the data of 2018, obtained by another group of researchers using a different method [22], allows us to draw a conclusion about the reliability of our results. According to [22], relatively high values of ^{137}Cs activity concentration in the Sea of Japan near the Chazhma Bay can be explained by the consequences of the accident in 1985. Interpretation of higher point values in the southern part of the Sea of Okhotsk, as well as near the Kamchatka Peninsula, requires further research. We have registered no high concentrations due to the lack of data in the areas indicated.

Analysis of both literature and our data shows that ^{137}Cs activity concentration in the seas studied in 2000–2018, including the period after the accident at the Fukushima Daiichi NPP, is in the range 1.0–5.1 Bq·m^{-3}, which corresponds to technogenic background for this radionuclide. Distribution patterns of ^{137}Cs in waters of Far Eastern seas have to be studied additionally.

Conclusion. Data on technogenic radionuclide ^{137}Cs content in surface waters of the Sea of Japan, the Sea of Okhotsk, and the Bering Sea have been obtained. It has been established that the maximum levels of radioactive cesium contamination are characteristic of surface waters of the Sea of Japan. Weak water exchange results in a gradual radionuclide accumulation in this water area. Contamination of adjacent water areas is insignificant; concentration fluctuations are within technogenic isotopes global background in the marginal seas of the Pacific Ocean. To reveal more complete information on ^{137}Cs distribution in Far Eastern seas, additional studies with more initial data are required.

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ОЦЕНКА СОДЕРЖАНИЯ ^{137}CS В ПОВЕРХНОСТНЫХ ВОДАХ ДАЛЬНЕВОСТОЧНЫХ МОРЕЙ ПО РЕЗУЛЬТАТАМ ЭКСПЕДИЦИОННЫХ ИССЛЕДОВАНИЙ 2018 ГОДА*

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По результатам экспедиционных исследований в 82-м рейсе НИС «Академик М. А. Лаврентьев» (01.06.2018–20.07.2018) выполнена оценка современных уровней объёмной активности техногенного радионуклида ^{137}Cs в поверхностных водах морей Дальнего Востока. Исследования проводили в северо-западной части Японского моря, южной части Охотского моря, прибрежной

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акватории Тихого океана в районе полуострова Камчатка, а также в западной части Берингова моря. Концентрацию ^{137}Cs в пробах морской воды определяли сорбционным методом с использованием двух последовательно соединённых адсорберов с последующим измерением содержания ^{137}Cs по гамма-излучению дочернего радионуклида ^{137m}Ba. Эффективность сорбции оценивали по разнице активностей на первом и втором адсорберах. Проведён сравнительный анализ уровней загрязнения исследуемых акваторий. Установлено, что объёмная активность ^{137}Cs в поверхностной воде Японского моря варьировала в пределах от (2,9 ± 0,1) до (5,1 ± 0,3) Бк·м$^{-3}$, в Охотском море — от (1,8 ± 0,1) до (2,3 ± 0,1) Бк·м$^{-3}$, в Беринговом море — от (1,7 ± 0,1) до (3,1 ± 0,1) Бк·м$^{-3}$. Максимальные концентрации ^{137}Cs отмечены в Японском море, что может быть связано с его изолированностью от других акваторий и с наличием вторичных источников поступления радионуклидов. В целом загрязнение прилегающих акваторий незначительно; флуктуации концентраций происходят в пределах глобального фона техногенных изотопов в окраинных морях Тихого океана.

Ключевые слова: ^{137}Cs, концентрация, морская вода, дальневосточные моря

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ADAPTATION OF NATURAL YEAST STRAINS TO HEAVY METAL AND RADIONUCLIDES SALTS*

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Ability of natural yeast strains to grow in conditions of high concentrations of heavy metal and radionuclides salts was studied. More than 500 strains were tested for resistance to salts of heavy metals (U, Cs, Sr, Ni, Ar, Cu, Cd, and Co) and to elevated temperature (t) (+37…+52 °C). Most of the strains tested were resistant to one or more selective factors. Combinations of (t, Cd, Cu, Co) and (Cd, Cu, Co) occurred with the highest frequencies: 36 and 26 %, respectively. Ability of isolated strains to grow in the presence of high concentrations of radioactive isotopes Cs and Ni and to bind them with high efficiency was established. The results showed the possibility of potential using of libraries of natural microorganisms for disposal of both radionuclides and heavy metals, which are the main pollutants of natural and anthropogenic objects, as well as the possibility of using of isolated and tested strains of microorganisms for concentrating metals from low-grade ores or mining industry waste. Phenotypes diversity revealed indicates probable existence of several mechanisms of resistance to high heavy metals concentrations.

Keywords: natural yeast strains, adaptation, heavy metals, radioisotopes ^{137}Cs and ^{63}Ni, bioremediation

Activity of industrial enterprises, especially metallurgical, mining, and nuclear ones, inevitably results in discharge of pollutants into the environment and in deterioration of ecosystems due to heavy metals accumulation in them [24]. For this reason, increasing attention has to be paid to potential health hazards caused by the presence of this type of pollutants in the environment. Their removal requires applying of economical and effective methods, and this leads to development of new technologies [24]. Disposal, ion exchange, and electrochemical and/or membrane processes are widely used for industrial wastewater treatment. However, application of these processes in some cases is impossible due to technical or economic reasons [12]. The search for new technologies for the removal of toxic metals from liquid waste leads to biosorption methods based on ability of various biosorbents, including microorganisms, to bind metals. Microorganisms in the environment play the main role both in elements circulation in nature and in formation of sedimentary rocks. They also affect geochemical properties of groundwater due to modification and transport of organic and inorganic pollutants [11]. While organic pollutants

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can be decomposed to CO_2 and water [17 ; 25], radionuclides can be only immobilized. When developing bioremediation methods, it has to be taken into account that at low concentrations many metals can play an important role in metabolic processes, but at high concentrations they often become toxic.

Biosorption is considered a way not only to remove toxic metals from solutions but also to obtain precious metals. Thus, the binding of heavy metals, including radionuclides, requires the search for microorganisms that both sorb metals selectively and remain viable in the presence of radioactive contamination with a level of volumetric activity up to 370 $kBq \cdot mL^{-1}$, as in technological waste [8]. It can be assumed that microorganisms with such properties can primarily live in natural and technogenic environments under conditions being extreme for their existence, as in the Kamchatka Peninsula and the Kuril Islands areas, as well as in technological waters of reactors, in water treatment systems of industrial enterprises, and in storage lakes of liquid technological waste from radiochemical plants.

The aim of this work was to study the possibility of using the collection of microorganisms for sorption of various heavy metals and radionuclides. The microorganisms were collected by the employees of the Petersburg Nuclear Physics Institute named by B. P. Konstantinov in the Kamchatka Peninsula and the Kuril Islands.

MATERIAL AND METHODS

The study was carried out using a collection of microorganisms (over 2000 yeast and yeast-like fungi strains) collected by the employees of the Petersburg Nuclear Physics Institute named by B. P. Konstantinov during expeditions to areas with geothermal activity (Kamchatka Peninsula; Kunashir and Iturup islands of the Kuril Chain). Initial substrate used for isolation of microorganisms was living plants (flowers, fruits, bark, leaves, and roots) and their fallen parts, as well as soil and insects. Samples were collected on volcanoes slopes, in valleys along rivers and streams, near hydrothermal vents, and inside active zones.

To identify natural strains from material canned, filters were transferred to Petri dishes with a dense enriched medium D (YPD; 2 % glucose; 1 % peptone; and 0.5 % yeast extract); from there, as the colonies grew at room temperature, the cells were inoculated again onto the dense D-medium by a streaking technique. Dishes with yeast-like fungi colonies were tested under a binocular magnifier and identified by morphological characteristics: color, shape, size, and surface character. Taxonomic determination was carried out using the method described in species guides [7 ; 13]. Not only the species name but also the numbers according to the collection catalog are given (indicated in the parentheses). The collection consists mainly of unicellular fungi that can exist in the medium containing fairly high levels of ions of almost all metals.

Sensitivity of fungi strains to high uranium concentrations was determined by the replica method [2] on dishes with agar and the nutrient D-medium containing 10, 120, and 150 $mmol \cdot L^{-1}$ of $^{238}UO_2(CH_3COO)_2$.

Selection of strains being resistant to high Ni content was carried out on dishes with a concentration gradient of nickel chloride. Nutrient agar was poured into sterile Petri dishes and left to cool down at an angle. After cooling, agar with the metal tested was inoculated (in this case, it was 10 $mmol \cdot L^{-1}$ of Ni). To evaluate nickel binding efficiency by the strains isolated, radioactive isotope ^{63}Ni was subsequently used.

Selection of fungi strains capable of growing in the presence of Cs^+ ions was carried out at various concentrations of stable cesium in the form of chloride (CsCl). So, a solution of 1 $mol \cdot L^{-1}$ of CsCl was prepared and added to the nutrient D-medium with agar so that final cesium concentration

was 10, 50, or 100 mmol·L^{-1}. Cell cultures were inoculated onto agar surface by a streaking technique; dishes were placed in a thermostat at +30 °C. Only the strains, being well-growing at maximum Cs^+ ions content, were used. In addition, from the strains selected, we used only those, that could grow in dishes containing CsCl and $SrCl_2$ at concentrations of 100 mmol·L^{-1}, *i. e.* were tolerant to several metals. Resistance was determined by the replica method.

Sensitivity of the strains selected to gamma irradiation inactivating effect was determined using an "Issledovatel" setup (^{60}Co) at a dose rate 100 Gy·min^{-1}.

To study the ability of free cells to bind radioactive ^{137}Cs or ^{63}Ni, cells from a culture, grown to a stationary phase in the D-medium, were inoculated onto fresh D-medium in a ratio 1:100; then either ^{137}Cs was added to 110 kBq·mL^{-1} or ^{63}Ni was added to 111 kBq·mL^{-1}. As they grew, two samples of equal volume (0.5 mL) were taken in parallel from each culture, transferred to 1.5-mL Eppendorf tubes, and deposited at 10,000 rpm for 10 minutes.

Amount of ^{137}Cs or ^{63}Ni in deposit and supernatant was determined using a Beckman LS 6500 counter (USA).

Efficiency of cesium or nickel radioactive isotopes binding by cells was determined as a percentage of the ratio of radioactivity in the deposit to the total sample radioactivity.

Efficiency of nickel binding by cells was optimized by changing glucose concentration in the growth medium.

For each strain, at least three independent experiments were made, according to which the mean value (see Fig. 3, Fig. 4, Fig. 5, and Table 1) and the mean standard error of a small sample were determined (Table 1).

RESULTS

Totally 2107 strains were isolated and microbiologically purified from the material collected. About 100 strains were identified. Among them, there were representatives of 21 species: *Candida haemulonii*, *Candida sake*, *Candida sorbosivorans*, *Cryptococcus albidus*, *Cryptococcus hungaricus*, *Cryptococcus laurentii*, *Debaryomyces hansenii*, *Pichia farinosa*, *Rhodotorula aurantiaca*, *Rhodotorula glutinis*, *Rhodotorula minuta*, *Rhodotorula mucilaginosa*, *Phaffia rhodozyma*, *Saccharomyces cerevisiae*, *Torulaspora delbrueckii*, *Tremella foliacea*, *Sporobolomyces roseus*, *Metschnikowia reukaufii*, *Sporidiobolus salmonicolor*, one representative of the genus *Bullera*, and one – of *Trichosporon*. Representatives of three classes were identified: Ascomycota, Basidiomycota, and imperfect yeast. The most common species were *Cryptococcus albidus* (20 strains) and *Debaryomyces hansenii* (7 strains). There are candidates for new species. About 100 yeast lines were isolated from a usual habitat on the Sakhalin. Species diversity revealed mainly corresponds to the data obtained when studying species composition of yeast living in the northern latitudes of Western Siberia and Alaska [21].

More than 500 strains were tested for resistance to salts of heavy metals (U, Cs, Sr, Ni, Ar, Cu, Cd, and Co) and to elevated temperature (t) (+37…+52 °C). Testing strain sensitivity to uranium salts is shown in Fig. 1. Strains being sensitive to low uranium concentrations were neither used nor identified further. The greatest resistance was shown by representatives of the genus *Rhodotorula*. Clones of *Rhodotorula minuta* (KI-20-1a) were also nickel-resistant. Totally 72 % of the strains tested were resistant to one or more selective factors. The most frequent combinations were (t, Cd, Cu, Co) and (Cd, Cu, Co): 36 and 26 %, respectively.

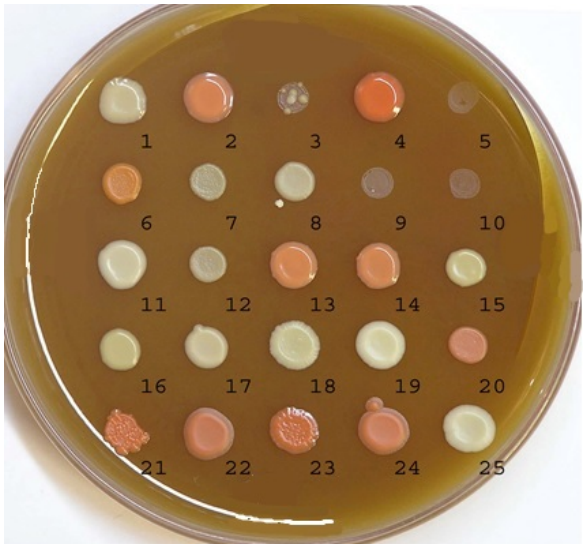

Fig. 1. Testing yeast strains sensitivity to uranium salts (10 mmol·L^{-1}):
1 – unidentified strain;
2 – *Rhodotorula mucilaginosa* (KI-20-4) strain;
3–5 – unidentified strains;
6 – *Phaffia rhodozyma* (KI-54-1) strain;
7–11 – unidentified strains;
12 – *Candida sake* (KI-38-2) strain;
13–17 – unidentified strains;
18–19 – separate clones of *Candida haemulonii* (KII-29-2a) strain;
20–24 – *Rhodotorula minuta* (KI-20-1a) strains;
25 – clone of *Candida haemulonii* (KII-29-2a) strain

Totally 30 strains with various resistance signs were tested for their ability to grow in the presence of non-radioactive ^{87}Sr (as oxide) and ^{133}Cs (as cesium chloride). Strains capable of growing at high cesium concentrations (up to 100 mmol·L^{-1}) were isolated. The representatives of the species *Rhodotorula minuta* (KI-17-5-1) and *Rhodotorula mucilaginosa* (KI-215-4) were the most resistant ones.

Nickel-resistant strains were selected among strains being resistant to several metals (Fig. 2). Clones of *Sporobolomyces roseus* (C26-2-1) and *Candida haemulonii* (KII-29-2a) strains showed high resistance to nickel (up to 5 mmol·L^{-1}). They were also resistant to uranium salts.

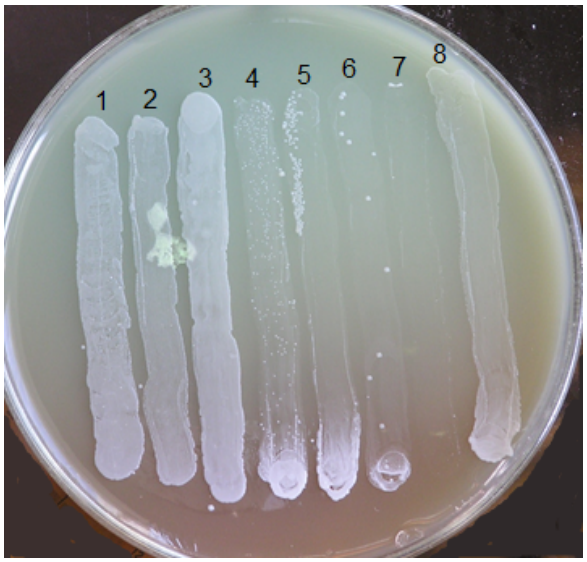

Fig. 2. Testing yeast strains sensitivity to nickel salts:
1–3 – clones of *Sporobolomyces roseus* (C26-2-1) strain;
4 – *Pichia farinosa* (KI-174-4a) strain;
5 – *Pichia farinosa* (KI-6-7a) strain;
6 – *Debaryomyces hansenii* (KI-126-1a) strain;
7 – *Saccharomyces cerevisiae* XII$_7$ strain, diploid;
8 – *Candida haemulonii* (KII-29-2a) strain

Sensitivity of the strains selected to "acute" ^{60}Co γ-irradiation is shown in Fig. 3 in comparison with that of *Saccharomyces cerevisiae* XII$_7$ strain. Among them, there are strains both more and less sensitive to γ-irradiation, being characterized with DMF (dose modification factor at the level of D_{37}) 0.7 to 1.15. *Rhodotorula minuta* (KI-17-2) isolate appeared to be the most radioresistant one.

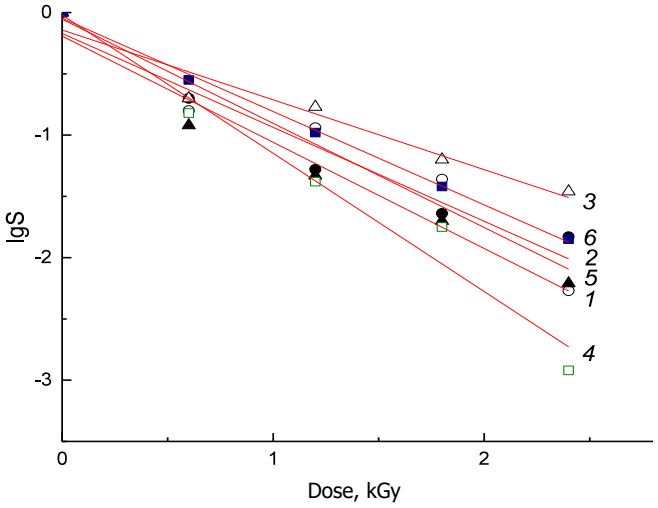

Fig. 3. Survival (lgS) of strains, selected for testing ^{137}Cs binding effectiveness, after "acute" ^{60}Co γ-irradiation:
1 – *Rhodotorula minuta* (KII-110-3) strain;
2 – *Rhodotorula minuta* (KI-20-1a) strain;
3 – *Rhodotorula minuta* (KI-17-2) strain;
4 – *Rhodotorula minuta* (KI-17-5-1) strain;
5 – *Rhodotorula mucilaginosa* (KI-215-4) strain;
6 – *Saccharomyces cerevisiae* XII_7 strain

The strains obtained were tested for their ability to grow in a medium with radioactive isotopes, in particular ^{137}Cs at a concentration up to 110 kBq·mL^{-1}, at different temperature and pH values, and when grown in different growth media. Several strains of the genus *Rhodotorula* have shown the ability to bind ^{137}Cs with efficiency 80–90 % (Fig. 4).

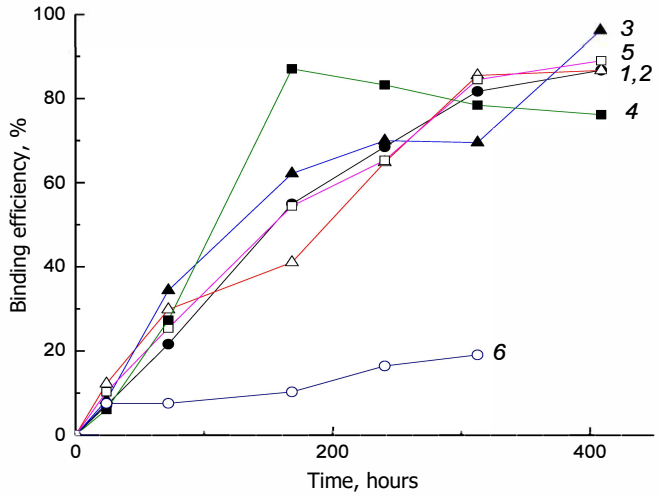

Fig. 4. Efficiency of ^{137}Cs binding by free cells from growth medium at pH ~ 6 during growth:
1 – *Rhodotorula minuta* (KII-110-3) strain;
2 – *Rhodotorula minuta* (KI-20-1a) strain;
3 – *Rhodotorula minuta* (KI-17-2) strain;
4 – *Rhodotorula minuta* (KI-17-5-1) strain;
5 – *Rhodotorula mucilaginosa* (KI-215-4) strain;
6 – *Escherichia coli* AB1157 strain

It follows from the results obtained (see Fig. 4) that when grown for 400 h, yeast-like fungi *Rhodotorula minuta* and *Rhodotorula mucilaginosa* bind ^{137}Cs much more efficiently than bacteria *Escherichia coli*.

Efficiency of ^{63}Ni binding, as that of ^{137}Cs before, was determined in percent – as a ratio of the radioactivity of cells deposited by centrifugation to the total activity of deposit and supernatant (Fig. 5).

It was found that *Rhodotorula glutinis* and *Sporobolomyces roseus* strains show fast kinetics of ^{63}Ni accumulation, while *Rhodotorula mucilaginosa* and *Rhodotorula minuta* after a long growth are characterized with a maximum binding percentage (~ 95 %), significantly exceeding this of *Saccharomyces cerevisiae*. To increase nickel binding efficiency by the strains tested, glucose was added to the growth medium with a concentration varying from 2 to 10 % (Table 1). *Rhodotorula glutinis* and *Rhodotorula mucilaginosa* responded positively to the additional energy source, binding up to 96–99 % of the metal.

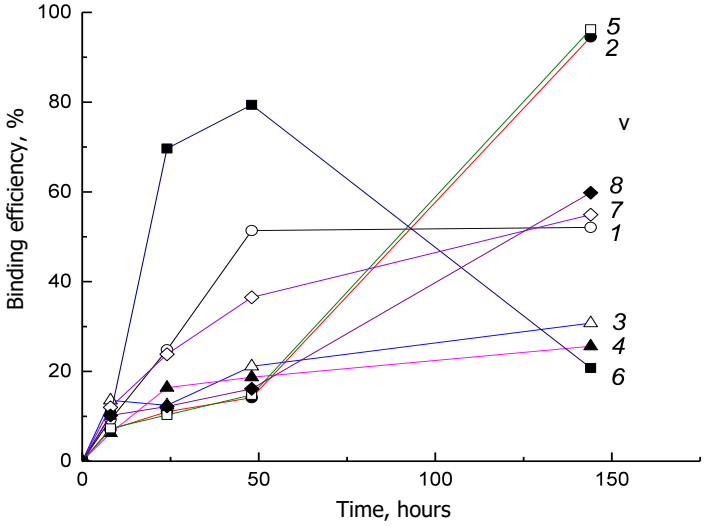

Fig. 5. Efficiency of ^{63}Ni binding (%) by free cells from growth medium at pH ~ 6 during growth:
1 – *Rhodotorula glutinis* (KI-216-4) strain;
2 – *Rhodotorula mucilaginosa* (KI-20-4) strain;
3 – *Cryptococcus albidus* (KII-III-24) strain;
4 – *Cryptococcus albidus* (KII-III-19) strain;
5 – *Rhodotorula minuta* (KII-110-3) strain;
6 – *Sporobolomyces roseus* (C-26-2-1) strain;
7 – *Saccharomyces cerevisiae* (C-20-2) strain;
8 – *Candida haemulonii* (KII-29-2a) strain

Table 1. Efficiency of ^{63}Ni binding (%) by free cells from growth medium at different glucose concentration

Strain	Time, h	Glucose concentration, %		
		2	5	10
Rhodotorula glutinis (KI-216-4)	0	0	0	0
	8	5.1 ± 0.5	9.6 ± 0.9	13.9 ± 0.5
	24	22.4 ± 0.2	28.2 ± 0.8	36.4 ± 0.4
	48	28.7 ± 0.4	40.6 ± 0.4	92.2 ± 0.6
	72	24.9 ± 0.2	50.6 ± 0.2	96.4 ± 0.7
	144	17.9 ± 0.2	86.5 ± 0.4	96.2 ± 0.3
Rhodotorula mucilaginosa (KI-20-4)	0	0	0	0
	8	6.8 ± 0.4	4.6 ± 0.9	14.8 ± 0.6
	24	8.7 ± 0.5	17.6 ± 0.2	16.2 ± 0.5
	48	36.1 ± 0.7	25.5 ± 0.1	23.0 ± 0.5
	72	24.4 ± 0.5	84.5 ± 1.0	45.7 ± 0.5
	144	83.8 ± 0.3	97.7 ± 0.5	99.3 ± 1.6
Rhodotorula minuta (KII-110-3)	0	0	0	0
	8	3.6 ± 0.7	7.4 ± 0.5	9.7 ± 0.4
	24	10.8 ± 0.4	19.8 ± 0.3	26.8 ± 0.4
	48	21.7 ± 0.2	27.9 ± 0.6	24.5 ± 0.3
	72	20.7 ± 0.6	30.1 ± 0.5	37.9 ± 0.6
	144	76.1 ± 0.5	65.8 ± 0.2	48.2 ± 0.3
Sporobolomyces roseus (C-26-2-1)	0	0	0	0
	8	10.0 ± 0.7	10.2 ± 0.3	13.5 ± 0.5
	24	67.6 ± 0.7	77.9 ± 0.6	63.9 ± 0.6
	48	26.4 ± 0.3	45.4 ± 0.4	31.7 ± 0.2
	72	28.5 ± 0.7	29.2 ± 0.3	40.6 ± 0.1
	144	32.0 ± 0.8	31.9 ± 0.3	32.0 ± 0.6

DISCUSSION

The uniqueness of yeast strains collection of the Petersburg Nuclear Physics Institute named by B. P. Konstantinov is determined by geographical peculiarity of the sampling sites. On the Kamchatka Peninsula, practically isolated from the mainland, there are about 60 volcanoes. Only half of them are active; however, hydrothermal and mud emissions of different temperature, containing various natural inorganic compounds, continue functioning on the slopes of extinct volcanoes. The Kuril Islands also abound in areas being characterized with manifestation of various emissions. Therefore, yeast and yeast-like fungi collected there, *i. e.* under conditions of constant strong environmental pressure, have to be highly resistant both to physical factors (elevated temperature, increased radioactive background, or increased intensity of UV radiation) and chemical ones (increased concentration of heavy metals salts and extreme pH values). Among these microorganisms, there might be those capable of efficiently accumulating ions of highly toxic heavy metals and radionuclides. *Rhodotorula* strains isolated by us showed the ability to grow at high concentrations of heavy metals and high radioactive background. Moreover, they were able to effectively bind these metals, in particular cesium and nickel.

To date, the main pollutants of liquid low-level waste (hereinafter LLW) are long-lived radionuclides ^{137}Cs ($T_{1/2}$ = 30.2 years) and ^{90}Sr ($T_{1/2}$ = 28.8 years). Only now, the problem of environmental protection has become the main one in the sphere of fissile material production. Obviously, level of costs for solving waste disposal problems might turn out to be almost the same as for main production processes. At the same time, to ensure radiochemical plants environmental safety, it is very important to prevent the risk of radionuclides entering groundwater and their outlet to soil surface. The approaches, currently being developed in the sphere of bioremediation, include both *ex situ* and *in situ* methods [6 ; 22 ; 23 ; 25], which makes it possible to find comprehensive solutions for both open storage reservoirs and pools for storing nuclear fuel.

Any methods of liquid LLW purification from ^{137}Cs are costly; all is determined by requirements to water and air quality. Liquid LLW are accumulated in large volumes, and this stimulates the search for cheap methods of purification from radionuclides and metals. Bioremediation methods, *i. e.* using microorganisms for this purpose, are today considered the most promising ones. The strains of natural yeast of the genus *Rhodotorula*, isolated by us, showed high ^{137}Cs binding efficiency with its activity up to 110 kBq·mL^{-1}.

Besides radionuclides, heavy metals, such as Ni, pose a great environmental hazard. Nickel is the most common industrial pollutant. Its level in the soil is 3–100 mg·kg^{-1}; in tailings from gold mining operations it is 580 mg·kg^{-1}, and in Tanzania it is 11,200 mg·kg^{-1}. In unpolluted and slightly polluted river waters, nickel concentration usually ranges from 0.8 to 10 μg·dm^{-3}; in polluted ones, Ni content amounts to several tens of mg per 1 dm^3. In seawater, average nickel concentration is 2 μg·dm^{-3}, in groundwater it is ~ 10^3 μg·dm^{-3}. In groundwater, washing nickel-containing rocks, Ni concentration sometimes increases to 20 mg·dm^{-3} [1 ; 3 ; 5].

The most toxic and carcinogenic nickel state is +4. Being catalysts, Ni compounds play an important role in blood-forming processes. Its increased concentration has a specific effect on the cardiovascular system. Nickel is a carcinogenic element capable of causing respiratory illnesses. It is believed that free nickel ions (Ni^{2+}) are approximately 2 times more toxic than its complex compounds [4]. Nickel excess causes hypoglycemia, asthma, nausea, headache, and nasal and lung cancer. The mechanisms of Ni toxicity are diverse; their action ultimately leads to cell membranes

destruction [9 ; 10 ; 14 ; 15 ; 16]. Again, the strains of natural yeast of the genus *Rhodotorula* binding nickel, that were isolated from the ecological niche of extremophiles, seem to be promising for bioremediation and for production processes.

Using both native and genetically modified organisms is on biotechnologists' agenda. The results of this work show the possibility of using natural strains but isolated from extreme living conditions (they already attract much attention [20]). Further study of extremophilic microorganisms involving omics technologies [18] will help in optimizing binding mechanisms [19] and stepping towards efficient cell-free systems.

Conclusions:

1. The results obtained show the possibility of potential using a library of natural microorganisms for disposal of both radionuclides and heavy metals, being the main pollutants of natural and technogenic objects, as well as the possibility of using isolated and tested strains of microorganisms for concentrating a number of metals from low-grade ores or mining industry waste.
2. The diversity of phenotypes revealed, namely multiple resistance, indicates that most likely there are several tolerance mechanisms.

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ВЫЯВЛЕНИЕ АДАПТИВНОСТИ ПРИРОДНЫХ ШТАММОВ ДРОЖЖЕЙ К СОЛЯМ ТЯЖЁЛЫХ МЕТАЛЛОВ И РАДИОНУКЛИДОВ*

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Изучена способность природных штаммов дрожжей расти в условиях высоких концентраций солей тяжёлых металлов и радионуклидов. Свыше 500 штаммов проверены на устойчивость к солям тяжёлых металлов (U, Cs, Sr, Ni, Ar, Cu, Cd, Co) и к повышенной температуре (t) (+37…+52 °C). Бóльшая часть изученных штаммов оказалась устойчива к одному или нескольким селективным факторам. С максимальной частотой — 36 и 26 % — возникают комбинации (t, Cd, Cu, Co) и (Cd, Cu, Co) соответственно. Установлена способность отобранных штаммов расти в условиях высокой концентрации радиоактивных изотопов Cs и Ni и связывать их с высокой эффективностью. Полученные результаты показали потенциальную возможность использования библиотеки природных микроорганизмов для осаждения как радионуклидов, так и тяжёлых металлов (основных загрязнителей природных и техногенных объектов), а также возможность применения выделенных и изученных штаммов микроорганизмов для концентрирования металлов из малообогащённых руд или из отходов добывающей промышленности. Обнаруженное разнообразие фенотипов свидетельствует о том, что существует, скорее всего, несколько механизмов устойчивости к высоким концентрациям тяжёлых металлов.

Ключевые слова: природные штаммы дрожжей, адаптация, тяжёлые металлы, радиоизотопы ^{137}Cs и ^{63}Ni, биоремедиация

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MERCURY ACCUMULATION IN SUSPENDED MATTER OF FOAM AND WATER OF THE BLACK SEA*

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The ability of suspended matter to concentrate mercury may be the prevailing factor in Black Sea purification. As a result of sedimentation, suspended particles transport pollution from the surface layer of the water column and, as a consequence, can deposit them in bottom sediments, thus participating in self-purification of marine area. Suspended matter, as a dispersed phase of an aqueous medium, considered as a heterogeneous dispersed system, can be more saturated with mercury than water itself, as a dispersion medium. In this work, contribution of dissolved and suspended forms of mercury to its total content was determined, and concentrating ability of suspended matter relative to mercury, which affects biogeochemical self-purification of waters from mercury, was estimated. All water samples were separated into filtrate and suspension by filtration through nucleopore filters with a pore diameter of 0.45 μm. Measurements of mercury concentration were carried out using a Hiranuma-1 analyzer by the method of atomic absorption spectrophotometry. Concentration of dissolved mercury in water was determined per liter, while in suspended matter – per liter and per gram of dry weight. Prevalence of dissolved form of mercury was revealed regardless of the season, with its percentage varying from 66.3 to 85.8 % of total mercury concentration. Average content of suspended form varied in the range of 14.2–33.7 % of its total form. Values of the dry weight of suspended matter (m_{ss}) varied from 0.1 to 15.0 mg·L^{-1} over the entire period studied, and an accumulation coefficient of mercury in suspended matter (K_{ss}) varied from n·10^3 to n·10^7. Significant contribution of suspended form of mercury in sea foam to its total content in stormy weather was established. With dry weight of suspended matter in seawater reaching 9.6 mg·L^{-1}, the concentration of dissolved form of mercury reached 55 ng·L^{-1}, and the concentration of suspended one reached 20 ng·L^{-1}. In sea foam, the concentration of suspended sedimentary matter was of 895.2 mg·L^{-1}; mercury concentration reached 200 ng·L^{-1} in dissolved form and 260 ng·L^{-1} in suspended one. Total mercury concentration in sea foam in this case exceeded the threshold limit value (100 ng·L^{-1}) for seawater. The accumulation coefficient of mercury in suspended matter (K_{ss}) was 3.8·10^4 for seawater and 1.5·10^3 for foam. Such distribution of mercury in sea suspension, foam, and water, as well as K_{ss} values obtained, may indicate high significance of suspended matter in self-purification of marine area. At a low mercury content in water, the concentrating ability of suspended matter, characterized by relatively high values of its mercury accumulation coefficient, becomes a very significant factor in the sedimentation self-purification of waters from mercury; however, with an increase in water pollution with mercury, the effect of this factor decreases.

Keywords: mercury, suspended matter, sea foam, Black Sea

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Mercury is a substance of the I hazard class and one of the most environmentally significant pollutants of the Black Sea [14]. As known, at mercury concentration of 0.1 μg·L^{-1}, vital activity of unicellular algae is suppressed [12]. At mercury concentration of 0.018 mg·L^{-1}, biochemical processes of self-purification are inhibited in waters, and at 2.0 mg·L^{-1} they stop [1 ; 4].

Mercury can enter the environment from various natural and anthropogenic sources. Volcanic activity, degassing of the Earth's crust, and evaporation from water surface followed by wind transport can be considered the main mercury natural sources. With Danube River waters only, mercury inflow into the Black Sea is estimated at 48.7–58.9 t·$year^{-1}$ [16], and its inflow into entire marine area from other sources – at 80 t·$year^{-1}$ [17]. Mercury anthropogenic sources in the Black Sea include industrial and municipal wastewater, ship repair facilities, and marine transport.

According to data published, the predominant factor in sedimentary water purification is a concentrating ability of suspensions [2 ; 10]. Due to sorption, mercury concentration in suspended matter can be quite considerable. As a result of sedimentation, suspended particles transport pollution from the surface layer of the water column and, as a consequence, can deposit them in bottom sediments, thus participating in self-purification of marine area. In stormy weather (mainly in shallow shelf and coastal areas), the upper layer of bottom sediments mixes with the bottom water layer; due to biogeochemical cycle, pollution inflows back into the water column. At the same time, surface water of a coastal water area is intensively filled with suspended sediment and is therefore a qualitatively new convenient object for studying the processes of self-purification of marine environment from mercury. Dispersed sedimentary matter, like almost all biotic and abiotic components of marine ecosystems, can be more saturated with mercury compared to water, considered as a dispersion medium.

The aim of this work was to determine the contribution of dissolved and suspended forms of mercury to its total content and the concentrating ability of suspended matter relative to mercury, as well as to estimate percentage of mercury accumulation by suspension, which characterizes contribution of suspended form of mercury to total form in a "suspension – water" system. A data array on mercury content in the Black Sea in 2011–2017 was analyzed, and mercury concentration in sea foam in 2018 was studied.

MATERIAL AND METHODS

To identify the contribution of dissolved and suspended forms of mercury to total one, published and unpublished data on mercury content in the Black Sea for 2011–2017 were used [9 ; 10]. Sampling stations are shown in Fig. 1. Water for the study was sampled during research cruises of the RV "Professor Vodyanitsky" (No. 70, 72, 79, 80, 88, 90, 92, 93, 96, 99, and 100), as well as in Sevastopol bays. In stormy weather in 2018, water and foam samples were taken from the surface layer of the Black Sea (44°39.167′N, 31°50.445′E).

All water samples were separated by filtration through pre-weighed nucleopore filters with a pore diameter of 0.45 μm into two parts: filtrate and suspension on the filters. Then, the suspension was dried under natural conditions and again weighed using a Sartorius microanalytical balance with a measurement error of 0.1 mg. Dry weight of the suspended matter was calculated from the difference between the filter mass after and before filtration. After that, the filter with the dry suspension was processed according to GOST 26927 (All-Union State Standard). Measurements of mercury concentration were carried out by flameless atomic absorption spectrophotometry using a Hiranuma-1 analyzer. To calibrate it, certified

standard samples of mercury ion solution GSO 7879-2001 were used. Analysis of several calibration solutions with mercury concentration of 0.2, 0.4, 0.6, 0.8, and 1 μg·L^{-1} (10 replicates each) showed a reproducibility of the results with a relative error not exceeding 2 %.

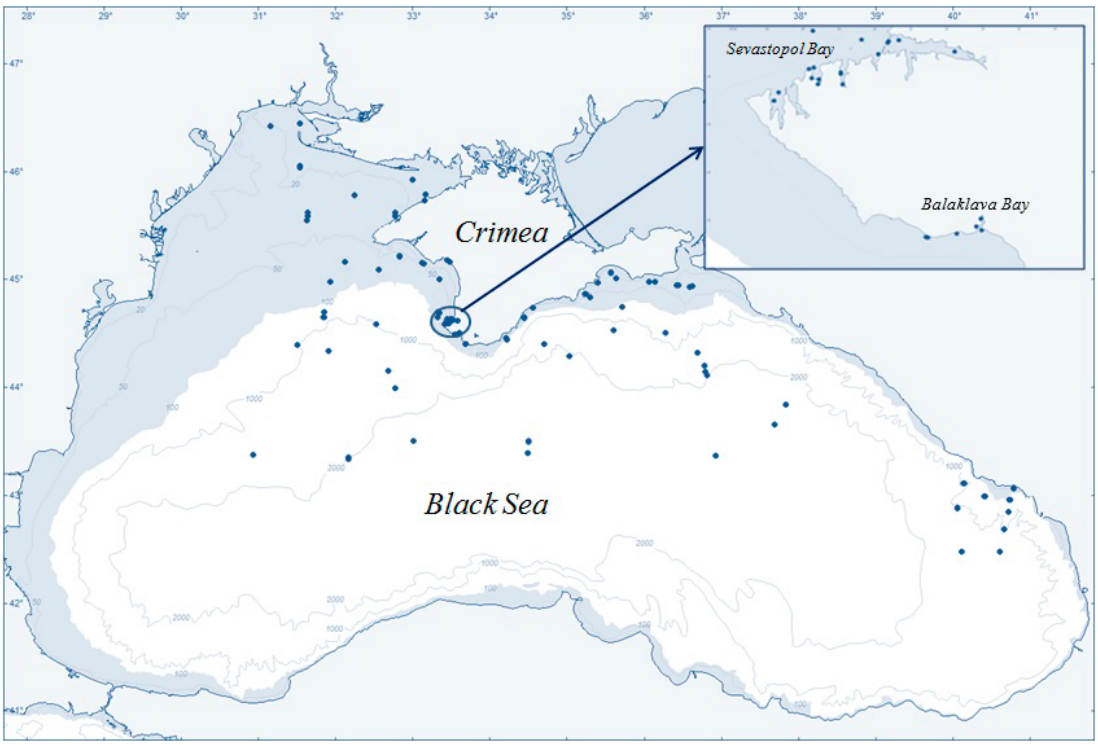

Fig. 1. Map of sampling in the Black Sea [13]

Concentration of dissolved form of mercury in water was determined per liter, and in suspended matter – per liter and per gram of dry weight.

To characterize the concentrating ability of suspended matter, the accumulation coefficient of mercury (K_{ss}) was calculated [7]:

$$K_{ss} = \frac{1000 \cdot C_{ss}}{C_w}, \quad (1)$$

where C_{ss} is specific mercury concentration in suspended matter (suspended substance), ng·g^{-1};

C_w is concentration of dissolved form of mercury in water, ng·L^{-1}.

Dependence of the percentage of mercury accumulation by suspended matter from aquatic environment on accumulation coefficients (K_{ss}) and concentration of suspended matter 10^{-6}B was calculated by the formula [6]:

$$A_1 = \frac{K_{ss}}{K_{ss} + \frac{1}{10^{-6}B}} (\%), \quad (2)$$

where $B = \frac{P_1}{P_2}$;

P_1 is mass of dry suspension;

P_2 is mass of water equal to 10^6 g;

10^{-6}B is suspension concentration in the aquatic environment in parts per million (mg·L^{-1}).

RESULTS AND DISCUSSION

Data for 2011–2017 were analyzed by season and depth. For each data group, average concentrations of various forms of mercury in ng·L^{-1} were calculated (Fig. 2). The maximum average annual concentration of total form of mercury was registered in 2014, and the minimum one – in spring of 2012 (Fig. 2A). The results showed the prevalence of dissolved form of mercury (Fig. 2B) with a variation in its percentage in the range of 66.3–85.8 % of total mercury concentration. The average concentration of suspended form was 14.2–33.7 % of the concentration of its total form.

In this case, the values of the dry weight concentration of suspended matter varied 0.1–15.0 mg·L^{-1} over the entire period studied.

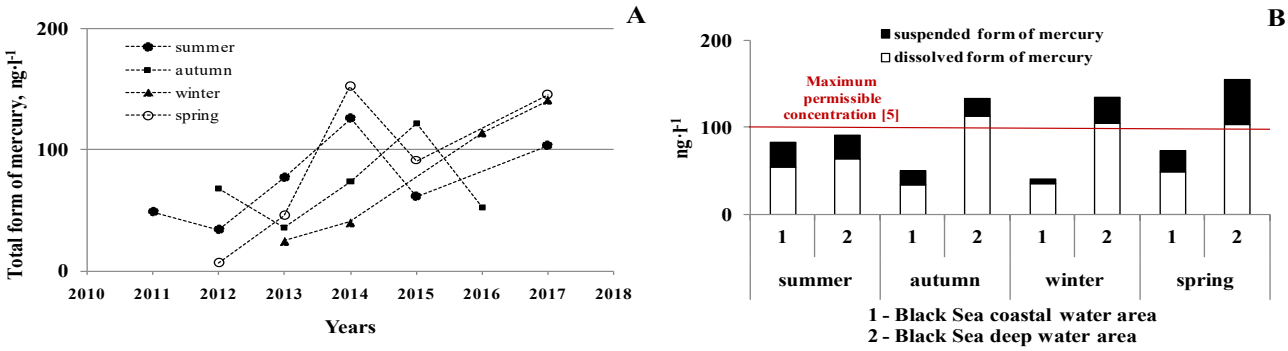

Fig. 2. A – average annual concentration of total form of mercury in the Black Sea in 2011–2017; B – average concentrations of dissolved and suspended forms of mercury during different seasons

Fig. 2B shows that in summer, both in coastal and deep-water areas of the Black Sea, the average concentrations of dissolved and suspended forms of mercury are approximately equal, with total content not exceeding threshold limit value (hereinafter TLV) for seawater equal to 100 ng·L^{-1}. In other seasons of the year, for coastal water areas of the Black Sea, the average mercury concentration is comparatively lower, and for deep-water areas it is much higher. Fig. 2B shows that in spring, the average concentrations of dissolved and suspended forms of mercury, both in coastal and deep-water areas, are higher compared to those in autumn and winter. An increased contribution of suspended form of mercury to its total content is also observed, which indicates activation of accumulating ability of the suspension relative to mercury. This is most likely to be due to spring increase of primary producing ability of biotic component of the suspension, in particular phytoplankton, resulting from increasing impact of two factors: heat and light. The increased concentration of dissolved mercury in deep-water areas of the Black Sea during these three relatively low-temperature seasons (autumn, winter, and spring), compared to coastal waters, is most likely associated with the low accumulating ability of suspended matter relative to mercury and with the corresponding reduced eliminating ability of the suspension to transport mercury by sedimentation from the surface layer to the bottom since it was previously described in literature that total suspension of surface water in the Black Sea and the Sea of Azov near the Crimean Peninsula is regularly decreasing from coastal to open deep-sea waters [8].

The prevalence of the values of suspended and dissolved forms of mercury in summer season, both for coastal and deep-water areas of the Black Sea, over mercury content in coastal waters in relatively low temperature seasons (autumn, winter, and spring) is most likely associated with an increase in the primary

producing ability of biotic component of the suspension (mainly phytoplankton) [3] and with a corresponding increase in its eliminating ability to transport accumulated mercury from the surface layer towards bottom sediments.

Table 1 shows the average values for the entire data array, as well as the ranges of variation of suspended matter specific dry mass in different seasons of the year. The minimum content of suspended matter was registered in summer (0.99 $mg \cdot L^{-1}$) and winter (0.60 $mg \cdot L^{-1}$) seasons in deep-water areas of the Black Sea. The maximum average values of suspended matter (m_{ss}) were observed in winter (2.96 $mg \cdot L^{-1}$) and spring (3.90 $mg \cdot L^{-1}$) periods in Crimean coastal waters.

Table 1. Average values of suspension concentration and specific mercury concentration in suspension from Black Sea water area in 2011–2017 (figures in brackets indicate ranges of variation)

Season of the year	Area under study	Suspension concentration (m_{ss}), $mg \cdot L^{-1}$	Specific mercury concentration in suspension (C_{ss}), $ng \cdot g^{-1}$ of dry weight
Summer	Coastal water area of Crimea	1.75 (0.3–10)	30,197 (408–500,000)
	Deep-water area of the Black Sea	0.99 (0.1–3.1)	53,038 (4839–320,000)
Autumn	Coastal water area of Crimea	1.67 (0.6–7)	9625 (614–30,769)
	Deep-water area of the Black Sea	1.08 (0.2–3)	23,353 (1447–100,000)
Winter	Coastal water area of Crimea	2.96 (0.5–14.7)	5144 (314–41,667)
	Deep-water area of the Black Sea	0.60 (0.1–3.4)	131,317 (3333–1,100,000)
Spring	Coastal water area of Crimea	3.90 (0.5–15)	17,375 (825–85,000)
	Deep-water area of the Black Sea	1.62 (0.5–3.6)	10,831 (2861–26,400)

Based on suspension weight ($g \cdot L^{-1}$) and mercury concentration in it ($ng \cdot L^{-1}$), mercury concentration in suspended matter ($ng \cdot g^{-1}$) was calculated (see Table 1). The minimum mercury concentration in suspension was 314 $ng \cdot g^{-1}$ in coastal water area of Crimea in winter. The highest value (1,100,000 $ng \cdot g^{-1}$) was registered in deep-water area of the Black Sea in winter. Calculated by formula (1), the accumulation coefficient of mercury in suspended matter (K_{ss}) varied from $n \cdot 10^3$ to $n \cdot 10^7$.

Fig. 3 shows a graphical depiction of a dependence of change in the accumulation coefficient of mercury in suspended matter (K_{ss}) on its concentration in water (C_w) for different seasons of the year and water areas. The graph (Fig. 3D) shows that in spring in coastal area of the Black Sea, the values of K_{ss} varied with an increase in C_w with a statistical validity of $R^2 = 0.73$. In the deep-water areas of the Black Sea in the same season, the dependences of K_{ss} on C_w had a low coefficient of approximation validity ($R^2 = 0.04$). In summer, R^2 values amounted to 0.01 for coastal water area of the Black Sea and 0.32 for deep-water area (Fig. 3A). In autumn, this parameter had the value 0.64 for coastal water area and 0.25 for the deep-water one (Fig. 3B). In winter, $R^2 = 0.01$ for deep-water areas of the Black Sea and $R^2 = 0.50$ for coastal water area (Fig. 3C). As a result, the most reliable trends were identified for coastal waters, with the exception of summer season.

The dependences obtained (Fig. 3) had a low coefficient of determination in summer in coastal water area (Fig. 3A); it was also low in winter (Fig. 3C) and spring (Fig. 3D) in the deep-water area. This indicates different representativeness of the data, as well as different ability of suspensions to accumulate mercury from coastal and deep-water areas in different seasons of the year. In general, by the approximating dependence in other cases, we can say that with an increase in the concentration of dissolved form of mercury in water (C_w), concentrating ability of suspended matter decreases.

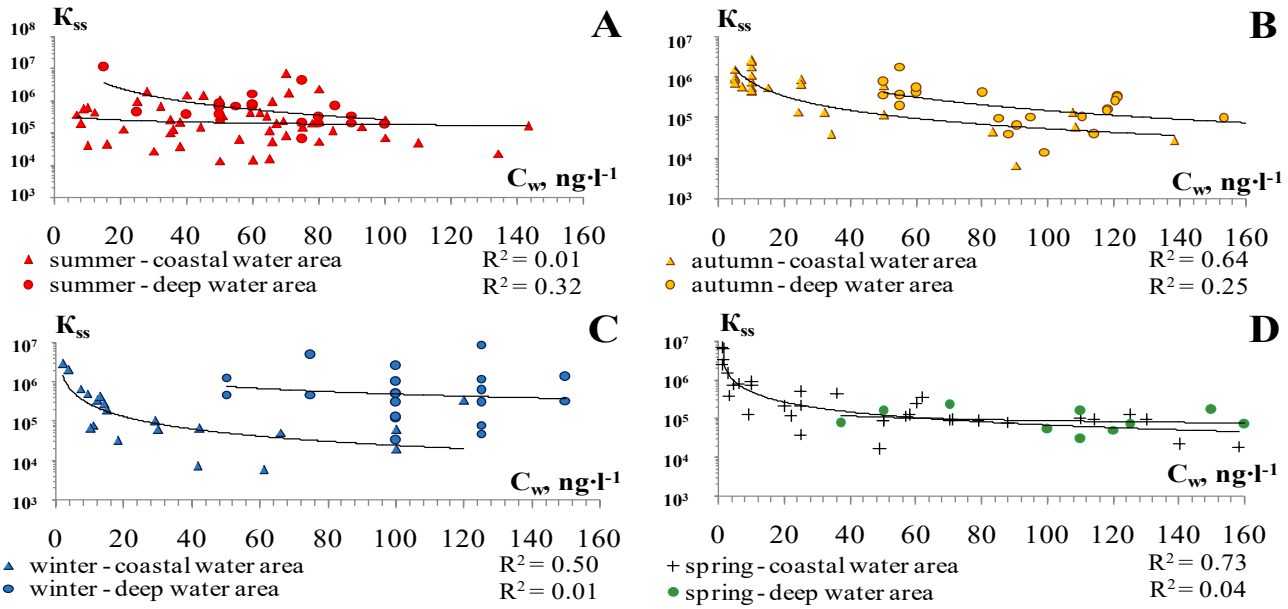

Fig. 3. Dependence of change of the accumulation coefficient of mercury in suspended matter (K_{ss}) on concentration of dissolved form of mercury in water (C_w, ng·L^{-1}) during different seasons (A – summer; B – autumn; C – winter; and D – spring) and in different water areas

Using formula (2), a dependence of the percentage of mercury accumulation by suspended matter from marine environment on the accumulation coefficient was calculated (Fig. 4).

According to Fig. 4, the percentage of mercury accumulation by suspension varies with an increase in K_{ss} with almost the same statistical validity for different seasons and Black Sea areas, with the exception of spring season in deep-water area. According to the data obtained, with $K_{ss} > 10^6$, almost all mercury is accumulated by suspended matter of seawater, which indicates its high concentrating ability.

The dependence of the percentage of mercury accumulation by suspension on C_w for different seasons and water areas has slightly pronounced trends (Fig. 5), with the exception of spring period in the deep-water area ($R^2 = 0.83$) (Fig. 5D). Moreover, in all cases, there is a decrease in a ratio of suspended form of mercury with an increase in the concentration of dissolved form in water, which is in full agreement with the functional dependence expressed by formula (2).

Previously, when studying the mechanism of foam formation on seawater surface, it was found that organic matter of seawater transforms from dissolved state into foam and suspension since fragments of the shells of bursting foam bubbles turn into dispersed particles [11].

In this article, the effect of storm surge on ratio and magnitude of different forms of mercury in water was investigated. In stormy weather, the concentration of suspended sedimentary matter in seawater was 9.6 mg·L^{-1}, and in sea foam – 895.2 mg·L^{-1} (Fig. 6).

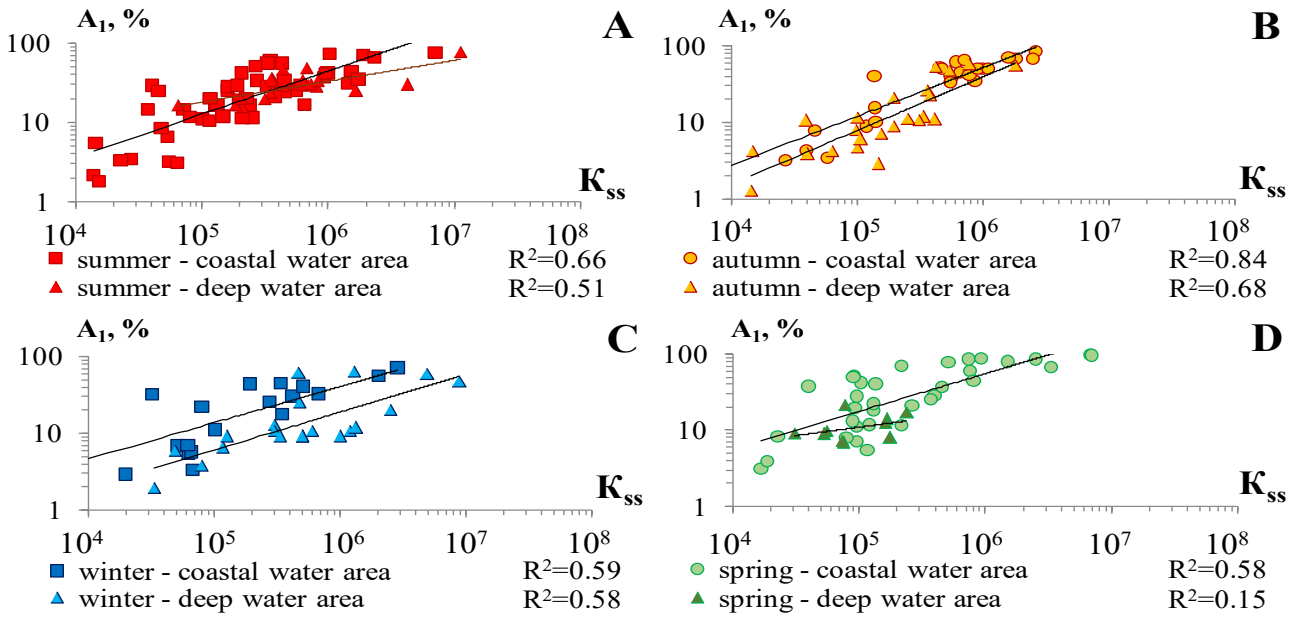

Fig. 4. Dependence of the percentage of mercury accumulation by suspended matter (A_1, %) on the accumulation coefficient (K_{ss}) during different seasons (A – summer; B – autumn; C – winter; and D – spring) and in different water areas

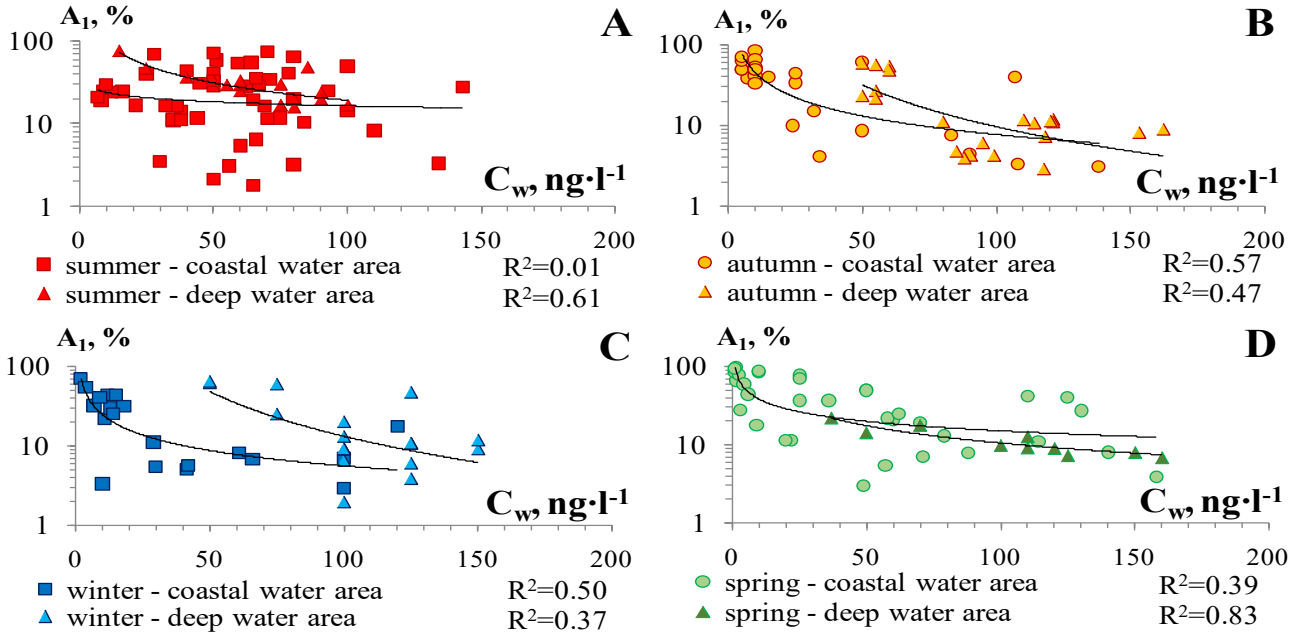

Fig. 5. Dependence of the percentage of mercury accumulation by suspended matter (A_1, %) on dissolved form of mercury (C_w, ng·L^{-1}) during different seasons (A – summer; B – autumn; C – winter; and D – spring) and in different water areas

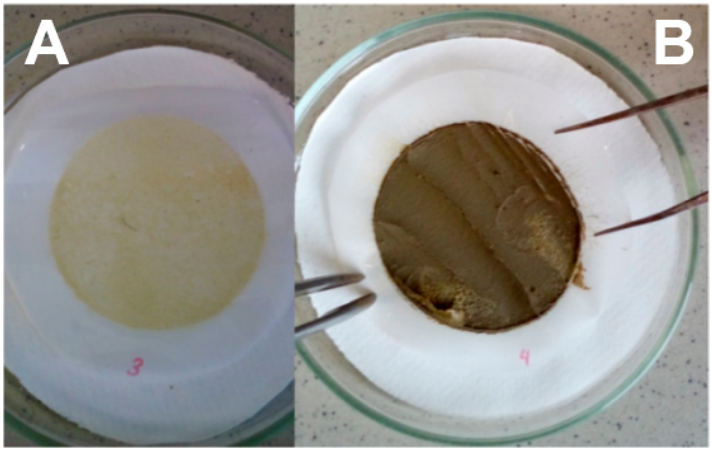

Fig. 6. A – suspended matter obtained from seawater; B – suspended matter obtained from sea foam

The concentration of dissolved form of mercury in seawater was 55 ng·L^{-1}, and in sea foam it reached 200 ng·L^{-1}, exceeding TLV (100 ng·L^{-1}) [5]. Values of suspended form of mercury were 20 ng·L^{-1} in seawater and 260 ng·L^{-1} in sea foam (Fig. 7). In this case, the concentration of total mercury in sea foam exceeded not only TLV for seawater but also standards for bottom sediments (300 ng·L^{-1}) [15]. Mercury concentration in suspended sediment was 2083 ng·g^{-1} of dry weight for suspension obtained from seawater and 290 ng·g^{-1} of dry weight for suspension from sea foam. The accumulation coefficient of mercury by suspended matter (K_{ss}) for seawater was $3.8 \cdot 10^4$, and for foam – $1.5 \cdot 10^3$. Such a distribution of mercury in sea foam and water, as well as K_{ss} values obtained, may indicate a high concentrating ability of marine sedimentary suspensions and their high significance in self-purification of marine area.

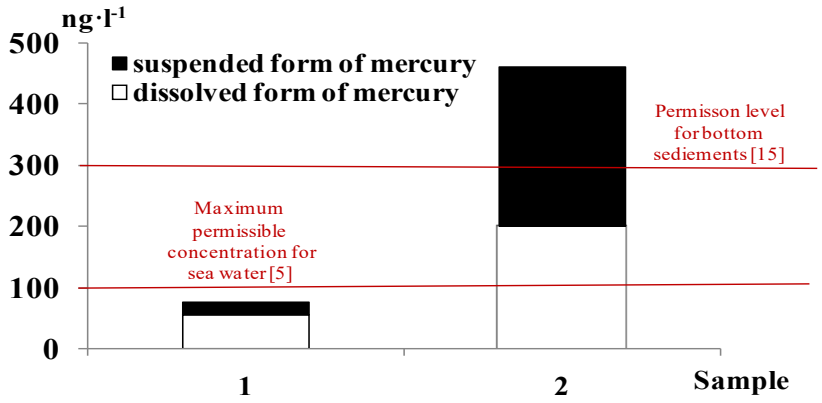

Fig. 7. Sample 1 – concentration of total mercury in seawater, ng·L^{-1}; sample 2 – concentration of total mercury in sea foam, ng·L^{-1}

Conclusion. In the Black Sea, dissolved form of mercury predominates regardless of the season, with a variation in its percentage in the range of 66.3–85.8 % of total mercury concentration. The accumulation coefficient of mercury by suspended matter varied from n·10^3 to n·10^7; at its values > 10^6, almost all mercury was accumulated by suspensions. At low mercury concentrations in water, the concentrating ability of suspensions, due to relatively high K_{ss} values, is a significant factor in sedimentary self-purification of water, but its effect decreases with increasing water pollution by mercury. Concentration of suspended form of mercury makes a significant contribution to total mercury concentration, especially in sea foam. The redistribution of sedimentary suspended matter into foam can serve

as a source of mercury remobilization in seawater. Therefore, the limits of changes in the accumulation coefficient can be decisive indicators in self-purification of marine environment. They can be used to solve the problems of limiting mercury emissions to the Black Sea, which can help in the timely identification of possible environmental hazard.

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КОНЦЕНТРИРОВАНИЕ РТУТИ ВО ВЗВЕШЕННОМ ВЕЩЕСТВЕ ПЕНЫ И ВОДЫ ЧЁРНОГО МОРЯ*

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Способность взвешенного вещества концентрировать ртуть может быть превалирующим фактором в очищении водной толщи Чёрного моря. В результате седиментации взвешенные частицы выносят загрязнения из поверхностного слоя воды и в итоге могут депонировать их в донных осадках, участвуя таким образом в процессах самоочищения морской акватории. Взвешенное вещество как дисперсная фаза водной среды, рассматриваемой в качестве гетерогенной дисперсной системы, может быть более насыщено ртутью, чем сама вода как дисперсионная среда. В данной работе определён вклад растворённой и взвешенной форм ртути в её общее содержание и оценена концентрирующая способность взвешенного вещества в отношении ртути, обуславливающая биогеохимическое самоочищение вод от ртути. Все пробы воды разделяли на фильтрат и взвесь путём их фильтрации через нуклеопоровые фильтры с диаметром пор 0,45 мкм. Измерения содержания ртути проводили на анализаторе «Хиранума-1» методом атомно-абсорбционной спектрофотометрии. Концентрацию растворённой ртути в воде определяли в пересчёте на литр, а во взвешенном веществе — на литр и на грамм сухой массы. Выявлено превалирование растворённой формы ртути независимо от сезона года с варьированием её процентного содержания в диапазоне 66,3–85,8 % от общей (суммарной) концентрации ртути. Средняя концентрация взвешенной формы составила 14,2–33,7 % от её общего содержания. При этом значения концентрации взвешенного вещества ($m_{взв}$) варьировали от 0,1 до 15,0 мг·л$^{-1}$ за весь исследованный период, а коэффициент накопления ртути взвешенным веществом ($Кн_{взв}$) изменялся в диапазоне от n·10^3 до n·10^7. Определён значительный вклад

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взвешенной формы ртути в её общее содержание в морской пене, образованной в штормовую погоду. Так, при концентрации взвешенного вещества в морской воде 9,6 мг·л$^{-1}$ концентрация растворённой формы ртути имела значение 55 нг·л$^{-1}$, а взвешенной — 20 нг·л$^{-1}$. В морской пене концентрация взвешенного осадочного вещества составила 895,2 мг·л$^{-1}$, а концентрация ртути достигла 200 нг·л$^{-1}$ в растворённой форме и 260 нг·л$^{-1}$ — во взвешенной. Содержание общей (суммарной) ртути в морской пене при этом превышало предельно допустимую концентрацию (100 нг·л$^{-1}$) для морской воды. В данном случае $Кн_{взв}$ для морской воды был равен $3{,}8 \cdot 10^4$, а для пены — $1{,}5 \cdot 10^3$. Такое распределение ртути в морской взвеси, пене и воде, а также полученные значения коэффициента накопления свидетельствуют о большой важности взвешенного вещества в самоочищении морской акватории. При низком содержании ртути в воде концентрирующая способность взвешенного вещества, характеризуемая относительно высокими значениями его коэффициента накопления ртути, становится весьма значимым фактором в седиментационном самоочищении вод от ртути, однако при повышении загрязнения вод ртутью влияние этого фактора снижается.

Ключевые слова: ртуть, взвешенное вещество, морская пена, Чёрное море

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APPLICATION OF THE G. G. POLIKARPOV CONCEPTUAL MODEL OF CHRONIC ACTION ZONALITY OF IONIZING IRRADIATION DOZE RATES TO BIOSPHERE OBJECTS IN APPLIED HYDROBIOLOGY*

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Evolution of the approach to assessing ionizing radiation effects on living organisms is briefly discussed in this paper. Using the example of Black Sea hydrobionts, possibility of applying the G. G. Polikarpov conceptual radiochemoecological model of chronic action zonality of ionizing irradiation dose rates in nature to assess ecological exposure of technogenic radioisotopes ionizing radiation on aquatic biota was shown. In applied hydrobiology, this model can serve as the basis for a complex approach in assessing aquatic biota ecological state and its prediction for a wide range of ^{239,240}Pu activity concentration in seawater. The necessity of combined use of biogeochemical and equidosimetric indicators of radionuclide behavior in a water area is emphasized. In particular, for predictive dosimetric assessments, it is important to take into account quantitative characteristics of accumulative ability of Black Sea hydrobionts and a type of radioelement biogeochemical behavior, reflecting peculiarities of plutonium biogeochemical migration in a marine ecosystem.

Keywords: assessment of aquatic biota ecological state, Black Sea, biogeochemical migration, redistribution of ^{239,240}Pu radioisotopes, dose commitments, hydrobionts, G. G. Polikarpov conceptual model

Applied hydrobiology is designed to study consequences of water bodies pollution by technogenic substances and processes of water quality formation as a result of the influence of ecosystem abiogenic and biogenic components on redistribution of technogenic substances in water bodies, as well as to offer scientifically based criteria and approaches for assessing hydrobionts ecological state. This is necessary for rational use and management of aquatic ecosystems while maintaining environmentally acceptable water quality, as well as for development of scientific basis for rationing supply of technogenic substances to water bodies and their separate water areas.

These questions are especially relevant for the Black Sea as an inland sea, anthropogenic impact on which is great, in particular in coastal areas. The area of the Black Sea drainage basin is more than 2.3 million km^2, and both biogenic and toxic substances come from it, including plutonium technogenic radioactive isotopes [13 ; 43 ; 44]. The main sources of ^{239,240}Pu in the Black Sea include global radioactive fallout and emissions after the Chernobyl Nuclear Power Plant (hereinafter NPP)

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disaster [13 ; 23 ; 44]. As a result of the functioning of nuclear facilities, as well as after accidents, high activity concentration levels of anthropogenic radioisotopes have already been formed in some marine areas (the Irish Sea and some Arctic seas) and in freshwater bodies in various regions, including Eurasia territory (in the Southern Ural and Siberia, in 30-km zone around the Chernobyl NPP, etc.) [3 ; 8 ; 13 ; 24 ; 25]. In the Black Sea, plutonium activity concentration levels are quite low, but widespread use of these isotopes in nuclear technologies increases possibility of further radioactive contamination of marine areas with Pu.

This makes it necessary and urgent to develop approaches for assessing biota ecological state in water bodies and separate water areas, based on established patterns of plutonium behavior in aquatic ecosystems. Such studies are particularly relevant in the post-Chernobyl period, since technogenic radioisotopes, coming to the Black Sea in low concentrations not causing negative changes in its ecosystems, can be measured using physical methods of research and serve as radioactive tracers of natural processes [13]. This is a unique opportunity for studying processes and their quantitative characteristics in natural conditions (without violating ecosystems integrity) including migration and redistribution of technogenic radioisotopes in natural Black Sea ecosystems. Long ^{239,240}Pu half-life periods give reason to consider plutonium radioactive radiation a component of chronic anthropogenic factor, which is being formed in the present period because of technogenic human activity. The results obtained will allow not only assessing current environmental conditions of water areas and consequences of chronic exposure, but also predicting their possible change in case of an extreme increase in ^{239,240}Pu activity concentration levels in aquatic environment because of accidents or other unplanned or planned events.

The aim of our work is to consider briefly the evolution of views on the assessment of ionizing radiation effect on hydrobionts and to evaluate radiation exposure levels from technogenic alpha-emitting plutonium radioisotopes based on the use of the G. G. Polikarpov conceptual model of chronic action zonality of ionizing radiation dose rates in nature (hereinafter the G. G. Polikarpov conceptual model) as a part of a complex approach in assessing aquatic biota ecological state in a wide range of ^{239,240}Pu levels in seawater in relation to long-lived plutonium radioisotopes.

The effect of radioactive substances on living organisms is primarily due to ionizing radiation (hereinafter IR) emitted by a radioactive substance, namely quantity and quality of energy transferred to a living object from IR. Therefore, we dwell briefly on the evolution of representations in equidosimetry for the aim of assessing IR effect on living organisms.

Understanding of dosimetric criteria for assessing IR environmental effect on biota underwent a number of changes after the entry of technogenic radionuclides into the environment in the middle of the XX century. Initially, development of equidosimetry for biota was based on developments in radiation hygiene: human radiation protection. In radiobiology, the question on equidosimetry was relevant from the very beginning of studying IR effect on a living organism. This is due to the fact that ionizing radiations, having one common property (to ionize a substance), can be of different types: electromagnetic radiation, charged particles of different masses, neutral particles, etc. With the same amount of energy transferred per unit mass of living substances (absorbed dose, D, Gy = J·kg^{-1} [10]), they cause damaging effects of different levels in living organisms. Therefore, to assess the effect of different IR types on human body, a concept of an equivalent dose (H) was introduced in radiation hygiene, in which IR quality was taken into account through a radiation weighting factor (W_R) [10] (*i. e.* its relative biological effectiveness

when exposed to a living organism). The radiation dose commitment to body, depending on IR type, is estimated as the equivalent dose ($H = W_R \times D$, Sv) or the equivalent dose rate (HR, Sv·day^{-1} or Sv·year^{-1}) [10].

How was IR influence on biota assessed initially? In 1977, the International Commission on Radiological Protection (hereinafter ICRP) adopted a concept focusing on human protection. It stated as follows: if a human is properly protected, then, most likely, other living beings would be sufficiently protected [35]. Meanwhile, radiobiological research practice did not confirm this point of view. Often there were situations of complete people absence in a polluted environment, in which radiosensitive representatives of non-human biota could experience damaging and harmful radiation effects. This depends on intensity of organism interaction with the environment (for example, hydrobionts with aquatic environment) and on a number of other factors and conditions. Unlike biota, people can actively protect themselves from IR effect using various means and methods. These include the simplest but effective means: wearing overalls, respiratory and eye protection, vehicles use, radioprotectors taking, regulation of the time spent in radioactive pollution zone, etc. As a result, dose formation is not the same for people and biota. In many cases, biota representatives receive higher IR doses, while people receive lower and not dangerous IR doses. After all, only people are able to regulate and to actively reduce absorbed doses by special countermeasures (prevention and treatment, acceleration of radionuclides elimination from the organism, consumption of imported food and water, use of special technologies, etc.). Thus, in the same conditions, biota is exposed to a more intense impact than humans. According to a generalization of research results in the accident zone in the Southern Ural in 1957 [1], local people received doses 10–100 times less than wild vertebrates and higher plants. In the zone near the Chernobyl NPP, this difference was 30–120 times [15].

While working at the International Marine Radioactivity Laboratory of the International Atomic Energy Agency (hereinafter IAEA) in Monaco (1975–1979), G. G. Polikarpov actively studied the problem of assessing ecological IR effect on hydrobionts. In 1977, in Italy, at the XX congress devoted to radiation protection, he made a report, in which he first set out his conceptual model of the chronic zonality of IR dose rates effects on hydrobionts based on a synthesis of the results of his research and world literature on chronic irradiation effect on biota [39]. Noting the complexity of a unified assessment of IR effects on aquatic biota, due to different types of radiation, different radiosensitivity of species, ontogenetic stages of the same organism, different body tissues, and other features of radiation exposure to biota [33], G. G. Polikarpov proposed to divide the entire range of dose rates into separate zones: according to the effects (exposure level) they cause in living organisms [39] (Table 1). In this edition of the model, dose rate scale is presented in rad·year^{-1}.

Five zones with the lower boundary of the last one (Zone of Obvious Impact) of about 400 rad·year^{-1} (4 Gy·year^{-1}) were identified (Table 1). Attention was focused on little knowledge and a need for a broader study of hydrobionts radiosensitivity to protect them adequately from IR effect.

Since the 1990s, idea of environmental criteria being necessary for sufficient biota protection has been gaining the status of the official one. In 1991, ICRP concept was supplemented by an assertion that under conditions where humans are adequately protected, certain species may be exposed to detrimental radiation effects [36]. In accordance with IAEA and ICRP recommendations [32 ; 34 ; 49], the safe dose rate limit of 0.01 mGy·day^{-1} (4 Gy·year^{-1} rounded up to whole units) has been adopted for hydrobionts. Its exceeeding leads to negative consequences for biota populations. Radioecologists started applying the concept of equivalent dose and dose rate to biota using Gy or Sv

as units [11 ; 13 ; 28 ; 45]. It is significant that radiological conditions of water environment of the water body, forming a dose rate of 0.00001 Sv·year^{-1} for people drinking this water, create a dose rate of 0.03 Gy·year^{-1} in seals in the same water body [6]. In this case, the dose rate for seals is 3000 times higher than for humans. When assessing dose rate from ^{14}C being characterized by concentration factor 50,000 for freshwater fish [48], the dose rate of the internal irradiation of seals due to fish feeding can be estimated at 7.5 Gy·year^{-1}. Dose rates being even an order of magnitude lower than this (tenths of Gy·year^{-1}) cannot be considered safe for mammals [6]. The data obtained shows that when each human in a certain area receives permissible IR dose rates from drinking water, radiosensitive aquatic biota in the water body at the same time is not protected and receives unsafe IR dose rates.

Table 1. Zones of biological effect of ionizing radiation chronic irradiation in the first edition of the G. G. Polikarpov conceptual model according to [39]

Zone number	Zone name (biological exposure level)	Doze rate (rad·year^{-1}) – upper zone boundary
I	Uncertainty	4×10^{-3}
II	Radiation Well-being	4×10^{-1}
III	Physiological Masking	5×10^{0}
IV	Ecological Masking	4×10^{2}
V	Obvious Impact	4×10^{3}

Thus, the studies led to a transition from the anthropocentric approach to biota radiation protection (there, human protection was put at the forefront as a priority task in nature conservation, considering man the most radiosensitive species and the most vulnerable one) to an ecocentric approach. It is based on an eco-ethical worldview and on results of environmental research. This approach encourages each person and the whole society to realize that human as a biological species was born and develops as a part of an integral ecosystem (from local ecosystem to biosphere as a global one) and that his future depends entirely on ecosystem health and safety [13 ; 37]. Therefore, the focus is on protection and preservation of the ecosystem: all species of living organisms. Human, being a rational species, is responsible for preserving life on the planet, ensuring safe development, and biodiversity conservation in aquatic and terrestrial ecosystems [1 ; 2 ; 13 ; 34 ; 37]. It is also important that humans are not considered the most radiosensitive and most vulnerable species; scientific data on the radiosensitivity of all species and characteristics of dose formation in relation to non-human biota are taken into account [1 ; 13 ; 16 ; 20 ; 41 ; 42 ; 49 ; etc.]. The eco-ethical approach echoes the biosphere one, in which biota and humans are considered biosphere elements. To preserve it, a unified assessment system is needed to ensure safety of humans and aquatic ecosystem inhabitants [7]. ICRP recommendations of 2007 not only contain proposals on protection of human beings, but also consider “approaches designed to create principles for proving adequate environmental protection” [14]. Section 8 on environmental protection states as follows: “A more understandable, scientifically grounded unified concept is needed to assess relationships between exposure and dose, dose and effect, and the consequences of such effects on non-human biota”. An extensive research is needed “to provide pragmatic guidance in this sphere” [14].

To assess IR radiation hazard for biota, being based on the ecocentric approach, equidosimetric concepts, and generalization of long-term radiobiological and radioecological studies, G. G. Polikarpov developed the previously proposed model [11 ; 14 ; 41 ; 42] and formulated a conceptual model of zonality of chronic IR dose rates in nature: at all living organization levels from a cell to biological communities and biosphere as a whole (Fig. 1) [11 ; 13]. This model served as a basis for equidosimetric analysis of biota ecological state in relation to ^{239,240}Pu in a complex approach of hydrobionts ecological state assessment [19 ; 20], where the equivalent dose rate (Gy·year^{-1}) is used as the value of dose commitment [11 ; 13]. The use of equivalent dose rate is important in assessing IR environmental effect levels from those radiation types for which $W_R > 1$. For alpha-particles emitted by ^{239,240}Pu, $W_R = 20$ in radiation hygiene [10]. In our work, we used $W_R = 20$ for hydrobionts, since in the modern period there is no other valid accepted unified W_R value for alpha-radiation in respect to biota, although different relative biological effectiveness for different IR types was observed in animals. In addition, most of data for establishing W_R in human radiation protection have been obtained in animal studies [33]. In a review on this subject [31], researchers did not come to a final informed decision, although they recommended using an average value $W_R = 5$ for biota populations and indicated that ranges of W_R changes were 1–10 and 1–20 for deterministic and stochastic effects in biota, respectively. In the studies used in the analysis, W_R value varied in a wider range: 37–150 in publications of 1966–1995 and 1–50 in works of 1991–2003 [31]. The absence of accepted reasonable W_R value in relation to biota is also mentioned in ICRP publication No. 108, dedicated to environment protection from IR [33]. ICRP publications No. 103 and 108 [14 ; 33] indicate that in this situation, for biota, in relation to alpha-radiation, $W_R = 20$ is used, the same as in human radiation protection. Meanwhile, equivalent doses for biota are expressed in Gy (units of absorbed dose) and equivalent dose rate: in Gy·day^{-1} or Gy·year^{-1}, respectively [14 ; 33]. In this work, the equivalent dose rate for non-human biota was obtained by multiplying the dose absorbed by $W_R = 20$ and presented in Gy·year^{-1}.

In the modern period, various approaches to environmental standardization and assessment of biota ecological state in aquatic and terrestrial ecosystems are being developed. Plenty of research and generalization methods are used. Bioindication and biotesting, as well as mathematical modeling are applied; processes of migration and accumulation of anthropogenic substances are studied; effects on organisms at different biota organization levels (from genetic to biocenotic one) are investigated. An integral part is the development of approaches for assessing radiation dose commitments to biota and the equidosimetry use [3 ; 7 ; 9 ; 26 ; 27 ; 31 ; 42 ; etc.]. The ecosystem approach in assessing IR effect on biota is becoming increasingly important internationally [13 ; 29 ; 30 ; 33 ; 38 ; 40 ; 41]. The concept of using both reference biota representatives and a range of accepted reference (control) dose rates is being developed: the range of derived consideration reference levels (DCRL) in relation to representatives of different taxonomic groups of aquatic and terrestrial biota [33]. In this case, DCRL is considered Radioactive Dosage Zone, within which stochastic effects are likely to occur and which separates Background Dose Rate Ranges Zone and Deterministic Effects Zone. According to data available at the time of the problem analysis (2008), for 12 selected reference representatives of animals and plants, DCRL Zone, according to preliminary estimates, was 0.1–100 mGy·day^{-1} [33]. Therefore, the equivalent dose rate equal to 10 mGy·day^{-1} (4 mGy·year^{-1}), accepted by G. G. Polikarpov as the lower boundary of Damage to Ecosystems Zone (in accordance with previously formulated proposals of international organizations [32 ; 34 ; 49]), is still relevant,

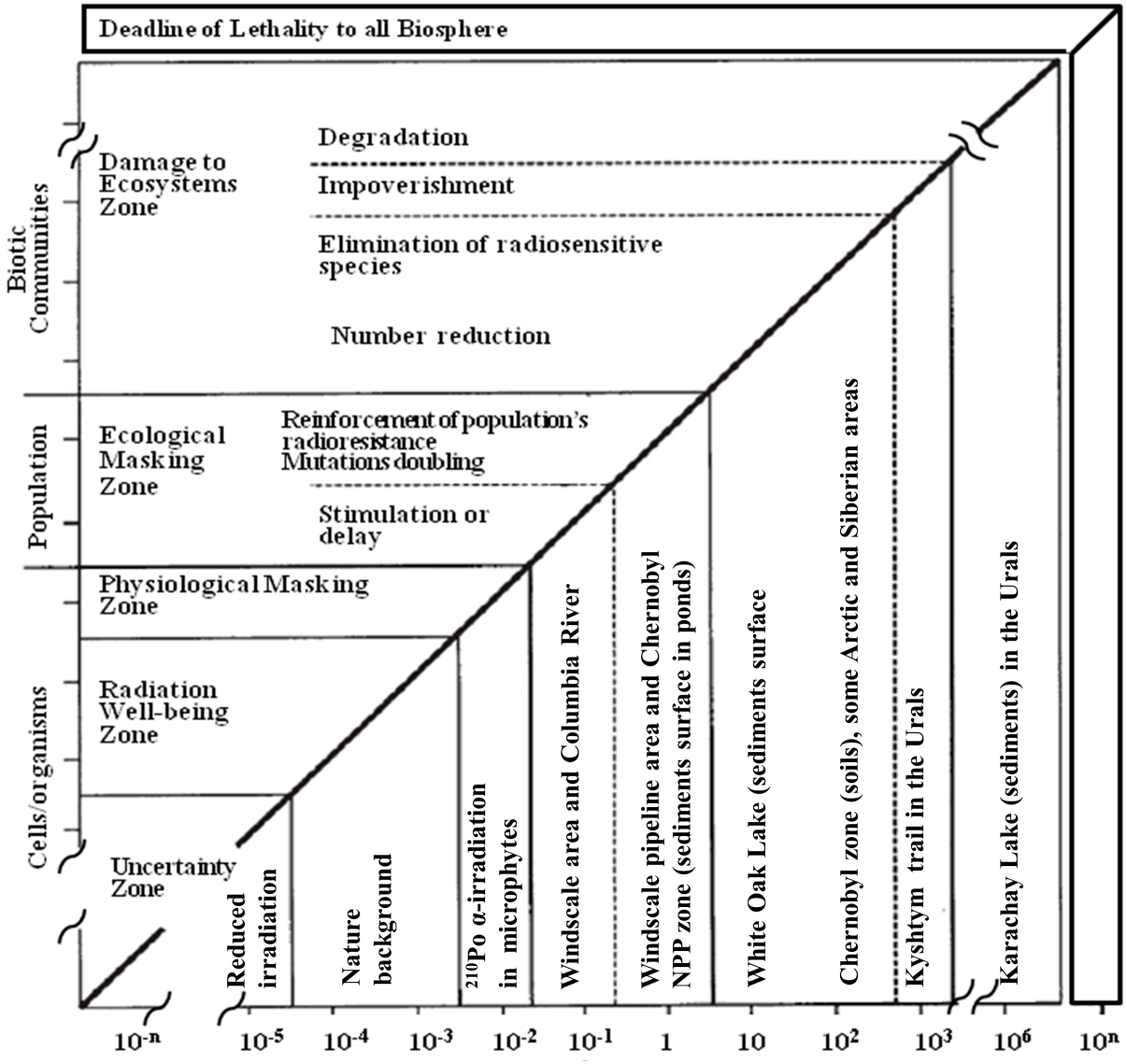

Fig. 1. Correspondence of ionizing radiation dose rate ranges and biological effect levels under chronic irradiation in the G. G. Polikapov conceptual model with examples of the state of existing contaminated aquatic biotopes, depending on dose rate level [11 ; 13]

and further research is required to clarify and revise it [33]. This was pointed out by G. G. Polikarpov paying attention to early stages of hydrobionts development, which are often more radiosensitive than adult ones [13].

As a rule, when considering the ecosystem approach, biota radiation protection focuses on the aspects of dose assessment and their effects. On the other hand, attention is paid to taking into account the diversity of structure and functions of ecosystems, their locations, and choice of reference animals and plants; this is undoubtedly necessary and important and is a very difficult task [12 ; 14 ; 29 ; 30 ; 33 ; 34 ; 38 ; 40 ; 49]. At the same time, attention is not focused on a role of ecosystem biogeochemical processes and a biogeochemical type of radioisotope behavior in the ecosystem determining the main ways of radioisotope redistribution in a water body. Meanwhile, these are very significant components participating in formation of radiation dose commitments to biota

in aquatic ecosystems [4 ; 9 ; 13 ; 16 ; 17 ; 21 ; 22 ; 24 ; 46]. One of the objectives of our work is to draw attention to consideration of migration aspect in assessing ecosystem ecological state in relation to IR effect, which source is anthropogenic radioisotopes entering the ecosystem. Significant results were achieved in this sphere, and a complex approach has been proposed by us to assess ecological status of marine areas in relation to long-lived radionuclides using the example of $^{239+240}$Pu [19 ; 20].

The complex approach is based on the premise as follows: different living organisms may experience different dose commitments being in the same aquatic environment, as it is seen from the examples above. Therefore, the complex approach combines assessment of state of aquatic environment and representatives of different groups of hydrobionts by mutual addition of biogeochemical [5 ; 16 ; 17 ; 18 ; 19 ; 20 ; 21 ; 46] and equidosimetric [13 ; 15 ; 19 ; 20 ; 40 ; 41] aspects of radioisotope presence in an aquatic ecosystem (Fig. 2). The biogeochemical approach implies taking into account real quantitative indicators of influence of characteristics and functioning processes of the ecosystem itself, its components, and physical and chemical features of the pollutant on its redistribution in the water body and, therefore, on the formation of its concentration in water.

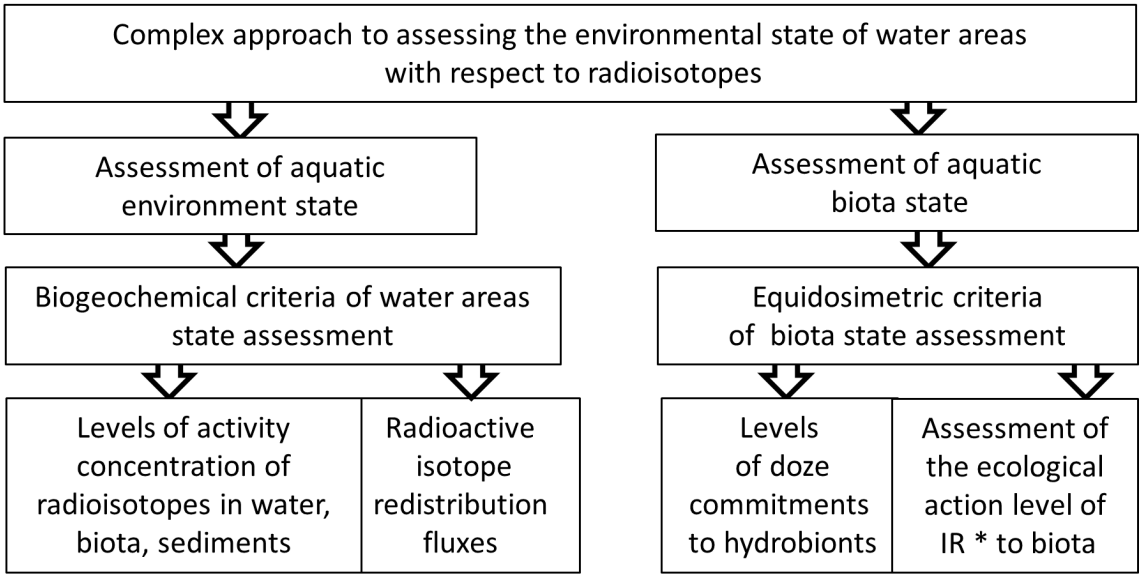

Fig. 2. Flowchart of the complex approach to assessing ecological state of water areas (IR* is ionizing radiation)

The main biogeochemical indicators are radioisotope activity concentration in water and a ratio of its input and removal fluxes. This ratio forms radioisotope activity concentration in water, and it should not exceed the permissible radioisotope activity concentration in water and biota (Fig. 3). Therefore, in order to assess biota ecological state in a water body, it is necessary to know permissible activity concentration ($C_{permissible}$, see Fig. 3) in water, the exceeding of which leads to negative consequences for hydrobionts populations, and to choose a method for determining the level of IR ecological influence from this radioisotopes level in water on biota of a water body. These questions can be solved by combining biogeochemical and equidosimetric aspects of radioisotopes presence in a marine ecosystem within

the framework of a complex approach to assess hydrobionts ecological state, which is closely related to migration processes and includes an assessment of the influence of different concentrations of technogenic substances on aquatic ecosystems biota.

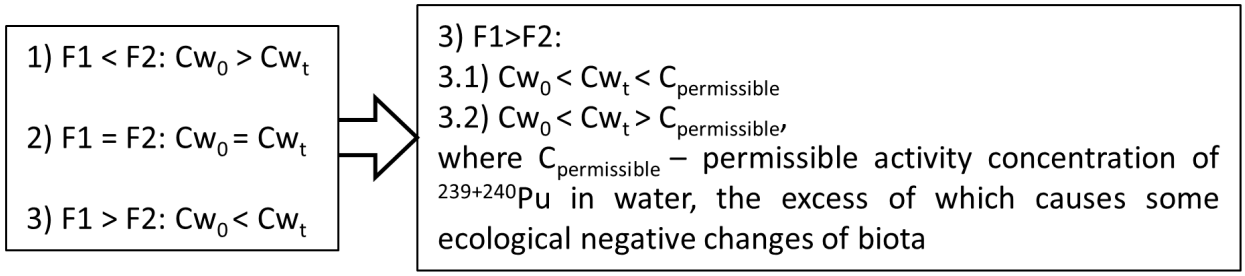

Fig. 3. Flowchart of formation of $^{239, 240}Pu$ activity concentration levels in water at different ratios of F1 and F2;
F1 is radioisotope input flux;
F2 is radioisotope removal flux from water environment ($Bq \cdot m^{-2} \cdot year^{-1}$ or $Bq \cdot m^{-2} \cdot day^{-1}$);
Cw_0 is radioisotope activity concentration in water at the initial moment of time (background),
Cw_t – at time t ($Bq \cdot m^{-3}$)

Determination of biogeochemical indicators is based on the study of migration aspect of plutonium radioecology in the Black Sea: behavior of radioisotopes in a natural ecosystem. It includes identification of a type of biogeochemical behavior of the radionuclide, determination of its levels in ecosystem components, assessment of radioisotopes input and removal fluxes from aquatic environment, and identification of leading mechanisms of these processes [19 ; 20 ; 21]. As a result of long-term observations in the Black Sea in the post-Chernobyl period, quantitative characteristics of plutonium radioisotopes redistribution in water areas were determined [13 ; 16 ; 17 ; 18 ; 46 ; 47], which made it possible to establish the pedotropic type of plutonium behavior in the Black Sea. On the basis of these data, it was determined that plutonium sedimentation flux with suspended matter into bottom sediments serves as the main removal flux from a water column [5 ; 16 ; 19 ; 47]. The concentration factors (C_f) of $^{239,240}Pu$ by biota representatives of different taxonomic groups of hydrobionts were also determined, being necessary for calculating dose rates of chronic internal IR irradiation of biota from $^{239,240}Pu$ [13 ; 15 ; 17 ; 46]. C_f values, along with radioisotope activity concentration level in aquatic environment, type of radionuclide biogeochemical behavior in a water body, and IR quality, play an important role in formation of dose rate level of chronic exposure in hydrobionts [17 ; 18 ; 19].

As an equidosimetric criterion for assessing IR influence on Black Sea biota, IR equivalent dose rate was used, with subsequent determination of its ecological exposure level through comparative equidosimetric analysis of data on dose rates using the G. G. Polikarpov conceptual model [13 ; 40 ; 41]. A comparative analysis of the ecological state in Black Sea areas and in stagnant water bodies of the 30-km zone of the Chernobyl NPP in relation to radioisotopes after the Chernobyl NPP accident in terms of radiation exposure levels to biota is presented in Fig. 4. At current $^{239+240}Pu$ activity concentration levels in components of Black Sea ecosystems, the dose rates, formed from their IR, do not affect negatively Black Sea biota. According to the zonality of ionizing radiations effect, the levels of their environmental action do not exceed the influence being characteristic of the Radiation Well-being Zone. IR dose

commitments from ^{239,240}Pu for molluscs and from a sum of $^{239+240}$Pu, ^{137}Cs, and ^{90}Sr for different groups of hydrobionts in the 30-km zone of the Chernobyl NPP exceeded background exposure levels. According to the G. G. Polikarpov conceptual model, these levels belong to the Physiological Masking Zone and the Ecological Masking Zone, and reach the lower boundary of the Damage to Ecosystems Zone.

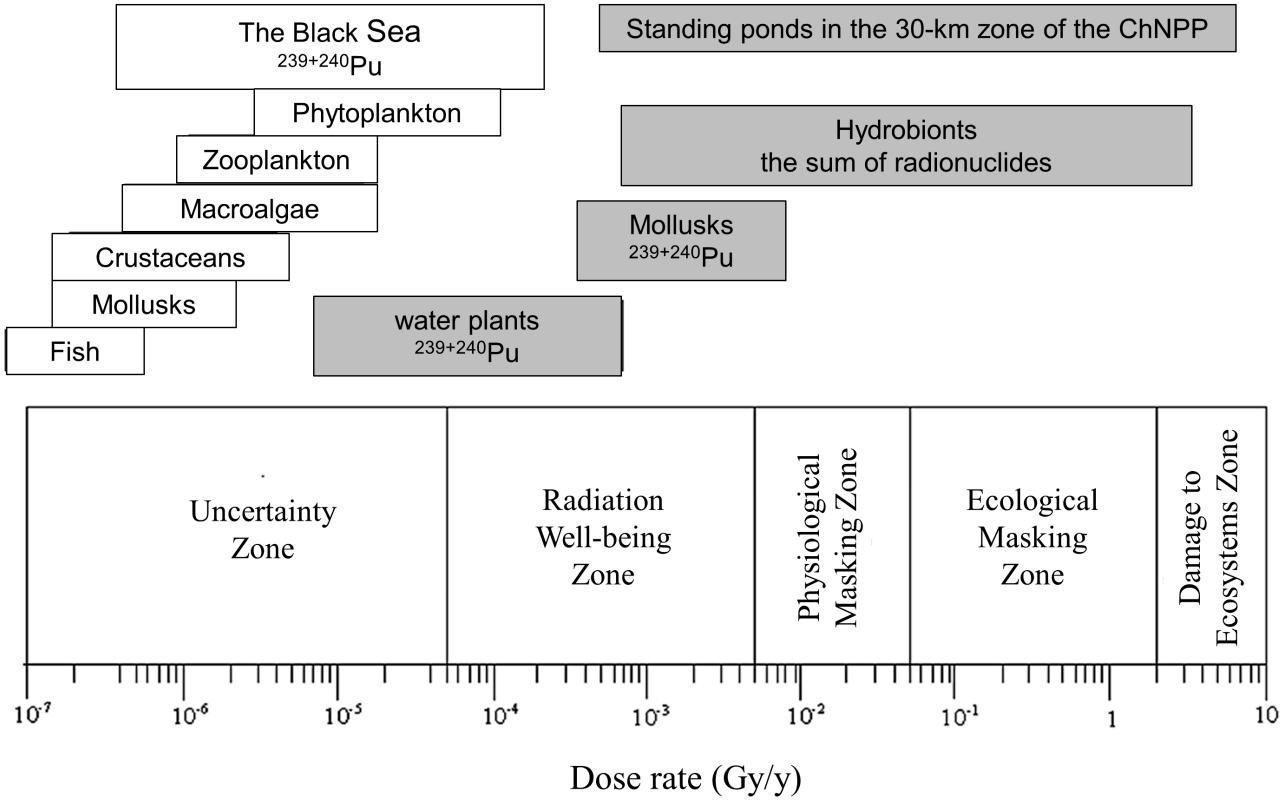

Fig. 4. Assessment of biological effect levels of ionizing radiation of plutonium radioisotopes, as well as of a sum of the main man-made dose-forming radionuclides (strontium, cesium, and plutonium) in the post-Chernobyl period

Calculation of dose commitments for Black Sea hydrobionts in a wide range of possible levels of ^{239,240}Pu activity concentration in water was performed according to known approaches [13 ; 15 ; 28], taking into account $W_R = 20$ for ^{239,240}Pu alpha-particles. The results of equivalent dose rate calculation are presented in Table 2. They reflect a relationship between the activity concentration of ^{239,240}Pu in water and the dose rate, and, therefore, the level of IR biological exposure to representatives of different groups of hydrobionts.

These data also illustrate relationship between biogeochemical and equidosimetric indicators for assessing aquatic environment and hydrobionts state. As it is evident from Table 2, at the same aquatic environment state with respect to ^{239,240}Pu levels, the level of these radioisotopes IR effect to different groups of hydrobionts is different, which is largely determined by accumulation capacity of hydrobionts in relation to plutonium. There is no doubt, that ontogenetic and radiobiological states of organisms can modify the lower boundary of the Damage to Ecosystems Zone; it will be refined as knowledge in this sphere accumulates.

Table 2. Dose commitments (HR is equivalent dose rate) at different levels of ^{239,240}Pu activity concentration in seawater (C_W Pu) and concentration factor in regard to ^{239,240}Pu (C_f Pu); 4 Gy·year^{-1} (IAEA and ICRP recommended dose rate limit, exceeding of which leads to negative changes in biota populations) is the boundary of Ecological Masking Zone and Damage to Ecosystems Zone (underlined in the Table) [32 ; 34 ; 42 ; 49]

Groups of hydrobionts	HR in hydrobionts at different C_W and C_f $^{239+240}$Pu, Gr·year^{-1}						
	C_W Pu, Bq·kg^{-1} / C_f Pu	0.000001	0.08	0.8	8	16	80
Phytoplankton	$1\cdot10^5$	$1\cdot10^{-4}$	$\underline{4\cdot10^0}$	$4\cdot10^1$	$4\cdot10^2$	$8\cdot10^2$	$16\cdot10^3$
Macroalgae	$5\cdot10^4$	$1\cdot10^{-5}$	$4\cdot10^{-1}$	$\underline{4\cdot10^0}$	$4\cdot10^1$	$8\cdot10^1$	$16\cdot10^2$
Zooplankton	$1\cdot10^3$	$1\cdot10^{-6}$	$4\cdot10^{-2}$	$4\cdot10^{-1}$	$\underline{4\cdot10^0}$	$8\cdot10^0$	$16\cdot10^1$
Molluscs	$5\cdot10^2$	$5\cdot10^{-7}$	$2\cdot10^{-2}$	$2\cdot10^{-1}$	$2\cdot10^0$	$\underline{4\cdot10^0}$	$8\cdot10^1$
Fish	$1\cdot10^2$	$3\cdot10^{-8}$	$1\cdot10^{-3}$	$1\cdot10^{-2}$	$1\cdot10^{-1}$	$2\cdot10^{-1}$	$\underline{4\cdot10^0}$

Summarizing the researches made, we have drawn up (Fig. 5) a general scheme of a complex approach to assessing water areas ecological state in relation to IR from long-lived radioisotopes [18 ; 19]. This approach takes into account specific biogeochemical characteristics of the ecosystem under study. First of all, these are biogeochemical sedimentation fluxes, accumulation capacity of ecosystem components, and hydrological regime of a water area. The features of the pollutant studied (type of radionuclide biogeochemical behavior and its physical-chemical and radiological characteristics) also play an important role. Taking these indicators into account makes it possible to more accurately assess self-purification capacity of photic layer surface waters (precisely in this particular ecosystem with respect to the pollutant under consideration). Applying the complex approach allows performing express assessments of current or expected level of pollutant environmental influence, as well as calculating fluxes of radioisotopes, at which they are formed, and time to reach control concentrations. Within the framework of the complex approach, it is recommended to use for the regulation a flux of radionuclides into the water area, avoiding contamination critical levels and preventing negative effect on biota.

It is also important, in our opinion, that the scheme-algorithm proposed focuses monitoring or expert studies not only on contamination levels in aquatic ecosystem components, but also on identifying basic patterns of radionuclide behavior in it. Of key importance are determination of a type of radionuclide biogeochemical behavior and studying of quantitative characteristics of biogeochemical processes in an ecosystem using radionuclides not only as a subject, but also as a method of research, *i. e.* as radioactive tracers. Such a scheme-algorithm can help in making decisions on the implementation of countermeasures necessary for the water area under study in case of radiation accidents and incidents and in predicting changes in biota ecological state.

Thus, based on the results of the study of leading processes determining redistribution of technogenic ^{239,240}Pu radioisotopes in the Black Sea, as well as taking into account their quantitative characteristics, identified main biogeochemical features of $^{239+240}$Pu behavior in the sea, levels of hydrobionts accumulation capacity, and received dose commitments to hydrobionts, applicability of the G. G. Polikarpov conceptual model was shown as the final link of a scheme-algorithm of current and predicted estimates of biota ecological state in relation to long-lived radionuclides for a wide range

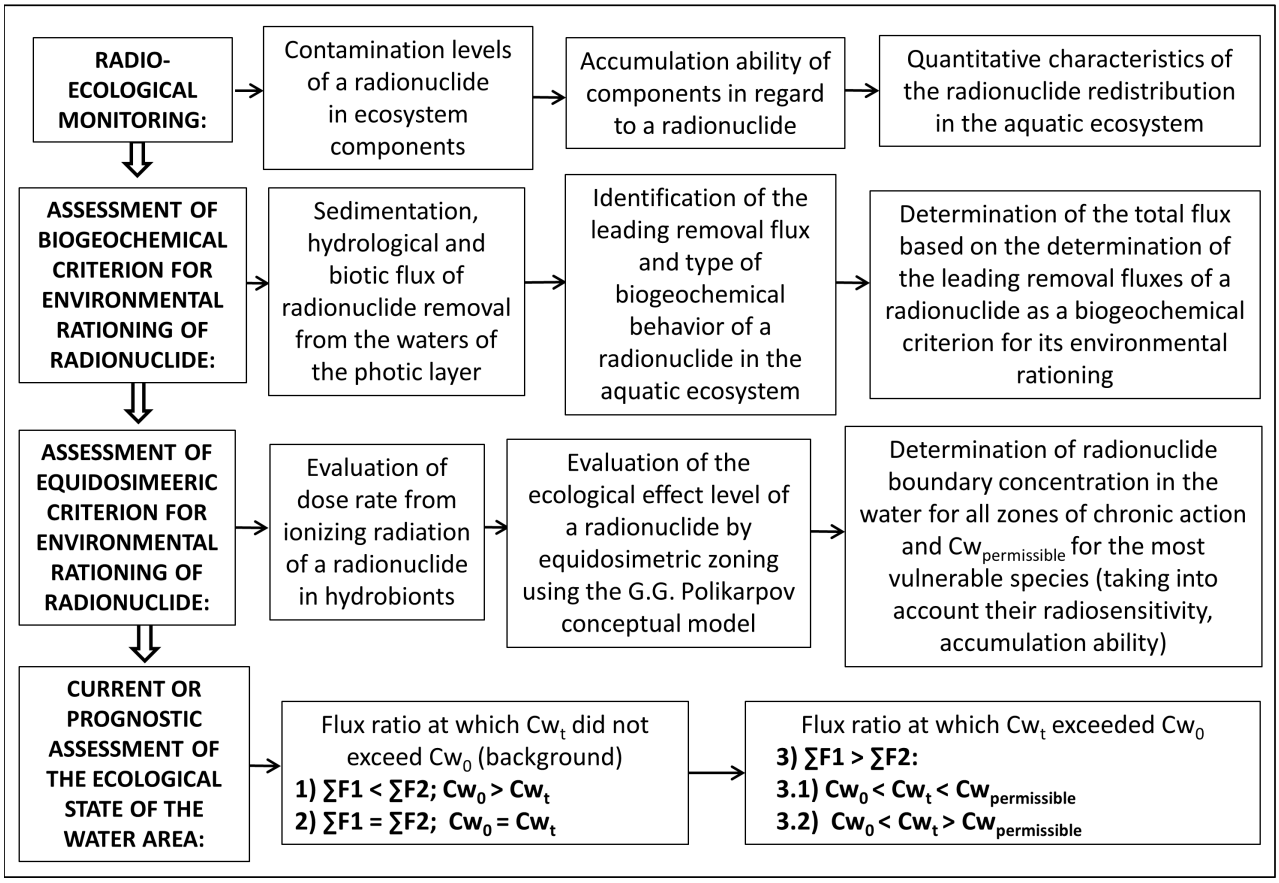

Fig. 5. Scheme for assessing biota ecological state (levels of expected ecological effect) in Black Sea water areas according to biogeochemical and equidosimetric criteria for a wide range of ^{239,240}Pu activity concentration in water;
F1 – ^{239,240}Pu input flux;
F2 – ^{239,240}Pu removal flux;
C_W – ^{239,240}Pu activity concentration in water;
Cw_0 – background level of C_W in water;
$C_{permissible}$ – ^{239,240}Pu activity concentration level in water, exceeding of which causes negative changes in hydrobionts populations

of $^{239+240}$Pu activity concentration in seawater. Attention was focused on the importance of taking into account biogeochemical indicators for predictive dosimetric assessments, in particular C_f, quantitatively characterizing accumulation capacity of Black Sea hydrobionts and type of radioisotopes biogeochemical behavior in a water area, as well as reflecting features of plutonium biogeochemical migration of it.

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ПРИМЕНЕНИЕ КОНЦЕПТУАЛЬНОЙ МОДЕЛИ ЗОНАЛЬНОСТИ ХРОНИЧЕСКОГО ДЕЙСТВИЯ МОЩНОСТЕЙ ДОЗ ИОНИЗИРУЮЩИХ ИЗЛУЧЕНИЙ НА ОБЪЕКТЫ БИОСФЕРЫ Г. Г. ПОЛИКАРПОВА В ПРИКЛАДНОЙ ГИДРОБИОЛОГИИ*

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В работе кратко рассмотрена эволюция подхода к оценке воздействия ионизирующей радиации на живые организмы. На примере черноморских гидробионтов показана возможность применения концептуальной радиохемоэкологической модели зональности действия хронического облучения ионизирующих излучений в природе Г. Г. Поликарпова для оценки уровня экологического воздействия ионизирующего излучения от техногенных радиоизотопов на водную биоту. Эта модель может служить в прикладной гидробиологии основой комплексного подхода в оценке экологического состояния водной биоты и его прогноза для широкого диапазона концентраций активности ^{239,240}Pu в морской воде. Подчёркивается необходимость совместного применения биогеохимического и эквидозиметрического показателей поведения радиоизотопов в водоёме. В частности, для прогнозных дозиметрических оценок важно учитывать количественные характеристики концентрирующей способности черноморских гидробионтов и тип биогеохимического поведения радиоэлемента, отражающие особенности биогеохимической миграции плутония в морской экосистеме.

Ключевые слова: оценка экологического состояния водной биоты, Чёрное море, биогеохимическая миграция, перераспределение радиоизотопов ^{239,240}Pu, дозовые нагрузки, гидробионты, концептуальная модель Г. Г. Поликарпова

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