Evaluation of metal content in perch of the Ob River basin

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Abstract. The geochemical features of river perch in the River Ob basin have been studied (the upper and middle reaches of the Ob River and the lower reach of the Tom River). The contents of Ag, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sn, W, Zn, Hg in perch's soft tissue are defined by the methods of ICP AES and stripping voltammetry, that of mercury in bones – by the atomic absorption method using mercury analyzer PA-915+. The distribution series of metal absolute concentrations in perch's soft tissue from the Ob River basin are plotted: Fe > Zn > Cu > Mn, typical for uncontaminated or slightly metal contaminated water bodies. In soft tissue of the studied samples the metal content does not exceed the permissible values. The mercury content in bones of studied samples is in the range 0,036-0,556 mg/kg. The mercury concentration is higher in bones in comparison with soft tissue in all samples.

1. Introduction

Interest in the content of the chemical elements in fish of Ob basin is related to the anthropogenic impact on natural water bodies that disturbs the natural cycle of chemical substances in the biosphere, and to the direct impact of those chemicals on human health.

The information on composition and amount of the metals can be found in the research of the fish (e.g. perch) muscle and bones chemical composition. Fish take the upper trophic level in aquatic ecosystems biocenosis and have a pronounced ability to accumulate elements [1]. Elevated levels of metals in fish indicate their significant concentration in the aquatic medium.

The average metal content in perch soft tissue of the Upper Ob River according to [2] was respectively: Cu – 0.94; Mn – 2.24; Fe – 61.87; Zn – 9.29; Pb – 0.28; Cd – 0.12; Hg – 0.015 mg/kg. According to the data of 1990, 1991, and 2000, the changes in the element content in the River Tom ranged in the following way: Cu – 0.73- 0.2; Zn – 8.5-14; Pb – 0.08-3.92; Cd – 0.01-0.23; Hg – 0.11-0.76 mg/kg [3]. In 2000, in contrast to 1990-1991, in the samples of fish soft tissue from the Tom River the contents of metals (Co, Ni, Cu, Cd, Hg and Pb) were considerably less, which is likely to be a consequence of decreasing the concentrations of these metals in abiotic river ecosystem components within this period.

Thus, there is an objective need for systematic data analysis on the same metals in the same time period in the lower reaches of the Tom River and the upper and middle reaches of the Ob River, where there are densely populated settlements of the Tomsk region.

The purpose of the work is as follows:

- To identify the geochemical characteristics of perch of the Ob River basin by examining its muscle and bone

- To estimate the quality of the river perch, as one of the staple food of the Ob River basin residents.

The stages of the work are: sampling the fish; sample preparation for atomic emission spectrometry ICP, voltammetry and atomic absorption analysis; determination of the elements contained in the bone and muscle tissue of the fish; data analysis.

For a number of reasons the river perch was chosen as an object of the analysis [2]: it accumulates the toxicants in much higher concentrations compared to those in the environment; its migration is of low intensity; it has large population; it has a relatively long life cycle; it can be of a relatively large size that makes possible to take enough quantity of samples; it is suitable enough for catching and sampling the organs and tissues; it is representative in terms of determining the degree of contamination according to the certain morphophysiological and environmental parameters.

2. Materials and methods

2.1. Study area, Sampling and preparation

The samples of perch were taken in June – July, 2014 in the upper and middle reaches of the Ob River and in the lower reach of the Tom River (figure 1). The point observation network was used during the sampling (15 points in total). The total mass of one sample was 500 to 700 grams, it included at least 7 to 10 fish. The muscle tissue was separated and crushed with a plastic tool. The bone tissue was taken out of the fish and subjected to drying and grinding.

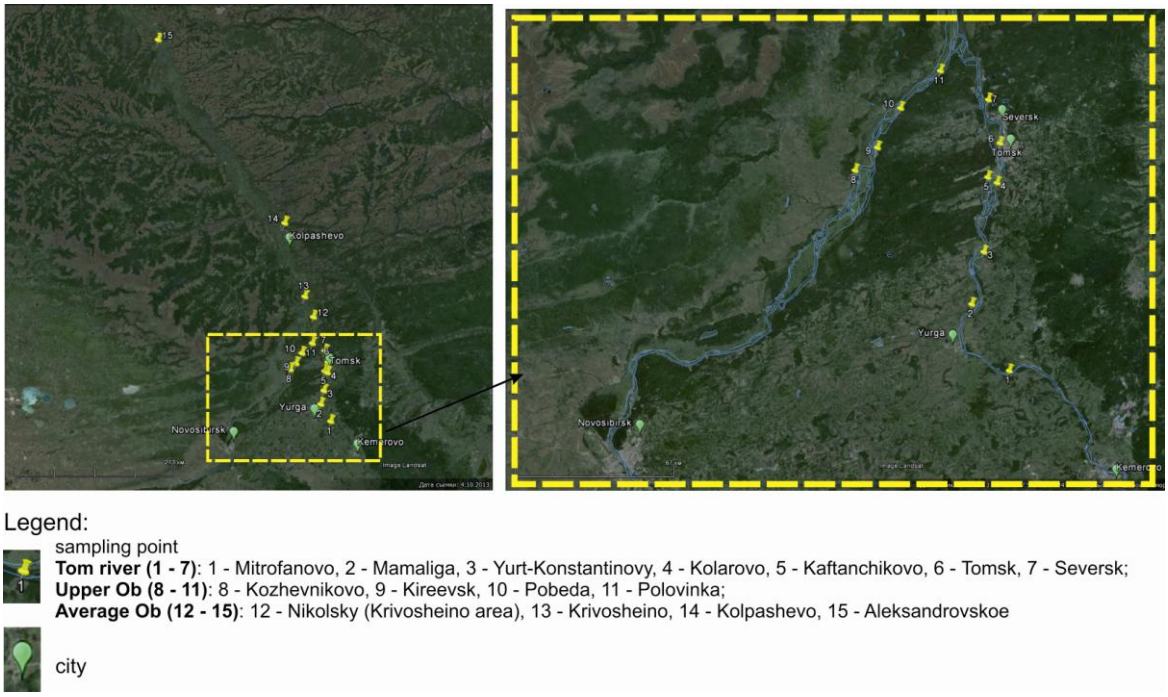

Figure 1. Scheme of perch sampling point.

2.2. Analysis

The quantitative analysis of muscle tissue samples for the content of Ag, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sn, W, Zn was performed by atomic emission spectrometry with inductively coupled plasma «iCAP 6300 Duo» (ThermoScientific Company), with sensitivity being 10^{-8}-10^{-9} per cent and with accuracy results up to 20 to 50 per cent depending on the element detected. The content of Hg, As, I, Se, Zn, Cd, Pb, and Cu in the perch muscles was determined by stripping voltammetry method. There is satisfactory convergence of these methods.

The content of Hg in the perch bone tissue was examined by the absorption method using the mercury analyzer RA-915+ equipped with the auxiliary device PYRO-915.

3. Results and discussion

The elements content analysis of the fish species muscle tissue revealed the following: most of the metals concentrations (Ag, Bi, Cd, Co, Cr, Mo, Ni, Sn, W) is lower than the sensitivity of the procedures being used, the average content of Cu, Fe, Mn, Zn, Se, I, As, Pb, and Hg in perch muscle does not exceed the permissible values for food products [4].

The content of iron (Fe) in the perch muscle tissue ranges from 6.44 to 24.2 mg/kg, the maximum concentration of the element was detected in the samples 1 and 14 (figure 2). It is impossible to draw a definitive conclusion about the causes and sources of elevated concentrations of Fe in the above mentioned sites of the Ob River basin without carrying out some additional research.

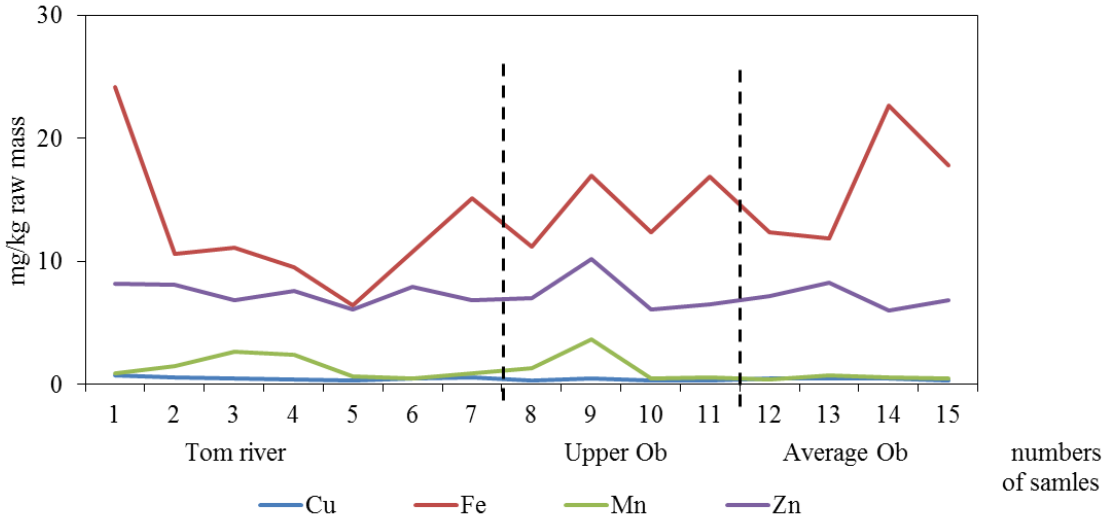

Figure 2. The content of metals in muscle tissue of perch caught in the Ob River basin, according to the results obtained by ICP AES.

In terms of decrease in metal absolute concentration in the perch muscle tissue the distribution series are built (figure 3). The first series corresponds to the fish tissue samples No. 1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 13, 14, and 15. For samples number 6 and 12, the second series of element distribution is typical.

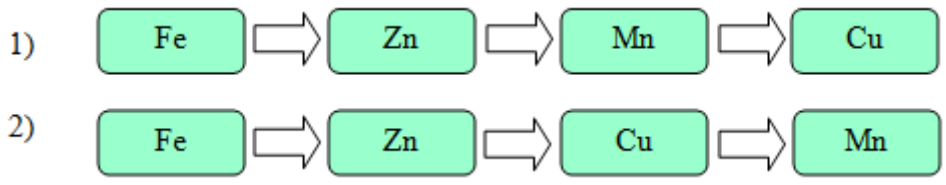

Figure 3. Series of metal absolute concentration in the perch muscle tissue, the Ob River basin.

In general, in all the investigated samples of muscle tissue, iron (Fe) and zinc (Zn) were predominant. This confirms the available literature data on high concentrations of these elements in fish, and significant accumulation coefficients compared to those of other metals. This fact is

explained by the intensive accumulation of microelements (Fe, Zn) in the organism, actively involved in a number of physiological processes (breath, blood formation, deposition, excretion, etc.).

The important fact is that the resultant distribution series correspond to the fish caught in uncontaminated or slightly metal contaminated waters [3]. In such species of ichtyofauna the content of Fe, Zn, Co, and Mn are predominant, zinc in almost all samples being an absolute leader after iron. Cu and Mn can interchange with each other. Co, Ni, Cd, Hg, are, as a rule, in the right side of the series, Hg and Cd being the rightmost.

In the samples of perch muscle tissue taken in the Tom River in, Pb follows Zn, thus reflecting its high accumulation in fish (table 1) [3]. However, the research of 1991 showed that copper follows zinc, not lead.

Table 1. Metal Content Ranking in Muscle of Perch in the Tom River.

Year	Ranked sequences
1990	Zn>Pb>Mn>Hg>Cu>Cd>Ni
1991	Zn>Cu>Mn>Pb>Co>Ni>Cd>Hg

One of the most harmful elements polluting the biosphere, possessing the highest toxicity index rate among heavy metals is mercury (Hg), due to its ability to block the protein molecules, break down their biosynthesis, cause mutagenic changes in DNA [5]. No positive effect of mercury on living organisms is established.

The analysis revealed that the content of mercury in the samples studied is in the range 0.036 to 0.556 mg/kg, the content of the element in all the test samples being higher in bone tissue in comparison with that in muscle tissue, which can be explained by the property of mercury to accumulate toxic elements (figure 4). Many researchers revealed similar trend of toxic elements accumulation in bones of living organisms [6-7].

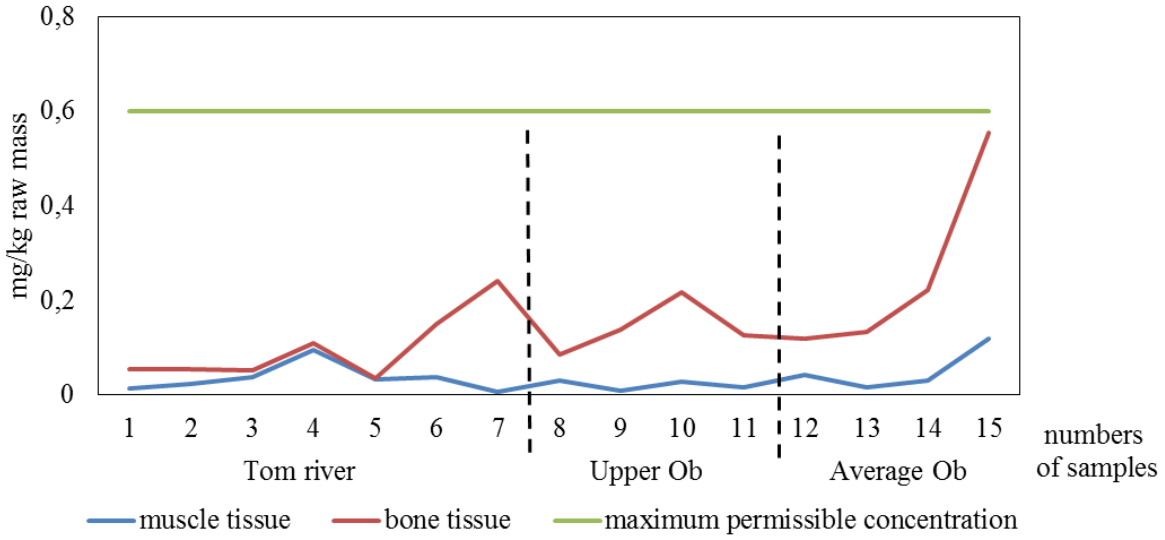

Figure 4. Comparison of mercury content in muscle and bone of perch of the Ob basin.
Note: Muscle tissue was investigated by stripping voltammetry, bone tissue was investigated by atomic absorption method.

In addition, the results of the study carried out has shown that the mercury levels in samples of the river fish of the Ob River basin do not exceed the maximum permissible concentration, except for the area of intensive oil production - 0.556 mg/kg, wet weight. This fact is not an unambiguous evidence

of anthropogenic factor influence, but we cannot exclude that the extraction and the use of oil and gas make a substantial contribution to mercury emission into the environment [7].

Mercury can pollute the atmosphere when gas is burnt in flares, and then, can settle on the water surface with precipitation. Fish, involved in the upper trophic level of the hydroecosystem, actively accumulate various elements, including mercury from the water surface.

4. Conclusion

As a result of the study, the following conclusions are made: in muscle tissue of perch of the Ob River basin the content of the following elements can be established: Cu, Fe, Mn, Zn, the maximum permissible concentration not being exceeded. The obtained distribution series of metals in perch muscle tissue correspond to the fish from uncontaminated or slightly metal contaminated waters. As compared to the mercury content in the soft tissue, it is higher in the bone tissue of the river perch. The maximum permissible concentration is not exceeded. All the studied samples of perch of the Ob River basin do not pose any hazard to the human health as a consumer of fish.

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