

# Seasonal and Spatial Variation of Water Quality in the Lumina-Rosu Lakes System, Danube Delta, Romania

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# Abstract

The main aim of the present scientific paper is to assess water quality of the surface water of various lakes located in the Lumina-Rosu interdistributary depression, Danube Delta, Romania. As specific objectives, the paper considered to spot the main potential sources of contamination and their environmental impacts on aquatic ecosystems. Equally, the purpose of the article is to emphasize the importance of monitoring the water quality of the Danube Delta, for preserving these unique natural water resources and their ecosystem services (fresh water, biodiversity, flood control, recreation, nutrient cycling, fishing and other traditional activities, ecotourism). Surface water samples collected from several control sections situated on the main tributaries and canals, as well as from lakes were investigated physically (T° - C, EC - µS/cm, TDS - mg/L, turbidity - NTU units, TSS - mg/L) and chemically (pH - units, DO - mg/L, N-NO2 - mg/L, N-NO3 - mg/L, P-PO43 - mg/L, Chla - mg/L, SiO2 - mg/L, TOC - mg/L, SO4<sup>2-</sup> - mg/L, S<sup>2</sup> - mg/L, H<sup>2</sup>S - mg/L and synthetic detergents - mg/L). Generally, the hydro-physicalchemical characteristics and water quality assessment of the surface waters of the lakes manifest the combined effect of both processes occurred in the catchment (weathering, sediment supply and transport), as well as the in situ lake processes (photosynthesis, sediment mixing, biogeochemical cycling, evaporation, eutrophication, productivity changes). Overall, the physical and chemical characteristics of the sampling sites investigated at high waters of the Danube are quite similar to those measured at low waters. The differences that mainly occurred within the lakes are more related to the limnological variables and the local environmental conditions. Anyway, a significant seasonal variation was noticed in the lakes, during the dry period, when different physical and chemical characteristics appeared to be influenced by high air temperature, lack of precipitation, low water level regime, low dissolved oxygen level regime, all related to climate change effects etc. Moreover, the anthropogenic factor that left its mark on some physical-chemical characteristics of water should not be omitted either. However, the results obtained within this study did not show such alarming values as might have dangerous effects on the investigated aquatic environments. The water quality information within this case study may be used for improving the understanding of the water quality issues and to better coordinate and plan for future monitoring activities in and around the Danube Delta environment. The results will contribute to updating the existing database with relevant information for a sustainable future of the Danube Delta and in similar areas that are subjected to such environmental challenges.

Keywords: water quality, environmental impact, lumina-rosu lakes, Danube delta, Romania

#### Introduction

River-dominated delta's social-ecological systems are vulnerable to natural hazards like droughts, floods, windstorms, sea-level rise, coastal flooding, salinity intrusion etc., [1, 2]. Besides, the effects of industrialization, urbanization and intensification of agricultural practices manifested in the last decades [3, 4, 5, 6] resulted in serious environmental issues, such as pollution. Water quality variations in time and space in river delta systems [7] is one of the most significant issues of water management influencing ecosystem products and services (freshwater supply, productive agriculture and aquaculture, fuel sources etc.) [8, 9], as well as ultimately, human health.

Danube Delta ecosystems are very dynamic, including both fresh and brackish waters, and they are vulnerable to numerous natural and anthropogenic pressures that may considerably change their natural dynamics and have negative consequences on their structure and function [10]. The natural and anthropogenic stressors behave differently on a spatial and temporal scale, determining an oxygen deficiency, nutrient enrichment and eventually, eutrophication [11, 12]. Generally, the quality of the transitional waters

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from the Danube Delta macro-ecosystem depends on the local and regional drivers, *i.e.*, the interaction of the River Danube with the Black Sea, geomorphological characteristics of the aquatic basins, landscape, geological substrate, and climate changes (droughts, floods, variations of river water level, increase in air temperature etc.) (Figure 1).

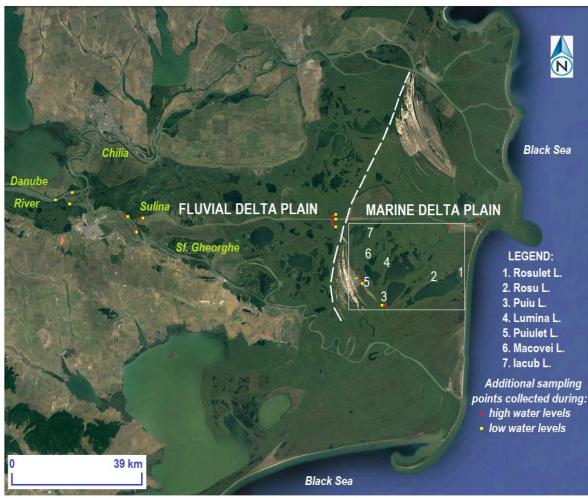


Fig. 1. Map of the Danube Delta Biosphere Reserve showing the location of the Lumina-Rosu interdistributary depression, including lakes Rosulet, Rosu, Puiu, Lumina, Puiulet, Macovei and Iacub, along with additional sampling points collected from the main tributaries and canals.

Most often, water quality may be altered by pollutants transported by the Danube River, originating from direct wastewater discharges and polluted surface runoff. Pollutants and fertilizers from agricultural practices can originate from both upstream and downstream point and non-point sources [13]. Danube Delta ecosystems are protected under national and international agreements as UNESCO World Heritage Sites, Biosphere Nature Reserve and Wetland of International Importance [14]. In these circumstances, it becomes important to assess water quality for a sustainable water management in the Danube River-Danube Delta-Black Sea macro-ecosystem which is a continuously changing environment. Furthermore, the European Water Framework Directive [15] appeals to all Europeans waters (rivers, lakes, transitional and coastal waters) to reach a good ecological status (by 2015, and the latest by 2027). Because these lakes are included within the Danube Delta Biosphere Reserve ecoregion, periodic environmental evaluations are necessary to ensure a superior level of environmental protection to maximize the water quality status, sustainability of the aquatic biodiversity and migratory birds, as well as human health. To achieve the main objectives of the EU WFD, we proposed a case study, looking at water quality of several lakes from the Lumina-Rosu interdistributary depression, Danube Delta, Romania. This new data will bring a better understanding of the natural system and will contribute to better coordinate and plan monitoring activities in and around the Danube Delta. These results will contribute to updating the existing database with relevant information for future actions for a sustainable use of the Danube Delta.

# **Material and Methods**

**Study Area.** The Danube Delta Biosphere Reserve is the largest river delta wetland in Europe shaped by the interaction of the Danube River (flow energy, fluvial input etc.) and the Black Sea (wave energy and littoral current regime, sea-level changes etc.) hydrodynamic environmental processes [16]. Danube Delta comprises two specific geomorphological units: fluvial delta plain, in the west and the fluvio-marine delta plain, in the east and south, separated by the "Jibrieni-Letea-Raducu-Ceamurlia-Caraorman" sand banks alignment [17] (Figure 1). The case study area covers the fluvio-marine delta plain, specifically lakes Rosulet, Rosu (1445 ha), Puiu (865 ha), Lumina (1676 ha), Puiulet (508 ha), Macovei and Iacub (591 ha), belonging to Lumina-Rosu interdistributary depression (Figure 1), which mostly remain in a natural regime. These lakes are connected to the Sulina branch through canals, so they are less influenced by the direct alluvial input (water and sediment) of the river. The major water circulation within the western part of the interdistributary depression is done by the main *Crisan-Caraorman* Canal, which also supply the flow-through lakes as Puiu and Rosu. The northern sector of the depression receives water through *Vatafu-Imputita* Canal. Water

discharge of the flow-through pair of lakes Rosulet-Rosu is done by inlets and outlets as *Busurca* Canal and *Tataru* Canal [18]. Several other channels maintain the supply of the lakes, as: *Rosu-Imputita* Canal, *Tatanir* Canal, *Puiu* Canal, *Mocansca* Canal and *Tataru-Litoral Canal* (Figure 2). The investigated sites represent a good example for the environmental exposure to different types of natural and anthropogenic stressors.

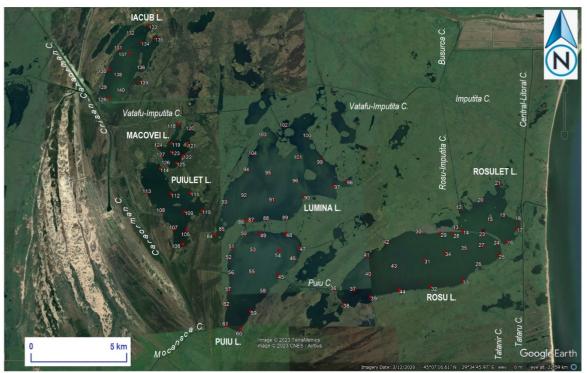


Fig. 2. Enlarged map of the investigated lakes with sampling sites shown in red marks

**Sample Collection.** The water quality status within each lake is controlled mainly, by how much water flows in and out of the lake, being dependent by the natural trend regimes of the Danube River flow, precipitation and evaporation. The sampling of water took place during 2022, with the R/V "Istros" of the National Institute for Marine Geology and Geo-ecology - GeoEcoMar, Bucharest, Romania, within two distinct periods of high and low water levels of the Danube River (Figure 3). During the first campaign (May 2022) a period characterized by high water levels, several water samples from the following lakes were taken: Rosulet (11 samples), Rosu (22 samples) and Puiu (18 samples) (Figure 2). Afterwards, in the second campaign (August 2022), at low water levels, the following lakes were assessed: Lumina (21 samples), Puiulet (10 samples) Macovei (10 samples) and Iacub (13 samples) (Figure 2). It should be mentioned that in 2022 the level of the Danube River in the Romanian sector registered the lowest historical levels, reaching the lowest flow rate in the last 100 years [19].

**Physical and Chemical Analysis.** During this investigation, several water quality parameters as temperature, pH, dissolved oxygen, electrical conductivity and total dissolved solids were measured *in situ*, at each sampling location, using the WTW Multiparameter Field Meter - 3630 IDS. Laboratory measurements and analysis were done using a Hach-DR6000 UV-VIS Spectrophotometer and Hach-2100 Portable Turbidimeter, to determine the levels of nitrite-nitrogen, nitrate-nitrogen, phosphate-phosphorus, silica content, chlorophyl" a", total organic carbon, sulphates, turbidity, total suspended solids, sulfide, hydrogen sulfide and synthetic detergents.

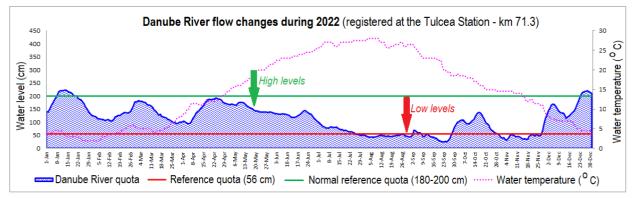


Fig. 3. The variations in the flow of the Danube River during the year 2022.

#### **Results and Discussions**

The water quality assessment was performed mainly in accordance with the nationally approved normative (Order 161/2006) that includes the conditions of certain surface water quality standard classes (Class I-very good; Class II-good; Class III-moderate;

Class IV-poor; class V-bad), as well as other reference standards which can be found in the specific research literature.

The main physical parameters assessed in this study will be discussed further below.

*Water temperature (T°-C)* is influenced by the local climatic conditions, being closely related to the evolution of the air temperature, characteristic of the seasons [20] and the dynamic action of the wind. Thus, the values fell within the limits of the natural variability of the investigated areas. The recorded water temperature values varied within small limits, in the two specific investigation periods. Consequently, during the period of high-water level, the following values were found: control sections (17.4-23.1°C), Rosulet L. (19.3-21.1 °C), Rosu L. (20.7-22.9 °C) and Puiu L. (21.0-23.1 °C). During the time of low-water level, the ranges of variation were the following: control sections (26.70-28.50°C), Lumina L. (24.80-27.10°C), Puiulet L. (26.5-27.5°C), Macovei L. (27.1-30.3°C) and Iacub L. (28.90-31.90°C), intervals which are consistent with the seasonal variations.

*Electrical conductivity (EC- \muS/cm)* measurements carried on water samples showed that they meet Class I (500  $\mu$ S/cm) category (very good) [21]. The values showed that no significant differences were recorded between both specific investigation intervals. During the period of high-water level, the values were relatively low, *i.e.*, control sections (389-404  $\mu$ S/cm), Rosult L. (408-443  $\mu$ S/cm), Rosu L. (374-448  $\mu$ S/cm), Puiu L. (311 -443  $\mu$ S/cm). A similar pattern of low EC values for each location was observed during the time of low-water level: control sections (367-420  $\mu$ S/cm), Lumina L. (326-406  $\mu$ S/cm), Puiulet L. (324-348  $\mu$ S/cm), Macovei L. (318-386  $\mu$ S/cm) and Iacub L. (292-359  $\mu$ S/cm).

*Total dissolved solids (TDS - mg/L)*. The entire series of all analyzed water samples were included in the range of natural variations (0 - 1000 mg/L) [22, 23]. No significant difference occurred neither between the locations nor between the seasons. The following fields of variation were met during the period of high-water level: control sections (195-202 mg/L), Rosulet L. (204-222 mg/L), Rosu L. (187-224 mg/L), and Puiu L. (156-222 mg/L). A similar trend of low TDS values for each location was noticed during the time of low-water level: control sections (184-210 mg/L), Lumina L. (163-203 mg/L), Puiulet L. (162-174 mg/L), Macovei L. (159-193 mg/L) and Iacub L. (146-180 mg/L).

*Turbidity (NTU units)* levels showed a wide range of variation within the investigated water samples. For instance, during the period of high-water level, several samples collected from the control sections localized on the main tributaries (Tulcea-Mm 34.5, Sf. Gheorghe-km 108, Sulina-Mm 33, Sulina-Mm 14, Old Danube Meander-near Mm14, Sulina-Mm 2, Sulina-Mm 0 and Crisan-Caraorman Canal) showed a variability of values that decreased from upstream (Tulcea) to downstream (Sulina). The water samples collected from these control sections are characterized as relatively moderate turbidity waters (>10 NTU), having ranging values (10.1-34.7 NTU). Instead, the lacustrine water samples (Rosulet L., Rosu L. and Puiu L.) are characterized as low turbidity waters (< 10 NTU). The ranges of variation in the lacustrine waters were: Rosulet L. (1.31-2.83 NTU), Rosu L. (1.88-5.10 NTU) and Puiu L. (0.87-9.96 NTU). By contrast, during the time of low-water level, a wide range of variation in the occurrence of relatively higher turbidity level patterns was noticed. This was to be predicted, since it is a response to seasonality, which is triggered by: Danube River low water levels, disruption of bottom sediments and resuspension, summer algal growth etc.). Thereby, the analyzed water samples collected from the main tributaries (Danube-Mm 14, Chilia-km114, Tulcea-Mm 42, Tulcea-Mm 34, Sf. Gheorghe-km 108, Sulina-Mm 33, Sulina-Mm 14, Old Danube Meander-near Mm14, and Crisan-Caraorman Canal) are classified among relatively moderate turbidity waters (>10 NTU), having ranging values (10.60-31 NTU). Subsequently, lakes as Lumina (11.70-54.20 NTU), Puiulet (29.3-55.9 NTU) and Macovei (12.9-42.4 NTU) are characterized as moderate turbidity waters (< 50 NTU). Contrary, Iacub L. (23.20-83.80 NTU) is characterized as a relatively high turbidity water (< 100 NTU).

*Total suspended solids (TSS–mg/L).* TSS values were relatively lower during high waters, in contrast with higher TSS values occurred in all samples investigated during low waters. The majority of samples collected in May and high-water level indicated TSS values (< 40 mg/L) included in the acceptable category of the freshwater environment [24], as follows: control sections (12-39 mg/L), Rosulet L. (3-6 mg/L), Rosu L. (3-10 mg/L) and Puiu L. (3-16 mg/L). Alternatively, much relatively higher TSS contents (> 40 mg/L) were noticed in water samples collected in August and low-water level, as: control sections (18-43 mg/L), Lumina L. (31-78 mg/L), Puiulet L. (50-84 mg/L), Macovei L. (25-53 mg/L) and Iacub L. (32-93 mg/L).

The main chemical parameters will be presented further.

*Water pH (pH units).* The variation range of the pH values determined in all sampling points was relatively narrow, ranging from 7.56 to 9.93 which indicates that the water in the investigated locations corresponded to various categories as: neutral water ((6.5-8.5 pH units), [21], slightly alkaline water (> 8.5 pH units) and alkaline water (> 9 pH units). In this case, the seasonal pattern of pH values for each location measured was not noticed. The ranges of pH variation determined during the high-water level period, were: control sections ((7.68-8.36), Rosulet L. ((8.13-8.93), Rosu L. ((7.90-8.64)) and Puiu L. ((7.72-9.79)). Afterwards, during the low-water level period similar pH variations were noticed, as: control sections ((7.56-8.52)), Lumina L. ((8.27-9.13), Puiulet L. ((8.61-9.15), Macovei L. ((7.57-8.86)) and Iacub L. ((8.49-9.93)). Each of these investigated locations is differently influenced by the natural and anthropogenic factors. In the present case, the relatively higher pH values can be attributed to the local conditions of the transitional environment. However, there are no obvious indications of acidification/alkalinity in the investigated water samples. In general, the pH investigated in the vast majority of freshwater lakes is in the neutral – slightly alkaline range. In transitional environments (lacustrine and brackish waters), high pH values are not unusual, and most often represent the result of several factors such as: microbial activity, microbial sulfate reduction, the degradation process (ammonification), or, the process of water evaporation associated with high concentrations of sodium and magnesium carbonates [25].

**Dissolved oxygen (DO-mg/L)**. Generally, the DO contents measured in all stations varied, for different categories of water quality as: well-oxygenated surface waters (8 mg/L), moderate-oxygenated surface waters (5-7 mg/L) [21], and poor-oxygenated surface waters ( $\leq 5mg/L$ ) [26]. During the high-water level period, the DO variations were comprised in the following intervals, as: control sections (4.1-5.35 mg/L), Rosulet L. (4.53-9.22 mg/L), Rosu L. (3.36-7.94 mg/L) and Puiu L. (4.70-9.70 mg/L). The lowest DO values occurred in both control sections, as well as in some lake locations are probably due to specific local conditions (Figure 4). At low waters, similar or much higher DO contents were noticed in the investigated locations: control sections (5.64-8.01 mg/L), Lumina L. (5.77-8.51 mg/L), Puiulet L. (8.06-10.73 mg/L), Macovei L. (3.39-10.03 mg/L) and Iacub L. (9.19-16.19 mg/L). The amount of DO in the water is facilitated by the dynamic flow regime of the water and the action of the winds. DO concentration discrepancies, including DO pronounced decreases in certain investigated water samples, are probably due to temperature fluctuations, or could be attributable to decomposition of large amounts of organic matter, or increased turbidity levels. For example, the lowering of water levels in lakes is a process that occurs naturally in the summer (dry periods with high temperatures and low water levels of the Danube River, macrophyte vegetation abundances etc.), when the flow of water courses (internal recirculation) through the network of tributaries and canals slows down. As the water moves more slowly, it mixes less

with the air causing DO concentration decreases. The DO lower content triggers acute eutrophication, which affects the vital processes of aquatic life including fish life cycle.

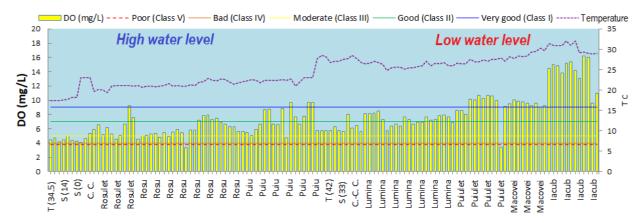


Fig. 4. Seasonal and spatial variation of DO (mg/L) in investigated sampling stations

*Nitrite-nitrogen (N-NO<sub>2</sub><sup>-</sup> - mg/L).* The concentrations of N-NO<sub>2</sub><sup>-</sup> values did not show a great variability, meeting the requirements (0.01 mg/L) settled for the first-class quality (very good). Alternatively, the water quality at specific sampling locations was included in class II category (0.03 mg/L) (good). The ranges of N-NO<sub>2</sub><sup>-</sup> variations within the high-water level period, were the following: control sections (0.0110-0.0280 mg/L), Rosulet L. (0.0100-0.0290 mg/L), Rosu L. (0.0050-0.0330 mg/L) and Puiu L. (0.0080 -0.0520 mg/L). The results showed that no significant differences were recorded between the two seasons. Thereby, the ranges of N-NO<sub>2</sub><sup>-</sup> variations within the dry period, were included into the following intervals: control sections (0.0200-0.0350 mg/L), Lumina L. (0.0050-0.0270 mg/L), Puiulet L. (0.0050-0.0360 mg/L), Macovei L. (0.0050-0.0360 mg/L) and Iacub L. (0.0060-0.0150 mg/L). Nitrites (NO<sub>2</sub><sup>-</sup>) become toxic to aquatic life at relatively low concentrations, therefore a periodical assessment of water quality is mandatory. Among anthropogenic sources in the catchment there are: wastewater treatment plant effluents, industrial effluents, intensive agriculture, intensive urban development, mining activities (impurities and residues) etc.

*Nitrate-nitrogen (N-NO<sub>3</sub><sup>-</sup> - mg/L).* The results of N-NO<sub>3</sub><sup>-</sup> included the tested samples in the category of class I quality (1 mg/L) [21]. The obtained values were very low, and did not exceed the threshold for the first-class quality. As well, there is any significant difference occurring between the seasons. Accordingly, during high waters, the N-NO<sub>3</sub><sup>-</sup> variations were: control sections (0.0110-0.0280 mg/L), Rosulet L. (0.0100-0.0290 mg/L), Rosu L. (0.0050-0.0330 mg/L), Puiu L. (0.0080-0.0520 mg/L). Following that, the ranges of N-NO<sub>3</sub><sup>-</sup> variations within low waters, were the following: control sections (0.0400-0.2900 mg/L), Lumina L. (0.0100-0.0300 mg/L), Puiulet L. (0.0100-0.0400 mg/L), Macovei L. (0.0100-0.1200 mg/L) and Iacub L. (0.0100-0.0200 mg/L).

**Orthophosphate (P-PO** $_{4}^{3-}$  - mg/L). The P-PO $_{4}^{3-}$  levels in the investigated freshwater environments showed a great spatial and seasonal variability (Figure 5). In general, relatively lower values that did not exceed the threshold for the second class of water quality (good) (0.2 mg/L) occurred between the stations. Nevertheless, different investigated water samples, exceed the threshold for the third-class of quality (moderate) (0.4 mg/L), as well as the fifth-class of quality (poor) (> 0.9 mg/L). As a result, the ranges of P-PO $_{4}^{3-}$  variation determined during the high-water level period, were: control sections (0.0633-0.1633 mg/L), Rosulet L. (0.0300-1.2366 mg/L), Rosu L. (0.0266-1.2333 mg/L), Puiu L. (0.0366-0.1766 mg/L). Subsequently, during low-water comparable P-PO $_{4}^{3-}$  variations were noticed, as: control sections (0.0760-1.6860 mg/L), Lumina L. (0.0560-0.7930 mg/L), Puiulet L. (0.0500-0.8500 mg/L), Macovei L. (0.0330-1.7760 mg/L) and Iacub L. (0.0530-1.3630 mg/L). In the present case, it is quite challenging to find out a reasonable explanation for why the concentration of P-PO $_{4}^{3-}$  had peaked or registered such increments, considering the different sampling location where the increments occurred. Diffuse source of phosphate contamination may come from both natural origins (atmospheric deposition, natural decomposition of rocks and minerals, dissolution of soluble inorganic materials, decomposition of plant or animal biomass, sedimentation etc.), as well as from human activities, which contribute to domestic, agricultural and/or industrial contamination. Therefore, continuous monitoring of water quality is necessary, since higher concentrations of phosphates, represent a risk for the normal functioning of aquatic ecosystems, leading to eutrophication (excessive growth of benthic algae or other aquatic species), oxygen deficiency and the reduction of biodiversity.

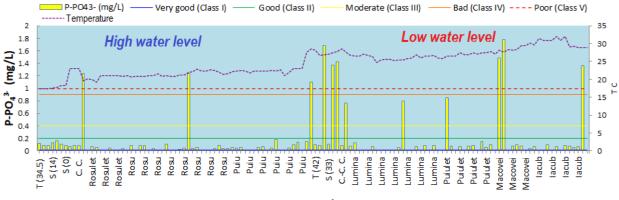


Fig. 5. Seasonal and spatial variation of P-PO43- (mg/L) in investigated sampling stations

*The chlorophyl" a" (Chla - \mu g/L).* Chlorophyll as a measure of algal (phytoplankton) biomass in the investigated water samples showed clearly a seasonal variability. The results of the samples collected during the high hydrological regime, indicated lower values of Chla content below the threshold for first-class quality category (very good) (25  $\mu g/L$ ). The variation ranges were relatively narrow, as follows: control sections (4.11-16.08  $\mu g/L$ ), Rosulet L. (2.25-3.86  $\mu g/L$ ), Rosu L. (1.71-11.89  $\mu g/L$ ) and Puiu L. (1.22-13.00  $\mu g/L$ ). This pattern of Chla lower values obtained at high waters (May 2022) was somehow predictable since chlorophyll "a" concentration was closely related to local specific environmental factors that control the development of phytoplankton, such as lower temperature, significant precipitation. In August, Chla displayed a greater variability: control sections (5.36-53.07  $\mu g/L$ ), Lumina L. (37.36-121.09  $\mu g/L$ ), Puiulet L. (90.45-142.94  $\mu g/L$ ), Macovei L. (49.62-125.66  $\mu g/L$ ) and Iacub L. (74.22-301.55  $\mu g/L$ ). Previous studies in the area [27, 28] have described the seasonal variability of Chla, with a minimum in winter and a maximum towards the end of summer. Nutrient concentrations in surface water are higher in winter and spring than in summer, but high summer temperatures lead to increased rates of remineralization, which can subsequently serve as a source of nutrients for primary production throughout the warm season [29], allowing phytoplankton to use and benefit from all their potential by growing in high concentrations. Chlorophyll concentrations in lakes are subject to several interacting factors, involving climatic conditions, lake depth, nutrient inputs, mixing regime, within the watershed.

Silica content (SiO<sub>2</sub> - mg/L). Silica is a sort of colloidal material (< 0.4 µm) considered an important nutrient for aquatic vegetation as phytoplankton algae (diatoms), as well as, macrophytes. Silica content, in addition to nutrient information, is a proxy indicator related to potential eutrophication. Within this study, the dissolved silica concentration showed a variability of values between the investigated stations. Anyways, the obtained values were low, bellow the conventional limit of rivers and lakes variation (1-30 mg/L) [30]. Furthermore, there is any considerable difference occurring between the seasons. As a result, during the high-water period, the SiO<sub>2</sub> variations were comprised in the following intervals, as: control sections (0.60-3.80 mg/L), Rosulet L. (0.43-2.82 mg/L), Rosu L. (0.29-1.71 mg/L), Puiu L. (0.266-2.283 mg/L). Next, the ranges of SiO<sub>2</sub> variations within the low-water period, were the following: control sections (0.58-3.35 mg/L), Lumina L. (1.57-4.21 mg/L), Puiulet L. (3.12-5.1 mg/L), Macovei L. (2.13-4.61 mg/L) and Iacub L. (2.14-3.99 mg/L)

*Total organic carbon (TOC - mg/L).* TOC is a quantitative measure of the organic matter content (dissolved and particulate organic substances) in water, that provide an indication of potential organic contamination [31]. The obtained results were related to typical limits of natural water variations (1-30 mg/L) [32]. In the high-water level period, the TOC levels showed some variability. The majority of values were low, and did not excessively transcend the typical limits of natural water variations, excepting three sampling sites from lakes linked to excessive amounts of organic loading (more than 30 mg/L) (*i.e.,* Rosu L:DD22-42=82.5 mg/L; Puiu L:DD22-45=88 mg/L; Puiu L:DD22-62=88 mg/L). In these stations, alluvial contents of inputs and outputs between lakes, as well as local environmental conditions (redistribution and remineralization of sedimentary organic carbon) are likely to contribute to the higher TOC concentrations. Variations occurred within the wet period were comprised in the following intervals, as: control sections (4.31-22.9 mg/L), Rosulet L. (12.2-30.1 mg/L), Rosu L. (0.89-82.5 mg/L), Puiu L. (13.6-88 mg/L). Next, within the dry season and low-water level period, any notable difference occurring between the stations was indicated. The values were below the established limit (< 30 mg/L), such as: control sections (3.31-11.80 mg/L), Lumina L. (9.19-14.20 mg/L), Puiulet L. (0.48-23.1 mg/L), Macovei L. (8.16-14.3 mg/L) and Iacub L. (10.50-24.30 mg/L).

Sulphates (SO<sub>4</sub><sup>2-</sup> mg/L). Sulphates are commonly found in the environment and may occur in natural waters and wastewaters as dissolved sulphate ion (SO<sub>4</sub><sup>2-</sup>). The origin of SO<sub>4</sub><sup>2-</sup> in freshwater environments implicate natural sources (mineral weathering, volcanic activity, decomposition and combustion of organic matter, oxidation of sulphides etc.), and anthropogenic inputs (acid mine drainage, fertilizer leaching from agricultural soils, wetland drainage, agricultural and industrial wastewater runoff). Cumulative SO<sub>4</sub><sup>2-</sup> levels in freshwater ecosystems predispose to several biogeochemical process disturbances. In this case, there were not noticed significant seasonal differences in trends between the investigated stations. The results revealed that there were relatively increasing trends of SO<sub>4</sub><sup>2-</sup> concentrations during high waters (May 2022), while decreasing level trends occurred during low water (August 2022). Anyway, the majority of results were below the threshold for the first-class quality (60 mg/L). In consequence, during the high-water, the SO<sub>4</sub><sup>2-</sup> concentrations were included in the following intervals, as: control sections (25-70 mg/L), Rosulet L. (34-41 mg/L), Rosu L. (29-39 mg/L), Puiu L. (28-79 mg/L). Afterwards, the ranges of SO<sub>4</sub><sup>2-</sup> concentrations within low-water level period, were the following: control sections (27-37 mg/L), Lumina L. (23-30 mg/L), Puiulet L. (22-28 mg/L), Macovei L. (25-43 mg/L) and Iacub L. (15-31 mg/L).

Sulfide (S<sub>2</sub><sup>-</sup> - mg/L) and hydrogen sulfide (H<sub>2</sub>S - mg/L). Knowing the values of these parameters (S<sub>2</sub><sup>-</sup> and H<sub>2</sub>S) is extremely important in evaluating the degree of pollution, expressing the level of load with sulphureous bacteria, the lack of oxygen and the occurrence of anaerobic processes from wastewaters. The analyzes performed for these indicators showed that the tested water samples have a low content of both S<sup>2-</sup> and H<sub>2</sub>S with values below the maximum permissible values (0.5 mg/L) [33].

*Synthetic detergents (mg/L)*. Lately, the use of synthetic detergents is increasing, as a result of increased urban development. Determination of the synthetic detergent concentrations in surface waters is essential since they are considered an important contaminant with serious direct and indirect impact to natural ecosystems affecting flora and fauna species. The most frequent source of detergents in aquatic environment comes from different origins as residential wastewaters, and from specific industries. The concentration of synthetic detergents (mg/L), tested in the investigated water samples, showed a great variability (Figure 6).

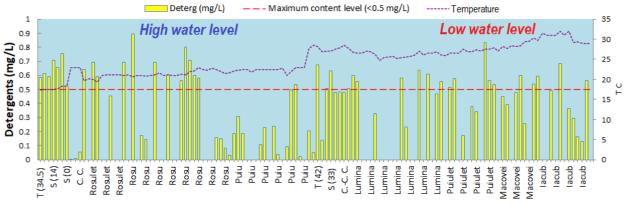


Fig. 6. Seasonal and spatial variation of synthetic detergents (mg/L) in investigated sampling stations

The results revealed that there were increasing and decreasing trends at different stations in two different seasons, without a particular significance. Several water samples have values below the recommended threshold limit values (< 0.5 mg/l) [31]. Oppositely, various disparate water samples exceeded the imposed limits for good water quality. As a result, during the high-water level period, the detergent concentrations were included in the following intervals: control sections (0.001-0.756 mg/L), Rosulet L. (0.456-0.691 mg/L), Rosu L. (0.0850-0.8930 mg/L), Puiu L. (0.0220 -0.5320 mg/L). Next, within the low-water period, the ranges of detergent concentrations were: control sections (0.05-0.67 mg/L), Lumina L. (0.23-0.63 mg/L), Puiulet L. (0.17-0.83 mg/L), Macovei L. (0.25-0.60 mg/L) and Iacub L. (0.13-0.68 mg/L).

#### Conclusions

The study aimed to decipher the influence of natural and anthropogenic stressors and their impact on several representative ecosystems that are included in the DDBR area, a region with great national and international ecological value. The results indicated that the physical-chemical characteristics of the surface waters investigated in this study were mainly controlled by the seasonal limnological variations, and less strongly by the seasonal and spatial variations in the water level fluctuation of the Danube River. It is true that the river is the main controlling factor for the majority of hydrological and bio-geo-chemical processes during the one year, especially related to the dissemination of water to the lacustrine inter-distributary areas. The river being in a continuous movement, has the capacity to dilute, transport and dissolve several alluvial constituents and potential contaminants faster than in the lacustrine ecosystems. The lakes are also dynamic ecosystems, continuously evolving over time in response to their changing environment. In conclusion, the negative impacts of a decreased water flow of the Danube, the lowest level in 100 years, did not severely impact the investigated areas. This is most probably due to the adaptive capacity and resilience of delta's wetlands and aquatic environments.

In this context, the physical-chemical characteristics of the sampling sites investigated within the high waters are quite similar to those stations surveyed during the low waters of the Danube River. The differences that mainly occurred within the lakes are more related to the limnological variables and the local environmental conditions. Anyway, the significant seasonal variation was noticed in the lakes during the dry period when different physical and chemical characteristics appeared to be enhanced by high air temperature, lack of precipitation, low water level, low dissolved oxygen level regime etc. Moreover, the anthropogenic factor that left its mark on some physical-chemical characteristics of water should not be omitted either. However, the results obtained within this study did not show such alarming values as might have dangerous effects on the investigated aquatic environments. The water quality information within this case study may be used for improving the understanding of the water quality issues and to better coordinate and plan future monitoring activities in and around the Danube Delta environments. The obtained results will contribute to updating the existing database with relevant information for sustainable Danube Delta future conservative actions in similar areas that are subjected to environmental challenges.

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## References

- J.P.M. Syvitski, A.J. Kettner, I. Overeem, E.W.H. Hutton, M.T. Hannon, G.R. Brakenridge, J. Day, C. Vorosmarty, Y. Saito, L.Giosan and R.J. Nicholls, "Sinking deltas due to human activities". Nature Geosci, 2, pp. 681-686 (2009), https://doi.org/10.1038/ngeo629
- 2. L. Giosan, J. Syvitski, S. Constantinescu and J. Day,"Climate change: Protect the world's deltas", Nature Comments, 516, pp. 31-33 (2014).
- 3. R. J. Nicholls, P. P. Wong, V. Burkett, C. D. Woodroffe and J. Hay,"Climate change and coastal vulnerability assessment: scenarios for integrated assessment" Sustain. Sci., 3, pp. 89-102 (2008).
- 4. M. R. Lowi,"Rivers of Conflict, Rivers of Peace", Journal of International Affairs, 49(1), pp.123, (1995).
- V. Lauria, I. Das, S. Hazra, I. Cazcarro, I. Arto, S. Kay, P. Ofori-Danson, M. Ahmed, M.A.R.H. Hossain, M. Barange and J.A. Fernandes, "Importance of fisheries for food security across three climate change vulnerable deltas", Sci. Total Environ., 640-641, pp. 1566-1577 (2018), https://doi: 10.1016/j.scitotenv.2018.06.011
- R. J. Nicholls, S. Brown, P. Goodwin, T. Wahl, J. Lowe, M. Solan, J.A. Godbold, I.D. Haigh, D. Lincke, J. Hinkel, C. Wolff and J.-L. Merkens, "Stabilization of global temperature at 1.5°C and 2.0°C: implications for coastal areas" Phil. Trans. R. Soc. A, 376 (2119), pp. 20160448, (2018), https://doi: 10.1098/rsta.2016.0448.
- 7. R. Costanza, M. Kemp and W. Boynton, "Scale and biodiversity in estuarine ecosystems", in Biodiversity loss: Economic and Ecological issues, edited by C. Perrings, Karl-Göran Mäler, C. Folke, and Bengt-Owe Jansson, Cambridge: Cambridge University Press, pp. 84-125, (1995)
- 8. C. Savage, S. F. Thrush, S.M. Lohrer and J. E. Hewitt, "Ecosystem services transcend boundaries: estuaries provide resource subsidies and influence functional diversity in coastal benthic communities". PLoS ONE, edited by Senjie Lin, 7, (8), p. e42708 (2012), https://doi.org/10.1371/journal.pone.0042708
- W.N. Adger, H. Adams, S. Kay, R. J. Nicholls, C.W. Hutton, S.E. Hanson, Md. M. Rahman and M. Salehin, "Ecosystem Services, Well-Being and Deltas: Current Knowledge and Understanding", in Ecosystem Services for Well-Being in Deltas, edited by R. Nicholls, C. Hutton, W. Adger, S. Hanson, M. Rahman, M. Salehin, Palgrave Macmillan, Cham., pp. 3-27 (2018), https://doi.org/10.1007/978-3-319-71093-8\_1
- 10. N. Panin,"Global changes, sea level rise and the Danube Delta: risks and responses", Geo-Eco-Marina, 4, pp. 19-29 (1999).
- L. D. Galatchi, and M. Tudor,"Europe as a source of pollution The main factor for the eutrophication of the Danube Delta and Black Sea", in Chemicals as Intentional and Accidental Global Environmental Threats, edited by L. Simeonov and E. Chirila, NATO Security through Science Series, Springer, Dordrecht, pp. 57-63 (2006), https://doi.org/10.1007/978-1-4020-5098-5\_5,
- 12. L. Török, Z. Török, E. M. Carstea and D. Savastru, "Seasonal Variation of Eutrophication in Some Lakes of Danube Delta Biosphere Reserve" Water Environ Res., Jan 1; 89(1), pp. 86-94 (2017), https://doi: 10.2175/106143016X14733681696248, PMID: 28236829.
- 13. C. Gasparotti,"The Main Factors of Water Pollution in Danube River Basin" Euro Econ., 33, pp. 93-106, (2014).
- 14. Ramsar Convention, "Convention on Wetlands of International Importance especially as Waterfowl Habitat", Ramsar (Iran), 2 February 1971, UN Treaty Series No. 14583, As amended by the Paris Protocol, 3 December 1982, and Regina Amendments, 28 May 1987, Ramsar Convention on Wetlands, Gland, Switzerland, (1987).
- 15. European Union Council, "Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy", Official Journal of the European Communities, 43(L327), pp. 1-73 (2000).
- 16. N. Panin, L. Tiron Dutu and F. Dutu,"The Danube Delta: An overview of its Holocene evolution", Méditerranée, 126, pp. 37-54 (2016).
- 17. N. Panin, "Danube Delta: Genesis evolution and sedimentology", GeoEcoMarina, 1, pp. 11-34, (1996).
- 18. B.V. Driga,"Danube Delta. Water circulation system", Institutul de Geografie al Academiei Române, Editura Casa Cartii de Stiinta, Cluj Napoca, Romania, pp. 256 (2004), [in Romanian
- 19. https://www.afdj.ro
- 20. https://www.accuweather.com/ro/ ro/tulcea/

- 21. Order no. 161/2006, "Normative concerning the classification of surface water quality to establish the ecological status of water bodies" (Romanian Order MEWM no. 161/2006), Annex C-Elements and physico-chemical quality standards in water, published in Romanian Official Monitor, part I, 511 bis, from 13th of June (2006) [in Romanian
- 22. J.H. Lehr, T.E. Gass and W.E. Pettyjohn, "Domestic Water Treatment", McGraw Hill Book Co.; New York, NY, USA, pp. 272 (1980).
- 23. J. De Zuane, "Handbook of Drinking Water Quality" (2nd ed.), John Wiley and Sons, ISBN 0-471-28789-X, pp. 575 (1997).
- 24. ANZECC 2000 Guidelines,"Australian and New Zealand Guidelines for Fresh and Marine Water Quality", http://www.mfe.govt.nz/fresh-water/tools-and-guidelines/anzecc-2000-guidelines
- 25. W.D. Grant,"Introductory chapter: Half a Lifetime in Soda Lakes", in Halophilic Microorganisms, edited by A. Ventosa, Springer-Verlag Berlin Heidelberg, pp.17-31 (2004).
- 26. https://www.niwa.co.nz
- 27. F.N. Güttler, S. Niculescu, F.Gohin, "Turbidity retrieval and monitoring of Danube Delta waters using multi-sensor optical remote sensing data: An integrated view from the delta plain lakes to the western–northwestern Black Sea coastal zone", Remote Sensing of Environment, 132, pp. 86–101, (2013). https://doi.org/10.1016/j.rse.2013.01.009
- 28. A.M. Constantinescu, "Reconstructing changes in sediment input from the Danube into the Black Sea", PhD Thesis, pp. 249 (2020).University of Stirling, United Kingdom. http://hdl.handle.net/1893/31886
- 29. M.W. Kemp and W.R. Boynton, "Spatial and temporal coupling of nutrient inputs to estuarine primary production: the role of particulate transport and decomposition", Bulletin of Marine Science, 35, pp. 522–535, (1984).
- D. Chapman, "Water Quality Assessments, A Guide to Use of Biota, Sediments and Water in Environmental Monitoring", Second Edition, Published on behalf of UNESCO, WHO, UNEP. E /FNSPON. London. Great Britain, University Press, Cambridge, pp. 626 (1996).
- 31. M. Chen, G. Zeng, J. Zhang, P. Xu, A. Chen and L. Lu, "Global Landscape of Total Organic Carbon, Nitrogen and Phosphorus in Lake Water", Sci Rep, 5, 15043 (2015), https://doi.org/10.1038/srep15043
- 32. https://www.for.gov.bc.ca/hts/risc/pubs/aquatic/interp/interp-01.htm
- 33. GD 188, Government Decision No. 188/ 20.03.2002 for approving the rules on the conditions of discharging wastewater into the aquatic environment as amended by HG 352/11.05.2005, Romanian Official Monitor, No.187, 20 March 2002, (2002), [in Romanian].