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ASSESSMENT OF CONTAMINATION OF THE ESTUARINE AREA OF THE NORTHERN DVINA RIVER BY CALCULATING BACKGROUND CONCENTRATIONS (Fe, Mn, Zn, Cu, Cd, Pb, and Ni)

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This publication is a continuation of research on the quantitation of the heavy metal contamination level (Fe, Mn, Zn, Cu, Cd, Pb, and Ni) in the ecosystem components of the estuarine area of the Northern Dvina River. To assess the contamination level with these metals in the ecosystem of the Northern Dvina estuarine area in the spot of the highest anthropogenic load (the area of Novodvinsk – Arkhangelsk – Severodvinsk urban agglomeration), we use the method of comparative analysis of the study object with the background plot – the river section above urban development. Using spatial mapping of the enrichment factor values for the aquatic ecosystem components, areas with abnormal excess of metal content in mollusc tissues, bottom sediments, and bottom water layer were determined. As established, the area adjacent to the city center and to an industrial zone on the left bank is subject to the highest anthropogenic load in the water area of the river delta top. The most likely sources of contamination with the considered heavy metals are the inflow of surface wastewater (meltwater and rain storm runoff), untreated municipal wastewater, and direct short-range atmospheric transport. The analysis of mollusc tissues proved to be a more informative and indicative approach to the assessment of the heavy metal contamination in water areas with complex hydrological and hydrochemical environmental gradients than the analysis of bottom water layer and bottom sediments.

Keywords: estuarine area of the Northern Dvina River, background concentrations, heavy metals, enrichment factor, bivalves

Rivers draining huge basins are the main source of inflow from land to sea of dissolved and suspended matter, *inter alia* organic matter, trace elements, and biogenic substances. The bulk of these substances, inputted from drainage basins, are deposited in estuarine areas of rivers – in the zone of freshwater and saltwater mixing; hence, the information on the state of the estuarine areas of rivers can help in characterizing both the marine environment and drainage basin area (Kotova et al., 2020). Moreover, coastal cities and manufacturing enterprises are mostly concentrated in the estuarine areas of rivers since there is a need for a constant source of freshwater. The works carried out to assess the heavy metal content in the ecosystem components of the estuarine area of the Northern Dvina River (Neverova et al., 2014, 2016) using threshold limit values (hereinafter TLVs) revealed the need to apply an approach with the calculation of conditional background concentrations typical for the research area. Mosaicity and high variability of the metal content in abiotic and biotic components of the aquatic ecosystem of the estuarine area of the Northern Dvina were recorded as well. The highest values of the heavy metal concentrations in water, bottom sediments, and hydrobiont tissues were observed (with no regularities) in local areas and for certain metals.

At the first stage of the work (Neverova et al., 2014), to quantify the heavy metal content in bottom water, bottom sediments, and tissues of macrobenthic species in the Northern Dvina delta, we compared the results obtained with the generally accepted state standards – TLVs. Importantly, concentrations of all metals in the entire studied section exceeded the standard. The results of observations carried out by the Northern Directorate for Hydrometeorology and Environmental Monitoring (Obzory zagryazneniya okruzhayushchei sredy, 2021) also annually show increased concentrations (up to 2–6 TLV) of Mn, Fe, Zn, and Cu. In various documents issued by environmental organizations, such excess is associated with the consequences of economic activities. However, in the estuarine area of the Northern Dvina River, there are no enterprises with high heavy metal content in technological processes. This fact demonstrates as follows: the existing state standards (TLVs) cannot be unified for all the types of aquatic ecosystems and for different climatic, geographic, and geochemical conditions. To date, most researchers dealing with this problem (Venitsianov et al., 2015 ; Wozniak & Lepikhin, 2018 ; Khorudzhaya, 2002) agree that it is unacceptable to apply uniform TLV norms to all regions; technogenic loads on ecosystems have to be standardized based on regional geochemical peculiarities. Moreover, the TLVs themselves have not been established for the vast majority of the aquatic ecosystem components, in particular for bottom sediments and tissues of benthic species.

To quantify the contamination level of the ecosystem components when having no TLVs, several models are usually applied to compare heavy metal concentrations obtained with metal natural content in the ecosystem (background values). The values of the indicator, which were established for the area not under direct anthropogenic load, can be used as the background ones. However, almost all the types of aquatic ecosystems are now affected by human activities (for example, resulting from long-range atmospheric transport or agricultural work in the depths of the drainage basins), and we can only talk about conditional background values. In this work, we chose as a background plot the river section above the spot of the highest anthropogenic load (above the area of Novodvinsk – Arkhangelsk – Severodvinsk urban agglomeration). To assess the background values of the heavy metal concentrations in water, bottom sediments, and mollusc tissues, we use the median and mean absolute deviation (*MAD*) obtained for a set of sampling points in the background plot. This method is recognized as the most sensitive one for calculating metal background levels in the analysis of contamination of components of the environment (Lukashev, 2007 ; Reimann et al., 2005).

The aim of this work is to quantify the level of heavy metal contamination in the Northern Dvina River in the spot of the highest anthropogenic load, applying the method of comparative analysis with conditional background values and calculating the mean metal concentrations in the tissues of hydrobionts and in their habitat by nonparametric statistics methods; based on the spatial distribution of the enrichment factor values, to draw a conclusion about the main sources of contamination in the studied river section (household wastewater of Arkhangelsk and Novodvinsk, industrial enterprises in these cities, *etc.*).

MATERIAL AND METHODS

The Northern Dvina River and its tributaries in the northern Russian Plain belong to the White Sea basin. In the Northern Dvina basin, the main part of the region's industrial potential is concentrated. The estuarine area of the river can be attributed to the most developed territories from the standpoint of industry and transport in the north of the Russian Federation; the area is under significant anthropogenic load. The estuarine area of the Northern Dvina includes a vast section of the lower river reach from the Pinega confluence to the delta sea edge and the southeastern Dvina Bay of the White Sea (Fig. 1). "The upper boundary of the estuarine area is at the Pinega River estuary, where tidal level fluctuations are no longer observed. The sea boundary runs along the slope of depths in the Dvina Bay, approximately along the 8-meter isobath. The river section in the estuarine area has a length of 135 km along the navigable fairway" (Gidrologiya ust'evoi oblasti Severnoi Dviny, 1965).

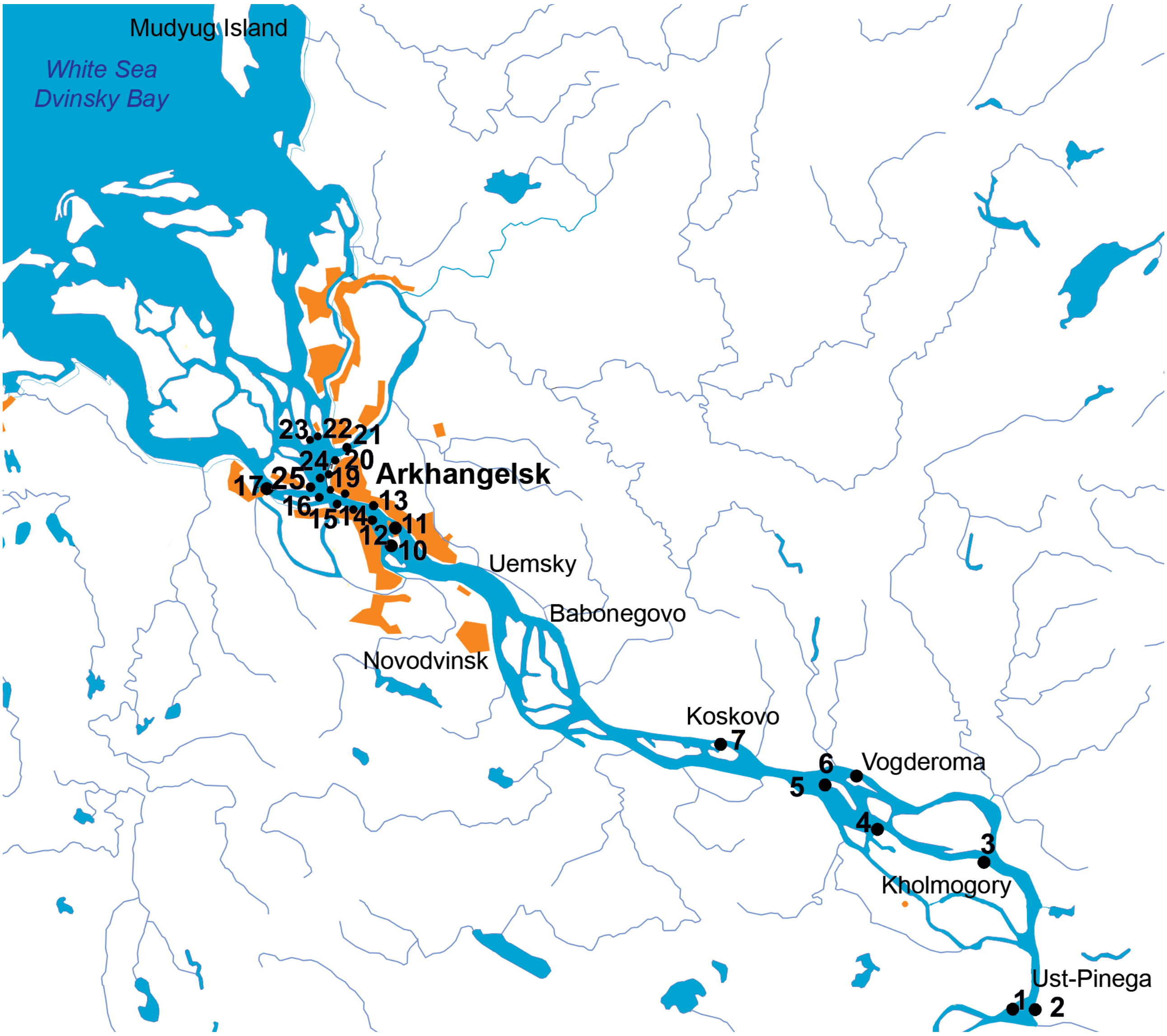

Fig. 1. Schematic map of the estuarine area of the Northern Dvina River with sampling points of bottom water layer, bottom sediments, and bivalves (points 1–7, the background plot; points 10–25, Arkhangelsk)

On the Northern Dvina, about 50 km from its confluence into the White Sea, Arkhangelsk is located; city quarters stretch for about 40 km along the right river bank. On the left bank, within the boundaries of Arkhangelsk, there are numerous industrial sites and low-rise residential areas, wooden buildings mostly, which stretch all the way to Novodvinsk.

To compare the heavy metal content, we chose the river section from Koskovo village to the upper boundary of the estuarine area (Ust-Pinega village) as the background plot (see Fig. 1, sampling points 1–7). Bivalve molluscs were sampled from their habitats simultaneously with bottom sediments and water in the estuarine area of the Northern Dvina at late July – August in 2009–2018. Molluscs were sampled by standard methods (Rukovodstvo po metodam, 1983) manually with a hydrological landing net or, at depths exceeding 1.5 m, with diving equipment. For the analysis, molluscs of the same age and size were selected from the sample and placed in vessels with water to cleanse their intestines; after this procedure, soft tissues were separated from shells and subjected to mineralization with concentrated nitric acid when heated. The preparation of biological samples for analysis is described in detail in the State Standard 26929-94 (2010).

The dominant benthic species in the studied river section, depending on biotope, are as follows: for solid substrate, bivalves *Dreissena polymorpha* (Pallas, 1771); for silted sand, *Anodonta anatina* (Linnaeus, 1758), *Unio pictorum* (Linnaeus, 1758), and *Pisidium* sp.; and for silt, Oligochaeta and Ghironomidae. To identify bivalve species, molecular genetic analysis was carried out according to the method (Bolotov et al., 2015). It showed that we have selected the most typical representatives of large bivalves for our area as objects for studying the heavy metal accumulation in tissues: *Anodonta anatina* (hereinafter duck mussel) and *Unio pictorum* (hereinafter painter's mussel). For *Dreissena*, no genetic analysis was performed: according to (Makhnovich, 2016), the mussels of this genus in the Northern Dvina belong to the species *Dreissena polymorpha* (Pallas, 1771). The analysis carried out earlier (Neverova et al., 2014, 2016) revealed that oligochaetes accumulate the maximum amount of metals; at the same time, due to technical difficulties in their sampling (primarily because of their small size), large bivalves are a more convenient object for studying the heavy metal accumulation.

Bottom water layer was sampled in accordance with the State Standard R 51592-2000 (2008), fixed with nitric acid, and, when transferred to a laboratory, subjected to mineralization when heated for analysis according to the Federal Environmental Regulatory Document 14.1:2.214-06 (2006). After preliminary drying to an air-dry state, bottom sediment samples were subjected to water bath–assisted extraction with 5 M nitric acid solution according to the Guidance Document 52.18.191-89 (Metodika vypolneniya izmerenii, 1990). All the solutions obtained (extracted tissues and bottom sediments; water) were analyzed by atomic absorption spectrometry on a novAA 315 spectrometer (Analytik Jena AG); in them, total content of Fe, Mn, Zn, Cu, Cd, Pb, and Ni was determined. The analysis was carried out at "Critical technologies of the Russian Federation in the field of environmental safety in the Arctic" core facility at the Federal Center for Integrated Arctic Research (Arkhangelsk).

All the empirical data obtained were preliminary assessed for compliance with the law of normal distribution using the Shapiro–Wilk test (Subbotina & Grzhibovskii, 2014). It showed that the distribution of most of the values obtained on the metal content in mollusc tissues, bottom water, and bottom sediments differs from the normal one. Therefore, to estimate the mean heavy metal content in mollusc tissues and in mollusc habitat at the background plot, we used the criteria of nonparametric statistics:

the median and *MAD*, defined as the median of absolute deviations from the median of all data (Lukashev, 2007 ; Reimann et al., 2005 ; Tukey, 2008). In this case, the background values were calculated by the formula:

$$C_f = Me_f \pm 2MAD\,, \tag{1}$$

where C_f is the background value of the studied indicator;

Me_f is the median value of a set of measured values (X_f) for the background plot;

MAD is the median of a set of absolute values of the differences between the measured X_f value and the median of a set of measured values for the background plot ($|X_f - Me_f|$).

To quantify the contamination level in certain areas of the riverbed, the metal content at a separate point was compared with the value of the upper limit of the background concentration using their ratio – the enrichment factor:

$$X_i/(Me_f + 2MAD)\,, \tag{2}$$

where X_i is the measured concentration value at the *i*-th sampling point.

If the ratio of the obtained metal concentration at a sampling point to the value of the upper limit of the background concentration is ≤ 1, the metal concentration at this point will be considered within the background fluctuation; if >1, the concentration will be considered increased.

Within the framework of the statistical analysis, to check the homogeneity of the sets of the heavy metal concentrations obtained for the background plot and for the area under direct anthropogenic load, an analysis was performed using the nonparametric Mann–Whitney *U* test.

To assess the spatial distribution of the enrichment factor values in heavy metals of the ecosystem components according to the data obtained at the sampling points, we used isoline schematic maps. Those were built in the Surfer software package; a data grid was created by the radial basis function interpolation. Since it is not an accurate interpolation method, the limits of maximum and minimum values were set manually.

RESULTS AND DISCUSSION

Bottom water layer. After processing the data obtained with the criteria of nonparametric statistics (the median and *MAD*), the following heavy metal concentrations were obtained in the bottom water layer for the background plot (points 1–7): Ni – (0.005 ± 0.003) $mg \cdot dm^{-3}$; Cd – (0.0038 ± 0.0026) $mg \cdot dm^{-3}$; Zn – (0.015 ± 0.011) $mg \cdot dm^{-3}$; Cu – (0.006 ± 0.001) $mg \cdot dm^{-3}$; Mn – (0.087 ± 0.023) $mg \cdot dm^{-3}$; and Fe – (0.420 ± 0.060) $mg \cdot dm^{-3}$. Pb content was below the detection limit. When testing the hypothesis that two compared sets (for the background plot and the river area within the city limit) belong to the same general population using the Mann–Whitney *U* test, we obtained statistically significant differences at $p \leq 0.05$ for Ni concentration alone.

Bottom sediments. Background concentrations for upper layer of bottom sediments had the values as follows (points 1–7): Ni – (3.64 ± 1.10) $mg \cdot kg^{-1}$; Pb – (1.02 ± 0.68) $mg \cdot kg^{-1}$; Cd – (0.14 ± 0.05) $mg \cdot kg^{-1}$; Zn – (9.91 ± 6.44) $mg \cdot kg^{-1}$; Cu – (4.65 ± 6.94) $mg \cdot kg^{-1}$; Mn – (86.85 ± 43.30) $mg \cdot kg^{-1}$; and Fe – (422.53 ± 298.60) $mg \cdot kg^{-1}$. When testing the hypothesis that two compared sets belong to the same general population, we obtained statistically significant differences at $p \leq 0.05$ for Cd and Pb content in bottom sediments for areas above and below the city limit. At the same time, the median of Cd concentration in the section of points 1–7 (see Fig. 1) was higher than in the river section adjacent to the city quarters. We associate this result with the noted increased Cd content in sediments in the drainage basin of the Northern Dvina in the background plot (Zimovets & Fedorov, 2013) and Cd behavior at the chemical boundary of the Pinega and Northern Dvina rivers mixing, when Cd can be displaced from compounds with organic ligands and deposit in bottom sediments in the form of a poorly soluble hydroxide (Dinu & Shkinev, 2020).

Bivalve molluscs. To assess the differences in the heavy metal accumulation in the tissues of two bivalve species, we used the Mann–Whitney *U* test for the entire set of samples of the estuarine area of the river. This test revealed no differences in the processes of the heavy metal accumulation in the tissues of painter's and duck mussels at $p \leq 0.05$ for all metals studied. In addition to analysis of the main pair of species, *Anodonta* and *Unio*, a pairwise comparison of the sets with another bivalve, *Dreissena polymorpha*, was carried out. For this species, the difference was shown in accumulation of all metals. However, in the present work, we do not use this species, though it is promising for ecotoxicological research, since we did not obtain sufficient field material in the studied section of the Northern Dvina. Due to the unfavorable effect of abiotic factors on molluscs of this species (lack of substrates for attachment, high reach velocities, rather low summer water temperatures, *etc.*) (Makhnovich, 2016), the density of *Dreissena* settlements does not provide enough material for monitoring. Perhaps, we will carry out a similar work based on *Dreissena polymorpha* analysis later.

For painter's mussel samples for areas above and below the city limit, the test did not reveal significant differences at $p \leq 0.05$ for all metals studied. For duck mussel, statistically significant differences at $p \leq 0.05$ were recorded for Zn, Cu, and Ni. For painter's mussel, background concentrations calculated by the formula (1) had the values as follows: Ni – (0.13 ± 0.04) $mg \cdot kg^{-1}$; Pb – (0.10 ± 0.09) $mg \cdot kg^{-1}$; Cd – (0.09 ± 0.03) $mg \cdot kg^{-1}$; Zn – (18.46 ± 8.93) $mg \cdot kg^{-1}$; Cu – (1.01 ± 0.33) $mg \cdot kg^{-1}$; Mn – (308.91 ± 128.21) $mg \cdot kg^{-1}$; and Fe – (91.38 ± 93.93) $mg \cdot kg^{-1}$. For duck mussel, the values were the following: Ni – (0.06 ± 0.08) $mg \cdot kg^{-1}$; Pb – (0.12 ± 0.01) $mg \cdot kg^{-1}$; Cd – (0.06 ± 0.03) $mg \cdot kg^{-1}$; Zn – (11.61 ± 5.37) $mg \cdot kg^{-1}$; Cu – (0.59 ± 0.11) $mg \cdot kg^{-1}$; Mn – (252.33 ± 182.83) $mg \cdot kg^{-1}$; and Fe – (86.06 ± 86.06) $mg \cdot kg^{-1}$. We published the data on the background heavy metal content in the bivalves in the estuarine area of the Northern Dvina River earlier in (Neverova & Chupakov, 2018).

Thus, a comparative analysis of the sets of metal concentrations for the background plot (B) and the city area (C) using the Mann–Whitney *U* test revealed several differences between them. The following significant relationships were established: for bottom water layer, B(Ni) < C(Ni); for bottom sediments, B(Pb) < C(Pb) and B(Cd) > C(Cd); and for *Anodonta*, B(Ni) < C(Ni), B(Zn) < C(Zn), and B(Cu) < C(Cu). These results characterize the effect of household activity on Ni, Pb, Zn, and Cu content in the ecosystem components of the estuarine area of the river. However, analyzing the data obtained, we note a high mosaicity in the metal concentration in the river water area (Neverova et al., 2014, 2016), which indicates a key role of local peculiarities of the sampling point (presence of a local source of contamination and spots with different hydrodynamic characteristics of waters and other granulometric composition of bottom sediments, as well as many other local factors – up to the predominant macrophytic species). Therefore, along with the "classical" scheme for the analysis of the results obtained (comparison of the sets), in order to quantify the differences in the metal content in mollusc tissues between the background plot and the river area within the boundaries of Arkhangelsk, we compared metal content at separate points with the value of the upper limit of the background concentration (formula (2), Table 1).

Table 1. Values of X_i / ($Me_f + 2MAD$) enrichment factor in the study objects

Sampling point No.	Object	Ni	Pb	Cd	Zn	Cu	Mn	Fe
10	Bottom water layer	0.56	–	0.25	**1.00**	**1.07**	0.27	0.41
	Bottom sediments	0.81	0.65	0.47	0.46	0.20	0.39	**1.37**
	Anodonta	–	–	–	–	–	–	–
	Unio	–	–	–	–	–	–	–
11	Bottom water layer	0.78	–	0.26	0.67	**1.21**	0.36	0.45
	Bottom sediments	**1.24**	**1.05**	0.37	0.79	0.61	**1.13**	**1.90**
	Anodonta	0.95	**1.12**	0.77	0.96	0.97	0.88	0.4
	Unio	–	–	–	–	–	–	–
12	Bottom water layer	**1.05**	–	0.65	0.38	0.52	0.21	0.16
	Bottom sediments	0.74	0.05	0.03	0.29	0.31	0.35	0.33
	Anodonta	0.8	0.41	**1.08**	0.87	**1.21**	0.16	0.19
	Unio	–	–	–	–	–	–	–
13	Bottom water layer	**3.44**	–	0.45	**2.00**	0.52	0.23	0.23
	Bottom sediments	0.60	0.40	0.07	0.32	0.29	0.41	0.33
	Anodonta	–	–	–	–	–	–	–
	Unio	–	–	–	–	–	–	–
14	Bottom water layer	**1.00**	–	–	0.39	0.50	0.37	0.42
	Bottom sediments	**1.27**	0.47	0.08	0.51	0.28	0.76	0.31
	Anodonta	0.6	–	**1.58**	**1.37**	**1.63**	0.44	0.71
	Unio	–	–	–	–	–	–	–
15	Bottom water layer	**2.13**	–	–	0.95	0.52	0.29	0.33
	Bottom sediments	**1.45**	0.54	0.14	0.63	0.31	0.93	0.36
	Anodonta	–	–	–	–	–	–	–
	Unio	0.22	0.07	0.96	0.34	0.8	0.44	**1.18**
16	Bottom water layer	–	–	0.43	0.50	0.36	0.42	0.67
	Bottom sediments	**3.12**	**2.03**	0.63	**1.48**	**3.44**	**2.01**	**1.71**
	Anodonta	**1.46**	**1.06**	0.95	**1.38**	**1.56**	0.92	**1.79**
	Unio	–	–	**1.84**	**1.53**	0.08	0.13	0.53
17	Bottom water layer	0.56	–	0.32	**1.23**	0.36	0.17	0.24
	Bottom sediments	**1.16**	0.14	0.56	0.52	0.36	0.48	0.38
	Anodonta	–	–	–	–	–	–	–
	Unio	–	–	–	–	–	–	–
18	Bottom water layer	0.56	–	0.02	0.67	0.71	0.49	0.62
	Bottom sediments	0.94	0.90	0.14	0.84	0.26	0.28	0.32
	Anodonta	**2.07**	–	**54.15**	**1.05**	**1.44**	0.42	**1.31**
	Unio	0.31	0.16	0.73	0.59	0.55	0.22	0.54
19	Bottom water layer	**1.34**	–	0.04	**1.70**	0.50	0.47	0.22
	Bottom sediments	0.83	**6.42**	0.04	0.39	0.27	0.49	0.33
	Anodonta	0.91	0.58	0.69	**1.72**	**1.08**	0.92	0.83
	Unio	–	–	–	–	–	–	–

Continue on the next page…

Sampling point No.	Object	Ni	Pb	Cd	Zn	Cu	Mn	Fe
20	Bottom water layer	**1.89**	–	0.08	0.90	0.50	0.25	0.13
	Bottom sediments	0.83	0.28	0.10	0.31	0.25	0.75	0.34
	Anodonta	0.8	0.12	0.83	**1.15**	0.99	0.4	0.61
	Unio	–	–	–	–	–	–	–
21	Bottom water layer	0.11	–	0.11	1.00	0.50	0.31	0.54
	Bottom sediments	0.54	0.38	0.33	0.26	0.31	0.36	0.96
	Anodonta	**1.09**	**1.55**	0.85	**1.15**	**1.27**	0.44	0.96
	Unio	–	–	–	–	–	–	–
22	Bottom water layer	0.44	–	0.16	0.10	0.71	0.09	0.23
	Bottom sediments	**2.77**	**1.25**	0.63	**1.45**	**1.08**	**1.47**	0.66
	Anodonta	0.56	0.42	0.68	0.48	0.71	0.45	0.14
	Unio	–	–	–	–	–	–	–
23	Bottom water layer	0.67	–	–	0.47	0.52	0.33	0.50
	Bottom sediments	0.83	0.13	0.05	0.31	0.21	0.28	0.36
	Anodonta	**2.02**	–	**1.19**	**1.07**	**1.41**	0.15	0.52
	Unio	–	–	–	–	–	–	–
24	Bottom water layer	**1.91**	–	–	0.41	0.51	0.15	0.13
	Bottom sediments	0.58	0.17	0.09	0.20	0.20	0.44	0.30
	Anodonta	0.53	–	**2.29**	**1.62**	0.67	0.45	0.35
	Unio	0.4	**1.09**	0.61	0.26	0.20	0.16	0.17
25	Bottom water layer	–	–	0.18	1.00	0.71	**1.34**	**1.41**
	Bottom sediments	0.95	0.38	0.12	0.68	0.33	0.44	**2.37**
	Anodonta	–	–	–	–	–	–	–
	Unio	0.60	0.62	0.69	0.77	0.66	0.58	0.98

Note: a dash (–) denotes either no molluscs found or metal concentrations being below the detection limit; in bold, the values corresponding to excess of the calculated background level are highlighted.

Visualizing the results obtained (see Table 1), we built schematic maps of the contamination in the river water area with heavy metals (Figs 2–5). The Mann–Whitney *U* test did not show differences in the accumulation processes between two mollusc species; therefore, when building the maps and when having data for duck mussel and painter's mussel, we used the arithmetic mean of the coefficient values in their tissues. As mentioned above, we did not apply an accurate interpolation method. For calculating the data grid for isoline maps, we used radial basis function interpolation: the location of sampling points is heterogeneous, and the use of accurate interpolation methods, *e. g.* triangular linear interpolation, is difficult. On the schematic maps 2–5, colored fields of values of enrichment factors > 1 may slightly deviate from sampling points, overlap land areas, *etc.*; these are common errors in the building of isoline maps. However, the general trends in the data distribution undoubtedly persist, and the clarity of the information presentation covers minor inaccuracies.

At all sampling points located in the area, where the river flows through the city center, there is (see Table 1) an excess of the calculated background concentrations in terms of Ni content in bottom water layer (Fig. 2A) and in bottom sediments (Fig. 2C), as well as in Zn content in mollusc soft tissues (Fig. 2F). At local sampling points in the city center, concentrations higher than the calculated background ones were recorded for two heavy metals: for Zn, in upper layer of bottom sediments (Fig. 2D); for Ni, in bivalve tissues (Fig. 2E).

Fe and Mn content in bottom water layer mostly does not exceed the background values calculated by us throughout the entire area (Fig. 3A, B). In upper layer of bottom sediments, Mn concentrations were higher than the background ones in the entire area of the Northern Dvina River adjacent to the city center; Fe concentrations (Fig. 3C), in local areas upstream and downstream of the city center. It needs to be highlighted that it is Fe and Mn compounds in water that are considered the main contaminants throughout the Northern Dvina watercourse – from the headwaters to the estuarine area (Gosudarstvennyi doklad, 2013 ; Kharakteristika zagryazneniya, 2021). In mollusc tissues, Fe concentrations higher than the calculated background ones were recorded at all points in the city center; Mn concentrations were lower than the background ones at all sampling points (Fig. 3E).

Cd content in the studied river section did not exceed the calculated background concentrations in bottom water layer and bottom sediments (Fig. 4A, C). As mentioned above, the median of Cd content was higher in the background plot than in the area of the river adjacent to the city quarters. In mollusc tissues, Cd concentration was higher than calculated for the entire water area in the city center (Fig. 4E). In 2014, in this area, the maximum absolute value of Cd concentration (5.12 $mg \cdot kg^{-1}$ wet weight) in duck mussel tissues was recorded; it exceeded the calculated background concentrations by more than 50 times (Table 1), wherein mollusc tissues were dark in color. This indicator was excluded from the set when building the maps due to its extreme value.

Cu content in bottom water layer above the calculated background concentration was registered in local areas of the watercourse along the right bank adjacent to the center of Arkhangelsk (Fig. 4B, D). When comparing this indicator with the TLV for the fishery industry, we saw as follows: in these areas, Cu content was ten times higher than the standardized one (Neverova et al., 2016). Cu concentration in bottom sediments above the calculated background one was recorded at points downstream of the central city quarters, in spots, where reaches slow down due to morphological features of the riverbed (Fig. 4D).

Pb content in bottom water layer throughout the studied section was below the detection limit of the method; in upper layer of bottom sediments, it exceeded the background values calculated by us at all sampling points in the area, where the river flows through the central city quarters (Fig. 5A). In mollusc tissues, Pb concentrations exceeded the background ones in sampling points above and below the city center (Fig. 5B).

As for bottom sediments, two areas are distinguished, where background concentrations are exceeded for all metals. These are sampling points 16 (the area at the Nikolsky branch mouth) and 22 (near Molodezhny Island) (see Fig. 1). Point 16 is located downstream of numerous industrial areas on the left bank of the Northern Dvina, in spots, where reaches slow down, which is associated with morphological features of the riverbed. Point 22 is located in the zone of macrophyte thickets, which is also the spot, where the reach slows down. As a result of these peculiarities, in these areas, bottom sediments deposit and accumulate, which are carried by reaches with metals sorbed on them.

In contrast to concentrations in bottom water layer and bottom sediments, in mollusc tissues, there is an excess of content of most of the metals studied: values above the calculated upper background ones are recorded at all sampling points along the riverbed in the city center – both on the right and left banks (Figs 2E, F; 3E; 4E, F; 5E, F).

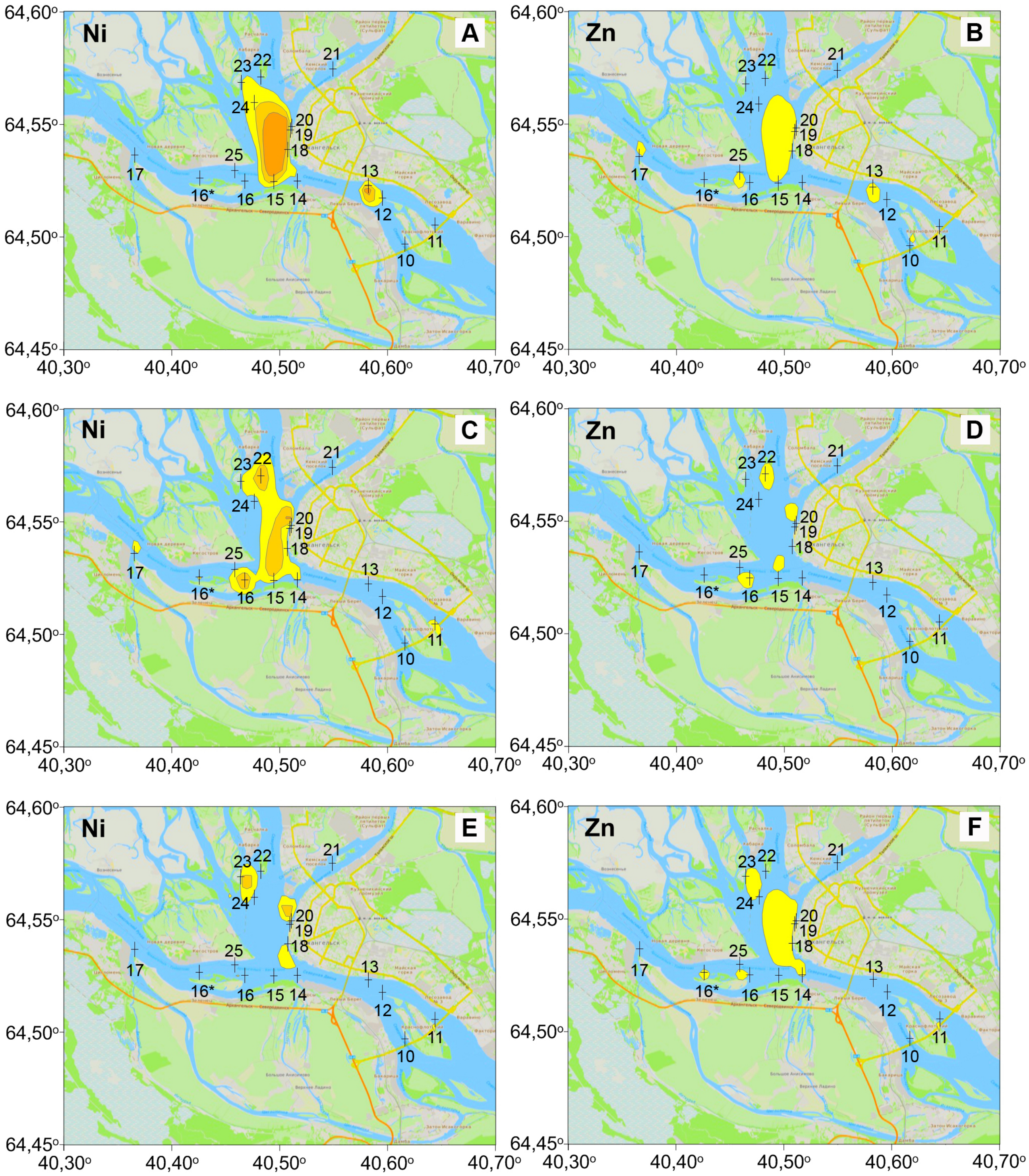

Fig. 2. Excess of the background level of Ni content (A, in bottom water layer; C, in bottom sediments; E, in mollusc tissues) and Zn content (B, in bottom water layer; D, in bottom sediments; F, in mollusc tissues). The gradation scale is shown in Fig. 5

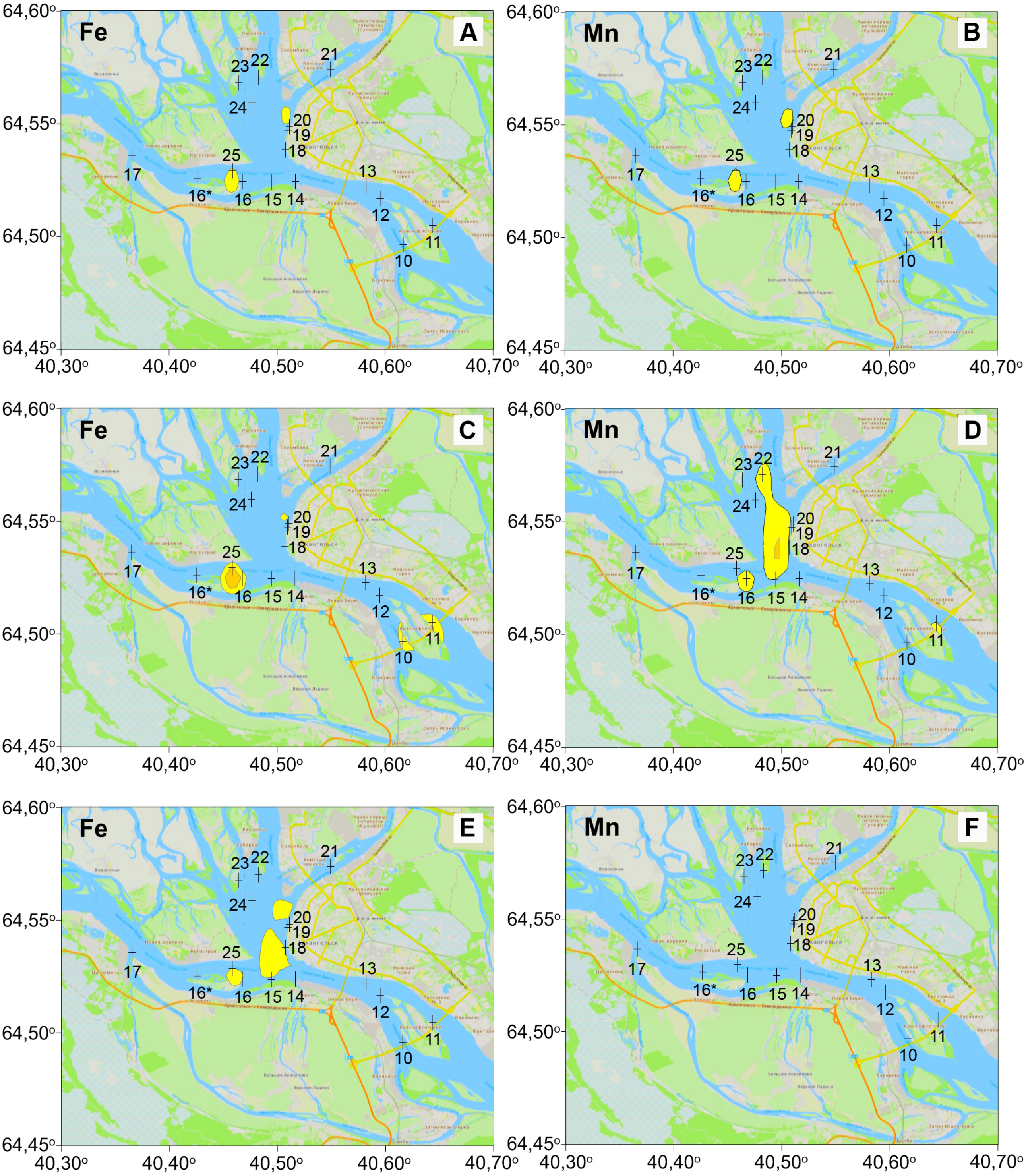

Fig. 3. Excess of the background level of Fe content (A, in bottom water layer; C, in bottom sediments; E, in mollusc tissues) and Mn content (B, in bottom water layer; D, in bottom sediments; F, in mollusc tissues). The gradation scale is shown in Fig. 5

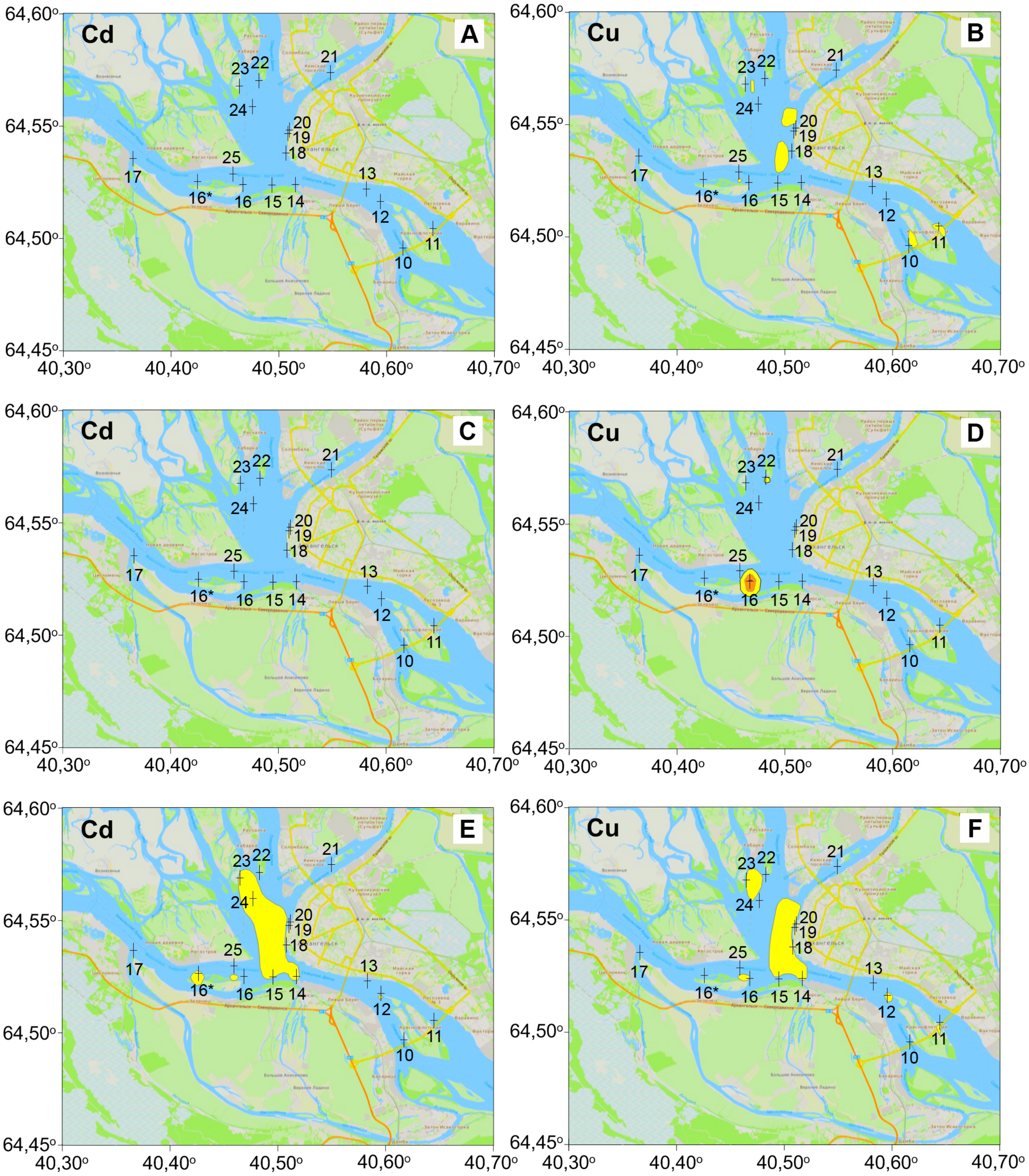

Fig. 4. Excess of the background level of Cd content (A, in bottom water layer; C, in bottom sediments; E, in mollusc tissues) and Cu content (B, in bottom water layer; D, in bottom sediments; F, in mollusc tissues). The gradation scale is shown in Fig. 5

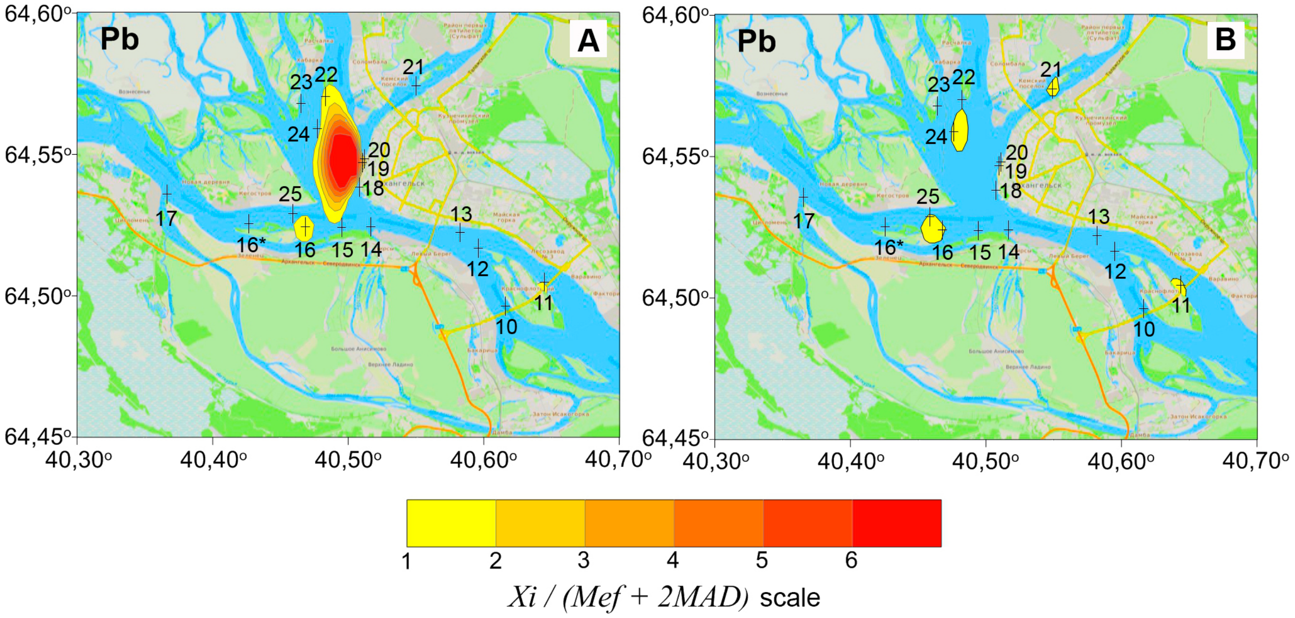

Fig. 5. Excess of the background level of Pb content (A, in bottom sediments; B, in mollusc tissues)

Analyzing the data obtained, it can be concluded as follows: Ni and Zn are inputted into bottom water layer from a single source (there is a significant positive Ni/Zn correlation; $R = 0.55$; $p \leq 0.05$; $N = 16$), with drains of drainage and storm sewers into the river water area on the right bank. There are local inflows of metals from an industrial hub located along the left bank of the Northern Dvina, where, along the river, insufficiently treated drains of domestic and drainage and storm sewers from the southern Arkhangelsk are inputted. The inflow of untreated domestic wastewater into the area of the city beach (points 18–20, Fig. 1) of the Northern Dvina is mentioned already in the publication of the 1920s (Lopato, 1927). Bottom sediments of the river section studied are enriched in Pb [> 6 background concentrations (b. c.)] and Ni (> 3 b. c.) throughout the entire area, where the river flows through the city center, both on the right and left banks. Local areas of the river in the city center and above and below central quarters are enriched in Fe (> 1 b. c.), Mn (> 1 b. c.), Cu (> 3 b. c.), and Zn (> 1 b. c.). In mollusc tissues, the calculated background values were exceeded for all metals, except for Mn.

Conclusions:

1. The excess of the heavy metal content over conditional background concentrations in the section of the Northern Dvina River adjacent to the central city quarters was revealed, which is associated with the inflow of rainwater and meltwater into the water area with insufficiently treated drains of domestic and drainage and storm sewers. For Cd and Pb, short-range atmospheric transport can be another major source of input. As shown in the study of the White Sea drainage basin contamination with the heavy metals from the atmosphere (Shevchenko et al., 2020), the proximity to a motorway significantly affects the enrichment of the snow cover with these two elements.
2. The analysis of the heavy metal content in mollusc tissues is more informative and indicative than the analysis of bottom water layer and bottom sediments. Sedentary benthic species, in particular bivalves, can serve as indicators of this contamination in the aquatic ecosystems: being filter feeders,

they accumulate relatively higher heavy metal concentrations in their tissues during feeding and respiration than in the habitat. Moreover, being less mobile than bottom sediments and water, molluscs can concentrate contaminants in a spatial aspect.

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ОЦЕНКА ЗАГРЯЗНЕНИЯ УСТЬЕВОЙ ОБЛАСТИ РЕКИ СЕВЕРНОЙ ДВИНЫ МЕТОДОМ РАСЧЁТА ФОНОВЫХ КОНЦЕНТРАЦИЙ
(Fe, Mn, Zn, Cu, Cd, Pb, Ni)

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Данная публикация является продолжением работ по количественной оценке уровня загрязнения тяжёлыми металлами (Fe, Mn, Zn, Cu, Cd, Pb, Ni) компонентов экосистемы устьевой области реки Северной Двины. Для оценки уровней загрязнения указанными металлами экосистемы устьевой области Северной Двины в районе наибольшего антропогенного воздействия (район городской агломерации Новодвинск — Архангельск — Северодвинск) мы используем метод сравнительного анализа объекта исследования с условно-фоновым участком, приняв за него участок реки, расположенный выше городской застройки. С применением пространственного картирования значений коэффициентов обогащения для компонентов водной экосистемы были выделены районы с аномальным превышением содержания металлов в тканях моллюсков, донных отложениях и придонном слое воды. Установлено, что наибольшей антропогенной нагрузке в акватории вершины дельты реки подвержен район, примыкающий к центральной части города и к промышленной зоне на левом берегу. Наиболее вероятными источниками загрязнения рассмотренными тяжёлыми металлами можно назвать попадание поверхностных сточных вод (талые и дождевые ливневые стоки), неочищенные коммунально-бытовые стоки и прямой ближний атмосферный перенос. Анализ тканей моллюсков проявил себя как более информативный и показательный подход к оценке загрязнения тяжёлыми металлами акватории со сложными гидрологическими и гидрохимическими градиентами среды, чем анализ придонного слоя воды и донных отложений.

Ключевые слова: устьевая область реки Северной Двины, фоновые содержания, тяжёлые металлы, коэффициент обогащения, двустворчатые моллюски