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2. The investigation of the water quality and bed-sediment conditions in Cutetchi Lake, Danube Delta, Romania

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Abstract: Danube Delta includes many ecosystems functioning in a dynamic environment that could be considered, each of them, as ”natural laboratories”. In this sense, Cutetchi Lake was chosen for conducting practical investigations (August 2016) and the obtained data will be used to evaluate the impacts associated with natural factors or human-related activities. Water samples were investigated for physical parameters and water-quality constituents. Bed-sediments samples were analyzed for the main lithological components and trace elements to identify the levels, distribution and the potential sources of heavy metals in surficial accumulations. Related environmental standards were used to evaluate the water and sediment quality. Results indicate that, in the surface water the mean concentration of the environmental indicators ranged mainly in line with sampling points and generally agreed with reference standard: transparency (0.94 m), dissolved oxygen (8.98 mg/l), temperature (22.39 ^{o}C), conductivity (392.2 µS/cm), total dissolved solids (196.1 mg/l), pH (7.91), Eh (22 mV), turbidity (5.06 NTU), total suspended solids (9.25 mg/l), nitrite-nitrogen (0.01 mg/l), nitrate-nitrogen (0,02 mg/l), soluble orthophosphates (0.17 mg/l), sulphates (25,5 mg/l), silica (6,8 mg/l). The mean sediment parameter values were: moisture (23.13 %), dry sediment content (76.87 %), total organic matter (73.53 %), total carbonates (7.48 %) and minerogenic fraction (18.98 %). In the bed-sediment, the average metal content was: Zn (102.17 mg/kg), Ni (44.77 mg/kg), Cr (73.23 mg/kg), V (75.30 mg/kg), Co (9.38 mg/kg), Pb (24.83 mg/kg), Cu (58.70 mg/kg), Cd (0.82 mg/kg) etc., and individual values only incidentally exceed the maximum recommended level. This work could be a basis for the ongoing evaluation processes of water and sediment quality.

Keywords: assessment, bed-sediment, Cutetchi Lake, human impact, water samples

INTRODUCTION

In agreement with information sources, the greatest wetland in Romania, the Danube Delta, including the Razim – Sinoie Lagoon System, too (5800 km^2 of which 3510 km^2 are in the Romanian domain) is the second largest and well-preserved of the Europe deltas (Gâștescu and Știucă, 2008). Resultantly, since 1991, was included in UNESCO World Heritage as the reservation of the biosphere at a national and regional level (*i.e.,* DDBR), as national park in the IUCN (*i.e.,* International Union for Conservation of Nature) protected area categories, as well as Wetland of International Importance (*i.e.,* Ramsar Sites) as defined by the Ramsar Conventions of wetlands.

The environmental problems facing the Danube Delta are many and diverse, of which is mentioned the natural physical and ecological processes that varied in time and space, and continuing with anthropogenic stressors (*e.g.,* industrial wastes, discharge of domestic and agricultural wastes derived from Danube River upstream and regional settlements, eutrophication, biodiversity decline, coastal erosion etc.), directly affecting the water quality in the Danube Delta and those occurred throughout its terrestrial ecosystems which have an indirect effect. The Danube Delta is subject to fluctuating arrangements to disarrangements stages as a result of important changes in the proximate influences of sediment input from the Danube River and redistribution by marine coastal processes (Panin and Jipa, 1998). During the last decades has been in an overall construction stage, triggered by the conversion works undertaken to improve agriculture, aquaculture and forestry, as well as different hydro-technical works aiming to the development of water regulation, irrigation systems and the fishery exploitation potential of water bodies. In this context, the Danube Delta requires a special attention in terms of environmental protection, ecosystems and biodiversity conservation, despite considerable conservation efforts which have taken place lately.

The Danube Delta is located in the northwestern part of the Black Sea, between 44°25' and 45°37' N latitude and between 28°45' and 29°46' E longitude, bounded by the Bugeac Plateau to the North and by the Dobrogea Unit to the South. This complex deltaic edifice is surrounded by varying landforms and traversed by the Danube branches and multiple tributaries, natural and artificial channels, supporting habitat for a vast biological diversity with numerous species of flora and fauna. As a consequence of increasing anthropogenic pressure, the Danube Delta is an area of interest, in particular, due to the implications of upstream contamination, urban and agricultural runoff, wastewater effluent, recreational and commercial boating activities, atmospheric depositions etc.). This deltaic area includes many ecosystems functioning in a dynamic environment that could be considered, each of them, as „natural laboratories". In this sense, Cutețchi Lake was chosen for conducting practical investigations (August 2016) and the obtained data will be used to evaluate the impacts associated with natural factors or human-related activities. Cutețchi Lake (also found under the name "Lacul cu Cotețe") is located in the Sireasa - Șontea - Fortuna Depression, namely in the Purcelu area (-2/ -4 m altitude in this lake depression) that includes some other shallow lakes as Carasu and Purcelu (Fig. 1).

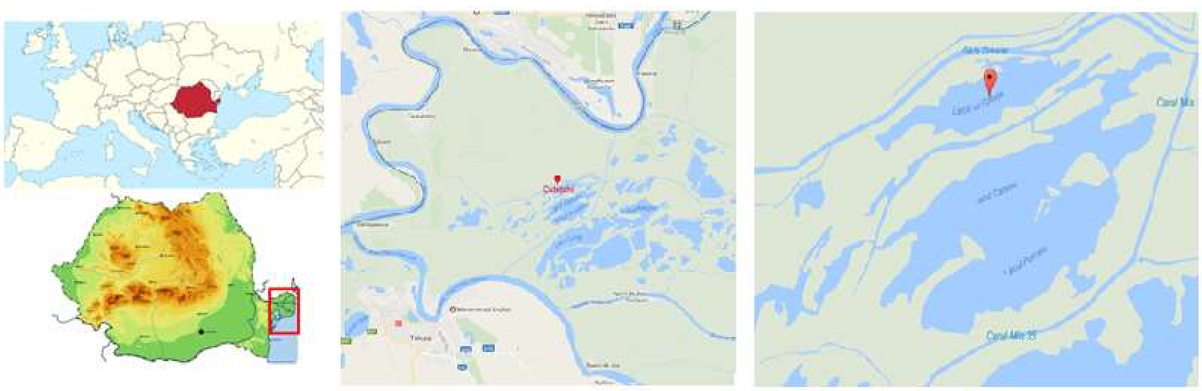

Figure 1 Study area located in the Danube Delta, Romania

The northern boundary of the Cutețchi Lake is represented by the Sireasa channel, the northeast part is limited by the Purcelu channel, the southern part of the Carasu Lake, and the rest of the area is surrounded by water meadows and marshes. The area of these lakes and their surroundings are characteristic of the fluvial delta that is adapted to the high amplitude of the flood wave, having specific flora (*i.e.*, white and yellow water lilies, galleries of willows) and fauna species (cormorants, herons, egrets etc.). The lake environment hosts specific vegetation around its surroundings and diverse fauna, making the site significant for scientific reasons (under physical-chemical, biological and geochemical aspects). This lake was chosen to investigate the quality of the environment (water and sediment) due to the position occupied within the details edifice, being to some extent directly influenced by the Danube River influx of water and sediments. Therefore, this paper performs an environmental assessment (based on physical-chemical characteristics of water and bed- sediments) of the Cutețchi Lake that could be impaired by the anthropogenic impact on the water and sediment quality.

MATERIALS AND METHODS

The research was focused on specific field work, subsequent laboratory analysis, data processing and results from interpretation.

Study area and environmental setting

Cutețchi Lake (Fig. 1) is located in the upper fluvial delta plain, more exactly in the Sireasa - Șontea - Fortuna Depression. Ten sampling stations have been established within the study area (Cutețchi Lake) from which to assess changes in their local environmental conditions within the driest period (August 2016). The location and number of sampling sites are shown in Figure 2. These stations, labeled from *DD16-107* to *DD16-121*, are located as follows: *DD16-107* (44°14'56.9", 28°54'8.9"), *DD16-108* (44°15'7.0", 28°54'26.3"), *DD16-109* (44°15'9.3", 28°54'17.2"), *DD16-110* (44°15'2.4", 28°54'2.9"), *DD16-111* (44°15'1.6", 28°53'48.3"), *DD16-117* (44°14'57.8", 28°53'52.2"), *DD16-118* (44°14'56.6", 28°53'42.3"), *DD16-119* (44°15'0.5", 28° 53'29.2"), *DD16-120* (44°14'52.0", 28°53'32.5"), and *DD16-121* (44°14'50.3", 28° 53'4.1").

Field and Laboratory Procedures

In situ parameters were measured at the sampling spots aboard the ″Istros″ Research Vessel owned and operated by the GeoEcoMar Institute, and *ex situ* parameters were analyzed at other laboratories in agreement with the standard methods.

Specific equipment was used for monitoring the water physical-chemical parameters, such as: WTW Multiline P4 Multiparameter (dissolved oxygen, temperature, electrical conductivity, total dissolved salts, pH, and redox potential), HACH 2100Q (turbidity), HACH 5000 - UV-Vis – Spectrophotometer (nitrates, nitrites, phosphates, sulfates), and HI 83200 Multiparameter Photometer (other common chemical constituents). The concentrations of nitrate, nitrite, orthophosphate and sulphate levels (mg/l) in collected water samples were determined using colorimetric determination with the Hach Lange 5000-UV-Vis spectrophotometer according to the specific method for each parameter (Hach DR 5000, Spectrophotometer Procedures Manual, 2005). The reagents used for the analysis were purchased from Hach (Hach Lange, Romania). As well, other chemical constituents in water samples (Ca, Mg, Cr, Cu, Fe, Mn and Ni) were analyzed with the aid of Hanna Multiparameter Bench Photometer for Laboratories Model HI 83200 (Hanna instruments) in line with the specific method for each parameter (HI 83200 - Instructions Manual). The chemical reagents and buffer solutions used for the test were acquired from Hanna (Hanna Instruments, Romania).

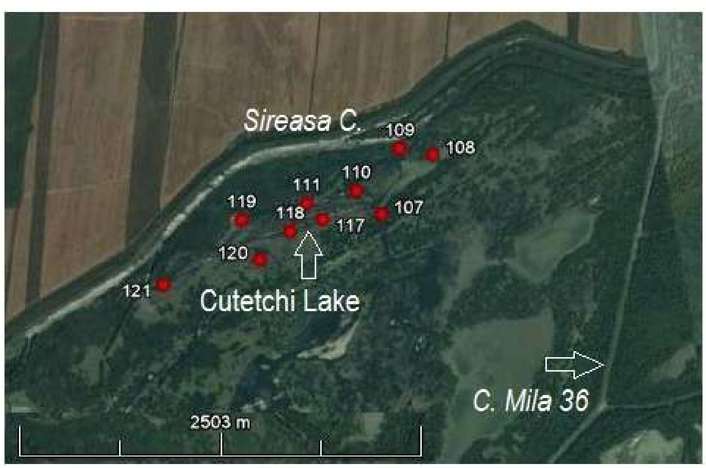

Figure 2 The locations of the sampling stations in the Cutețchi Lake

The sampling of the bed-sediments (sediment-water interface, 0 -20 cm) was achieved using a Van-Veen type grab sampler. The percentage estimation of the main lithological components represented by the total organic matter content (TOM %), total carbonates (CAR %) and siliciclastic fraction (SIL %) was performed by lithological analysis (LOI Method). For quantifying the lithological components (expressed as a percentage), through the calcination method (Dean, 1974; Heiri et al., 2001; Santisteban et al., 2004) it was used as a high-temperature electric furnace SNOL 8.2/1100°C.

Determinations of major components in surficial sediment samples (Fe_2O_3, TiO_2, MnO, Rb, Sr, Cr, Zr and V) were probed by an X-ray fluorescence spectrometry on a VRA - 30 XRF sequential spectrometer, fitted with an X-ray tube with chromium anode, directly on compacted powders. An analyzer crystal LiF 200 was employed to select the characteristic wavelengths, measurements being done with a Na (Tl) J scintillation detector. Titration methods were used for analyzing $CaCO_3$ (Black, 1965) and TOC (total organic carbon), (Gaudette *et al.*, 1974). Determination of MnO, Cr, Zn, Ni, Co, Cu and Pb were analyzed by flame atomic absorption spectrometry and Cd by electro-thermal atomic absorption spectrometry on a Pye Unicam SOLAAR 939E double beam absorption spectrophotometer with deuterium lamp background correction. The precision and accuracy of the AAS and XRF chemical analysis were accomplished with several SRMs (Standard Reference Material) from the US Geological Survey, NIST and IAEA. Compared with the certified concentrations, recovery for AAS varied from 93.2% - Co to 99.4% - Pb, while for XRF the recovery range was 90.3% (Zr) - 104.4% (Sr). Precision, expressed as the coefficient of variation for 6 replicate determinations varied for FAAS between 0.8% (Zn) and 4.5% (Mn), for XRF from 0.2% (Fe_2O_3) to 6.2% (V), the highest variability has been recorded for Cd - 12.5%, GFAAS determination. All chemicals used in the experiments were of analytical reagent grade.
The graphical representation was created using the Surfer Software (Golden Software, Inc., 2011).

RESULTS AND DISCUSSIONS

Surface water characteristics

The water physical-chemical quality indicators can vary in consonance with the natural local circumstances that characterize the considered perimeter (*e.g.,* seasonal flows, rainfall, drought, freshwater inflows etc.) and/or subsequently as a result of potential Danube River upstream and regional anthropogenic pressures. Accordingly, is important to analyze some specific physical and chemical environmental parameters, and their seasonal and spatial variations, too.

Water quality assessment was accomplished in line with water quality guidelines in Romania - Order of the Ministry of Environmental and Water No.161/2006 (for the Approval of the Norm Concerning the Reference Objectives for the Surface Water Quality Classification, Official Journal of Romania, Part 1, No 511 bis). In addition, it has also resorted to other normatives in order to evaluate the total dissolved solids content (http://www.theinfolist.com/php/SummaryGet.php?FindGo=Total%20dissolved%20solids), turbidity levels (STAS 6323 – 88), total suspended solids (ANZECC 2000 Guidelines), the oxidation-reduction potential (Sigg, 2000) and silica levels (http://www.freedrinkingwater.com/water_quality/quality2/j-24-typical-concentrations-for-silicates-ground-n-surface-waters.htm).

The results (expressed as an average value) of the main physical – chemical parameters are shown in the Table 1.

Thermal regime and pH –The distribution of the surface water temperature expressed as an average (20.4 °C) was in line with the seasonal climate variations during August. The water reaction (pH) present values that is included in the normal range for pH in the surface water system which is 6.5 to 8.5 units of pH. The highest value (8.22 pH unit) was recorded in the sampling station labelled DD16-119, and the lowest value (7.55 pH unit) was reported in the sampling station DD16-109. It can be stated that the recorded values give the water a slightly alkaline character.

Oxygen regime – In this study, dissolved oxygen levels (4.95 -12.78 mg/l, respectively 57.2 – 143.40 %) show values which are in conformity with environmental standard (Oder 161/2006), showing in general, well-aerated waters. The lowest value (4.95 mg/l) was noticed in DD16-109 sampling site, and the highest value (12.78 mg/l) was listed in DD16-120. Abnormalities in oxygen concentration could be linked to a number of natural (summer fluctuations as a result of the increased growth of plants and algae, intensive photosynthesis, respiration, and decomposition, etc.) or human related factors (different type of discharges). The distribution of oxygen (mg/l) content and pH (unit) determined in the surface water samples of Cutețchi L. are graphically plotted in the figure 4 (a-b).

Table 1 Summary of the physical-chemical parameters analyzed in the water samples

Value	***T***	***pH***	***O_2***	***O_2***	***N -NH_4***	***N -NO_2^-***	***N NO_3^-***	***P -PO_4^{3-}***
	(ºC)	***(units)***	***(mg/l)***	***(%)***	***(mg/l)***	***(mg/l)***	***(mg/l)***	***(mg/l)***
min	22.2	7.55	4.95	57.2	0.05	0.01	0.01	0.14
max	22.7	8.22	12.78	143.4	1.22	0.01	0.02	0.2
mean	22.39	7.91	8.98	101.52	0.38	0.01	0.02	0.17
Value	***P***	***EC***	***TDS***	***SO_4^{2-}***	***Ca***	***Mg***	***Turb***	***TSS***
	(mg/l)	***(µS/cm)***	***(mg/l)***	***(mg/l)***	***(mg/l)***	***(mg/l)***	***(NTU)***	***(mg/l)***
min	0.1	379	189.5	22	80	45	1.73	5
max	0.5	401	200.5	32	160	50	11.3	15
mean	0.325	392.2	196.1	25.5	127.5	47.5	5.06	9.25
Value	***VDS***	***ORP***	***SiO_2***	***Cr***	***Cu***	***Fe***	***Mn***	***Ni***
	(m)	***(mV)***	***(mg/l)***	***(µg/l)***	***(mg/l)***	***(mg/l)***	***(mg/l)***	***(g/l)***
min	0.7	13	5.91	2	0.06	0.01	0.2	0.03
max	1.5	39	8.99	4	0.25	0.07	0.7	0.05
mean	0.94	22	6.8	3	0.115	0.025	0.5	0.0375

Nutrients regime – the measurements performed on random water samples show the following variations: the ammonia-nitrogen (N-NH_4^+) varies within a relatively wide range (0.05 -1.22 mg/l), the nitrite-nitrogen (N-NO_2^-) and nitrate-nitrogen (N-NO_3^-), varies within a relatively narrow range with a mean of 0.01 mg/l and, respectively, 0.02 mg/l; also, the soluble orthophosphates (P-PO_4^{3-}) and P varies within a relatively narrow range (0.14 - 0.20 mg/l, respectively, 0.1 – 0.5 mg/l). The test results of water samples of the above-stated nutrient monitoring indicators show that in general have not exceeded the limit. There have been noticed some exceptions, compared to environmental standard (Order 161/2006) therefore, the monitoring indicators of some tested samples meet class I, II and III water standard, exceeding the limit.

Salinity regime - Electrical conductivity levels (379 - 401 µS/cm), the concentrations of total dissolved solids (189.5 – 200.5 mg/l) and the levels of sulfates in various surface water samples (22 – 32 mg/l) were below the recommended limit stipulated by the norms. The concentration of calcium (Ca) is generally higher than those values established as a threshold for the class I and II water standard, with values fluctuating within a relatively wide range (80 – 160 mg/l). The magnesium (Mg) concentration varied within a relatively narrow range (45 – 50 mg/l), therefore, some water samples meet class I and II water standard.

Turbidity, total suspended solids, water transparency (Secchi disk visibility/VDS) - Turbidity values varied in a relatively wide variation interval (1.73 – 11.3 NTU), and individual values only incidentally exceed the recommended level. The distribution of the TSS concentration showed values included in a relatively narrow variation interval (5 -15 mg/l), with values corresponding to freshwaters. The transparency of water (Secchi disk) fluctuated between 0.7 - 1.50 m, with an average of 0.94 m.

Oxidation-reduction potential (ORP) - The ORP level probed in water samples falls within the normal variation range in natural waters, with values included in 13-39 mV interval.

Silica (SiO_2) content in surface water - The silica concentration fall within a narrow range, with values ranging from 5.91 to 8.99 mg/l, values included in the reference range of natural waters (5-25 mg/l).

Other specific environmental items, as Cr, Cu, Fe, Mn and Ni were tested in the water samples collected in August 2016. Mainly, the concentration of Cr, Cu, Fe and Ni were below the recommended limit; instead, levels of Mn meet class II and III water standard.

Lake sediment characteristics

Generally, the spatial differences in sediment composition are due to the complex interactions between the physical, geochemical, and biological processes within a depositional environment.

The bed-sediments gathered from Cuteţchi Lake are generally represented by alternations of fine organic mud and very fine silt fractions, with semi-compact close to compact consistency, with loose and unctuous aspect, rarely peat-like, showing a palette of variable colors (from gray-yellowish to dark-gray blackish) and having a fine gray-yellowish oxidation pellicle at the top. A number of plant traces (fine triturated plant material, leaves, and woody remnants), including traces of bioturbation (*Chironomidae* larvae), have been identified. These muds frequently contain shell debris and/or whole shells of *Anodonta, Viviparus, Planorbis, Limnea stagnalis* etc.

A general assessment of the bed-sediment composition (lithology) can be made in line with the weight percentages of the total organic matter, carbonates and minerogenic fraction content, determined by the total weight of dry sediment (G. van der Veer, 2006). The quantitative assessment of the minerogenic matter or mineral residue (the inorganic non-carbonate fraction) was performed using the LOI Method at 950-1000^{o}C (Digerfeldt *et al.,* 2000). Complementary, a common classification of lake sediments was taken into account being attributed to the percentage of the carbonate content (De Bakker and Schelling, 1989). Regarding the estimation of the carbonate content it has recourse to Loss On Ignition (LOI) Protocol (www.geog.cam.ac.uk/facilities/laboratories/.../loi.doc).
Results of analyses of the main lithological components are shown in Table 2.

Table 2. Summary of the physical-chemical parameters investigated in bed-sediments

Value	***TOM***	***CAR***	***SIL***	***WC***	***DM***	***$CaCO_3$***	***TOC***	***Fe_2O_3***	***TiO_2***	***MnO***	***Zr***
	%	***%***	***%***	***%***	***%***	***%***	***%***	***%***	***%***	***%***	***µg/g***
min	62.23	3.56	9.33	17.22	65.29	12.42	4.26	3.88	0.31	0.043	79
max	87.11	11.89	32.03	34.71	82.78	35.06	7.27	5.93	0.83	0.139	216
mean	73.53	7.48	18.98	23.13	76.87	23.54	5.86	5.06	0.54	0.08	119.80
Value	***Sr***		***Rb***	***Zn***	***Ni***	***Cr***	***V***	***Co***	***Pb***	***Cu***	***Cd***
	µg/g		***µg/g***	***µg/g***	***µg/g***	***µg/g***	***µg/g***	***µg/g***	***µg/g***	***µg/g***	***µg/g***
min	186		66	72.2	34	40.7	49	6.71	12.63	36.12	0.449
max	341		123	117.6	51.5	97.5	115	11.37	32.34	73.12	1.282
mean	270.3		96.7	102.17	44.77	73.23	75.30	9.38	24.83	58.70	0.82

The analyzed lithological parameters show that the main component of the bed-sediments collected from Cuteţchi L. is represented by the fraction of the total organic matter with a high share, over 50 % of the total weight of dry sediment, presenting a mean value of 73.53% and a relatively narrow range of variation with values between 62.23 - 87.11%.

The total carbonate content involves a significant percentage with average values of over 1% of the total dry sediment weight, ranging from 3.56 to 11.89 % and an average of 7.48 %.

The minerogenic part has low values, below 50 % of the total dry sediment weight, falling within a relatively wide range of variations, ranging from 9.33 to 32.03% and an average of 18.98 %.

The environmental conditions related to the Cutețchi Lake recently deposited sediments are slightly influenced by the significantly large amounts of organic matter. Here predominates the distribution of the autochthonous material (*e.g.*, the settlement of vegetable and organic detritus constituents). The type of the recent sedimentary deposits accumulated in this lake is characterized by sediments rich and very rich in organic matter (organic muds subordinated followed by the organic-mineral muds). Based on the obtained results (Fig. 3), it can be considered that the sediments of Cuteţchi L., fall within the field of *organic sediments*, and subordinated to the *organo-mineral* type with relatively significant carbonate content.

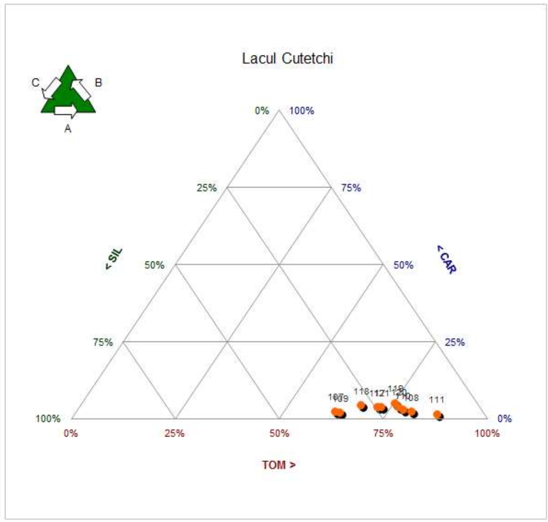

Figure 3 The ternary diagram representing the total organic matter (TOM %), carbonates (CAR %) and siliciclastic fraction (SIL %) in Cuteţchi Lake.

The areal distribution of the investigated lithological parameters (*i.e.,* TOM %, CAR % and SIL %) analyzed in the bed-sediments of Cutețchi Lake are graphically plotted in the figure 4 (c, d, e).

Related to the chemical composition of lake sediments from Cutețchi Lake a brief review will be made. Results of analysis for major, minor constituents and heavy metals of the bed-sediment samples are given in Table 2.
The concentration of major, minor and other constituents identified in the bed-sediments of Cutețchi Lake are graphically plotted in the figure 4 (f-v).

The major constituents' distribution did not reveal a consistent pattern. In this study, our intent is to identify the distinct technophyllic heavy metal concentrations as Ni, Cu, Pb, Zn and Cd. The results were related to Order No. 161/2006 and/or Order No 756/1997, to evaluate the sediment quality status.

In this sense, it can be said that were observed some differences between samples. For all that, it should be noted that the obtained concentration were generally low. Anyway, it was recorded overruns exceeding the established thresholds for the elements as Ni, Cu and Cd. Nevertheless, at this stage it cannot be accurately stated if the accumulation of these elements in the bed-sediments could be linked with pollution caused by human-related activities in the surrounding watershed, or is due to natural processes related to the geochemical background of lake sediments. Within the scope of the analyzed heavy metals, no considerable differences between samples were observed, they occur generally in relatively low concentrations, have only minor variations, and they seem rather to reflect a natural background distribution and their concentration not posing levels of potential effect.

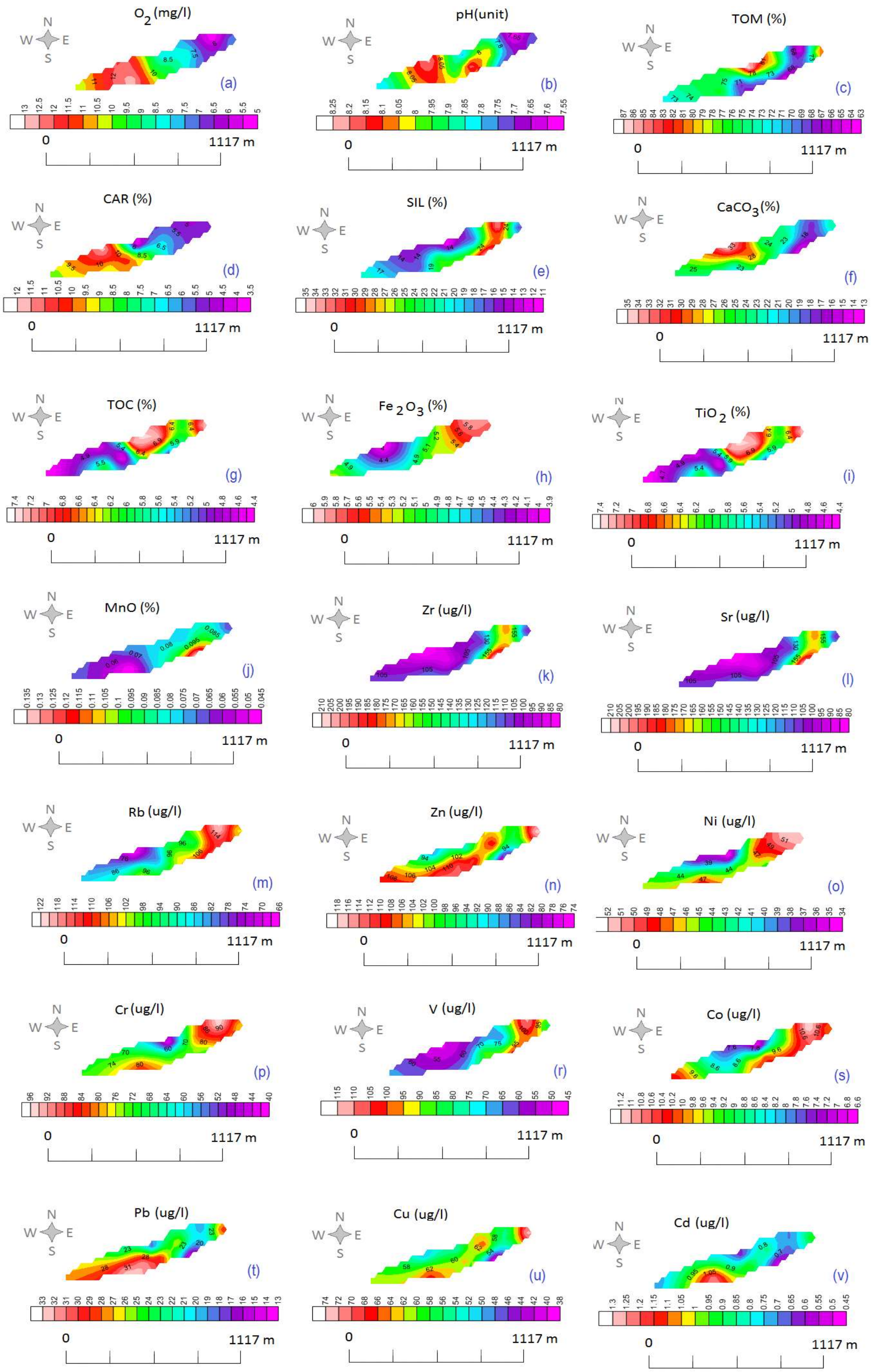

Figure 4 The spatial distribution of some physical-chemical parameters in the surface water (a-b), and, respectively, in the bed-sediments (c-v) from Cutețchi Lake.

CONCLUSIONS

Shallow lakes (as is Cutețchi Lake, in this case) come out with particular functional and structural characteristics due to their location within the Danube Delta, their position towards the Danube River influx of water and sediments, and the secondary hydrographic network, as well.

Water quality in an aquatic ecosystem depends on the many physical - chemical and biological circumstances. The results indicated that the water quality of the different samples, disclosed suitable environmental conditions relative to different physical-chemical environmental variables. The environmental indicators ranged mainly in line with sampling points and generally agreed to a reference standard. Some inadvertent findings were observed, but without triggering a level that will pose a potential negative effect. It is important to note that the analyses of water submit an instantaneous image of the lake's environmental circumstances at the moment of sampling.

The percentage distribution results of the physical sediment parameters (moisture, dry content, total organic matter, total carbonates and siliciclastic fraction) also fluctuate in function of the specific local conditions of the studied areas. As regards the heavy metals, individual values only incidentally exceed the maximum recommended level. Further studies are necessary in order to conclude a causal association between the accumulations of these elements and to relate them to different source areas, as well as to investigate their dispersal patterns in terms of in lake geochemical processes.
In conclusion, this study attempts to supply the environmental knowledge related to environmental issues databases by presenting the main characteristics of water and sediments and assessing these data in the context of the freshwater environmental quality status.

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