DISTRIBUTION AND MOVEMENT OF WATER–SOLUBLE GEOCHEMICAL ELEMENTS IN A PEAT BOG DURING ENVIRONMENTAL CHANGES AND HUMAN IMPACTS IN THE EASTERN CARPATHIANS IN ROMANIA[•]

EGY TŐZEGLÁP VÍZOLDHATÓ GEOKÉMIAI ELEMEINEK ELOSZLÁSA ÉS MOZGÁSA A KÖRNYEZETI VÁLTOZÁSOK ÉS EMBERI HATÁSOK TÜKRÉBEN, A KELETI-KÁRPÁTOKBAN

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Abstract

This paper presents the result of geochemical analysis of the peat bog at Homoródszentpál Kerek-tó (Round Lake). The bog is situated in Homoród Hills of the Eastern Carpathians in Romania. The primary objective of this study was to analyse the water–soluble geochemical composition of a 7500 year long peat record and compared previous sedimentological and pollen analytical data. The selected water–soluble elements (Fe, Mn, Ca, Mg, Na and K) concentrations were determined using flame AAS. The 560 cm long sedimentary core consists of an upper lake and a lower marsh phase, which show different geochemical characteristics. The elemental distribution describes the paleoenvironmental and palaeohydrological changes and indicates different evolution stages of the bog system. Through our results, water–soluble Fe and Mn could be linked to the mineral component of the sediment while the Ca shows biophilic origin. The Na, K and Mg show affinity both to the organic and inorganic material.

Kivonat

Kutatásunkban a homoródszentpáli Kerek–tó tőzegláp geokémiai vizsgálatának eredményeit mutatjuk be. A láp a Keleti-Kárpátokban a Homoródi-dombságban található, Romániában. A tanulmány elsődleges célja a 7500 éves tőzegrétegsor vízoldható elemtartalom meghatározása volt, valamint a korábbi szedimentológiai és pollen elemzési adatokkal való összehasonlítása. A kiválasztott vízoldható elemek (Fe, Mn, Ca, Mg, Na, K) koncentrációját AAS atom abszorpciós spektroszkópiával határoztuk meg. Az 560 cm hosszú üledékes mag egy felső tavi és egy alsó lápi fázisból áll, melyek eltérő geokémiai jellemzőket mutatnak. Az elemek eloszlása leírja a paleokörnyezeti változásokat és megmutatja a láp különböző fejlődési szakaszát. Eredményeink szerint a vízben oldódó Fe és Mn az üledék ásványi anyagával mutat kapcsolatot, míg a Ca biofil eredetet mutat. A Na, K és Mg kapcsolatot mutat mind a szerves, mind a szervetlen anyaggal.

KEYWORDS: PEAT BOG, WATER–SOLUBLE ELEMENTS, ATOMIC ABSORPTION SPECTROMETRY, PALEOENVIRONMENT.

KULCSSZAVAK: TŐZEGLÁP, VÍZOLDHATÓ ELEMEK, ATOM ABSZORPCIÓS SPEKTROMETRIA, PALEOKÖRNYEZET.

Introduction

Peat and lake sediments which accumulated in situ are important paleoenvironmental archives (Mackareth 1965).

The peat records are appropriate for reconstructing the palaeoclimatic, paleoenvironmental and paleo-ecological changes (Blytt 1876; Sernander 1892), These changes could be reconstructed using many different methods, for instance radiocarbon dating, pollen and macrofossil analysis, testate amoebae, geochemical and isotope analysis.
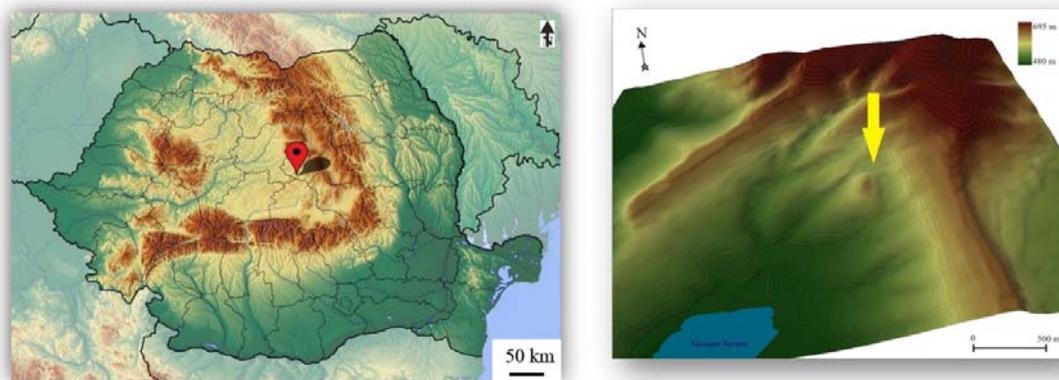
Fig. 1.: Relief map of Romania within the studied site (Round Lake at Săntpaul) and the location of core site on the 3D map

1. ábra: Románia domborzati térképe a vizsgálati helyszínnel (Kerek–tó, Homoródszentpál) és a fúrás helyszíne a 3D–s domborzati modellen

The Round Lake peat sequence formed between 7500 cal BP and the 16th century (depth of sediment: ca. 560–104 cm), when as a result of increased human activities the basing was gradually infilled. During the 19th century a fishing pond was created by damming (Tapody 2016; Tapody et al. 2018).

In this paper, we compared the previously published results of sedimentological and palinological investigations (Tapody et al. 2018 with the new geochemical results).

The aim of this study is to understand and present the geochemical behaviour of the analysed elements in peat deposits, and define the interaction between chemical changes and environmental, climatic and hydrological changes.

The site studied

The Round Lake (latitude 46°11′56.24″N and longitude 25°25′00.37″E) is a dried-out lake situated on the south-western foothills of the Hargita Mountains of the Eastern Carpathians in Romania (**Fig. 1.**).

The average elevation of the lake is 547 m a.s.l. and the surface is 2–3 hectares. The basin of the lake developed as a result of down-slope mass wasting promoted by thawing permafrost during the Late Glacial/Postglacial transition (Vandenberghe et al. 2014; Ruszkiczay–Rüdiger & Kern 2016; Tapody 2016; Tapody et al. 2018). The bedrock consists of Tertiary silty clay layers at the bottom overlain by Late Tertiary – Quaternary volcanic tuff and tuffite (Szakács & Seghedi 1995; Pécskay et al. 1995). The sampled core is 560 cm long and did not reach the bottom of the bog. The core sequence represents

ca. 7500 years (Tapody et al. 2018). The lower 460 cm of the sequence is represented by various peat layers, and the overlying top 100 cm of the sequence is represented by sediments of the pond created at the end of the Middle Ages (Tapody et al. 2018).

The Carpathians are a transitional area between continental climates and the oceanic ones from east to the west, as well as between boreal climates in the north and Mediterranean climates in the south. Precipitation in the Eastern Carpathians ranges from 1,400 to 1,600 mm/year. These general characteristics vary in terms of radiation and the circulation of air masses, and are directly reflected in plant associations and soils, and consequently indirectly reflected in all the natural components of the mountainous environment (UNEP, 2007; JRC, 2010).

Materials and Methods

560 cm–long undisturbed core was taken by Russian peat corer from the centre of the former lake in June 2015. The sediment core was extracted by a 5–cm–diameter sealed liner tube and it was sub-sampled at 2–4 cm intervals for palaeobotanical, sedimentological, geochemical analysis. The main lithostratigraphic features of the core were described using Troels–Smith (1955) system, as the method developed for unconsolidated sediments.

This study is focused on the geochemical characteristics of the lake. The sedimentological and radiocarbon and palynological methodology and results are described in detail in Tapody et al. (2018).
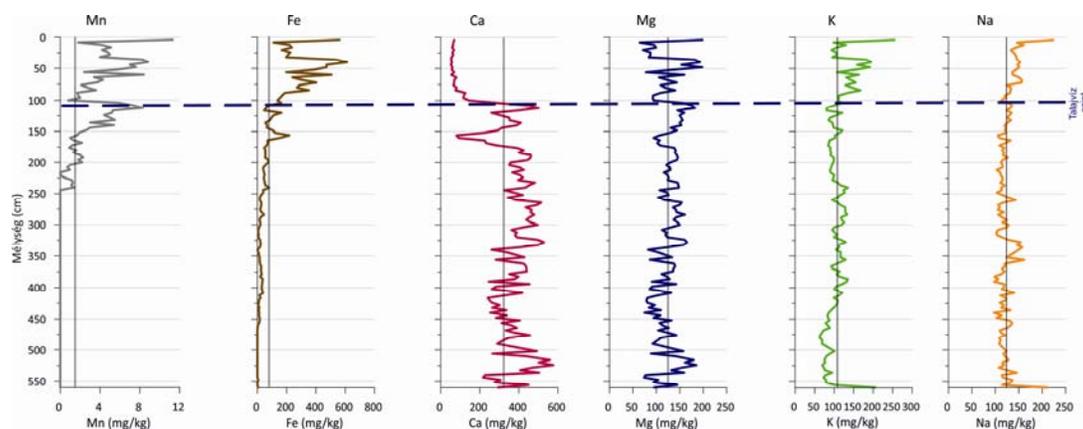
Fig. 2.: The concentration of water–soluble elements in the peat core and the water table. The black line represents the mean value.

2. ábra: A vízoldható elemtartalom a rétegsorban, megjelölt talajvízszinttel. A fekete vonal az átlagot jelöli.

Table 1.: Sedimentological description of the core profile of Round Lake

1. táblázat: A Kerek-tó fúrómagjának szedimentológiai leírása

Depth (cm)	Troel-Smith category	Lithostratigraphy
0-102	Lc1As3	Greyish red calcareous silty clay lake sediment
102-198	Lc1Th1As2	Dark brown calcareous silty clay with limonite precipitates
198-254	Th2Lc1As1	Blackish brown mixed reed and sedge peat with calcareous silty clay
254-260	Th3Lc1	Blackish brown mixed reed and sedge peat with carbonate rich silt
260-284	Th2Lc1As1	Blackish brown mixed reed and sedge peat with calcareous silty clay
284-290	Th3As1	Grey-black mixed reed and sedge peat with clay
290-292	Th2Lc1As1	Blackish brown mixed reed and sedge peat with calcareous silty clay
292-320	Th3As1	Grey-black mixed reed and sedge peat with clay
320-362	Tb3As1	Deep-red *Sphagnum* peat mixed with clay
362-366	Th2Lc1As1	Blackish brown mixed reed and sedge peat with calcareous silty clay
366-382	Th3Lc1	Deep-red mixed reed and sedge peat with calcareous silty clay
382-392	Th2Lc1As1	Blackish brown mixed reed and sedge peat with calcareous silty clay
392-510	Th3As1	Deep-red mixed reed and sedge peat with clay
510-530	Tb3As1	Dark brown *Sphagnum* peat mixed with clay
530-560	Th3As1	Deep-red mixed reed and sedge peat with clay

Table 2.: Water–soluble elements mean concent-ration (mg/kg) in the Round Lake whole section, compare to the lake and the bog phase.

2. táblázat: Vízoldható elemek átlag koncentrációi a teljes Kerek-tó szelvényében összehasonlítva a tavi és a lápi fázissal.

	Total section 0-560 cm	Lake phase 0-100 cm	Bog phase 100-560 cm
Mn	1.51	4.58	0.81
Fe	83.43	304.04	33.74
Mg	125.41	120.63	126.48
Ca	319.67	74.04	374.99
Na	125.06	143.45	120.92
K	108.13	139.30	101.11

The core for geochemical was sub-sampled at 4 cm intervals. Applied method was the first step of the five–step extraction–digestion method by Dániel (2004). The water–extractions of the unseparated samples gave information about the water–soluble elements from weathered minerals (like carbonates and salts), precipitates and ions bound slightly onto the mineral surface (Dániel, 2004). The distributions of concentrations of Mn, Fe, Ca, Mg, Na and K could indicate the changes in the bog conditions which describe the paleoenvironmental and palaeohydrological changes.

Samples were grounded and air-dried at 105 °C for 24 hours. 100 ml double–distilled water was added to 1.0 g sample. The samples were shaken for 6 hours at 160 rpm. The resulting suspension was filtered and diluted to 50 ml. 1 ml 65% (m/m) HNO3 was added for storage (Dániel 2004). Element concentrations were determined by flame AAS (Perkin–Elmer 100) using conventional standards of known concentrations.

Statistical analysis was performed by using SPSS 25.0 statistical software package and we used Spearman rho correlation coefficient.

Results

Stratigraphy of the Round Lake sediment

The sediments of the Round Lake could be divided into 3 main zones. The first zone from the surface to 100 cm depth is a lake sediment phase which a result of silt up in the Medieval Age. The second zone is a transition phase the lake sediment with mixed reed and sedge remains. The third zone between 198 cm and 560 cm is composed of mixed peat. This zone dominantly consists of reed and sedge peat, but Sphagnum peat is also present in two sections (320–362 cm and 510–530 cm). When the core was pulled out, the compression closed the hole, so the core did not reach the underlying bedrock. (**Table 1.**).

Elemental composition

The whole core section is characterised by various peat accumulation and inorganic sediment deposition. These changes can be observed in the content of water–soluble elements (**Fig. 2.**). In the case of the studied elements, it can be observed that they behave differently in both the lake (0–100 cm) and the bog phases (100–560 cm). The accumulation depends on various conditions, but overall, the lake phase have higher mean Mn, Fe Na, K and lower Ca and Mg concentrations which is the reverse of the bog phase (**Table 2.**).

In the correlation matrix of the whole section of the Round lake seen in **Table 3.** A strong positive correlation between Fe–Mn, Ca–Mg, Fe–Ash yield and Mn–Ash yield, and strong negative correlation between Ca–Fe, Ca–Ash yield. Furthermore, the correlation matrix for the lake and the bog phases were examined separately (**Table 4., Table 5.**). It can be clearly seen that in the lake phase Mg shows a strong correlation with Fe and Mn, while it has a negative correlation with Ca, meanwhile in the correlation matrix of the bog phase is similar to the whole section correlation matrix.

The distribution of Fe and Mn concentrations has similar trends along the whole section. From the surface to 104 cm is the first sedimentation layer which is a calcareous silty clay lake sediment. In this section, all analysed elements except the calcium showing high concentrations near the surface. There are three significant Mn and Fe peaks well correlated with each other. From 160 cm downward the amount of the two elements decreases.

The trends of Na and K contents are similar in the bog phase, and they show small fluctuation along the section. The higher K and N contents are recorded in the upper 104 cm (**Table 2.**). Significant peaks are detected between 36–83 cm, which is similar to Fe, Mn and Mg peaks. High Na concentrations were also recorded at depths 256–260 cm, 334–366 cm and 532–536 cm. These peaks overlap with higher plant–containing lithologic layers (Th3Lc1, Tb3As1, Th3As1) and layer boundaries.

The Ca and Mg concentrations from the base of the core to 112 cm have similar distributions. At the depth of 112 cm, the Ca concentration sharply decreased and remains at low values in the whole upper section of the core. Unlike Ca, the content Mg in the upper section is correlated with Fe and Mn distribution.

Table 3.: Spearman's rank correlation coefficient matrix between the concentration of analysed elements and ash yield in total section. **Correlation is significant at the 0.01 level (2–tailed). *Correlation is significant at the 0.05 level (2–tailed).

3. táblázat: Spearman–féle rangkorrelációs koefficiens mátrix az elemkoncentrációk és a hamutartalom között a Kerek tó teljes szelvényében. ** a korreláció szignifikáns 0.01 szintnél, * a korreláció szignifikáns 0,05 szintnél.

	Mn	Fe	Mg	Ca	Na	K
Fe	0.86**					
Mg	0.23**	0.15				
Ca	-0.47**	-0.48**	0.57**			
Na	0.42**	0.32**	0.13	-0.30**		
K	0.23**	0.51**	0.18*	-0.21*	0.28**	
Ash y.	0.82**	0.94**	0.08	-0.49**	0.29**	0.53**

Table 4.: Spearman's rank correlation coefficient matrix between the concentration of analysed elements and ash yield lake phase. **Correlation is significant at the 0.01 level (2–tailed). *Correlation is significant at the 0.05 level (2–tailed).

4. táblázat: Spearman–féle rangkorrelációs koefficiens mátrix az elemkoncentrációk és a hamutartalom között a tavi fázisban ** a korreláció szignifikáns 0,01 szintnél, * a korreláció szignifikáns 0,05 szintnél.

	Mn	Fe	Mg	Ca	Na	K
Fe	0.79**					
Mg	0.61**	0.91**				
Ca	-0.75**	-0.50*	-0.26			
Na	0.62**	0.56**	0.43*	-0.45*		
K	0.52**	0.86**	0.96**	-0.15	0.40*	
Ash y.	0.52**	0.16	-0.10	-0.77**	0.29	-0.15

Table 5.: Spearman's rank correlation coefficient matrix between the concentration of analysed elements and ash yield bog phase. **Correlation is significant at the 0.01 level (2–tailed). *Correlation is significant at the 0.05 level (2–tailed).

5. táblázat: Spearman–féle rangkorrelációs koefficiens mátrix az elemkoncentrációk és a hamutartalom között a lápi fázisban ** a korreláció szignifikáns 0,01 szintnél, * a korreláció szignifikáns 0,05 szintnél.

	Mn	Fe	Mg	Ca	Na	K
Fe	0.79**					
Mg	0.35**	0.29**				
Ca	-0.08	-0.05	0.81**			
Na	0.12	-0.02	0.22*	0.07		
K	-0.08	0.33**	0.13	0.12	0.03	
Ash y.	0.73**	0.91**	0.26**	-0.06	-0.06	0.41**
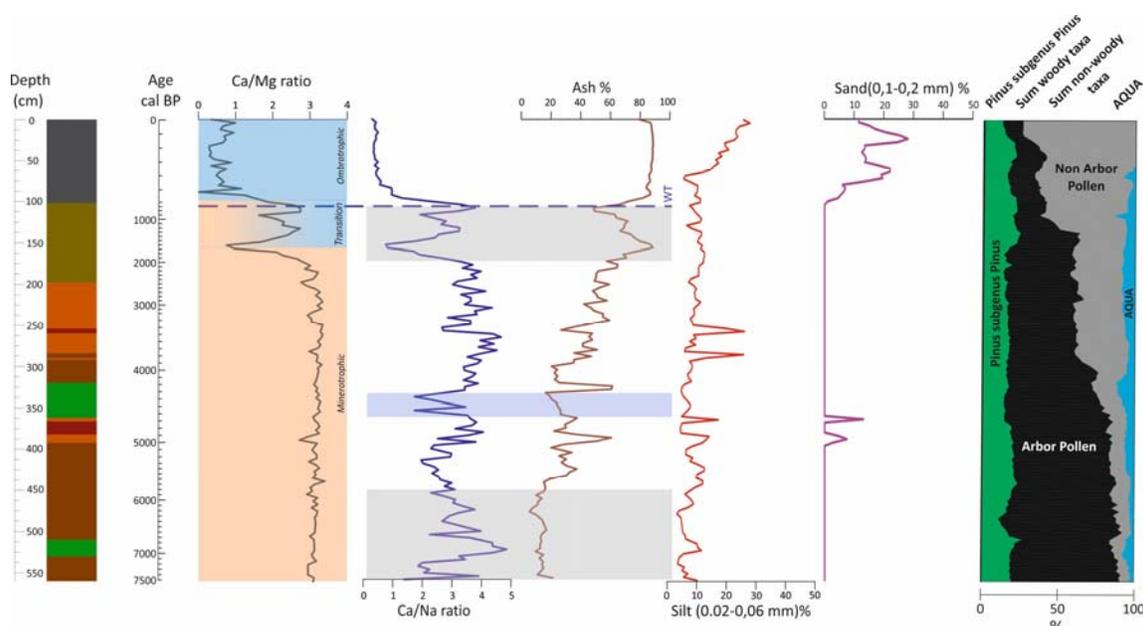
Fig. 3.: Comparable representation of the Ca/Mg ratio, Ca/Na ratio, Ash% content, coarse silt and fine sand content and a summarised pollen data from Tapody et al. (2018).

3. ábra: Összehasonlító ábra a Ca/Mg arány, Ca/Na arány, Hamu % tartalom, durva kőzetliszt %, finom homok % és az összesített pollen ábrával Tapody et al. (2018)-ból átvéve.

Discussion

The analysed concentration of elements show a significant change between the peat-land and the lake phase at about 104 cm, as well as at the time of the sampling (May 2015) the water table was at 104 cm.

The Fe and Mn are lithogenic elements, but their content depends on the environmental factors that control post–depositional processes (Schittek et al. 2015, Muller et al. 2006, 2008), which affected just the upper part of the section. Therefore, the concentration of water–soluble Mn and Fe are well correlated with the ash content (**Fig. 3.**). This section is a silty clay lake phase which derived from the weathering of mineral sediments. Both elements under anaerobic condition are mobile and accumulate above the water level (Damman 1978; Shittek et al. 2015).

In the previous studies (Mackereth 1966; Engström & Wright, 1984; Dániel 2004) it is elaborated that the contents of Na, K, Mg can indicate both chemical and physical weathering of soil in the past. The higher K contents in the uppermost section indicate intensive erosion and significant peaks correlate with Mn and Fe peaks that could originate from the feldspars in inorganic sediment (Mackareth 1966). The highest Na values are detected in the purest plant–based peat (mixed sedge and reed peat) where the Na accumulating

species could fix the Na and K ions (Kustár et al. 2016.; Braun et al. 1993; Beeton, 1965).

The Ca and Mg concentration trend is similar in the bog phase and different in the lake phase. Ca is a well–known biophilic element (Gorham et al. 2005). For adequate growth in plants is normally around 0.5% shoot dry matter (Batty & Younger, 2004). There is a clear similarity between the Ca concentration and the Arbor pollen concentrations, which could derive from the deciduous tree fallen leaves. The Arbor pollen concentration sharply decreased, and the Non–Arbor Pollen (NAP) was gradually increasing at 150 cm which correlates the time of the Great Migration and the Hungarian Conquest (ca.1600–900 cal BP). These cultures put an expand pressure on the bog environment by deforestation and pasturelands (Tapody et al. 2018).

The Ca/Na ratio is usable for weathering rates (Watmough & Aherne 2008, Bailey et al. 2003, Federer et al. 1989). In these studies suggest that the disturbance of forest ecosystems, like harvesting cause depletion of available calcium (Ca) pools like lakes. Based on the Ca/Na ratios three sections of sediments were defined in the Round Lake profile. As the bedrock is volcanic and the calcium concentration correlates with arbor pollen, in contrast to the ash content, it was hypothesized that the Ca/Na ratio can indicate the changes in the surface vegetation of the bog. Therefore, the Ca/Na ratio was compared with the ash content and summarised pollen diagram. If we

compare the Ca/Na ratio with the ash content, we can see that some sections change in the same, others in opposite directions. It is important to note that the source of calcium (Ca) can be derived from the dissolution of mineral particles and leaching from the secondary accumulation of deciduous tree leaves.

The ash yield calculated from the LOI contains both inorganic mineral matter and inorganic components of plant tissues. In this regard, the Ca/Na ratio, the ash content, the fine sand, and coarse silt content are compared. In the 560–450 cm section, there are fluctuating high Ca/Na peaks with a low ash content of 10–20%. There is a sharp peak between 510–530 cm which coincides with the first Sphagnum layer and coarse silt peak. At this stage, the AP pollen rates are between 85% and 95%, the Round Lake was surrounded by rich deciduous forest.

In the next stage (450–360 cm) the ash content rises 40–50% and the Ca/Na ratio is around 2–3%. Between 390 and 360 cm, there are 3 lithologic layers within the section the Ca/Na peak coincides with the Th3Lc1 layer and the ash peaks with the Th2Lc1As1 layers. Between 360–330 cm, a Ca/ Na peak coincides with the second Sphagnum level. Between 330 and 180 cm, the Ca/Na and ash contents move in the same direction. The Ca and Na trends are very similar because the sedge and reeds that build up the peat could fix the Na. There are no major fluctuations in the coarse silt at this stage, except for two peaks, which are at the boundary of the layers. It is assumed that a significant portion of the ash content may have been due to inorganic plant residues, which may be true for sedge and reed. The forest vegetation gradually decreased at 180 cm to ca. 60%.

Between 180 and 100 cm, the change in Ca/Na is opposite to the ash content. This phase is a transitional phase between the lake and the bog. The major part of the sediment is made up of inorganic mineral matter, but the bog vegetation is also present. At 150–140 cm, AP pollen is reduced by 10% and further 20% towards the surface. At the groundwater level the Ca/Na ratio is high, but the ash content decreases. In the upper 100 meters is the lake phase, the ash content is high and the Ca/Na ratio drops below 1%.

The Ca/Mg ratio is used to determine the peat trophic status. The trophy depends on the source of the water and the nutrient supply. Minerotrophic peats receive nutrients from rainwater and incoming surface and groundwater, while ombrotrophic peat collects nutrient solely from the rainwater. Ombrothropic peat can not get in contact with ground or surface water because the peat forms a dome above the terrain level.

One procedure to determine the trophic status is to compare the Ca/Mg ratio of the peat with those of the local rainwater. If the Ca/Mg ratio of the peat exceeds the local rainwater level the peatland must have an additional source of Ca, so it is minerotrophic otherwise ombrotrophic (Weiss et al. 1997, 2002; Shotyk 1988, 1996, 2002; Muller et al. 2006; Lähteenoja et al. 2009).

The rainwater Ca/Mg ratio from the region (Giurgeu basin and Ciuc basin) is between 4–6 (Szép et al. 2018). The Round Lake Ca/Mg ratio values are under the rainwater values (**Fig. 3.**). For minerotrophic peats the ratio is usually higher than1.0. Conversely, it is less than 1.0 for ombrotrophic peats (Mattson et al. 1944; Chapman 1964, Verhoeven 1986; Shotyk 1988). Thus, sections, already defined based on the Ca/Mg ratio could be additionally described as: The lower section (560–160 cm) peat condition is a minerotrophic, between 150–100 cm is a transition phase, and the top 100 cm were ombrotrophic. It seems contradictory that the highest inorganic content lake sediment section (top 100 cm) show ombrotrophic condition. This will be a scope of our future investigation.

Conclusion

This paper describes the geochemical data analysis of the peat deposit in Round Lake to define paleoenvironmental conditions over the past 7500 years. According to the results, there are two main phase in the development history of Round Lake. The top 104 cm sediment based on lake phase and the bottom part is a manifold peat deposit.

The peat core unfolds a complex development of the bog that was influenced by climate, hydrology the vegetation and the environment. The analysed element suggests that:

(1.) The Mn and Fe concentration derived from the mineral matter of the catchment basin. The water–soluble components are only detectable above the water table because they are mobile in water.

(2.) The high Ca content unambiguously derived from the deciduous forest vegetation surround the bog. However, the vegetation has a significant effect on Ca content, the distribution is influenced by the hydrological conditions of the bog, such as the precipitation, fluctuation of groundwater level and the peat vegetation.

(3.) The Na and K are essential elements to all plants, and they could be accumulated in plant tissues. The highest concentration of the Na is on the surface below the living layer the Na and K could be leached.

(4.) The highest concentration of Mg and K are revealed in the inorganic mineral phase, besides they firmly bond the vegetation and a secondary

accumulation in peat may occur. The vegetation of different peat binds calcium, magnesium differently, which can determine the minerotrophic and ombrotrophic phase.

Acknowledgments

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