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Dynamics of microelements (B, Al) in the water samples from the Prut river during the 2020 year

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Abstract
The purpose of this research was to study the dynamics of microelement content, the correlation between the main forms of migration of microelements (B, Al) - dissolved and suspended forms, except colloidal, and to study their seasonal variation. The main form of migration of the metalloid B in the waters of the Prut river is the dissolved one, while the migration form of Al is the suspensions. In this research, the content of the mentioned microelements was investigated in the water samples collected from the Prut River in 2020 (winter, spring, summer, and autumn) from 7 collection points. The microelements were determined using atomic absorption spectrophotometry (Perkin-Elmer AAnalist 400 atomic absorption spectrophotometer). The importance of determining trace elements in natural waters is determined by a number of issues, including the need to monitor the environment and assess environmental risks and assess their influence on living systems. The results of studying these forms of migration (dissolved and suspended) allow us a fuller understanding of their role in the migration of microelements in aquatic ecosystems in the system "water-suspensions-underwater deposits-hydrobionts".
Keywords: water, microelements, migration, Prut river.

1. INTRODUCTION

Water - the most universal and important medium of migration of chemical elements in the earth's crust [1].

Research on the migration of trace elements is of considerable interest for hydrobiology, ecology, and hydrochemistry. The study and understanding of the migration processes of chemical elements are of imperative importance for the development of the theory on the functioning of freshwater ecosystems [2]. Penetrating into surface waters, trace elements play an important role as biocatalysts that prevent or stimulate life processes. [3].

Some of the main factors that determine the distribution and migration of trace elements in the "water-suspension" system, including sediments (not found in this study) are: relief dismemberment, amount of precipitation, physicochemical characteristics of rocks, soil and water, as well as the hydrology and status of the aquatic fauna and the chemical characteristics of the microelements themselves. Of major importance are also human activities, such as hydrotechnical constructions, chemicalization, and irrigation of agricultural land and wastewater disposal. [4].

The migration capacity of microelements in surface waters and their forms of migration are conditioned by endogenous factors - the properties of the elements themselves, and by exogenous factors - the physico-chemical particularities of the environment, redox conditions, pH size, temperature, the presence of complexing agents, suspended substances, the vital activity of hydrobionts and others [3].

The dynamics of the ratio of soluble and suspended forms in the migration of microelements is conditioned by several factors: the size of water pH, water mineralization, quantity and composition of organic substances and suspended substances, hydrological regime of rivers, and the vital activity of hydrobionts. The correlation between suspended and dissolved forms of migration of microelements in river waters is important in assessing their influence on living systems and has great significance in hydrogeochemical research, characterizing the denudation processes in river basins [3].

In the last years, a lot of ecotoxicological research has appeared aimed at assessing the anthropogenic impact on the dynamics of microelement content in rivers [2], which is increasing year by year and leads to irreversible changes in the aquatic environment. Human economic activity also makes significant adjustments to the distribution and migration of trace elements in aquatic ecosystems. For example, the construction of accumulation lakes on rivers significantly changes the ratio of suspended and dissolved forms of migration both downstream and in its regulated part, and in connection with the decrease in water flow rate, sedimentation processes of suspended substances increase [3].

Numerous studies on the effect of metals and other chemical elements on aquatic organisms indicate that the boundaries between beneficial and harmful effects are in a narrow range of concentrations, and optimal concentrations for some organisms may be toxic or insufficient for others [5].

Metal Al as well as metalloid B, along with other microelements have a significant biochemical role in the functioning of aquatic ecosystems, their action on living systems is often similar to that of catalysts in chemical reactions [6].

2. EXPERIMENTAL

Water samples and suspensions were collected seasonally: winter, spring, summer, autumn, including during the flood (June) in the Prut river on the territory of the Republic of Moldova and Lake Costesti-Stinca (lower sector) in 2020 from 7 collection points (Fig. 1.).

Fig. 1. The river Prut sampling sites: Criva, Costesti-Stinca, Braniste, Leuseni, Cahul, Cislita-Prut, Giurgiulesti.

Water samples were filtered directly into the field through 0.45 micron pore diameter membrane filters using the Sartorius filtration system. Thermo Scientific iCAP 6000 inductively coupled plasma optical emission spectrometer (ICP-OES) was used to analyze the content of B and Al in dissolved and suspension forms [7].

Field sampling and chemical laboratory analysis were performed according to hydrochemical methods [8].

3. RESULTS AND DISCUSSION

Boron. Boron enters the water both naturally and in anthropogenic ways. Anthropogenic activity is the basic factor of pollution of the Prut river with B. The main source would be the use of B as a fertilizer in agriculture [9] [10], being one of the essential nutrients for plants [11]. Other important sources of B pollution are the glass and glass products, ceramics, and metallurgy industries.

The chemical forms of B in water are primarily influenced by adsorption-desorption reactions and depend on the pH and concentration of B in the solution. In natural waters, B exists as undissociated boric acid and borate anion, which are both stable and highly soluble. At acidic and neutral pH, B exists in solutions in the form of undissociated boric acid, while at an alkaline pH, it is present as borate ions [12].

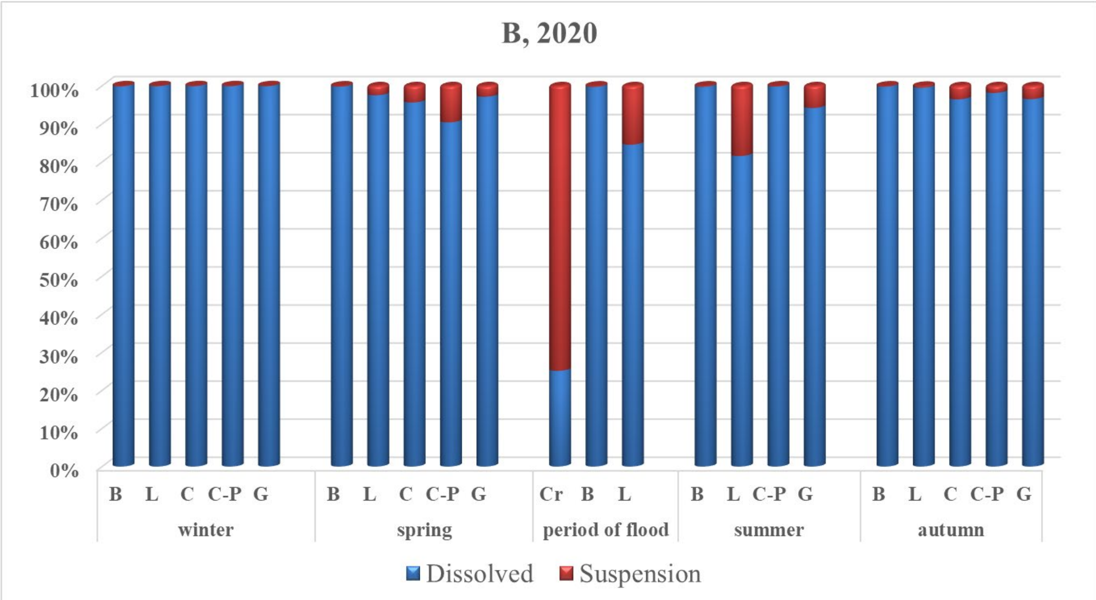

Fig. 2. The Boron ratio between dissolved and suspensions forms in Prut waters on seasons (Cr – Criva, B – Braniste, L – Leuseni, C – Cahul, C-P – Cislita-Prut, G – Giurgiulesti), 2020 year.

The main form of migration of B throughout the year in the Prut river was the dissolved one (Fig. 2). And it represents in most points over 90% of the total concentration of B in water. Only at the point of Criva during floods does B predominate in suspensions.

The limits of variation of the B concentration during 2020 were: in water - from 30.1 µg/l to 147.5 µg/l, in suspensions from 0.1 µg/l to 89.6 µg/l. The highest concentrations in dissolved form were determined in winter at the collection points Leuseni, Cahul, Cislita-Prut, and Giurgiulesti, and the lowest concentrations in summer during the floods at Criva, Braniste, and Leuseni. For suspensions, the highest concentration was determined at Criva during the floods, and the lowest concentrations were detected at all collection points in winter, and at Braniste point throughout the year (Fig. 3).

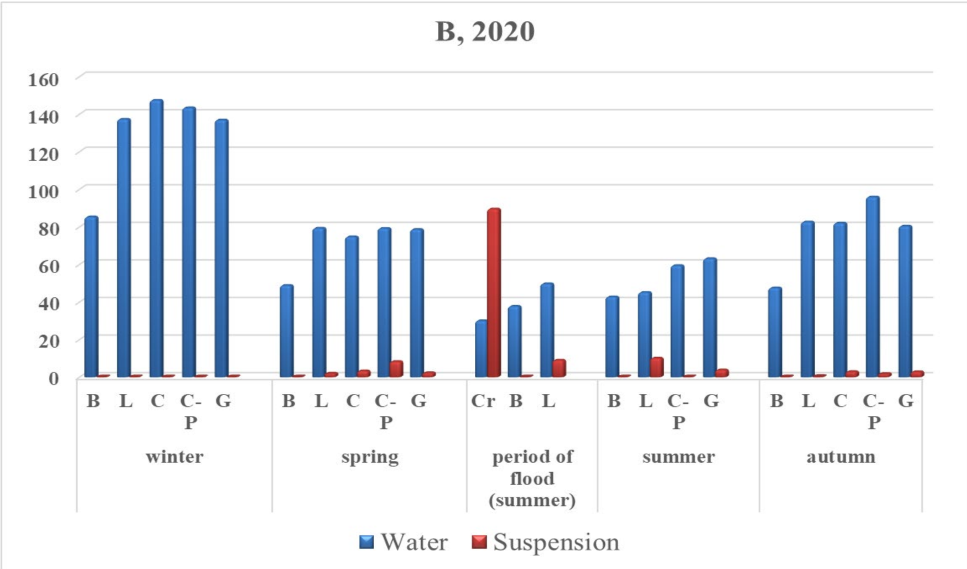

Fig. 3. Boron concentration dynamics in Prut waters mg/l on the seasons (Cr – Criva, B – Braniste, L – Leuseni, C – Cahul, C-P – Cislita-Prut, G – Giurgiulesti), 2020 year.

According to the drinking water quality requirements of the Republic of Moldova, the total concentrations of B are below the CMA limit of 1 mg/l [13].

Aluminium. Aluminium can enter surface water in both anthropogenic and natural ways. The natural factors have a major influence on the concentrations of Al in the waters of the Prut river. The European Union and the World Health Organization have set a limit on the concentration of Al in water of 200 μg/l, with a recommended concentration of 50 μg/l [14]. According to the requirements of drinking water quality in the Republic of Moldova for Al CMA is 200 μg/l [13].

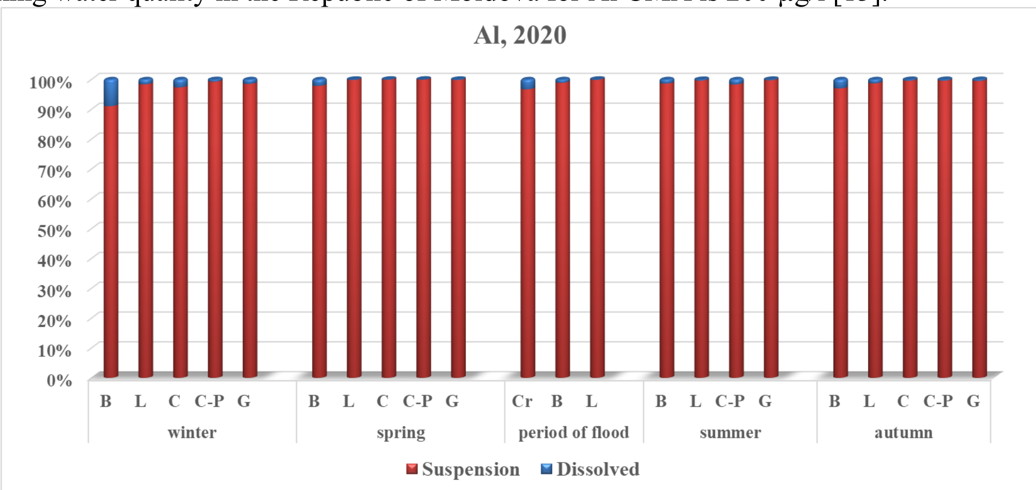

Fig. 4. The Aluminium ratio between dissolved and suspensions forms in Prut waters on seasons (Cr – Criva, B – Braniste, L – Leuseni, C – Cahul, C-P – Cislita-Prut, G – Giurgiulesti), 2020 year.

Al dissolved in rivers with neutral pH is found in low concentrations, between 1-50 μg/l, characteristic of the Prut River. At acidic pH, Al dissolved concentrations can increase considerably. During 2020, Al dissolved concentrations in the waters of the Prut river ranged from 2.1 to 13.2 μg/l, the lower limit being determined at the Braniste collection point, in spring, and the upper limit was determined at Criva during the floods (Fig. 4).

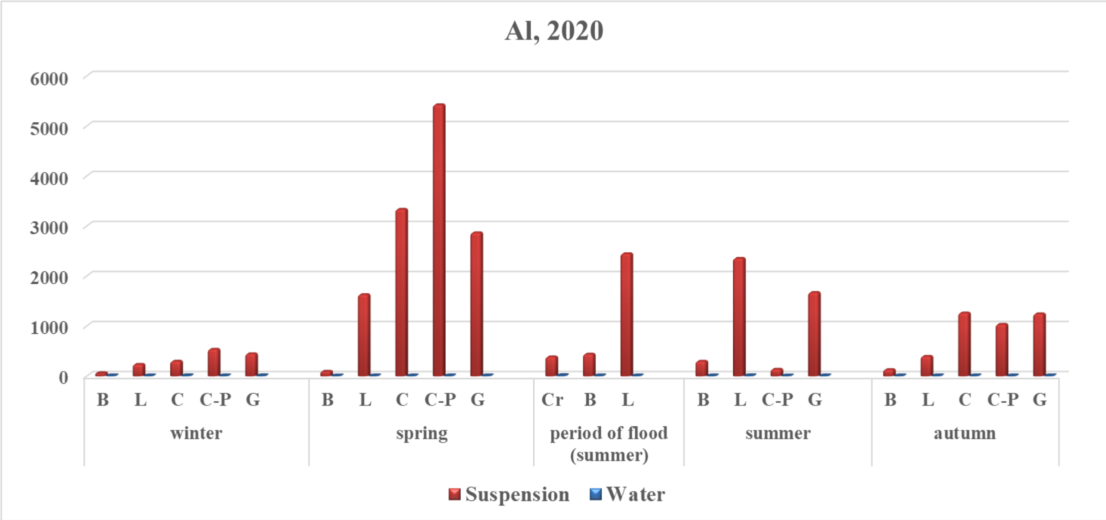

Fig. 5. Aluminium concentration dynamics in Prut waters mg/l on the seasons (Cr – Criva, B – Braniste, L – Leuseni, C – Cahul, C-P – Cîslita-Prut, G – Giurgiulesti), 2020 year.

In the Prut river as in most surface waters [15], Al migrates in the form of suspensions. There is also a direct link between the amount of mineral suspensions in the water and the amount of Al in the suspension. As the amount of mineral suspensions increases, the concentration of Al in the suspension increases. The limits of variation of the Al concentration in suspension were between 62.1 - 5428 µg/l. The highest concentrations were determined in spring and the lowest in winter (Fig. 5).

The high concentrations of Al are also due to the fact that it is the most abundant metal in the Earth's crust. Even though it is a common metal, Al is considered a toxic element. [16] The Al content of the suspensions reduces its chemical and biological activity, due to the fact that with the deposition of the suspensions there is a self-purification of the water and a decrease in its toxicity. However, it should be noted that suspended Al can negatively influence the vital activity of fish.

The toxicity of Al in water depends on pH. At neutral pH, Al is insoluble, a fact characteristic of the Prut river. Al toxicity is limited by the extremities of pH. The highest toxicity is attested at acidic pH. At basic pH, toxic effects may also occur. However, some studies show that exposure of fish to Al at pH 8.7 can ameliorate the toxic effects of high pH, compared to exposure to the same pH, but in the absence of Al [16].

4. CONCLUSIONS

1. Boron concentrations in the waters of the Prut river are within the CMA limits established for drinking water in the Republic of Moldova. Al concentrations in the Prut river exceed the CMA in most collection points except Braniste point, where the concentrations are in the CMA limits.
2. The main forms of migration for the studied microelements in the waters of the Prut river in 2020 were: Al - in suspension, B - in dissolved form.
3. The seasonal dynamics of the studied microelement concentrations were diverse. The highest concentrations of Al were determined in spring and the lowest in winter. B concentrations in winter were highest and in summer lower.

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