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# The content, dynamics and migration of As in the Prut River during the 2020-2023 years

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**Abstract**
Arsenic is an immunotoxic element that can be found in living organisms, being a part of many important biochemical processes. It interacts with different groups of proteins, lipids and, in increased quantities, affects oxidative processes. As a toxic element, arsenic concentrations are limited in drinking water and food products by Community Directives and national regulations. From2020 to2023, we investigated the dynamics of this element in the water and suspended matter from the Prut River ecosystems within the Republic of Moldova. The sources of pollution with arsenic compounds are various pesticides, herbicides, metallurgical enterprises and power plants that use fossil coal and fuel oil. The pollution with pharmaceutical preparations that contain arsenic compounds should also be mentioned. Arsenic compounds enter the body of animals and humans in increased quantities primarily through polluted air, especially in industrial areas near thermal power plants and facilities such as metallurgical, military, chemical and pharmaceutical plants, as well as through drinking and mineral water, grapes, fruits, seafood (fish, snails, algae), medicines, pesticides and herbicides. The risk of arsenic accumulation is also increased in tobacco smokers.

**Keywords:** arsenic, Prut, river, migration, water.

## 1. INTRODUCTION

Typically, in natural waters, the content of As is found in very low concentrations, being within the limits of 1–10 µg/L [2, 3], which aligns with the As values for drinking water indicated by the WHO (10 µg/L ) [3], the characteristic values also observed in the Prut River. Both natural and anthropogenic factors are responsible for the arsenic pollution of aquatic ecosystems . Cases are known when in regions with geothermal activity, where thermal waters with high concentrations of arsenic reach the surface, lead to surface water pollution. Such regions include Yellowstone National Park in the USA and the Taupo volcanic geothermal area in New Zealand [5]. As a result of human activity, arsenic can reach aquatic ecosystems from metallurgical enterprises, paint, pigment, ceramic manufacturing, thermal power plants coal and fuel oil using. A very important source of pollution is agricultural activity. Until the '70s of the last century, about 80% of pesticides, insecticides and herbicides contained in their composition simple inorganic salts of arsenic [2]. Even today, in the case of heavy rains, considerable concentrations of arsenic can be transported from agricultural fields into aquatic ecosystems.

In aquatic ecosystems, As migrates both in suspension and in dissolved form [1], but predominantly in the latter, that's why most researches are directed to study them [2, 3]. It is well known that arsenic is a very toxic metalloid, especially its inorganic forms [5]. The main inorganic forms are represented by arsenate (As(V)) and arsenite (As(III)), with arsenite being tens of times more toxic than arsenate. Compared to organic forms, inorganic ones are 70-100 times more toxic [2]. The main forms of arsenic in water are $AsO_3$, $AsO_4$, and in aquatic ecosystems with a high sulfur content it can also exist in the form of $As_2S_3$, $HAs_2S_4$, $As_2S_4^{2-}$. In oxidizing conditions, $AsO_3^-$ and $AsO_4^-$ are present, and in reducing conditions-compounds of arsenic with sulfur [1]. Due to the low toxicity of organic compounds, many countries have not established maximum permissible limits in fish products [5]. Moreover, in studies it is mentioned [5] that fish with strong homeostasis can control the content of arsenic in the body, preventing the accumulation of this microelement in large quantities.

The status and transformation of As in aquatic ecosystems is mainly conditioned by the Eh and pH of the environment, but microorganisms also play an important role in the transformation of arsenic. For example, during the period of intense phytoplankton development, As(V) is rapidly reduced to As(III) and methylated forms [2]. Additionally, some studies in Bangladesh [6] demonstrate that in the presence of oxidants, the mobilization of arsenic compounds from sediments and their penetration into aquatic ecosystems can take place. Nitrates used as fertilizers in agriculture can also be oxidizers.

Some authors [3] mention that there is a strong correlation between the content of As and Fe in the sediments.

## 2. EXPERIMENTAL

Water samples and suspensions were collected seasonally-winter, spring, summer, and autumn- from 7 sampling points along the Prut River on the territory of the Republic of Moldova between 2020 and 2023. (fig. 2.1).


*Fig. 2.1. The Prut River sampling sites: Criva, Braniște, Sculeni, Leuseni, Cahul, Caslita-Prut, Giurgiulesti.*

Directly in the field, the water samples were filtered through membrane filters with a pore size of 0,45 µm, to separate dissolved metals from solid suspensions, using the Sartorius filter system.

Under laboratory conditions, water samples were subjected to microwave acid digestion at elevated temperatures, and to pressure in hermetically sealed ultrapure PTFE vessels using SpeedWave four SW-4 (Berghof) (fig. 2.3.) for spectroscopic analysis. Hydrochloric and nitric acids, used in digestion, were purified using the distillacid “BSB-939-IR” apparatus (Berghof).

After digestion, the acid solutions were evaporated in ultrapure PFA vials in the HotBlock SC 151 unit (Environmental Express) (fig. 2.2.), then brought to volume with deionized water.


*Fig. 2.2. Digester for liquid samples, HotBlock SC 151 (Environmental Express).*

*Fig. 2.3. Microwave digester for solid and semi-liquid samples, SpeedWave four SW-4 (Berghof)*

Multi-element spectral measurements entailed reading the spectral emissions in both axial and radial modes using the Thermo Scientific iCAP 6200 Duo spectrometer (Thermo Fisher Scientific) (fig. 2.4.) [7]. Aerosol atomization was achieved with an inductively coupled plasma torch in a continuous argon flowat 5 bar pressure. Analyte signal intensity readings were correctedbased on the percentage recoveries of Sc (scandium) [9] as the internal standard . A solution containing approximately 10 mg(Sc)/l was used as an internal standard. Reference spectral lines of Sc (scandium) at 188.060, 227.318, 361.384 and 391.181 nm were used. Spectral lines (nm) 189.042 and 193.759 were used to identify arsenic.

*Fig. 2.4. Atomic emission spectrometer Thermo Scientific iCAP 6200 Duo*

The methods used for water sampling were based on water sampling regulations in accordance with the current legislation [8].

## 3. RESULTS AND DISCUSSION

During the years 2020-2023, the content of As in water oscillated between 0.3 – 4.93 µg/L. According to the information from previous investigations (2013-2014) [5], concentrations ranging between 0.2-2.4 µg/l were determined. In investigations carried out by Romanian colleagues during the years 2015-2019, average arsenic values of up to 2 µg/l were determined [7].

Average annual seasonal variations (fig. 3.1.) of As in years 2020, 2022 and 2023 were not pronounced. However, in the autumn of the year 2021, values were observed to be 3 times higher than those in spring and summer. A clear trend of increasing concentrations was observed across all seasons over the years.

Moreover, while average annual concentrations of 1.3-1.5 µg/l were detected in 2020-2021 - values consistent with those detected in previous investigations- a considerable increase in the average concentrations of arsenic in water was observed in the year 2022, and especially in the year 2023,reaching 4 µg/l. These concentrations practically exceed 3 times the average annual content of the years 2020-2021.

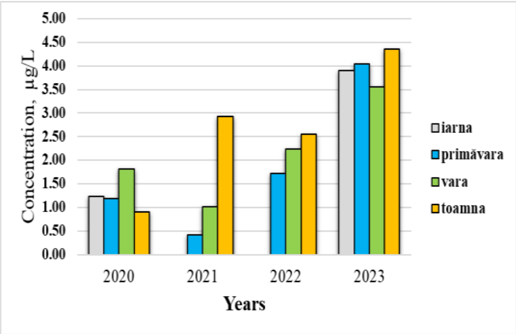


*Fig. 3.1. Multiannual average seasonal concentrations of As.*

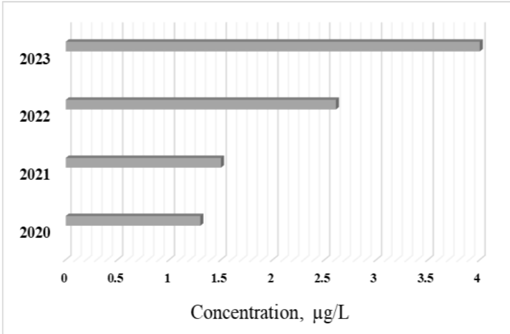


*Fig. 3.2. The dynamics of the average of annual concentrations of As.*

In all studied points (Braniste, Sculeni, Leuseni, Cahul, Caslita-Prut, Giurgiulesti) a clear tendency of increasing the average annual concentrations of As in water was observed, which is a worrying fact (fig. 3.3. – fig. 3.8).

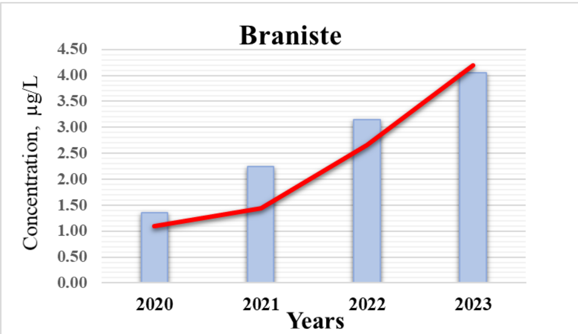


*Fig. 3.3. Multiannual average concentrations of As in Braniste.*

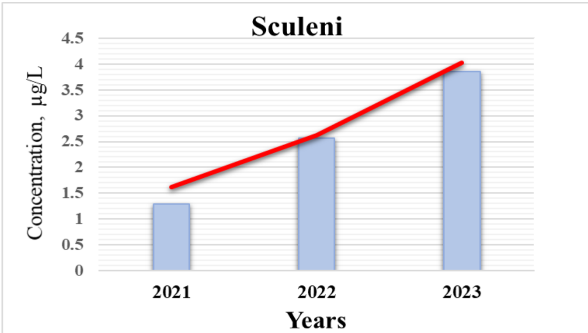


*Fig. 3.4. Multiannual average concentrations of As in Sculeni.*

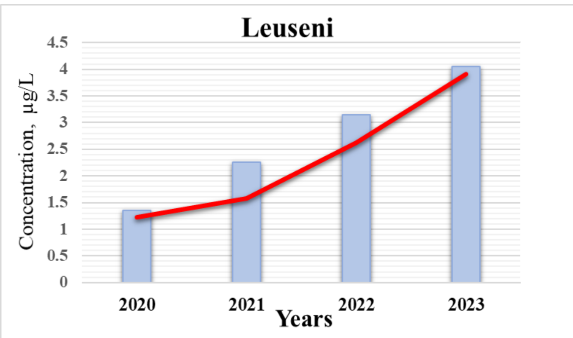


*Fig. 3.5. Multiannual average concentrations of As in Leuseni.*

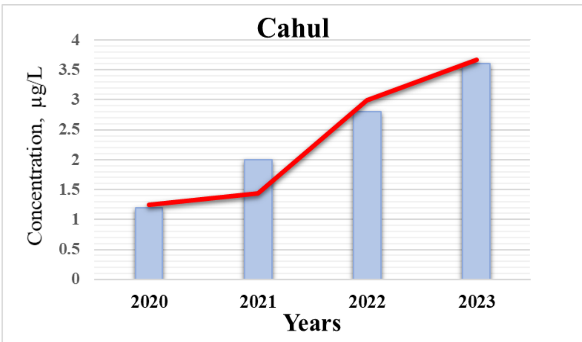


*Fig. 3.6. Multiannual average concentrations of As in Cahul.*

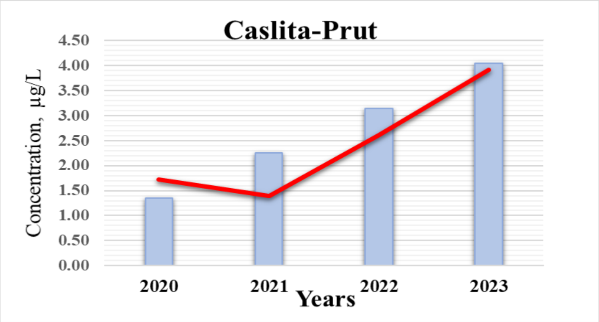


*Fig. 3.7. Multiannual average concentrations of As in Caslita-Prut.*

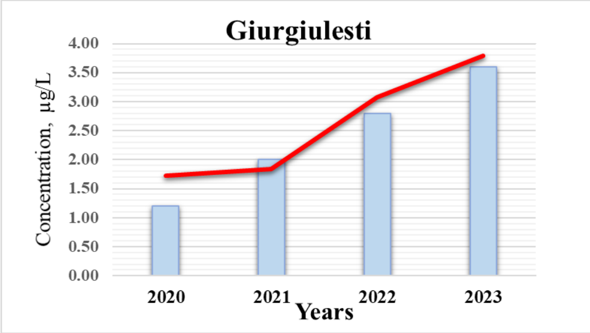


*Fig. 3.8. Multiannual average concentrations of As in Giurgiulesti.*

As mentioned previously, As migrates in natural waters mainly in dissolved form, characteristic to the Prut River (fig. 3.9.). About 70% of the total Arsenic concentration is found in dissolved state.

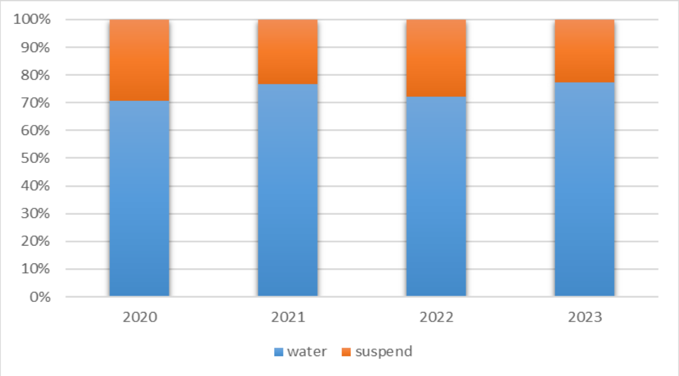


*Fig. 3.9. The ratio between dissolved and suspended forms of arsenic.*

Also, there is a strong correlation between As and Fe content in the sediments. The following correlation coefficients were determined for the studied years: $R_{2020}$ = 0,9303, $R_{2021}$ =0,9793, $R_{2022}$ =0,8349, $R_{2023}$ =0,9173.

## 4. CONCLUSIONS

1. Arsenic concentrations in water are below the drinking water limit of 10 µg/L.
2. During the year 2023, a considerable increase of about 3 times was observed in the average annual concentrations of As in water, compared to the years 2020-2021, which represents a reason for concern and increased attention for As, in the following period.
3. In the Prut River, during the studied period, As migrates primarily in dissolved form, representing about 70% of the total concentrations.
4. In general, the concentrations of arsenic did not present risks for aquatic organisms in the Prut River, but the narrow toxic limits indicate the need for continuous monitoring of this element in water.

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