Original article

# Trace Elements in the Components of the Aquatic Ecosystem of the North Crimean Canal and Irrigated Farmland

## V. Yu. Proskurnin, N. Yu. Mirzoeva, O. D. Chuzhikova \*, M. O. Vakhrushev

A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russia \* e-mail: olga88.chp@ya.ru

#### Abstract

For 2022–2023, the concentrations of trace elements (Be, V, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Ag) were determined in the aquatic ecosystem of the North Crimean Canal, adjacent irrigated soils and cultivated irrigated agricultural crops. The content of all studied elements was determined in their acidic concentrates and mineralizates in accordance with State Standard of Russia 56219-2014 by mass spectrometry with inductively coupled plasma on a PlasmaQuant MS Elite mass spectrometer (AnalytikJena, Germany) on the basis of the collective use center "Spectrometry and Chromatography", A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS. The concentrations of heavy metals and trace elements in the aquatic ecosystem of the North Crimean Canal allowed safe use of the Dnieper water both for drinking and for other economic needs of Crimea. The maximum relative increase in the heavy metals pool due to irrigation of fields with the Dnieper water was for Mo (up to 0.1 %), Zn, Sb and Pb (no more than 0.04 %), which cannot affect the ecological state of the irrigated lands. In soils, a systematic excess of the maximum permissible concentrations was observed for Cd (up to 230 %) both in rice and wheat fields as well as in virgin lands. In rice and wheat crops, the maximum permissible levels for grain and grain fodder for Fe, Ni, Cd, As were exceeded. In the wheat ear, maximum permissible levels were exceeded for Fe (by 24 %), Ni (by 110 %) and As (by 70 %). Maximum permissible concentrations in rice grain were exceeded for Cu (by 29 %), Cd (by 150 %) and Pb (by 438 %), and in wheat grain – for Cd (by 360 %) and Pb (by 300 %). It was revealed that insignificant amounts of trace elements brought with the Dnieper water through the North Crimean Canal cannot have a noticeable effect on the irrigated farmland of Crimea. The detected excesses of maximum permissible concentrations and maximum permissible levels of trace elements in soils and agricultural crops are probably due to the activities of industrial enterprises in the north of the peninsula.

**Keywords**: North Crimean Canal, heavy metals in soil, heavy metals in plants, heavy metals in water, irrigated soils, agricultural plants, heavy metal pollution

**Acknowledgments**: The work was carried out within the framework of the Russian Science Foundation Grant, Project No. 23-26-00128: "The role of the North Crimean Canal irrigation system in the processes of transfer of long-lived radionuclides of Chernobyl origin, heavy metals, as well as hydrocarbons with Dnieper water to irrigated farmland of the Crimea".

© Proskurnin V. Yu., Mirzoeva N. Yu., Chuzhikova O. D., Vakhrushev M. O., 2024



This work is licensed under a Creative Commons Attribution-Non Commercial 4.0 International (CC BY-NC 4.0) License

**For citation**: Proskurnin, V.Yu., Mirzoeva, N.Yu., Chuzhikova, O.D. and Vakhrushev, M.O., 2024. Trace Elements in the Components of the Aquatic Ecosystem of the North Crimean Canal and Irrigated Farmland. *Ecological Safety of Coastal and Shelf Zones of Sea*, (3), pp. 123–138.

# Микроэлементы в компонентах водной экосистемы Северо-Крымского канала и орошаемых сельхозугодий

# В. Ю. Проскурнин, Н. Ю. Мирзоева, О. Д. Чужикова \*, М. О. Вахрушев

Институт биологии южных морей имени А. О. Ковалевского РАН, Севастополь, Россия \* e-mail: olga88.chp@ya.ru

### Аннотация

В 2022-2023 гг. в водной экосистеме Северо-Крымского канала, орошаемых почвах вдоль него и выращиваемых поливных сельскохозяйственных культурах были определены концентрации микроэлементов Be, V, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Ag. Содержание всех изучаемых элементов определяли в их кислотных концентратах и минерализатах в соответствии с ГОСТ Р 56219-2014 методом массспектрометрии с индуктивно-связанной плазмой на масс-спектрометре PlasmaQuant MS Elite (AnalytikJena, Германия) на базе НО ЦКП «Спектрометрия и хроматография» ФИЦ ИнБЮМ. Концентрации тяжелых металлов и микроэлементов в водной экосистеме Северо-Крымского канала были безопасны для использования днепровской воды в качестве питьевой, а также для других хозяйственных нужд Крыма. Максимальное относительное увеличение пула микроэлементов вследствие орошения полей днепровской водой было определено для Мо (до 0.1 %), а также для Zn, Sb и Pb (не более 0.04 %), что не может существенно влиять на экологическое состояние орошаемых земель. В почвах как рисовых и пшеничных полей, так и целинных земель наблюдалось систематическое превышение предельно допустимой концентрации Cd для почв сельхозугодий (до 230 %). В культурах риса и пшеницы обнаружено превышение максимально допустимых уровней содержания Fe, Ni, Cd, As для зерна и зернофуража. В колосе пшеницы максимально допустимые уровни Fe были превышены на 24 %, Ni - на 110 %, As - на 70 %. В зерне риса были превышены предельно допустимые концентрации для продуктов питания Cu (на 29 %), Cd (на 150 %) и Pb (на 438 %), а в зерне пшеницы – Cd (на 360 %) и Pb (на 300 %). Выявлено, что незначительные количества микроэлементов, приносимые с днепровской водой по Северо-Крымскому каналу, не могут оказать ощутимого эффекта на орошаемые сельхозугодья Крыма. Обнаруженные превышения предельно допустимых концентраций и максимально допустимых уровней микроэлементов в почвах и сельскохозяйственных культурах обусловлены, вероятно, деятельностью промышленных предприятий на севере полуострова.

Ключевые слова: Северо-Крымский канал, тяжелые металлы в почве, тяжелые металлы в растениях, тяжелые металлы в воде, орошаемые почвы, сельскохозяйственные растения, загрязнение тяжелыми металлами

Благодарности: работа выполнена в рамках гранта РНФ, проект № 23-26-00128: «Роль оросительной системы Северо-Крымского канала в процессах переноса долгоживущих радионуклидов чернобыльского происхождения, тяжелых металлов, а также углеводородов с днепровской водой на поливные сельхозугодья Крыма». Для цитирования: Микроэлементы в компонентах водной экосистемы Северо-Крымского канала и орошаемых сельхозугодий / В. Ю. Проскурнин [и др.] // Экологическая безопасность прибрежной и шельфовой зон моря. 2024. № 3. С. 123–138. EDN MHWSYU.

## Introduction

The North Crimean Canal (NCC) was constructed and brought into operation in 1971 with the objective of providing a sustainable water supply to Southern Ukraine and Crimea. The arid climate of the Crimean peninsula presents significant challenges to agricultural production. Consequently, the operation of the NCC system is of great strategic importance for the water supply of the vast agricultural lands in the northern and north-western parts of the peninsula<sup>1</sup> [1]. Among the agricultural crops grown on the peninsula, rice and wheat are of particular importance [2, 3]. In 2022, after an eight-year break in the regular operation of the canal, the supply of the Dnieper water to Crimea via the NCC was resumed [4]. One of the most important indicators of the quality of used water is the content of heavy metals (HM) and other trace elements in it. It is advisable to monitor this indicator both in soils irrigated with this water and in agricultural crops grown on them [5, 6]. In order to ascertain the potential adverse effects of the Dnieper water supplied by the NCC on the quality of irrigated agricultural crops cultivated on the peninsula, it is essential to gain an understanding of the patterns of HM redistribution within the following system: water – irrigated soils – irrigated agricultural crops.

The objectives of the study are as follows:

a) determination of the current quality of the Dnieper water supplied along the NCC with respect to trace elements (Be, V, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Ag), including heavy metals;

b) quantification of the levels of transfer of these elements from water to irrigated soils located along the NCC and agricultural crops grown on them;

c) comparison of the obtained results with the sanitary norms established in the Russian Federation regarding the content of HM and other trace elements in the studied objects.

This study is the first of its kind to examine the objectives set and the number of elements studied in the sampled objects in the NCC area and in the adjacent irrigated farmland. Consequently, it is a pioneering piece of research.

## Material and methods

To determine trace elements, including HM, water and suspended matter samples were taken directly from the NCC bed and diversion canals. Soil samples of fields irrigated with water from the NCC as well as rice and wheat grown on them

<sup>&</sup>lt;sup>1)</sup> Sokolov, A.A., 1964. [*Hydrography of the USSR (Land Waters)*]. Leningrad: Gidrometeoizdat, 535 p. (in Russian).

were taken in the areas of the villages of Krepkoe and Ilyinka and the city of Dzhankoy (the village of Pobednoe), (Fig. 1, Table 1). Samples were collected between April 2022 and May 2023, and the concentration of 15 trace elements (Be, V, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Tl, Pb) was determined. The dissolved forms of the determined elements were extracted from water by their extraction concentration as diethyldithiocarbamates using carbon tetrachloride,



Fig. 1. Scheme map of sampling in the area of the North Crimean Canal (2022–2023). Sampling stations: 1 - main bed of the NCC, Armyansk area; 2 - main bed of the NCC, Krasnoperekopsk area; 3 - the village of Krepkoe, Krasnoperekopsk area; 4 - branch of the NCC, the village of Ilyinka, Krasnoperekopsk area; 5 - the village of Pobednoe, Dzhankoy area). Water reservoirs: MR – Mezhgornoe, SKR – Starokrymskoe, FR – Feodosiyskoe, FrR – Frontovoe, LR – Leninskoe, SR – Samarlinskoe, StR – Stantsionnoe (Kerchenskoe)

Table 1. Coordinates of sampling stati	ions
--	------

Study area	Sampling coordinates (N, E)
1. NCC main bed (Armyansk area)	46°07.208', 33°41.426'
<ul><li>2. NCC main bed</li><li>(Krasnoperekopsk area)</li></ul>	45°57.261', 33°49.184'
<ul><li>3. The village of Krepkoe</li><li>(Krasnoperekopsk area): wheat field paddy fields</li></ul>	45°55.419', 33°54.223' 45°56.097', 33°55.029'
4. NCC branch (Krasnoperekopsk area), the village of Ilyinka	45°50.067', 33°45.600'
5. NCC main bed, the village of Pobednoe (Dzhankoy area), irrigated field	45°45.500', 34°26.230'

in accordance with Regulatory Document 52.10.243-92. The determined elements were extracted from solid samples (soils, suspended matter, stems and grains of rice and wheat) by acid mineralization followed by filtration in accordance with Federal Environmental Regulations 16.2.2:2.3.71-2011. The content of all studied elements was determined in their acidic concentrates and mineralizates in accordance with State Standard of Russia 56219-2014 by mass spectrometry with inductively coupled plasma on a PlasmaQuant MS Elite mass spectrometer (AnalytikJena, Germany) on the basis of the collective use center "Spectrometry and Chromatography" A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS. The mass spectrometer was calibrated using standard solution "Calibration Multielement Standard IV-28, HNO<sub>3</sub>/HF, 125 mL" (Inorganic Ventures) by plotting a calibration straight line across solutions with dilution degrees of the standard covering the full range of element concentrations to be determined. The measurement procedure included at least seven repetitions for each measured element in each sample. The measurement time of each m/z ratio was determined by the intensity of the detector response to the presence of a particular element in solution and ranged from 0.01 to 0.1 s. The relative error of measurement was determined for all measured elements, with a maximum value of 10 % observed.

To assess water quality, the obtained values of element concentrations were compared with the maximum permissible concentrations (MPC) established by Sanitary Regulations and Standards 1.2.3.3685-21<sup>2)</sup> for domestic and drinking water use (MPC<sub>DD</sub>). It should be noted that such MPCs are also applied to waters used for irrigation. As the local population catches and consumes the fish that inhabit the canal, the obtained values were also compared with MPC recommended for waters of water bodies for fishery purposes<sup>3)</sup> (MPC<sub>fish</sub>). The values of element concentrations determined in soils were compared with MPC (MPCsoil) (or approximately permissible concentrations (APC<sub>soil</sub>)) values established for agricultural soils<sup>2)</sup>. In addition, since farming in Crimea is primarily based on chestnut soils with pH > 5.5, the MPC<sub>soil</sub> (APC<sub>soil</sub>) values for clay and loam soils with pH > 5.5were used where applicable. The transfer of elements with the NCC waters to irrigated fields was estimated based on the average norm of specific mass of arable horizon of soil 3000 t ha-1 (in accordance with Sanitary Regulations and Standards 2.1.7.573-96) and maximum water consumption rates for irrigation of fields with spring grain crops in Rostov Oblast as similar in soil type and climatic features to the Crimean peninsula, up to 4140 m<sup>3</sup>·ha<sup>-1</sup>·year<sup>-1</sup> (in accordance with State Standard of Russia 58331.3-2019). Agricultural crop quality was assessed according to the temporary maximum permissible levels (MPL) for grain and grain fodder for farm animals<sup>4)</sup> and MPC for cereals as a human foodstuff (MPC<sub>food</sub>) (Sanitary Regulations and Standards 2.3.2.560-96). Regularities of trace elements accumulation by agricultural crops from soils were characterized by conversion factors (F<sub>c</sub>) calculated as the ratio of the concentration of the element in the crop (part of the crop)  $C_{\rm crop}$  to the concentration of the element in the soil under this crop  $C_{\rm soil}$ .

## **Results and discussion**

Table 2 shows the results of measurements of trace elements concentrations in the Dnieper water of the NCC used for irrigation, in irrigated soils and crops.

Fig. 2 shows the assessment of the NCC water quality in relation to trace elements content in 2022–2023.

<sup>&</sup>lt;sup>2)</sup> Popova, A.Yu., 2021. Sanitary Regulations and Standards СанПиН 1.2.3.3685-21 *Hygienic Norms* and Requirements to Ensure Safety and/or Harmlessness of Habitat Factors for Humans (as Amended for 30 December 2022). Moscow, 469 p. (in Russian).

<sup>&</sup>lt;sup>3)</sup> On the Approval of Water Quality Standards for Water Bodies of Commercial Fishing Importance, Including Standards for Maximum Permissible Concentrations of Harmful Substances in the Waters of Water Bodies of Commercial Fishing Importance: Order of the Ministry of Agriculture of Russia dated December 13, 2016, No. 552 (in Russian)

<sup>&</sup>lt;sup>4)</sup> Tretyakov, A.D. and Zaichenko, A.I., 1987. Temporary maximum permissible level (MPL) of the content of some chemical elements and gossypol in feed for farm animals and feed additives (approved by the Main Veterinary Department of the State Agro-Industrial Committee of the USSR on 7 August 1987). Moscow.

	Water		0.1	Agricultural
Element	Dissolved form Tot	Total concentration	5011	crops
Pb	0.05-0.19	0.70–1.96	8.63-70.82	0.86–7.68
Cd	0.02–0.37	0.10-0.61	0.56-6.64	0.07 - 1.00
Zn	6.42–113.83	8.51–117.38	63.47-122.07	3.70-26.79
Cu	0.64–2.29	1.16–3.01	20.02-59.43	1.24-12.87
Fe	0.63–2.83	36.69–230.71	$10.2 \cdot 10^{3} - 42.7 \cdot 10^{3}$	33–2941
Co	0.02–0.06	0.04–0.14	11.33–15.42	0.02–0.89
Ni	0.76–1.39	1.24–2.26	38.22-51.65	0.39–4.21
Mo	0.02-0.21	0.34–0.65	0.45-2.85	0.03-1.33
Sb	0.008-0.015	0.014-0.023	0.03-0.22	< 0.01-0.03
As	0.01-0.20	0.06-0.27	4.91-10.91	<0.10-0.85
V	0.16-0.61	0.33-0.96	43.94–76.39	<0.10-5.40
Tl	< 0.001 - 0.005	0.001-0.006	0.11-0.27	< 0.001-0.017
Se	<0.03-0.19	<0.03-0.19	0.75-3.29	<0.30-0.32
Ag	< 0.001	< 0.001-0.11	0.12-0.32	< 0.01
Be	< 0.01	<0.01-0.01	0.80-1.30	<0.001-0.086

T a ble 2. Concentrations of trace elements in the water ( $\mu g \cdot L^{-1}$ ), in the soil and in the agricultural crops ( $mg \cdot kg^{-1} D.W.$ )

It should be noted that RF normative documents <sup>2), 3), 5), 6) regulate the content of dissolved forms of elements only. On the basis of the analysis of the data obtained, it was found that the concentrations of trace elements in the water (both in their dissolved and total (suspended) forms) did not exceed MPC<sub>DD</sub> <sup>2), 5), 6)</sup> throughout the period of the studies.</sup>

With regard to MPC<sub>fish</sub><sup>3)</sup>, a single exceedance of twice the standard for zinc concentration in the water (dissolved form) was observed in March 2023 under low level conditions prior to the start of water supply.

<sup>&</sup>lt;sup>5)</sup> Kurlyandsky, B.A. and Sidorov, K.K., eds., 2003. Hygienic standard FH 2.1.5.1315-03. Maximum permissible concentrations of chemical substances in the water of water bodies of household and cultural and domestic water use: approved by the Decree of the Head State Sanitary Doctor of the Russian Federation from 30 April 2003 no. 79. Moscow: Neftyanik, 152 p. (in Russian).

<sup>&</sup>lt;sup>6)</sup> Mazaev, V.T., 2002. Sanitary Regulations and Standards SANPIN 2.1.4.1074-01. Drinking Water. Hygienic Requirements for Water Quality of Centralised Drinking Water Supply Systems. Quality Control (Approved by the Chief State Sanitary Doctor of the Russian Federation on 26 September 2001, no. 24). Moscow, 103 p.



Fig. 2. Ratio of average ( $C_{av}$ ) and maximum ( $C_{max}$ ) concentrations of dissolved forms of trace elements (TE) in the North Crimean Canal water to MPC<sub>DD</sub> (*a*) and MPC<sub>fish</sub> (*b*) in 2022–2023

It was determined that the maximum concentration factors (C<sub>f</sub>) of elements by suspensions were observed for Fe  $-n \cdot 10^7$ , slightly lower values of C<sub>f</sub> were observed for As, Mo, Cd and Pb  $-n \cdot (10^5 \div 10^6)$ , the values of C<sub>f</sub> did not exceed  $n \cdot 10^5$ for V, Co, Ni, Cu, Se, Sb and Tl, and the values of this coefficient were minimal for Zn and varied in the range of  $n \cdot (10^3 \div 10^4)$ . Such high values of C<sub>f</sub> determine the most efficient sedimentation self-purification of the NCC waters from Fe, As, Mo, Cd and Pb, to a lesser extent from V, Co, Ni, Cu, Se, Sb and Tl and the least efficient from Zn.

Concentrations of dissolved forms of Be and Ag were below their detection limits: for Be  $-0.01 \ \mu g \cdot L^{-1}$ , Ag  $-0.001 \ \mu g \cdot L^{-1}$ . Fig. 2 shows the ratios of the detection limits to the corresponding MPC values for these elements.

Fig. 3 shows the assessment of the quality of arable soils of agricultural lands and adjacent virgin land plots in the north of Crimea with regard to the content of trace elements in them.



Fig. 3. Ratio of trace elements (TE) concentrations ( $C_{TE}$ ) in soils of arable (*a*) and virgin (*b*) land plots in the north of Crimea to the maximum (MPC<sub>soil</sub>) and approximately (APC<sub>soil</sub>) permissible concentrations of TE in soils in 2022–2023

A systematic excess of MPC<sub>soil</sub> was observed for Cd – up to 230 % – both in rice and wheat fields (the village of Krepkoe, Fig. 1, Table 1) as well as in virgin lands (the village of Krepkoe, the village of Ilyinka, Fig. 1, Table 1). The vertical distribution of Cd in arable soils indicated an increase in its concentration with the depth of the bedding layer. Maximum exceedance of MPC<sub>soil</sub> for Cd in the rice field in this area appeared to be due to homogenisation of surface soil layers by mechanical processing. Minor exceedance of MPC<sub>soil</sub> for As was observed only in virgin soil adjacent to the rice field near the village of Ilyinka (Fig. 1, Table 1), with no exceedances observed in the arable soil itself.

Fig. 4 shows the results of calculation of ranges of specific pools of trace elements in arable soils of the studied fields and of elements supply with the NCC waters used for irrigation.

The results of calculations (Fig. 4) show that the maximum values of metal supply to irrigated soil with irrigation water are expected for Fe  $-0.43\div0.95$  kg·ha<sup>-1</sup> (0.001 % of the pool) and Zn  $-0.05\div0.11$  kg·ha<sup>-1</sup> (0.03 % of the pool).







Fig. 4. Ranges of specific pools of microelements (*a*) in arable soils of Crimea (P<sub>TE</sub>) and assessment of the absolute (*b*) and relative (*c*) changes in these pools ( $\Delta P_{TE}$ ) due to the supply with the North Crimean Canal waters used for irrigation

At the same time, the maximum relative increase in the pool of trace elements due to irrigation is expected for Mo (up to 0.1 %), Zn, Sb and Pb (not more than 0.04 %), which, obviously, will not affect the ecological state of the irrigated lands.

Calculations of conversion factors ( $F_c$ ) of elements from irrigated soils to rice and wheat crops grown on them show that with respect to many elements their concentration in grain in relation to the stem of the studied crops is observed. To quantify this concentration, magnification coefficients ( $C_m$ ) were calculated as the ratio of the concentration of trace elements in the grain to the concentration in the plant stem. Figs. 5 and 6 show the results of such calculations.

It was demonstrated (see Figs. 5 and 6) that, of the trace elements (Fe, Ni, Co, Cu, Zn, Mo, Sb, Cd and Pb) reliably measured in rice cultivation, all elements except Cd exhibited a greater accumulation in the grain than in the stems. In contrast, the accumulation of Cd in wheat grain was found to be significantly higher than that of other elements, while Sb and Mo were more concentrated in plant stems. This discrepancy highlights the distinctive physiological characteristics of rice and wheat crops.



Fig. 5. Coefficients  $F_c$  (conversion factor) (*a*) and  $C_m$  (magnification coefficient) (*b*) of the trace elements for rice crops in the village of Krepkoe



Fig. 6. Coefficients  $F_c$  (conversion factor) (*b*) and  $C_m$  (magnification coefficient) (*b*) of the microelements for wheat crop in the village of Ilyinka (Krasnoperekopsk area) and the village of Pobednoye (Dzhankoy area)

Fig. 7 shows the results of quality assessment of the studied crops with respect to their trace elements content.

In a rice crop from the village of Krepkoe, maximum permissible levels for Fe content in grain and grain fodder as animal feed were exceeded in grain by 49 % and for Ni – by 214 %, while Cd concentrations in rice stems reached maximum permissible levels<sup>4</sup>.

In a wheat crop from the village of Ilyinka, maximum permissible levels for Fe were exceeded in ear by 24 %, for Ni – by 110 %, for As – by 70 %, and in wheat stems, Fe and As content exceeded maximum permissible levels by 52 and 68 %, respectively. MPC<sub>food</sub><sup>7), 8)</sup> in rice grain were exceeded for Cu by 29 %, for Cd – by 150 %

<sup>&</sup>lt;sup>7)</sup> Trukhachev, V.I., Tolokonnikov, V.P. and Lysenko, I.O., 2005. [*Food as an Environmental Factor: A Textbook for the Discipline of Biology and Bioecology*]. Stavropol: AGRUS, 182 p. (in Russian).



Fig. 7. Ratio of trace elements concentrations in rice and wheat crops ( $C_{TEc}$ ) to MPL (maximum permissible levels for grain and grain fodder for livestock feed) (*a*) and MPC<sub>food</sub> (MPC for grains and cereals as human food products) (*b*)

and for Pb – by 438 %, and in wheat grain from a field near Dzhankoy, the Cd content exceeded MPC<sub>food</sub> by 360 %, Pb – by 300 %.

The findings of the study indicated that during the 2022-2023 period, the Dnieper water in the NCC met the standards set forth by the Russian Federation for the concentration of trace elements in water intended for household use, drinking and irrigation. Exceedances of MPC<sub>soil</sub> for Cd and As were detected in both arable and virgin soils, which, as noted earlier, is due to the activities of industrial enterprises, including chemical industry, located in the north of the peninsula [13, 14]. Exceedance of maximum permissible levels of some trace elements in agricultural crops was also observed, which is connected with transfer of these elements from soils and their concentration by plants.

<sup>&</sup>lt;sup>8)</sup> State Committee for Sanitary Supervision and Disease Control, 1997. SANPIN 2.3.2.560-96. [2.3.2 Food Raw Materials and Food Products. Hygienic Requirements to Quality and Safety of Food Raw Materials and Food Products]. Moscow: Goskomepidnadzor Rossii, 269 p. (in Russian).

## Conclusion

In 2022–2023, during the period of the NCC operation from the moment of resumption of the Dnieper water inflow through the canal system (March 2022, after eight years of its absence since 2014) and until the termination of water supply to the canal ecosystem (after the destruction of Kakhovka Hydroelectric Power Plant in June 2023), studies were conducted to determine the concentrations, migration and distribution of trace elements (Be, V, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Ag), including HM, in the NCC water, irrigated soils and growing irrigated crops.

It was determined that the concentrations of HM and microelements in the aquatic ecosystem of the NCC allowed safe use of the Dnieper water both for drinking and for other economic needs of Crimea.

The concentrating capacity of suspended matter in the NCC water was determined, expressed by concentration factors (C<sub>f</sub>), the values of which varied in the range from  $n \cdot 10^7$  (for Fe) to  $n \cdot 10^3$  (for Zn). Such high values of C<sub>f</sub> of the investigated elements cause effective sedimentation self-purification of the NCC waters from HM and other pollutants.

Systematic exceedances of MPC<sub>soil</sub> for Cd up to 230 % were observed both in rice and wheat fields and in virgin soils. Exceedances of MPC<sub>food</sub> for Cu (by 29 %), Cd (by 150 %) and Pb (by 438 %) were noted in rice grain and MPC<sub>food</sub> for Cd (by 360 %) and Pb (by 300 %) – in wheat grain from a field near Dzhankoy. The revealed exceedances of MPC and maximum permissible levels of trace elements in soils and crops are probably caused by the activities of industrial enterprises in the north of the peninsula.

The results of calculations of trace elements and HM pools supply to irrigated soils showed that even maximum values of metals supply with irrigation water (they do not exceed 0.001 % of the pool for Fe) would not affect the ecological state of irrigated lands. In other words, insignificant amounts of trace elements brought with the Dnieper water through the NCC cannot have a noticeable effect on the irrigated farmland of Crimea. At the same time, estimation of trace elements content in agricultural crop grain and grain fodder requires additional monitoring studies.

The results obtained can be used to devise strategies for the prevention of chemical contamination of irrigated agricultural lands in Crimea, thereby addressing the challenges of sustainable development in the Crimean region and the Black Sea regions of Russia as a whole.

### REFERENCES

- 1. Shevchenko, M.A., ed., 1989. [Hydrology and Hydrochemistry of the Dnieper River and its Reservoirs]. Kiev: Naukova Dumka, 216 p. (in Russian).
- 2. Koba, V.P. and Sakhno, T.M., 2020. Soil Fertility and Yielding Capacity of Grain and Leguminous Crops in the Crimea. *ArgoEcoInfo*, (2) (in Russian).
- Rodin, I.K. and Klepova, I.K., 2023. [Distribution of Cultivated Areas of Agricultural Crops in the Republic of Crimea after 2014]. In: RSAU, 2023. Proceedings of VII International Scientific and Practical Conference: The Ecological State of the Natural Environment and the Scientific and Practical Aspects of Modern Agricultural Technologies. Ryazan, 6 April 2023. Ryazan: Ryazan State Agrotechnological University Named after P. A. Kostychev, pp. 351–354 (in Russian).

- 4. Mirzoeva, N., Tereshchenko, N. and Korotkov, A., 2022. Artificial Radionuclides in the System: Water, Irrigated Soils, and Agricultural Plants of the Crimea Region. *Land*, 11(9), 1539. https://doi.org/10.3390/land11091539
- Ulesov, A.S., Tsedrik, E.S., Stich, A.A. and Gutsalova, A.A., 2020. [The Problem of Increasing Levels of Heavy Metals in Crop Irrigation Water]. In: RSAU, 2020. International Scientific-Practical Conference to the Memory of Corresponding Member of RAAS and KAS, Academician of MAEL and RAVN Bochkarev Y. V. 'Integrated Approach to Scientific and Technical Support of Agriculture'. Ryazan, 9 December 2020. Part II. Ryazan: RGATU, pp. 340–343 (in Russian).
- Chernykh, N.A., The Cuong Ngo, Tran Quoc Hoan, Baeva, Yu.I. and Grachev, V.A., 2018. The Regularities of Heavy Metals and Arsenic Accumulation in the Vegetation of Riverside Depending on the Level of Technogenic Load. *Journal of Pharmaceutical Sciences and Research*, 10(4), pp. 800–804. Available at: https://www.jpsr.pharmainfo.in/documents/Volumes/vol10Issue04/jpsr10041823.pdf [Accessed: 8 September 2024].
- Perevolotskaya, T.V. and Anisimov, V.S., 2017. Regularities of Migratory Processes of Heavy Metals in the System "Soil – Agricultural Plant" on the Example of the Coefficient of Accumulation of Cu, Zn, Pb, Cd in Grain Crops (Grain of Wheat and Barley). *Problemy Sovremennoy Nauki i Obrazovaniya*, (10), pp. 27–32 (in Russian).
- Koretskaya, A.S., Andreeva, G.Yu. and Nikonova, G.N., 2023. The Content of Heavy Metals in the Soil-Grain System. *Bulletin of Michurinsk State Agrarian University*, (4), pp. 96–100 (in Russian).
- Lukyanova, E.S. and Fedotov, V.A., 2024. Features of Accumulation of Heavy Metals in Soil and Grain Crops. *Trace Elements in Medicine*, 25(2), pp. 54–55 (in Russian). http://doi.org/10.19112/2413-6174-2024-25-2-23
- Bashmakov, D.I. and Lukatkin, A.S., 2009. [Ecological and Physiological Aspects of Accumulation and Distribution of Heavy Metals in Higher Plants]. Saransk: MRSU, 236 p. (in Russian).
- Krupnova, T.G., Rakova, O.V., Popkova, M.A. and Gavrilkina, S.V., 2023. Distribution of Some Heavy Metals in Winter Wheat at Different Stages of its Development. Bulletin of the South Ural State University. Series "Chemistry", 15(3), pp. 148–158. EDN UNIELM. https://doi.org/10.14529/chem230308
- Inisheva, V.D., Kurbanova, V.Yu., Fedorova, E.A., Shapovalova, A.A., Shapovalova, A.A., Naronova, A.A., 2018. Adsorption Properties of Rice in Relation to Salts of Heavy Metals. In: USMU, 2018. Proceedings of III International Scientific and Practice Conference of Young Scientists and Students "Issues of Modern Medical Science and Health Care" III Forum of Medical and Pharmaceutical High Schools in Russia "For Qualitative Education". Ekaterinburg, 03–05 April 2018. Ekaterinburg: USMU, pp. 592–595 (in Russian).
- Evstafeva, E.V., Bogdanova, A.M., Minkina, T.M., Sushkova, S.N., Baranovskaya, N.V., Mandzhieva, S.S. and Antonenko, E.M., 2018. Heavy Metal Content in Soils of Residential Territories of Crimea Republic. *Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering*, 329(10), pp. 19–29. https://doi.org/10.18799/24131830/2018/10/2101 (in Russian).
- 14. Lisetskii, F.N., Marinina, O.A., Poletaev, A.O. and Zelenskaya, E.Ya., 2020. Comparative evaluation of pollution by heavy metals of ploughed and fallow land at various duration of agropedogenesis. *Journal of Agriculture and Environment*, (3). https://doi.org/10.23649/jae.2020.3.15.2

Submitted 29.02.2024; accepted after review 25.03.2024; revised 17.06.2024; published 25.09.2024

#### About the authors:

Vladislav Yu. Proskurnin, Junior Research Associate, A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Av., Sevastopol, 299011, Russian Federation), ORCID ID: 0000-0002-2176-9228, Scopus Author ID: 55653290000, Researcher ID: H-4611-2018, *v\_proskurnin@ibss-ras.ru* 

Natalya Yu. Mirzoeva, Leading Research Associate, Head of the RchBD, A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Av., Sevastopol, 299011, Russian Federation), Ph.D. (Biol.), ORCID ID: 0000-0002-8538-2436; Scopus Author ID: 55623414000; Researcher ID: Q-9393-2016, *natmirz@mail.ru* 

Olga D. Chuzhikova, Junior Research Associate, A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Av., Sevastopol, 299011, Russian Federation), ORCID ID: 0000-0002-4518- 2624, Scopus AuthorID: 57205198922, Researcher ID: X-4583-2019, *olga88.chp@ya.ru* 

**Maxim O. Vakhrushev**, Leading Engineer, Graduate Student, A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Av., Sevastopol, 299011, Russian Federation), *140393@inbox.ru* 

#### Contribution of the authors:

**Vladislav Yu. Proskurnin** – setting goals and objectives, performing chemical analysis and measuring concentrations to determine microelements, including HMs, analytical data processing, writing the manuscript

**Natalya Yu. Mirzoeva** – setting goals, objectives, analyzing the results obtained, discussing the results, writing the article

**Olga D. Chuzhikova** – sample preparation and chemical analysis to determine the concentrations of heavy metals and microelements, drafting the article

**Maxim O. Vakhrushev** – participation in expeditions, sampling and preparation of samples, participation in chemical analysis to determine the concentrations of heavy metals and trace elements in the objects under study

All the authors have read and approved the final version of the manuscript.