

Simulation of Heavy Metal Pollution of Watercourses in the Basin of the Nizhnekamskoe Reservoir

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Abstract—The physically based ECOMAG-HM model, developed to simulate heavy metal cycles in large river basins, was used to study the spatial and temporal regularities in the formation of copper and zinc distributions in water bodies in the basin of the Nizhnekamskoe Reservoir. Maps of the mean annual concentrations of the metals in river network and the mean annual modules of diffuse runoff with its genetic components have been compiled. The contributions of point and diffuse sources to river water pollution by copper and zinc have been evaluated. To specify the estimates of the effect of economic activity on river water pollution, numerical experiments have been carried out to simulate the scenarios of an increase in the amount of metals discharged as wastewater components, wastewater emergency volleys, and complete elimination of anthropogenic impact on a drainage basin.

Keywords: river basin, ECOMAG-HM model, diffuse pollution, point sources, heavy metals, copper and zinc runoff, economic activity scenarios

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INTRODUCTION

The discharges of poorly treated wastewater, originating from industrial, municipal, and agricultural enterprises, have been long regarded as the major sources of pollution of water bodies. That is why the water-protection programs are based on the concept of reducing wastewater discharges from controlled point sources. As can be seen from state statistical reports, the amount of pollutants in wastewater composition has decreased considerably over the past decades [4, 6]. However, the respective decrease in pollutant concentrations, which could be expected, did not take place in many water bodies [8, 18].

The present-day technical and natural conditions of water quality formation show that many sources of uncontrollable diffuse pollution appear in river basins: individual elements of basin geosystems (soils, groundwater, and bottom sediments), polluted under the effect of long-term anthropogenic impact, and the anthropogenic pollution sources themselves (territories of industrial enterprises; areas occupied by dumps and industrial wastes; municipal solid waste landfills; agricultural and transport facilities, etc.) [13, 23–25]. The available data show that pollutant input from uncontrollable diffuse sources into the watercourses of the Volga basin can be greater than that from point sources [3, 9, 10, 29]. Similar data are available for some largest European rivers [12, 28, 33].

The development of water-protection strategies and appropriate measures for their implementation in river basins requires the good knowledge of the processes of water quality formation under current natural and technogenic conditions and the contributions of various types of sources to river water pollution. The present-day system used to control pollutant input into water bodies fails to allow such estimates to be made because of the imperfect accounting system of industrial water users, providing their statistical reports on wastewater discharges [7]; the incorrectness of the data on wastewater discharge in reports of individual enterprises [7, 19, 27, 29]; the absence of pollution monitoring from diffuse sources. The best indicators of diffuse pollution are medium-size and, especially, small rivers; however, sites of regular hydrochemical observations are mostly located on large rivers at wastewater discharges from large enterprises, towns and settlements, as well as individual industrial facilities.

A way out of this situation is to describe and simulate the formation processes of river runoff, water chemistry and quality for the entire river basin areas, including those not covered by observations, based on spatially distributed physically based models with a unified regional set of parameters derived from data from a relatively sparse network of hydrochemical monitoring and physical–geographic analysis of runoff formation factors. The best known among the

models of this type in Russia is ECOMAG [15]. The model is well adapted to describing processes in river basins with mixed rain and snow nourishment, as well as to the structure and composition of hydrometeorological data in Russia. The hydrological block of ECOMAG has been many times tested on numerous large river basins and used in practical hydrological calculations, forecasts, and water resources management problems [15]. The hydrochemical block of the model has been verified on as little as two river systems. Study [14] demonstrates the potentialities of the hydrochemical block of the model as an expert system for assessing nickel pollution of small rivers under various operation scenarios of Pechenganikel Mining Plant in northwestern Kola Peninsula. In [16, 31], the model was verified against data on the large river basin of the Nizhnekamskoe Reservoir with watercourses showing high concentrations of heavy metals (HM).

The objective of this study is to deepen the knowledge of the effect on river water quality produced by various processes, taking place in the drainage basin of the Nizhnekamskoe Reservoir under the current technical and natural conditions:

- to study the hydrochemical regime of watercourses in the basin, including those not covered by hydrochemical observations, with the construction of maps of mean annual concentrations of copper and zinc in river network, and to identify zones with higher concentrations of metals in river water;

- to compile and analyze maps of mean annual modules of river runoff and the chemical runoff of copper and zinc, as well as its genetic components;

- to evaluate the contributions of natural and anthropogenic components to the formation of hydrochemical runoff of copper and zinc;

- to evaluate the contribution of point sources to river water pollution under different scenarios of metal inputs with wastewater;

- to evaluate the time scale of drainage basin self-purification from metals at a decrease in anthropogenic load.

NATURAL AND ECONOMIC CHARACTERISTICS OF THE STUDY OBJECT

The drainage basin of the Nizhnekamskoe Reservoir (NKR), located in the South-Ural region of Russia on the Kama River between the Nizhnekamskii and Votkinskii hydropower systems, is 186 thous. km² in area; its major portion (142 thous. km²) is the Belaya R. basin. Almost 2/3 of the area in the western and central parts of the drainage basin are plains; the eastern part is the Ural Folded Mountain Area.

The climate of the territory is continental. It changes from that of semiarid steppe regions in the southwest, where the annual precipitation varies within the range of 300–400 mm and the normal annual air temperature is ~3°C, toward wetter regions

(northeastern and eastern mountain-forest), where the annual precipitation is >600 mm and the normal annual temperature is below 1°C. The climatic difference between various parts of the drainage basin determine the pronounced latitudinal zonality of vegetation (steppe, forest steppe, and forest zones), complicated by the vertical belts in the Ural Mountains. The soils (black earth, sod-podzol, gray forest) show high humus content and heavy mechanical composition. Well drained mountain soils are widespread in the eastern part of the drainage basin.

The rivers are mostly recharged by snowmelt water. The spring flood accounts for >60% of annual runoff volume. The mean annual lateral inflow into the NKR is 36.5 km³, of which 26.1 km³ is due to the Belaya R.

For many decades, copper and zinc have been among the most common pollutants of surface water in the region. Their concentrations in water bodies at the hydrochemical monitoring gages are often in excess of the maximal allowable concentrations. The natural waters show high concentrations of HM because of the considerable concentrations of ore-forming elements in the rocks. The industrial development of the region, associated with the development of mineral deposits, started almost 300 years ago and had been taking place subject to no environmental limitations. The ancient antropogenically transformed mining landscapes, modern industrial plants for mining and treating mineral resources, large populated localities and their infrastructure objects are additional sources of metal input onto the drainage basin [23].

In the soil that inherits the chemistry of the soil-forming rocks, metals form strong complexes with humic substances, and they are removed from it very slowly: the half-removal period of copper from soil is more than 1000 years and that of zinc is 500 years [11]. The heavily dissected relief determines a higher erosion level of the soil. Enriched with microelements, eroded soils facilitate HM input into water bodies with sediments. In river runoff, many metals migrate as components of suspension rather than solutions. According to [26], the average proportion of dissolved to suspended forms of copper migration in rivers is ~1 : 1, and that of zinc is 1 : 20.

The drainage basin contains many objects of economic activity, which serve as sources of HM input into water bodies. In the eastern part of the drainage basin, such sources are mining enterprises, and in its western and central parts, these are oil production and processing, chemical and petrochemical, metallurgical, mechanic engineering and power-production plants, and storages of production and consumption wastes. In the recent years, the amount of pollutants entering water bodies from controllable point sources decreases (Fig. 1), though the reasons of this are not clear: possibly, this is due to a decrease in the water consumption and disposal volumes [6, 17] or the

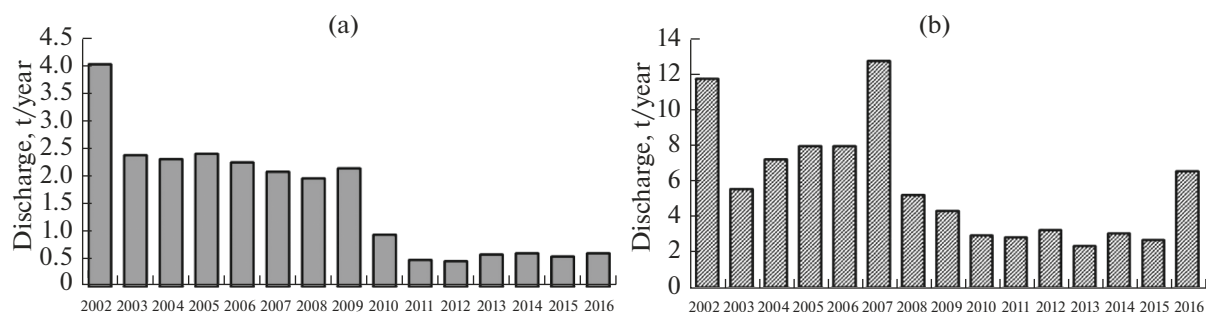


Fig. 1. Dynamics of discharges into water bodies of the NKR basin of (a) copper and (b) zinc in the composition of wastewater from industrial plants [6].

decrease in the number of the monitored water users that present statistical reports of 2-TP (vodkhoz) form [7].

The strongest pollution source in the region is Ufa City with a population of more than one million. The city hosts about 200 large and medium-size production facilities, including three oil-processing plants, synthetic-alcohol, engine-building, oil-processing equipment, cable, and other plants. Municipal Unitary Enterprise (MUE) Ufavodokanal implements centralized water supply and disposal of the forming wastewater, as well as wastewaters of most urban plants after their local treatment on the site. According to state accounting data, MUE Ufavodokanal accounts for ~35% of the volume of wastewater discharge in the region [5, 6].

In studies [22, 29], the correctness of the data presented in the report forms 2-TP (vodkhoz) was checked by comparing data on pollutant concentrations in the wastewater discharged into the Belaya R. by MUE Ufavodokanal with mass balance estimates of pollutants contained in river water in the segment between two gages: 500 m downstream and 500 m upstream of the wastewater discharge site of the plant over a long-term period. The comparison of these data showed a considerable difference. In most cases, the calculated values were greater than those in the data of HM statistics. In some cases, the actual amount of the metals in wastewaters was 1–2 orders of magnitude greater than the HM mass given in reports. The difference can be due to shortcomings in the existing system of wastewater chemistry control at plants. In the absence of instruments for automatic monitoring of pollutant concentrations in wastewaters at the plants, the amounts of discharged pollutants are evaluated either based on occasional water samples or indirectly, based on the production volume. Such approach inevitably introduces considerable errors to the evaluation of actual pollutant discharges from point sources [19, 27].

ECOMAG-HM MODEL

HM turnover in NKR basin (on its surface, in the soil, and in groundwater and river water) was simulated with the use of the semi-distributed physically based model ECOMAG-HM (ECOLOGICAL Model for Applied Geophysics—Heavy Metals) [16], operating with a daily time step and consisting of two main blocks: a hydrological submodel of runoff formation and a hydrochemical submodel of pollutant migration and transformation. The first submodel describes the processes of hydrological cycle: snow cover formation and melting, soil freezing and melting, infiltration of snowmelt and rain water into soil, evaporation, soil moisture dynamics, the formation of surface, subsurface, groundwater, and river runoff. This model block was tested against data on largest river basins in the Northern Hemisphere (the Volga, Lena, Amur, Mackenzie, etc.), located in different physico-geographic zones with different runoff formation conditions, nourishment types, and the hydrological regime of water bodies [15].

The hydrochemical submodel describes the migration processes of nonreactive pollutants in a river basin: their accumulation on the surface of the river basin and dissolution by snowmelt and rain water, seepage of dissolved pollutants into the soil, interaction with soil solution and the solid phase of the soil. The migration of dissolved pollutants in river basin depends on the rate of hydrological processes. Therefore, the hydrological characteristics that are determined in the hydrological block of the model are used as entries for the hydrochemical submodel. The model also takes into account pollutant inputs from point sources. The equations, algorithms, and the results of tests of this model block have been described in [16, 31].

DATA SUPPORT OF THE MODEL

The model was adapted to the NKR basin with the use of computer technology of the Information-Modeling Complex IMC ECOMAG [15]. The complex contains the calculation module of the mathematical

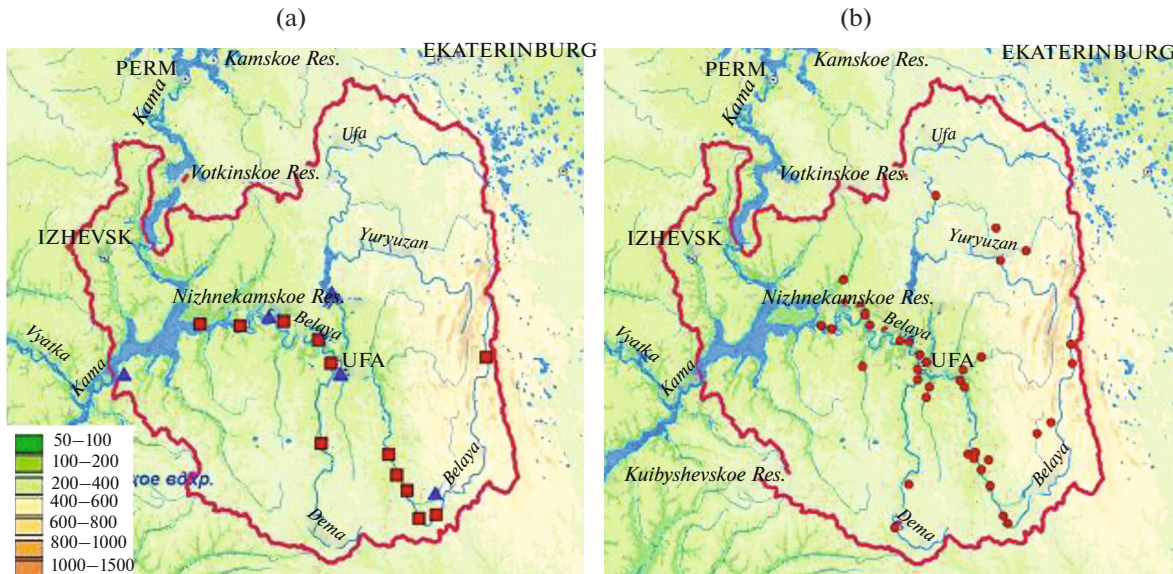


Fig. 2. Location of monitoring sites in the NKR basin: (a) observation points of runoff (triangles) and wastewater discharges (squares); (b) Roshydromet hydrochemical monitoring stations.

model and instruments for information and technological support of this module, i.e., thematic digital electronic maps, a technology for automated division of the drainage basin into elementary drainage basins (model cells) and schematization of river network, databases of land surface characteristic, databases of hydrometeorological, hydrochemical, and water-management data, database management systems and instruments for geoinformation processing of spatial data, as well as an administration system.

The model schematization of NKR drainage basin and river network with the use of IMC ECOMAG based on digital thematic maps of the region (topography, hydrographic network, soils, and landscapes) contained 503 elementary model drainage basins with an average area of ~ 400 km²; in addition to the main river, the model river network includes 50 first-order tributaries, 131 second-order tributaries, 63 third-order tributaries, and 8 fourth-order tributaries [16, 31]. In each elementary drainage basin, the hydrological and hydrochemical processes were simulated at four levels: in the formation zone of surface runoff, in the surface soil layer, in the underlying deeper layer, and in soil water. In the cold season, the storage capacity of snow cover is included. The scheme is concluded by the consideration of the processes of runoff and pollutant transformations in the river network.

The data for the calculations and boundary conditions for the model were represented in the form of daily fields of weather characteristics (air temperature and moisture content and precipitation) collected in NKR basin at 56 weather stations. Data on the daily water discharges at five hydrological gages were used

to calibrate parameters (2001–2007) and validate (2008–2013) the hydrological submodel.

The initial conditions in the hydrochemical submodel in terms of metal concentrations (copper and zinc) in soils in NKR drainage basin were specified based on microelement concentrations in the ploughed soil layer in the Republic of Bashkortostan, given in the atlas [2], with the incorporation of similar data on the nearby administrative units in the NKR basin. The concentrations of metals in precipitation and confined subsoil water, which feed perched groundwater in the aeration zone of soils, were taken constant based on the weighted mean concentrations given in [1, 21]. The data on point anthropogenic sources of river water pollution were represented by data on metal discharges with wastewaters in 12 large populated localities in the Belaya R. basin (Fig. 2a) based on statistical reports 2-TP (vodkhoz) over period 2004–2007. The hydrochemical submodel was tested against data on the dynamics of metal concentrations in river water at 34 gages in the Belaya R. and its tributaries (Fig. 2b), collected by Roshydromet services over period 2004–2007.

The major portion of the physically based model parameters were specified with the use of IMC ECOMAG and global databases of cartographic data on the region (characteristics of soils, vegetation, and landscapes). Some parameters of the hydrological block of the model were chosen in the course of calibration by differences between the calculated and actual daily runoff hydrographs at gages. The values of hydrochemical submodel parameters, the initial values of which were specified by [1, 21, 32], were calibrated and specified based on data on concentration dynam-

ics of copper and zinc in river water at hydrochemical monitoring sections.

TESTING ECOMAG-HM MODEL

The results of testing the hydrological block of the model by comparing the simulated and actual runoff hydrographs at five hydrological gages in NKR basin (Fig. 3) show an acceptable agreement between the calculated and observed data [16, 31]. Additional successful tests of the model for river network segments not covered by hydrometric observations were carried out through comparing the calculated map of the mean annual runoff modules with a map of modules given in [20] based on observed data (Fig. 4).

The hydrochemical block of the model was tested by comparing the calculated and measured concentrations of copper and zinc in different sections of river network with different time averaging. The low frequency of measurements at hydrochemical monitoring sections (as a rule, 4 to 12 measurements per year), as well as the considerable errors in the determination of HM concentrations in water samples (~50%) restrict the applicability of conventional statistical hydrological criteria to compare the results of model calculations of the annual change in HM concentrations and episodic data of hydrochemical measurements (Figs. 5a, 5b) [30]. More reliable estimates can be derived from these data for the characteristics averaged over long periods.

Figures 5c, 5d give examples of the comparison of diagrams representing the annual distribution of zinc concentrations averaged over four years by quarters. The results show that the statistically significant coefficients of correlation between the calculated and averaged measured metal concentrations for all 34 gages are as follows: in the case of copper $R = 0.55$ only for the second quarter (spring flood period) with maximal concentration values; and in the case of zinc $R = 0.50$ and $R = 0.69$ for the second and third quarters, respectively.

The spatial differences between the mean annual metal concentrations at the hydrochemical monitoring stations are given in Fig. 5d in the order of their location from the upper reaches of the Belaya R. toward the dam of the Nizhnekamskii Hydropower Station. The coefficients of correlation between the calculated and measured mean annual concentration values vary from 0.58 for copper to 0.60 for zinc, thus showing that the model satisfactorily reproduces the major spatial and temporal regularities in the formation of the runoff of metals in the basin and their concentrations in river network [30].

MAPPING HEAVY METAL CONCENTRATIONS IN RIVER WATER

The results of calculations were used to map the concentrations of copper and zinc in watercourses in

NKR basin, including in areas not covered by hydrochemical observations (Fig. 6). The maps show the distribution of the calculated mean annual concentrations obtained by averaging their daily values in the elements of model river network. The thickness of the line reflects the concentration of copper or zinc in river network in accordance with the legend. The maps demonstrate the spatial dynamics of metal concentrations on NKR drainage basin. The results of mapping show (Fig. 6) that the mean annual concentration of copper in the major portion of NKR basin is in excess of the MAC for water bodies used for fishery (1 $\mu\text{g/L}$), while the mean annual concentration of zinc is below the respective MAC (10 $\mu\text{g/L}$). This can also be seen from the mean annual metal concentrations in the river network averaged over measurement data at 34 Roshydromet stations, which are 3.9 $\mu\text{g/L}$ (~4 MAC) for copper and 4.7 $\mu\text{g/L}$ (~0.5 MAC) for zinc.

Maps in Fig. 6 show local areas in the drainage basin not covered by hydrochemical observations with a high pollution level of river water. For example, in small rivers emptying into the rivers of Ai, Yuryuzan, and lower Ufa (shown by ovals in Fig. 6), maximal normal annual metal concentrations are 5–6 times greater than the respective values averaged over NKR basin. The comparison of maps of the spatial distribution of metal concentrations in river network shows their close correlation with metal concentrations in soil [2].

SIMULATING THE FIELDS OF GENETIC COMPONENTS OF DIFFUSE RUNOFF OF METALS

The algorithm for determining various genetic components of diffuse runoff of copper and zinc from NKR drainage basin was as follows. The daily fields of weather characteristics for all model elementary drainage areas were used to calculate metal discharges into the local river network by the surface, soil and groundwater, and total runoff. Averaged values of the daily fields of metal runoff over a long period were used to map the fields of mean annual modules of the surface, subsurface, and total runoff of metals into river network (Figs. 7, 8).

The maps show the spatial distribution of various genetic components of diffuse runoff of metals in the NKR basin. The comparison of the maps of modules of the total (Figs. 7a, 8a) and subsurface (Figs. 7c, 8c) runoff shows their close correlation with the spatial distribution of metal concentrations in soils. This can be seen from the higher values of copper runoff modules in the eastern and northeastern parts of NKR basin and maximal values of the modules of zinc runoff north of Ufa. The lower values of the modules of surface runoff of metals (Figs. 7b, 8b) in the eastern part of the basin are due to the higher permeability of soils in the piedmonts of the Southern Urals, and they

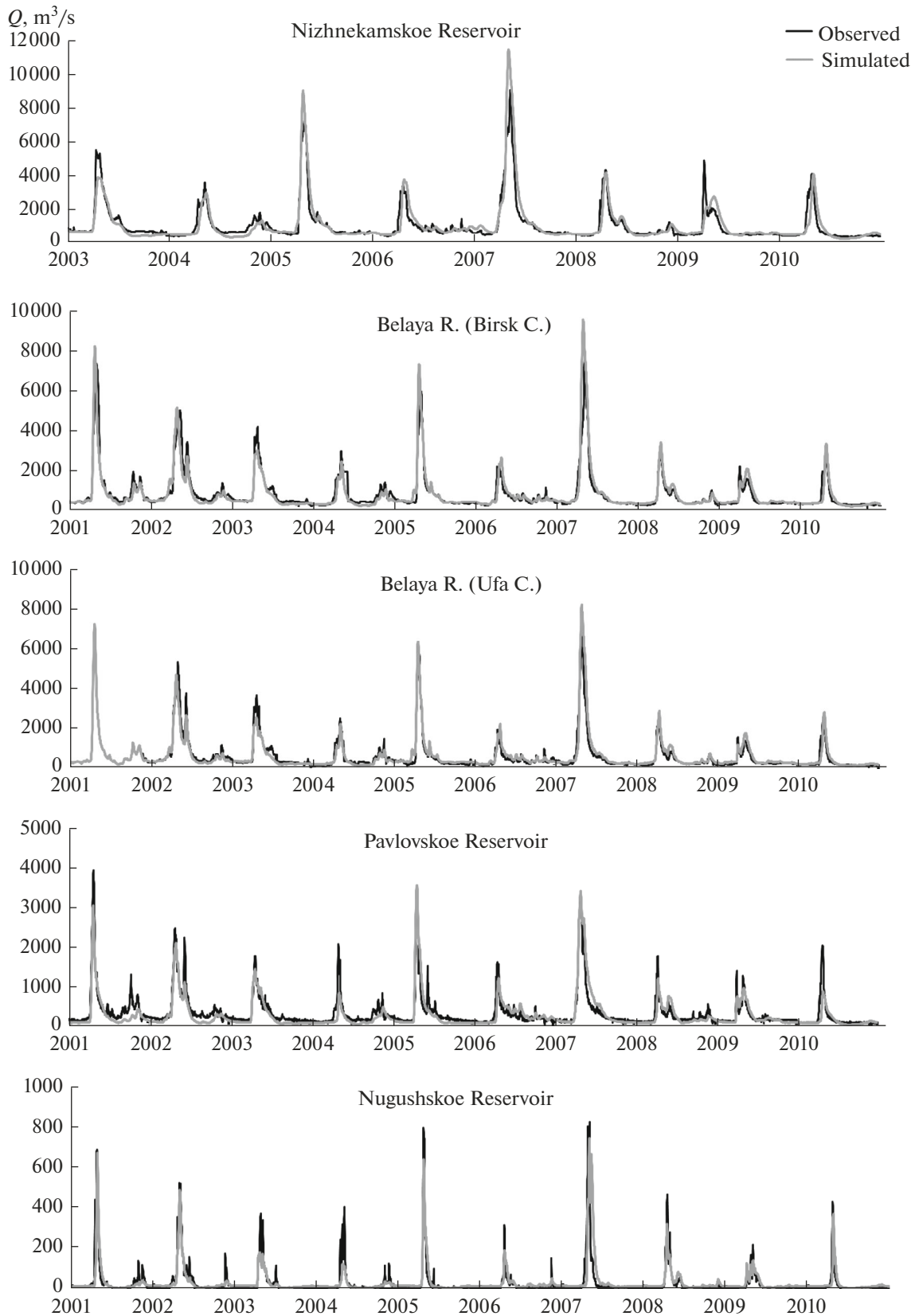


Fig. 3. Observed (dark line) and simulated (light line) hydrographs of the Belaya R. and inflow into the reservoirs in the NKR basin.

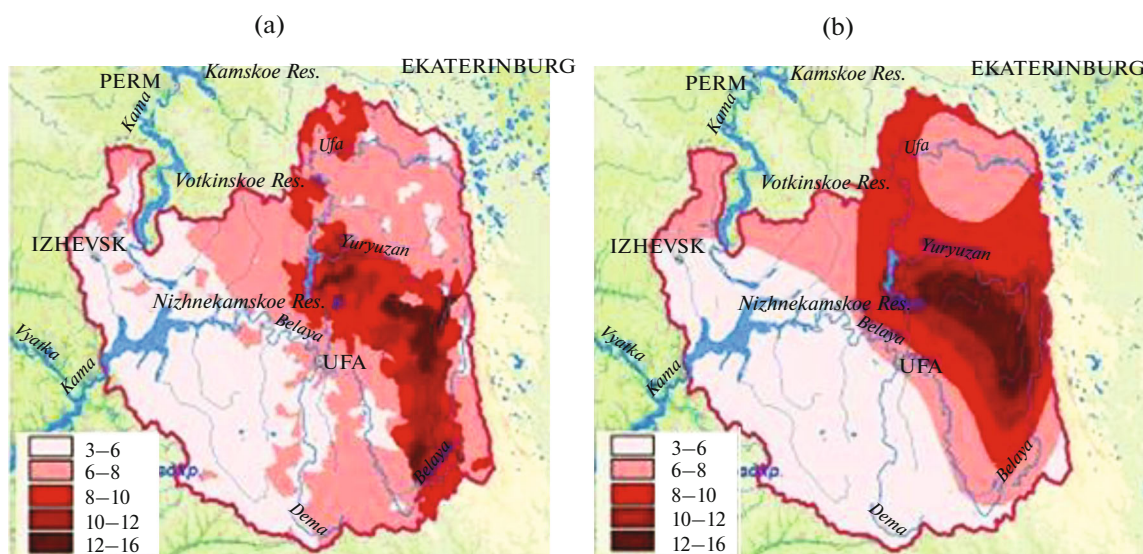


Fig. 4. (a) Simulated and (b) observed (according to SC 435-72) maps of water runoff module in NKR basin, L/(s km²).

also can be seen in river valleys in soils of lighter texture.

The comparison of the modules of surface and subsurface runoff shows (Figs. 7b, 7c, 8b, 8c), that the discharge of copper and zinc into river network forms mostly due to the subsurface component. The share of the runoff of metals by surface water in the major portion of the drainage basin is less than half of metal runoff with subsurface water, except for the western part of the basin, where the modules of surface metal runoff are comparable or somewhat greater than their washout by subsurface runoff.

ASSESSING THE CONTRIBUTIONS OF POINT AND DIFFUSE SOURCES INTO RIVER WATER POLLUTION

Model balance calculations were used to evaluate the contributions of point (controlled wastewater discharges) and diffuse sources to river water pollution. The results of balance calculations are given in Table 1. The data on point sources were taken from the data on metal discharges with wastewater based on the forms of statistical reports 2-TP (vodkhoz). The actual discharge of metals from the drainage basin in NKR (Table 1) was evaluated as the product of the observed annual water inflow into the reservoir multiplied by the measured mean annual metal concentration in the last station of hydrochemical monitoring on the Belaya R. before its inflow into NKR (Dyurtly station).

The model balance calculations show that ~80% of the total metal discharges into watercourses in NKV drainage basin is formed by their washout from subsurface stratum. The surface washout accounts for ~20% of copper and ~15% of zinc runoff. The propor-

tions of HM entering river network with wastewater discharges are relatively low, amounting to ~1% and ~4% of the total copper and zinc runoff, respectively. A considerable portion of metals washed out from the watershed is accumulated with sediments in bottom deposits: on the average, ~45% of copper and 60% of zinc.

The comparison of the calculated and actual runoff of metals into NKR shows the satisfactory reproduction of its year-to-year dynamics. The differences between the compared values are due to the large errors in determining metal concentrations in river water.

SIMULATING THE SCENARIOS OF ECONOMIC ACTIVITY ON NKR DRAINAGE BASIN

A series of numerical experiments was carried out to give a more detail estimate of the effect of economic activity on river water pollution; these experiments considered the following scenarios: an increase in the amount of metals discharged with wastewater at all 12 populated localities with controlled discharges; a volley input of a large amount of HM into a watercourse, resulting from an emergency wastewater discharge in a populated locality; a complete elimination of anthropogenic impact on the drainage basin.

Scenario 1. An Increase in the Amounts of Metals Discharged with Wastewaters

The scenarios used in the calculations implied an increase in metal concentrations in wastewater by factors of 10, 20, 40, 60, 80, and 100 relative to the existing level (given in reports 2TP (vodkhoz)) for 12 pop-

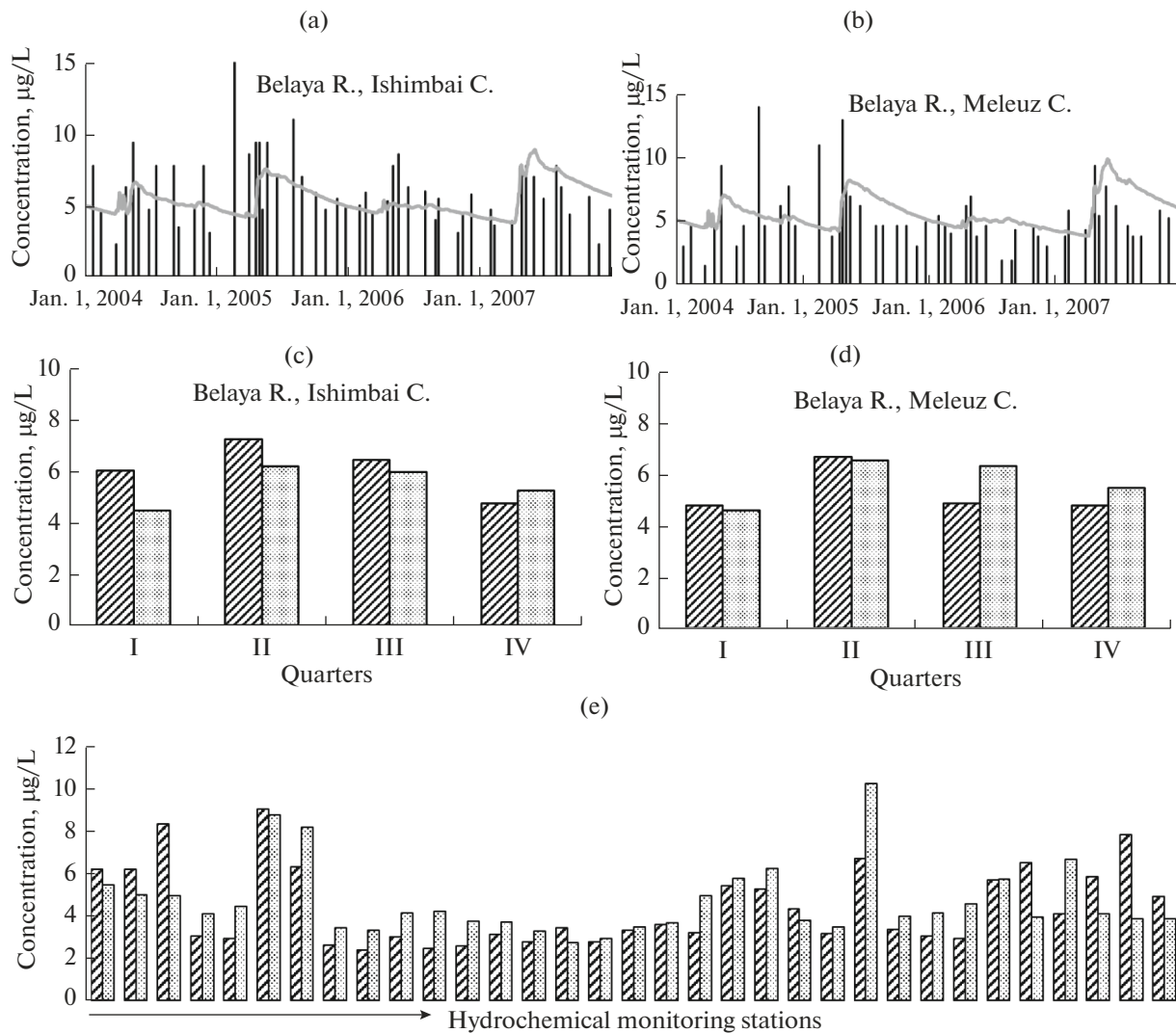


Fig. 5. Observed (diagonally hatched and dark columns) and simulated (light hatching and light line) zinc concentration in river water, $\mu\text{g/L}$, in hydrochemical monitoring sections over period 2004–2007: (a, b) concentration dynamics with daily resolution; (c, d) mean annual distribution of concentrations; (e) mean annual concentrations at hydrochemical monitoring stations; the arrow shows the flow direction in the Belaya R.

ulated localities. In reality, such an increase can be due to an increase in industrial production or because of a more objective and accurate presentation of data in reports 2TP (vodkhoz), regarding the amounts of pollutants discharged by water users with wastewaters. The rates of wastewater discharges were assumed to be constant within a year.

Figure 9 exemplifies the plots of calculated annual variations of copper concentration in the Belaya R. at Ufa City given the actual wastewater discharges, as well as at an increase in copper content of the discharged wastewaters by factors of 20 and 60. As can be seen from the calculations, at the current level of copper concentration in wastewater, its concentration in river water increases in periods of higher water abundance (spring flood and freshets) because of metal

inputs mostly from diffuse sources (Fig. 9a). The same regularity was typical of zinc.

An increase in metal discharges with wastewaters is accompanied by an increase in their concentrations in river water. As the concentration of metals in wastewater increases relative to the existing level by a factor greater than some critical value, the concentrations of metals in periods with higher water abundance become minimal. This is a result of the dilution of the heavily polluted industrial wastes by much less polluted snowmelt and rain water. Therefore, at an increase in the concentrations of metals in wastewater above some critical level, the relationship between their concentration in river water and river flow rate ($C = f(Q)$) changes to the opposite. As can be seen from plots in Figs. 9b, 9c, when the factor of copper

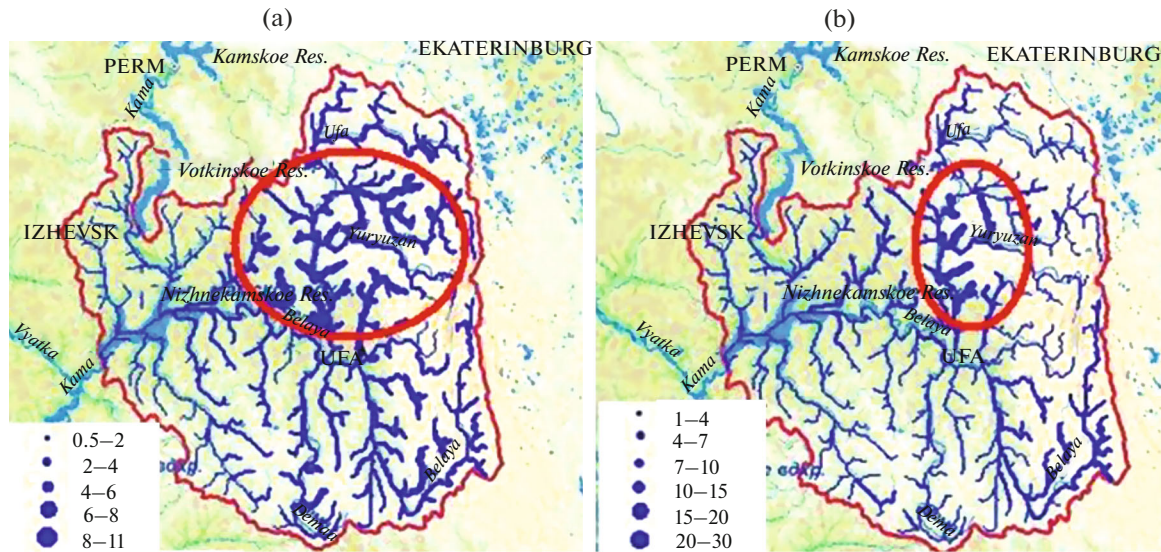


Fig. 6. Distribution of the simulated mean annual concentrations of (a) copper and (b) zinc in river water in the NKR basin over 2004–2007, µg/L.

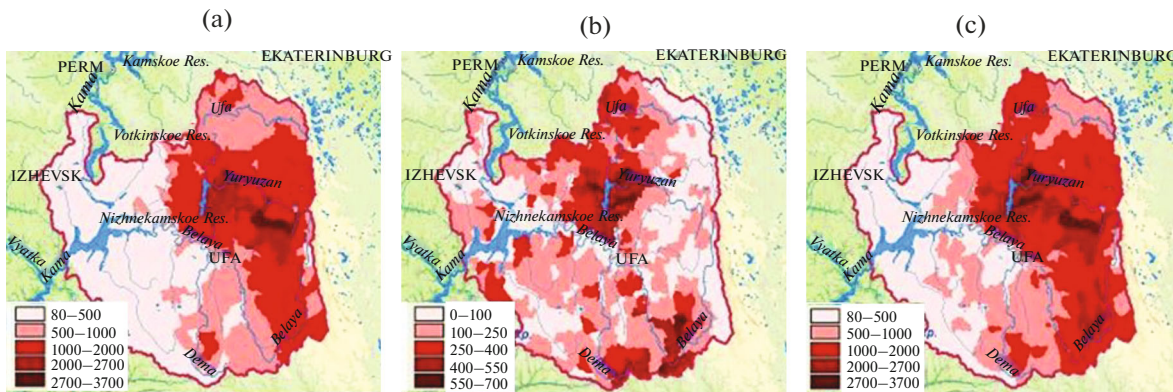


Fig. 7. Calculated values of mean annual copper runoff module in the NKR basin over period 2004–2007, g/(year km²): (a) total, (b) surface, and (c) subsurface runoff.

concentration in wastewater increases to 20, such change in the dependence $C = f(Q)$ takes place at the section downstream of the Ufa City. At a 60-fold increase in copper concentration in wastewater, this effect manifests itself in both sections, either upstream or downstream of Ufa City.

The results of numerical experiments for each section were used to construct nomograms (Fig. 10), showing the critical levels of anthropogenic load (the multiplication factors of the metals discharged with wastewaters relative to the existing level (given in reports 2TP (vodkhoz)), at which such changes are taking place. In particular, as follows from Fig. 10b, the relationship between water discharge and copper concentration at a section in the Belaya River downstream of Ufa changes to the opposite at a decrease in

discharges by a factor of 20 or more. At an increase of discharges by more than 40 times, the relationship also changes in the section upstream of the city (Fig. 10a). Similar changes take place in the relationship between river water discharge and its zinc content: in the section downstream of the city, at an increase in discharges by a factor of ≥ 10 , and at the section upstream of the city, by a factor of 60, i.e., the critical multiplication factor of the metals discharged with wastewater in the section upstream of the city is always greater. This is due to the fact that $\sim 82\%$ of the copper and $\sim 87\%$ of the zinc in all controlled discharges in the NKR drainage basin enter the river from Ufa City territory within the segment between these two sections. The inflow of a large tributary, the Ufa R., into the Belaya R. within the city, increasing its water abundance by $>40\%$, is not enough to dilute water to com-

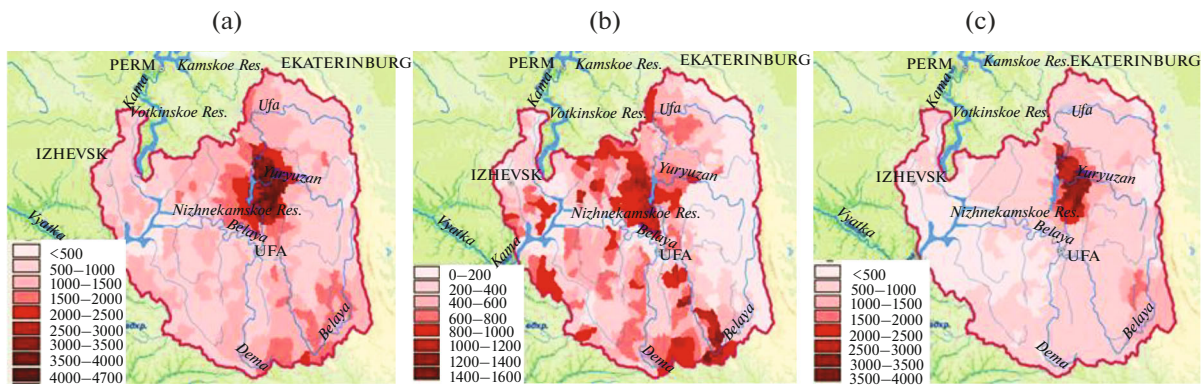


Fig. 8. Calculated values of mean annual runoff module of zinc in the NKR basin over period 2004–2007, $\text{g}/(\text{year km}^2)$: (a) total, (b) surface, and (c) subsurface runoff.

pensate for the critical multiplication factor at the sections upstream and downstream of the city.

As follows from Figs. 10a, 10b, at an increase in Belaya R. water discharge in Ufa C. up to $>3500 \text{ m}^3/\text{s}$, either upstream or downstream of the city, the curves of the relationship between copper concentration and water discharge at different scenarios of wastewater discharges asymptotically approach the value of $\sim 6 \mu\text{g}/\text{L}$, i.e., the calculations show that, at high water discharges, the contribution of point sources is minimized, and the concentration of metals in river water is mostly determined by the maximal exchange capacity of the drainage basin at HM leaching from the soil stratum at intense precipitation or snow melting, forming maximal water discharges.

At an increase in metal concentration in wastewater, the contribution of point sources to NKR pollu-

tion increases considerably (Fig. 11a). Thus, at an increase in metal concentrations in wastewater by a factor of 20, the contribution of point sources is $\sim 20\%$ for copper and 44% for zinc, while at an increase by a factor of 100, the contributions are ~ 53 and 80% , respectively.

The increase in the concentrations of metals in the discharged wastewaters leads also to an increase in their export by river water into the reservoir (Fig. 11b). Thus, at an increase in the discharge of the metals by a factor of 100, the amounts of copper and zinc discharged into the NKR increase by factors of ~ 2 and ~ 4 , respectively.

Scenario 2. Simulation of an Emergency

An extreme situation was simulated, leading to an inflow of a large amount of HM into the stream. Such

Table 1. Calculated values of various genetic components of hydrochemical runoff of metals and its actual values from the NKR, t/year

Year	Diffuse runoff from the drainage basin into the river network		Discharge into river with wastewaters	Settling with sediments onto river bed	Runoff of metals into the NKR	
	surface runoff	subsurface runoff			calculated	actual
Copper						
2004	25	130	2.3	82	75	127
2005	50	192	2.4	106	138	166
2006	18	123	2.3	78	65	54
2007	68	252	2.1	130	192	129
Mean	40.3	174.3	2.3	99	118	119
Zinc						
2004	22	165	7.2	125	69	97
2005	46	207	7.9	152	109	109
2006	14	153	7.9	114	61	97
2007	61	265	12.7	186	153	155
Mean	35.8	197.5	8.9	144.3	98	114.5

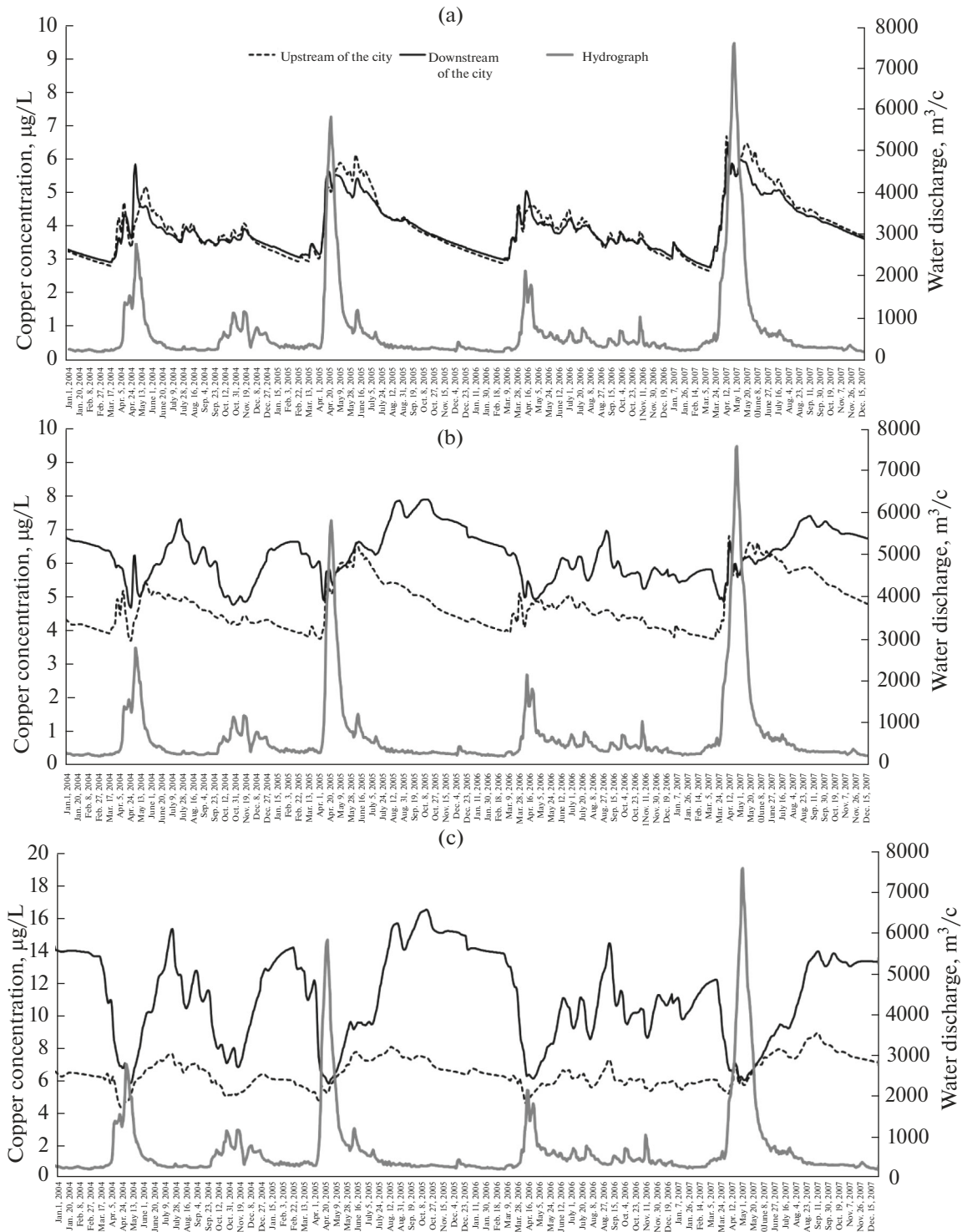


Fig. 9. Annual distribution of copper concentration in river water at Belaya R.—Ufa C. section (upstream and downstream of the city) under different scenarios of economic activity in the NKR basin: (a) at the actual copper concentration in wastewater (according to 2TP (vodkhoz)); (b) at an increase in copper concentration in wastewater by a factor of 20; (c) at an increase in copper concentration in wastewater by a factor of 60.

situation can be a result of an emergency at liquid waste storage, volley wastewater discharges because of unstable functioning of plants, unauthorized discharges of untreated polluted wastewaters, etc. The

algorithm of the scenario was as follows. Specified at the entry to the model were different amounts of metals discharged within a day at some point in the river network. Next, the concentrations of metals in river

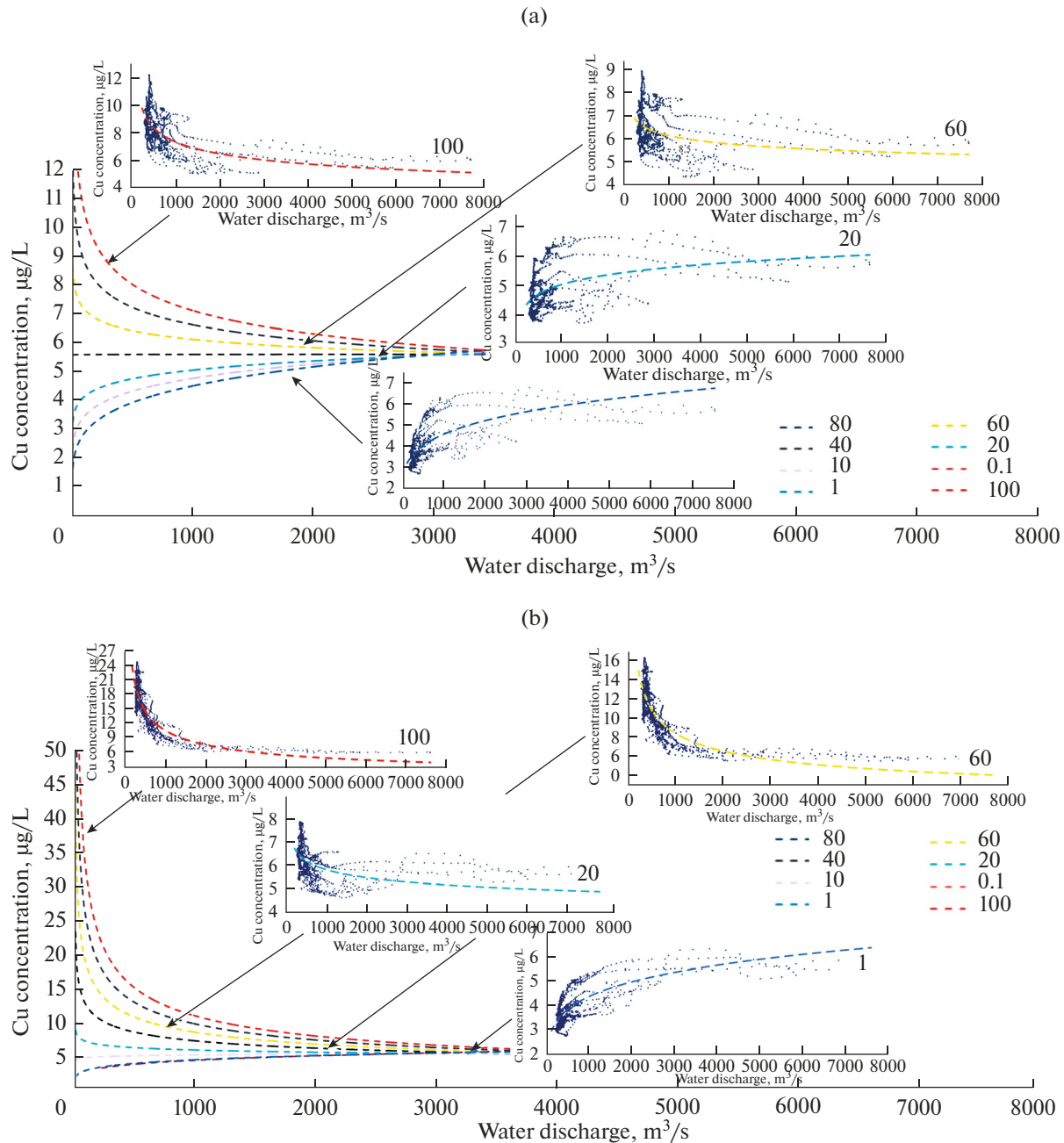


Fig. 10. Dependence between water discharge in the Belaya R. at Ufa C. (in sections (a) upstream and (b) downstream of the city) and copper (Cu) concentration in river water under different scenarios of copper concentrations in wastewater: (1) actual copper concentration in wastewater (according to 2TP (vodkhoz)); 10, 20, 40, 60, 80, 100 are scenarios of copper concentration increase in wastewater by factors of 10, 20, 40, 60, 80, and 100, respectively.

water were calculated at different points downstream of the emergency discharge site. As an example, Fig. 12 gives the results of calculation of variations of the maximal copper concentration along the river under different scenarios of its volley input (5000, 4000, 3000, 2000, 1000, 500, and 100 kg) into the

Belaya R. near Salavat C. Calculations show that, as the pollution patch is moving downstream from its discharge site, copper concentration is rapidly decreasing because of dilution by water from Belaya R. tributaries and copper settling onto river bed along with sediments. As near as in Ufa C. (~200 km from

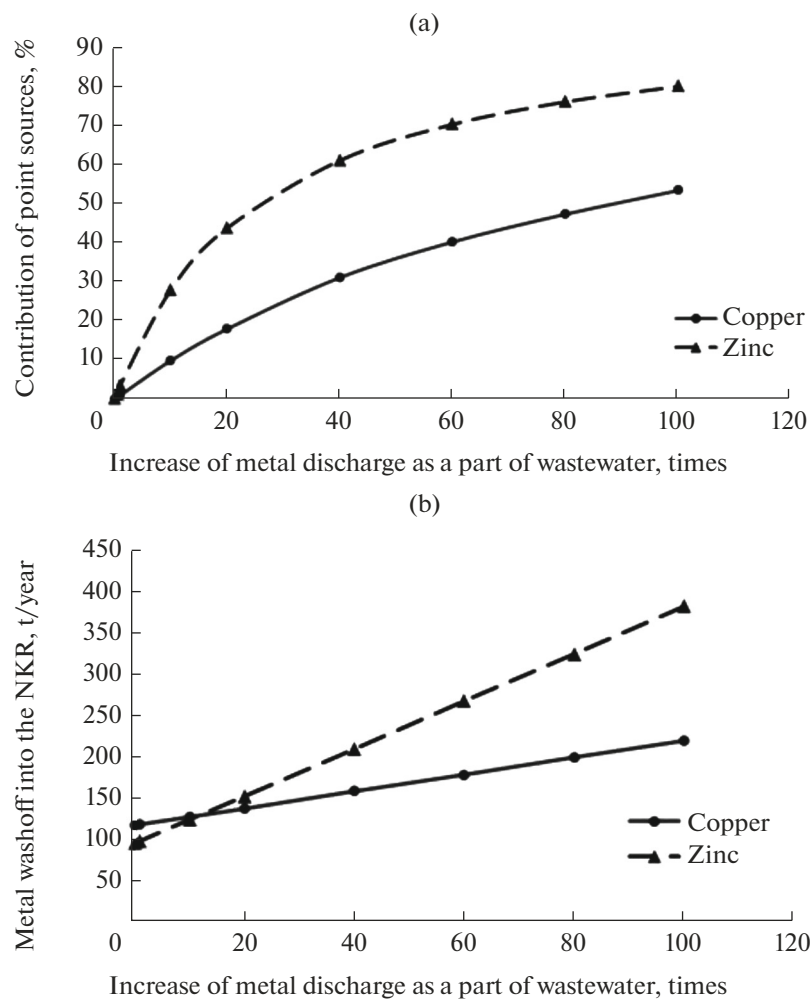


Fig. 11. Dynamics of the characteristics of anthropogenic impact on the NKR at an increase in metal concentrations in the discharged wastewater: (a) the share of point sources in metal discharge; (b) washoff of metals into the reservoir.

the discharge site), the maximal concentration of copper decreases by ~2 orders of magnitude.

Scenario 3. Exclusion of Anthropogenic Impact on the Drainage Basin

The time scale of drainage basin self-purification from HM was evaluated under a scenario of zero anthropogenic impact on NKR drainage basin. The wastewater was assumed to contain neither copper nor zinc, and the release of metals into the atmosphere with industrial emissions and hence the concentrations of metals in precipitation were assumed zero. The concentration of metals in confined groundwater was reduced to the least in the range of values typical of groundwater in the examined region.

Under such conditions, numerical experiments for assessing the dynamics of copper and zinc content of river water were carried out for 400 years ahead. The meteorological forcing data were given in the form of series of weather elements from weather stations in

NKR basin over 33 years from 1979 to 2011. The final results for December 31, 2011 were recorded at the initial point of January 1, 1979, and thus the calculations for the 33-year series were reiterated.

The maps of metal contents of soils showed that the copper reserves in the top half-meter soil layer in NKR drainage basin were ~1 million t (Fig. 13a), and those for zinc were ~550 thousand t. The mean annual copper runoff from the watershed into the channel network in the beginning of the calculation period was 147 (Fig. 13b), and that of zinc, ~156 t/year. Calculations for 200 years ahead showed a decrease in the export of copper and zinc from the drainage basin to 140 and 147 t/year, respectively. Four hundred years later, the mean annual export of copper and zinc into the channel network kept decreasing, amounting to 135 and 140 t/year, respectively. Thus, in the absence of external impacts in the calculation period, slow purification of the drainage basin was taking place with a decrease in the copper content of soil to ~950 thousand t (Fig. 13a) and zinc to ~500 thousand t.

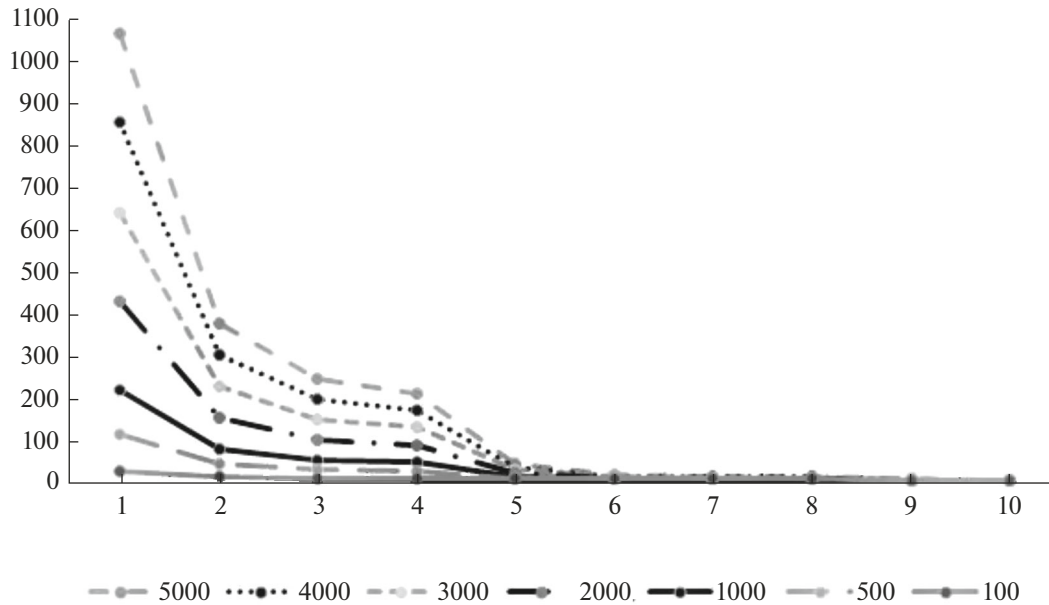


Fig. 12. Variations of the maximal copper concentration in river water, $\mu\text{g/L}$, under various scenarios of its volley discharge into the Belaya R. (5000 kg, ..., 100 kg) near Salavat C. at hydrochemical stations: (1) Salavat C., (2) Ishimbai C., (3) upstream of Sterlitamak C., (4) downstream of Sterlitamak C., (5) upstream of Ufa C., (6) downstream of Ufa C., (7) upstream of Blagoveshchensk C., (8) downstream of Blagoveshchensk C., (9) downstream of Birsk C., (10) downstream of Dyurtly C.

The decrease in the copper and zinc reserves in the drainage basin caused a decrease in their concentration in the river network. Calculations showed that, over the 400-year period of self-purification of NKR basin, the mean annual concentrations of copper and zinc in river water have been decreasing by 7–8%. The low rate of the decrease of copper and zinc concentrations in river water allows their current mean annual concentrations to be recommended as background values in the NKR basin.

CONCLUSIONS

The spatial and temporal regularities in the formation of water quality and chemical runoff of HM (copper and zinc) in NKR drainage basin were studied with the use of ECOMAG-HM software complex. The results of calculations are compared with data of hydrological and hydrochemical observations and showed a good agreement between the calculated and actual characteristics of water flow and a satisfactory reproduction of spatial and temporal regularities in the formation of metal concentrations in river water in NKR basin.

The results of simulation were used to map the mean annual concentrations of copper and zinc in river network. The concentration of copper in river water in the major portion of the basin was found to be in excess of the MAC, while zinc concentration was below its MAC. At the same time, watershed areas not covered by hydrochemical observations were identified where the pollution level of small rivers was con-

siderable, and the concentrations of metals were 5–6 times their normal annual values in NKR basin.

The normal annual modules of diffuse flow of copper and zinc were calculated and mapped. The spatial distribution of various genetic components of diffuse metal flows was established.

The contributions of natural and anthropogenic components of the hydrochemical runoff of copper and zinc were evaluated. Balance calculations showed that the washout of metals from soil mass accounts for ~80% of the total metal runoff, while the surface washout, for up to 20%. About half of the metals washed out from the drainage basin accumulates in bottom deposits with sediments. The shares of HM entering river network with wastewater discharges are not large ($\leq 4\%$ of heavy metal runoff into the NKR).

The contributions of point sources to river water pollution were evaluated under different scenarios of metal discharges with wastewaters. It was found that some level of anthropogenic load onto water bodies can cause changes in their hydrochemical regime. When the concentrations of metals in discharged wastewater reach some critical level, their maximal concentrations in river water will be observed in the phase of water regime, in which, before the critical level is reached, the concentrations were minimal. In addition, the calculations showed that the contribution of point pollution sources at large water discharges is minimized, and the concentration of metals in river water asymptotically tends to a constant value and becomes determined mostly by the maximal

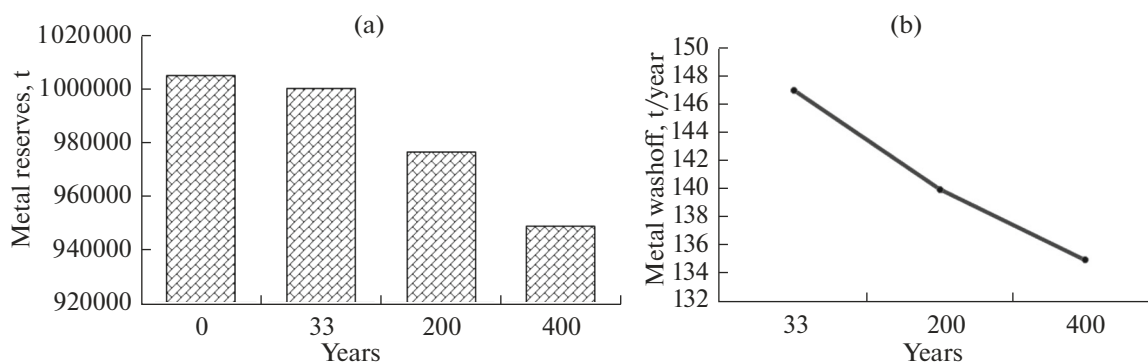


Fig. 13. Changes in the copper content in the NKR drainage basin: (a) copper reserves in soil, t; (b) copper washoff into river network, t/year.

exchange capacity of the drainage basin at HM wash-off into river network at intense precipitation or snow melting.

Calculations for an emergency leading to an input of a considerable amount of HM into the Belaya R. showed that their concentrations rapidly decrease with the motion downstream from the site of emergency discharge because of the dilution by water of tributaries of the Belaya R. and settling of metals onto river bed along with sediments (by ~2 orders of magnitude at a distance of 200 km from the discharge site).

Estimates of the time scale of drainage basin self-purification from HM at a decrease of anthropogenic load showed that, under a scenario of its complete absence over a 400-year period, the reserves of metals in the drainage basin and the normal annual concentrations of copper and zinc in river water are very slowly decreasing by 7–8%. This allows the current mean annual values to be recommended as the background concentrations of HM in the NKR basin.

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REFERENCES

1. Abdrakhmanov, R.F., Chalov, Yu.N., and Abdrakhmanova, E.R., *Presnye podzemnye vody Bashkortostana* (Fresh Groundwater of Bashkortostan), Ufa: Informreklama, 2007.
2. *Atlas Respubliki Bashkortostan* (Atlas of the Republic of Bashkortostan), Yaparov, I.M., Ed., Ufa: Kitap, 2005.
3. Belyaev, S.D., On the issue of taking into account the differentiation of natural environment when planning water protection measures, *Geograf. Vestn.*, 2017, no. 4, vol. 43, pp. 81–96.
4. Blokov, I.P., *Okruzhayushchaya sreda i ee okhrana v Rossii. Izmeneniya za 25 let* (Environment and Its Protection in Russia. Changes over 25 Years), Moscow: Sovet Grinpis, 2018.
5. Gordienko, V.S., Water treatment plants in Ufa today, *Vodosnabzh. Sanit. Tekh.*, 2001, no. 5, pp. 9–11.
6. *Gosudarstvennyye doklady o sostoyanii prirodnnykh resursov i okruzhayushchei sredy Respubliki Bashkortostan za 2005–2016 gg.* (State Reports on the State of Natural Resources and the Environment in the Republic of Bashkortostan over 2005–2016).
7. *Gosudarstvennyi doklad "O sostoyanii i ispol'zovanii vodnykh resursov Rossiiskoi Federatsii v 2016 godu"* (State Report "On the State and Use of Water Resources of the Russian Federation in 2016"), Moscow: NIA-Priroda, 2017.
8. *Kachestvo poverkhnostnykh vod Rossiiskoi Federatsii. Informatsiya o naibolee zagryaznennykh vodnykh ob'ektakh Rossiiskoi Federatsii (Prilozhenie k ezhegodnikam 2011, 2013, 2015, 2016)* (Surface Water Quality in the Russian Federation. Information about the Most Heavily Polluted Water Bodies in the Russian Federation (Appendix to Yearbooks of 2011, 2013, 2015, 2016)).
9. Kirpichnikova, N.V., Major pollution sources in the reservoir, in *Ivan'kovskoe vodokhranilishche. Sovremennoe sostoyanie i problemy okhrany* (The Ivankovo Reservoir. Current State and Protection Problems), Moscow: Nauka, 2000, pp. 30–62.
10. Lepikhin, A.P., Bogomolov, A.V., Voznyak, A.A., Lyubimova, T.P., and Parshakova, Ya.N., Diffuse pollution of surface water bodies of Solikamsk–Berezniki Industrial Center: extent, genesis, *Gorn. Ekho*, 2019, no. 1, vol. 74, pp. 27–31.
11. Maistrenko, V.N., Khamitov, R.Z., and Budnikov, G.K., *Ekologo-analiticheskii monitoring superekotoksikantov* (Ecological-Analytical Monitoring of Superecotocicants), Moscow: Khimiya, 1996.
12. Mikhailov, S.A., *Diffuznoe zagryaznenie diffuznykh ekosistem: metody otsenki i matematicheskie modeli* (Diffuse Pollution of Diffuse Ecosystems: Methods of Assessment and Mathematical Models), Barnaul: Den', 2000.
13. Moiseenko, T.I. and Gashkina, N.A., *Formirovanie khimicheskogo sostava vod ozer v usloviyakh izmeneniya okruzhayushchei sredy* (Formation of Water Chemistry

- in Lakes under Changing Environment), Moscow: Nauka, 2010.
14. Motovilov, Yu.G., Estimates of anthropogenic pollution of river basins by heavy metals based on ECOMAG model, *Sb. Nauch. tr. "Nauchnoe obespechenie realizatsii "Vodnoi strategii Rossiiskoi Federatsii na period do 2020 goda" (Coll. Sci. Pap. "Scientific Support of the Implementation of "The Water Strategy of the Russian Federation for the Period up to 2020")*, 2015, vol. 1, pp. 335–343.
 15. Motovilov, Yu.G. and Gel'fan, A.N., *Modeli formirovaniya stoka v zadachakh gidrologii rechnykh basseinov (Runoff Formation Models in Problems of River Basin Hydrology)*, Moscow: Ross. Akad. Nauk, 2018.
 16. Motovilov, Yu.G. and Fashchevskaya, T.B., Spatially distributed model of heavy metal runoff in a river basin, *Voda: Khim. Ekol.*, 2018, nos. 1–3, pp. 18–31.
 17. *Nauchno-populyarnaya internet-entsiklopediya "Voda Rossii" (Popular-Science Internet-Encyclopedia "Water of Russia")*.
 18. Nikanorov, A.M., Minina, L.I., Lobchenko, E.E., Emel'yanova, V.P., Nichiporova, I.P., Lyampert, N.A., Pervysheva, O.A., and Lavrenko, N.Yu., *Dinamika kachestva poverkhnostnykh vod krupnykh rechnykh basseinov Rossiiskoi Federatsii (Dynamics of Surface Water Quality in Large River Basins in the Russian Federation)*, Minina, L.I., Ed., Rostov-on-Don: Gidrokhim. Inst., 2015.
 19. Selezneva, A.V., Anthropogenic load on rivers from point pollution sources, *Izv. Samar. Nauh. Ts. Ross. Akad. Nauk*, 2003, vol. 5, no. 2, pp. 268–277.
 20. SN 435-72. *Ukazaniya po opredeleniyu raschetnykh gidrologicheskikh kharakteristik (Guides for Estimating Hydrological Characteristics)*, Leningrad: Gidrometeoizdat, 1972.
 21. *Tendentsii i dinamika sostoyaniya i zagryazneniya okruzhayushchei sredy v Rossiiskoi Federatsii po dannym mnogoletnego monitoringa za poslednie 10 let. Analiticheskii obzor (Trends and Dynamics of the State and Pollution of the Environment over the Past 10 Years. An Analytical Review)*, Chernogaev, G.M., Ed., Moscow: Rosgidromet, 2017.
 22. Fashchevskaya, T.B., Krasnogorskaya, N.N., and Rogozina, T.A., On the effect of "Ufavodokanal" plant on water quality in the Belaya river, *Materialy mezhdunarod. nauch. konf. "Ekologicheskie i gidrometeorologicheskie problemy bol'shikh gorodov i promyshlennykh zon" (Mater. Intern. Sci. Conf. "Ecological and Hydrometeorological Problems and Industrial Zones")*, St. Petersburg.: Izd. Ros. Gos. Gidromet. Univ., 2006, pp. 80–82.
 23. Fashchevskaya, T.B., Motovilov, Yu.G., and Shadiyanova, N.B., Natural and anthropogenic variations of the concentrations of iron, copper, and zinc in water streams of the Republic of Bashkortostan, *Water Resour.*, 2018, vol. 45, no. 6, pp. 873–887.
 24. Khublaryan, M.G. and Moiseenko, T.I., Water quality, *Herald Russ. Acad. Sci.*, 2009, vol. 79, no. 5, pp. 230–236.
 25. Chernogaeva, G.M., Kuz'mich, V.N., and Berdnikov, S.V., Problem of standardization of chemical runoff from a drainage area, *Meteorol. Gidrol.*, 2003, no. 3, pp. 75–86.
 26. Shul'kin, V.M., Heavy metals in river and coastal marine ecosystems, *Extended Abstract of Doctoral (Geogr.) Dissertation*, Pacific Geograph. Inst., Far-Eastern Branch, Russ. Acad. Sci., Vladivostok, 2007, 38 p.
 27. Shcherbakov, B.Ya., Chilikin, A.Ya., and Izhevskii, V.S., Valley discharges of production wastewaters and their effects, *Ekol. Prom-st. Ross.*, 2002, no. 6, pp. 39–41.
 28. EPA-State Approach to Instream Monitoring for NWQI.EPA, 2013. Electronic Resource. www.epa.gov/sites/production/files/2015-09/documents/nwqi-monitoringapproach-2013-state-april30.pdf.
 29. Fashchevskaya, T.B., Polianin, V.O., and Fedosova, L.V., Structural analysis of water quality formation in an urban watercourse: point, non-point, transit, and natural, *Water Resour.*, 2018, vol. 45, suppl. 1, pp. S67–S78.
 30. Moriasi, D.N., Arnold, J.G., Van Liew, M.W., Bingner, R.L., Harmel, R.D., and Veith, T.L., Model evaluation guidelines for systematic quantification of accuracy in watershed simulations, *Trans. ASABE*, 2007, vol. 50, no. 3, pp. 885–900.
 31. Motovilov, Yu.G. and Fashchevskaya, T.B., Simulation of spatially-distributed copper pollution in a large river basin using the ECOMAG-HM model, *Hydrol. Sci. J.*, 2019, vol. 64, no. 6, pp. 739–756.
 32. Sauve, S., Manna, S., Turmel, M.-C., Roy, A.G., and Courchesne, F., Solid-solution partitioning of Cd, Cu, Ni, Pb and Zn in the organic horizons of a forest soil, *Environ. Sci. Technol.*, 2003, no. 37, vol. 22, pp. 5191–5196.
 33. Vink, R. and Peters, S., Modelling point and diffuse heavy metal emissions and loads in the Elbe basin, *Hydrol. processes*, 2003, vol. 17, pp. 1307–1328.

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