Ecological and chemical characteristics of small river Arguzikha (Zeya-Bureya plain, Russia)

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Abstract. The article considers the results of research from 2015 to 2019 on the study of hydrochemical indicators and the content of heavy metals in the ecosystem components of the small Arguzikha river , a left-Bank tributary of the Amur river (water, bottom sediments, macrophytes, birds ' feathers). High oxygen content in the water (8.8-15.9 mgO_2/dm^3) and high BOD_5 values (6-12 mgO_2/dm^3) in the middle and lower reaches of the Arguzikha river indicate the process of eutrophication. The value of permanganate oxidability (6.8-15.5 mgO/dm^3) characterizes the high content of organic substances in water. In the spring, nitrate nitrogen (3.45-6.39 $mgN-NO_3^-/dm^3$) was found in the water of the Arguzikha river, which had a pyrogenic origin. In the summer the rainy season was dominated by ammonium nitrogen (2.34 $mgN-NH_4^+/dm^3$). The high content of total phosphorus (0.337-0.609 mg/dm^3) in the river water was in the spring. In the spring of 2015, the concentration of lead in the lower reaches of the river reached 6.36 $\mu g/dm^3$, during the subsequent time, the lead content in the Arguzikha water was less than the MPC. Toxic concentrations of lead (> 30 mg / kg) and manganese (> 300 mg/kg) were found in macrophytes of *Nymphoides peltata* and *Myriophyllum spicatum*. In the feathers of waterfowl of the Arguzikha river the content of heavy metals decreases in a row Fe>Zn>Cu>Pb>Mn>Cr>Ni>Co>Cd. The feathers of *Anas acuta* and *Anas querquedula* contained Pb 17.7 mg/kg and 22.2 mg/kg, Cd 0.15 mg/kg and 0.08 mg/kg, respectively.

1 Introduction

The natural landscapes of the Zeya-Bureya plain have changed as a result of human activity. Here is the largest agro-industrial complex in the Russian far East, animal husbandry is developing, and huge areas of land are plowed for growing grain crops, soybeans, and rapeseed. Such changes have negatively affected the biodiversity of biocenoses. The use of mineral fertilizers and herbicides contributed to the accumulation of heavy metals in the soil [1]. During floods and inundations, heavy metals entered the water of small rivers from the surface layers of the soil. The quality of small rivers deteriorated due to the introduction of organic substances, heavy metals, nitrogen and phosphorus compounds into the water from the soil. Mass plowing of land in the floodplains of small rivers of the Zeya-Bureya plain, deforestation, construction of reservoirs, and application of fertilizers to the soil contributed to changes in the water quality of small rivers [2, 3]. Macrophytes enrich water with oxygen during photosynthesis, participate in the process of

self-purification of small rivers, and extract heavy metals from sediments and water. Heavy metals can have a toxic effect on macrophytes [4]. Macrophytes are sensitive indicators of anthropogenic pollution [5, 6]. Higher water plants serve as habitat and food for birds [3]. Small rivers of the Zeya-Bureya plain are tributaries of the Amur river, the river banks are usually swampy. The preserved wetlands are home to rare and endangered bird species that need protection. Accumulation of heavy metals in the habitat has a negative impact on birds, contributes to disease and death of birds [7]. Pollution of the environment with heavy metals leads to a violation of the reproductive function of birds and a decrease in the growth rate of Chicks [8]. All this has determined the importance of studying the accumulation of heavy metals in the components of the ecosystem of small rivers. The aim of this work is to study the ecological state of the Arguzikha river based on hydrochemical indicators and the content of heavy metals in water, river bottom sediments, macrophytes and bird feathers.

2 Object and methods of research

The object of study was water, sediments, rivers Arguzikha, macrophytes and bird feathers. The area where the research was conducted is the small Arguzikha river , a left tributary of the Amur river. The Arguzikha river flows into the Amur river 1892 km from the mouth, the length of the watercourse is 47 km. Samples were collected in four sections: I - the river below the village of Lermontovka (N 50°4′4″, E 127°53′58″), II - reservoir Rozdol'ne (N 50°1′1″, E 127°50′37″), III - the river below the village of Kuropatino (N 49°58′56″, E 127°39′5″ e.l.), IV - lower reaches of the river (N 49°55′06″, E 127°29′03″). Arguzikha river flows through agricultural landscape of southern Zeya-Bureya plain. The river flows through an open space, only in the lower reaches of the river the banks are overgrown with shrubs and trees, mainly willows. For a long distance, the river is completely blocked from above by a carpet of floating plants, mainly reeds. Fires easily move from one Bank to the other, destroying ground vegetation. In the lower reaches of the Arguzikha river there are unique wetlands of the Muravyevsky reserve, where about 300 species of birds live, including those that are under protection - the red-crowned crane, the Oriental stork, the hooded crane and the Daurian white-naped crane. In the reeds of the river Arguzikha, which sometimes completely cover the water surface to nest Schrenck's Bittern, Brown-cheeked Rail, Oriental Reed-warbler, Northern Reed Bunting. On Razdolnoye reservoir come to feed Grey Heron, Great Cormorant. Flocks of Garganey, Common Teal and Northern Pintail stop during migrations. The presence of field roads and a small distance from the village attract poachers here. Fires in the spring destroy surface vegetation, depriving birds of nesting conditions.

Water sampling was carried out during the low water period in May, July and October 2015-2019 in accordance with GOST R 51592-2000. Macrophytes and sediments were collected in the summer of 2016. Macrophytes were washed with distilled water and dried in a drying Cabinet at a temperature of 50 °C for 1 hour. Bottom sediments were also dried at 50 °C for 1 hour. The birds' feathers were selected in the fall of 2019. Sample preparation was carried out on the complex "Temos-Express TE-1", based on the destruction of interfering organic substances by thermal action together with oxidizers (HNO_3, H_2O_2). Heavy metals in aquatic plants, bottom sediments, and bird feathers were determined by voltammetric method using the STA-1 complex (Tomsk). Heavy metals in the waters of the Arguzikha river were determined by atomic absorption method using the quantum Z. ETA spectrophotometer. Hydrochemical indicators were performed in accordance with federal regulatory documents on nature conservation.

3 Research results and discussion

3.1 Hydrochemical parameters of river water Arguzikha

The water temperature in the river corresponded to the hydrological time of year: 9-10 °C in spring (the third decade of April - the first decade of may), 21-24 °C in summer (the second decade of may - the second decade of September), 2-4 °From autumn (the third decade of September - the first decade of October). The acid-base properties (pH) of the waters of the small Arguzikha river in points I - III were within the norm (4.46 - 8.29) with the exception of autumn water samples in the Razdolnoye reservoir (8.70). In the lower reaches of the river, the pH value was higher than normal (8.59-9.31). The highest values of water pH were observed in summer and autumn due to the high biological productivity of phytoplankton. Minimum values of specific electrical conductivity of water were observed in spring, maximum values in summer (table 1). The waters of small rivers in this region are low-mineralized and soft [2, 3]. The water Color of the Arguzikha river ranged from 22 degrees of color in spring to 115 degrees of color (Cr-Co) in summer, the maximum value of color was observed in the water of the Razdolnoye reservoir in spring-172 degrees of color. The color of water depends on the type of soil, the content of iron and manganese compounds in the water.

Table 1. Electrical conductivity, pH and color of the waters of the small river Arguzikha.

River	pH			SEC, µS / cm			Color, ° (Cr-Co)		
	Spring	Summer	Autumn	Spring	Summer	Autumn	Spring	Summer	Autumn
I	7.46	7.89	8.20	175	339	231	82	101	27
II	7.58	8.29	8.70	100	124	80	172	51	36
III	7.62	7.90	7.90	171	187	142	80	55	22
IV	8.59	8.7	9.31	179	190	150	89	115	58

Note: The table shows the average values of indicators.

The water of the river Arguzikha contains a large amount of oxygen. The exception is the low oxygen saturation of water (52 %) in the river below the village of Lermontovka (I) in summer. The river water has high values of permanganate oxidability (PO), which characterizes the high content of organic substances in the water. In the fall, after severe summer floods, the PO value along the entire length of the river decreased. High oxygen saturation of water and high BOD_5 values (table 2) in the middle and lower reaches of the Arguzikha river indicate the process of eutrophication.

In spring and summer, BOD_5 reached 6.1 - 13.1 mgO_2/dm^3 in the middle and lower reaches of the river, and 2 mgO_2/dm^3 in the upper reaches of the river. In the autumn after the flood, BOD_5 in the water of the II and III sections decreased, which is associated with the intensity of self-cleaning processes in the river, and in the I section, on the contrary, increased. Range IV has the highest values of dissolved oxygen in water, BOD_5, and PO during the entire growing season.

Among nitrogen compounds in the water of the Arguzikha river, the dominant position is occupied by ammonium nitrogen, the content of which was especially high in the summer during the rainy season and reached 2.34 $mgN\text{-}NH_4^+/dm^3$.

Table 2. Oxygen indicators of the water of the small river Arguzikha.

River	Dissolved oxygen, mgO_2/dm^3			BOD_5, mgO_2/dm^3			PO, mgO/dm^3		
	Spring	Summer	Autumn	Spring	Summer	Autumn	Spring	Summer	Autumn
I	8.8	4.2	13.0	2.0	1.4	7.1	15.5	14.8	6.1
II	10.8	12.9	13.6	6.8	8.2	4.0	11.7	11.2	5.8
III	12.2	15.8	13.8	6.1	12.7	3.9	7.5	6.8	5.4
IV	13.2	15.9	14.6	7.9	13.1	6.1	9.35	14.9	9.9

The concentration of ammonium nitrogen did not meet the standard (MPC= 0.39 mgN-NH_4^+/dm^3). Nitrogen compounds entered the water of the river from the surface layers of the soil of agricultural arable land during the flood. In spring, along the entire length of the river, nitrate nitrogen in the amount of 3.45 - 6.39 mgN-NO_3^-/dm^3 was detected in the water, which had a pyrogenic origin. Fires cause large concentrations of nitrate nitrogen to appear in water [9]. Authors of works [10, 11] name as the reason for the high concentration of nitrogen compounds in river waters leaching of nitrogen fertilizers from agricultural fields, runoff from livestock farms into the river.

The content of nitrite nitrogen in the spring in the water of the Razdolnoye reservoir reached 0.017 mgN-NO_2^-/dm^3. during the research period, nitrites were detected in other river channels in the amount of 0.002 - 0.005 mgN-NO_2^-/dm^3 (table 3). Nitrogen compounds affect the quality of river water during the rainy season, and phosphorus compounds are the main factor in the dry season [12]. Different forms of nitrogen had significant seasonal variations and varied quantitatively in space. In the content of nitrogen compounds, there is a seasonal dynamics: in the autumn, they contain a minimum amount in the water, since nitrates are assimilated by aquatic plants. Nitrogen forms in water are interconnected with physical and chemical parameters in different seasons of the year, with the processes of nitrification and denitrification that occur in rivers [13].

The high content of total phosphorus in the river water was noted in the spring. Phosphates were of pyrogenic origin, since every year grass is burned in floodplains and on agricultural land, and fires occur. Phosphates in bodies of water fall as a result of agricultural activities, because phosphorus is included in fertilizers. In such conditions, affecting the eutrophication of the reservoir, the process of cyanobacteria flowering occurs. Many types of blue-green algae are very toxic and have a harmful effect on human health. Excess phosphorus in the catchment area of the river is carried with the current and is the cause of a serious global water quality problem - eutrophication of the reservoir [14]. A high concentration of total phosphorus indicates hypertrophy of argusi. In the autumn after the flood, the phosphate content in the river was minimal (table 3).

The content of cadmium in the river water during the research period did not exceed the norm. In the spring of 2015, the lead content in the lower reaches of the river reached 6.36 µg/dm^3, during the subsequent study period, the lead content in the Arguzikha water was less than the MPC. The contents of zinc and copper in the water of the river Arguzikha exceeded the fisheries standard. Maximum concentrations of heavy metals were observed in the lower reaches. The highest concentrations of heavy metals in water were observed in summer. Due to heavy rains and floods, heavy metals were washed out of the surface layers of the soil of agricultural fields and fell into the river. The high content of manganese and iron in the water is due to a natural factor. The formation of the chemical composition of

natural waters is influenced by soil, rocks, terrain features, climatic conditions, and flooding. The high iron content in the streams of the Amur basin is due to the presence of iron-containing minerals in the soils and rocks of taiga territories. The presence of ferromanganese films and nodules is clearly visible in wetlands. In autumn, the concentration of heavy metals throughout the river decreased (table 4).

Table 3. The content of nutrients in the water of the small river Arguzikha.

River	Ammonium nitrogen, $mgN-NH_4^+/dm^3$			Nitrate nitrogen, $mgN-NO_3^-/dm^3$			Total phosphorus, mg/dm^3		
	Spring	Summer	Autumn	Spring	Summer	Autumn	Spring	Summer	Autumn
I	0.40	2.34	0.36	3.45	0.46	0.06	0.337	0.133	0.007
II	0.22	1.67	0.07	4.78	0.48	0.06	0.439	0.028	0.026
III	0.13	1.61	0.06	4.01	0.49	0.06	0.476	0.048	0.004
IV	0.62	2.04	0.44	6.39	0.48	0.06	0.609	0.120	0.030

Table 4. The level of heavy metals in the water of the small river Arguzikha, $\mu g / dm^3$.

River	Pb	Cd	Cu	Zn	Fe	Mn
I	0.95±0.5	0.11±0.02	3.7±1.2	12.8±1.2	100±13.9	157±15
II	2.07±1.1	0.08±0.05	4.0±1.2	11.2±1.2	250±30.2	443±31
III IV	1.18±0.9 3.67±1.1	0.11±0.1 0.16±0.2	2.0±0.2 12.44± 1.2	9.3±1.0 18.83±2. 1	150±18.2 640±64	183±18 230±23
MPC$_{f-r}$	6	5	1	10	100	10
MPC$_{h.-d.c.-p}$	10	1	1000	1000	300	100

Note: MPC $_{f-r}$ is the maximum permissible concentration of fisheries, MPC $_{h.-d.c.-p}$ is the maximum allowable concentration of household and drinking and cultural purposes.

3.2 Heavy metal Content in the bottom sediments of the Arguzikha river

The final link in the cycle of technogenic elements in the landscape is the bottom sediments of reservoirs. Accumulation of pollutants in bottom sediments may cause secondary contamination of reservoirs. Therefore, the accumulation of heavy metals in bottom sediments is actively studied [15-17]. The level of heavy metals in the bottom sediments of the small river Arguzikha decreases in the series: Fe>Mn>Zn>Cu>Pb>Cd (Table 5). The level of cadmium, lead, copper and zinc in the bottom sediments of small rivers does not exceed background values. The background is the level of heavy metals in uncontaminated bottom sediments of lakes in Muravyovsky Park [18]. Low content of heavy metals was observed in the bottom sediments of the Arguzikha river in the summer of 2016.

Table 5. The level of heavy metals in bottom sediments of the small river Arguzikha, mg/kg.

River	Pb	Cd	Cu	Zn	Fe	Mn
Arguzikha	5.2±1.6	0.11±0.03	28.8±2.8	32.1±0.3	9090±270	184±55
Background values	6 -10	0.1 – 0.3	3-13	28 -78		125-900

3.3 The Content of heavy metals in macrophytes of the river Arguzikha

Water plants for birds are a habitat and shelter from predators. Birds use rdests, duckweed, seeds, rhizomes, and young shoots of macrophytes for food, so the accumulation of heavy metals in aquatic plants creates a risk of exposure to pollutants on birds. A very important task was to study the content of heavy metals in hydrophytes. *Nymphoides peltata* is a very decorative aquatic plant that takes root with a creeping underwater rhizome, included in the Red books of various regions of Russia. *Myriophyllum spicatum* is a hydrophyte submerged and floating in the water column. The content of heavy metals in macrophytes of the river Arguzikha decreases in a row: Fe>Mn>Pb>Zn>Cu>Cd (table 6). Macrophytes of the Arguzikha river contained a deficient concentration of copper (2-5 mg/kg), normally - cadmium and zinc. Toxic concentrations of lead (> 30 mg / kg) and manganese (> 300 mg/kg) were found in macrophytes of *Nymphoides peltata* and *Myriophyllum spicatum L.* (table 6). The toxic effect of lead on plants is associated with a violation of fundamental biochemical processes - photosynthesis, mitosis, growth. The most typical manifestation of the toxic effects of manganese is ferruginous chlorosis [4].

Table 6. The average level of heavy metals in aquatic plants of the small river Arguzikha, mg / kg.

Macrophyte	Pb	Cd	Cu	Zn	Fe	Mn
Nymphoides peltata (S.G.Gmel.) O.Kuntze	35.0±3.5	0.002	2.0±0.2	31.0±3	786±79	536±53
Eleocharis ussuriensis Zinserl.	12±1.2	0.001	8±0.8	9.0±0.9	380±4	140±14
Myriophyllum spicatum L.	30.5±3.2	0.006	2.5±0.5	29.3±1.1	658±66	422±42

K. Peng and colleagues (2008), studying the content of heavy metals in macrophytes *Potamogeton pectinatus* L. and *Potamogeton malaianus* Miq. rivers of a large industrial city in China under conditions of man-made pollution, found the following concentrations: CD 1.96±1.13 mg/kg and 1.85±1.3 mg/kg, respectively, Pb 32.1±12.2 mg/kg and 15.5±7.36 mg/kg, Mn 513±23.7 mg/kg and 819±23.1 mg/kg, Zn 71.9±15.1 mg/kg and 106±34.0 mg/kg, Cu 32.1±12.2 mg/kg and 32.1±12.2 mg/kg.kg [19]. In the macrophyte *Hydrilla verticillata* (L. fil.) Royle under conditions of agricultural pollution, the Pb content was 45.3±4.5 mg/kg, Zn 137±14 mg/kg, Cu 17±1.7 mg/kg, Mn 8050±805 mg/kg [3]. Submerged hydrophytes can accumulate heavy metals in large quantities. The content of Zn, Cu, Mn and Pb in macrophytes depends on the content of these elements in water and bottom sediments [3, 19].

3.4 Heavy metal Content in bird feathers

Birds are at the top of the food chain, widespread, long-lived, sensitive to changes in the environment, accumulate pollutants, so they are bioindicators of environmental pollution. The accumulation of pesticides and organic pollutants in birds is actively studied [20-22]. The content of heavy metals is studied in various organs and tissues of birds - in the blood, liver and muscles, and bones of birds [21, 23]. A non-invasive way to obtain information is to detect heavy metals in eggshells and bird feathers [24, 25]. There are recommendations for use in monitoring the environment of Chicks and birds of the first year of life, especially if they are migratory birds [22]. However, adult birds can be used for environmental monitoring [21, 24]. Researchers pay attention to the study of various types of birds. Birds

of prey are an important indicator of heavy metal pollution due to their high trophic level [25]. To monitor local environmental pollution, passerines are successfully used, since this is the most numerous order of birds. These birds differ significantly in appearance, lifestyle, habitat conditions, and methods of food production [8]. Current research works are studies on the determination of heavy metals in the habitat of birds of wetlands that are threatened with extinction [24, 26, 27], waterfowl [28].

Heavy metals accumulate during feather growth and contact with the environment. For some chemicals, concentrations measured in feathers may differ significantly from concentrations in tissues and organs. There are differences between concentrations in different types of feathers and internal tissues of birds for different classes of pollutants [25]. Different types of contour feathers differed greatly in their content of heavy metals, in particular lead. Downy feathers have been studied as an alternative biomonitoring [29]. You can collect feathers during molting, but the issue of external contamination is of great concern. Feathers do not always reflect the actual concentrations of pollutants in the bird's body, but can be used to record man-made loads in the bird's habitat. The content of heavy metals in bird feathers often indicates exogenous contamination [30]. The microelement composition of plumage depends on the place of permanent or temporary residence of birds. By the content of heavy metals in the plumage of birds, you can determine the nesting or wintering place of an individual. The bird's feather contacts the circulatory system during growth. In this case, to determine endogenous contamination, the feathers must be thoroughly washed before the study and special training should be carried out. Feathers should be stored in conditions that are protected from potential sources of contamination and degradation (light, moisture) before research [31].

Table 7. Heavy metal concentration in bird feathers, mg/kg.

Name	Pb	Cd	Zn	Cu	Fe	Mn	Co	Ni	Cr
Northern Pintail *Anas acuta* (Linnaeus, 1758)	17.7±0.2	0.15	60.2±6.0	26.3±3.4	80.1±36.0	4.9±2.2	0.29±0.1	2.7±0.4	3.1±0.4
Garganey *Anas querquedula* (Linnaeus, 1758)	22.2±0.1	0.08	61.6±6.7	32.6±2.4	87±35.2	12.2±1.7	0.3±0.08	3.3±0.3	4.3±0.4

The feathers of the Northern Pintail Anas acuta and Garganey Anas querquedula waterfowl of the Argusikha river contained iron, copper and zinc in the largest quantities, and cobalt and cadmium in the smallest. The content of heavy metals in the feathers of birds decreased in a row Fe>Zn>Cu>Pb>Mn>Cr>Ni>Co>Cd. The ratio of elements that has developed during the evolution of the biosphere is due to the biological role of elements and geochemical conditions of the environment. High lead content was found in waterfowl feathers (table 7). The presence of heavy metals in the feathers of birds inhabiting the river reservoir Arguzikha, testified about exogenous contamination.

4 Conclusions

The river water Arguzikha are characterized by high oxygen saturation. High oxygen content and high BPC5 values in the middle and lower reaches of the Arguzikha river indicate the process of eutrophication. In spring and summer, high values of permanganate

oxidability (PO) were observed, which characterizes the high content of organic substances in water. In the fall, after severe summer floods, the PO value along the entire length of the river decreased. The high content of phosphates and nitrates found in spring samples had pyrogenic origin. In summer, the river water contained the largest amount of ammonium nitrogen, which was introduced into the river from the surface layers of soil during rains. The lowest concentrations of nitrogen and phosphorus compounds were after the flood in autumn.

The content of cadmium in the water of the Arguzikha river did not exceed the standard. In the spring of 2015, the lead content in the lower reaches of the river reached 6.36 µg/dm^3, during the subsequent study period, the lead content in the Arguzikha water was less than the MPC. Macrophytes contained high concentrations of lead and manganese. In the feathers of waterfowl the content of heavy metals decreased in a row: Fe>Zn>Cu>Pb>Mn>Cr>Ni>Co>Cd. The elements found in bird feathers were of external origin. The results obtained in a small river Arguzikha is an important step for the study of anthropogenic load on small rivers Zeya-Bureya plain. They are necessary for developing solutions for environmental protection and efficient land use, and the use of environmentally friendly technologies in agriculture.

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