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Loss of ignition as a proxy indicator for assessing the lithological composition of the recent sediments accumulated in some freshwater lakes from the Danube Delta, Romania

Irina Catianis, Silviu Rădan, and Dumitru Grosu

National Institute of Marine Geology and Geoecology - GeoEcoMar,
Bucharest/Dimitrie Onciul Street/024053 Bucharest,
Romania

ABSTRACT: The paper asserts the percent horizontal and vertical distribution of the main lithological components (the total organic matter, total carbonates and minerogenic clastic fraction) in the grab surface layer and core sediment samples of some fluvial - Danubian lakes. The study is corroborated on the analysis of 144 grab sampling stations and 6 Hydro-Bios sediment cores collected during 2010-2013. Evaluations of the above mentioned parameters considered in surface sediments, and in samples from distinct cores have been defined by *Loss on Ignition* (LOI) method. By using the total organic matter concentration results in the grab sediment, as a proxy, it was tried to be pursued the source of the organic matter input into the lakes during the recent period. Evaluating the mean areal distribution values of the total organic matter, the shallow water depth, and assuming the *autochthonous* input as a main contributing source, it was exhibited that the investigated lakes are over-supplied with organic material, passing through a continuous shallowing environments due to a strong siltation of the canals and streams. The assessment of the vertical distribution results reported a distinctive pattern with infrequent dominantly organic layers interposed with sequences of minerogenic clastic contents. These fluctuations indicate seasonal shifts that have repercussion on the depositional environment conditions on some moments in time. The results obtained by *LOI* method yields excellent, medium or small correlation between the variations in the investigated parameters.

KEYWORDS: core sediment, Danube Delta, surficial sediment, total carbonates, total organic matter

1 INTRODUCTION

Each lake can yield a numerous type of uses, starting from being centers for human settlements with the whole suite of issues associated as habitation, water supply, boating, navigation, commercial and recreational fisheries, as well as provide relevant data about its evolution on different time scales, degradation of water and sediment quality induced by human activities and other environmental changes at the local and regional scale.

The importance of studying aquatic sediments to outline their origin and characteristics for different goals has experienced an accelerated progress in the recent decades. The benefit of it has been widely studied by the means of many researches ([1], [2], [3], [4]), that emphasizes the major role of the interrelations between sediments, water, soluble elements and particulate matter in the aquatic environment. Thus, in these circumstances, any disturbance which is going to take place in sediments, or in water, will be directly reflected in the lacustrine environment.

The lake sediments are generally composed of clastic material (clay, silt and sand), organic detritus, in-situ chemical precipitates, or a mixture of these components. Their proximate distribution is attributable to *allochthonous* sources (upstream inputs, the nature of the local catchment area, aeolian sediment transport, climate, etc.), as well as for *autochthonous* inputs (the age and the geological substrate of the lacustrine depositional environment along with in-lake related biogeochemical processes).

Specifically, lake sediments are very important in assessing the potential environmental impacts of anthropogenic activities and natural inputs on the composition of the lacustrine sediments, as well as the water quality characteristics of lakes.

2 MATERIAL AND METHODS

2.1 GEOMORPHOLOGY AND THE ENVIRONMENTAL SETTING OF THE STUDY AREA

The Danube Delta is considered as one of the most important and well preserved deltas from Europe, after the Volga Delta, being the natural interface between the extents of land through the medium of the Danube River and the western Black Sea coastline ([5]). The Danube Delta was granted UNESCO World Heritage Site Status in 1991, is listed as a Biosphere Reserve nationwide in Romania, as well as IUCN (International Union for Conservation of Nature) National Park, site of global importance.

Evaluated as an international waterway, the Danube River is one of the most important European connection routes, passing through several countries. It is also denominated as the ”Amazon” of Europe ([6]), due to the paramount importance of the natural reservation and wildlife areas developed along its course, within Europe. Before discharging into the Black Sea *via* Danube Delta, the Danube River branches out into three main distributaries: Chilia (northerly), Sulina (in the central part) and Sf. Gheorghe (south), (see Fig. 1).

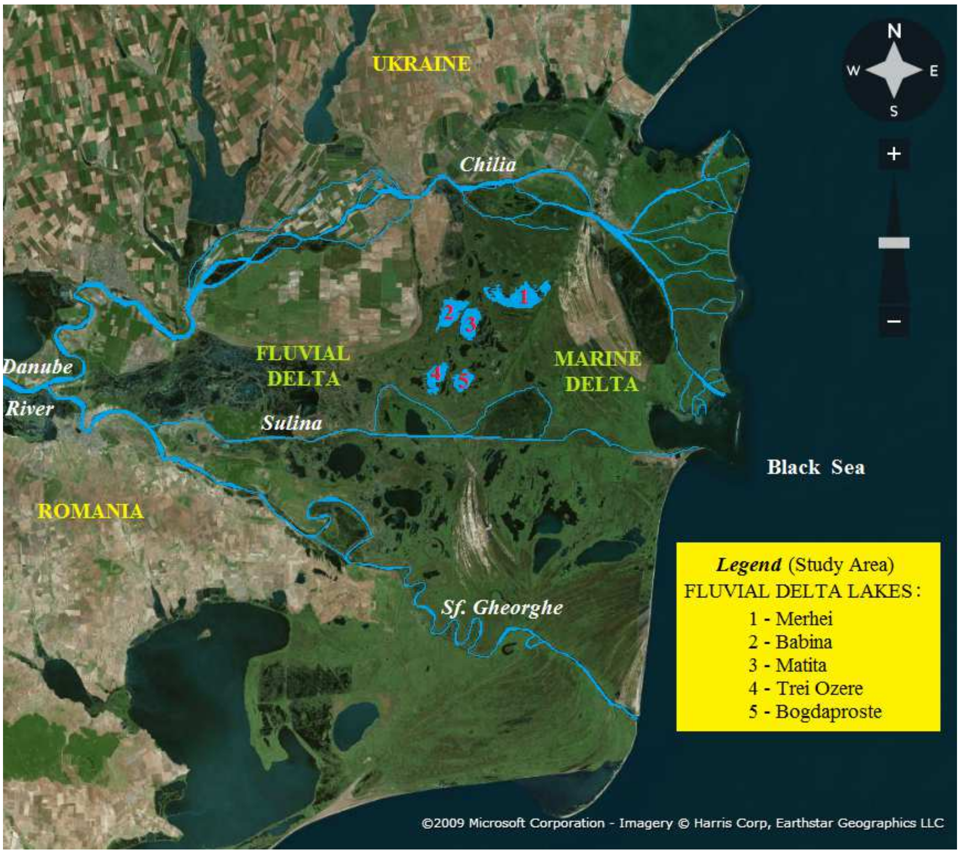

Fig. 1. General view of the Danube Delta and the location of Fluvial Danube Delta lakes where the research was performed. (Satellite image freely available on web services ([7]), Location: Latitude 45°11'7" N, Longitude 28°58'23" E)

The approximate surface of the Danube Delta area is 4152 km2, of which the most part of it (3446 km^2) stretches on the Romanian territory, and a northern smaller part that lies in Ukraine (see Fig. 1). The Danube Delta is a low alluvial plain, predominantly represented by a unique and complex landscape of wetlands, marshes, canals, watercourses and lakes. In terms of geomorphological processes, acts as a very dynamic system, stimulated by strong subsidence and important sediment accumulation, being the youngest landform of Europe, created by the deposition of sediments (sand, silt) brought by the Danube River. The Danube Delta consists of two principal components – the fluvial delta plain (a more elevated unit located in the western part) and the fluvio-marine delta plain (a subjacent unit positioned between the eastern part and the Black Sea coastline), (see Fig. 1). The initial littoral ridge: Jibrieni-Letea-Răducu-Ceamurlia-Caraorman-Sărăturile-Perișor-Lupilor splits these major units ([8]).

Both in the past and today, the water flow and sediment transport in the lower Danube River represents the driving force that controls and processes the Danube Delta development and evolution, under sedimentological, geomorphological and geoecological aspects ([9]). Several interdistributary depressions characterized by primary or secondary specific hydrographic network have been developed between the Danube branches.

The present paper focuses on the study of lake sediments (grab and core) from the Matița - Merhei - Trei Ozere depression that belongs to the fluvial delta plain.

The Matița - Merhei - Trei Ozere Unit, considered as a weakly clogged lacustrine depression area ([10]), is situated between Chilia (Cernovca Branch and Chiliei Grind), in the northern part, and Sulina distributaries (the big ”M” of the Old Danube Branch), in the south (see Fig. 1). This area is placed far enough away from the main arms of the Danube River, thereby the lakes situated in the central-northern part of the unit, are not considerably influenced by the water and sediments provided by the fluvial intake.

The Matița - Merhei - Trei Ozere is one of the dominant lake systems in the Danube Delta, being individualized by the presence of several lakes that cover the entire central part of the fluvial depression. The total water area is about 5701.74 ha (106 lakes). From north to south (see Fig. 2), between the aquatic basins is distinguished: Merhei (1137.47 ha), Matița (641.83 ha), Babina (427.35 ha), Bogdaproste (400.19 ha), Trei Ozere (433.5 ha), ([11]), as well as other lakes, but smaller in size. These lakes are interconnected by the related secondary hydrographic network of inlets and canals (e.g., Eracle, Lopatna, Dovnica, Răducu, Bogdaproste, Sulimanca and Roşca), ([12]).

The system of canals and other small streams present a reversible capacity, aiming to supply (at high water level), and respectively to discharge (at low water level) of the surrounded Danube River distributaries (Chilia and Sulina), ([10]). The main canals that facilitate the inflows and outflows are represented by: Sulimanca, Dovnica, Suez, Lopatna, Rădăcinoasele, Stipoc, Eracle and Bogdaproste (positioned from north to south, see Fig. 2).

2.2 FIELD WORK

During the interval between 2010 and 2013, several sediment samples have been investigated from the Merhei, Babina, Matița, Trei Ozere and Bogdaproste lakes. The sediment samples have been collected in sediment deposition areas, in certain inland lakes from the Matița - Merhei - Trei Ozere Unit. These zones have been chosen depending on the inlet/outlet drainage system that would link with the specific retention basins, as well as their waterways accessibility. The overall aim of this multi-year lake sediment sampling application is to yield a baseline sediment quality characterization.

The sampling expeditions were conducted aboard the R/V ”Istros”, a fluvial and coastal research vessel, managed by the National Institute for Research and Development of Marine Geology and Geoecology – GeoEcoMar, Romania.

The geographical localization of the sampling points was recorded using the Global Position System (GPS).

To evaluate the surficial bottom type sediments (the top 15 – 20 cm of the recent sediments), one hundred and forty-four samples have been collected by hand, using a Van-Veen grab sampler.

To augment the sediment material information under the water-sediment interface (about a maximum depth of 55 cm), six core samples have been gathered through Hydro-Byos gravity corer. Immediately, after the sampling, in-situ, on the R/V ”Istros” board, the grab sediment material was described, sub-sampled, partitioned in single-use plastic containers and stored in cold conditions until their delivery to the laboratories for subsequent analyses. On board, the short cores have been split horizontally; as the sediment core was extruded, slices of 1-3 thickness have been cut and distributed in labelled sample containers.

To be used in the laboratory analyses, an amount of about 100 grams of grab and core sediment was set apart.

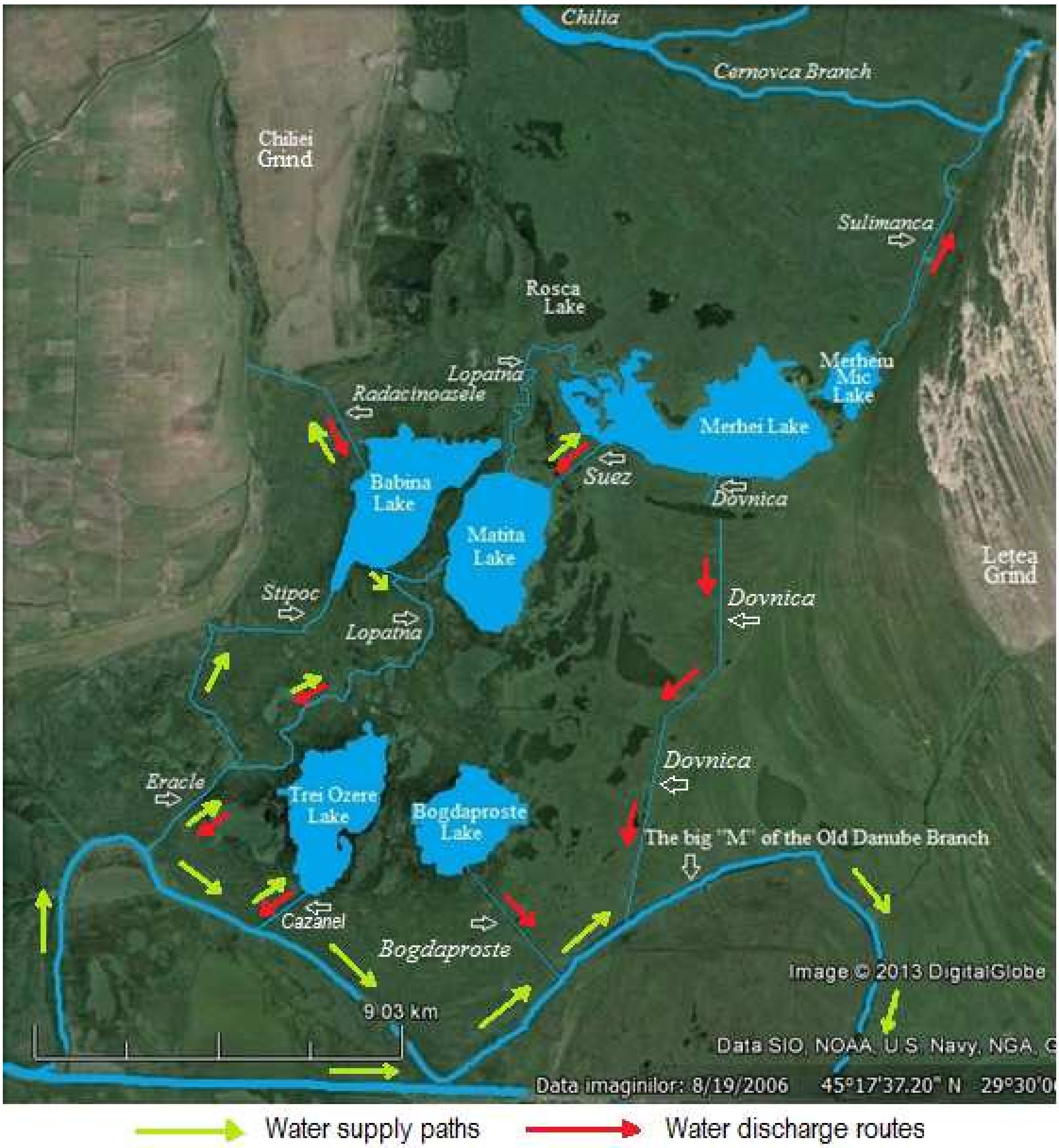

Fig. 2. Detailed view of the sample area locations, and the water circulation of the Matița - Merhei - Trei Ozere Depression (after, [10]), (sources of image: freely available on web services [13], modified).

2.3 Laboratory Methods

Laboratory analyses and sedimentological characterizations were conducted to provide more information that can be applied to evaluate the current sediment quality status of these lakes, to perform a medium-term monitoring in order to develop proposals for rehabilitation and improvement of the lake ecosystems, there, where it is sorely needed.

In this study, several surface sediment samples and some cores were investigated with respect to the visual sedimentological characterization (e.g., observations of the physical parameters as color, structure, texture, grain size, the dominant lithological composition etc.), loss on drying at 105°C (for determining the percentage of moisture and dry sediment content), as well as loss on ignition at 550°C and 950°C (for establishing the percentage of total organic matter and, respectively, total carbonates).

2.3.1 THE VISUAL DESCRIPTION OF THE GRAB AND CORE SEDIMENT SAMPLES

The macroscopic structure of the collected sediment represents the primary types of examinations performed *in situ*, being then supplemented with laboratory observations.

The deltaic lakes, as any other inland bodies of stagnant water, act as a storage place for several materials brought into it by *allochthonous* and *autochthonous* sources (water flow, wind, products resulting from metabolic activities of plant and animal organisms etc.). These materials are represented by the fragments of rocks, fine particles of minerals and organic debris.

The investigated lakes are influenced more or less by the direct intake waters loaded with suspended solids from the Danube River.

Thereby, the grab sediment samples collected from these lakes are characterized by the presence of fine-medium and sometimes coarser particles (due to finely triturated vegetal fragments) of yellowish – gray – dark gray color of non-compacted and non-cohesive silts ([14]); the prevalent material is of organic origin, the silts being consisted of numerous vegetal fragments of reed, leaves, fragile and depigmented shell debris (e.g., *Viviparus viviparus, Dreissena polymorpha, Anodonta cygnea*, various types of *Cardiidae* species), insect larvae (*Chironomidae*) etc. A strong saprogenic odor was noticed in most grab samples.

The short sediment cores (at most 55 cm length) were predominantly gathered from the central area of the following lakes: Matița (2 cores), Babina (3 cores) and Bogdaproste (1 core).

The cores consist of an alternation of lithological sequences represented by silt, clay, silty clay sometimes with dispersed sand-sized granules intervals or intercalated with argillaceous and peaty material (see Fig. 6).

The visual observations of the sediment cores have generally allowed the identification of the following type of deposits based on their color and outward aspect: a fluffy layer of yellowish dark gray to dark gray of organic mud (silt) that accumulates at the top of the core. The interval comprising the median part of the core is represented by different units of sediments that are variable in color (ranging from greenish light gray to dark grayish) and grain size (fine to coarser particles). The lowermost part of the core is characterized by sediment layers that become increasingly more compact alternating in color and grain size, too. A more or less dense and vertical distribution of remnants of shells (various species of *Gastropods*, *Dreissenidae, Cardiidae* etc.), bits of reed, plant residues and clear burrowing that occurs along downwards, has been noticed.

2.3.2 GRAIN SIZE ANALYSIS

The grain size analysis yields basic information regarding the preliminary investigations of lacustrine sediments. Since the aim of this paper is not to use specifically the particle size analysis in order to identify and characterize the fine-coarse-grained, stagnant sediment layers in freshwater lake sediments it will be presented just some grain-size background references. Several data regarding the macroscopic characterizations and grain-size categories of sediments from different Danube Delta lakes were previously published by [15], [16], as well as by [17]. The grain size determinations were carried out with a Laser Particle Sizer. The results accomplished in other anterior surveys showed that the sediments collected from these areas are mainly composed of fine particulate organic material, with a particle size dominated by silt or clay (0.0039 to 0.0625 mm/0.00006 to 0.0039 mm, accordingly with the Udden-Wentorth scale), ([18], [19]), sometimes even coarser. Actually, the prevalence of silt represents a disintegration stage caused by the decomposition of live or dead plant and animal debris (microscopic algae, waste matter etc.), as well as the chemical decaying of various chemical products brought by the fluvial input, or which there exist in the respective lake water mass. The large majority of the organic material within the lakes considered in this study, has *autochthonous* origin, so that the particle size it is not linked excessively to the hydrodynamic conditions and potential sediment transport.

2.3.3 THE MOISTURE AND DRY SEDIMENT CONTENT

The moisture content of lake sediments is a very important evidence as it varies between wide limits in the same set of grab or core sediment samples. The dry sediment content is useful to analogize with the results obtained by ignition loss, showing also the degree of material compaction. The water and the dry matter content were determined volumetrically by the classical laboratory Loss On Drying method (LOD_{105oC}). The sediment samples were weighed (using a readable and accurate to 0.1 mg, Partner AS 110/C/2 Analytical Balance), placed in pre-weighted crucibles and dried overnight at 105 ±5°C (using a Universal Memmert oven), cooled in the dry atmosphere of a desiccator, and then re-weighed again.

The results are expressed as a percentage of the mass (%), using the following empirical formulas:

$$W_{dm}\ [LOD_{105}{}^{o}{}_{C}\ (\%)] = \left(\frac{m_{c-}\ m_a}{m_{b-}\ m_a}\right) \text{ x } 100 \qquad (1)$$

$$W_{wc}\ [LOD_{105}{}^{o}{}_{C}\ (\%)] = \left(\frac{m_{b-}\ m_c}{m_{b-}\ m_a}\right) \text{ x } 100 \qquad (2)$$

Where:

W_{dm} = the weight of the dry matter of the sediment sample expressed in percentages;
W_{wc} = the weight of the water content of the sediment sample expressed in percentages;
ma = the mass of the empty crucible in grams;
mb = the mass of the crucible containing the wet sediment matter in grams;
mc = the mass of the crucible containing the dry matter in grams, dried at 105°C;

2.3.4 ESTIMATION OF THE MAIN LITHOLOGICAL COMPONENTS FROM SEDIMENTS BY LOSS ON IGNITION

The determination of the total organic matter, total carbonates and minerogenic clastic material content was performed by sequential weight Loss On Ignition (LOI) Method at 550°C and respectively, 950°C. The sequential loss on ignition is a customary and universally used procedure applied to the sediments in order to assess their organic matter and carbonate content through weight loss after ignition ([20], [21], [22] [23], [24]).

This technique involves the completion of two phases of heating, at 550°C and respectively, 950°C. The weight loss during the phases is exactly measured by weighing the sediment samples before and after the ignition, being strictly associated with the total organic matter and total carbonate content of the sediment sample. The leftover material that remains after a two-phase of ignition, it is considered to be the minerogenic clastic material (the residue of ignition).

In the first stage of heating, the organic matter is oxidized at 500-550°C. The dried sediment samples (at 105°C) are ignited in a SNOL 8.2/1100 furnace at 550°C for two hours, cooled in a desiccator, and re-weighted. In the second stage of burning, the carbon dioxide is released from carbonate at 900-1000°C, leaving instead the oxides. The dried sediment samples (at 550°C) are ignited again in the furnace at 950°C for two hours, cooled in a desiccator, and re-weighted. The loss on ignition (LOI) is expressed as a weight percentage of the dry mass, applying these empirical formulas:

$$W_{dm}\ [LOI_{550}{}^{o}{}_{C}\ (\%)] = \frac{(m_{c} - m_d)\ x\ 100}{(m_{c} - m_a)} \qquad (3)$$

$$W_{dm}\ [LOI_{950}{}^{o}{}_{C}\ (\%)] = \frac{(m_{d} - m_a)\ x\ 100}{(m_{c} - m_a)} \qquad (4)$$

Where:

W_{dm} = the weight of the dry matter of the sediment sample expressed in percentages;
ma = the mass of the empty crucible in grams;
mc = the mass of the crucible containing the dry matter in grams, dried at 105°C;
md = the mass of the crucible containing the dry matter in grams, dried at 550°C;
me = the mass of the crucible containing the dry matter in grams, dried at 950°C;

The results obtained from this method have been presented in the horizontal (areal) form distribution maps. The areal distribution maps have been plotted by Golden Software Inc. Surfer 8 Program.

3 RESULTS AND DISCUSSION

The sediment status represents an important issue of a freshwater ecosystem, as it is in interconnection with the water mass and several communities of aquatic organisms (pelagic and benthic) that are dependent on each other, as well as on their environmental conditions.

It is well known, that the depositional zones of lakes accumulate and store different types of sediments along the time. Assessing the physical composition of these deposited sediments contribute to obtain information about environmental change tendencies related to natural or anthropic factors, as determinants, in terms of past or medium/long-term evolution of the main characteristics of the Danube Delta environment. Lately, several scientific papers have taken into considerations different research studies about the sediments of the Danube Delta ([25], [26], [27], [28], [29], [30]). Although, due to the fact that there is not too much published data, there has been a growing interest to disseminate as many results as possible related to lithological characteristics of the Danubian lakes.

The deposited sediments placed on the bed of the lakes contain two main constituents as, an inorganic one (derived from upstream sediment flux or from the erosion of the lake geological substratum), and an organic part (provided by the decaying plant and animal matter, biological production and decomposition, plant and animal debris). The purpose of this paper is to evaluate the distribution of the main lithological components (the percentage of the total organic matter, total carbonates and minerogenic clastic material) from the sediment-water interface (grab) and bottom sediments (core). A significant contribution of the primary source of organic matter to these lake sediments is represented by the aquatic plants living in the water lake, or terrestrial plants that grow up on the lake edges. The association between the excessive development of the phytoplankton corroborated with the biomass of macroalgae and macrophytes result in a superabundant development of the biological productivity during the warmer months ([31]).

The predominant vegetation species of the Matița - Merhei - Trei Ozere Unit is represented by floating algae, periphyton, macrophytes and reed beds found mainly in the central part, and a subordinated association of reed and rush towards the adjacent edge areas of lakes.

Another source of organic matter is represented by the inputs resulted from plankton biomass, different in-lake biological processes caused by plant and animal organisms, residues etc.

Presumably, the nature and distribution of the total carbonate contents investigated in the collected sediment samples have an authigenic origin (due to the chemical precipitation and recristalization or, due to the mechanical abrasion of *autochthonous* or *allochthonous* skeletal or non-skeletal carbonate elements). Laboratory sample preparation has considered as much as possible the removal of the visible shell debris present in the material.

3.1 THE GRAB HORIZONTAL DISTRIBUTION PROFILES OF THE LITHOLOGICAL COMPONENTS OF THE INVESTIGATED LAKE SEDIMENTS

The accumulation of the recent sediments in the investigated freshwater lakes was assessed by linking the field observations and drainage basin morphology with the measurement and the analogy of the main lithological components investigated for 144 sampling stations. The percentage distributions of the investigated lithological components of the grab sediments are shown in the table 1.

As it was previously mentioned the lakes belonging to the Matița - Merhei - Trei Ozere Unit, are situated relatively further away from the Danube River water supply.

More than that, the accumulation of sediments from tributaries or streams and canals is supposed to decrease considerably as a result of their landscape context, as well as due to their temporary character. The anthropogenic factors such as river engineering and management has not a significant impact in this perimeter, the majority of the investigated lakes being under natural conditions.

The analysis carried out to figure the moisture and dry matter contents in the surficial sediments show different variations that are certainly dependent on the local specificities and the dynamics of the investigated lakes (see Table 1), as well as due to sediment sample's lithological type.

MERHEI LAKE

The Merhei Lake is located in the northern compartment of the Matița - Merhei - Trei Ozere Unit, being contiguous with the Letea grind (the access is only possible by boat). This lake is characterized by a poor water circulation due to the long distance from the main hydrological network of the Danube River (e.g, Chilia branch), (see Fig. 2). Also, the secondary hydrological network is rather poorly represented by some small streams and canals that are affected by long-term siltation.

The areal distribution of the total organic matter content in the Merhei Lake present maximal concentrations (values between 75 - 85%) that covers almost the entire surface of the lake (see Fig. 3).

The results were plotted together (meaning the data for Merhei and Merheiu Mic Lakes), taking into consideration the small area of the Merheiu Lake. The increased concentrations of the organic material accumulated on the bottom of this lake could be linked to the stagnant environmental conditions. Therefore, the organic matter is considered to be of *autochthonous* origin. Some exceptions of this trend occur in the northern part (namely in the Merheiu Mic Lake, 40 - 75 %), as well as in the southeastern part of the Merhei Lake (50 - 75 %), zones that are relatively in connection with the Sulimanca (north) and Dovnica (south) stream inputs. The water currents, even at lower rates can substantially impede the accumulation of the organic matter.

Generally, the distribution of the total carbonate content (%) contains values between 0.38 - 8 %. A zone of maximal concentration is observed in the central part of the lake. More than likely, the source of total carbonate content (in weight percent) is attributed to the carbonate detritus (fragments of shells, skeleton structural parts, internal waste products).

The minerogenic clastic fraction (the leftover material) reveals areas with both minimal and maximal values (there is an inverse correlation with the organic matter). Factors as, weak lake circulation, abundant sub-aquatic plants and substantial organic settlings are consistent with the quiescent environmental status of the lake.

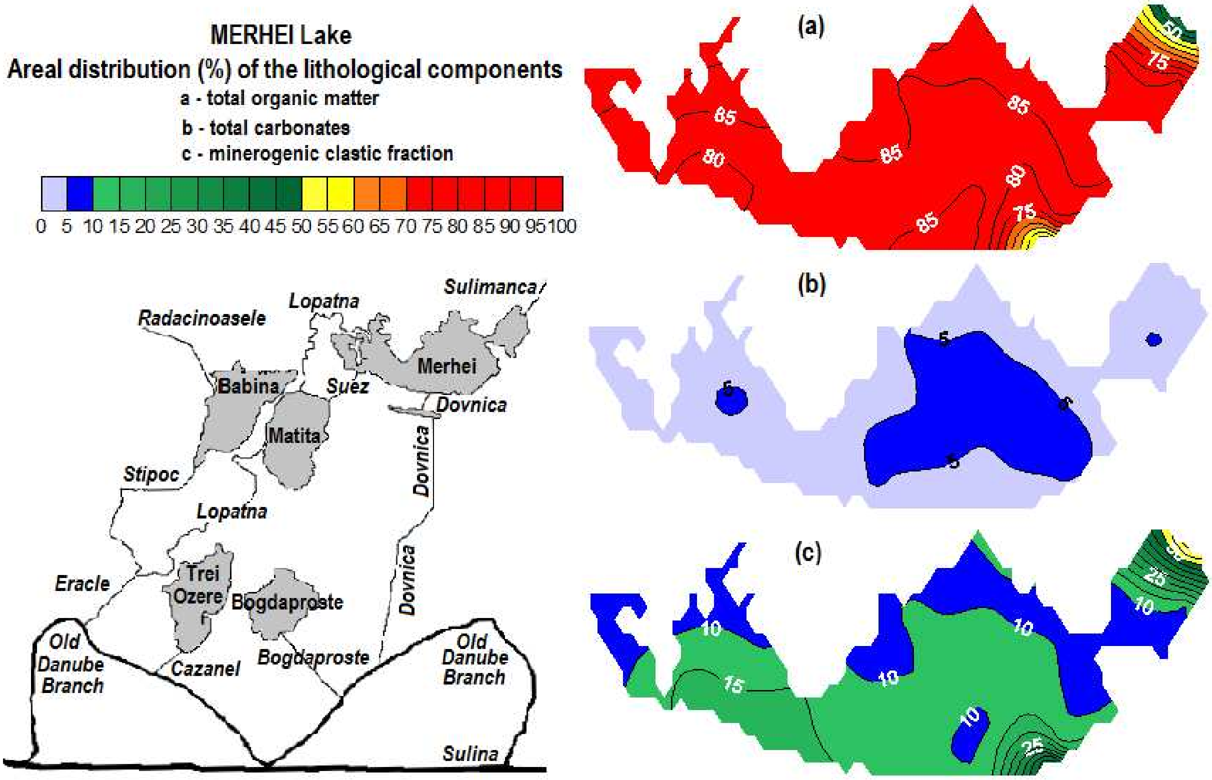

Fig. 3. Areal distribution and concentrations (%) of the investigated parameters in surficial sediments from Merhei Lake.

BABINA AND MATIȚA LAKES

To some extent, this pair of lakes is in the same stagnant environment, characterized by a considerable distance from the Danube River arms (e.g., Chilia and Sulina arms), a rather low rate of the surface water flow and sediment transport by streams and canals, and a richness of underwater plants.

The concentration of the total organic matter content, show areas with various values (34.36 - 84.58 %) that occur in different sediment sample locations in the Babina Lake (see Fig. 4).

In the northwestern sector of the lake, there is an area with relatively low values of the total organic matter, that could be associated with the Rădăcinoasele Canal (preventing probably the deposition of the organic material due to the water currents). The values of the total carbonate concentrations in grab sediments are registered between 1.06 - 13.89 % interval. The increase of several percent occurs in the northern part of the lake. The values obtained for the minerogenic clastic fraction content, are in the 12.87 - 63.74 % range. An apparent increase take place in the northeastern part of the lake near the Rădăcinoasele Canal. As it was previously noted, the concentration of the minerogenic clastic fraction is frequently inversely related to the total organic matter content.

Concerning the total organic matter distribution in the Matița Lake it can be said that here prevails quite high contents, therefore this lake is entirely dominated by sediments full of organic matter (53.20 - 82.25 %).

The total carbonate content of the Matița surface sediments (2.69 - 8.55 %) is primarily attributed to the organogenous constituents (e.g., shells and skeleton pieces of different species). A relatively increase of the total carbonate several percents covers approximately three quarters of the lake surface.

The minerogenic clastic fraction contains a moderate percentage with values included in the 13.26 - 42.49 % range.

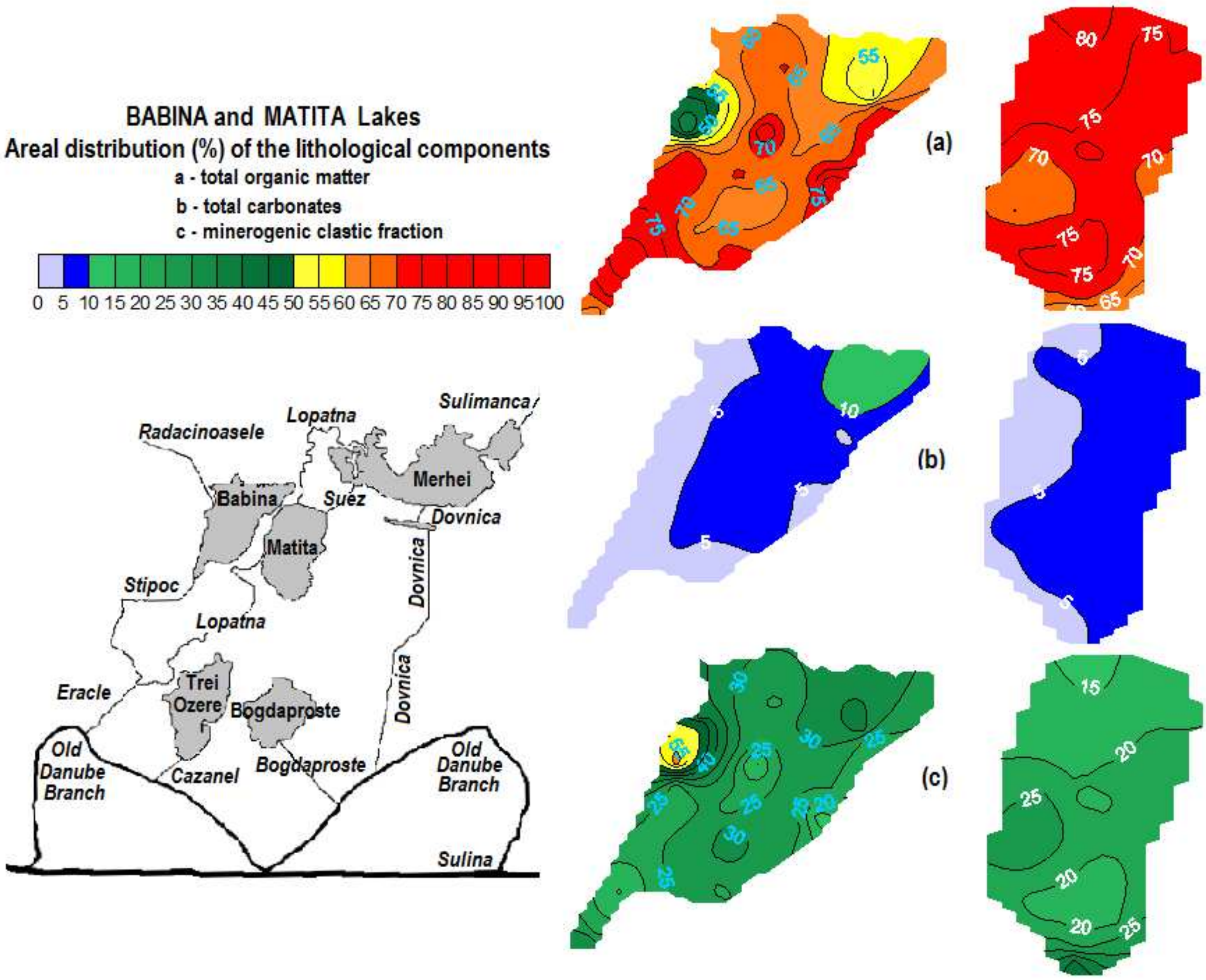

Fig. 4. Areal distribution and concentrations (%) of the investigated parameters in surficial sediments from Babina and Matița Lakes.

Table 1. The percentage distribution content (min./max./mean) of the lithological components of the grab/core sediment samples

Lake	**Lake/Core Location**		**Number of samples**	**The dry sediment content (%)**			**The moisture content of sediment (%)**			**Total organic matter (%)**			**Total carbonates (%)**			**Minerogenic clastic fraction (%)**		
	Latitude N	*Longitude E*		**Min. value**	**Max. value**	**Mean value**	**Min. value**	**Max. value**	**Mean value**	**Min. Value**	**Mean value**	**Max. value**	**Min. value**	**Mean value**	**Max. value**	**Min. value**	**Mean value**	**Max. Value**
GRAB SEDIMENT SAMPLES																		
Merhei	45°19′15.7″	29°26′48.2″	45	73,65	87,50	81,38	12,50	26,35	18,62	28,12	92,63	82,99	0,38	8,00	3,78	5,92	68,15	13,22
Babina	45°18′20.7″	29°20′28.3″	33	35,21	77,09	53,57	22,91	64,79	46,43	34,36	84,58	67,63	1,06	13,89	4,95	12,87	63,74	27,42
Matița	45°17′46.1″	29°22′8.0″	25	53,70	88,66	72,94	11,34	46,30	27,06	53,20	82,25	72,93	2,69	8,55	5,74	13,26	42,49	21,33
Trei Ozere	45°14′24.1″	29°19′4.6″	21	71,07	89,81	84,78	10,19	28,93	15,22	57,72	88,72	79,68	1,90	8,09	4,74	9,30	40,12	15,58
Bogdaproste	45°14′5.9″	29°21′37.9″	20	72,61	81,99	78,82	18,01	27,39	21,18	54,85	91,37	81,63	1,28	6,91	3,71	7,28	43,09	14,66
CORE SEDIMENT SAMPLES																		
Matița (DD10-01)	45°17′41.76″	29°22′8.94″	27	29,53	75,93	56,05	24,07	70,47	43,95	4,62	55,58	15,85	5,34	18,17	10,09	34,47	90,00	74,06
Matița (DD11-01)	45°17′49.8″	29°22′12.5″	23	67,08	81,35	73,49	18,65	32,92	26,51	11,81	85,69	58,11	3,26	12,29	6,47	10,77	79,74	35,43
Babina (DD10-18)	45°18′6.78″	29°20′6.18″	25	53,23	92,81	69,11	7,19	46,77	30,89	3,13	69,69	26,95	1,06	10,69	4,08	23,56	93,52	68,98
Babina (DD10-106)	45°18′19.4″	29°20′22.6″	21	60,19	77,15	67,91	22,85	39,81	32,09	10,43	79,66	55,55	0,99	9,48	5,47	15,38	88,09	38,98
Babina (DD11-49)	45°18′00.4″	29°20′05.4″	15	59,41	82,40	74,68	17,60	40,59	25,32	2,97	83,07	33,79	3,96	15,59	6,30	12,97	89,97	59,90
Bogdaproste (DD13-104)	45°14′01.4″	29°21′27.4″	24	40,22	77,67	58,89	22,33	59,78	41,11	3,10	82,97	49,80	1,40	15,17	4,20	12,63	91,35	46,00

Also, in this situation, it is assumed that the *autochthonous* inputs (e.g., physical, chemical and biological in-lake processes) of this couple of lakes (Babina and Matița) contribute to outlining the areal distribution pattern of the lithological components. This is consistent with the weak connection with the hydrographic system, low sedimentation rate, as well as the abundance of submersed aquatic vegetation.

TREI OZERE AND BOGDAPROSTE LAKES

The couple of lakes Trei Ozere and Bogdaproste, located in the southern compartment of the Matița - Merhei - Trei Ozere Unit, exposed the same trend of the lithological component distribution. The local environmental conditions are quite different in comparison with those mentioned above, meaning the nearest distance from the Danube River intake, benefiting moderately of an active water circulation. Nevertheless, the status of these shallow depth lakes is influenced by phytoplankton-macrophyte dominated species etc.

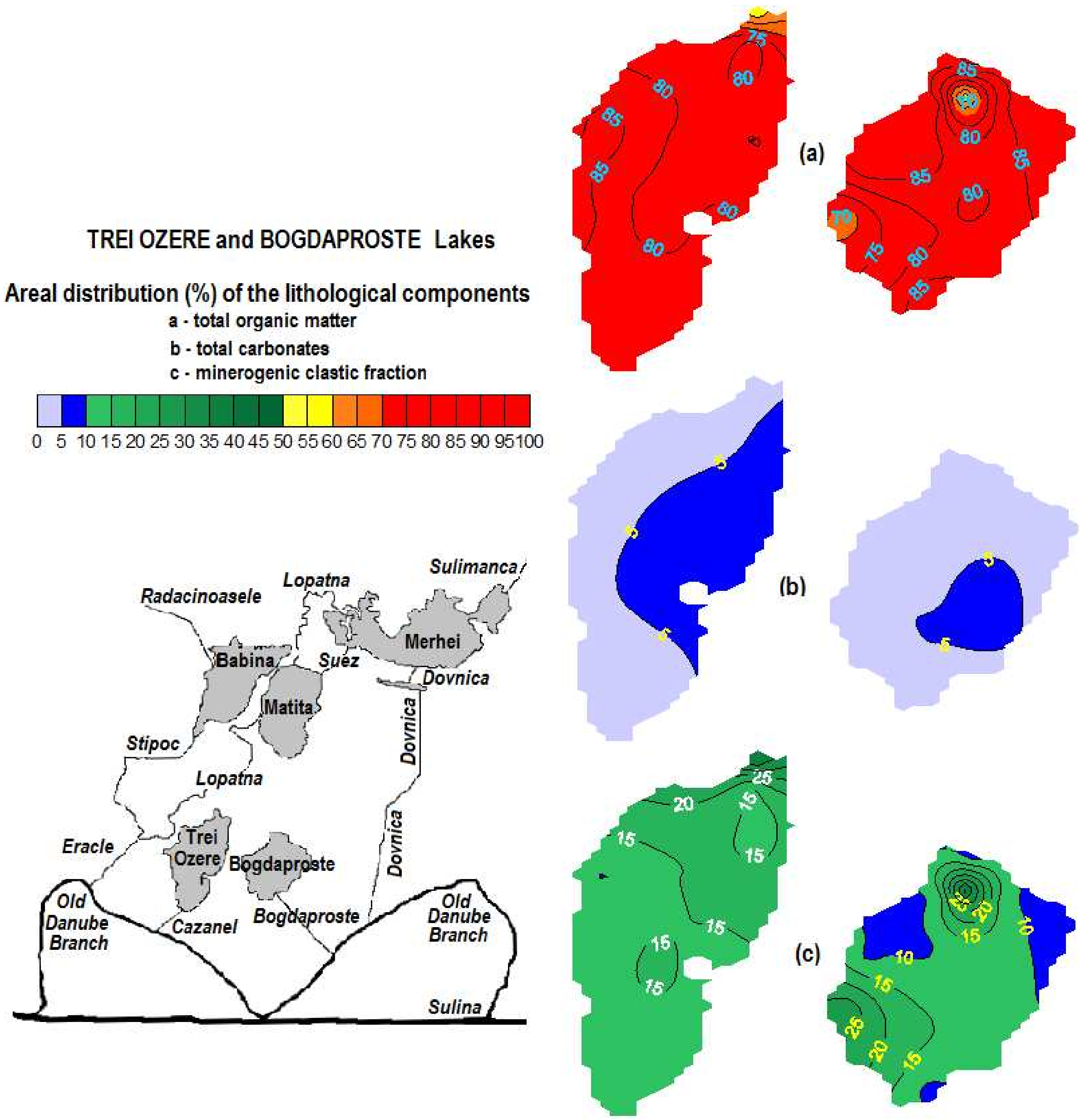

Fig. 5. Areal distribution and concentrations (%) of the investigated parameters in surficial sediments from Trei Ozere and Bogdaproste Lakes.

So, the total organic matter distribution in the Trei Ozere Lake is defined by high values ranging from 57.72 - 88.72 % (see Fig. 5). This suggests quiescent environmental conditions that control the accumulation of the organic matter input (vegetal and fauna settled on the bottom of lakes). The total carbonate content (1.90 - 8.09 %) reveals some increased percents in the eastern half of the lake. The minerogenic clastic fraction areal distribution includes a moderate percentage with values fluctuating from 9.30 up to 40.12 %.

Over its entire surface, the Bogdaproste Lake exhibit zones of maximal concentration of the total organic matter content (54.85 - 91.37 %). The organic settlement dominates this lake, too. The total carbonates content values (1.28 - 6.91 %) are somewhat lower compared to the other investigated lakes. An increase of several percent outline a spot area within the southeastern part of the lake. A variation of the minerogenic clastic fraction content (7.28 - 43.09 %) was noticed in different sediment sample locations that are related to the concentration of the organic matter content, with which is often inversely correlated.

3.2 THE CORE VERTICAL DISTRIBUTION PROFILES OF THE LITHOLOGICAL COMPONENTS

This investigation includes the analysis of core lake sediment lithological composition, some basic data, related to past and recent environmental changes. From the investigated area, three lakes were short cored, namely Matița, Babina and Bogdaproste.

Matița Lake lies in the northern compartment of the Matița - Merhei - Trei Ozere Unit. Two cores, labelled as DD10-01 and DD11-01, were extracted from this lake, during 2010 and 2011, respectively, in order to identify the lithological horizons and their analogy with the vertical distribution of the investigated parameters. The short core DD10-01, sampled near the central part of the lake, reached a maximum depth of 55 cm, and the DD11-01 core, was picked a short distance away towards the north end, being probed to a depth of 53 cm.

Babina Lake is situated in the middle compartment of the above mentioned unit. Three sediment cores designated as DD10-18, DD10-106 and DD11-49 were gathered from this lake, during 2010 and 2011. The first core (DD10-18) was taken from the middle of the lake, reaching at a depth of 55 cm and the other one (DD10-106), was drawn relatively towards the north end of the lake, going into 44,5 maximum depth. The third core (DD11-49), sampled in the south end direction, was captured the bottom lake sediments to the depth of 53 cm.

Within the Bogdaproste Lake, located in the southern compartment of the Matița - Merhei - Trei Ozere Unit, was collected one core, termed as DD13-104, during 2013. The core was probed near the center of the lake and reached a maximum depth of 48 cm.

A very generalized lithological description of the recovered sediments is summarized in the graphical representation of the lithological columns from the Fig. 6. A composite image of each of the short sediment cores has been plotted using Paint-Microsoft Windows, aiming to identify any similarities among the six cores. The depths are presented in centimeters from the bottom surface of the lake. The majority of the fresh core sediment characterization was performed on R/V board. The color codes of the lithological columns have been chosen aleatory.

Generally, all the log cores are homogenous in composition (texture and structure), exhibiting a fluctuation of intervals with remarkably organic and inorganic depositions.

In reference to visual description, these lake short cores mainly exhibit 3 distinct divisions: the top, the middle part and the bottom section. The upper part of the core, comprise intervals of green-dark gray, soft, unconsolidated fine-grained (silt and clay) organic lake bottom mud accumulations, mixed with debris flow deposits.

Sometimes these accumulations that generically represent the median part of the core, are standing over sandy or argillaceous deposits. As the sediment layers go down deeper, they become increasingly more compact. All these layers have a variable content of an organic material.

For a general overview it is noticed that the short cores collected from the Matița and Babina lakes exhibit relatively the same pattern of the sediment layer arrangement, in comparison with the Bogdaproste Lake that does not show a similar distribution patterning. A unique peaty coarse-grained sediment material layer packet is evidenced here, along with silty argillaceous enclaves, as well as peaty silt enclaves.

The distribution and the associations of this strata can be linked to the fact that the layers are deposited in a different environment (e.g., poor drainage flow conditions, grain-size and distribution, slowing rates of organic matter decomposition).

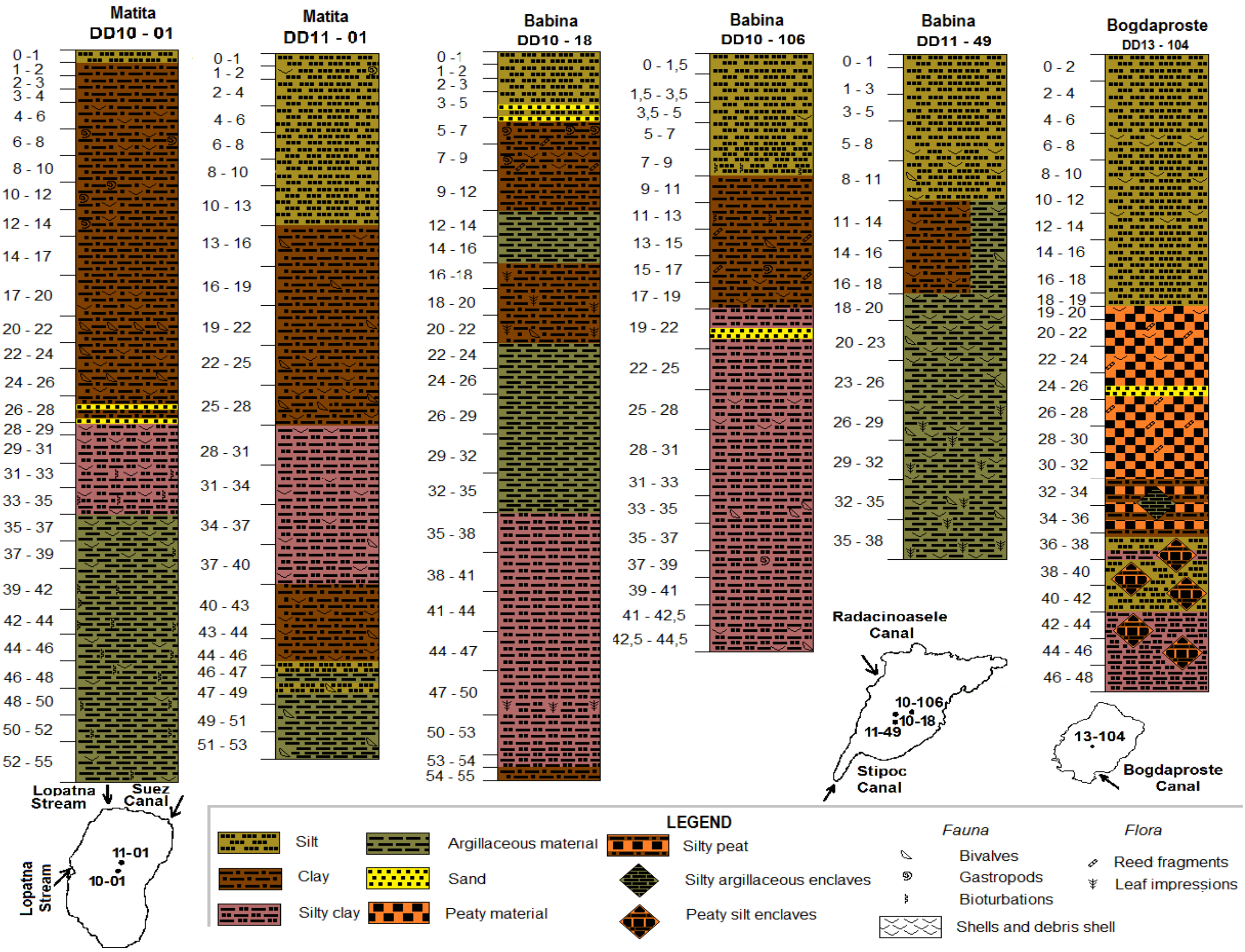

Fig. 6. The uppermost sedimentological layers captured in short cores from Babina, Matița and Bogdaproste Lakes

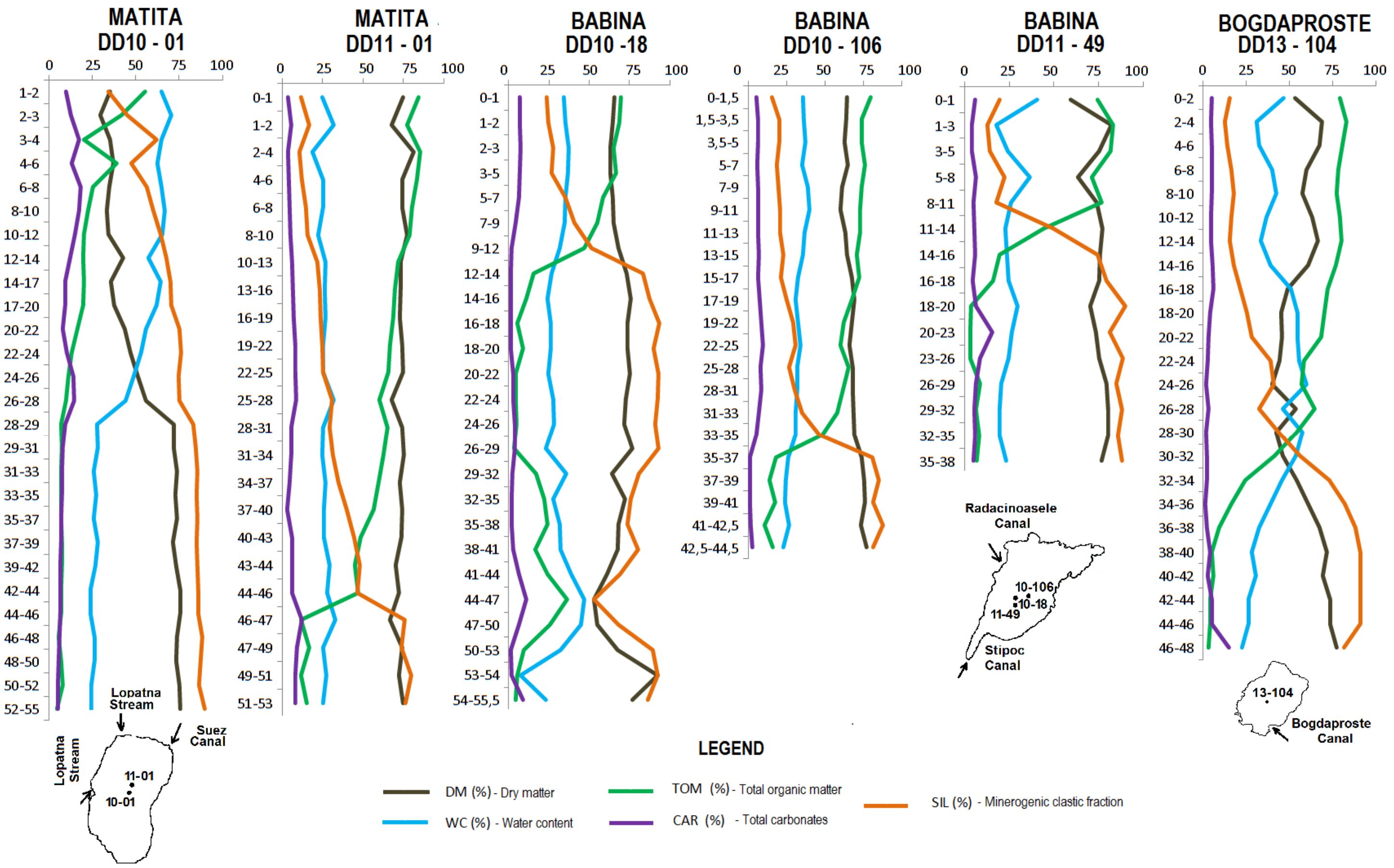

Fig. 7. Vertical distribution (%) of the investigated parameters (dry matter, water content, total organic matter, total carbonates and minerogenic clastic fraction) within the short cores sediments from Babina, Matița and Bogdaproste Lakes.

The total organic matter, the total carbonates and the minerogenic contents were measured to indicate if there exist any change patterns of these parameters during the time. The percentage distribution of the short core sediment parameters is shown in the table 1.

The results obtained from the LOD_{105oC} (Loss on drying) measurements performed to determine the moisture and dry matter contents, does not indicate major changes regarding the lithological profiles of the investigated lake sediment cores. The typical water content and dry matter tendencies, are complementary with depths, but their magnitude is unequal. Generally, the diagrams are characterized by a rapid loss of water in the upper part of the cores, and then it has noticed a downward decrease trend (showed with blue lines). The water content is inversely related to the amount of the dry matter content (showed with brown lines).

A relatively continuous water content variation was noticed in the cores (DD10-01 and DD11-01) collected from the Matița Lake. This might suggest that the particle settling has been accumulated during a quiescent depositional environment. Instead, a discontinuous water content variation was observed in the other cores, gathered from the Babina and Bogdaproste lakes (DD10-18, DD10-106, DD11-49 and DD13-104).

An explanation for this situation may be related to different changes of the environmental conditions during the sediment deposition (external and internal physical-chemical factors, grain-size, lithology type etc.). Thereby, it can be appreciated that in the investigated area, it was evidenced a fairly normal degree of the water and dry mater content spatial variability between lakes, related to their local environmental conditions.

By using the Loss On Ignition ($LOI_{105/550/950^{\circ}C}$) method, some interesting results regarding the vertical distribution of the total organic matter, total carbonates and minerogenic clastic contents, have been obtained.

The general total organic matter and minerogenic clastic content are, equally with depth, although their degree of variation is dissimilar. In the upper part of the majority of cores, it is observed a quite high content of the total organic matter (showed with green lines) which then downward decreases. The total organic matter content is inversely correlated with the minerogenic clastic fraction (showed with orange lines). Each investigated cores has a specific high increase of the total organic matter percentage and a corresponding low percentage of minerogenic material (when the total organic matter values increase, the minerogenic fraction values decrease). This tendency persists downcore with fluctuating high and low percentages of the total organic matter and minerogenic material values.

For example, the DD10-01 core collected from the Matița Lake display some clear high/low peaks in total organic matter (values ranging from 4.62 to 55.58 %) and an interrelated low/high peaks in percentage minerogenic part (33.47 - 99.00 %), at a core depth of 3-4 cm, 4-6 cm and 6-8 cm (see Fig. 7).

Starting from the 6-8 cm interval, the organic matter, content, registered a quite linear downward decrease. This trend is similar in the other core, DD11-01, gathered from the same lake. Some distinct peaks of the organic matter content (11.81 - 85.69 %) and a corresponding low of the clastic material (10.77 - 79.74 %) were observed at 1-2 cm and 2-4 cm intervals. Then, the total organic matter gradient shows a relative continuum shape until the core depth of 44-46 cm, after which began to suddenly decrease. A strong negative correlation has been noticed between the total organic matter and minerogenic variables (see Fig. 8-Ac).

The three cores taken from Babina lakes shows a different pattern distribution regarding the investigated parameters (the total organic matter and the minerogenic fraction) (see Fig. 7).

For instance, the values of the total organic matter content (3.13 - 69.69 %) measured in the DD10-18 core, reveal a discontinuous downward decrease between 0-29 cm. Then, a gradient increase it is noticed at a core depth of 38-41 cm, that afterwards shows a low, but undeviating decrease in the percent of organic matter below 41 cm, downcore. At 44-47 cm a high peak of the total organic matter is registered, that then continue to decrease.

Certainly, that the minerogenic fraction percent values (23.56-93.52 %), are inversely correlated with the organic matter distribution (see Fig. 8-Cc).

The similar non-linear total organic matter distribution is evidenced also in the DD10-106 (10.43 - 79.66 %) and DD11-49 (2.97 - 83.07 %) cores, with values that downward decrease; a corresponding high/low percent of minerogenic fraction in DD10-106 (15.38 - 88.09 %) and DD11-49 (12.97 - 89.97 %) was registered (see Fig. 8-Dc and 8-Ec).

The last core, DD13-104, gathered from the Bogdaproste Lake, also present increased percentages of total organic matter values (3.10 - 82.97 %) at the top of the core, that then downward consistently decrease (see Fig. 7).

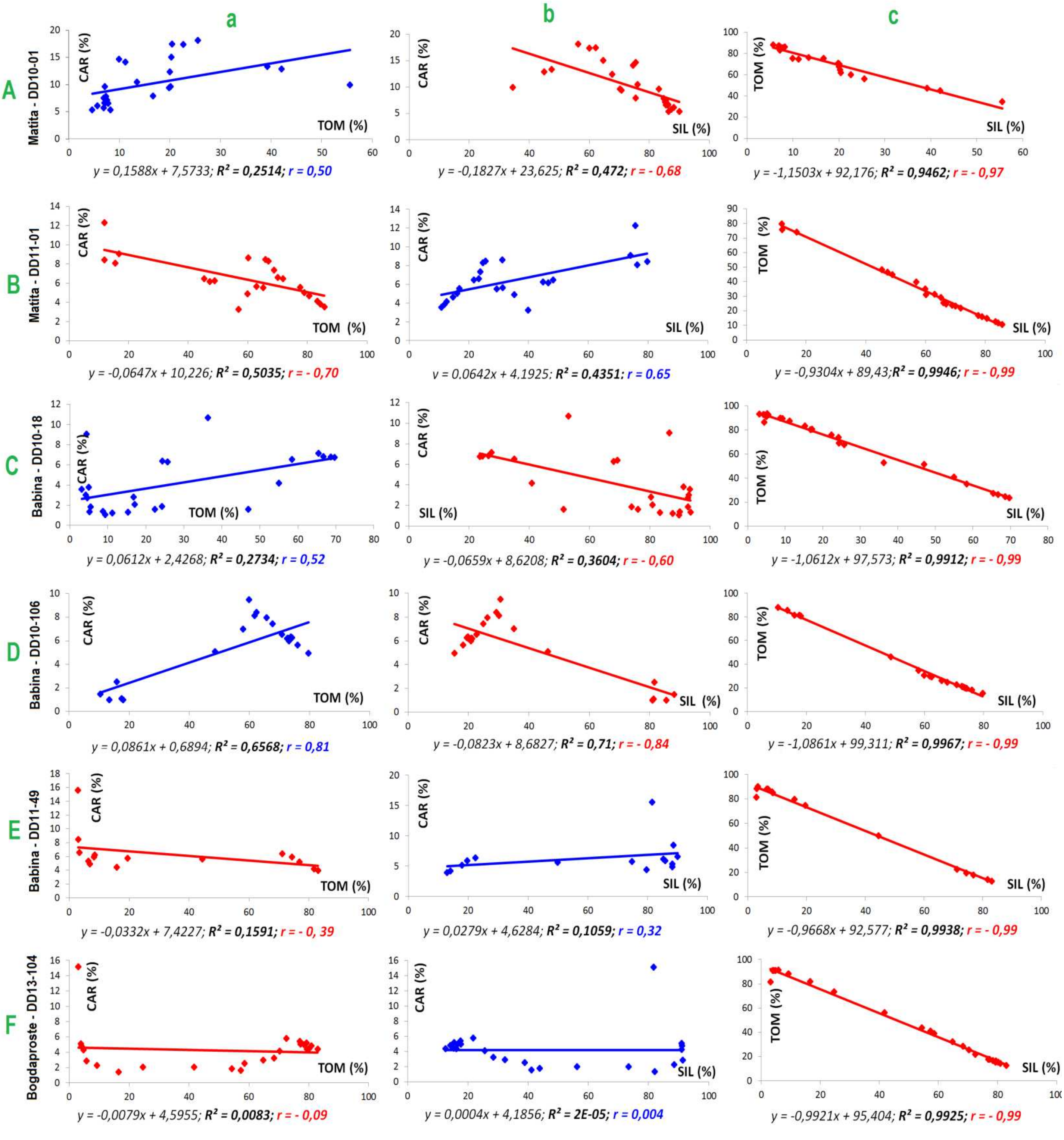

Fig. 8. Scatter diagrams and correlations between investigated parameters within the short cores sediments from Babina, Matița and Bogdaproste Lakes.

The minerogenic content (12.63 - 91.3 %) record high or low values, correspondingly with the total organic matter part, with which is inversely correlated (see Fig. 8-Fc).

The percent total carbonate results obtained from the investigated lakes show approximately the same orientation (see Fig. 7).

The determination of the total carbonate content (showed with violet lines), generally, registered different percent values.

For instance, the following values have been encountered in DD10-01 (5.34 - 18.7 %) and DD11-01 (3.26 - 12.29 %), respectively, cores extracted from Matița Lake (see Fig. 7).

The core collected quite close to each other, from the same Babina Lake (see Fig. 7), present similar values, as: DD10-18 (1.06 - 10.69 %), DD10-106 (0.99 - 9.48 %) and DD11-49 (3.96 - 15.59 %).

The core DD13-104, picked from Bogdaproste Lake (see Fig. 7), present values ranging from 1.40 - 15.17 %. There are some distinct high or low peaks, encountered along the investigated cores. A possible reason for the higher values could be linked to biogenic accumulations (debris shell or skeletal remains) or due to bio-induced precipitate.

In all investigated cores from Matița, Babina and Bogdaproste lakes (DD10-01, DD11-01, DD10-18, DD10-106, DD11-49 and DD13-104) a discontinuous gradient with respect to the total organic matter vertical distribution, was observed (see Fig. 7).

The variable peaks (higher or lower) encountered at different core depths could be related to the past environmental sedimentation process dynamic conditions.

It is assumed that the particular local conditions (e.g., the storage regime as the inflow and outflow of the lakes, intense biological activity and chemical processes etc.) have allowed the organic matter deposition in higher amounts.

The lower peaks of the total organic matter may be associated with an inorganic contribution affluence that prevails in some moments in the environment.

The discontinuous gradient applies also to the minerogenic clastic content, a trend that occurs in all investigated cores.

4 CONCLUSIONS

The accumulation of recent sediments in the investigated shallow lakes depends on several factors as the geological and geomorphological lake context, local and regional water and sediment transport capacity, climate influences, the prevalence composition of the flora and fauna associations that exist in that environment etc.

The obtained results, reveal that the areal distribution pattern of the most recent surface sediment cover accumulations of the investigated lakes had a uniform distribution. The only one category that is distinguished here is represented by the organic matter-rich sediments. The mean value of the total organic matter concentrations is very high in all lakes, as it follows: Merhei (82.99 %), Matița (72.93 %), Babina (67.63 %), Bogadaproste (81.63 %) and Trei Ozere (79,68 %).

The ranges of the mean value in total carbonate contents are also uniform, being recorded the following values: Merhei (3.78 %), Matița (5.74 %), Babina (4.95 %), Bogdaproste (3.71 %) and Trei Ozere (4.78 %).

In this sense, it can be said that the probed lake sediments have similar characteristics, incorporating largely organic matter-rich sediment type (about 80 % total organic matter), low in carbonate content (to around few percent of the total carbonates).

It appears that, the autochthonous source (biological and microbiological production and decomposition within the water body) plays a major role, dominating in this area, any contrast being registered between lakes.

Even the Bogdaproste and Trei Ozere lakes, located in the southern part of the Matița-Merhei-Trei Ozere Unit, and which are considered that are standing hydrologically open (through Sulina Arm), does not present any difference in surface sediment characteristics.

Concerning the core sediments it can be said that the entire suite of deposited sediments are layered, being disposed as flat sheets, more or less thick. The type of sediment accumulations ranges in depth. The layers are characterized by fluctuating different color (from greenish light gray to dark grayish), grain-size (silty clay - fine sand), as well as other constituents (debris shells, plant fragments etc.).

By looking at the lithological composite image of each of the sediment cores gathered from Matița and Babina lakes no major differences were found. However, the exception is given by the core collected from Bogdaproste Lake, characterized by the existence of a unique peaty coarse-grained sediment material layer, that is not rediscovered in the other cores. This suggests that these particular layers were deposited in a different manner in function of freshwater inflow variability and local lake conditions (specificity, dynamics, climate).

The in-depth distribution of the total organic matter is particularly within all investigated sediment cores, and frequently varying within the same aquatic basin. A possible cause of this situation could be represented by the seasonal climatic shifts (droughts alternating with floods), suggesting contrasting depositional environments on a local scale.

Generally, the vertical distribution pattern of the total carbonates is uniform with values included in the same approximate range. The encountered inconsistencies could be related to internal local changes (debris shells, skeletal remains or bio-induced precipitate).

The lake basins considered relatively hidrologically open (e.g., Bogdaproste and Trei Ozere), as well as lake basins considered relatively hidrologically close (e.g., Merhei, Matița and Babina) have been investigated. The results showed that the lake basins intercommunicates with the hydrological network (streams and canals) in diversified ways that are controlled by seasonally induced lake-level shifts (water depth, water and sediment influx), autochthonous productivity and local unstable depositional environment conditions.

The Loss of Ignition has proved to be a fast and reliable method relating to the global assessment of the main lithological components of the grab and core collected sediments, contributing to the identification of the main type of surficial sediment deposited, and respectively in the top 55 centimeters of the bottom of lakes. The hydrographic parameters and the nature of the deposited materials rule the local variations of the total organic matter and total carbonates in the investigated lakes.

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