

## DISTRIBUTION OF HEAVY METALS IN THE DANUBE RIVER ECOSYSTEM AND THE IMPACT ON THE ENVIRONMENT. A REVIEW

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### Abstract

*The Danube Basin collects water from nineteen countries and is exposed to significant amounts of pollutants. Heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), nickel (Ni), zinc (Zn), copper (Cu), aluminum (Al) are considered critical contaminants of aquatic ecosystems, given their high predilection to enter and accumulate in food chains. The primary sources of heavy metal pollution consist of discharges from agricultural waste, industrial and urban wastewater into the aquatic environment, as well as mining activities. Given their persistence in the environment, it is required to conduct studies on heavy metal concentrations to understand their implications for aquatic life and to assess biomagnification through food chains. For this purpose, various pollution indices are utilised to evaluate the chemical speciation of metals within the environmental system. Shortly, it is essential to prioritize the development of technologies that can facilitate the recovery of harmful heavy metals, while mitigating potential risks to the environment.*

**Key words:** bioaccumulation, Danube River, heavy metals.

### INTRODUCTION

The Danube River is one of the most essential in Europe, covering around 2.860 kilometres and crossing ten countries: Germany, Austria, Slovakia, Hungary, Croatia, Serbia, Romania, Bulgaria, Moldova, and Ukraine. It is an important river for the economy, transportation, drinking water, agriculture, and biodiversity (Popa et al., 2018).

The Danube Delta Biosphere Reserve (UNESCO protected area) forms at the mouth of the Danube into the Black Sea, making it one of the world's largest deltas and the second largest in Europe. It is also one of Europe's largest wetlands and a refuge for numerous bird, fish, and plant species. This area is ecologically, economically and geographically important, having a significant impact on the environment and economy of the riparian regions since it is an important place for fishing and tourism (Mindrescu et al., 2022).

The Danube has numerous important tributaries coming from different regions of Central,

Eastern and South-Eastern Europe, such as Inn, Morava, Drava, Sava, Tisa, Iskar, Olt, Siret, Prut and Velika Morava, which play an important role in supplying the river with water, but also with pollutants, significantly influencing water quality and disrupting the ecological equilibrium (Culicov et al., 2022). Sources of pollution with these metals can be natural or anthropogenic. The natural sources can include volcanic eruptions, weathering, wildfires, while anthropological sources can be mining, chemical and metallurgical industries, industrial waste discharges, agriculture (using pesticides and fertilizers), and through transportation or construction activities (Benhadji et al., 2025). Human activity in river basins and deltas causes pollutants to be released into the air, soil and water. The principal pollutants found in aquatic systems include volatile organic compounds, pharmaceutical compounds, plant nutrients, suspended solids, microbial pathogens, and parasites (Paul, 2017). Among these pollutants are also heavy metals (HMs), which are chemical elements with a high density that can

pose serious risks to both human health and the ecosystem, such as lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), nickel (Ni), zinc (Zn), copper (Cu), aluminium (Al) (Zaynab et al., 2022). Because of their widespread distribution, toxicity, persistence in the environment and capacity for bioaccumulation, heavy metals represent a critical contaminant of aquatic ecosystems (Jarić et al., 2011). In the past years, monitoring heavy metals in the aquatic environment has become a priority for authorities. The presence of heavy metals can be examined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Mikala Okouyi et al., 2024), inductively coupled plasma mass spectrometry (ICP-MS) (Calmuc et al., 2021), atomic absorption spectrometry (Lazarević et al. 2022), atomic fluorescence spectrometry (AFS), X-ray absorption spectroscopy (XAS) and X-ray fluorescence spectrometry (XRF) (He et al., 2024).

This study assesses the heavy metal concentration of the surface water, sediment, and biota of the Danube River, as well as the environmental impact.

## MATERIALS AND METHODS

### Sources of heavy metals

**Aluminum (Al)** is one of the most abundant metallic elements in the Earth's crust and occurs naturally only in the +3-oxidation state ( $Al^{3+}$ ), typically in combination with elements such as oxygen, silicon, and fluorine.  $Al^{3+}$  is a key component of various minerals, including mica, feldspars, and clays. Aluminum enters the environment through natural processes such as rock weathering and volcanic activity, as well as anthropogenic activities, including aluminum production, coal combustion, mining, waste incineration, motor vehicle emissions, fireworks, packaging, toothpaste, vaccines, antiperspirants, and certain pharmaceuticals such as buffered aspirin and antacids (Alasfar & Isaifan, n.d.; Briffa et al., 2020; Closset et al., 2022).

**Arsenic (As)** is a crystalline metalloid that occurs naturally in the environment. It originates from both natural processes - such as wildfires, pedogenesis, dust storms, volcanic and geothermal activity - and anthropogenic sources including electroplating, smelting, fossil fuel

combustion, production of glass, pharmaceuticals, insecticides, pesticides, fertilizers, electronics, mining, and wood preservation (Briffa et al., 2020; Byeon et al., 2021; Liu et al., 2022; Zhang et al., 2022; Wang et al., 2023; Sevak & Pushkar, 2024). In aquatic systems, the dominant and most toxic inorganic forms are arsenate ( $As^{5+}$ ) and arsenite ( $As^{3+}$ ) (Jeong et al., 2023).

**Cadmium (Cd)** is a highly toxic heavy metal found abundant in Earth's crust, usually in combination with ores of copper, zinc and lead. Natural cadmium emissions arise from rock weathering, volcanic eruptions, dust transport, marine aerosols, forest fires, and soil erosion (Khan et al., 2022; Jeong et al., 2023; Oladimeji et al., 2024). Anthropogenic sources include electroplating, metal coatings, mining, plastics stabilization, cement manufacturing, paint pigments, battery production, fossil fuel combustion, pesticide and fertilizer use, as well as incineration of municipal and sewage sludge (Briffa et al., 2020; Khan et al., 2022; Jeong et al., 2023; Oladimeji et al., 2024).

**Chromium (Cr)** particularly in the  $Cr^{+3}$  and  $Cr^{+6}$  oxidation states, is one of the most toxic heavy metals naturally present in water and soil due to geological processes like weathering. Anthropogenic contributions include metal processing, chromate production, leather tanning, stainless steel welding, electroplating, cement and pigment manufacturing, textile dyeing, mining, coal and oil combustion, fertilizer application, thermal power generation, and the paper industry (Briffa et al., 2020; He et al., 2020; Tumolo et al., 2020; Ayele & Godeto, 2021; Kolarova & Napiórkowski, 2021; Prasad et al., 2021; Jeong et al., 2023).

**Copper (Co)** is naturally present in the form of sulphide and oxide ores, salt minerals, and native copper deposits. It is released into the environment via volcanic activity, geological deposits, and the weathering and erosion of rocks and soils (Rehman et al., 2019). Copper contamination of water can occur through corrosion of pipes and plumbing fixtures (Alkhanjaf et al., 2024). Human-induced sources include mining, smelting, metal and electronics manufacturing, discharge of industrial wastewater, wood preservatives, antifouling paints, fossil fuel combustion, urban runoff, fertilizers, fungicides, and pesticides

(Rehman et al., 2019; Briffa et al., 2020; Izydorczyk et al., 2021; Jeong et al., 2023).

**Lead (Pb)** is a trace metal found naturally in reduced quantities in the environment, with unknown role in cells, but extremely toxic even at low concentrations, which can be bioaccumulated by aquatic organisms (Valová et al., 2010). It can be found in galena and can be generated by volcanic activities, weathering and erosion (Briffa et al., 2020; Jeong et al., 2023), but it is predominantly produced due to anthropogenic sources such as metal processing, battery production industry, lead-based paints, lead in gasoline, mining, smelting, automobiles production, metal plating, agricultural fertilizers, insecticides, pesticides, waste disposal (batteries and electronics), unsuitable industrial waste, ammunitions and projectiles, lead crystal glass, pipes, glass screens, cable covers (Briffa et al., 2020; Jeong et al., 2023; Raj & Das, 2023; Oladimeji et al., 2024).

**Mercury (Hg)** is a non-essential, persistent, and highly toxic metal that bioaccumulates and biomagnifies in aquatic ecosystems. Naturally, mercury is emitted from the Earth's crust, wildfires, erosion of mercury-containing rocks, volcanic activity, geothermal processes, weathering, and evaporation from surface water (Budnik & Casteleyn, 2019; de Almeida Rodrigues et al., 2019; Jeong et al., 2023; 2024). Anthropogenic sources include chlor-alkali and thermal power plants, manufacturing of batteries, thermometers, and fluorescent lamps, ore smelting, agriculture, fossil fuel combustion, sewage, industrial wastewater, and cultural practices such as fish-based diets (Budnik & Casteleyn, 2019; de Almeida Rodrigues et al., 2019; Briffa et al., 2020; Kolarova & Napiórkowski, 2021; Jeong et al., 2023; 2024). Mercury exists in elemental ( $Hg^0$ ), inorganic ( $Hg^+$ ,  $Hg^{2+}$ ), and organic forms (e.g., methylmercury –  $MeHg^+$ ) (Kumar et al., 2024; Tsui et al., 2025).

**Nickel (Ni)** is a potentially toxic element commonly present in soil and aquatic systems. Natural inputs include rock weathering, wildfires, and volcanic activity (Gauthier et al., 2021), while anthropogenic sources include alloy manufacturing, pigment production, tannery wastewater, fossil fuel combustion, stainless steel manufacturing, battery production, electroplating, automobile and

refinery emissions (Briffa et al., 2020; Wang et al., 2020; El-Naggar et al., 2021).

**Zinc (Zn)** is an abundant trace element in the Earth's crust, primarily found in sulphide minerals like sphalerite (Zn, Fe) S. Anthropogenic sources of zinc include metal processing, mining, municipal wastewater discharges, galvanization, smelting, electroplating, cosmetics, sunblock, deodorants, and vitamin supplements (Seto et al., 2013; Briffa et al., 2020; Jeong et al., 2023).

These pollutants mainly come from metallurgical, chemical, mining industries and urban wastewater, having a major impact on water quality and aquatic ecosystems (Simionov et al., 2021a). Identifying the sources of contamination is essential for developing effective monitoring, control and remediation strategies.

In **Austria**, the city of Linz serves as a major industrial centre where metallurgical and chemical processes are potential sources of contamination (Winkler et al., 2018). This is further compounded by the Inn River, which traverses Switzerland, Austria, and Germany, and receives industrial runoff from regions such as Bavaria, where lead (Pb), zinc (Zn), and copper (Cu) have been detected in elevated concentrations (Saeed et al., 2023). In **Slovakia**, the industrial area near the capital Bratislava includes oil refineries and chemical facilities that may release hazardous substances into nearby watercourses (Culicov et al., 2022), with additional input from the Morava River, which transports agro-industrial pollutants and legacy contaminants from former industrial facilities in Slovakia (Vesković et al., 2024). In **Hungary**, the accumulation of industrial residues from bauxite processing, particularly in the form of "red mud", poses a major environmental threat, owing to elevated concentrations of aluminium (Al), iron (Fe), and cadmium (Cd), with implications for both ecosystem integrity and public health (Winkler et al., 2018). The capital Budapest hosts active industrial and port areas, contributing to the metal load of the Danube, mainly through metallurgical and chemical activities (Culicov et al., 2022). The Drava River, which flows through Hungary as well as Italy, Austria, Slovenia, and Croatia, adds further contamination originating from mining, agriculture, and industry (Šorša et al., 2022). In

**Serbia**, heavy industrial activity along the Danube in Belgrade is a key source of contaminants, with metal processing facilities discharging trace elements such as lead and zinc directly into the river (Subotić et al., 2013). The Sava River, Serbia's most significant tributary, passes through major industrial cities like Zagreb and Belgrade, transporting both metallic and organic pollutants (Vuković et al., 2012; Jovanović et al., 2017). Further inland, the Velika Morava River carries industrial effluents from central Serbia's densely populated areas (Culicov et al., 2022). In **Romania**, the city of Galați, with one of the country's largest steel producers, is a major source of industrial emissions (Ioniță et al., 2014; Iticescu et al., 2014; Georgescu et al., 2023). Although industrial activity in Turnu Măgurele has diminished, the persistence of contaminants from former chemical plants continues to raise ecological concerns. Similarly, Drobeta-Turnu Severin presents industrial activities, such as shipyard operations, that may continue to influence water quality (Georgescu et al., 2023). The Tisza, flowing through five countries including Romania, has been affected by pollution by mining-related accidents in Maramureș that released cyanide and metal contaminants downstream (Kraft et al., 2006). The Olt River has been affected by longstanding pollution from the chemical and mining sectors around Râmnicu Vâlcea (Iordache et al., 2022), while the Siret and Prut Rivers are influenced by both agriculture and urban development across Ukraine, Moldova, and Romania (Calmuc et al., 2021; Burdenyuk et al., 2023; Georgescu et al., 2023). In **Bulgaria**, the industrial cities of Ruse and Vidin host chemical and metallurgical facilities whose discharges further burden the Danube's ecological balance (Culicov et al., 2022). Similarly, the Iskar River carries pollutants from industrial areas in Sofia and northern Bulgaria into the Danube (Angelova et al., 2020).

These tributaries highlight the complexity and scale of the challenges related to heavy metal pollution in the Danube basin.

### **Analytical Techniques for Heavy Metals Determination**

Several analytical techniques are available for detecting and quantifying heavy metals in

environmental samples, each with specific advantages and limitations depending on the matrix and target elements. ICP-OES and AAS are commonly used for water, sediment, and biota analysis, both providing detection limits around 0.1-10 ppb. ICP-OES enables simultaneous multi-element analysis, high throughput, and reduced matrix effects compared to AAS, though spectral interferences may occur in complex samples (Mikala Okouyi et al., 2024). AAS is a well-established method offering high precision for single-element determinations, though it is limited to sequential analysis and requires complete digestion of solid matrices (Lazarević et al., 2022). ICP-MS offers exceptional sensitivity (0.001-0.1 ppb), supporting ultra-trace analysis, wide dynamic range, and applications in isotopic and speciation studies, though it may be affected by polyatomic and isobaric interferences (Burada et al., 2015; Calmuc et al., 2021). AFS, with detection limits between 0.01 and 1 ppb, is highly sensitive for select elements such as Hg, As, and Se, offering good selectivity and low background noise, although its applicability is limited to a narrow range of elements and can be influenced by molecular and matrix interferences (Abdelmonem et al., 2025). For elemental speciation and oxidation state determination, XAS provides detailed structural information in solid, liquid, and biological samples. This non-destructive, element-specific technique requires advanced facilities and complex data interpretation (Hu et al., 2020). Lastly, XRF allows rapid, non-destructive analysis of solid matrices like sediments and dried biota, with detection limits of 1-10 ppm. While effective for screening and minimal sample preparation, it offers lower sensitivity for trace-level elements and is less suitable for light elements or complex organic matrices (Lu et al., 2023).

## **RESULTS AND DISCUSSIONS**

### **Status of heavy metal in Danube River water, sediments and biota**

Extensive studies have been carried out by several researchers on heavy metal pollution of river Danube (Table 1). A research group (Saeed et al., 2023) studied the concentrations of arsenic, chromium, copper, nickel, lead and zinc

in the water of the river Danube at Dunaföldvár, Baja and Hercegszántó (Hungary) between 2013 and 2019 and reported temporal and spatial variations in heavy metal distribution. Concentrations of Zn reached up to  $19.39 \mu\text{g}\cdot\text{L}^{-1}$ , Cu up to  $4.4 \mu\text{g}\cdot\text{L}^{-1}$ , and Ni exceeded  $3 \mu\text{g}\cdot\text{L}^{-1}$  in some sites. Other study presents (Popescu et al., 2022) the levels of As, Cd, Hg, Pb and Zn in several Romanian sites along the Danube during 2020. It was found that arsenic levels, though low ( $0.09\text{--}0.14 \mu\text{g}\cdot\text{L}^{-1}$ ), were present throughout all sampling stations, while Pb concentrations ranged from 0.21 to  $0.31 \mu\text{g}\cdot\text{L}^{-1}$  and Zn levels were notably high, up to  $21.1 \mu\text{g}\cdot\text{L}^{-1}$ . Simionov and his team (Simionov et al., 2021b) also conducted an important study on the

concentrations of As, Cd, Cu, Ni, Pb and Zn in surface waters collected from Galați and Tulcea. The highest recorded values were for Zn ( $57 \mu\text{g}\cdot\text{L}^{-1}$ ), Cu ( $6.7 \mu\text{g}\cdot\text{L}^{-1}$ ), and Ni ( $8.2 \mu\text{g}\cdot\text{L}^{-1}$ ) around Galați, while Pb reached up to  $3.1 \mu\text{g}\cdot\text{L}^{-1}$  and Cd  $0.14 \mu\text{g}\cdot\text{L}^{-1}$ . These values significantly exceeded those reported in upstream areas and reflect strong anthropogenic influence, likely related to industrial and urban discharge. A seasonal assessment was performed in Croatia (Redžović et al., 2023) at Medsave and Jarun, where Al, Cd, Cr, Cu, Ni, Pb and Zn were monitored in water samples. Aluminum levels reached  $3.94 \mu\text{g}\cdot\text{L}^{-1}$ , and Cd was found up to  $0.030 \mu\text{g}\cdot\text{L}^{-1}$ .

Table 1. Concentrations of heavy metals in water of the Danube River and adjacent areas

Sampling area/Country	Survey period	Heavy metals								References
		Al ( $\mu\text{g}\cdot\text{L}^{-1}$ )	As ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Cd ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Cr ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Cu ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Hg ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Ni ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Pb ( $\mu\text{g}\cdot\text{L}^{-1}$ )	
Dunaföldvár, Hungary	April - September (2013-2019)	-	1.21	-	1.45	4.29	-	2.55	1.22	16.45
Baja, Hungary		-	1.27	-	1.3	4.17	-	2.64	1.61	14.78
Hercegszántó, Hungary		-	1.34	-	1.42	4.4	-	2.64	1.42	17.66
Dunaföldvár, Hungary		-	1.35	-	1.8	3.48	-	3.1	1.14	12.93
Baja, Hungary		-	1.37	-	1.11	3.74	-	2.87	1.2	11.98
Hercegszántó, Hungary		-	1.20	-	1.49	4.11	-	2.86	1.45	14.38
Bazias, Romania	October - March (2013-2019)	-	1.31	-	1.44	4.03	-	2.27	1.14	16.8
Divici, Romania		-	1.30	-	1.07	3.33	-	2.41	0.93	14.35
Coronini, Romania		-	1.27	-	0.93	3.37	-	2.29	1.37	14.44
Liborajdea, Romania		-	1.45	-	1.01	3.71	-	2.71	1.03	16.25
Svinița, Romania		-	1.28	-	1.58	3.81	-	2.45	1.3	12.79
Dubova, Romania		-	1.46	-	1.42	3.62	-	2.3	1.12	16.13
Gura Văii, Romania		-	1.70	-	1.83	3.79	-	2.6	1.55	15.8
Drobeta - Turnu Severin, Romania		-	1.60	-	1.65	4.17	-	2.8	1.34	19.39
Tigănași, Romania		-	0.09	0.004	-	-	0.011	-	0.21	21.1
Galati, Romania		-	0.12	0.009	-	-	0.017	-	0.24	18.5
Tulcea, Romania	July-September 2020	-	0.12	0.008	-	-	0.012	-	0.28	20.1
Pietrei pond, Romania		-	0.14	0.012	-	-	0.014	-	0.21	18.5
Barcaz Lake, Romania		-	0.10	0.014	-	-	0.011	-	0.21	17.9
Soschi Lake, Romania		-	0.11	0.008	-	-	0.009	-	0.22	19.1
Black Sea Sf. Gheorghe, Romania		-	0.09	0.0011	-	-	0.010	-	0.22	19.7
Black Sea Perisor, Romania		-	0.11	0.042	-	-	0.009	-	0.22	19.4
Jarun, Croatia		-	0.14	0.088	-	-	0.015	-	0.31	18.1
Medsave, Croatia	April 2018	-	2.8	0.14	-	6.7	-	8.2	3.1	57
Tulcea, Romania		-	2.7	0.05	-	4.1	-	4.4	1.4	3
Pietrei pond, Romania		-	3.9	0.004	-	0.5	-	1.1	0.7	0.5
Barcaz Lake, Romania		-	1.7	0.02	-	2.6	-	2.9	0.8	5
Soschi Lake, Romania		-	2.4	0.01	-	1.1	-	1	0.5	8
Black Sea Sf. Gheorghe, Romania	Winter 2018	-	1	0.06	-	1.8	-	7	1	4
Black Sea Perisor, Romania		-	0.4	0.04	-	1.4	-	11	0.9	2
Medsave, Croatia		-	2.11	-	0.013	< 0.060	0.696	-	0.80	0.024
Jarun, Croatia		-	1.96	-	0.020	0.396	0.648	-	1.13	0.043
	Spring 2019	-	3.94	-	0.030	0.298	1.46	-	1.61	0.043
	Summer 2019	-	3.46	-	0.021	0.421	0.838	-	1.06	0.050
	Autumn 2019	-	0.38	-	0.013	< 0.060	0.606	-	1.12	0.046
	Winter 2018	-	1.79	-	0.017	0.327	1.17	-	2.03	0.050
	Spring 2019	-	1.69	-	0.012	0.272	0.476	-	1.88	0.049
	Summer 2019	-	1.73	-	0.023	0.419	1.21	-	2.39	0.039
	Autumn 2019	-	-	-	-	-	-	-	-	1.20

This study emphasized seasonal fluctuations, with higher concentrations typically recorded during summer and autumn months. Heavy

metal contamination in sediments is a critical indicator of long-term pollution in riverine ecosystems (Table 2).

Table 2. Concentrations of heavy metals in river and lake sediments along the Danube Basin

Sampling area/Country	Survey period	Heavy metals							References
		Al ( $\mu\text{g}\cdot\text{g}^{-1}$ )	As ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Cd ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Cr ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Cu ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Ni ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Pb ( $\mu\text{g}\cdot\text{g}^{-1}$ )	
Galati, Romania	April 2018	-	11	0.6	23	26	34.9	11	130
Tulcea, Romania		-	7	0.5	18	19	29.7	10	100
Pietrei pond, Romania		-	10	0.7	26	30	36.7	11	150
Barcaz Lake, Romania		-	10	0.7	22	40	39.8	12	140
Soschi Lake, Romania		-	13	0.7	18	34	27.6	8	100
Black Sea Sf. Gheorghe, Romania		-	2	0.05	8	3	8.9	3	30
Black Sea Perisor, Romania		-	1.4	0.01	5	2	5.2	2	17
Tamis, Serbia		-	28.10	1.13	81.76	90.50	40.46	35.22	164.92
Tisa, Serbia		-	16.54	2.12	12.69	77.58	60.56	49.22	312.12
Sava, Serbia		-	9.84	2.57	69.08	28.71	78.49	27.29	149.84
Danube, Serbia		-	15.05	2.75	14.24	98.79	82.17	91.45	353.91
Medsave, Croatia	Winter 2018	5310	-	0.045	16.2	5.11	8.69	4.92	14.4
	Spring 2019	8300	-	0.063	14.5	5.30	8.14	4.04	18.6
	Summer 2019	8960	-	0.086	13.6	4.24	7.51	4.86	18.0
	Autumn 2019	9270	-	0.088	13.1	4.07	7.51	5.11	18.3
Jarun, Croatia	Winter 2018	5090	-	0.037	19.9	4.58	10.4	3.77	10.4
	Spring 2019	8790	-	0.051	19.6	5.77	11.2	4.90	16.8
	Summer 2019	7720	-	0.078	19	5.42	10.2	5.69	15.5
	Autumn 2019	7660	-	0.070	14.5	4.49	7.50	5.28	15.8
Danube, Serbia		-	17.8	-	183	56	97	-	328
Insula Chici	Autumn 2018	-	-	0.30	-	4.30	16.03	5.90	58.84
Bac 1 (Braila)		-	-	0.59	-	10.72	29.12	8.96	118.54
Bac 2		-	-	0.74	-	17.39	27.88	12.57	120.76
Chiscani, Romania		-	-	0.50	-	12.58	22.31	8.49	87.43
Priza Dunarii, Romania		-	-	0.50	-	12.54	20.53	7.93	84.15
Siret, Romania		-	-	0.46	-	7.60	14.00	5.17	62.39
Libertatea, Romania		-	-	0.57	-	11.81	19.99	7.28	84.65
Cotul Pisicăi, Romania		-	-	0.54	-	10.24	22.09	21.14	77.64
Prut, Romania		-	-	0.54	-	7.89	16.28	4.84	64.48
Grindu, Romania		-	-	0.76	-	13.42	23.90	7.55	146.23
Luncavita, Romania		-	-	0.53	-	6.68	24.83	7.83	85.40
Isaccea, Romania		-	-	0.63	-	9.79	24.76	6.84	96.11
Somova, Romania		-	-	0.75	-	16.64	28.35	8.29	121.38
Vard Amo, Romania		-	-	0.57	-	15.17	38.81	8.11	117.01
Tulcea, Romania		-	-	0.53	-	9.42	16.94	5.34	69.97
Insula Chici	Spring 2019	-	-	0.59	-	10.31	20.17	6.02	78.69
Bac 1 (Braila)		-	-	0.65	-	11.65	19.33	6.05	84.21
Bac 2		-	-	0.99	-	25.01	35.80	13.78	177.33
Chiscani, Romania		-	-	0.63	-	8.97	16.04	6.41	73.57
Priza Dunarii, Romania		-	-	0.57	-	10.08	24.58	5.70	95.67
Siret, Romania		-	-	0.41	-	7.55	19.09	4.17	71.27
Libertatea, Romania		-	-	0.46	-	7.47	17.65	5.68	63.21
Cotul Pisicăi, Romania		-	-	0.78	-	19.47	28.49	10.35	131.50
Prut, Romania		-	-	0.46	-	9.29	17.40	4.31	66.06
Grindu, Romania		-	-	0.65	-	17.18	27.41	8.33	121.05
Luncavita, Romania		-	-	0.72	-	27.50	50.46	14.64	161.24
Isaccea, Romania		-	-	0.77	-	20.75	32.55	9.87	146.53
Somova, Romania		-	-	0.82	-	23.29	39.03	9.90	154.34
Vard Amo, Romania		-	-	0.48	-	9.29	25.85	6.76	81.26
Tulcea, Romania		-	-	0.52	-	10.07	28.13	8.01	86.43

A collaborative study (Simionov et al., 2021b) analysed sediment samples from Galați, Tulcea, Pietrei Pond, Barcaz Lake, and Soschi Lake in Romania, detecting As, Cd, Cr, Cu, Ni, Pb and Zn at varying levels. The maximum values reached  $0.7 \mu\text{g}\cdot\text{g}^{-1}$  for Cd,  $40 \mu\text{g}\cdot\text{g}^{-1}$  for Cu, and  $150 \mu\text{g}\cdot\text{g}^{-1}$  for Zn, while arsenic was found in concentrations up to  $13 \mu\text{g}\cdot\text{g}^{-1}$  in Soschi Lake. Recent findings in Serbia (Kašanin-Grubin et al., 2023) highlight significant contamination in sediments from the Danube, Sava, Tisa and Tamiš rivers. In the Danube, Cd reached  $2.75 \mu\text{g}\cdot\text{g}^{-1}$ , Cu up to  $98.79 \mu\text{g}\cdot\text{g}^{-1}$ , and Zn  $353.91 \mu\text{g}\cdot\text{g}^{-1}$ . Lead (Pb) was also present at concerning levels, up to  $91.45 \mu\text{g}\cdot\text{g}^{-1}$ , while Cr measured  $14.24 \mu\text{g}\cdot\text{g}^{-1}$ , indicating severe industrial pollution. A Croatian study (Redžović et al., 2023) conducted a seasonal assessment at Medsave and Jarun. Aluminum concentrations ranged from 5310 to  $9270 \mu\text{g}\cdot\text{g}^{-1}$ , and cadmium reached up to  $0.088 \mu\text{g}\cdot\text{g}^{-1}$ . While heavy metal values were moderate compared to other regions, seasonal variation influenced levels of Cr, Ni, and Zn, with higher concentrations typically observed in spring and summer.

Calmuc et al., 2021 assessed sediment contamination between Braila and Tulcea,

Romania. At Grindu, Zn reached up to  $146.23 \mu\text{g}\cdot\text{g}^{-1}$  and Cu  $13.42 \mu\text{g}\cdot\text{g}^{-1}$ . At Luncavița and Somova, Cd exceeded  $0.70 \mu\text{g}\cdot\text{g}^{-1}$ , and Cu surpassed  $27.50 \mu\text{g}\cdot\text{g}^{-1}$ . Elevated levels of Ni, Pb, and Zn suggest strong anthropogenic input, especially near industrial zones and confluence areas. Heavy metals accumulation in fish provides valuable insight into bioavailability and potential human health risks (Table 3). The investigation performed (Simionov et al., 2021b) focused on several species sampled from Galați, Tulcea, Pietrei Pond, Barcaz Lake, Soschi Lake, Black Sea Sf. Gheorghe, Black Sea Perisor (Romania). They determined that liver tissues generally exhibited higher concentrations of metals than muscle. Notably, Cd reached  $0.8 \mu\text{g}\cdot\text{g}^{-1}$  in *Cyprinus carpio* liver, while Zn levels peaked at  $157 \mu\text{g}\cdot\text{g}^{-1}$ , indicating significant bioaccumulation. In addition, Jovičić et al., 2024 assessed metal content in *Rutilus rutilus* and *Blicca bjoerkna* from Veliko Ratno Ostrvo and Višnjica (Serbia), identifying the presence of As, Cr, Cu, Hg, Ni, Pb and Zn. Zinc concentrations were the highest, up to  $27.64 \mu\text{g}\cdot\text{g}^{-1}$ , while Cr and Ni also showed moderate levels.

Table 3. Concentrations of heavy metals in biota from Danube Basin

Sampling area/Country	Species	Sample type	Survey period	Heavy metals							References
				As ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Cd ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Cr ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Cu ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Hg ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Ni ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Pb ( $\mu\text{g}\cdot\text{g}^{-1}$ )	
Galati, Romania	<i>Abramis brama</i>	muscle	April 2018	-	0.02	-	0.4	-	-	0.025	4.38
		liver		-	0.3	-	10	-	-	0.043	25.6
	<i>Leuciscus aspius</i>	muscle		-	0.02	-	0.2	-	-	0.005	5.14
		liver		-	0.24	-	2	-	-	0.27	12.6
	<i>Alosa immaculata</i>	muscle		-	0.02	-	0.4	-	-	0.01	3.6
		liver		-	0.11	-	1	-	-	0.02	25.9
	<i>Silurus glanis</i>	muscle		-	0.03	-	0.5	-	-	0.015	7.6
		liver		-	0.14	-	3	-	-	0.03	20.6
Tulcea, Romania	<i>Cyprinus carpio</i>	muscle		-	0.15	-	2	-	-	0.013	20.6
		liver		-	0.73	-	7	-	-	0.03	74.4
	<i>Silurus glanis</i>	muscle		-	0.02	-	5.4	-	-	0.005	7.4
		liver		-	0.17	-	12	-	-	0.015	25.6
	<i>Carassius gibelio</i>	muscle		-	0.12	-	5	-	-	0.004	32.9
		liver		-	0.8	-	8	-	-	0.016	157
	<i>Silurus glanis</i>	muscle		-	0.08	-	0.4	-	-	0.013	13.3
		liver		-	0.03	-	2	-	-	0.16	94.7
Barcaz Lake, Romania	<i>Cyprinus carpio</i>	muscle		-	0.2	-	1.4	-	-	0.024	4.1
		liver		-	0.6	-	2.5	-	-	0.012	17.2
	<i>Silurus glanis</i>	muscle		-	0.06	-	1.4	-	-	0.02	37.9
		liver		-	0.07	-	3	-	-	0.03	133
	<i>Carassius gibelio</i>	muscle		-	0.02	-	3	-	-	0.014	16.7
		liver		-	0.015	-	5.4	-	-	0.156	35.9
Soschi Lake, Romania	<i>Cyprinus carpio</i>	muscle		-	0.006	-	0.5	-	-	0.009	5
		liver		-	0.06	-	2	-	-	0.013	16.1
	<i>Esox lucius</i>	muscle		-	0.001	-	1.4	-	-	0.002	7.7
		liver		-	0.02	-	8	-	-	0.013	34
	<i>Silurus glanis</i>	muscle		-	0.002	-	0.5	-	-	0.003	15
		liver		-	0.002	-	3.2	-	-	0.015	43
	<i>Carassius gibelio</i>	muscle		-	0.005	-	2.3	-	-	0.016	31
		liver		-	0.02	-	5.5	-	-	0.07	72

Sampling area/Country	Species	Sample type	Survey period	Heavy metals							References	
				As (µg·g⁻¹)	Cd (µg·g⁻¹)	Cr (µg·g⁻¹)	Cu (µg·g⁻¹)	Hg (µg·g⁻¹)	Ni (µg·g⁻¹)	Pb (µg·g⁻¹)	Zn (µg·g⁻¹)	
Black Sea Sf. Gheorghe, Romania	<i>Trachurus m. ponticus</i>	muscle liver	April 2018	0.4	0.02	-	0.3	-	-	0.015	6	Simionov et al., 2021b
				0.9	0.09	-	2	-	-	0.034	22	
Black Sea Perisor, Romania	<i>Alosa immaculata</i>	muscle		0.4	0.02	-	0.4	-	-	0.021	4	Jovičić et al., 2024
		liver		0.7	0.12	-	2	-	-	0.03	31	
	<i>Mugil cephalus</i>	muscle		0.3	0.05	-	5	-	-	0.021	8	
		liver		2.3	0.62	-	35	-	-	0.06	35	
Veliko Ratno Ostrovo, Serbia	<i>Rutilus rutilus</i>	muscle	April 2021	0.019	-	0.019	0.264	0.080	0.480	0.023	9.002	Jovičić et al., 2024
		Blicca bjoerkna ( <i>Abramis brama</i> )		0.115	-	0.110	0.202	0.109	0.317	0.028	12.935	
Višnjiča, Serbia	<i>Rutilus rutilus</i>	muscle		0.072	-	0.020	0.566	0.081	0.158	0.029	27.641	Bjedov et al., 2025
		Blicca bjoerkna ( <i>Abramis brama</i> )		0.048	-	0.051	0.269	0.050	0.591	0.024	12.228	
Spačva, Croatia Podravljje, Croatia Mužilovčica, Croatia Strug, Croatia Kopački rit, Croatia Stara Drava, Croatia Reka, Croatia	<i>Cybister lateralimarginalis</i>	-	Spring - Summer 2023	420	39	-	-	630	-	40	-	Bjedov et al., 2025
				510	113	-	-	250	-	150	-	
				530	28	-	-	690	-	80	-	
				470	42	-	-	560	-	210	-	
				390	19	-	-	520	-	200	-	
				1440	29	-	-	360	-	160	-	
				570	24	-	-	500	-	640	-	
Zemun, Serbia	<i>Carassius auratus gibelio</i>	muscle	October 2013	139	57	-	-	994	-	30	-	Jovanović et al., 2017
				189	52	-	-	222	-	48	-	
				109	21	-	-	110	-	19	-	
				258	59	-	-	393	-	59	-	
				105	23	-	-	106	-	32	-	
				160	68	-	-	208	-	58	-	
Grocka, Serbia	<i>Carassius auratus gibelio</i>			172	51	-	-	139	-	40	-	
				239	62	-	-	325	-	62	-	
				154	27	-	-	161	-	28	-	
				333	82	-	-	466	-	84	-	
				153	36	-	-	162	-	37	-	
				211	69	-	-	260	-	69	-	

## Effects of heavy metals

Heavy metals present significant ecotoxicological threats to aquatic ecosystems, exerting their toxicity through a variety of mechanisms, including oxidative stress, neurotoxicity, enzymatic inhibition, impaired reproduction, and disruption of metabolic homeostasis. **Lead** accumulates in tissues such as gills, muscles, gonads, and digestive glands, where it mimics essential metals like copper, zinc, and iron, disrupting physiological functions (Jeong et al., 2023). Its affinity for sulphydryl groups leads to enzymatic inhibition, including suppression of heme synthesis and antioxidant defense, resulting in lipid peroxidation, protein degradation, and DNA damage (Raj & Das, 2023; Oladimeji et al., 2024). **Cadmium**, although not subject to

biomagnification, bioaccumulates extensively and replaces essential metals in enzymatic systems, impairing cell signalling and inducing oxidative stress, calcium imbalance, and DNA damage (Khan et al., 2022; Jeong et al., 2023). Its toxicity is evident even at low concentrations, causing growth reduction and neurotoxicity in species such as *Daphnia magna* and *Ostrea edulis* (Abd Elnabi et al., 2023). Moreover, cadmium persists in sediments and alters microbial activity and plant growth, destabilizing ecosystem processes (Kolarova & Napiórkowski, 2021; Oladimeji et al., 2024). **Mercury**, particularly as methylmercury (MeHg), is one of the most dangerous aquatic pollutants due to its ability to bioaccumulate and biomagnifies along food chains (Jeong et al., 2023). MeHg, formed under anoxic or even oxic

conditions, is readily absorbed by phytoplankton, initiating trophic transfer and causing severe neurotoxicity and structural deformities in fish (Kumar et al., 2024; Tsui et al., 2025). It also crosses the blood-brain barrier, accumulating in organs and impairing immune responses (Briffa et al., 2020). **Arsenic**, influenced by pH, redox conditions, and organic matter, accumulates in sediments via adsorption to iron and manganese oxides, from where it may be remobilized (Wang et al., 2023). The inorganic form, arsenite ( $\text{As}^{+3}$ ), is particularly toxic and bioavailable, accumulating in the liver and gills and causing oxidative stress, growth inhibition, and apoptosis (Jeong et al., 2023; Sevak & Pushkar, 2024). Although bioreduction is common in food chains, certain arsenic forms, such as arsenobetaines, may undergo biomagnification (Zhang et al., 2022). **Chromium**, especially as  $\text{Cr}^{+6}$ , is mutagenic and carcinogenic, affecting fish, invertebrates, and aquatic plants through oxidative stress, reproductive toxicity, and developmental inhibition (He et al., 2020; Ayele & Godeto, 2021).  $\text{Cr}^{+6}$  reduces photosynthesis in aquatic flora, while  $\text{Cr}^{+3}$  can cause more severe effects in fish (Prasad et al., 2021; Jeong et al., 2023). **Nickel**, although essential for some microorganisms, becomes toxic at high concentrations, accumulating in gills, liver, and kidneys, where it induces respiratory disturbances and ionic imbalance (Gauthier et al., 2021). Sensitivity varies by species, with gastropods and vascular plants being more susceptible than fish or algae (Blewett & Leonard, 2017; Wang et al., 2020). **Zinc**, an essential trace element, becomes toxic in excess, disturbing calcium metabolism in freshwater fish, leading to hypocalcemia and mortality (Jeong et al., 2023). While phytoplankton may mitigate its toxicity by supporting microbial metabolism, invertebrates often suffer from reduced respiration and excretion, leading to restricted growth (Seto et al., 2013). **Aluminum**, particularly soluble at low pH, accumulates in tissues such as the brain in species like *Oncorhynchus mykiss*, where it causes neurotoxicity, oxidative stress, inflammation, and acetylcholinesterase inhibition (Closset et al., 2022). Its toxicity is form-dependent, with monomeric inorganic species being most harmful. Finally, **copper**, though an essential

micronutrient, is highly toxic at elevated levels, even exceeding the toxicity of cadmium or lead in some cases (Jeong et al., 2023). Cu disrupts enzymatic activity, reproduction, and neurological function, and may become remobilized from sediments under climate-induced changes, amplifying ecological risks (Izydorczyk et al., 2021; Cui et al., 2024). Its impact is compounded by its widespread use in industry and agriculture and its influence on drinking water toxicity under varying pH and hardness conditions (Rehman et al., 2019).

## CONCLUSIONS

Heavy metal pollution in the Danube basin is the result of industrial, urban and agricultural sources, both along the river and from its major tributaries. The use of modern analytical methods and the precise identification of critical areas is essential to understand the dynamics of pollution and to implement coherent monitoring and remediation measures.

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