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Using the carbon content and isotope stratigraphy in
sediment cores to reconstruct the lake and catchment
history of large boreal lakes in Finland

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ABSTRACT

Lake sediment study helps in reconstructing the histories of past climate, the associated environmental conditions, and the land use changes affecting several processes in lake and catchment area. As there has been less studies in large boreal lakes compared to small lakes, this thesis study the carbon (C) content and stable isotopes stratigraphy in large lakes Kallavesi and Oulujärvi located in Finland, with the aim to check if the amount of C, the C/N ratio and the isotopes of C ($\delta^{13}\text{C}$) can be used for assessing the autochthonous and allochthonous sources of organic matter, productivity rates and the decomposition processes in the lake and their changes associated with environmental changes. The studied sediment core represents the whole Holocene. Two sediment cores, one from the North basin and one from the South basin of Kallavesi and three cores from the central basin of Oulujärvi were sliced every 1 cm in the first 10 cm and every 5 cm in the deeper parts. The sediment slices were measured for wet weight and put in oven for drying at 105 °C overnight. The dry weight was taken, and homogenizing was done with plastic hammer. 20 mg of dry homogenized powdered sediment was encapsulated in a tin capsule for analyzing C % and isotopes of C in isotope ratio mass spectrometer connected to elemental analyzer. Top sediments from Kallavesi have higher C % but low $\delta^{13}\text{C}$ compared to sediments from Oulujärvi with a high C % mean of 6.3 ± 0.64 (4.69 -7.22) and low $\delta^{13}\text{C}$ mean of -30.51 ± 0.24 (-30.7 – - 29.9) and despite these differences by lake, there are general trends with depths where C and C/N are decreasing and $\delta^{13}\text{C}$ is increasing. The high C accumulation in the top sediment with a mean of 4.45 ± 1.75 (2.14 - 7.31) is being reduced towards the bottom sediment with a mean of 0.06 ± 0.04 (-0.2-0.17) due to decomposition of OM and maybe also lower C accumulation rates in the past. The low C/N ratio with a mean of 7.08 ± 2.57 (0.9 -13.5) point that most of the OM in the lake sediments were from the algae production within the lake with low inputs of terrestrial plants, despite there are few moments with peaks of C/N suggesting periods of high contribution of allochthonous OM (terrestrial plants). The more negative values of $\delta^{13}\text{C}$ in the top sediments with a mean of -29.17 ± 1.21 (-31.46 – - 27.83) indicated low decomposition process of OM while more positive values towards bottom with a mean of -26.90 ± 0.50 (-27.81 – -25.91) indicated high decomposition process with high mineralization of C and diagenesis. This thesis provides a better estimation of C accumulation in lake sediments and points to autochthonous origin (algae) as the main source of OM in large boreal lakes. However, due to the results of this study it should be contrasted using other biogeochemical proxies (e.g. biomarkers,lipids...etc.) also including more sites to see how the C accumulation and the source of OM change in the sediments of large lakes from near tributaries towards more pelagic areas.

Foreword

I am grateful for the practical and moral support received from many people throughout my research process. I express my sincere gratitude to my Supervisor Carlos Palacin Lizarbe (Post Doctoral Researcher) and Hannu Nykänen (FT, Dos. Water RC coordinator) for their guidance, suggestions and insightful comments that inspired me to accomplish this thesis. I owe deep gratitude to my husband Robin Lama and family members for their immense support and encouragement. Special thanks to my friends Shovana Khaitu, Aamna Batool, Hishila Sujakhu, Sajan Khaitu and Udip Thapa Magar for their support to this study.

Abbreviations

C	Carbon
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EA IRMS	Elemental Analyzer Isotope Ratio Mass Spectrometer
Km ²	Square kilometer
N	Nitrogen
NH ₄	Ammonium
N _{tot}	Nitrogen total
OC	Organic carbon
OM	Organic Matter
P	Phosphorous
P _{tot}	Phosphorous total
POC	Particulate organic carbon
TOC	Total organic carbon
TOM	Total organic matter
tOM	Terrestrial organic matter
°C	Degree Celsius
δ ¹³ C	Carbon isotope
km ²	square kilometer
µg/l	Micrograms per liter
m a.s.l	Meters above sea level
mg/l	Milligrams per liter
Pg	petagrams
‰	Per mill
%	Percentage

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1 Introduction

Lake sediment providing information on histories of past climates and the associated environmental conditions and land use changes is one tool for the reconstruction of the processes in lake and lake catchment area (Douglas, 2013). Lake sediments contain evidence of local and regional changes and histories of deglaciation and sediment deposition (Meyers, 2003). Lake sediment contains organic matter (OM) both of autochthonous formed within the lake or allochthonous origin formed from the surrounding catchment. The catchment has an important role in the inputs of OM to the lake. Boreal headwater catchments consist of coniferous forest, peat land and agricultural land (Rantakari, 2010). Human impacts such as slash and burn agriculture practice and deforestation (Myllyntaus et al., 2002) causes alteration to catchment areas. The amount of carbon (C) in the lake sediment helps to understand the productivity in a lake (Köster et al., 2005). It has also been mentioned that lake has significant role in the carbon cycle (Kortelainen et al., 2004). Boreal lakes are affected by climate (Itkonen et al., 1999) both in contemporary time and historically during sediment formation.

Stable isotopes are non-hazardous due to which many research are done to solve environmental issues. Isotopes provide information on nutrient balance and human impact on the watershed (Fry, 2006). Activities such as deforestation, agricultural activities and infrastructure development leads to eutrophication which can be seen as change in composition of C content and isotope of C ($\delta^{13}\text{C}$) (Köster et al., 2005). C isotope values in lake are vital for assessing the sources of organic matter (OM), analyzing nutrient status and productivity rates (Choudhary et al., 2009). A higher accumulation rate of OM and higher C amount provides information on high aquatic productivity in lakes. Increased productivity increases $\delta^{13}\text{C}$ values of newly formed OM in the lake sediment. The $\delta^{13}\text{C}$ with C/N ratio helps in identifying sources of OM and its degradation in lake sediment (Meyers, 2003). C isotopes acts as indicator of various changes in cycles of OM in lakes over the period of time (Herczeg et al., 2001). The alteration of OM through post burial diagenesis in sediments can alter the overall isotopic composition of C and N isotopes and further hinder the vital indicators of past productivity (Hodell & Schelske, 1998; Lehmann et al., 2002).

This study measures C %, C/N and $\delta^{13}\text{C}$ as they are important proxies to assess the autochthonous and allochthonous sources of organic matter, nutrient status, productivity and the decomposition processes in the lake sediment and their associated changes with environmental changes.

2 Literature Review

2.1 History of lake in Finland

About 10,000 years ago, during the post-glacial era, lakes formation occurred in Finland. Lake formation began in North Karelia's supraaquatic regions prior to 11,000 BP as a result of land emergence from beneath ice sheet before 11,000 BP (Hyvärinen, 1973; Tikkanen, 2002). Afterwards about 10,300 BP, the height of water in the Baltic Ice Lake decreased than the nearby oceans leading to the creation of small lakes. Along with the continuation of formation of many lakes, most of the lakes were formed due to the Baltic Sea being divided into distinct basins at various phases to form an individual basin. Meanwhile there also occurred haphazard uplifting of the land resulting in sloping of the land surface. This phenomenon caused flooding in numerous lakes which changed the direction of flow. Since the flooding, numerous changes occurred in the main watershed during the period of 8500-4500 years ago, leading to the shift in the outflow waterways. Over time, a significant number of small lake became shallow as a result of high sedimentation along with deep outlet channels (Tikkanen, 2002).

In Northern and Eastern regions of Finland, the subaquatic areas emerging after the disappearance of the continental ice sheet were located above Baltic shoreline known as supra-aquatic. Soon the deglaciation process resulted in the formation of many lakes in supra-aquatic terrain. In this region, the basins in the supra-aquatic initially consisted of fine minerogenic sediment, silt and varved clay and organic sediment which deposited at the bottom of the lake. Many of those existing lakes were formed because of ice damming and covered large areas in front of receding ice. The sedimentation history of subaquatic basins is complex and relies on multiple factors such as their formation time, rate of upliftment and the morphology of both the newly formed coastlines and the basins. During the early Holocene era, a rapid uplift rate contributed to the swift formation of lake basin from the waters of the Baltic basin with deposition of organic matter (Pajunen, 2000).

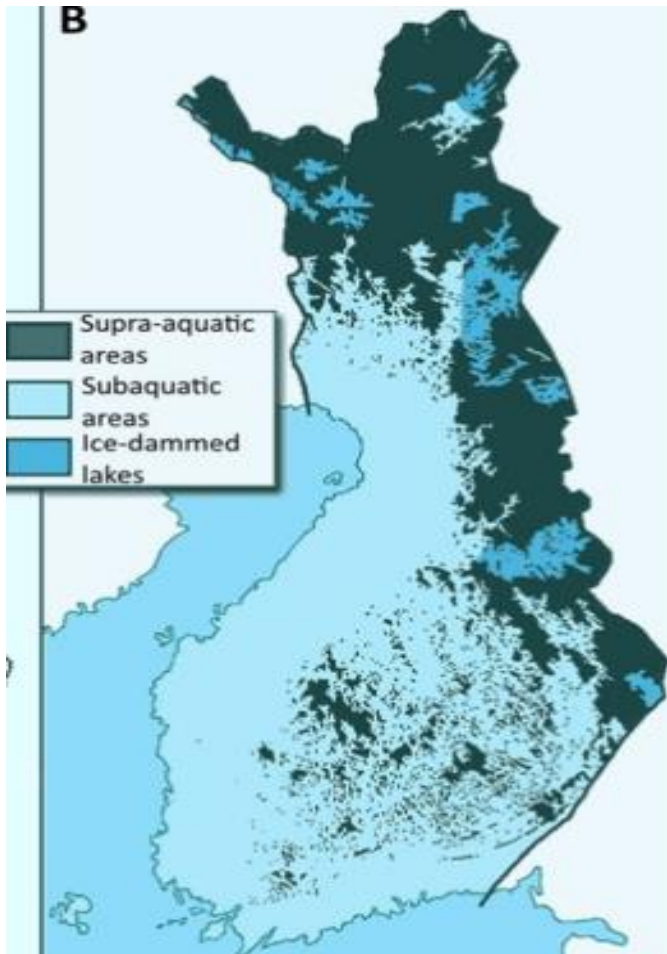


Figure 1: Map showing the Supra-aquatic areas which were not washed with waters. (Heiskanen et al., 2020).

2.2 Shoreline and isolation of lake basins

The uppermost Baltic coastline delineates the boundary between supra-aquatic and subaquatic landscapes. In the Northwest region, the age of the highest shoreline declines in relation to the retreating ice in the Southern areas of Finland. In the Salpausselkä zone, the highest shorelines formed during the late-glacial Baltic ice lake stage with elevations ranging from 100 -165 m a.s.l. Similarly, to the North of Salpausselkä zone in south-central Finland, extending to a line passing through Pori, Jyväskylä, and Kajaani, the shoreline dates to the Yoldia Sea stage of the Baltic, with elevations ranging from 120 - 185 meters. Moving further North, the highest shoreline in Ostrobothnia represented the Ancylus lake stage with elevation ranging from 185m-200 m a.s.l. towards the northern side of lake OJ and 220-200 m a.s.l. near Rovaniemi within the Arctic circle. In the North, the highest shoreline is observed to be newly formed. The shorelines of the Baltic Ice Lake were formed approximately between 12500-11500 years ago, the highest Yoldia Sea shorelines formed between 11,500 and about 10,800 y.a. and the highest Ancylus lake shorelines between 10,800 and 10,000 years ago (Pajunen, 2000).

The highest shorelines quickly formed due to the rapid upliftment and retreating of ice, as mentioned in (Saarnisto, 1981; Salomaa, 1982) the shoreline displacement in different regions of Finland indicated an uplift of 10 meters per century. This prompt uplift led to the isolation of lake basins from Baltic. The lake isolations are evident in oldest lakes in Southeast Finland, where many lakes became disconnected because of the Baltic ice lake draining approximately 30 m to the level of Yoldia Sea around 11,500 years ago. The origin of individual lakes has great importance within the Finnish lake district for the development of Ancylus lake. It experienced a rapid decline in the water level in Baltic basin caused due to opening of new outlet in Ancylus lake. These isolation of the lakes from the Baltic basin is evident in the sediments at the bottom of the lakes (Pajunen, 2000).

2.3 Temperature in lake

The large lakes found within the lake District have experienced uneven warming in spring not primarily due to the large areas covered by basin between North and South, but due to associated varying circumstances dominant on the shores as well as open waters. For example, a covered harbour facing the South direction receives ample amount of sunlight and acts as efficient suntrap, and the presence of thick forest can further enhance radiation absorption along the shore. Due to this phenomenon the mean temperature of water is high up to 15°C. After the ice melts the water has temperature ranging from 2°C- 4°C (Kuusisto, 1999).

In summer lakes with high depth undergo stratification. With the arrival of midsummer, the thermocline that exists at a depth of around five meters experiences a low temperature drop of 2-3 degrees within each meter. In the case of early summer where there is presence of high winds, the thermocline tends to occur at higher depth. Conversely, following a period of quiet weather, one can anticipate a significant temperature drop or the development of an extra thermocline nearer to the top of the lake. Typically, the water on the surface in the Southern and Central Finland remains relatively warm, hovering around 19-22°C (Heikkilä & Lindholm, 2006).

2.4 Lake sediments and its role in carbon cycle

Various OM and inorganic particles forming from different sources enter boreal lakes and ultimately go down to the bottom of the lake forming sediments. This sediment plays a vital part in the water cycle and serves both as a provider and reservoir of C. The settled OM in the bottom of the lake aids in the deposit of OC (organic carbon) facilitates the removal of C in terms of active short-term C cycle. In the long run these sediments represent a long-term C

sink. There also occurs active ongoing microbial process on the lake sediments that helps in the decomposition processes. The continuous microbial decomposition aids in the mineralization of OC to CO₂. The recycling process within the lake system results in additional emissions of CO₂ and CH₄ into the atmosphere (Chmiel, 2015). According to Kortelainen et al. (2004), lake sediments have more capacity to store C than the existing plantation soils and biomass.

The transportation of particulate organic matter to boreal lakes acts as significant contributor to the deposition of OC in lake sediments. In the lake process where dissolved organic carbon (DOC) transforms into POC (Particulate organic carbon), highlights the importance as significant contributor to the accumulation of OC in sediment within the lakes in boreal region (Von Wachenfeldt & Tranvik, 2008). Various factors also influence the formation of CO₂ and CH₄ in sediments through their impact on organic carbon OC mineralization. The origin of OM is important as it helps in determining mineralization rates. The degradation performance by microorganisms is faster for autochthonous OC compared to allochthonous OC (Burdige, 2007; Chmiel, 2015). Temperature also plays a significant role on OC mineralization in sediments, higher the temperature, increased is the mineralization rate. Similarly, the availability of oxygen facilitates the mineralization rates along with the CH₄ production. In case of anoxic conditions, degradation rate typically decreases, resulting in low CO₂ production, while promoting methane production (Chmiel, 2015).

2.5 Organic matter in lake sediments

Organic matter is formed from the decayed plant existing in the aquatic ecosystem and from the land plants surrounding the lake and catchment areas. For example, algae, grasses, shrubs and trees These OM further gets deposited at the bottom of the lake. The dominance of these plant groups in contributing OM in lake sediments is highly impacted by different factors including lake shape, watershed terrain and the abundance of plants found within the lake and its watershed. So, the OM in lake sediments is either formed mainly from algae in certain lakes to predominantly originating from terrestrial sources in others. OM formed from the terrestrial plants has $\delta^{13}\text{C}$ value of about -28‰. The lake which consists of newly formed OM from algae present in the lake itself has C/N value from 4-10 and the OM formed from the terrestrial plants has C/N ratio of 20 and higher (Meyers, 2003).

During the initial stages of diagenesis, the degradation process of OM components leads to alterations in elemental compositions and C/N ratio of OM in sediments. For example, C/N ratio of contemporary wood samples are greater than those wood which has undergone burial in

the sediments (Meyers & Ishiwatari, 1993).

The research conducted on sediment cores in Lake Alexandrina showed increased $\delta^{13}\text{C}$ values of about 3 ‰ from the lowermost section to increased value of -21 ‰ at a depth of 150 mm. Subsequently, the value decreased by 5 ‰ to around -27 ‰ within the uppermost 100 mm of the core. The C: N mass ratio <11 indicated that OM found in the sediment is predominantly derived from aquatic plant found in the lake and less input from terrestrial plants. Also, the fluctuation of $\delta^{13}\text{C}$ signifies an alter from predominant input of inorganic carbon from the surrounding terrestrial sources to growing influence of marine-derived sources. This type of alteration occurred due to initiation of water diversion in the late 1800s (Herczeg et al., 2001).

2.6 Carbon study in lake sediments

The ongoing climatic changes will cause changes in the temperature and precipitation patterns and impacting the Arctic lakes (Bring et al., 2016). Climate change is anticipated to activate allocation of OM from the neighbouring watersheds to lakes in the Arctic regions as evidenced by approximately 2 Pg of organic carbon stored in glaciers. This could result to increase in amount of terrestrial carbon in lake sediments (Schuur et al., 2015; Wauthy et al., 2018). Climate warming leads to increment of local vegetation in the North which results in greater supply of OM to lakes. So, understanding the source of OM is crucial as terrestrial dissolved organic matter (DOM) plays a significant part in providing energy to lake ecosystems (Osburn et al., 2019).

Study done on 31 lake sediments core to determine the storage of C and its accumulation rate found the average C stored in small lakes were comparatively higher than the large lakes. In Finnish lake sediments, the carbon stored is about 780 million tonnes. The average C accumulation rate was found to be lower with the decreasing lake size (Pajunen, 2000).

Research on implication on what will be the future of C in warm and arid conditions in lakes of Greenland found that DOM comprised both allochthonous terrestrial and autochthonous macrophytes. Autochthonous algae were predominantly stored in lake sediments and this pattern remained consistent regardless of variations in the hydro-climatic conditions across the gradient (Osburn et al., 2019). The author also found C/N value for soil and macrophytes were found to be higher with the increasing precipitation (Osburn et al., 2019).

A study done in varved lake sediment in Sweden found that if the loss of C is less over the time then C/N ratio increases (Gälman et al., 2008). A study from Lake Sattal in India found that the bottom sediments may undergo diagenesis causing mineralization in OC (Choudhary et al., 2009).

3 Study Objectives and Hypothesis

The objectives of the study are:

1. To determine the C content and isotopes stratigraphy in sediment cores in large boreal lakes
2. To reconstruct the past environmental changes of the lake and its catchment.

3.1 Hypothesis

- i. The presence of high C content in the sediments indicates higher productivity of the lake and catchment area, and perhaps more favourable climate
- ii. Higher $\delta^{13}\text{C}$ indicates higher decomposition of OM
- iii. Higher C/N ratio (>20) evidence higher proportion of terrestrial OM, while lower C/N (<10) a higher proportion of algal OM and microbial biomass
- iv. Higher OM content deposits on the top which is partially decomposed with time (depth), increasing OM content with depth evidence periods with increased productivity of the catchment and or of the lake

4 Material and Methods

The sediment study was conducted in laboratory at University of Eastern Finland (UEF). The sediment cores used in this study is from Geological Survey of Finland (GTK). These long sediment cores were in tubes of diameter 5.8 cm and 2-3 m long. The practical work was conducted in the lab from October till November 2023. The total number of samples in this study was 411.

4.1 Sample preparation

The respective sediment cores of KV and OJ were taken out from the freezer stored at -18 °C and brought to the UEF lab for defrost overnight. The core was cut open with the help of Stanley knife carefully. The core was marked with marker at 1cm in the first 10 cm and the deeper part was divided at 5 cm per slice and photograph of opened core was taken before slicing. The core was sliced with the help of a self-made plastic spatula and the samples were put into the plastic bags (Food and freezer bags1 L,) withstanding temperatures (-40°C - 115 °C). Plastic tools were used to allow metal analyses of the cores later.

4.2 Homogenizing sediment sample for Carbon analysis

The dried sediment samples in bags were homogenized using a rubber hammer. The hammering was done with precaution to avoid sample loss. The powdered sediment sample for C, N and stable isotope analyses were put into 2mL Eppendorf tubes using small steel spatula.

4.3 Water content

The wet weight of the sediment sample was taken with the help of electronic precision weighing balance. The samples were placed on the trays and put in the oven overnight at 105 °C for drying. The dried sediment sample was taken out from oven the next day and the dry weight was measured. The water content percentage of the sediment samples was calculated using the formula.

$$\text{Water content (\%)} = \frac{\text{Wet weight of the sediment sample(g)} - \text{dry weight of the sediment sample(g)}}{\text{Wet weight of the sediment sample(g)}} * 100 \quad (1)$$

4.4 Bulk density

The dry and wet bulk density of the sediment sample was calculated using the formula of (Pajunen, 2000).

$$\text{Dry bulk density } (\delta_{\text{dry}}) = \frac{\text{Dry sediment mass(g)}}{\text{Volume of the core(cm}^3\text{)}} \quad (2)$$

$$\text{Wet bulk density } (\delta_{\text{wet}}) = \frac{\text{Wet sediment mass(g)}}{\text{Volume of the core(cm}^3\text{)}} \quad (3)$$

4.5 Loss in ignition (LOI)

LOI was initially done to obtain some ideas about carbon and nitrogen amount in the sample in order to estimate the correct amount of sample for IRMS analysis. LOI was analyzed from set of 36 samples. The dried homogenized sediment samples of lake Kallavesi and Oulujärvi was used for LOI. The empty crucibles marked with numbers were taken and kept in the (Nabertherm muffle furnaces) oven at 550 °C for an hour and put into desiccator with the help of tongs to cool at room temperature. The weight of the empty crucible was noted. The weighed sediment sample 1-2 g was put into crucible and the weight was noted. The crucible containing the homogenized weighed sample was put in for burning at 550 °C for two hours. The burned sediment samples were left to cool in the desiccator at room temperature and weighed by micro balance. LOI is calculated using the formula of (Pajunen, 2000).

$$\text{LOI (\%)} = \frac{[\text{Weight of a empty crucible + dry sediment sample(g)}] - [\text{weight of empty crucible (g)} + \text{burned sample}]}{\text{Dry weight of the sediment sample(g)}} * 100 \quad (4)$$

4.6 Study area map

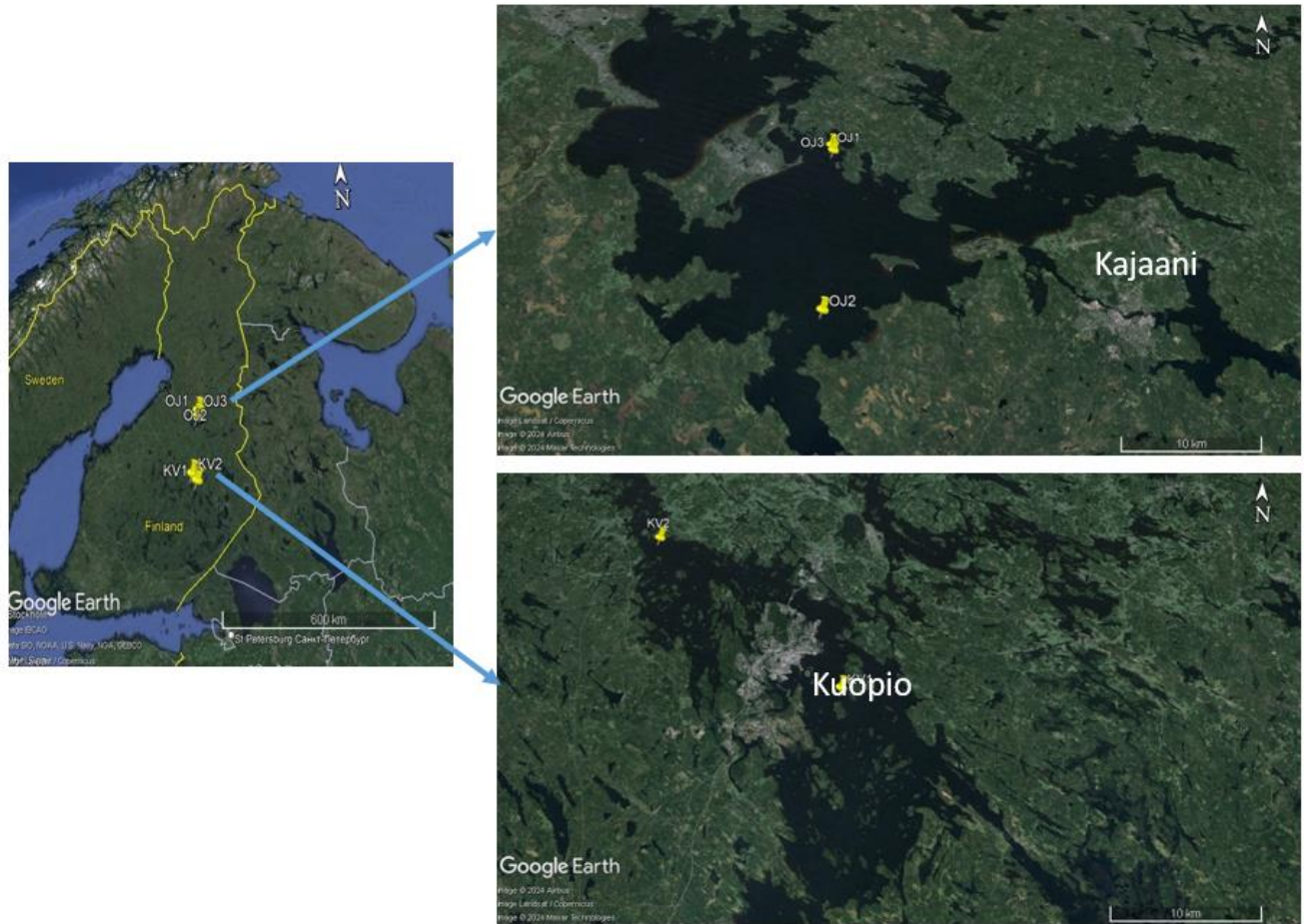


Figure 2: Map of the study showing locations of the sediment study points. Google Earth (2024).

4.7 Lake kallavesi

Lake Kallavesi is medium size lake found in eastern Finland in Kuopio area. The area of the lake is 517.00 km² and with a maximum depth of >60m. It lies at 81.8 ma.s.l. (62° 49' 0"N 27° 47' 0" E). The lake is mesotrophic. The lake consists of brown water and is of medium humic type (Järvi-Meri Wiki, 2024a). The regressions and transgressions observed in Saimaa Lake complex have led to significant fluctuations in the lake basins of KV. These changes have influenced the rate of sedimentation and erosion. In KV there was transgression of over 10 meters succeeded by a regression exceeding 20 meters. The catchment area of lake KV is 13000 km². The percentage compositions of catchment area consists of water, agriculture land, peatland, forestry land and built-up area are 12, 8.5 ,17, 62 and 0.60 % respectively. The PH of the lake is 7.3 with N_{tot} and P_{tot} concentrations of 593 and 17µg/l respectively. TOC concentration is 8.2 mg/l (Pajunen, 2000).

4.8 Lake Oulujärvi

Lake Oulujärvi is one of the large lakes located in the provinces of Kainuu and North Ostrobothnia. It lies at 122.2 ma.s.l. (64° 19' 60.00" N 27° 14' 60.00" E). The area of the lake is 865.02 km² and with a maximum depth of 35m. The lake is mesotrophic. It consists of well oxygenated and clean water (Järvi-Meri Wiki, 2024b). It consists of three major basins Niskanselkä, Arjanselkä and Paltaselkä. Lake OJ basin was formed due to Ancyclus regression and has undergone transgression of more than 12 m in east resulting in upliftment as explained in (Koutaniemi & Keränen, 1983). As a result of transgression there has been a rise in water level of 10-15 m. The catchment area of lake OJ is 20000 km². The percentage compositions of catchment area consist of water, agriculture land, peatland, forestry land and built-up area are 13, 2.0, 27, 58 and 0.21 % respectively. The pH of the lake is 7.0 with N_{tot} and P_{tot} concentrations of 240 and 15 µg/l respectively. TOC concentration is 6.5 mg/l (Pajunen, 2000).

4.9 Carbon % and C ‰ analysis

Carbon content of the sediment sample was determined. For, low range dried sediment sample, 10mg (8-14) mg was weighed in tin capsule with the help of microbalance and encapsulated. For high range sediment sample, 30mg (25-35) mg was weighed in tin capsule and encapsulated. Both the encapsulated sediment sample was sent for IRMS as a trial in the first phase to predict the right amount of sample needed for C % and δ¹³C analysis in this research. In the second phase after the right amount of sediment sample was predicted, 20mg (18-23) mg dried sediment sample was weighed in tin capsule with the help of microbalance and encapsulated.

The analysis of δ¹³C, C % and N % of the sediment samples was conducted at University of Eastern Finland, Kuopio, using an elemental analyzer coupled to an isotope ratio mass spectrometer (EA- IRMS), which included a Thermo Finnigan DELTA XP Plus IRMS, Flash EA 1112 Series Elemental Analyzer, and a Conflow III open split interface (Thermo Finnigan, Bremen, Germany)(Gil et al., 2022).

5 Results

This table will focus on 3 geochemical proxies (C%, C/N and $\delta^{13}\text{C}$), see in Table 1 the information provided by these proxies, and the main results obtained in this study, including :1) main trend with sediment depth, 2) site/lake variability, and 3) periods of change, i.e. deviations (either a peak or a drop) from the main trend with depth indicating periods with an intense environmental change.

Table 1. Organic geochemical proxies.

Variables	Information	Main trend with depth	Sites/lake variability	Periods of Change
C %	Amount of C present in the OM and proxy of systems productivity (Köster et al., 2005)	C content decreases with depth	Top sediment KV has a higher C % than OJ.	KV1: High C content peak at 250 cm depth ~ 6000 yr BP KV2: C content drop at 35cm depth
C/N	Values (4-10) indicates algae OM Value >20 indicates terrestrial plants OM (Meyers, 2003)	C/N value decreases with depth	Top sediment KV2 has highest C/N ratio in top cm and shows steep decrease.	KV2 and OJ2 Peak in C/N observed in KV2 at depth of 0-1 cm in OJ2 at a depth of 50-75 cm ~ 1000 yr BP and at depth 350 cm ~ 5600 yr BP
$\delta^{13}\text{C}$	Higher $\delta^{13}\text{C}$ values when higher decomposition of OM (Meyers & Ishiwatari, 1993) Diagenesis (Herczeg et al., 2001; Hodell & Schelske, 1998)	$\delta^{13}\text{C}$ value increases with depth, particularly for the bottom half of the OJ cores	Top sediment More negative $\delta^{13}\text{C}$ values in KV than in OJ	KV1 and OJ2 KV1 depth >125 cm ~2900 yr BP, $\delta^{13}\text{C}$ increases happens earlier while later in OJ2 at depth >275 cm ~ 4200 yr BP

The following table 2 summarizes the main results of the whole dataset by sites which includes mean, standard deviation, standard error with minimum and maximum values. The results plotted against depth (time) are shown in the following pages.

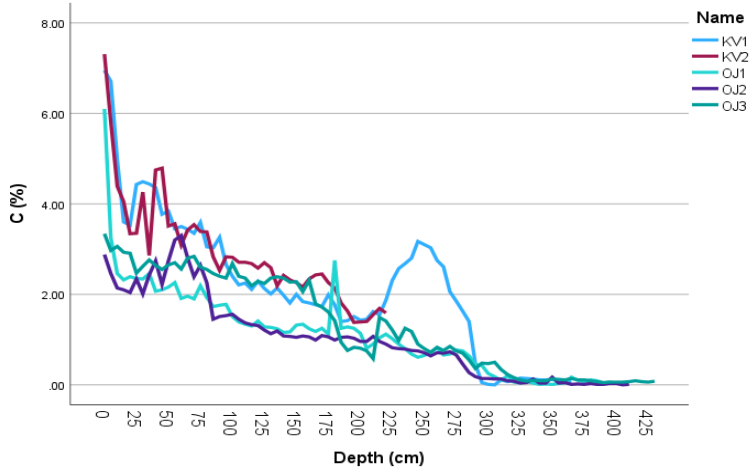
Table 2. Summary of the main result for the whole dataset by site.

		N	Mean	Std. Deviation	Std. Error	Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
C (%)	KV1	82	2.6361	2.03157	.22435	2.1897	3.0825	.00	7.14
	KV2	53	3.3623	1.52938	.21008	2.9407	3.7838	1.38	7.31
	OJ1	89	1.3769	1.27014	.13463	1.1093	1.6444	.01	6.10
	OJ2	92	1.1652	.98854	.10306	.9605	1.3699	-.02	3.30
	OJ3	95	1.4700	1.14403	.11738	1.2369	1.7031	.05	3.37
	Total	411	1.8583	1.60677	.07926	1.7025	2.0141	-.02	7.31
C/N	KV1	82	6.841	1.8268	.2017	6.440	7.243	2.8	10.5
	KV2	53	8.983	1.3844	.1902	8.601	9.365	5.9	12.6
	OJ1	89	7.448	1.9225	.2038	7.043	7.853	4.7	11.1
	OJ2	92	5.752	3.3594	.3502	5.056	6.448	.9	13.5
	OJ3	95	7.169	2.5662	.2633	6.647	7.692	1.5	11.1
	Total	411	7.081	2.5723	.1269	6.832	7.330	.9	13.5
$\delta^{13}C$ (‰)	KV1	82	-27.8502	1.51581	.16739	-28.1833	-27.5172	-30.13	-24.58
	KV2	53	-30.8913	.35421	.04865	-30.9890	-30.7937	-31.46	-29.45
	OJ1	89	-28.1713	.73363	.07776	-28.3259	-28.0168	-29.27	-26.23
	OJ2	92	-28.4052	.96860	.10098	-28.6058	-28.2046	-29.80	-25.91
	OJ3	95	-28.1692	.79061	.08112	-28.3302	-28.0081	-29.70	-26.43
	Total	411	-28.5099	1.34584	.06639	-28.6404	-28.3794	-31.46	-24.58

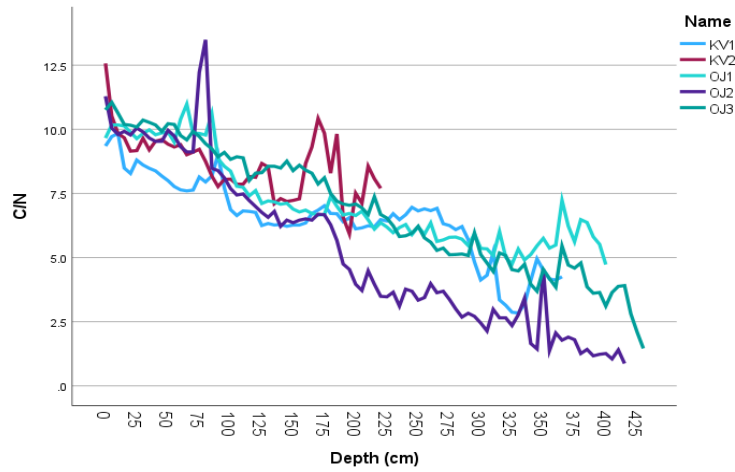
5.1 Main trends with depth

In The overall findings of this study are presented in figure 3. The C content decreases with depth in all the sediment sites, which is due to the general decomposition of OM over time (Fig. 3A). The bottom part of the sediment cores has low C % i.e. oldest sediments formed during the initial stages of lake formation. C/N ratio show a similar pattern with depth (Fig. 3B). This results from C degrading preferentially in comparison to N, decreasing the C/N ratio. A pattern of increasing $\delta^{13}C$ values with depth is found in (Fig. 3C), except for KV2, which has low $\delta^{13}C$ values compared to all the other sediment sites. This is a shorter core ~ 225 cm, while ~ 410 cm for the rest of the cores. The increasing $\delta^{13}C$ value with depth is more pronounced in the bottom part of the cores from OJ. More positive $\delta^{13}C$ value indicate higher microbial activity induced decomposition of OM (Meyers & Ishiwatari, 1993).

A



B



C

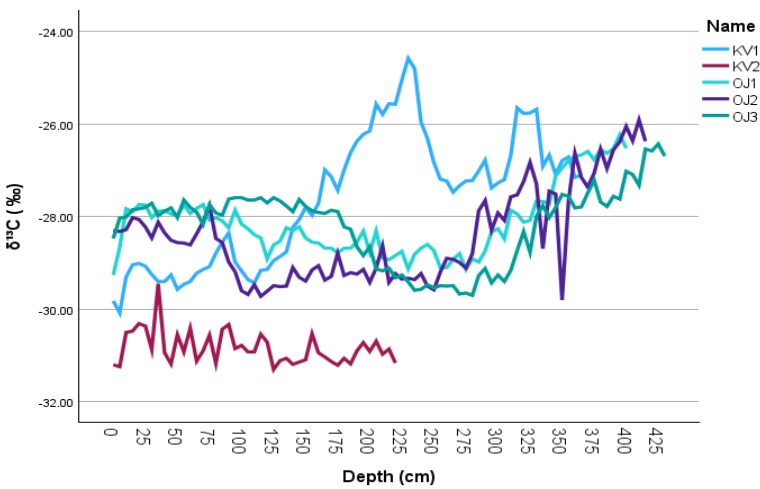
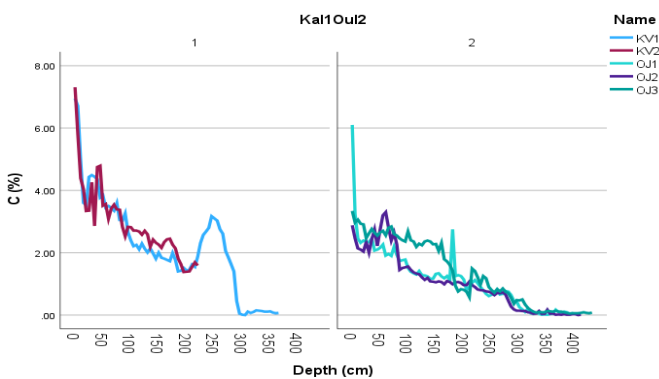


Figure 3. C % (top), C/N(middle) and $\delta^{13}\text{C}$ (bottom) with sediment depth for five studied sites in Kallavesi lake, Southern basin (KV1) and Northern basin (KV2), and in the Central basin of the Ouljarvi lake, near the shoreline (OJ1 and OJ3) or in a more pelagic area (OJ2).

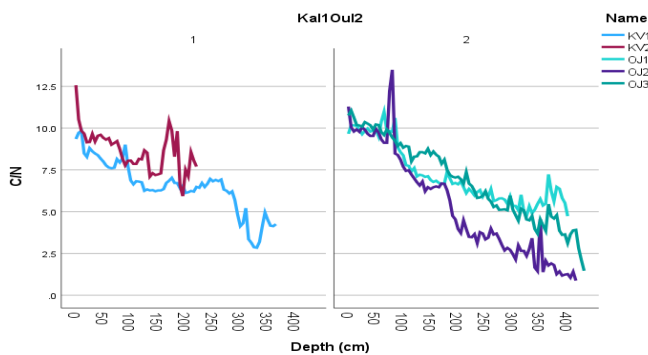
5.2 Differences between the lakes

At the lake scale, the C content in KV is higher compared to OJ (Fig. 4A). Similar C/N ratio for all sites with the more distinct values in OJ2, with a peak at 75 cm depth and lower values from > 200 cm depth in (Fig. 4B). Regarding the $\delta^{13}\text{C}$ values, KV1 and KV2 show changing trends while all OJ sites had more similar trends trends with increasing $\delta^{13}\text{C}$ values from around a depth of 215 cm onwards.

A



B



C

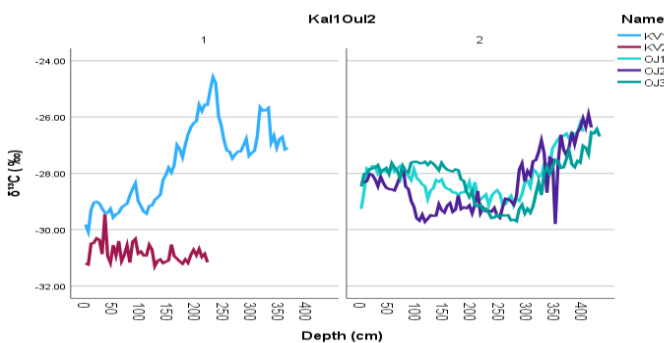
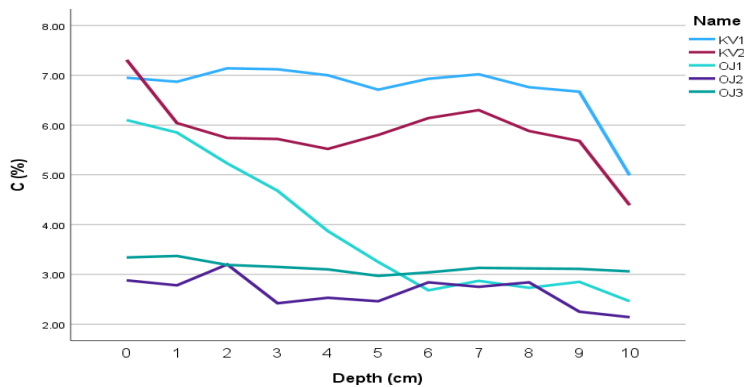


Figure 4. C %, C/N and $\delta^{13}\text{C}$ with depth for Kallavesi (right) and Oulujärvi (left) lakes.

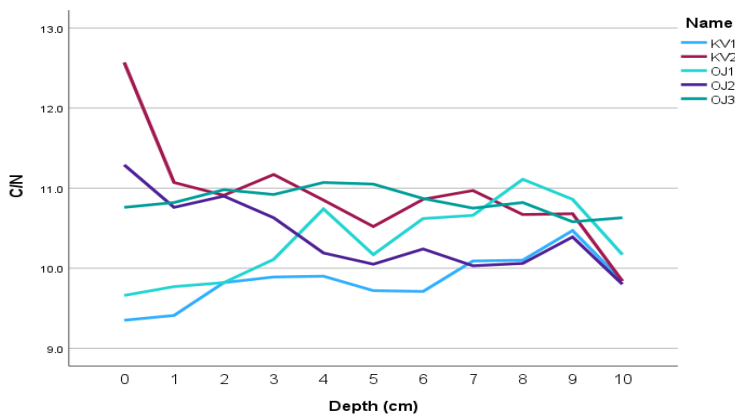
5.3 Top sediments

The top 10 cm sediments were analyzed every centimeter (Fig. 5), while deeper sediments were analyzed at reduced spatial resolution (every 5 cm, Fig. 3). In the top sediment, C content varies from 3-7 % between sites. KV has a higher C % than OJ (Fig. 5A), due to reprocessing and decomposition with depth. In the top sediment, more negative $\delta^{13}\text{C}$ values in KV which also has higher amount of TOC than OJ in water column (Pajunen, 2000).

A



B



C

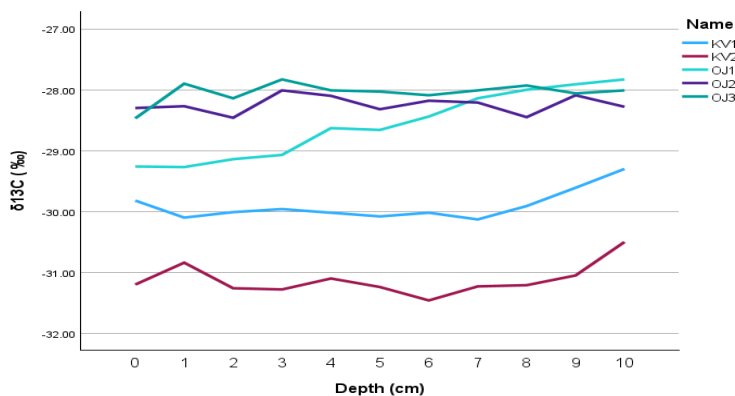


Figure 5. C %, C/N and $\delta^{13}\text{C}$ with depth for the top 10 cm in five studied sites.

5.4 Sediment dating

The dating of the core shown in (Fig. 6) is used to relate time (Year BP) for the formation of sediments with respect to depth in our study. (e.g. see in the bottom Fig. 7). This study does not date the sediment core but uses the dating sediment core references as it is near to the location of our study sites (Fig. 6). OJ dating is more comprehensive and complete with 13 dates, with respect to KV1 which consists of only two dates. Moreover, there is only Cs dating available for the Kallavesi Northern basin, where KV2 is located. Cs dating provides dating only for the recent sediments.

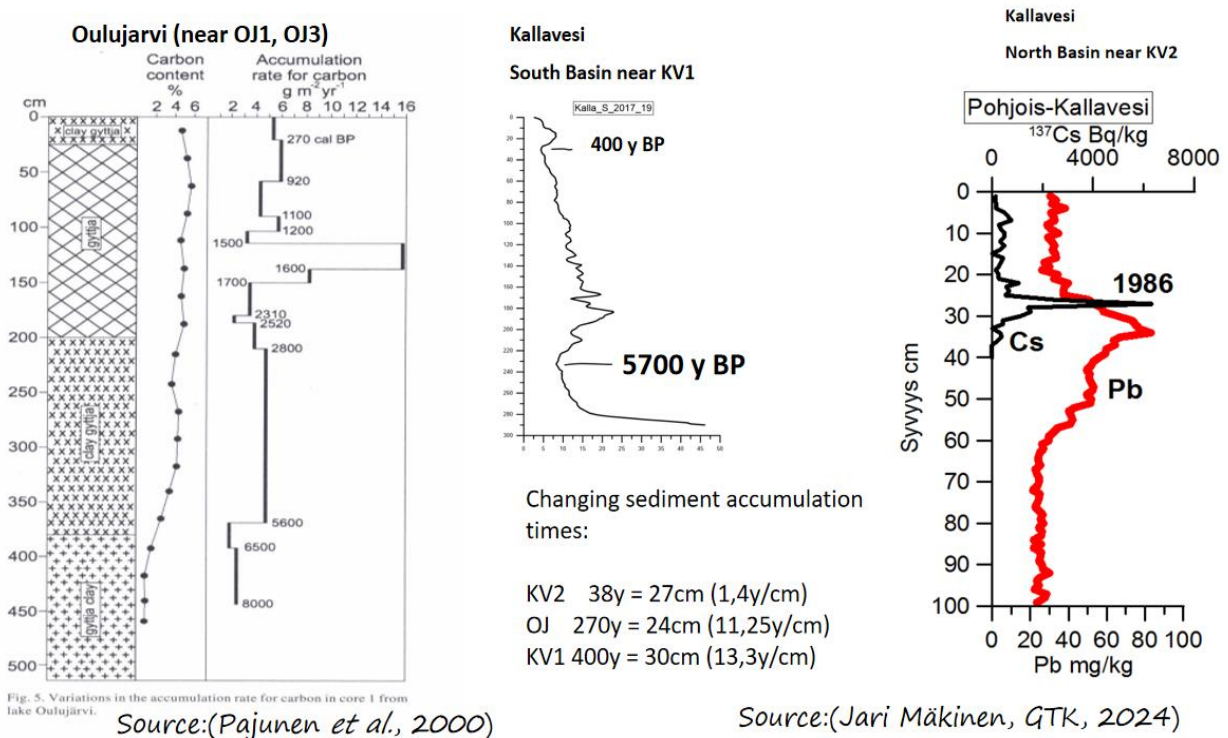


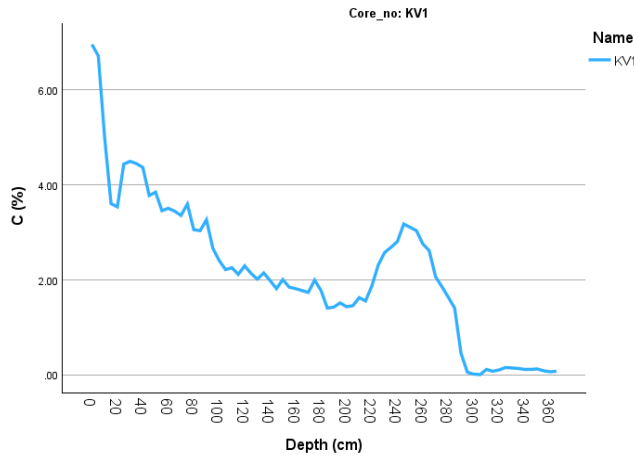
Figure 6. Dating of sediment core for the two studied lakes Kallavesi and Oulujarvi. (Mäkinen, 2024) (Pajunen, 2000).

5.5 Site variability

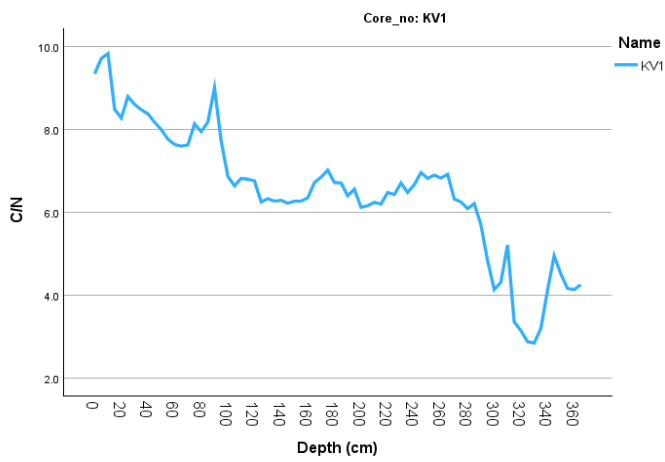
A glance at the sediment profile for each site helps to identify the periods of significant environmental change, when the depth trend deviated from the main trend, either with a peak or a noticeable dip.

KV1 is located at the southern basin of Kallavesi and the site with high amount of C relates to the higher algae productivity in the lake (Pu et al., 2020). Additionally, KV1 proximity to Kuopio is also located near to the city aids in increased OM inputs and nutrient loadings. In KV1 a notable peak is observed at depth \sim 220-300 cm around (5700- 8000 yr BP) for C content is interpreted as the period of lake formation with warm climate (Itkonen et al., 1999). The sediment deposited during this period predominantly consists of algae. The further decrease in carbon content after a depth of 300 cm, \sim 8300 yr BP, suggests increased inputs of minerogenic matter, likely from a more mineral-rich catchment area during that period with higher $\delta^{13}\text{C}$ values indicating enhanced carbon mineralization and a high degree of organic matter decomposition. Similarly, at same depth low C/N ratio is observed indicating low OM content with C mineralization higher than N degradation. There is a steady increase in $\delta^{13}\text{C}$ values after depth ($>$ 125 cm) in \sim 2900 yr BP. More positive δ values implies more decomposition OM and non-OM limitation, pointing to warmer climate. A deviation with a dip at a depth of 20 cm in \sim 130 yr BP indicates the periods with low C content. Similarly, at a depth around 95 cm in \sim 2100 yr a peak in C/N ratio is observed suggesting episodes of TOM inputs with terrestrial plants.

A



B



C

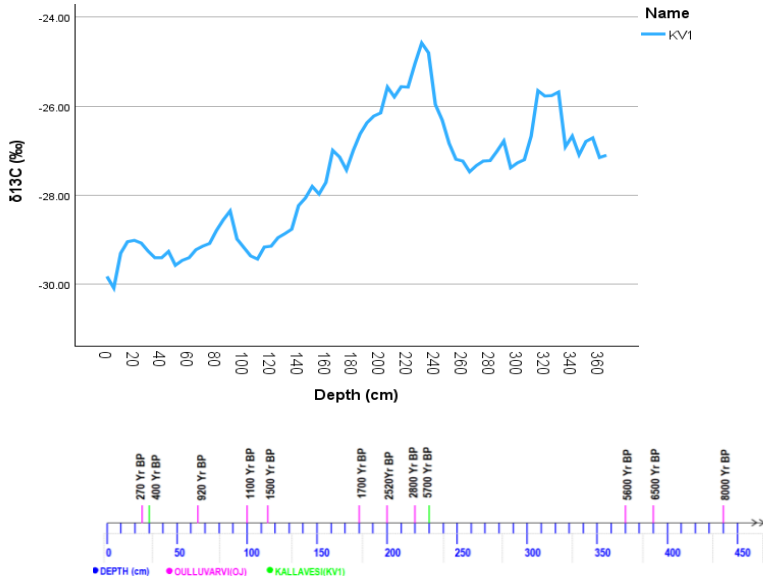
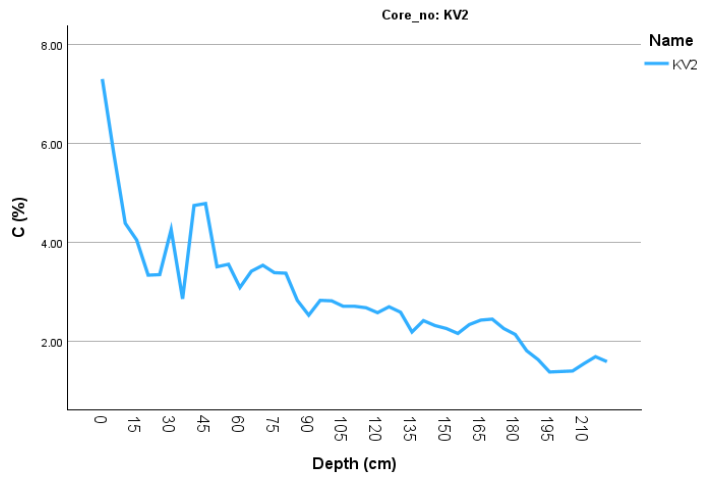


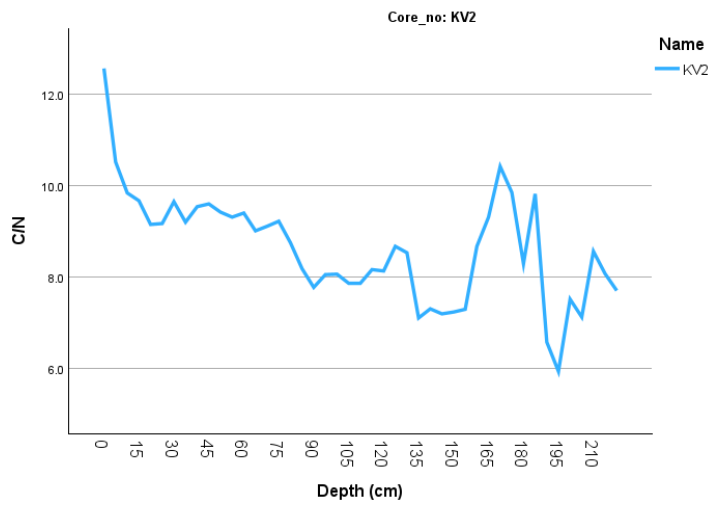
Figure 7. C% (top), C/N (middle) and $\delta^{13}\text{C}$ (bottom) with depth at site KV1. In the depth-time axis at the bottom end appears the depth (cm, in blue) while the time in years before present for OJ in pink and KV in green (see figure 6 for further details).

KV2 is located at the northern basin of Kallavesi and has a similar high C amount as in KV1 and high sedimentation rate (1.4 cm/yr, Fig. 5). In KV2 a sharp drop in C content is seen at around 30 cm depth with high values of $\delta^{13}\text{C}$ indicating the rapid decomposition of OM. At \sim depth of 35-50 cm a peak in C amount is observed indicating high OM in sediment. Similarly, \sim depth 155 -170 cm indicates the possible episode of tOM input with a peak observed in C/N ratio. The highest value of C content is seen in the top sediment indicating the presence of high amount of OM with partial decomposition. At a depth around 180-195 cm, a steady decrease in C/N ratio is seen due to mineralization of C. The overall C/N ratio in KV2 indicates the source of OM is from the algae and present in the lake. The higher value of C/N ratio at the top sediment indicates the terrestrial OM inputs (Meyers, 2003). The $\delta^{13}\text{C}$ values remained consistent with low values as shown in (Fig. 8)

A



B



C

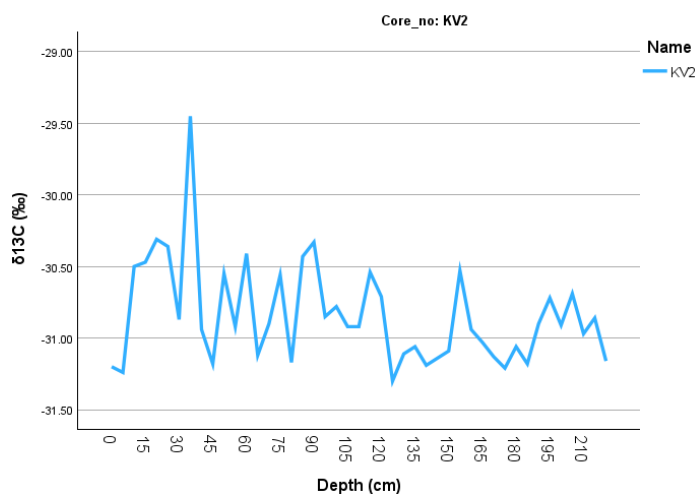
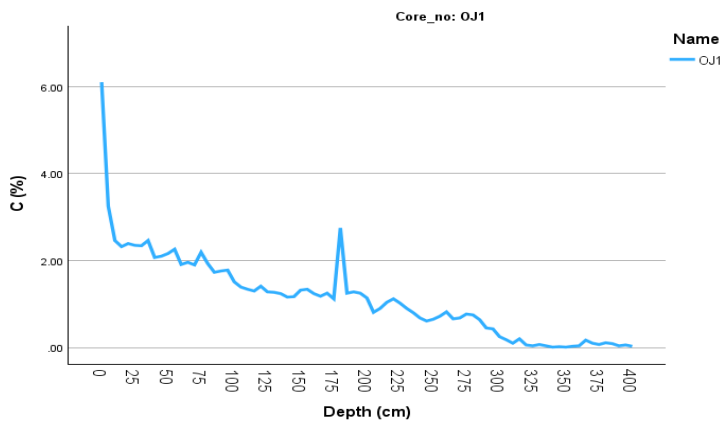


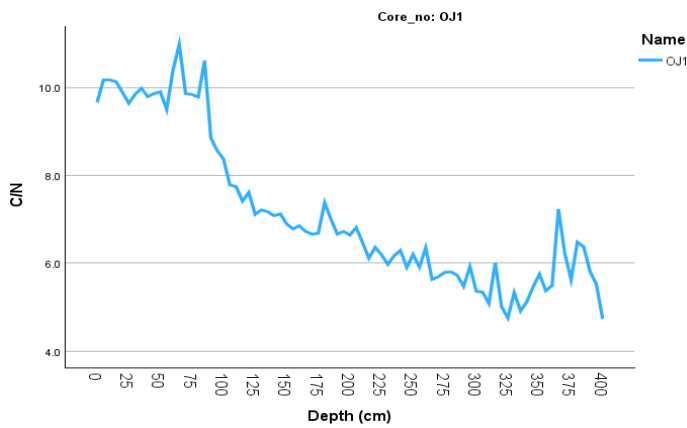
Figure 8. C% (top), C/N (middle) and $\delta^{13}\text{C}$ (bottom) with depth at site KV2.

OJ1 as OJ3 is the site which is located towards the north in the central basin of the lake near to the littoral. This site is close to the shoreline and near to the OJ site 2 studied in (Pajunen, 2000). This site faces erosion and transportation processes with accumulation only in the deep part of the basins (Pajunen, 2000). The amount of C content for OJ1 shows a similar trend of C % decreasing with depth. The high C/N ratio at the depth of around 65 cm with low C content in ~ 900 yr BP shows high inputs of tOM and conversion of OC to inorganic form. A notable peak is observed at a depth of 175 cm in ~ 2400 yr BP indicating high carbon content and high productivity in the lake system (Köster et al., 2005). Similarly, at depth > 275 in ~ 4200 yr BP shows low C content but with increased value of $\delta^{13}\text{C}$ as shown in (Fig. 9A) indicates OM formed from algae present in the lake (Meyers, 2003). After depth (>325 cm) in ~ 5100 yr BP, C content is consistent and very low indicating the presence of minerogenic matter in large amount as it could be the pre state of the lake. For C/N ratio a deviation is observed at depth of 370 cm in ~ 6000 yr BP.

A



B



C

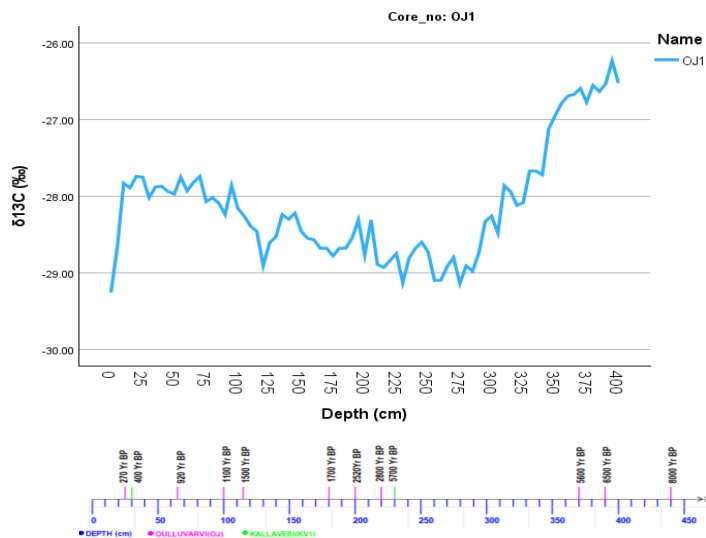
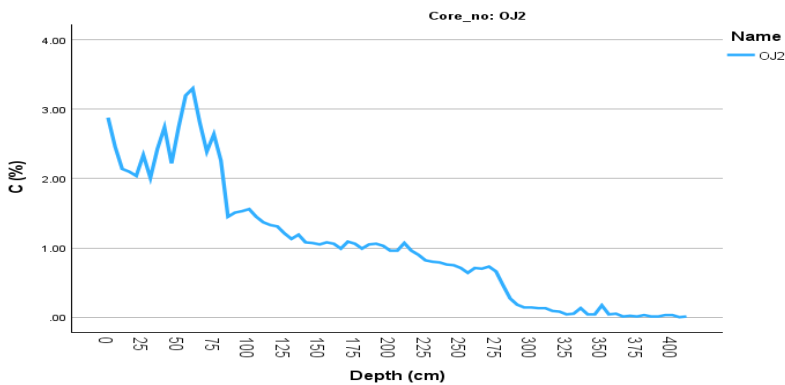


Figure 9. C% (top), C/N (middle) and $\delta^{13}\text{C}$ (bottom) with depth at site OJ1.

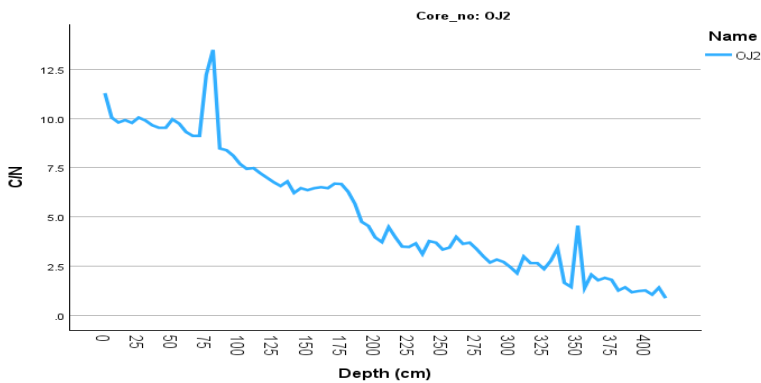
Site OJ2 in the central basin of Oulujärvi is located further south, being in the middle of the basin is a very pelagic site with less influence of the catchment. Site OJ2 has more pelagic component catchment influence. In OJ2 at depth 25-75 cm around 270 yr BP to 1000 yr BP shows high productivity in the

lake system due to presence of fresh OM with high carbon content. At a depth of 75 cm \sim 1000 yr BP shows the highest value of C/N indicating the high terrestrial plant inputs and a mix of algal sources. At depth \sim 100 cm in \sim 1100 yr BP shows lower $\delta^{13}\text{C}$ with decreased C content towards the bottom. The $\delta^{13}\text{C}$ values increases at depth $>$ 275 cm in \sim 4200 yr BP indicating diagenesis and decomposition of OM. A sharp drop is seen at a depth 350 cm in \sim 5600 yr BP showing lowest value of $\delta^{13}\text{C}$ with low C content. After depth $>$ 350 cm \sim 5600 yr BP consistent lowest values of C is observed at the bottom sediment.

A



B



C

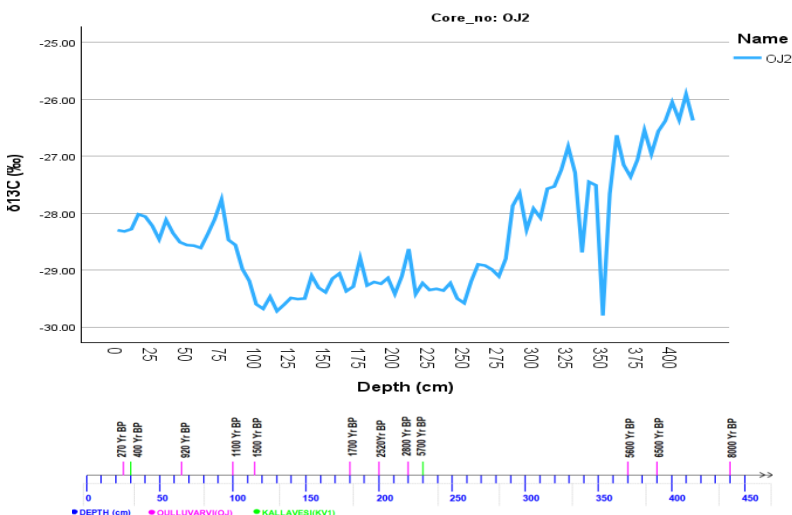


Figure 10. C% (top), C/N (middle) and $\delta^{13}\text{C}$ (bottom) with depth at site OJ2.

Site OJ3 is located towards the north in the central basin of the lake near to OJ1 and near to the shoreline. A deviation (marked drop) is observed at a depth of 215 cm in ~ 2800 yr BP indicates low amount of C with high OM degradation. After depth >225 cm in ~ 3300 yr BP, C % keeps on decreasing with lowest values observed at the bottom. In OJ3 \sim depth > 300 cm in ~ 4700 yr BP shows increased $\delta^{13}\text{C}$ values relating to rapid decomposition of OM. The C/N ratio decreases continuously with increasing depth except at a depth of 370 cm in ~ 6000 yr BP with slightly increased values showing high algal productivity.

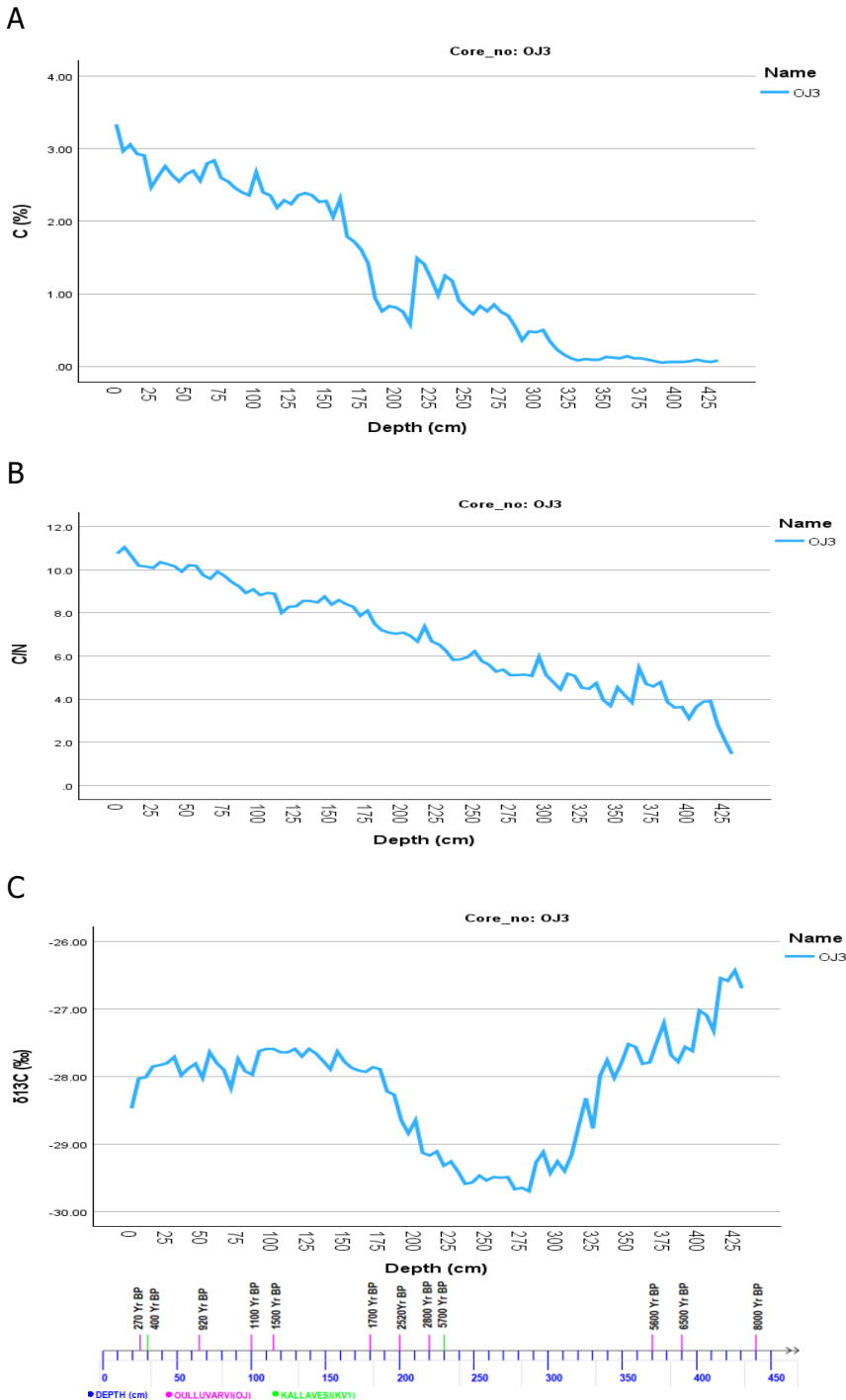


Figure 11. C% (top), C/N (middle) and $\delta^{13}\text{C}$ (bottom) with depth at site OJ3.

5.6 Correlation between the studied variable

Almost all the studied variables have a significant correlation with each other (Table 3). Depth has a strong correlation with six variables C/N (-0.896) Dry Bulk Density (0.842), C% (-0.821), Magnetic-susceptibility (0.808), LOI (-0.776), N% (-0.762) but the correlation with $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ is lower. C% is highly correlated with N% (0.968), as both elements are mainly in their organic form, this also explains the high correlation (0.943) with OM (LOI), depth (-0.821), Dry Bulk Density (-0.785), C/N (0.768) and Magnetic susceptibility (-0.712). The correlation with $\delta^{13}\text{C}$ is lower and no significant correlation with $\delta^{15}\text{N}$. C/N and depth have a strong correlation (-0.896) followed by Dry Bulk Density (-0.817), LOI (0.814), C% (0.768), Magnetic susceptibility (-0.695), N % (0.638). The correlation is low with $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. The value of $\delta^{13}\text{C}$ is highly correlated with LOI (-0.568) followed by magnetic susceptibility (0.505) and the low correlation are noticed for five variables, N% (-0.482), C% (-0.471), Dry Bulk Density (0.449), depth (0.448) and C/N (-0.369) at 0.01 level where $\delta^{15}\text{N}$ is significant with $\delta^{13}\text{C}$ at 0.05 level. Similarly, the significant values for other variables in the study are shown in table 3.

Table 3. Correlation matrix of the studied variables.

		Correlations								
		Depth (cm)	C (%)	N (%)	C/N	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	Dry Bulk Density (g/cm ³)	Magnetic-Susceptibility	LOI (%)
Depth (cm)	Pearson Correlation	1	-.821**	-.762**	-.896**	.448**	.303**	.842**	.808**	-.776**
	Sig. (2-tailed)		<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001
	N	411	411	411	411	411	411	411	299	29
C (%)	Pearson Correlation	-.821**	1	.968**	.768**	-.471**	-.086	-.785**	-.712**	.943**
	Sig. (2-tailed)	<.001		<.001	<.001	<.001	.082	<.001	<.001	<.001
	N	411	411	411	411	411	411	411	299	29
N (%)	Pearson Correlation	-.762**	.968**	1	.638**	-.482**	-.097	-.750**	-.672**	.864**
	Sig. (2-tailed)	<.001	<.001		<.001	<.001	.050	<.001	<.001	<.001
	N	411	411	411	411	411	411	411	299	29
C/N	Pearson Correlation	-.896**	.768**	.638**	1	-.369**	-.146**	-.817**	-.695**	.814**
	Sig. (2-tailed)	<.001	<.001	<.001		<.001	.003	<.001	<.001	<.001
	N	411	411	411	411	411	411	411	299	29
$\delta^{13}\text{C}$ (‰)	Pearson Correlation	.448**	-.471**	-.482**	-.369**	1	.101*	.449**	.505**	-.568**
	Sig. (2-tailed)	<.001	<.001	<.001	<.001		.041	<.001	<.001	.001
	N	411	411	411	411	411	411	411	299	29
$\delta^{15}\text{N}$ (‰)	Pearson Correlation	.303**	-.086	-.097	-.146**	.101*	1	.063	.320**	-.206
	Sig. (2-tailed)	<.001	.082	.050	.003	.041		.203	<.001	.284
	N	411	411	411	411	411	411	411	299	29
Dry Bulk Density (g/cm ³)	Pearson Correlation	.842**	-.785**	-.750**	-.817**	.449**	.063	1	.872**	-.826**
	Sig. (2-tailed)	<.001	<.001	<.001	<.001	<.001	.203		<.001	<.001
	N	411	411	411	411	411	411	411	299	29
Magnetic-Susceptibility	Pearson Correlation	.808**	-.712**	-.672**	-.695**	.505**	.320**	.872**	1	-.795**
	Sig. (2-tailed)	<.001	<.001	<.001	<.001	<.001	<.001	<.001		<.001
	N	299	299	299	299	299	299	299	299	23
LOI (%)	Pearson Correlation	-.776**	.943**	.864**	.814**	-.568**	-.206	-.826**	-.795**	1
	Sig. (2-tailed)	<.001	<.001	<.001	<.001	.001	.284	<.001	<.001	
	N	29	29	29	29	29	29	29	23	29

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

LOI is a proxy for OM content, there is a positive correlation between LOI and C indicating that most of the C is in the OM (not in mineral form) as expected in silicic and granitic catchments in Finland. Any variation in the carbon content is directly associated with variations in the LOI values. The high R² value of 0.88 indicates a strong correlation between the percentage of LOI and carbon. Similarly, all the R² value for different sites shows significant correlation as shown in table 4.

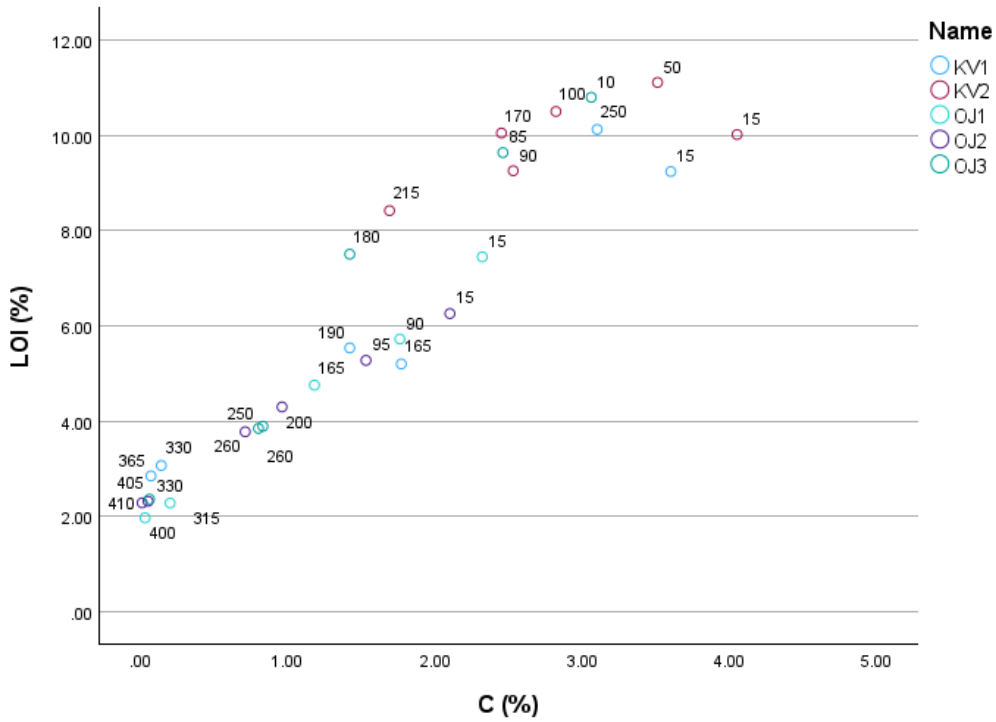


Figure 12. LOI with C% for all studied sites.

Table 4. Regression matrix of the studied variables.

Cores	Equation	R ²
All cores	$LOI = 2.33 + 2.41C$	0.88
KV1	$LOI = 2.61 + 2.02C$	0.93
KV2	$LOI = 7.62 + 0.8C$	0.50
OJ1	$LOI = 1.86 + 2.35C$	0.99
OJ2	$LOI = 2.32 + 1.93C$	0.99
OJ3	$LOI = 2.01 + 3.01C$	0.96

There is a weak negative correlation between the C % and $\delta^{13}\text{C}$, as indicated by the R^2 value of 0.21. The value of $\delta^{13}\text{C}$ decreased due to the large inputs of C. Other factors also affect how $\delta^{13}\text{C}$ values fluctuate. The degree of the C % and $\delta^{13}\text{C}$ correlation change when assessing for core alone (Table 5), being more explanatory in KV1 and no explanatory in OJ2 and OJ3. Apart from OJ3, where a low input of C enhances the value of $\delta^{13}\text{C}$, all the R^2 values in (Table 5) indicate an inverse association between C % and $\delta^{13}\text{C}$. In the appendix there are scatter plots to see one to one trend between the variables.

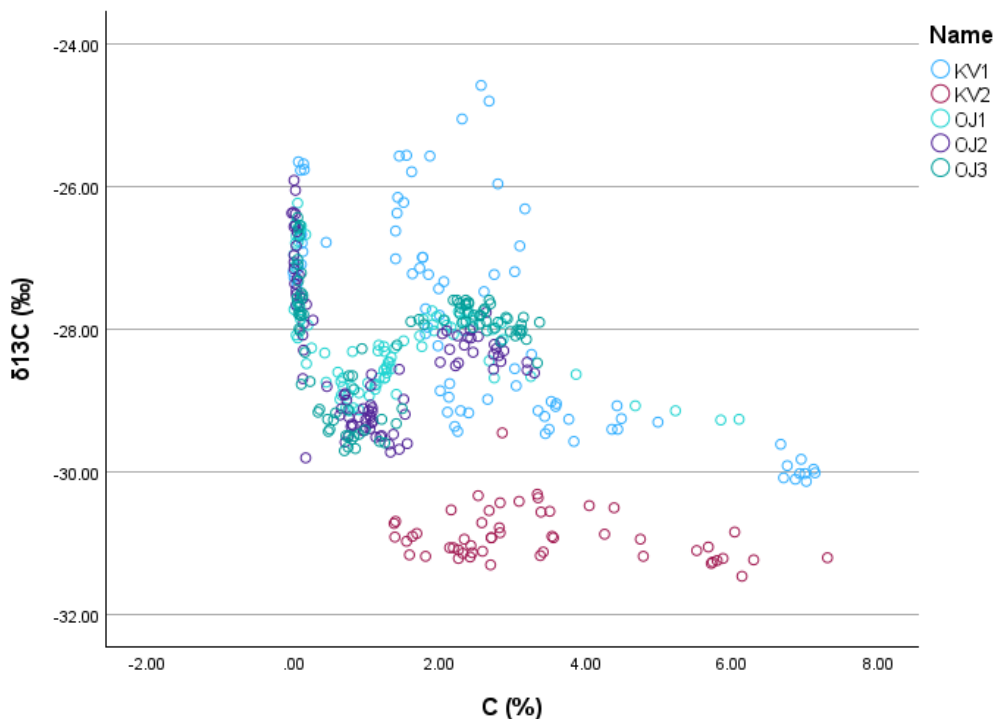


Figure 13. LOI with C% for all studied sites.

Table 5. C% and $\delta^{13}\text{C}$ linear equation and R squared for all the studied sites.

Cores	Equation	R^2
All cores	$\delta^{13}\text{C} = -14.16 - 0.56\text{C}$	0.22
KV1	$\delta^{13}\text{C} = -24.36 - 0.97\text{C}$	0.52
KV2	$\delta^{13}\text{C} = -31.77 - 1.14\text{C}$	0.06
OJ1	$\delta^{13}\text{C} = -18.4 - 0.7\text{C}$	0.16
OJ2	$\delta^{13}\text{C} = -7.21 - 0.3\text{C}$	0.09
OJ3	$\delta^{13}\text{C} = 7.12 + 0.2\text{C}$	0.01

6 Discussion

The result of the study revealed C content decreasing with depth in all sediment sites; this could be because OM degrades over time by microbial processes. It was shown that microbial activity caused more reduction in OM that was buried in the lake bottom (Meyers, 2003). The result with high C content found in the top sediment of this study relates to recent productivity in lake (Köster et al., 2005) warm climate (Itkonen et al., 1999) and partial decomposition in the newly formed OM. Conversely, the bottom sediment in this study was found to have lower C % may be due to presence of minerogenic materials with high influx of minerals from the barren catchment. This bottom sediment is the oldest sediment formed after deglaciation during the early Holocene representing the periods of initial sedimentation. In lake sediments the OM content and its preservation also depends on various factors such as its burial rate and oxidation of degradable compounds (Hodell & Schelske, 1998). The low C amount found in this study indicates presence of algal matter in the lake sediment (Pu et al., 2020) but with faster degradation of autochthonous OC by microbial activities (Burdige, 2007), resulting in lower preservation of C in lake sediment.

KV shows higher C content compared to OJ could be due to presence of higher amount of TOC as mentioned in Pajunen (2000). Boreal lakes were found to be affected by climate periods now and in the past (Itkonen et al., 1999). Around 6000 yr BP, lake had high production of algae as seen in (Fig. 7A) in KV1 may be due to the presence of warm climate (Itkonen et al., 1999). C content is found to be decreasing from the top sediment towards the bottom. The top sediment in this study has high mean value of 4.4 compared to the study in Lake Alexandrina (Herczeg et al., 2001). In the top sediment KV has a high C % compared to OJ due to KV1 receiving OM inputs and nutrient loading from city of Kuopio and low OM decomposition observed in KV2. Loss in catchment vegetation can also have significant impact in input of OM and nutrients to lake, potentially affecting C content (Köster et al., 2005) in the lake sediments. The reason why this study showed low C % could be due to influx of mineral as a result of soil erosion from the nearby catchments (Köster et al., 2005) and due to low C storage in large lakes compared to small lakes (Pajunen, 2000). Despite low amount of C content in lake sediment, it can still play an significant role in the carbon cycle (Kortelainen et al., 2004) and act as a C sink especially in the boreal regions (Chmiel, 2015).

In this study the C/N ratio decreased with depth in all the sediment sites; this could be due to conversion of OC to inorganic form and microbial activities leading to temporary confinement of nitrogenous materials in form of NH_4^+ (Meyers & Ishiwatari, 1993). The C/N ratio is highly

correlated to depth in this study portraying the changes in sources and composition of OM with changing environment conditions over time. The high C/N ratio relates to the influences of catchment with more terrestrial plants inputs and at the same time microbial mineralization of N relative to C in diagenetic process (Herczeg et al., 2001) resulting in less relative loss of C compared to N (Gälman et al., 2008). The low C/N ratio suggests algae and aquatic plants are predominantly present in the lake (Meyers, 2003) with high microbial biomass. The high C/N ratio in KV2 indicates the high inputs of TOM from the surrounding catchment due to its presence near the shoreline.

The top sediment in this study has a higher C/N ratio indicating a higher amount of terrestrial OM input from the catchment areas (Meyers, 2003). Although top sediment has high C/N ratio, a drastic drop seen in OJ2 may be due to rapid decomposition of OM. The bottom sediment in this study has low C/N ratio which indicates the sources of OM are from the algal sources and contains a higher proportion of microbial biomass. The result from this study contradicts with other studies where C/N ratio was found increasing with depth for e.g. lake Ontario (Hodell & Schelske, 1998) and lake Lugano (Lehmann et al., 2002). The C/N values were found to be 9.6 in large lakes (Pajunen, 2000) which is lower in this study with an average value of 7.07. The C/N ratio is similar for KV and OJ in the top sediment ~ 10 . Similarly, the C/N ratio were found to be ~ 10 for the surface sediment study in Southwest Greenland (Osburn et al., 2019) and varved lake sediment in Sweden (Gälman et al., 2008) is a similar to the mean values of top sediment in this study. The sediment study from lakes at Green land coast showed the sources of OM to be predominantly autochthonous (Osburn et al., 2019). Their findings agree to this study results with low C/N ratio.

This study shows that carbon content decreases while the $\delta^{13}\text{C}$ values increases with depth. The more positive $\delta^{13}\text{C}$ values towards the bottom of the sediment suggests the lake with enhanced decomposition process of OM (Meyers & Ishiwatari, 1993) and diagenetic process (Choudhary et al., 2009). In this study the top sediment values with more negative of $\delta^{13}\text{C}$ indicates inputs of terrestrial OM inputs as mentioned in Torres et al. (2012) and low decomposition. The top sediment in this study has slightly higher value of $\delta^{13}\text{C}$ with a mean value of -29.17 ‰ compared to mean value of -30 ‰ (Choudhary et al., 2009). In the top sediment KV has more negative $\delta^{13}\text{C}$ values compared to OJ. These negative $\delta^{13}\text{C}$ value refers to presence of allochthonous with human interferences (Choudhary et al., 2009). The lower value of $\delta^{13}\text{C}$ refers to decreased in CO_2 availability for phytoplankton (Hodell & Schelske, 1998). KV2 has the lowest $\delta^{13}\text{C}$ value < -30 ‰ confirms the inputs of forest plants (Talbot &

Johannessen, 1992). According to Choudhary et al. (2009) the diagenetic processes in bottom sediments result in increased $\delta^{13}\text{C}$ values due to the mineralization of C. This aligns with the findings of this study, which show increased $\delta^{13}\text{C}$ values in the bottom sediments, while the top sediments have high carbon content and decreased $\delta^{13}\text{C}$ values.

The informativeness of these proxies also depends on the small-scale spatial variability of the sites. A crucial point to remember is that KV2 has a missing bottom core due to which it might contain less information of the deep sediments.

7 Conclusion

This study highlights the importance of studying the geochemical proxies to gain knowledge on the history and environmental changes in large boreal lakes needed for reconstruction of lake and their catchment. The results obtained from studying sediment cores from Kallavesi and Oulujärvi showed the general trends of C and C/N decreasing and $\delta^{13}\text{C}$ increasing with depths. Deviations from the overall pattern provided information about the times when the environmental changes occurred. Higher amount of C with increase in OM inputs and partial decomposition were observed in the top sediment which further decreased with depth and time. KV has higher C% but low $\delta^{13}\text{C}$ values compared to OJ in the top sediment. The low C/N ratio confirmed the primary source of OM was predominantly from algae production within the lake with less impact from the terrestrial inputs wherein the existence of the land plants was found more in the top sediment. More negative values of $\delta^{13}\text{C}$ were found in the top sediment indicating low decomposition process of OM while more positive values of $\delta^{13}\text{C}$ were found towards the bottom indicating high decomposition with mineralization of C. Compared to small lakes, the environmental changes in the sediment archive of large lakes are more difficult and challenging to interpret due to various factors such as former processing of OM until sedimentation and higher spatial variability in the lake.

References

- Bring, A., Fedorova, I., Dibike, Y., Hinzman, L., Mård, J., Mernild, S., Prowse, T., Semenova, O., Stuefer, S. L. & Woo, M. K., 2016. Arctic terrestrial hydrology: a synthesis of processes, regional effects, and research challenges. *Journal of Geophysical Research: Biogeosciences*, 121, pp.621-649.
- Burdige, D. J., 2007. Preservation of organic matter in marine sediments: controls, mechanisms, and an imbalance in sediment organic carbon budgets? *Chemical Reviews*, 107, pp.467-485.
- Chmiel, H. E., 2015. The role of sediments in the carbon cycle of boreal lakes. *Acta Universitatis Upsaliensis*.
- Choudhary, P., Routh, J. & Chakrapani, G. J., 2009. An environmental record of changes in sedimentary organic matter from Lake Sattal in Kumaun Himalayas, India. *Science of the Total Environment*, 407, pp.2783-2795.
- Douglas, M.S.V., 2013. Paleolimnology| Overview of Paleolimnology. *Encyclopedia of quaternary science*, pp.259-270.
- Fry, B., 2006. *Stable isotope ecology* (Vol. 521, p. 318). New York: Springer.
- Gälman, V., Rydberg, J., de- Luna, S. S., Bindler, R. & Renberg, I., 2008. Carbon and nitrogen loss rates during aging of lake sediment: Changes over 27 years studied in varved lake sediment. *Limnology and Oceanography*, 53, pp.1076-1082.
- Gil, J., Marushchak, M. E., Rütting, T., Baggs, E. M., Pérez, T., Novakovskiy, A., Trubnikova, T., Kaverin, D., Martikainen, P. J. & Biasi, C., 2022. Sources of nitrous oxide and the fate of mineral nitrogen in subarctic permafrost peat soils. *Biogeosciences*, 19, pp.2683-2698.
- Herczeg, A.L., Smith, A.K. and Dighton, J.C., 2001. A 120 year record of changes in nitrogen and carbon cycling in Lake Alexandrina, South Australia: C: N, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in sediments. *Applied Geochemistry*, 16(1), pp.73-84.
- Hodell, D. A. & Schelske, C. L., 1998. Production, sedimentation, and isotopic composition of organic

matter in Lake Ontario. *Limnology and Oceanography*, 43, pp.200-214.

Hyvärinen, H., 1973. The deglaciation history of eastern Fennoscandia-recent data from Finland. *Boreas*, 2, pp.85-102.

Itkonen, A., Marttila, V., Meriläinen, J. & Salonen, V.-P., 1999. 8000-year history of palaeoproductivity in a large boreal lake. *Journal of Paleolimnology*, 21, pp.271-294.

Järvi-Meri Wiki, 2024a. Kallavesi [Online]. Available: [https://www.jarviwiki.fi/w/index.php?title=kallavesi_\(14.972.1.001\)](https://www.jarviwiki.fi/w/index.php?title=kallavesi_(14.972.1.001)) [Accessed 01/04/2024].

Järvi-Meri Wiki, 2024b. Oulujärvi [Online]. Available: [https://www.jarviwiki.fi/w/index.php?title=kallavesi_\(14.972.1.001\)](https://www.jarviwiki.fi/w/index.php?title=kallavesi_(14.972.1.001)) [Accessed 04/01/2024].

Kortelainen, P., Pajunen, H., Rantakari, M. & Saarnisto, M., 2004. A large carbon pool and small sink in boreal Holocene Lake sediments. *Global Change Biology*, 10, pp.1648-1653.

Köster, D., Pienitz, R., Wolfe, B.B., Barry, S., Foster, D.R. and Dixit, S.S., 2005. Paleolimnological assessment of human-induced impacts on Walden Pond (Massachusetts, USA) using diatoms and stable isotopes. *Aquatic Ecosystem Health & Management*, 8(2), pp.117-131.

Koutaniemi, L. and Keränen, R., 1983. Lake Oulujärvi, main Holocene developmental phases and associated geomorphic events (Vol. 135). Suomalainen tiedeakatemia.

Kuusisto, E., 1999. Saimaa, a Living Lake. Tammi Publishers.

Lehmann, M. F., Bernasconi, S. M., Barbieri, A. & McKenzie, J. A., 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. *Geochimica et Cosmochimica Acta*, 66, pp.3573-3584.

Lindholm, T. and Heikkilä, R., 2006. Destruction of mires in Finland. Finland—land of mires. Finnish Environment Institute, Helsinki, pp.179-192.

Mäkinen, J., 2024. Re: GTK.

Meyers, P. A., 2003. Applications of organic geochemistry to paleolimnological reconstructions: a

summary of examples from the Laurentian Great Lakes. *Organic Geochemistry*, 34, pp.261-289.

Meyers, P. A. & Ishiwatari, R., 1993. Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry*, 20, pp.867-900.

Myllyntaus, T., Hares, M. & Kunnas, J., 2002. Sustainability in danger? Slash-and-burn cultivation in nineteenth-century Finland and twentieth-century Southeast Asia. *Environmental History*, 7, pp.267-302.

Osburn, C. L., Anderson, N. J., Leng, M. J., Barry, C. D. & Whiteford, E. J., 2019. Stable isotopes reveal independent carbon pools across an Arctic hydro-climatic gradient: Implications for the fate of carbon in warmer and drier conditions. *Limnology and Oceanography Letters*, 4, pp.205-213.

Pajunen, H., 2000. Carbon in Finnish Lake Sediments. Geological Survey of Finland.

Pu, Y., Werne, J.P., Meyers, P.A. and Zhang, H., 2020. Organic matter geochemical signatures of sediments of Lake Ngoring (Qinghai-Tibetan Plateau): A record of environmental and climatic changes in the source area of the Yellow River for the last 1500 years. *Palaeogeography, palaeoclimatology, palaeoecology*, 551, p.109729.

Rantakari, M., 2010. The role of lakes for carbon cycling in boreal catchments.

Saarnisto, M., 1981. Holocene emergence history and stratigraphy in the area north of the Gulf of Bothnia. *Suomalainen Tiedeakatemia*.

Salomaa, R., 1982. Post-glacial shoreline displacement in the Lauhanvuori area, western Finland. *Annales Academiae Scientiarum Fennicae AIII*, pp.81-97.

Schuur, E. A., McGuire, A. D., Schädel, C., Grosse, G., Harden, J. W., Hayes, D. J., Hugelius, G., Koven, C. D., Kuhry, P. & Lawrence, D. M., 2015. Climate change and the permafrost carbon feedback. *Nature*, 520, pp.171-179.

Talbot, M. R. & Johannessen, T., 1992. A high resolution palaeoclimatic record for the last 27,500 years in tropical West Africa from the carbon and nitrogen isotopic composition of lacustrine organic matter. *Earth and Planetary Science Letters*, 110, pp.23-37.

Tikkanen, M., 2002. Long-term changes in lake and river systems in Finland. *Fennia-International Journal of Geography*, 180, pp.31-42.

Torres, I.C., Inglett, P.W., Brenner, M., Kenney, W.F. and Ramesh Reddy, K., 2012. Stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) values of sediment organic matter in subtropical lakes of different trophic status. *Journal of paleolimnology*, 47, pp.693-706.

Von Wachenfeldt, E. & Tranvik, L. J., 2008. Sedimentation in boreal lakes—the role of flocculation of allochthonous dissolved organic matter in the water column. *Ecosystems*, 11, pp.803-814.

Wauthy, M., Rautio, M., Christoffersen, K. S., Forsström, L., Laurion, I., Mariash, H. L., Peura, S. & Vincent, W. F., 2018. Increasing dominance of terrigenous organic matter in circumpolar freshwaters due to permafrost thaw. *Limnology and Oceanography Letters*, 3, pp.186-198.

Appendix

Appendix 1: The descriptives table of the overall studied variables.

		Descriptives							
		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
Depth (cm)	KV1	74	182.50	107.529	12.500	157.59	207.41	0	365
	KV2	45	110.00	65.670	9.789	90.27	129.73	0	220
	OJ1	81	200.00	117.633	13.070	173.99	226.01	0	400
	OJ2	84	207.50	121.963	13.307	181.03	233.97	0	415
	OJ3	87	215.00	126.293	13.540	188.08	241.92	0	430
	Total		371	190.81	117.718	6.112	178.79	202.83	0
C (%)	KV1	82	2.6361	2.03157	.22435	2.1897	3.0825	.00	7.14
	KV2	53	3.3623	1.52938	.21008	2.9407	3.7838	1.38	7.31
	OJ1	89	1.3769	1.27014	.13463	1.1093	1.6444	.01	6.10
	OJ2	92	1.1652	.98854	.10306	.9605	1.3699	-.02	3.30
	OJ3	95	1.4700	1.14403	.11738	1.2369	1.7031	.05	3.37
	Total		411	1.8583	1.60677	.07926	1.7025	2.0141	-.02
C/N	KV1	82	6.841	1.8268	.2017	6.440	7.243	2.8	10.5
	KV2	53	8.983	1.3844	.1902	8.601	9.365	5.9	12.6
	OJ1	89	7.448	1.9225	.2038	7.043	7.853	4.7	11.1
	OJ2	92	5.752	3.3594	.3502	5.056	6.448	.9	13.5
	OJ3	95	7.169	2.5662	.2633	6.647	7.692	1.5	11.1
	Total		411	7.081	2.5723	.1269	6.832	7.330	.9
δ13C (‰)	KV1	82	-27.8502	1.51581	.16739	-28.1833	-27.5172	-30.13	-24.58
	KV2	53	-30.8913	.35421	.04865	-30.9890	-30.7937	-31.46	-29.45
	OJ1	89	-28.1713	.73363	.07776	-28.3259	-28.0168	-29.27	-26.23
	OJ2	92	-28.4052	.96860	.10098	-28.6058	-28.2046	-29.80	-25.91
	OJ3	95	-28.1692	.79061	.08112	-28.3302	-28.0081	-29.70	-26.43
	Total		411	-28.5099	1.34584	.06639	-28.6404	-28.3794	-31.46
N (%)	KV1	82	.2909	.19658	.02171	.2477	.3340	.00	.71
	KV2	53	.3472	.13305	.01828	.3105	.3838	.08	.58
	OJ1	89	.1478	.11380	.01206	.1238	.1717	.01	.61
	OJ2	92	.1651	.05646	.00589	.1534	.1768	.10	.33
	OJ3	95	.1660	.10390	.01066	.1448	.1872	.03	.31
	Total		411	.2101	.14602	.00720	.1960	.2243	.00
δ15N (‰)	KV1	82	3.1729	2.25624	.24916	2.6772	3.6687	-4.08	7.58
	KV2	53	2.4296	2.35598	.32362	1.7802	3.0790	-.94	9.53
	OJ1	89	4.6783	4.21647	.44695	3.7901	5.5665	-5.55	11.62
	OJ2	92	.1626	1.70566	.17783	-.1906	.5158	-5.77	3.42
	OJ3	95	2.1204	1.23617	.12683	1.8686	2.3722	-.38	6.02
	Total		411	2.4859	2.98362	.14717	2.1966	2.7752	-5.77
Water content (%)	KV1	82	58.0421	10.83729	1.19678	55.6609	60.4233	29.32	70.93
	KV2	53	66.3281	5.86742	.80595	64.7109	67.9454	50.11	82.63
	OJ1	89	50.8275	10.48603	1.11152	48.6186	53.0364	31.01	77.18
	OJ2	92	44.6893	8.64229	.90102	42.8996	46.4791	22.06	61.69
	OJ3	95	50.8015	12.78312	1.31152	48.1974	53.4055	24.42	95.17
	Total		411	52.8858	12.28366	.60591	51.6947	54.0768	22.06
Wet Bulk Density (g/cm3)	KV1	82	.9189	.27760	.03066	.8579	.9799	.38	1.64
	KV2	53	.6757	.15706	.02157	.6324	.7190	.32	.96
	OJ1	89	1.0701	.27404	.02905	1.0124	1.1278	.62	1.62
	OJ2	92	1.2480	.27647	.02882	1.1908	1.3053	.44	2.03
	OJ3	95	1.0198	.39911	.04095	.9385	1.1011	.34	2.10
	Total		411	1.0173	.34283	.01691	.9840	1.0505	.32
DryBulk Density (g/cm3)	KV1	82	.4060	.23317	.02575	.3547	.4572	.15	1.14
	KV2	53	.2209	.04035	.00554	.2098	.2321	.13	.33
	OJ1	89	.5422	.23771	.02520	.4922	.5923	.17	1.06
	OJ2	92	.7096	.25703	.02680	.6563	.7628	.25	1.44
	OJ3	95	.5441	.32118	.03295	.4787	.6095	.17	1.41
	Total		411	.5115	.28945	.01428	.4834	.5396	.13
MagneticSusceptibility	KV1	77	20.2094	23.54409	2.68310	14.8655	25.5532	1.30	111.92
	KV2	47	8.0685	2.68909	.39224	7.2790	8.8581	.60	13.79
	OJ1	84	47.2902	33.38581	3.64269	40.0451	54.5354	.10	132.64
	OJ2	91	43.2055	37.41734	3.92240	35.4130	50.9980	.00	114.00
	OJ3	0
	Total		299	32.9078	33.24809	1.92279	29.1238	36.6917	.00
LOI	KV1	6	6.0083	3.06053	1.24946	2.7965	9.2202	2.86	10.13
	KV2	6	9.8933	.94454	.38560	8.9021	10.8846	8.42	11.11
	OJ1	6	6.5583	5.58331	2.27938	6.990	12.4177	1.98	17.14
	OJ2	6	4.0383	1.58884	.64864	2.3709	5.7057	2.29	6.26
	OJ3	6	6.3450	3.46598	1.41498	2.7077	9.9823	2.37	10.80
	Total		30	6.5687	3.65197	.66676	5.2050	7.9323	1.98

Appendix 2: Co-ordinates points of the studied area.

Name	Coordinate
Kallavesi_2017_19 (KV-1)	62°51'41"N 27°45'41"E
Kallavesi_2014_13 (KV-2)	62°59'27"N 27°25'41"E
Oulujarvi-2018-3 (OJ-1)	64°22'20"N 27°14'38"E
Oulujarvi_2016_10 (OJ2)	64°13'22"N 27°14'48"E
Oulujarvi_2016_14(OJ3)	64°22'01"N 27°14'53"E

Appendix 3: Plots of C%, C/N and $\delta^{13}\text{C}$ with Dry Bulk density and Magnetic Susceptibility for all the studied sites.

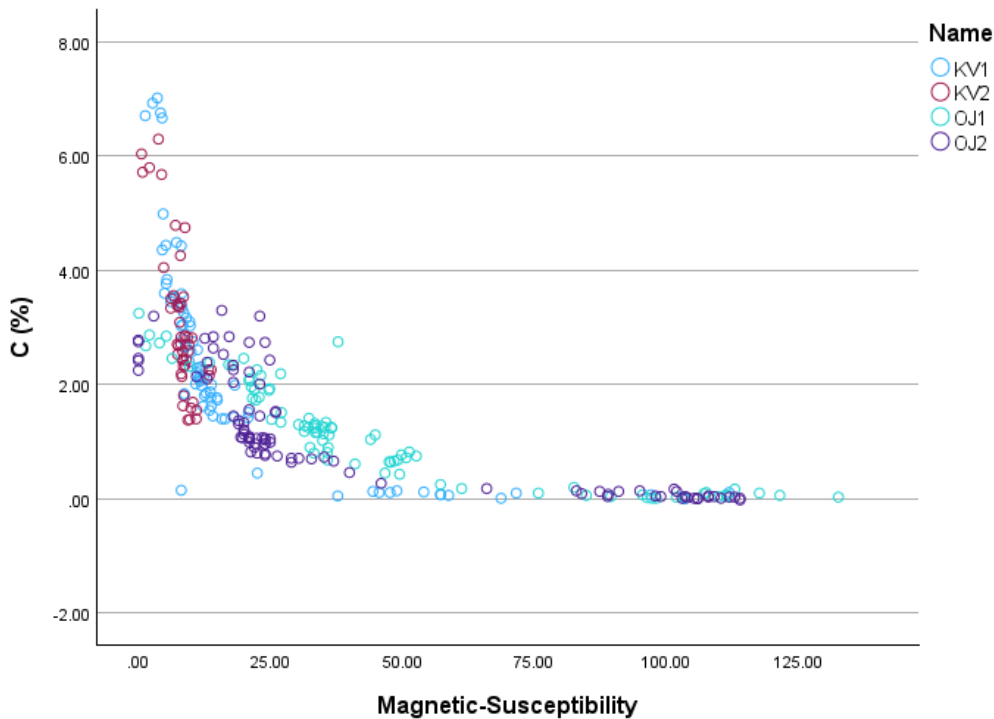


Figure i. C% with Magnetic- Susceptibility for all the studied sites.

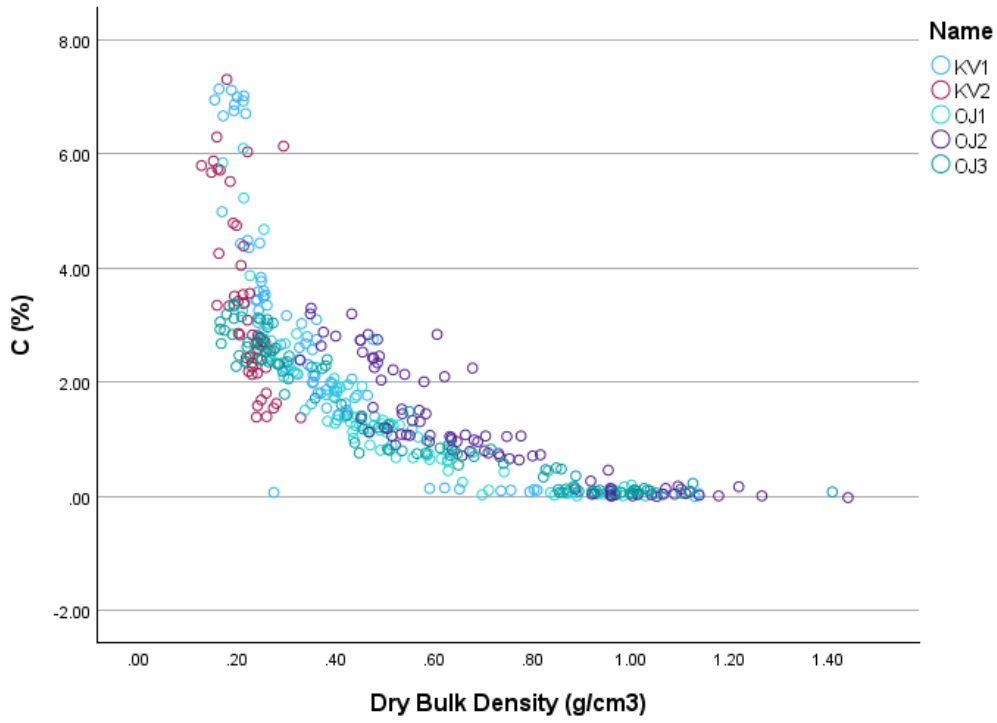


Figure ii. C % with Dry Bulk Density for all the studied sites.

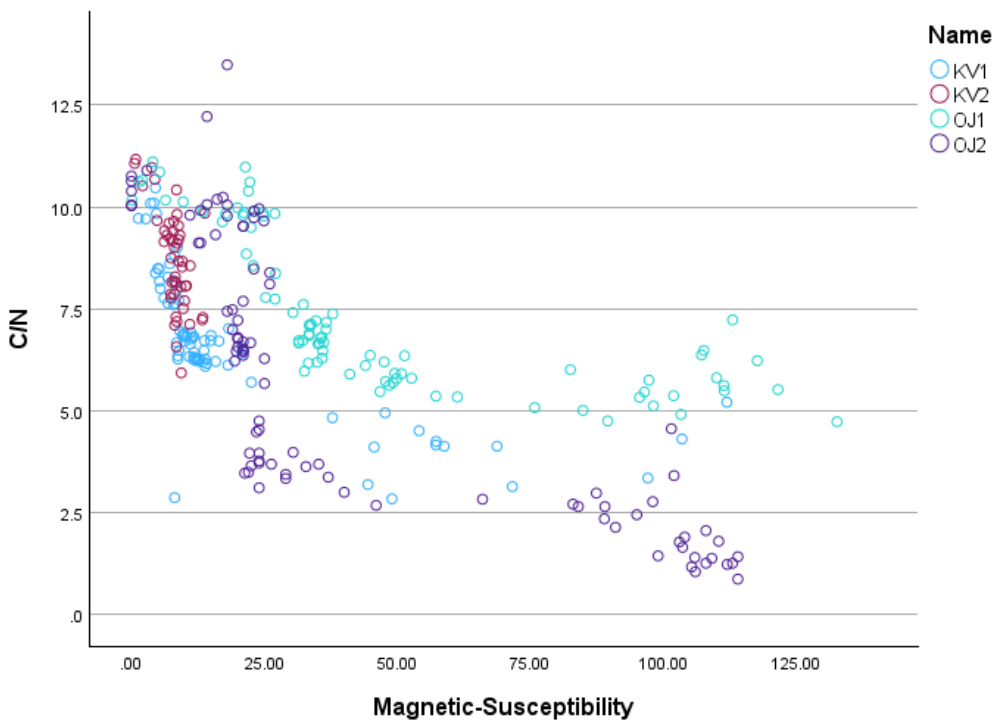


Figure iii. C/N with Magnetic- Susceptibility for all the different sites.

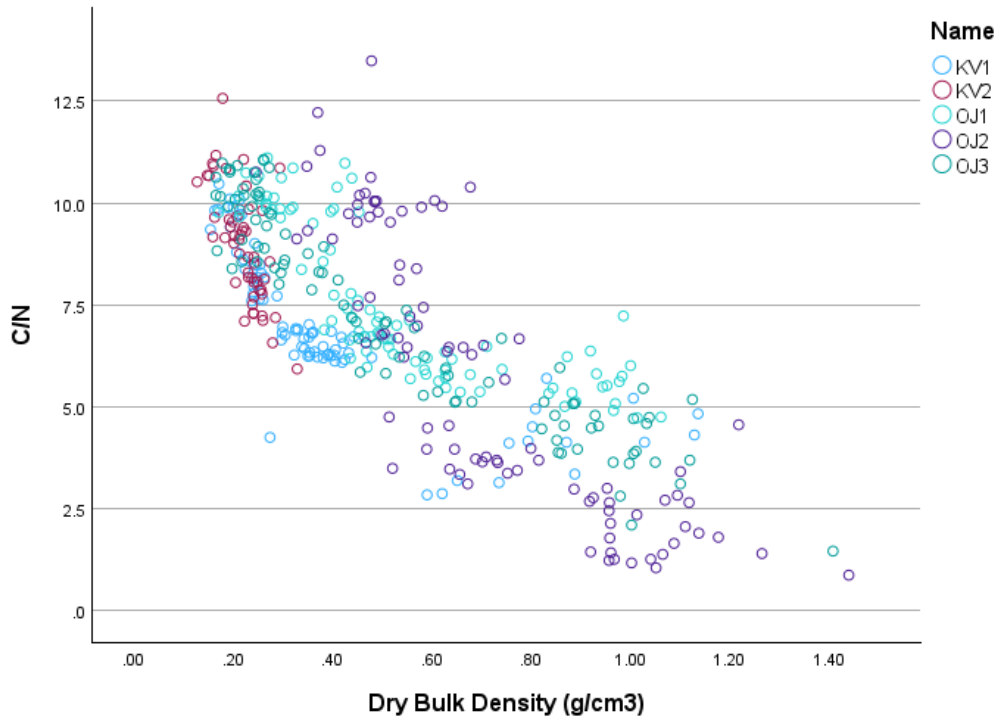


Figure iv. C/N with Dry Bulk Density for all the sites

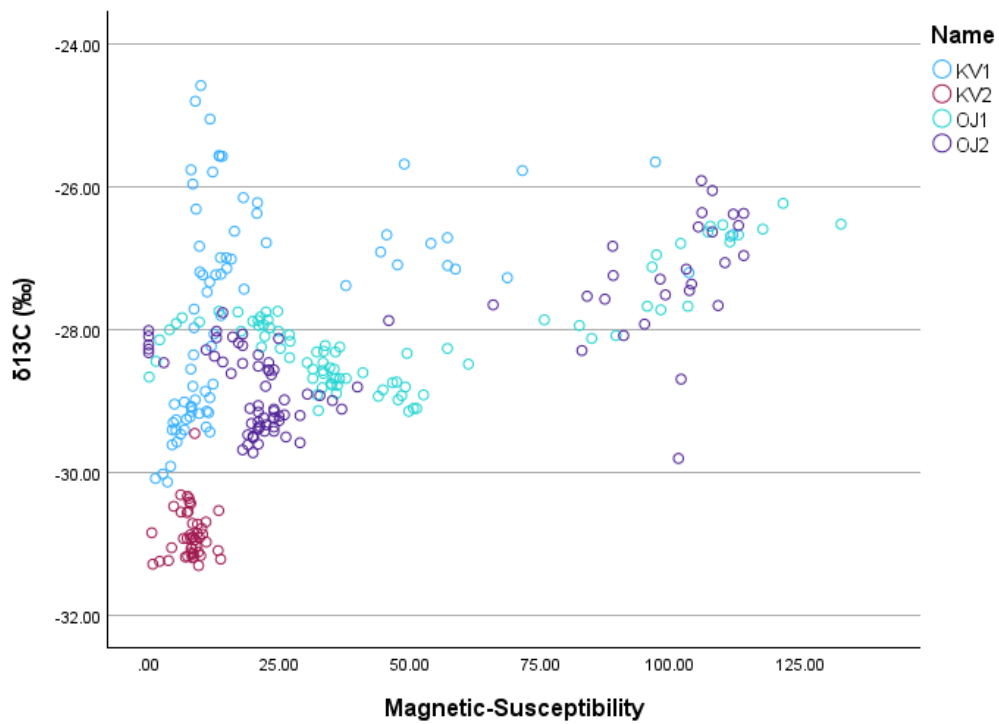


Figure v. $\delta^{13}\text{C}$ with Magnetic- Susceptibility for all the sites.

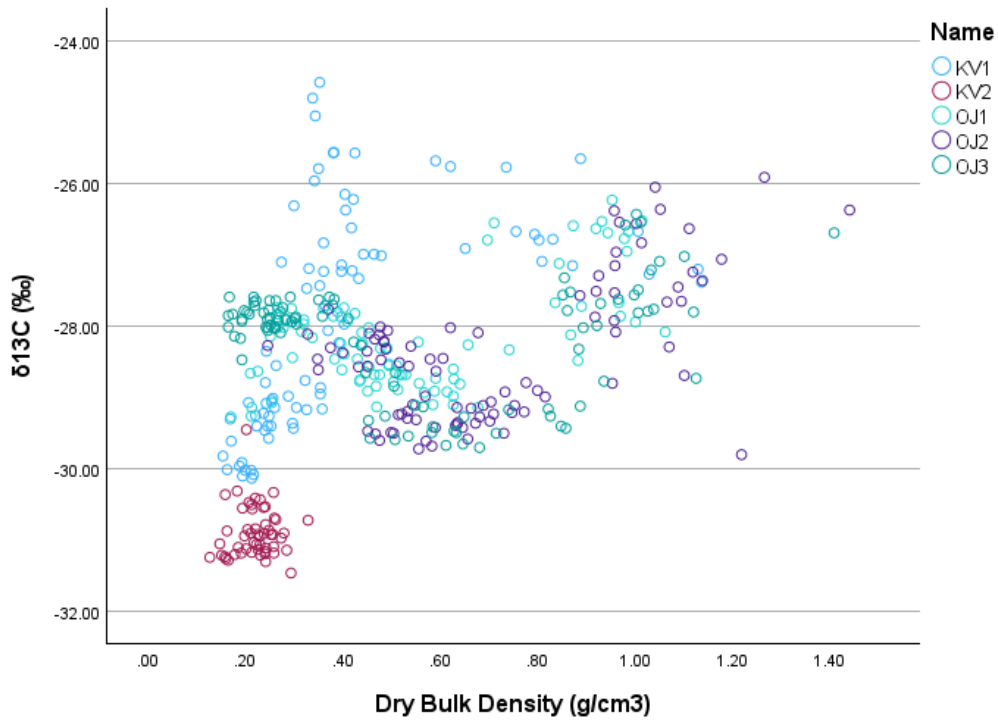


Figure vi. $\delta^{13}\text{C}$ with Dry Bulk Density for all the sites.

Appendix 4: Pictures of the studied sediment cores



Sediment core of KV2



Sediment core of OJ2



Sediment core of OJ3