WATER QUALITY ASSESSMENT IN A RIVER-SEA TRANSITION ZONE. RECENT RESULTS FROM DISTINCT AQUATIC ENVIRONMENTS OF THE DANUBE DELTA BIOSPHERE RESERVE AREA, ROMANIA

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Abstract. This study aims to compare the water quality in distinct aquatic systems, situated in different representative areas of the Danube Delta Biosphere Reserve, Romania - a unique natural area of national and international importance. These areas are largely populated by a vast diversity of aquatic organisms, including rare species of plants, animals, aquatic birds and fish, many of them being endangered species. Any imbalances in these ecosystems, owing to natural and human-induced changes in the water quality may affect aquatic life. In this sense, water samples were collected from the surface layer of a freshwater environment (i.e., Babina, Rădăcinoasele and Ciorticut lakes), as well as from mixed environments (i.e., Musura and Sahalin Bays) during August 2018. The following water guality indicators were considered: temperature, pH, dissolved oxygen, nitrite-nitrogen, nitrate-nitrogen, ammonium-nitrogen, orthophosphates, chlorophyll a, total organic carbon, silica, electrical conductivity, total dissolved solids, sulphates, turbidity, total suspended solids, transparency and oxido-reduction potential. These parameters were analysed and discussed in relation to national and international environmental standards. Maps of spatial distribution of some quality parameters were obtained, showing variation as a result of local specific environmental circumstances, which change in time and space. These results suggest that the environmental indicators measured in drought conditions and low water levels showed generally good to moderate water quality status, in spite of many local triggers associated with natural and anthropogenic causes that can alter or impair the quality of the water. After this investigation performed during August 2018, it can be appreciated that the analysed water samples maintain appropriate levels that are suitable for the ecological status of the investigated aquatic systems, and, as expected, the aquatic habitats are ecologically balanced environments. The paper recommends the routine monitoring and periodical testing of the water quality to create and develop a database to reflect the natural variation and humanrelated implications for water quality within these areas, and their short, medium and long-term evolution trends. The present work is important for water quality assessment to detect changes in water quality under human pressures and climate change and to protect and conserve these natural water resources.

Abbreviations: Ammonium-Nitrogen (N-NH₄⁺: mg/L), Before Present (BP years), Chlorophyll *a* (Chla: μ g/L), Danube Delta Biosphere Reserve (DDBR), Dissolved Oxygen Saturation (DO: %), Dissolved Oxygen Concentration (DO: mg/L), Electrical Conductivity (EC: μ S/cm), European Union (EU), Global Positioning System (GPS), Hectares (ha), Nitrate-Nitrogen (N-NO₃⁻: mg/L), Nitrite-Nitrogen (N-NO₂⁻: mg/L), Orthophosphates (P-PO₄³⁻: mg/L), Oxido-Reduction Potential (ORP: mV), Silica (SiO₂: mg/L), Sulphates (SO₄²⁻⁻: mg/L), Temperature (t: °C), Total Dissolved Solids (TDS: mg/L), Total Organic Carbon (TOC: mg/L), Total Suspended Solids (TSS: mg/L), Turbidity (NTU units), Water Depth (m), Water Framework Directive, (WFD), pH: (units), Water Transparency/Secchi Disc Depth (SDD: m), World Health Organization (WHO).

Key words: Danube Delta, environment assessment, brackish water, freshwater, physical-chemical characteristics, water quality

INTRODUCTION

Water quality is a global environmental issue due to several interconnecting factors. Generally, the quality of natural waters depends on both interrelated natural and human factors. The natural factors include the geological setting, flow regime, climate regime and associated changes, watershed, topography, soil, vegetation, biological processes etc. The anthropogenic factors include the main sources of contamination, as agricultural activities and land use, domestic and industrial pollution etc. (Hering *et al.*, 2015).

Aquatic systems represent indispensable resources for biodiversity and ecosystem stability, as well as for human needs, therefore it is important to survey and control the water quality. In addition to their basic uses as water resource, energy, transportation, tourism and fishing, the healthy aquatic ecosystems provide multiple ecosystem services (Ostrom *et al.*, 1993; Heal, 2000; Falkenmark, 2003) as basic elements of survival, improve community health, enhance security, and support good social relations. For instance, deltas and/or lagoons support biodiversity and provide recreation, natural protection and buffering of inland areas from floods and storms etc. (Russi *et al.*, 2013; Newton *et al.*, 2018). Water is a vital component in maintaining the healthy functioning of ecosystems while keeping them resilient to change (Costanza *et al.*, 1997).

Assessment of water quality is an integral part of a scientifically based routine environmental monitoring program. Water quality degradation is an imperative problem which is increasing in magnitude due to humanrelated activities (Sala et al., 2000; Kennish, 2002; Steffen et al., 2007; Ellis and Ramankutty, 2008; Ellis, 2011), that in turn contributes to climate change (Gleick, 1989; Crossland et al., 2005; Eisenreich, 2005; Milly et al., 2008; Ferguson and Maxwell, 2012) having negative consequences on natural waters as river, lakes, transitional and coastal waters. The Water Framework Directive (European Union Council -WFD, 2000) has established a distinct framework for the management, protection, and improvement of the quality of water resources, to which all member states across the EU have to join, aiming to achieve good status in all open water bodies (such as wetlands, rivers, and lakes). Many studies address pollution of water sources and investigate the quality of natural waters that are impaired with a wide range of contaminants (Anderson et al., 2002; Schulz, 2004; Meals et al., 2010; Reza and Singh, 2010; Dai et al., 2011; Sharpley et al., 2013). Moreover, eutrophication and harmful algae blooms cause a decrease in water quality (Newton et al., 2014).

Several studies have highlighted that the anthropogenic factors and climate change are increasing the environmental risk in many deltas of the world (Overeem and Syvitski, 2009; Syvitski *et al.*, 2009; Renaud *et al.*, 2013).The growing awareness of the negative impacts of these anthropogenic stressors has attracted significant interest in the study of various contaminants in the aquatic environment. The anthropogenically-derived water pollution has a major impact within aquatic ecosystems (Petrovic *et al.*, 2002; Sabater, 2008; Heathwaite, 2010), leading subsequently to reduce water species biodiversity (Helfrich *et al.*, 2009; Stevenson and Sabater, 2010; Stevenson, 2011), as organisms and vegetation that survive in water (MacFarlane and Burchett, 2000; Dudgeon, 2013), and/or to human health hazards (Ekpo *et al.*, 2013).

The current study examines some of the important water quality parameters, aiming at assessing the quality of water and identifying the interrelationship among the physical chemical parameters investigated in various aquatic systems in the *DDBR* (Danube Delta Biosphere Reserve) area. It also highlights the need of water quality monitoring on a regular basis and contributes with relevant information/data in order to sustain the water bodies quality, on short-, medium- and long-term.

DDBR is situated in south-eastern Romania, where the Danube River reaches the Black Sea (Gâștescu, 2007). With an area of around 580,000 ha surface, DDBR is a vast lowland that incorporates the two major hydrographic compartments, namely the Danube Delta and Razim-Sinoie Lagoon Complex. The interaction of the river's flow and the particular conditions characterizing the coastal area created a dynamic environment, a unique ecosystem supporting freshwater, brackish and saltwater communities. The delta is crossed by the main arms of the Danube River i.e., Chilia, Sulina and Sf. Gheorghe, as well as by the numerous channels, some of which are clogging, some are active, while others are only being drained by the flow of the Danube River. Alongside the hydrographic network of rivulets, channels and canals, almost the whole delta is spotted with numerous lakes, marshes and low-lying swamps (Gâștescu and Știucă, 2008).

The DDBR has a triple international status. UNESCO placed the DDBR area on its World Cultural and Natural Heritage List, being as well ranked as a Biosphere Nature Reserve. In addition, this area is designated as a Wetland of International Importance (Ramsar Site) under the UN Convention on Wetlands (Ramsar Convention, 1987).

Due to its importance, in terms of national and international heritage, it becomes imperative to assess the environmental quality status of DDBR, by integrating physical-chemical, biological and sedimentological data. Fragile and unique ecosystems of the DDBR area that provide a habitat for many species of plants and animals (Rose, 1992; Rose and Taylor, 1993) may be threatened by the upstream contamination (Kyle, 2006) of the Danube River, or as a result of local pollution sources and beyond. The negative impact of the hydro-technical works (through the lower Danube River) were investigated in the DDBR wetlands, considering a lot of aspects related to environmental changes (Wilson and Moser, 1994; Vădineanu et al., 1997; Panin et al., 1999; Romanescu, 2013; Oaie et al., 2015; Tiron Dutu et al., 2019), coastal erosion (Stănică et al., 2007; Stănică, 2012) and habitat degradation (Pavel et al., 2017). Other studies have approached some important inter-distributary depressions of the Danube Delta or perimeter areas in the lagoon southern sector (Rădan et al., 1997; Rădan et al., 2000; Friedrich et al., 2003; Postolache, 2006; Coops et al., 2008; Durisch-Kaiser et al., 2011; Romanescu et al., 2018), which have been evaluated in terms of environmental conditions.

MATERIALS AND METHODS

STUDY AREA

The Danube Delta is divided into three main depositional facies: delta plain, delta front and pro-delta (Panin, 1989). Delta plain is divided into two main regions, the upper or *fluvial delta plain*, to the west, a labyrinth of channels, and lakes, separated mainly by thick reed beds (Oostberg *et al.*, 2000) and the lower, *marine delta plain* to the east. The two units are separated by the Initial Spit (11700-9800 years BP) *i.e.*, Jibrieni – Letea – Caraorman – Sărăturile – Perişor – Lupilor (Panin, 1983; Panin *et al.*, 1983; Panin, 1989). The former unit comprises the active delta, with sand bars, beach areas and marginal lagoons.

This research was carried out for the determination of several key physical-chemical water quality parameters in three different sampling sites located in the *DDBR* area (Fig. 1), *i.e., Babina, Rădăcinoasele and Ciorticuț* lakes, belonging to a deltaic inter-distributary depression (Matița-Merhei), as well as *Musura* Bay and *Sahalin* Bay that belong to the coastal transition zones, between the Danube River environments and the Black Sea.

The *Babina*, *Rădăcinoasele and Ciorticuț* lakes are situated further from the main Danube River water and sediment supply, being connected to the main branches by a network of channels. Conversely, *Musura* Bay and *Sahalin* Bay are situated in a highly dynamic environment, in the transition area between the fresh and brackish water, being the interface between the river outflows and the sea, with which is directly connected *via* narrow or open outlets that vary in form, dimensions and locations. A brief description of the sampling sites is presented below.

■ Babina, Rădăcinoasele (Corciuvatele) and Ciorticuţ (Dracului) lakes belong to the Matița-Merhei interdistributary depression, located between Chilia and Sulina branches, and included within the *fluvial delta plain* (Fig. 1).

Babina L. (338 ha) is a shallow freshwater lake, belonging to the category of lakes with a large surface and relative active changes of waters, including a secondary hydrographic network (Gâştescu and Ştiucă, 2008). In this sub-unit, which is placed between Chilia and Sulina branches, the connected network of streams, channels and canals are Eracle, Lopatna, Dovnica, Răducu, Bogdaproste, Sulimanca, Roşca and Căzănel (Bondar and Panin, 2001; Năstase and Năvodaru, 2008).

Rădăcinoasele L. is part of the less extended category of lakes. It is located in the north-eastern part of the Babina Lake, and in the southern part of the Ciorticuţ Lake. The water transfer through the hydrographic network is done directly through *Babina* Lake.

Ciorticuț L. has a less extended area that *Rădăcinoasele*. The water exchange with *Rădăcinoasele* Lake is done through underwater vegetation in its southern part.

The water level in the *Babina*, *Rădăcinoasele*, and *Ciorticuț* lakes depends on the Danube river supply, as well as on

precipitation inputs. The major environmental threat to the conservation of these lake ecosystems is the progressive filling up of the reservoirs by particulate organic material, as well as the abundance of emergent aquatic vegetation. Another particularity of these lakes is represented by the banks and unconsolidated lake shorelines made up of growing reed (Phragmites australis) and bulrush (Typha latifolia) vegetation. This aspect was also emphasized by Vădineanu et al., (1992) who asserts that characteristics as their shallowness, large surface area and absence of firm and high borders, makes these lakes to become vulnerable to ecological effects of climate fluctuations (*i.e.*, light, temperature, wind strength and frequency). Due to the highly hydrodynamic natural conditions and similar natural changes of these lake shores, made up of floating vegetation, these three connected lakes can be considered one unit.

■ **Musura Bay** is a shallow semi-enclosed bay (about 1 - 2 m) with low salinity (1-5‰), located in the delta front, (Stănică *et al.*, 2007), namely in the area where Chilia and Sulina arms discharge into the Black Sea, with the tendency for further transformation into a lagoon (Fig. 1).

Geomorphologically, the Musura canal and Musura Bay are quite recent, and they were formed in the first half of the 20th century, by depositional alluvial processes, between the delta of Chilia and Sulina. At that time, the bay had a wide opening towards the sea (13 km) and depths over 12 m, therefore the water biocenosis met similar favourable marine condition. The recent geomorphological evolution of the Musura Bay triggered by the alluvial deposition and the rapid advancement of Chilia secondary delta in the northern part of the bay, including the construction of a new channel (9 km) at the mouth of Sulina branch (Stănică *et al.*, 2007), had an impact on accelerated narrowing of the bay's mouth. Consequently, in 2005, the opening towards the sea recorded 5 km, while the depth decreased to 2 m (Zinevici *et al.*, 2006).

The ecological long-term monitoring of the area reported the relative accelerated characteristics and spatial-temporal dynamics. The active and long-term changes generated a gradual shift from marine gulf stage to a half-enclosed bay, with many freshwater characteristics. The environmental variables, as decreasing trend in the level of water, the progressive reduction of the salinity (*i.e.*, 1942-12‰; 2005-0.18‰) and the geomorphological changes, have led to the establishment and proliferation of the typical freshwater vegetation. Therefore, the structure and functional diversity of plankton communities (*e.g.*, phyto-, zoo- and bacterioplankton) interchanged (Zinevici *et al.*, 2006; Zinevici and Parpală, 2007; Ionică *et al.*, 2008).

The major environmental issue related to Musura Bay is represented by the progressive clogging of this area, due to rapid sedimentation (Panin and Overmars, 2012; Stănică *et al.*, 2007; Stănică *et al.*, 2013). Most likely, in time, this bay tends to be sealed off due to an accelerated siltation process (Panin and Overmars, 2012).



Fig. 1. Sitemap location of the study area, including GPS sampling sites, marked by red dots (Base map: https://zoom.earth/, https://earth.google.com/web/ 2018)

■ **Sahalin Bay** is a shallow marginal body of water (about 1-2 m) located in the area where Sf. Gheorghe arm flows into the Black Sea, south of its mouth (Fig. 1).

The abundant supply of alluvial material brought by the branch into the sea has created a sandy barrier which extends over several kilometres (Panin, 1996). This sandy barrier partially tends to close off the Sahalin Bay. The aquatic area between the initial shoreline and the sandy barrier is a bay of several kilometres (in length and width), with low salinity (0-13.5‰) (GeoEcoMar, PN 09-41 03 04, phase 22/2015, unpublished data). Long-term monitoring identified significant coastal morphological changes in the structure and function of this ecosystem, especially throughout the past decades. The lake-forming process, by the merging of the Sahalin Island with the coast, continues even if the island is now a peninsula (split) (Gâștescu and Grigoraș, 2014). The dynamics of the Sahalin area are controlled both by longshore and crossshore processes. The result is a continuous elongation (in average 100-140m/year) of the spit which is also fed by alongshore sediment transport from the north and the river sediment supply (Sf. Gheorghe branch, also with

a significant discharge of alluvia), but the main cause of spit's lateral migration (over a 20m/year on average) is the over wash (Dan *et al.*, 2009).

5 km

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HYDROLOGICAL AND CLIMATE CONDITIONS

Water discharge, sediment transport and dissolved loads in the rivers considerably influence the geomorphology of the river channels, alluvial plains and deltas, and deliver numerous terrestrial materials to seas/oceans, that sustain the coastal and marine ecosystems (Cerda, 1998).

The Danube River carries to the Black Sea large amounts of allochthonous sediments from the upper, intermediate and lower Danube River catchment areas which are partially dispersed throughout the fluvial-deltaic lakes. Instead, the coastal areas can be supplied, in addition, with allochthonous sediments transported by wind currents. Considering that the Danube Delta fed by the water and sediment of the Danube, through its main channels to the coastal area, is important to mention its temporal variations during the year 2018 (Fig. 2), and its interrelations within and between investigated aquatic systems. Irina Catianis, Dan Vasiliu, Adriana Maria Constantinescu, Iulian Pojar, Dumitru Grosu – Water quality assessment in a river-sea transition zone



Fig. 2. Annual variations of the Danube River water level recorded at the Tulcea Port station

The sampling campaign took place in August 2018, when the climatic conditions were characterized by drought, with high temperatures (>30°C day temperature) and lack of precipitation. The growth of underwater vegetation was at its peak. A relatively lower mean value (116.95 cm) of the river water level was recorded (compared to the national average quota from Tulcea Port, which is 180 – 200 cm), (http://www. afdj.ro/ro/cotele-dunarii).

MATERIALS AND METHODS

SAMPLING AND ANALYTICAL PROCEDURES

Sampling campaign was carried out on board RV/Istros (NIRD GeoEcoMar) in August 2018, within the three sites described above. The sampling points (Fig. 3) were chosen to be evenly distributed in the lakes and bays concerned, and on the easier access basis.



Fig. 3. Maps showing the distribution of the sample points in *Babina, Rădăcinoasele* and *Ciorticuț* lakes (*i.e.,* the collected samples were enumerated from DD18-101 to DD18-121), *Musura* Bay (*i.e.,* from DD18-157 to DD18-163) and *Sahalin* Bay (*i.e.,* from DD18-172 to DD18-177), (Base map: https://earth.google.com/web/ 2018).

Table 1. A synopsis of the main physical-chemical parameters measured at sampling sites (The results are expressed as the minimum, maximum and mean values)

	Value	Physical-chemical parameters								
akes		ТоС	pH (unit)	D0 (mg/L)	DO (%)	N-NO ₂ ⁻ (mg/L)	N-NO ₃ ⁻ (mg/L)	N-NH ₄ + (mg/L)	P-PO ₄ 3 ⁻ (mg/L)	Chla (µg/L)
sele, Ciorticuț l	min	23.6	6.36	2.43	29.5	0.004	0.01	≤ 0.02	0.026	3.73
	max	28.2	7.92	12.21	154.3	0.015	0.05	≤ 0.02	0.183	68.03
	mean (n=21)	26.7	7.45	9.00	113.5	0.01	0.02	≤ 0.02	0.08	14.58
loas	Value	Physical-chemical parameters (continuation)								
Babina, Rădăci		TOC (mg/L)	SiO ₂ (mg/L)	EC (µS/cm)	TDS (mg/L)	50 ₄ 2 ⁻ (mg/L)	Turb. (NTU)	TSS (mg/L)	SDD (m)	ORP (mV)
	min	5.51	0.69	325	163	19	1.82	2	0.2	43
	max	28.02	5.42	409	205	28	12.4	11	0.8	99
	mean (n=21)	9.8	3.37	356.14	177.57	22.50	3.84	5.50	0.37	66.75
lusura Bay	Value	Physical-chemical parameters								
		ТоС	pH (unit)	DO (mg/L)	DO (%)	N-NO ₂ ⁻ (mg/L)	N-NO3 ⁻ (mg/L)	N-NH ₄ + (mg/L)	P-P0 ₄ 3 ⁻ (mg/L)	Chla (µg/L)
	min	26.6	7.63	7.53	94.7	0.008	0.01	<0.02	0.056	17.33
	max	27.2	8.7	10.72	136	0.008	0.01	<0.02	0.056	17.33
	mean (n=7)	26.9	8.17	9.59	120.63	0.008	0.01	<0.02	0.056	17.33
		Physical-chemical parameters (continuation)								
sn				Pnys	ical-cnemic	al paramete	rs (continuat	ion)		
Mus	Value	TOC (mg/L)	SiO ₂ (mg/L)	EC (μS/cm)	TDS (mg/L)	al paramete S0 ₄ 2 ⁻ (mg/L)	rs (continuat Turb. (NTU)	ion) TSS (mg/L)	SDD (m)	ORP (mV)
Mus	Value min	TOC (mg/L) 4.59	SiO 2 (mg/L) 3.66	EC (μS/cm) 385	TDS (mg/L) 193	al paramete SO ₄ 2 ⁻ (mg/L) 50	rs (continuat Turb. (NTU) 7.72	ion) TSS (mg/L) 14	SDD (m) 0.2	ORP (mV) -9
Mus	Value min max	TOC (mg/L) 4.59 4.59	SiO ₂ (mg/L) 3.66 3.66	EC (μS/cm) 385 4000	TDS (mg/L) 193 2000	al paramete SO ₄ 2 ⁻ (mg/L) 50 50	rs (continuat Turb. (NTU) 7.72 42	ion) TSS (mg/L) 14 53	SDD (m) 0.2 0.8	ORP (mV) -9 11
Mus	Value min max mean (n=7)	TOC (mg/L) 4.59 4.59 4.59	SiO ₂ (mg/L) 3.66 3.66 3.66	EC (μS/cm) 385 4000 11114.14	Ical-cnemica TDS (mg/L) 193 2000 557.29	al paramete SO ₄ ^{2°} (mg/L) 50 50 50	rs (continuati Turb. (NTU) 7.72 42 23.1	rss (mg/L) 14 53 31.571	SDD (m) 0.2 0.8 0.51	ORP (mV) -9 11 0
Mus	Value min max mean (n=7)	TOC (mg/L) 4.59 4.59 4.59	SiO ₂ (mg/L) 3.66 3.66 3.66	EC (μS/cm) 385 4000 11114.14	Ical-cnemica TDS (mg/L) 193 2000 557.29 Physical-	al paramete SO ₄ ^{2°} (mg/L) 50 50 50 chemical pa	rs (continuati Turb. (NTU) 7.72 42 23.1 trameters	ion) TSS (mg/L) 14 53 31.571	SDD (m) 0.2 0.8 0.51	ORP (mV) -9 11 0
Mus	Value min max mean (n=7) Value	TOC (mg/L) 4.59 4.59 4.59 ToC	SiO ₂ (mg/L) 3.66 3.66 3.66 PH (unit)	Phys EC (μS/cm) 385 4000 11114.14 D0 (mg/L)	Ical-cnemica TDS (mg/L) 193 2000 557.29 Physical- DO (%)	al paramete SO ₄ ^{2*} (mg/L) 50 50 50 chemical pa N-NO ₂ ⁻ (mg/L)	rs (continuat Turb. (NTU) 7.72 42 23.1 rameters N-N0 ₃ ⁻ (mg/L)	ion) TSS (mg/L) 14 53 31.571 N-NH₄ ⁺ (mg/L)	SDD (m) 0.2 0.8 0.51 P-PO ₄ ^{3*} (mg/L)	ORP (mV) -9 11 0 Chla (µg/L)
Mus	Value min max mean (n=7) Value min	TOC (mg/L) 4.59 4.59 4.59 ToC 25.7	SiO ₂ (mg/L) 3.66 3.66 3.66 PH (unit) 7.44	FC (μS/cm) 385 4000 1114.14 D0 (mg/L) 5.76	Ical-cnemica TDS (mg/L) 193 2000 557.29 Physical- DO (%) 70.5	al paramete SO ₄ ^{2°} (mg/L) 50 50 50 chemical pa N-NO ₂ ⁻ (mg/L) 0.008	rs (continuation Turb. (NTU) 7.72 42 23.1 rameters N-NO ₃ ⁻ (mg/L) 0.01	non) TSS (mg/L) 14 53 31.571 N-NH ₄ ⁺ (mg/L) 0.22	SDD (m) 0.2 0.8 0.51 P-PO ₄ ^{3°} (mg/L) 0.043	ORP (mV) -9 11 0 Chla (μg/L) 1.05
Mus	Value min max mean (n=7) Value min max	TOC (mg/L) 4.59 4.59 4.59 ToC 25.7 27.4	SiO ₂ (mg/L) 3.66 3.66 3.66 PH (unit) 7.44 8.73	FC (μS/cm) 385 4000 1114.14 D0 (mg/L) 5.76 9.26	Ical-cnemica TDS (mg/L) 193 2000 557.29 Physical- DO (%) 70.5 115.5	al paramete SO ₄ ^{2°} (mg/L) 50 50 50 chemical pa N-NO ₂ ⁻ (mg/L) 0.008 0.011	rs (continuat Turb. (NTU) 7.72 42 23.1 rameters N-NO ₃ ⁻ (mg/L) 0.01 0.02	ton) TSS (mg/L) 14 53 31.571 N-NH₄ ⁺ (mg/L) 0.22 0.51	SDD (m) 0.2 0.8 0.51 P-PO4 ^{3*} (mg/L) 0.043 0.056	ORP (mV) -9 11 0 Chla (µg/L) 1.05 18.98
in Bay Mus	Value min max mean (n=7) Value Min max mean (n=6)	TOC (mg/L) 4.59 4.59 4.59 4.59 25.7 27.4 26.4	SiO ₂ (mg/L) 3.66 3.66 3.66 PH (unit) 7.44 8.73 8.24	Phys EC (μS/cm) 385 4000 1114.14 D0 (mg/L) 5.76 9.26 8.31	Ical-cnemica TDS (mg/L) 193 2000 557.29 Physical- DO (%) 70.5 115.5 101.7	al paramete SO ₄ ^{2°} (mg/L) 50 50 50 chemical para N-NO ₂ ⁻ (mg/L) 0.008 0.011 0.01	rs (continuation Turb. (NTU) 7.72 42 23.1 rameters N-N0 ₃ ⁻ (mg/L) 0.01 0.02 0.01	non) TSS (mg/L) 14 53 31.571 N-NH₄ ⁺ (mg/L) 0.22 0.51 0.39	SDD (m) 0.2 0.8 0.51 P-P04 ^{3*} (mg/L) 0.043 0.056 0.05	ORP (mV) -9 11 0 Chla (μg/L) 1.05 18.98 6.59
ıhalin Bay Mus	Value min max mean (n=7) Value min max mean (n=6)	TOC (mg/L) 4.59 4.59 4.59 TOC 25.7 27.4 26.4	SiO ₂ (mg/L) 3.66 3.66 3.66 PH (unit) 7.44 8.73 8.24	FC (μS/cm) 385 4000 1114.14 D0 (mg/L) 5.76 9.26 8.31 Phys	Ical-chemica TDS (mg/L) 193 2000 557.29 Physical- DO (%) 70.5 115.5 101.7 ical-chemica	al paramete SO ₄ 2 ⁻ (mg/L) 50 50 50 chemical pa N-NO ₂ ⁻ (mg/L) 0.008 0.011 0.01 al paramete	rs (continuation Turb. (NTU) 7.72 42 23.1 rameters N-N03 ⁻ (mg/L) 0.01 0.02 0.01 rs (continuation	tion) TSS (mg/L) 14 53 31.571 N-NH₄ ⁺ (mg/L) 0.22 0.51 0.39 tion)	SDD (m) 0.2 0.8 0.51 P-PO₄ ^{3*} (mg/L) 0.043 0.056 0.05	ORP (mV) -9 11 0 Chla (μg/L) 1.05 18.98 6.59
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Sahalin Bay Mus	Value min max mean (n=7) Value min max mean (n=6) Value min	TOC (mg/L) 4.59 4.59 4.59 70C 25.7 27.4 26.4 TOC (mg/L) 3.15	Si02 (mg/L) 3.66 3.66 3.66 3.66 9H (unit) 7.44 8.73 8.24 Si02 (mg/L) 1.59	Phys EC (μS/cm) 385 4000 1114.14 D0 (mg/L) 5.76 9.26 8.31 Phys EC (μS/cm) 4000	Ical-chemica TDS (mg/L) 193 2000 557.29 Physical- DO (%) 70.5 115.5 101.7 ical-chemica TDS (mg/L) 2000	al paramete S04 ^{2°} (mg/L) 50 50 50 chemical paramete S04 ^{2°} (mg/L) 0.008 0.011 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01	rs (continuation Turb. (NTU) 7.72 42 23.1 rameters N-NO ₃ ⁻ (mg/L) 0.01 0.02 0.01 0.02 0.01 rs (continuation Turb. (NTU) 6.1	ton) TSS (mg/L) 14 53 31.571 N-NH₄ ⁺ (mg/L) 0.22 0.51 0.39 tion) TSS (mg/L) 10	SDD (m) 0.2 0.8 0.51 	ORP (mV) -9 11 0 Chla (μg/L) 1.05 18.98 6.59 ORP (mV) -72
Sahalin Bay Mus	Value min max mean (n=7) Value min max mean (n=6) Value min max	TOC (mg/L) 4.59 4.59 4.59 700 25.7 27.4 26.4 TOC (mg/L) 3.15 4.28	SiO ₂ (mg/L) 3.66 3.66 3.66 PH (unit) 7.44 8.73 8.24 SiO ₂ (mg/L) 1.59 3.06	FC (μS/cm) 385 4000 1114.14 D0 (mg/L) 5.76 9.26 8.31 Phys EC (μS/cm) 4000 17580	Ical-chemica TDS (mg/L) 193 2000 557.29 Physical- DO (%) 70.5 115.5 101.7 ical-chemica TDS (mg/L) 2000 8790	al paramete SO ₄ ^{2°} (mg/L) 50 50 50 chemical paramete N-NO ₂ ⁻ (mg/L) 0.011 0.01 al paramete SO ₄ ^{2°} (mg/L) 99 124	rs (continuation (NTU)) 7.72 42 23.1 rameters N-N03 ⁻ (mg/L) 0.01 0.02 0.01 rs (continuation rs (continuation (NTU)) 6.1 76.1	tion) TSS (mg/L) 14 53 31.571 N-NH₄ ⁺ (mg/L) 0.22 0.51 0.39 ion) TSS (mg/L) 10 40	SDD (m) 0.2 0.8 0.51 P-PO₄ ^{3*} (mg/L) 0.043 0.056 0.05 0.05 0.05	ORP (mV) -9 11 0 (μg/L) 1.05 18.98 6.59 ORP (mV) -72 28

Water samples were collected from the surface layer (0.5 – 1 m) using a 15 L plastic bucket.

The water temperature (°C), water depth (m), transparency (m), DO concentration (mg/L) and saturation (%), conductivity (μ S/cm), TDS (mg/L) and pH (units) (Table 1) were measured *in-situ*, using a WTW Multiline P4 Multiparameter. Other parameters as the ORP (mV), turbidity (NTU), TSS (mg/L), N-NO₂⁻(mg/L), N-NO₃⁻(mg/L), P-PO₄³⁻(mg/L), SO₄²⁻(mg/L), and SiO₂ (mg/L) (Table 1) were analyzed on board, immediately after water sampling.

The above-mentioned parameters were measured by the Hach 2100 P Turbidimeter, Portable Spectrophotometers HACH DR 5000 UV-Vis and DR 2000.

For ammonia-nitrogen (mg/L), TOC (mg/L) and chlorophyll a (µg/l) analysis, the water samples were collected in clean glasses/polyethylene bottles, then filtered through Whatman Sterile Mixed Cellulose Ester Membranes, 0.45-µm and kept frozen (for chlorophyll a and ammonium-nitrogen) or refrigerated (TOC) until subsequently analyses. Chlorophyll a was measured by UV-VIS spectrometry, after the pigment extraction with acetone 90% vol/vol, ammonium-nitrogen was also measured by UV-VIS spectrometry (phthalate method), while TOC concentration was determined using a TOC Analyzer with IR detector.

The assessment of water quality was mainly based on the national surface water quality standard classes stated in Order 161/2006, as follows: Class I (very good water quality), Class II (good), Class III (moderate), Class IV (poor) and Class V (bad), but also according to other national/ international reference standards existing in the specialized literature.

The obtained results within this study were processed as distribution maps of the main physical-chemical parameters using Surfer software – Golden Software, Inc., 2010, by kriging interpolation.

Statistical data processing was done using the program XLSTAT 7.5.2. Analysis of variance (ANOVA) and Fisher (LSD) test were used to examine seasonal chlorophyll a variation. The testing significance of differences between chlorophyll a means recorded in the investigated areas was performed by using t test (Student) at the significance level of 0.05. The same significance level was used for testing the significance of the correlation between chlorophyll a and some of the variables.

RESULTS AND DISCUSSION

Quality of surface water depends on the variability of the parameters that can change significantly both under the influence of natural conditions (changes in seasonal flows, precipitation patterns etc.), and as a result of anthropogenic impact (human activities and other industrial activities, wastewater discharges etc.). Therefore, a consistent monitoring both in time and space is important.

These three aquatic systems that were previously briefly presented i.e., Babina, Rădăcinoasele and Ciorticuț lakes, as well as Musura and Sahalin bays are characterized by particular environmental conditions. It is important to consider that Musura and Sahalin bays are situated in a highly dynamic environment that undergoes significant changes in short time, in comparison to Babina, Rădăcinoasele and Ciorticut lakes that are positioned in a confined environment. The morpho-dynamic evolution of these semi-protected environments, i.e., Musura and Sahalin bays, is triggered by the relative dominance of key forcing parameters, among which we mention: hydro-dynamic (floods and droughts) and morpho-lithological (alluvial deposition) factors, complex and dynamic climate regime (fluctuations of tides and winds), anthropogenic impact (hydro-technical works on the Danube River and its delta) etc.

Locally, the ecosystems taken into consideration within this study can be subjected to the impacts of humanrelated activities. In the surrounding areas there are small human settlements (i.e., old fishing villages) in which small agricultural activities or animal husbandry takes place, as well as other delta's specific traditional activities i.e., traditional fishing, illegal fishing, reed harvesting, tourism and navigation. In addition to day-to-day movements of merchant ships, which are creating water turbulence, mixing or/and sediment re-suspension on the main routes of navigation in the deltaic area, there are also several small passenger ferries which circulate and stop frequently in water-stations for commuters and tourists. Many waterways are used for tourism attraction, by involving cruise activities and sightseeing in the Danube Delta and Lagoon Complex Razim-Sinoie. The effects of these activities can be reflected in diffuse sources of contamination, which in turn may supply a high input of various contaminants into the waters.

The investigation of surface water in *Babina*, *Rădăcinoasele*, *Ciorticuț* lakes, as well as in *Musura* and *Sahalin* bays has been performed to evaluate the current quality status and its suitability for aquatic life ambient.

The main results are shown in Table 1 and they are plotted as the spatial variation of parameters at the water surface (Figs. 4, 5 and 6).

The pattern of the relative variation of the different physical-chemical parameters showed that all the examined water parameters are quite heterogeneous. Generally, all the surface water parameters examined at the *Babina*, *Rădăcinoasele, Ciorticuț* lakes, *Musura* and *Sahalin* bays are within the permissible limits according to different reference standards. However, incidentally, there have been encountered some local situations where some parameters have experienced slight variations or a decline.

WATER THERMAL REGIME AND PH

The water temperature is an important parameter for lake ecosystems, influencing the dynamics of physical-chemical

reactions, the concentration of dissolved gases (*e.g.*, oxygen), and vertical mixing (Delpla *et al.*, 2009). In the present study, the surface water temperature showed high values (23.6 – 28.2°C), in accordance with the high air temperature recorded in August 2018 (maxima between 29°C and 37 °C according to https://www.accuweather.com/ro/ro/tulcea/). One way ANOVA test applied for the surface temperature did not show significant differences between the studied areas.

The pH regime variability can be associated with natural factors and man-made inputs (Alan, 1995). Within this study, the pH values showed a heterogeneous spatial distribution, with a minimum of 6.36 measured in the southern part of the Babina L., and a maximum of 8.73 recorded in the Sahalin Bay, (Figs. 3, 4, 5 and 6). However, the one way ANOVA followed by multicomparison Fisher (LSD) test showed statistically significant lower pH values in the lakes, although they are within the national water quality standard (Order 161/2006) as compared with the bays (7.45 as compared to 8.17 in Musura and 8.24 in Sahalin, respectively). The lowest value (6.36) could be related to intense degradation processes of the organic matter by aerobic and anaerobic bacteria, releasing more carbon dioxide into the water. The pH in the water will affect what types of organisms can live in the stream. The pH values, from 6.5 to 8.2, generally obtained in our study are optimal for most aquatic organisms (Chapman, 1996; Pearce et al., 1999; Murdock et al., 2001). There is no sign of acidification/alkalinity of the investigated water samples as the pH values range, generally varied in the above-mentioned acceptable range. The obtained results were consistent with the results reported in other previous investigations in the DDBR area (Munteanu et al., 2012).

DO REGIME

In many freshwater habitats, low dissolved oxygen (DO) is one of the most important and ubiquitous stressors affecting the aquatic fauna (Butler and Burrows, 2007). The DO provides information on the levels of contamination, as well as for the determination of the productivity of an aquatic environment (Omar *et al.*, 2016). Generally, this study found that the DO content of all investigated sites (Figs. 4, 5 and 6) was above 4 mg/L which is considered as minimum requirement for aquatic growth (Maun and Moulton, 1991). Our values (Table 1) are also consistent with the minimum concentration of 5 mg/L of DO that is recommended to safeguard the lifesupporting capacity (https://www.niwa.co.nz/...dissolvedoxygen).

ANOVA test did not reveal statistically significant differences between the studied sites. However, slight higher DO concentrations were observed in the *Musura* Bay (mean of 9.59 mg/L), while slight lower DO concentrations were recorded in the *Sahalin* Bay (mean of 8.31 mg/L). Even if there were registered lower values in *Babina* L. (DD18-101 = 2.43 mg/L; DD18-106 = 3.21 mg/L; Fig. 3) within acceptable limits, < 4 mg/L, established for Class V of water quality (Order 161/2006), most of the DO content above

6 mg/L indicates that the studied sites are characterized by a healthy ecosystem with good water flow and good aeration (oxygenation) conditions (Figs. 4, 5 and 6). In dry periods there is a decrease in the amount of oxygen in the water that can be limited by high atmospheric temperature or by the abundant development of the underwater plants followed by the decaying process or by a cumulative effect of both. The low oxygen concentrations observed in the above-mentioned stations may be linked with the bacterial decomposition activity of organic matter, including decaying underwater plants. Organic matter decay generates oxygen depletion in freshwater systems (Schlautman and Han, 2001). It should be noted that our acquired results are comparable to those previously obtained in DDBR areas with similar environmental conditions (Rădan et al., 1997; Rădan et al., 2000; Munteanu et al., 2012; Catianis et al., 2016; Catianis et al., 2017).

NUTRIENT AND CHLOROPHYLL REGIME

ANOVA test did not show statistically significant differences between the studied sites in terms of $N-NO_2^-$, $N-NO_3^-$, $N-NH_4^+$, $P-PO_4^{3-}$, SiO₂, TOC and chlorophyll *a*.

Nitrite (N-NO2⁻) is a natural component of the nitrogen cycle in ecosystems, and its presence in the environment is a potential problem due to its toxicity to aquatic organisms (Jensen, 2003; Kroupová et al., 2005). N-NO2⁻ levels tested in this study (Table 1) were generally within the limits provided by the environmental standard (Order 161/2006), which is 0.01 mg/L, established for Class I (very good status) of water quality, but slightly elevated values of N-NO₂ (> 0.01 mg/L) were observed in two samples from Babina L. (DD18-105 = 0.011 mg/L; DD18-108 = 0.011 mg/L), one sample from Ciorticut L. (DD18-121 = 0.015 mg/L) and one sample from Sahalin Bay (DD18-174 = 0.011 mg/L) (Fig. 3). The intercomparison between investigated sampling sites exhibited the following mean values: Babina, Rădăcinoasele and Ciorticut - 0.01 mg/L, Musura Bay - 0.008 mg/L and Sahalin Bay - 0.01 mg/L. Usually, contaminant sources of N-NO₂-combine human sewage, livestock manure, illegal sanitary sewer connections, poorly functioning septic systems, fertilizers and erosion of natural deposits (Lucassen et al., 2004). The relatively higher levels of N-NO₂, which do not raise major contamination concerns, may be due to the entry of runoff containing human/animal manure or fertilizers into the water.

 $N-NO_3$ concentrations showed values within acceptable limits, < 1 mg/L, established for Class I of water quality, as suggested by the national reference standard (Order 161/2006).

 $N-NH_4^+$, regarded as an environmental parameter, serves as an indicator of contamination by anthropogenic sources (*i.e.*, organic matter decomposition, animal and human waste, urban and industrial effluent discharges, livestock manure and agricultural runoff). Referring to our results, a similar trend is also well-founded for $N-NH_4^+$ levels, meaning that generally, the obtained values were inside standard limits, < 0.4 mg/L, settled for Class I of water quality, *i.e., Babina, Rădăcinoasele, Ciorticuț* lakes and *Musura* Bay (values \leq 0.02), while in the *Sahalin* Bay (Fig. 3), two values (DD18-172 = 0.51 mg/L and DD18-174 = 0.45 mg/L) slightly exceeded the limit imposed on Class I (< 0.4 mg/L). In terms of N-NH₄⁺, statistically significant higher concentrations were found in the *Sahalin* Bay as compared with the other two sites.

Thus, all the investigated values obtained within this study are heterogeneous, hence there is a need for routine monitoring of the water. It is well-known that increased levels of $N-NH_{4^+}$ in surface water have toxic effects on the aquatic organisms (US-EPA, 2013).

Phosphates in water come from a range of sources as human and animal waste, phosphorus-rich bedrock, laundry, cleaning, industrial effluents, fertilizer runoff and/or the phosphorus re-mobilization at the sediment-water interface (Chapman, 1996). These phosphates become harmful when they exceed a certain level and can lead to excessive algal growth and the resultant eutrophication (Shock and Pratt, 2003). In the present study, $P-PO_4^{3-}$ levels at all sites (Table 1) were at or below the limit 0.1 mg/L, settled for Class I of water quality. Relatively elevated levels (> 0.1 mg/L) were noticed only in one sample of Babina L. and one sample of Ciorticut L. The results showed the following mean variations: Babina, Rădăcinoasele and Ciorticuț - 0.08 mg/L, Musura Bay - 0.056 mg/L and Sahalin Bay - 0.05 mg/L. However, in the current study, P-PO₄³⁻ levels were low at all sites, and their values do not require special concern. Similar nutrient levels have been reported in the DDBRA areas by another previous study (Török et al., 2008).

In aquatic ecosystems, nutrients are found in various forms, including ammonia, nitrate, nitrite, orthophosphate, dissolved carbon dioxide (CO₂), dissolved silica (SiO₂) etc. (Deas and Orlob, 1999). The existence of silicate in aquatic environments is very important for the development of a group of microorganisms as diatoms (Egge and Aksnes, 1992). Silica is an essential nutrient for macrophyte and diatom communities and can play a significant role in coastal eutrophication (Struyf and Conley, 2008). For the silica content, there are no national specific environmental standards. The silica concentration determined within this study was not significantly fluctuating and its measured values were below the range of natural water variation (5-25 mg/L), (http://www.freedrinkingwater.com/). The ranges of variations are: Babina, Rădăcinoasele and Ciorticuț (0.69 -5.42 mg/L; mean = 3.37 mg/L), Musura Bay (3.66 mg/L) and Sahalin Bay (1.59 - 3.06 mg/L; mean = 2.11 mg/L). Hence, it can be asserted that the investigated waters have lower silica content.

The concentration of chlorophyll *a*, a measure of the phytoplankton biomass, is considered a key indicator of eutrophication (Bricker *et al.*, 1999). The abundant development of various species of algae produces chlorophyll

and confers water its green pigmentation in productive areas, meaning excessive algae growth or algal blooms that often lead to reduced water clarity and light penetration (Hoyer et al., 2002). A large part of the surface waters with low nutrient levels include low Chla levels (< 2.5 g/L), but higher levels can be noticed if there is high nutrient availability (Chapman, 1996). In the current study, all investigated sites revealed lower Chla levels (Table 1), generally not exceeding the limit 25 µg/L settled for Class I of water quality, with one exception from Babina L., settled for Class II of water quality (25-50 µg/L). The ranges of average variations are: Babina, Rădăcinoasele and *Ciorticuţ* lakes $(3.73 - 68.03 \mu g/L; mean = 14.58 \mu g/L)$, Musura Bay (17.33 µg/L) and Sahalin Bay (1.05 – 18.98 µg/L; mean = 6.59 μ g/L). The results obtained within this study did not indicate a higher concentration of Chla levels in the investigated waters.

Determination of the TOC content in water is often used as a non-specific indicator of water quality to assess the degree of organic pollution of water. Most organic carbon in water bodies is natural in origin and is derived from living and decaying vegetation (LeChevallier et al., 1991). Since there are no national standards, our results were compared to those established by the Ministry of the Environment of British Columbia (1991), where TOC is expressed as mg/L, and the concentration in which it is found in natural waters may range from 1-30 mg/L. The TOC results obtained within this study (Table 1) fall within the range of natural water variation (1-30 mg/L). The ranges of variations are: Babina, *Rădăcinoasele* and *Ciorticuț* (5.51 – 28.02 mg/L; mean = 9.8 mg/L), Musura Bay (4.59 mg/L) and Sahalin Bay (3.15 - 4.28 mg/L; mean = 3.61 mg/L). Considering the obtained values that are enrolled within the range of natural water variation (1-30 mg/L) it can be appreciated that the tested waters are of good quality.

Conductivity

Electrical conductivity (EC) is a measure of the ability of water to conduct an electric current, being sensitive to variations in dissolved solids, generally mineral salts (Chapman, 2006), and it is measured on a scale from 0 to 50000 µS/cm (http://mrccc.org.au/wp-content/uploads/2013/10/ Water-Quality-Salinity-Standards.pdf). Commonly, the EC of the natural waters is anticipated to fluctuate between 50 and 1500 µS/cm (Bartram and Balance, 1996), whereas after the World Health Organization (WHO) requirements, the maximum permissible value of potable water is 2500 µS/cm (WHO, 2004). For the most freshwaters, the EC ranges from 10 to 1000-1500 µS/cm, and typical seawater may exhibit a conductivity level of about 50000 µS/cm. Low levels of salts are found naturally in waterways and are important for the development of plants and animals. Instead, elevated levels of above 1000 µS/cm encountered in contaminated freshwater with large amounts of land runoff, can generate issues related to aquatic ecosystems and complicated human uses (Chapman, 1996). In streams and rivers, the conductivity



Fig. 4. Spatial variation of physical-chemical parameters in surface water from Babina, Rădăcinoasele and Ciorticuț lakes

is influenced by factors as the type of soils, bedrocks, and existence of inorganic dissolved solids. Wastewaters or sewage leaks could increase conductivity due to the additional amount of chloride, phosphate, and nitrate (http:// water.epa.gov/). ANOVA test followed by the Fisher (LSD) comparison test showed statistically significant differences between areas in terms of conductivity. Thus, significant higher conductivities were observed in the Sahalin Bay (mean of 12461.67 µS/cm) as compared with the Musura Bay (mean of 1114.14 μ S/cm) and the lakes (mean of 356.14 μ S/ cm). The values varied significantly among the sampling sites, meaning that the fresh waters from Babina, Rădăcinoasele and Ciorticut lakes had low EC levels within acceptable limits, which is $< 500 \mu$ S/cm, established for Class I of water quality, in comparison to brackish waters of Musura Bay and Sahalin Bay, which showed a much higher value of the EC levels, exceeding the limit allowed even to class V of water quality, > 1300 μ S/cm, (Figs. 4, 5 and 6). The highest values of EC, registered in some sampling points from Musura and Sahalin bays, are related to the inputs of the dissolved salts originated from marine intrusions. Therefore, in these cases, it's not about water contamination, but saltwater-freshwater mixing, a natural occurring process in these areas, characteristic of seawater conductivity that is one million times higher than pure (deionized) water, because of the ions dissolved in the seawater (i.e., sodium, chloride, magnesium, sulphate, and calcium) (http://cdn2.hubspot.net/). Monitoring EC in these environments gives an indication of their evolution from freshwater to mixed and then brackish, in close relation to their morphology.

TDS is a measurement of inorganic salts, organic matter and other dissolved materials in the water (US - EPA, 1986). The concentration and composition of TDS in natural waters are defined by many elements as industrial effluent, the geology of the drainage area, changes in the water balance (by limiting inflow, by increased water use or increased precipitation), or by salt-water intrusion (Wetzel, 1983). Our results after the TDS measurements showed a similar trend to EC dynamics, since the EC serves as an indirect measure of TDS concentration. Thus, statistically significant higher TDS were measured in the Sahalin Bay as compared with the Musura Bay and lakes. The ranges of variations are: Babina, Rădăcinoasele and Ciorticuț lakes (163 - 205 mg/L; mean = 177.57 mg/L), Musura Bay (193 - 2000 mg/L; mean = 557.29 mg/L) and Sahalin Bay (2000 - 8790 mg/L; mean = 6230.83 mg/L) (Figs. 4, 5 and 6). Thereby, the tested waters from Babina, Rădăcinoasele and Ciorticuț lakes had low TDS levels, values that correspond to potable water (500 - 1000 mg/L) (DeZuane, 1997) and/or freshwater domain (0 - 1000 mg/L TDS), in opposition to Musura and Sahalin bays that exhibited higher values of TDS levels, but which are suitable for the marine domain (1000 - 30000 mg/L TDS). Since there are no national specific environmental standards our results were related to other reference literature (DeZuane, 1997; https:// en.wikipedia.org/). The high TDS load of Musura and Sahalin

bays may be attributed to the gradual transition from the freshwater to the seawater environment. The levels of TDS of the two bays are attributable to local specific environmental circumstances and therefore do not pose any environmental challenges.

In this study, the water salinity was estimated using EC and temperature measurement data (http://www.fivecreeks. org/monitor/sal.shtml). The investigated sampling sites showed a lower salinity in *Musura* Bay (≤ 2 %), in comparison to the *Sahalin* Bay (2.1 – 10.1%); mean = 7.1%).

Sulphate (SO₄²⁻) is widely distributed in nature and may be present in natural waters at concentrations ranging from a few to several hundred milligrams per litre (lowa Department of Natural Resources, 2009). Anthropogenic sources of sulphate may come from mine drainage wastes and smelters and from pulp and paper mills, textile mills, tanneries etc., (Delisle and Schmidt, 1977). The present study found that SO₄²⁻ level in all investigated sites (Table 1) was generally in conformity to the limits, < 60 mg/L, settled for Class I of water quality, but elevated levels of SO₄²⁻ which are characteristic for Class II (good status) of water quality (60 - 120 mg/L) were noticed in samples collected from Sahalin Bay. The ranges of variations are: Babina, Rădăcinoasele and Ciorticuț lakes (19 – 28 mg/L), Musura Bay (50 mg/L) and Sahalin Bay (99 – 124 mg/L). However, it cannot be stated that the investigated waters are contaminated with sulphates. SO₄²⁻, showed the highest concentrations in the Sahalin Bay (mean of 111.33 mg/L), followed by Musura Bay (mean 50.00 mg/L), and the Babina, Rădăcinoasele and Ciorticuț lakes (mean 22.50 mg/L). The level of the salinity regime (*i.e.*, EC, TDS, SO₄²⁻) measured in the two semi-enclosed bays are consistent with values obtained in other studies, especially in Sinoie Lake that belongs to the Razim-Sinoie Lagoon Complex (Dimitriu et al., 2008; Catianis et al., 2018). In this lake, water circulation is controlled by the two inlets that facilitate the mixing of fresh and brackish waters (i.e. Periboina and Edighiol Inlets, between Sinoie and the Black Sea) (Dinu et al., 2015).

TURBIDITY, TSS AND TRANSPARENCY

Turbidity, defined as an optical property of a liquid mainly caused by light scattering and to some extent by light absorption along the photons path length (Anderson, 2005) is routinely used to indicate water quality. Turbidity is created by the presence of suspended sediment such as clay, silt, finely divided organic and inorganic matter, and plankton and other microscopic organisms in the water body (Anderson, 2005). Although microbiological contamination is commonly associated with increases in turbidity, other factors, as silt and organic matter, may affect turbidity levels of water (http:// www.ec.gc.ca/water/en/info/gloss/e_gloss.htm#T). Hiah turbidity levels can impair water visibility and affect vegetal and animal aquatic life. In our study, the turbidity results were related to a national standard which stated that the limit of turbidity in drinking water is 5-10 NTU (STAS 6323-88). The ANOVA test, followed by Fisher (LSD) comparison



Fig. 5. Spatial variation of physical-chemical parameters in surface water from Musura Bay

test revealed significant higher values in both bays (means 23. 1 NTU in *Musura*, respectively of 26.8 NTU in *Sahalin*) as compared with the lakes (mean of 3.8 NTU). The lowest values of turbidity were found in *Babina*, *Rădăcinoasele*, *Ciorticu*; and *Musura* Bay, while some higher values were noticed in the *Sahalin* Bay (Figs. 4, 5 and 6). These peaks in turbidity levels may be attributed to continuous wind currents and waves which stir up the muddy bottom sediments of the shallow waters of the *Sahalin* Bay.

Water transparency (Secchi depth) values were read in a similar variation range, as follows: *Babina, Rădăcinoasele* and *Ciorticu*; (0.2 - 0.8m; mean = 0.3 m), *Musura* (0.2 - 0.8m; mean = 0.5 m) and *Sahalin* bays (0.3 - 0.8m; mean = 0.5 m).

TSS is a specific quantity measurement of all suspended solids, organic and inorganic, present in a water body (http:// www.ecy.wa.gov/). TSS arises from soil erosion, runoff, discharges, stirred bottom sediments or algal blooms. The increased amount of suspended solids in water can impair water guality for aguatic and human life, impede navigation and increase flood risks (Wood, 2014). The obtained results within this investigation were compared to a reference standard (ANZECC Guidelines, 2000) that recommended a permissible level of suspended solids of < 40 mg/L as acceptable levels of TSS in freshwater, as well as < 10 mg/L as acceptable levels of TSS in the marine environment. In this respect, TSS concentration in the investigated waters noted variability in the acquired results. Similar to turbidity, TSS showed significant higher values in both bays (31.5 mg/L in Musura and 24.7 mg/L in Sahalin, respectively) as compared with the lakes (5.5 mg/L) (Figs. 4, 5 and 6). The highest values of TSS were noticed in the Sahalin Bay. It should be noted that the difference between Musura and Sahalin is given by different local factors that control turbidity and TSS (i.e., geoecological setting, landscape and evolutionary processes, sedimentary regime, climate variations, salinity levels etc.).

Other measurements (GeoEcoMar, 2015 and University of Stirling, 2016, unpublished data), have found higher TSS values in Sahalin Bay, in both low (August) and high-water conditions (May, June). While Musura Bay is under the direct influence of the Chilia Branch water and suspended sediment discharge, and so both turbidity and TSS are controlled by it, Sahalin Bay is only partially influenced by the Sf. Gheorghe Branch water and sediment flux, through the channel Gârla Turcului and also the Ciotica canal. In this case, turbidity and TSS high values are probably created by a mix of phenomena. For instance, the direct discharge of water and suspended sediments through the two channels increases turbidity and TSS locally, in the north and east of the bay. The overall higher values are presumably generated by the re-suspension and stirring of the bottom sediments by wind and wind-induced waves. Also, the over-wash of the spit and the alongshore current formed by the Sf. Gheorghe plume which follows the shape of the spit creates the mix of fresh and brackish waters and suspended particles.

THE OXIDO-REDUCTION POTENTIAL (ORP)

ORP, is a measure (in millivolts), of the tendency of a chemical substance to oxidize or reduce another chemical substance. The values of ORP in oxic conditions are positive (higher than +50 mV), while the ORP values in anaerobic/ anoxic conditions are negative (less than -50 mV) (Eckenfelder and Grau, 1992).

Anoxia and hypoxia have been widely noticed in many coastal regions over the world *i.e.*, America, Africa, Europe, India, South-East Asia, Australia, Japan and China. In some places, anoxic/hypoxic zones could be linked both to human-related factors in coastal areas, which increases nutrient load into the marine ecosystems (Diaz and Rosenberg, 1995; Wu, 1999), or to natural factors. Inter-comparisons of the ORP level tested with our investigated samples varied as: *Babina, Rădăcinoasele* and *Ciorticuț* lakes (+43 – +99 mV; mean = +66.75 mV), *Musura* Bay (-9 – +11 mV; mean = 0 mV) and *Sahalin* Bay (-72 – +28 mV; mean = -28.5 m).Thus, all the investigated values obtained within this study fall within the ORP range of natural waters (-500 + 700 mV) (Chapman, 1996; Sigg, 2000) hence there is a need for routine monitoring of the water.

CONCLUSIONS

The present comparative study of the water quality was performed on two different types of environments, namely a freshwater environment (*i.e., Babina, Rădăcinoasele,* and *Ciorticuț* lakes), and a mixed environment (*i.e., Musura* and *Sahalin* bays).

The results obtained during the study were compared with different national and international environmental standards.

Overall, with an exception of few sampling points, the physical-chemical water quality parameters fall within the range of natural water chemistry, for both investigated environments, specifically, a freshwater and a mixed environment.

The outcomes showed a spatial differentiation of the variation of few quality parameters, mainly as a result of local specific environmental circumstances. Higher levels of EC, TDS, turbidity and TSS were noticed in the in the two semienclosed bays. These exceedances may be attributed to the very dynamic environments of the areas, particularly the interferences between the river influx and the sea. The impact of saltwater intrusions within these semi-protected aquatic environments (*i.e., Musura* and *Sahalin*) was determined as well.

The results suggest that, the environmental indicators measured in drought conditions and low water levels exposed generally good to moderate water quality status, in spite of many local triggers associated with natural and anthropogenic causes that can alter or impair the quality of the water. After this investigation performed during August



Fig. 6. Spatial variation of physical-chemical parameters in surface water from Sahalin Bay

2018, it can be appreciated that the analysed water samples maintain appropriate levels that are suitable for the ecological status of the investigated aquatic systems, and, as expected, the aquatic habitats are ecologically balanced environments.

This paper recommends the routine monitoring and periodical testing of the water quality to create and develop a database to reflect the natural variation and human-related implications for water quality within these areas, and their short, medium and long-term evolution trends.

As a conclusion, the present work is important for water quality assessment to detect changes in water quality under human pressure and climate change and to protect and conserve these natural water resources.

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