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IMPACT OF FLOOD DISCHARGE ON WATER QUALITY IN DANUBE RIVER BIFURCATIONS AND SELECTED LAKES (GORGOVA-UZLINA HYDROGRAPHIC UNIT)

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Abstract

Significant progress in water conservation and environmental preservation has been made through efforts by worldwide authorities in ecological water management. However, unexpected water pollution events continue to threaten water quality and biodiversity. Monitoring pollution levels in surface waters is essential for supporting aquatic ecosystem services and sustainability. This study aimed to quantify heavy metal pollution in several sampling sites to assess water quality and its impact on biodiversity. Elements like As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were analyzed using ICP-OES from samples collected during low-water (September 2024) and high-water (October 2024) conditions due to an upstream flood event. Results were compared to Romanian water quality standards. During low-water conditions, heavy metal concentrations were mostly below the limit for Quality Class I, except for Cd, which exceeded this limit. After the flood event, concentrations of most metals were within the Quality Class I limit. Still, Cd, Fe, and Pb showed varied results, with Ni levels ranging from very good to inferior water quality. Continuous monitoring is needed to prevent further degradation of delta ecosystems.

Key words*: concentration, flood event, heavy metal pollution, quality standard, surface water.*

INTRODUCTION

Fluvial-dominated delta ecosystems are vulnerable to the impacts of climate change induced by exogenous terrestrial pressures (droughts, river floods, intense storms, sediment starvation) and/or exogenous marine influences (erosion, sea-level rise, coastal flooding, saltwater intrusion) (Syvitski et al., 2009). Moreover, anthropogenic stressors represented by industrialization, urbanization, intensified agricultural practices and human intervention in catchment and delta plain land use contributed to significant environmental concerns, including water pollution (Nicholls et al., 2008). These ecosystems accumulate inorganic and organic compounds, heavy metals, nutrients, waste, plastic, pathogens, sediments, and other pollutants that heavily impact water quality (De Jonge, 2002). All these contaminants have harmful consequences on aquatic life, impeding vulnerable ecosystems and threatening biodiversity. Among chemical compounds, special attention must be paid to the toxic heavy metals from water and sediments, that can manifest bioaccumulation and biomagnification processing (Kumar et al., 2017) through the food web, compromising wildlife and ultimately affecting human health (Tovar-Sánchez et al., 2018). In addition to human-related activities, poor water quality may be endangered by flow rate fluctuations, precipitation, intense drought, weathering, soil erosion, etc. Thereby, successfully monitoring and assessing water quality and ecological status involves a multi-faceted approach that covers a wide range of physical and bio-geo-chemical variables and biotics of water in space and time (Chapman & Sullivan, 2022). In this context of concerns about the impacts of climate change on the fate of contaminants through unpredictable weather events, the subject of this scientific paper is included. The Danube River is the second-largest river basin in Europe, after the Volga River (Russia), emptying into the Danube Delta before reaching the Black Sea (Panin et al., 2016). The Danube River runs for a length of 2857 km, drains an area of roughly 801463 km^2, and traverses through or bordering ten European countries. Due to its pan-European character in socio-economic and cultural aspects (Padło et al., 2021) had attracted administrative authorities and technical governmental departments from several involved countries, supporting and expressing sustain for the environmental policies related to good environmental quality of natural resources. On its lower course (on the Romanian territory), the Danube has three branches: Chilia, Sulina, and Sf. Gheorghe. Chilia, the northern branch, has a length of 104 km, transporting 60% of the river's water and silt. Sulina, the middle arm, with a length of 71 km and carrying 18% of the Danube's flow, is considered the only navigable arm of the Danube, where large ships can enter. The southern branch, namely, Sf. Gheorghe Arm has a length of 112 km carrying 22% of the Danube's alluvial input. In the last few years, acute hydrological events have become more prevalent in the Danube River Basin, due to precipitation in the watershed, and/or a prolonged dry season. For example, the lower course of the Danube River recorded both historical high-flows (*i.e.,* 1970, 1991, 1998, 2002, 2005, 2010, 2013, 2014, 2018, 2019, 2024) and low-flows (*i.e.,* 1921, 2003, 2007, 2010, 2011,2012, 2015, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024) than the multi-year average. It is well known that the adaptive capacity and resilience of rivers are attributable to their dynamic characteristic and self-purification potential (Bennett & Rathbun, 1971). However, the acute effects of the Danube River flow fluctuations should not be overlooked, since they may have further ecological repercussions in the stable state of the Danube Delta shallow freshwater lakes assignable to extreme weather and climate events. Data on the flow of the Danube River in Romania are monitored by the National Authority for Romanian Waters and various meteorological and hydrological institutions. The river flow usually varies depending on the season and climatic conditions, and the values can be influenced by factors such as precipitation, snowmelt, the river regime in the upstream surrounding basins etc. The Danube Delta's surface area is roughly 4180 km^2, of which 3510 km^2 stands on Romanian territory. The delta evolved mainly from alternating layers of silt and sand, delivered by the Danube River over the past 10 to 12 thousand years, creating the complex network of channels, islands, and wetlands we see today. Its evolution is closely linked to river dynamics, sediment transport, and changes in sea levels (Gâștescu & Știucă, 2008). The delta is in a state of continuous change, shaped by both natural influences and human activity. It continues to grow and evolve as sediment accumulates, making it one of the most dynamic and recent landforms. The process of its formation is ongoing, with new islands and channels forming, while others may erode, resulting in a landscape that is both young and active. The present study aims to investigate seasonal changes in water quality and decipher the upstream flood event contribution of the lower Danube River to the spatial distribution of heavy metals in the water quality of several sampling sites investigated at the river bifurcations, including several Danube Delta lakes. Accordingly, the contents of ten (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) technophile elements (Ptitsyn, 2018) were analyzed. Consequently, systematic monitoring and assessment of the water quality's status is mandatory in deltaic aquatic environments of inestimable value from an ecological and unique biodiversity point of view.

MATERIALS AND METHODS

Study area

This investigation was performed at the Danube River bifurcations within its delta, specifically, at the *Ceatal Izmail* and the *Ceatal Sf. Gheorghe*, including several lakes attributed to the *Rusca-Gorgova-Uzlina* Hydrographic Unit, Danube Delta Romania. The selected sampling sites for this study illustrate a relevant example of the potential environmental impact of climate change (such as extreme weather events, including drought and flooding, wildfires, heavy rainfall, sea-level rise etc.). The Danube's bifurcations play an important role in the hydrological connectivity between the river's distributary branches and inter-distributary channels, streams, and lakes of the entire Danube Delta edifice. The *Rusca-Gorgova-Uzlina* Hydrographic Unit is situated in the western floodplain area, between the Sulina (north) and the Sf. Gheorghe (south) branches, and east of the Letea-Caraorman Spit (Panin et al., 2016) and is mainly characterized by a relatively dynamic hydrographic network influenced by the two above-mentioned branches, including, the *Litcov Canal* and the *Perivolovca Stream*.

Field sampling and data analysis

Field measurements and sample collection, preservation, preparation, and storage before any laboratory analyses were accomplished at the R/V "Istros" owed by the National Institute for Research and Development of Marine Geology and Geoecology-GeoEcoMar, Romania. In this study, several spot water samples were considered in two distinct hydrological periods of the Danube River's flow: low-water level (September 2024) and high-water level (October 2024) (Figure 1). During the low-water period (September), the Danube River's flow was at its lowest level, while a maximum amplitude was reached at the peak high-water stage (October), after an upstream flood event.

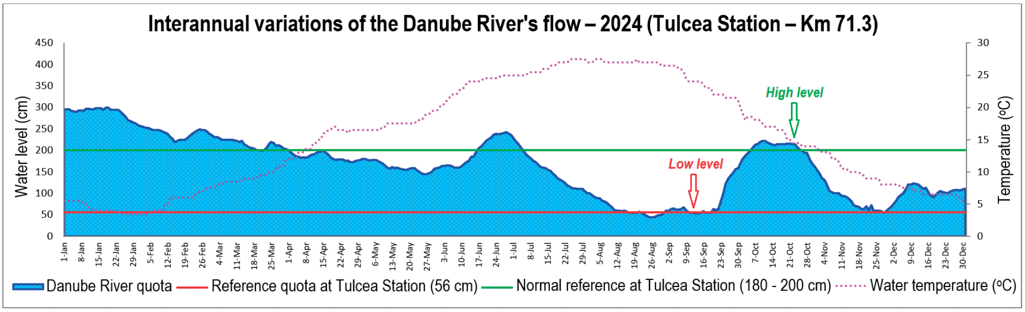

Figure. 1. Interannual variations of the Danube River's flow (Source Data: https://www.afdj.ro/ro/cotele-dunarii)

During the low-water period, the sampling sites were considered: *Ceatal Izmail, Ceatal Sf. Gheorghe*, including lakes such as *Uzlina, Isacova, Durnoliatca, Bleziuc-Pojarnia* and *Pojarnia* (Figure 2). Due to their proximity to the Sf. Gheorghe Branch alluvial input, these lakes are constantly filled, receiving appreciable amounts of water and silts. During the high-water period, the succeeding perimeters were investigated: *Ceatal Izmail*, *Ceatal Sf. Gheorghe*, *Cuzminţul Mare L., Rotund L., Rădăcinos L., Gorgova L., Gorgovăţ L., Potcoava de Sud L.*, *Litcov Canal* and *Old Danube River Meander* (Figure 2). The hydrological connection within these lakes varies mainly seasonally, alternating between relatively consistent connectivity with at least the *Old Danube River Meander via Litcov Canal*, and recurrent water deficiency (insufficient supply from rivers and streams), especially between lakes during the dry periods. The analysis to assess the environmental risk of heavy metals in freshwater deltaic environments was carried out using their spatial distribution, their content, and the possible origin of several investigated heavy metals. The sampling sites were chosen to determine the longitudinal distribution (along the upstream-downstream gradient of the Danube River bifurcations), including the horizontal distribution (along investigated lakes) of some specific heavy metals. For each site, 1-liter surface water samples for the chemical analyses were collected using sterile glass bottles at the sub-surface level (0-0.5 m) and close to the lake bottom. Nitric acid preservation of samples was performed in the field. Then, samples were filtered through a 0.45 μm membrane filter at the R/V "Istros" laboratory. After filtering, the bottle samples were plastic-bagged and iced quickly. Sample bottles were shipped to the analytical laboratory. Water samples were analyzed at a special and accredited (SR EN ISO/IEC 17025:2018) water testing laboratory ("The Pollution Control Department - Laboratory for water, soil, waste control"), from the National Research-Development Institute for Industrial Ecology - ECOIND, Bucharest, Romania. Ten selected heavy metals, namely As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, commonly present in surface waters due to anthropogenic sources were determined by inductively coupled plasma atomic emission spectroscopy (ICP-EOS). The method for the

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quantification of heavy metals levels in surface waters was performed according to the SR EN ISO 11885:2009 standard. Evaluation of the heavy metals content in the investigated water samples and their potential risk assessment was done in comparison with the Romanian water quality standards (Order 161/2006).

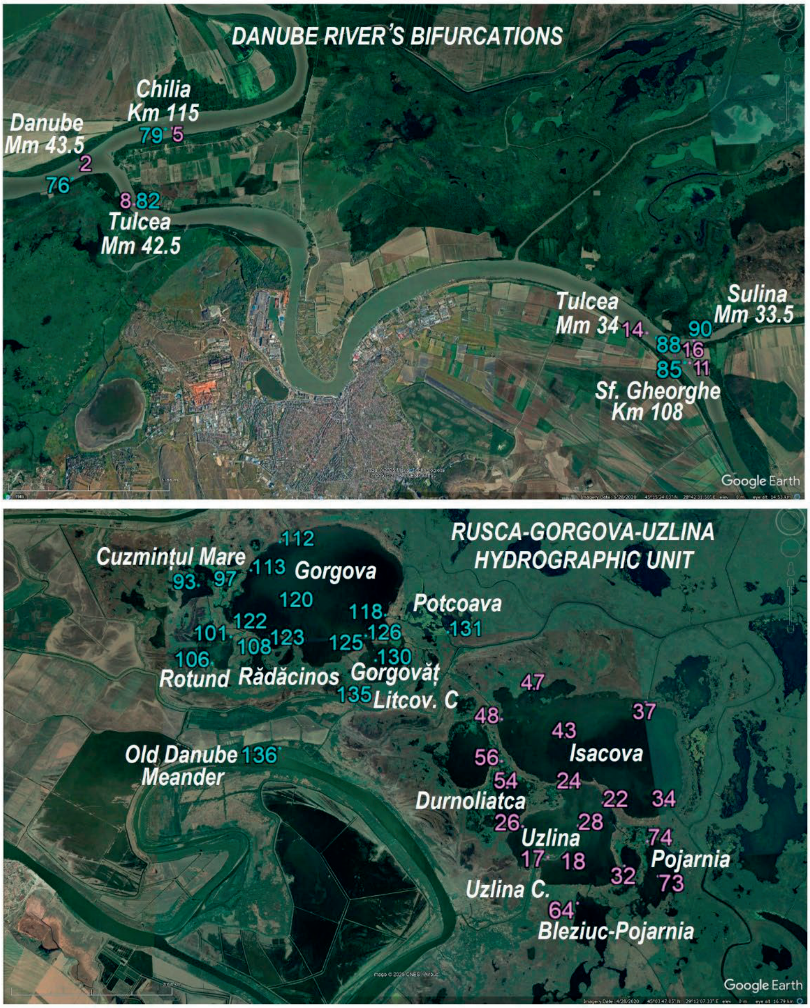

Figure 2. Location of the investigated perimeters. Pink dots mark the sampling sites during the low-water periods; Blue dots mark the sampling sites during the high-water periods (Base Map Source: https://www.google.com/maps/)

RESULTS AND DISCUSSIONS

Water quality and sustainable ecological ecosystems are fundamental to the proper functioning of the Danube River Delta region. The important benefits of healthy ecosystems contribute to maintaining good conditions for the wetlands and aquatic ecosystems of the Danube Delta which are of international ecological importance, being recognized worldwide as UNESCO World Heritage Sites, Biosphere Reserve, and Ramsar Site (Ramsar Convention, 1987). Correspondingly, water quality impairment may impact the ecosystem services provided by the Danube Delta (*i.e.,* unique and fascinating natural landscapes, habitats for flora and fauna species, reed resources, flood control, water supply, agricultural uses, recreational activities, tourism, fishing activities, etc.) (Cazacu & Adamescu, 2017). The Danube Delta ecosystems are vulnerable to the water quality of the Danube River, which could be contaminated by numerous pollutants such as toxic heavy metals and organic contaminants from upstream and local sources. All these contaminants may often end up in the Danube River and subsequently, the coastal area of the Black Sea. Generally, the Danube River water quality status is mainly correlated to anthropogenic activities (industrial use, wastewater discharges, agricultural practices) (Chitescu et al., 2021), past hydro-technical projects on the river that restrict the flow of water and sediment discharge downstream (Panin & Jipa, 1998), and to some extent to climate change and hydroclimatic extremes (such as floods and rainstorms, droughts and heatwaves etc.) (Leščešen et al., 2024). Consequently, various natural and anthropogenic stressors could be responsible for water quality degradation, water biodiversity loss, and affected ecosystem services (Belacurencu, 2007). In this study, the contents of heavy metals *i.e.,* As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, in water samples collected from several sampling locations of the Danube Delta area, were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-EOS). The reference values were used to determine and evaluate the heavy metals' water quality status and spatial distribution in investigated freshwater samples. The Romanian current legislation imposed the reference values (Order 161/2006 - Normative regarding the classification of surface water quality to establish the ecological status of water bodies). The reference values represent the maximum permissible values of pollutant concentration corresponding to the five-surface water quality standard classes: Class I (Very Good), Class II (Good), Class III (Moderate), Class IV (Poor), and Class V (Bad).

Heavy metals' distribution during the low-water period investigation

During the low-water period (September 2024), at the *Ceatal Izmail* bifurcation area, the *Danube* carried a flow of approximately 2851 $m^3 \cdot s^{-1}$ at the entrance to the delta. This was unequally distributed between the *Tulcea* - 1701 $m^3 \cdot s^{-1}$ and *Chilia* - 1168 $m^3 \cdot s^{-1}$ branches, in favor of the *Tulcea* branch. The average velocities on the profiles were between 0.34 and 0.4 $m \cdot s^{-1}$. The riverbed was symmetrical in the *Ceatal Ismail* bifurcation area, with velocities homogeneously distributed on the cross sections. At the entrance to the second hydrographic node at the *Ceatal Sf. Gheorghe* bifurcation area, the flow of the *Tulcea* branch was at the time of measurements approximately 1572 $m^3 \cdot s^{-1}$. The flow was unequally distributed between the *Sulina* - 643 $m^3 \cdot s^{-1}$ and *Sf. Gheorghe* branches - 955 $m^3 \cdot s^{-1}$. The average velocities on the profiles were between the values of 0.39 and 0.5 $m \cdot s^{-1}$, with higher values on the *Sulina Canal*. The riverbed of the three branches was asymmetric in the bifurcation area at the *Ceatal Sf. Gheorghe*, with velocities homogeneously distributed on the cross sections. The chemical analyses were performed for 24 spot water samples collected from *Ceatal Izmail* (at the *Danube - Mm 43.5, Chilia Arm - Km 115, Tulcea Arm - Mm 43.5*), *Ceatal Sf.* Gheorghe (at the *Tulcea Arm - Mm 43, Sulina Arm - Mm 33.5, Sf. Gheorghe Arm - Km 108*), including lakes such as *Uzlina, Isacova, Durnoliatca, Bleziuc-Pojarnia* and *Pojarnia* (Figure 3). During the low-water period, the values of the investigated heavy metals pointed to an insignificant variability related to the heavy metals' distribution between the collection points, in both investigated Danube River bifurcations, as well as deltaic lakes. The results are illustrated in Table 1. Following the results obtained for samples taken under hydrodynamic conditions of low-water levels of the Danube, it can be observed that the investigated heavy metals such as: As, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn recorded low concentrations, close to those corresponding to quality class I (very good condition), while, for the Cd element, the concentrations varied from one sampling station to another, incidentally exceeding the limit of class II (good condition). The dynamics of the investigated heavy metal concentrations during the low-water period will be presented further on.

Arsenic. The As concentration (μg/L) identified in the water samples presented a series of insignificant variations. Most of the obtained values were low, below the detection limit (< 2 μg/L), implicitly, below the limit corresponding to quality class I (10 μg/L).

Cadmium. The Cd concentration (µg/L) determined in the investigated water samples presented a series of interesting variations. Generally, most of the values were below the limit set for water quality Class I. However, values that slightly reached or exceeded the first two quality classes (Class I - 0.5 µg/L, Class II - 1 µg/L) were encountered in different samples taken from the investigated locations. For example, several sampling sites showed results that overpassed the limit set for water quality Class I (Figure 3): the *Sf. Gheorghe Arm - Km 108* (*DD24-11*), *Sulina Arm - Mm 33.5* (*DD24-16*), *Uzlina C.* (*DD24-17*), *Uzlina L.* (*DD24-26*) (situated close to the mouth of the connection canal with *Durnoliatca L.*), *Isacova L.* (*DD24-34*) (located in the south-eastern part of the lake, close to the mouth of the connection canal with *Perivolovca C.*), *Durnoliatca L.* (*DD24-49*) (located in the south-eastern part of the lake, close to the mouth of the connection canal with *Uzlina L.*) and *DD24-56* (situated in the northern part of the lake, close to the mouth of the connection canal with *Isăcel L.*). Alternatively, the concentration of Cd tested in water samples taken from *Tulcea Arm - Mm 42.5* (*DD24-08*) and *Uzlina L.* (*DD24-24*) (situated in the northern part of the lake, close to the mouth of a connection canal with *Isacova L.*) exceeded the limit set for water quality Class II.

Cobalt. The Co concentration (µg/L) tested in all collected water samples showed no significant variations. The majority of the results were below the limit set for water quality Class I (10 µg/L).

Chromium. The Cr concentration (µg/L) identified in the water samples collected during the low-water period showed no significant variations.

All the obtained values were low, below the limit set for water quality Class I (25 µg/L).

Table 1. Results of the heavy metal analysis in the investigated control sections (point samples) (Danube branches, canals, lakes, etc.) (low-water hydrodynamic conditions)

No. crt.	Location	Sample's indicative	As	Cd	Co	Cr_{tot}	Cu	Fe_{tot}	Mn	Ni	Pb	Zn
			µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	mg/L	µg/L	µg/L	µg/L
1	Danube Mm 43.5	DD24-02	<2.0	0.4	< 0.6	<2.0	2.7	0.024	0.002	<2.0	<2.0	5.8
2	Chilia Km 115	DD24-05	<2.0	<0.4	< 0.6	<2.0	<2.0	0.065	0.003	<2.0	<2.0	<5.0
3	Tulcea Mm 42.5	DD24-08	<2.0	1.1	< 0.6	<2.0	2.3	0.027	0.002	<2.0	<2.0	<5.0
4	Sf. Gheorghe km 108	DD24-11	<2.0	0.6	< 0.6	<2.0	6.2	0.025	0.005	<2.0	<2.0	<5.0
5	Tulcea Mm 34	DD24-14	<2.0	0.4	< 0.6	<2.0	2.5	0.028	0.003	<2.0	<2.0	10.8
6	Sulina Mm 33.5	DD24-16	<2.0	0.8	< 0.6	<2.0	<2.0	0.018	0.003	<2.0	<2.0	<0.5
7	Uzlina C.	DD24-17	<2.0	0.6	< 0.6	<2.0	2	0.056	0.009	<2.0	<2.0	<0.5
8	Uzlina L.	DD24-18	<2.0	<0.4	< 0.6	<2.0	2.3	0.039	0.005	<2.0	<2.0	6.8
9	Uzlina L.	DD24-22	<2.0	<0.4	< 0.6	<2.0	<2.0	0.028	0.004	<2.0	<2.0	<5.0
10	Uzlina L.	DD24-24	<2.0	1.6	< 0.6	<2.0	<2.0	0.018	0.008	<2.0	<2.0	<5.0
11	Uzlina L.	DD24-26	<2.0	0.6	< 0.6	<2.0	<2.0	0.021	0.003	<2.0	<2.0	<5.0
12	Uzlina L.	DD24-28	<2.0	<0.4	< 0.6	<2.0	<2.0	0.020	0.003	<2.0	<2.0	<5.0
13	Isacova L.	DD24-32	<2.0	<0.4	< 0.6	<2.0	<2.0	0.011	0.003	<2.0	2.3	<5.0
14	Isacova L.	DD24-34	<2.0	0.6	< 0.6	<2.0	2.1	0.012	0.005	2.1	<2.0	<5.0
15	Isacova L.	DD24-37	<2.0	0.5	< 0.6	<2.0	<2.0	0.026	0.012	2.2	2.9	<5.0
16	Isacova L.	DD24-43	<2.0	<0.4	< 0.6	<2.0	<2.0	0.026	0.022	2.9	<2.0	<5.0
17	Isacova L.	DD24-47	<2.0	0.4	< 0.6	<2.0	<2.0	0.022	0.010	2.6	<2.0	<5.0
18	Isacova L.	DD24-48	<2.0	<0.4	< 0.6	<2.0	<2.0	0.028	0.005	3.6	<2.0	<5.0
19	Durnoliatca L.	DD24-49	<2.0	0.7	< 0.6	<2.0	<2.0	0.025	0.006	2.8	<2.0	<5.0
20	Durnoliatca L.	DD24-54	<2.0	<0.4	< 0.6	<2.0	<2.0	0.007	0.021	2.6	<2.0	<5.0
21	Durnoliatca L.	DD24-56	<2.0	0.6	< 0.6	<2.0	<2.0	0.006	0.004	3.2	<2.0	<5.0
22	Bleziuc L.	DD24-64	<2.0	<0.4	< 0.6	<2.0	<2.0	0.020	0.002	3.6	<2.0	<5.0
23	Pojarnia L.	DD24-73	<2.0	<0.4	1	<2.0	<2.0	0.054	0.012	<2.0	<2.0	<5.0
24	Pojarnia L.	DD24-74	<2.0	<0.4	< 0.6	<2.0	<2.0	0.009	0.008	<2.0	2.9	<5.0

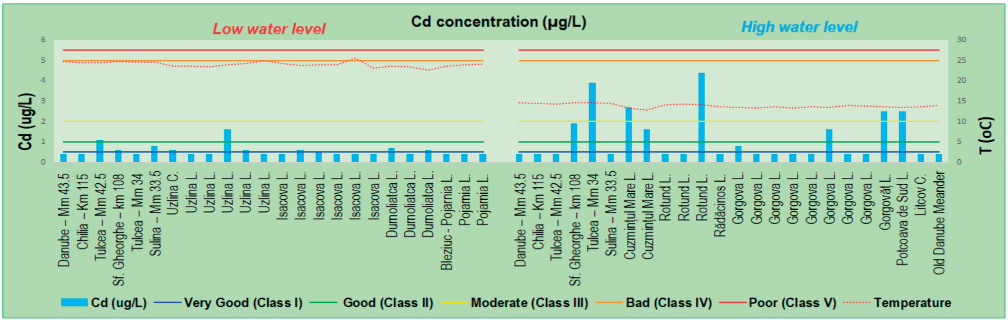

Figure 3. Cd (µg/L) concentration in investigated freshwater samples

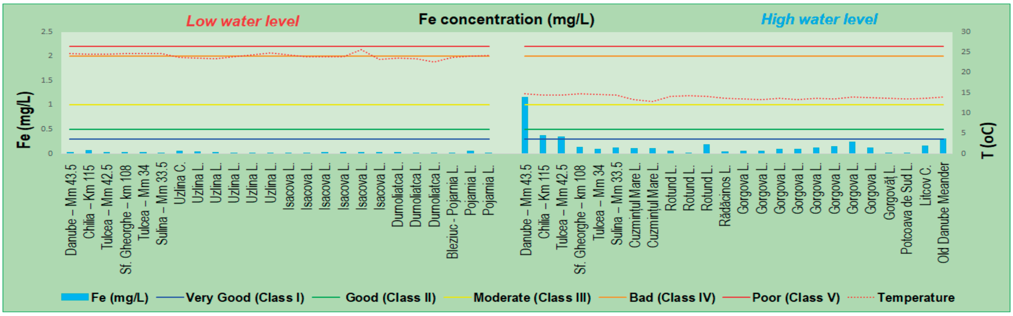

Figure 4. Fe (mg/L) concentration in investigated freshwater samples

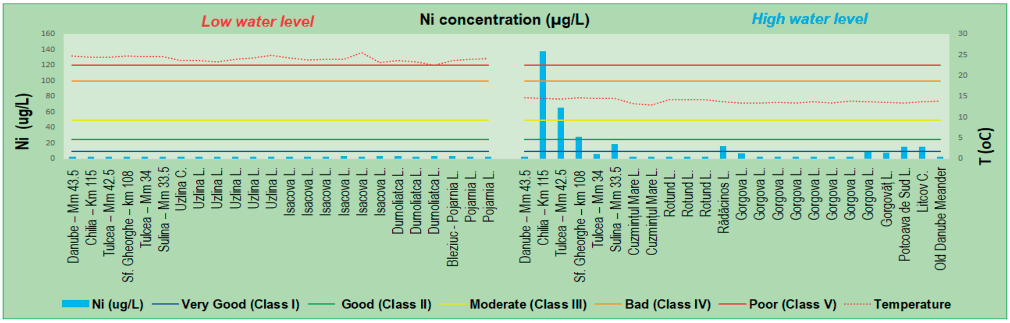

Figure 5. Ni (µg/L) concentration on investigated freshwater samples

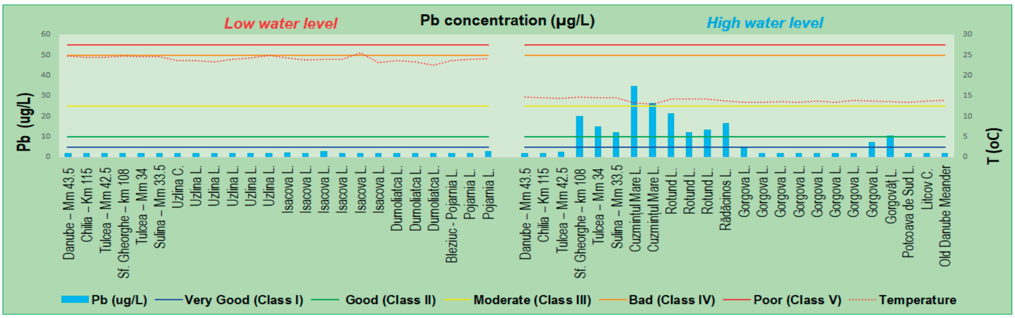

Figure 6. Pb (µg/L) concentration in investigated freshwater samples

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Copper. The Cu concentration (μg/L) measured in the water samples collected during the low-water period, showed no significant variations. All the values obtained were low, below the limit set for water quality Class I (20 μg/L).

Iron. During the low-water period, the Fe concentration (mg/L) defined in the water samples collected from all sampling points, showed no significant variations. All the obtained values were low, below the limit set for water quality Class I (0.3 mg/L) (Figure 4).

Manganese. The results showed an inconsiderable Mn concentration (mg/L) detected in the water samples collected from all sampling points. All the values were low, below the limit set for water quality Class I (0.05 mg/L).

Nickel. The Ni concentration (μg/L) spotted in the water samples collected during the low-water period showed no significant variations. All the value obtained were low, below the limit set for water quality Class I (10 μg/L) (Figure 5).

Lead. The Pb concentration (μg/L) observed in the water samples collected during the low-water period showed no significant variations. All the obtained values were low, below the limit set for water quality Class I (5 μg/L) (Figure 6).

Zinc. The Zn concentration (μg/L) noticed in the water samples collected during the low-water period showed no significant variations. All the obtained values were low, below the limit set for water quality Class I (100 μg/L)

Heavy metals' distribution during the high-water period investigation

The field expedition occurred when an impetuous increase in Danube water levels was expected due to a flood wave owing to storms and heavy rainfall coming from upstream countries. Consequently, during the high-water period (October 2024), at the *Ceatal Izmail* bifurcation area, the *Danube* carried a flow of approximately 6970 $m^3 \cdot s^{-1}$ at the entrance to the delta. This was unequally distributed between the *Tulcea* - 3896 $m^3 \cdot s^{-1}$ and *Chilia* - 3032 $m^3 \cdot s^{-1}$ branches. The average velocities on the profiles were between 0.72 and 0.93 $m \cdot s^{-1}$.

Table 2. Results of the heavy metal analysis in the investigated control sections (point samples) (Danube branches, canals, lakes, etc.) (high-water hydrodynamic conditions)

No. crt.	Location	Sample's indicative	As	Cd	Co	Cr_{tot}	Cu	Fe_{tot}	Mn	Ni	Pb	Zn
			μg/L	μg/L	μg/L	μg/L	μg/L	mg/L	mg/L	μg/L	μg/L	μg/L
1	Danube Mm 43.5	DD24-76	<2.0	<0.4	<0.6	<2.0	<2.0	1.160	0.005	<2.0	<2.0	67.6
2	Chilia Km 115	DD24-79	<2.0	<0.4	<0.6	<2.0	<2.0	0.379	0.004	138	<2.0	57.2
3	Tulcea Mm 42.5	DD24-82	<2.0	<0.4	<0.6	<2.0	<2.0	0.348	0.001	65.2	2.5	60.2
4	Sf. Gheorghe Km 108	DD24-85	<2.0	1.9	7.8	<2.0	<2.0	0.130	0.000	28.2	20	40
5	Tulcea Mm 34	DD24-88	<2.0	<0.4	7.6	<2.0	<2.0	0.092	0.000	5.5	14.8	59.6
6	Sulina Mm 33.5	DD24-90	<2.0	<0.4	<0.6	<2.0	<2.0	0.125	0.000	18.1	12.2	33.3
7	Cuzmințul Mare L.	DD24-93	<2.0	2.7	<0.6	<2.0	<2.0	0.111	0.003	<2.0	34.6	30.4
8	Cuzmințul Mare L.	DD24-97	<2.0	1.6	1.5	<2.0	<2.0	0.109	0.005	<2.0	26.4	35.7
9	Rotund L.	DD24-101	<2.0	<0.4	<0.6	<2.0	<2.0	0.052	0.000	<2.0	21.2	48.5
10	Rotund L.	DD24-102	<2.0	<0.4	<0.6	<2.0	<2.0	0.016	0.001	<2.0	12	25.4
11	Rotund L.	DD24-106	<2.0	4.4	4.7	<2.0	<2.0	0.188	0.024	<2.0	13.2	25.1
12	Rădăcinos L.	DD24-108	<2.0	<0.4	3.3	<2.0	<2.0	0.042	0.003	15.8	16.4	9.7
13	Gorgova L.	DD24-112	<2.0	0.8	<0.6	<2.0	<2.0	0.059	0.001	6.7	4.7	49.4
14	Gorgova L.	DD24-113	<2.0	<0.4	<0.6	<2.0	<2.0	0.056	0.003	<2.0	<2.0	30.8
15	Gorgova L.	DD24-118	<2.0	<0.4	<0.6	<2.0	<2.0	0.094	0.003	<2.0	<2.0	61.7
16	Gorgova L.	DD24-120	<2.0	<0.4	1.2	<2.0	<2.0	0.097	0.010	<2.0	<2.0	34
17	Gorgova L.	DD24-122	<2.0	<0.4	<0.6	<2.0	<2.0	0.123	0.008	<2.0	<2.0	<5.0
18	Gorgova L.	DD24-123	<2.0	1.6	2.1	2.3	<2.0	0.154	0.003	<2.0	<2.0	44.6
19	Gorgova L.	DD24-125	<2.0	<0.4	<0.6	2.2	<2.0	0.246	0.023	<2.0	<2.0	47.3
20	Gorgova L.	DD24-126	<2.0	<0.4	1.8	<2.0	<2.0	0.124	0.002	8.1	7.4	12.9
21	Gorgovăț L.	DD24-130	<2.0	2.5	<0.6	5.7	<2.0	0.003	0.006	7.7	10.6	37.8
22	Potcoava de Sud L.	DD24-131	<2.0	2.5	<0.6	6.3	<2.0	0.006	0.003	15.5	<2.0	10
23	Litcov C.	DD24-135	<2.0	<0.4	<0.6	<2.0	<2.0	0.167	0.010	14.9	<2.0	<5.0
24	Old Meander	DD24-136	<2.0	<0.4	1.3	<2.0	<2.0	0.306	0.009	<2.0	<2.0	30.6

At the entrance to the second hydrographic node at the *Ceatal Sf. Gheorghe* bifurcation area, the flow of the *Tulcea* branch was at the time of measurements approximately 3738 $m^3 \cdot s^{-1}$. The flow was unequally distributed between the *Sulina* - 1377 $m^3 \cdot s^{-1}$ and *Sf. Gheorghe* branch - 2328 $m^3 \cdot s^{-1}$. The average velocities on the profiles were between 0.76 and 0.95 $m \cdot s^{-1}$, with higher values on the *Sulina* Canal. The chemical analyses were fulfilled for 24 spot water samples collected from *Ceatal Izmail* (at the *Danube - Mm 43.5, Chilia Arm - Km 115, Tulcea Arm - Mm 43.5*), *Ceatal Sf. Gheorghe* (at the *Tulcea Arm - Mm 43, Sulina Arm - Mm 33.5, Sf. Gheorghe Arm - Km 108*), including *Cuzmințul Mare L., Rotund L., Rădăcinos L., Gorgova L., Gorgovăț L., Potcoava de Sud L.*, *Litcov Canal* and *Old Danube River Meander* (Figure 2). During the high-water period, the values of the investigated heavy metals showed a higher variability associated with the heavy metals' distribution between the collection points, in both investigated Danube River bifurcations, as well as in deltaic lakes. The results are shown in Table 2. In general, the content values of certain heavy metals (Cd, Fe, Ni and Pb) acquired within hydrodynamic conditions of high-water levels of the Danube (October 2024) were higher than the values obtained within the low-water level period (September 2024). Regarding the other investigated heavy metals (As, Co, Cr, Cu, Mn and Zn), they maintained a similar trend so that no significant exceedances were registered between the two seasons (September 2024 and October 2024). The distribution trend of these heavy metals had a pattern with low values, close to those corresponding to quality class I (very good condition), registered in all investigated sampling stations. The dynamics and changes in the concentrations of ten investigated heavy metals (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) during the high-water period will be shown below.

Arsenic. The As concentration (μg/L) identified in the water samples presented a series of insignificant variations. Most of the obtained values were low, below the detection limit (< 2 μg/L), implicitly, below the limit corresponding to quality class I (10 μg/L).

Cadmium. The Cd concentration (μg/L) determined in the investigated water samples presented a series of interesting variations. A part of the values was below the limit set for water quality Class I, but also were observed values that slightly reached or exceeded the first three quality classes (Class I - 0.5 μg/L, Class II - 1 μg/L, Class III - 2 μg/L) (Figure 3). The water sample that exceeded class I was encountered in the *Gorgova L.* (*DD24-112*) (situated in the northwestern part of the lake, close to the mouth of the connection canal with *Sulina Arm*). Then, the sampling sites with values higher than class II are represented by: *Sf. Gheorghe Arm - Km 108* (*DD24-85*), *Cuzmințul Mare L.* (*DD24-97*) (situated in the northeastern part of the lake, close to the mouth of a connection canal) and *Gorgova L.* (*DD24-123*) (located in the west southern part of the lake, close to the mouth of a connection canal with *Rădăcinos L.*). The water samples that overpassed the limit set for water quality Class III were noticed in: the *Tulcea Arm - Mm 34* (*DD24-88*), *Cuzmințul Mare L.* (*DD24-93*) (situated in the middle part of the lake), *Rotund L.* (*DD24-106*) (located in the southern part of the lake, close to the mouth of a connection canal with *Litcov C.), Gorgovăț L. (DD24-130)* (located in the middle of the lake) and *Potcoava de Sud L.* (*DD24-131*) (situated in the southern part of the lake, close to the mouth of a connection canal with *Litcov C.*).

Cobalt. The Co concentration (μg/L) identified in all collected water samples showed no significant variations. Most of the results were low values, below the limit set for water quality Class I (10 μg/L).

Chromium. The Cr concentration (μg/L) tested in the water samples collected during the high-water period showed no significant variations. All the value obtained was low, below the limit set for water quality Class I (25 μg/L).

Copper. The Cu concentration (μg/L) noted in the water samples collected during the high-water period showed no significant variations. All the values obtained were low, below the limit set for water quality Class I (20 μg/L).

Iron. During the high-water period, the Fe concentration (mg/L) identified in most of the water samples showed no significant variations, with low values, below the limit set for water quality Class I (0.3 mg/L). For all that, three samples slightly reached or exceeded the first quality class (Figure 4), namely: the *Chilia Arm - km 115* (*DD24-79*), the *Tulcea Arm - Mm 42.5* (*DD24-82*) and the *Old Danube Meander* (*DD24-136*). In addition, it was also noticed one sample overpassed the limit set for water quality

Class III (1.0 mg/L), specifically, the *Danube - Mm 43.5* (*DD24-76*).

Manganese. The results showed an insignificant Mn concentration (mg/L) detected in the water samples collected from all sampling points. All the values were low, below the limit set for water quality Class I (0.05 mg/L).

Nickel. Overall, the Ni concentration (µg/L) spotted in several water samples collected during the high-water period showed no significant variations, with low values, below the limit set for water quality Class I (10 µg/L). Even so, four water samples exceeded the first quality class, namely: the *Sulina Arm - Mm 33.5* (*DD24-90*), *Rădăcinos L.* (*DD24-108*) (situated in the northern part of the lake), *Potcoava de Sud L.* (*DD24-131*) (situated in the southern part of (situated close to the mouth of the connection canal with *Durnoliatca L.*), (situated close to the mouth of the connection canal with *Durnoliatca L.*), *135)*. The other two samples overpassed the limit set for water quality Class II (25 µg/L), namely, *Sf. Gheorghe Arm - Km 108* (*DD24-85*), and respectively, Class III (50 µg/L) at the *Tulcea Arm - Mm 42.5* (*DD24-82*). Finally, at the *Chilia Arm - Km 115* (*DD24-79*) was depicted a Ni concentration overpassed the limit set for water quality Class V (>100 µg/L) (Figure 5).

Lead. Almost half of the water samples investigated showed lower Pb concentration (µg/L), with values below the limit settled for water quality Class I (5 µg/L). Instead, the other half of the samples showed values that exceeded the first three quality classes (Class I - 5 µg/L, Class II - 10 µg/L, Class III - 25 µg/L). So, the following sampling sites revealed Pb concentration (µg/L) higher than Class I: *Gorgova L.* (*DD24-126*) (located in the south-eastern part of the lake, close to the mouth of a connection canal with *Gorgovăț L.*) and *Gorgovăț L.* (*DD24-130*) (located in the middle part of the lake). Then, the upcoming water samples were included in the quality class II: *Sf. Gheorghe Arm - km 108* (*DD24-85*), *Tulcea Arm - Mm 34 (DD24-88)*, *Sulina Arm - Mm 33.5* (*DD24-90*), *Rotund L.* (*DD24-101*) (located in the eastern part of the lake, close to the mouth of a connection canal with *Gorgova L.*), *Rotund L.* (*DD24-102*) (located in the northern part of the lake, close to the mouth of a connection canal with *Cuzmințul Mare L.*), *Rotund L.* (*DD24-106*) (located in the southern part of the lake, close to the mouth of a connection canal with *Litcov C.*), and *Rădăcinos L.* (*DD24-108*) (located in the northern part of the lake, close to the mouth of a connection canal with *Gorgova L.*). Relatively, higher values of Pb concentration corresponding to the quality class III were identified in: *Cuzmințul Mare L.* (*DD24-93*) (located in the middle part of the lake) and *Cuzmințul Mare L.* (*DD24-97*) (located in the eastern part of the lake, close to the mouth of a connection canal) (Figure 6).

Zinc. The Zn concentration (µg/L) determined in the water samples collected during the high-water period, showed no significant variations. All the obtained values were low, below the limit set for water quality Class I (100 µg/L).

The heavy metals investigated in the surface water samples collected under distinct hydrodynamic conditions (low and high water levels of the Danube River in 2024) show a varying degree of distribution, ranging from very low values below the detection limit, implicitly below the limit corresponding to Class I quality (very good status) to relatively higher values (in certain stations) that exceed the maximum allowed limit, corresponding to Class II (good status), Class III (moderate status), Class IV (poor status), and Class V (bad status). To some extent, the results obtained in this study are similar to those of previous research conducted on the Danube Delta ecosystems (Vignati, 2013; Vasiliu, 2021; Catianis, 2022). It is assumed that the increased concentrations of particular heavy metals (*i.e.,* Cd, Fe, Ni and Pb) observed during the high-water period may be due to the flood wave. When the flow of a river increases (*e.g.,* due to heavy rains, snowmelt, etc.), it can transport pollutants from the upstream areas of the watercourse. These pollutants may include chemicals, heavy metals, waste, and even pathogens. Increased flow can lift pollutants from upstream soil, sediments, and waters, transporting them downstream and affecting water quality. Particularly, during flooding, contaminants can be carried in much greater quantities than under normal flow conditions. Generally, even areas located far from the potential pollution sources can suffer from the transport of these pollutants, which may reach sensitive ecosystems or even drinking water sources. Higher concentrations of Cd, Fe, Ni and Pb in the investigated freshwater samples can be attributed to several natural and anthropogenic factors. Among the most relevant factors that could contribute to the increase in Cd, Fe, Ni, and Pb concentrations are industrial activities, mining, transportation, agricultural waste and fertilization practices, upstream contamination, atmospheric particle deposition, urban and industrial waste, illegal or uncontrolled discharges, soil erosion, sediment input, in-lake processes, etc. However, it should be noted that in the Danube Delta, there are sediments that may contain nickel in higher concentrations due to the natural geochemical background. Additionally, soil and rock erosion in the upstream areas of the delta may release nickel into the water. More than that, the combination of natural sedimentation, erosion, flood-induced transport, anthropogenic pollution, and geochemical factors leads to the higher concentration of heavy metals near the mouths of connecting channels with lakes. These areas may act as collection points for pollutants, both from upstream sources and from local environmental processes.

The impact of heavy metals on the aquatic environment. Higher concentrations of Cd, Fe, Ni and Pb in the Danube and the lakes of the Danube Delta represent a complex phenomenon, generated by both natural sources and anthropogenic influences, which requires constant monitoring. Their impact on the ecosystems of the Danube Delta depends not only on the concentrations of these metals but also on their interactions with other biological and physical-chemical factors in the area. Higher concentrations of Cd, Fe, Ni and Pb can lead to water pollution, affecting the health of aquatic ecosystems either through direct toxicity or by modifying the physical-chemical characteristics of the water. This can also disrupt biodiversity and the normal functioning of the ecosystem. Therefore, monitoring and managing this type of pollution are essential for protecting the environment of the Danube Delta.
Tracking heavy metal contamination in water and sediments is important for developing targeted management strategies to mitigate their impact on deltaic ecosystems. Heavy metal pollution disrupts ecosystem functions, such as nutrient cycling and water purification, leading to habitat degradation. It also threatens biodiversity by accumulating in aquatic organisms and affecting the food chain. Human health risks arise from contaminated fish and water, while economic impacts include reduced fish stocks, harmed agriculture, and decreased eco-tourism. To ensure long-term sustainability, advanced remediation, stronger policies, ecosystem restoration, and community involvement are essential to mitigate the effects of heavy metal contamination in the Danube River-Danube Delta-Black Sea system, which is important for both the surrounding regions and Europe.

CONCLUSIONS

The natural and anthropogenic factors leave their mark on the water quality of the Danube Delta ecosystems. The most evident impact of anthropogenic stressors is the influence of climate change (i.e., floods, droughts, geological factors, sediment matrix, etc.). The effects of climate change, particularly extreme weather events, have the potential to abruptly modify the physical-chemical, biological, and heavy metal characteristics of the Danube Delta ecosystems. Instantly, the contaminant load and soil processes may make the water more vulnerable to pollution, consequently affecting its ecological functions.
The water quality status within the Danube Delta region is primarily linked to seasonal fluctuations and, to a lesser extent, spatial variations in the hydrological regime of the Danube River. This study highlighted the influence of the Danube River during the high-water period, which showed a considerable increase in some heavy metal concentrations at certain sampling stations, compared to the low-water period when most of the values were negligible. Although the results were not alarming, being recorded only at specific stations, this study provided evidence that systematic monitoring and assessment of the water quality's status is essential in such deltaic aquatic environments, which are of inestimable ecological and biodiversity value.

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