ORGANIC MATTER DYNAMICS IN CORE SEDIMENTS OF HIGH ALTITUDE CHANDRATAL LAKE, HIMACHAL PRADESH

Dissertation submitted to Jawaharlal Nehru University for the award of the degree of

Master of Philosophy

Shamurailatpam Monica Sharma

School of Environmental Sciences
Jawaharlal Nehru University
New Delhi-110067, India
July 2017

जवाहरलाल नेहरू विश्वविद्यालय
Jawaharlal Nehru University
SCHOOL OF ENVIRONMENTAL SCIENCES
New Delhi-110067
Tele. 011-26704303, 4304

CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled **"Organic Matter Dynamics in the Core Sedimentsof High Altitude Chandratal Lake, Himachal Pradesh"** has been carried by Shamurailatpam Monica Sharma in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi under the supervision of Prof. AL Ramanathan, for the partial fulfillment of the award of degree of Master of Philosophy.

This work is original and has not been submitted in part or full for any other degree or diploma in any university or institution.

S. Monica Sh.
Shamurailatpam Monica
(Candidate)

Prof. S Mukherjee
(DEAN, SES)

प्रो.सौमित्र मुखर्जी / Prof. S. Mukherjee
डीन / Dean
पर्यावरण विज्ञान संस्थान
School of Environmental Sciences
जवाहरलाल नेहरू विश्वविद्यालय,
Jawaharlal Nehru University
नई दिल्ली 110067/New Delhi-110067

AL. Ra
Prof. AL Ramanathan
(Supervisor)

Acknowledgement

I would like to express my deepest gratitude to my supervisor Professor AL Ramanathan for his continuous support, patient guidance and useful critiques of this MPhil work.

I would also like to extend my gratitude to Dr Ratan Kar of Birbal Sahani Institute of Paleosciences, Lucknow for providing me with the opportunity to conduct Pollen grain analysis and assistance in keeping my progress on schedule. I would like to extend my heartfelt gratitude to Ruchika Ma'am for her untiring and timely help with the analysis. My warmest thanks to Dr. Abhijeet Mukherjee of Indian Institute of Technology, Khragpur, for offering me the resources for conducting the Amino Acid Analysis. I am very much thankful to Srimanti Ma'am for her care, encouragement and support in doing the extraction and analysis processes. I extend my gratefulness to my collegue Payal for her help in the entire extraction procedure and the non-teaching staff of IIT Kharagpur without whose help it would not be able to complete on time.

I also extend my appreciation to Prof. Garkoti, SES, JNU for providing me the opportunity to conduct Nitrogen Kjeldhal Digestion. I owe my obligation to Abhijit and Shailendra for assisting me throughout the performance of the analysis.

I would like to acknowledge the financial support I am receiving from the UGC funded NET-JRF. I would like to give my special thanks to the Dean of School of Environmental Sciences, Prof. S. Mukherjee for giving me the opportunity and providing with the necessary facilities to conduct this research project. In addition, I am grateful to Phauminsang Guite, administrative officer and to the coordinators of School of Environmental Sciences for their help in dealing with the administration. I am thankful to the staff of CIF, JNU (Gayakwad, Nitin, Bharadhawaj, Rashmi) for their help in instrumentation facility. I am also thankful to Anil Sharma for his timely delivery of lab equipment and chemicals.

I would like to thank Karuna, Sanjana, Om, Namrata, Prabhat and Swati for helping me during my analysis and giving me with valuable suggestions. I would like to thank Praveen, Arindan and Shailesh for giving assistance without any hesitation. I am also thankful to all my lab mates for their friendship and providing a stimulating academic environment.

I owe my loving thanks to all my classmates. Besides my sincere thanks to all my close friends for always being there for me and believing in me. Last but not the least I would like to thank my family for their constant care and encouragement without their support, this work would not have been possible.

Monica

Abstract

In the present study, we had studied a core sediment of 134 cm long, collected through piston corer from High altitude Chandratal Lake, a glacial fed lake, which is situated 4200 m above mean sea level in the Lahual Spiti district Himachal. The sediment core was analyzed for pollen grains, grain size, bulk parameters (TOC, TN, BSi) and Amino Acids (AA). Pollen grain study had identified four important climatic phases based on the change in frequency of pollen taxa and arboreal to non-arboreal ratios (AP/NAP). The overall pollen yield was quite low which was quite apparent, as it is an arid region. The dominance of extra-local pollens indicate their long distance transport from lower altitude. The C/N ratio of the core sediment range between 3.11-5.78 indicating in-situ production; phytoplankton and microalgae, as sources of organic matter (OM). Finer sediment of <0.002mm controlled the availability of organic carbon in the core sediment. Based on the biogenic silica (BSi), the comparative increased in its burial amount from around the depth of 28 cm indicated the warmer climatic condition. Amino acids based geochemical indicators such as Asp:β-Ala and Glu:GABA indicated relatively fresh organic matter in the upper part of core up to 28 cm than the bottommost core and except at the upper 4cm were extensive degradation had occurred. Amino acids based indices; reactivity index (RI) and lake degradation index (LI) were used. The comparatively low reactivity of OM with RI value of 0.66-3.09 revealed the relative slow rate in remineralization, LI values showed -2.07 to 1.42 with more negative values in the bottommost part of core from around 108 cm indicating the presence of relatively fresh OM in the sediment. Organic matter at the surface to 24 cm and 76-104cm were relatively degraded. The oxic:anoxic values fluctuate between 0.76-2.64 in the sediment core indicating the formation of sediment under both oxic and anoxic environment sequences. The overall climate regime in the studied region fluctuates between cold and arid to comparatively warmer and moist climate. Granulometry, origin of OM, microbial activities, redox potential and climate dependence of OM contents in sediment, denundational and erosional inputs of OM were the major processes controlling the sedimentary organic matter dynamics.

Keywords: High Altitude Lakes, TOC, TN, C/N, biogenic silica, amino acids, reactivity index, lake degradation index, oxic:anoxic, granulometry, microbial activities, climate.

ACRONYMS

AA - Amino Acids
AA-C - Carbon bound Amino acids
a m.s.l - Above mean sea level
AA-N - Nitrogen bound Amino Acids
Anox - Anoxic
AP - Arboreal Pollen
BP - Before Present
BSi - Biogenic Silica
C - Carbon
ca *Circa* (around)
DI - Degradation Index
THAA - Total Hydrolysable Amino Acids
N - Nitrogen
LI - Lake degradation Index
NAP - Non-Arboreal Pollen
OM - Organic Matter
Ox - Oxic
RI - Reactivity Index
TN - Total Nitrogen
TOC - Total Organic Carbon

Table of Contents

List of Figures

List of Tables

Chapter 1

INTRODUCTION

Lakes are considered as important archives of paleoenvironmental change because of its diverse range of organic matter derived from lake in-situ production and allochthonous production from its catchment area (Meyers and Lallier-Vergès, 1999). The relative importance of many potential sources of organic matter and their alteration in the post-depositional processes at varying regional environmental condition may reflect in the organic matter deposited in sediment at different time (Meyers, 1997). High Altitude Lake because of its geographical location and extreme climate condition have scanty biodiversity. Therefore, they have simple and shorter food web compare to other low-lying lakes. The remote location of high-altitude lake are in general less influenced by anthropogenic activities compare to lowland lakes. However, this condition does not essentially imply that these ecosystems are pristine, because many pollutants are introduced through regional and long-range transport (Sommaruga, 2001). The climate conditions in high altitude lakes are harsh and the ecosystem adapted in such region is particularly sensitive. Depending on the elevations of the lakes, they are ice and snow-covered for long periods, therefore they have a short growing period. Low temperature and low light levels during ice-covered seasons, act as a limiting factors for lake production (Ventelä et al., 1998). High altitude lakes have little nutrients and humic substances contribution and thus light penetration is high during the ice-free season (Sterner et al., 1997).

1.1 Evaluation of Paleo Environmental Conditions through Pollen Analysis

Pollens are particularly valuable in the reconstruction of past vegetation because of its extremely resilient nature and can be found in deposits in which other types of fossils are not common. They are also produced in enormous numbers, and can be retrieved in great quantities, they can be treated statistically and quantitative variations can be adequately controlled (Faegri and Iversen, 1950). The result of a pollen analysis, the pollen record, is represented by a pollen diagram which summarizes the results of field and laboratory investigations. However, interpretation of the pollen diagram is a strenuous task as many factors influences the pollen deposition, such as the pollen grains deposited in abnormal settings, the pollen rain influenced by extraordinary factors, conditions of sedimentation, preservation deviant etc. Besides, differential in production and dispersal by different species (Ritchie, 1995) are other constraints in the pollen diagram interpretation. Thus, pollen grains are often underrepresented or overrepresented in the pollen diagram. At the same time, to overcome the limitations of pollen analysis, certain assumptions are taken up, such as, pollen grains are produced in great quantity, and they show high degree of uniformity in the dispersal (Faegri and Iversen, 1950).

Extensive studies have been carried out in various environments including lacustrine environment by using pollen as a tool to reconstruct paleoclimate (Kotliya, 1997, 2013; Kar, 2002; Prasad 2006; Nautiyal 2009; Trivedi 2009; Rawat et al. 2015).

1.2 Bulk Parameters approach for lake productivity

Among the bulk parameters, TOC/TN ratio (atomic ratio, "C/N", used hereafter) is the most accepted indicator for the quality of organic matter in sediments (Huston and Deming, 2002). All living organisms require comparatively lesser amount of the carbon (C) compared to nitrogen (N). The ratio of C and N is an important factor in determining whether the organic matter is easily decomposable by the organisms or not. The lowering of C/N ratios in sediment with time might be an indicator to microbial immobilisation of nitrogenous material accompanied by the remineralisation of carbon (Sollins et al., 1984). Besides, C/N ratio provides information to discriminate the percentage contribution of aquatic and terrestrial organic matter to the lake sediments (Menzel et al., 2014). This is accompanied by the assumption that C/N ratios of between 4 and 10 represent unaltered algal organic matter, whereas C/N ratios of 20 and above indicate from land derived vascular plants (Redfield et al., 1963; Ishiwatari and Uzaki,1987; Ruttenberg and Goni, 1997; Emerson and Hedges, 1988; Meyers, 1994; Lehmann et al., 2002). The discrimination in source of organic matter is due to the absence of cellulose in algae and its greater abundance in terrestrial vascular plants. Although the C/N ratios of organic matter in sediments can changed because of selective degradation of organic matter components during early diagenesis (Meyers 1995, 2003), these values is still using by various workers for source indicators of organic matter in sediments (Bernasconi et al., 1997; Ostrom et al., 1997; Hodell and Schelske, 1998; Mishra, 2014).

Lakes of high latitudes and altitudes are particularly sensitive to climate change respond because they are seasonally covered with ice and have short growing seasons, therefore even a slight changes to their growing period have huge impacts on their biological productivity (Smol, 1988). Diatoms are typically the dominant photoautotrophs in high altitudes lakes (Douglas and Smol, 1999); BSi provides a direct measurement of the diatoms abundance and gives a reliable proxy for productivity in such lakes (Conley and Schelske, 2001). Sedimentary BSi is predominantly influenced by the lake production, clastic sedimentation rate and the post depositional preservation of siliceous organisms (Smol, 2000). The production of a lake is predominantly dependent on the water temperature, amount of lights receiving and the availability of nutrients (Wetzel, 2001). Hence, BSi could record on specific lakes changes that are not directly related to climate. In high altitude lake, which is seasonally covered with ice the extent and duration of the ice cover is the dominant factor affecting the lake production which in turn is a climate dependent (Douglas and Smol, 1999). However, various non-climatic factors such as geomorphic and hydrologic setting may interfere in the reconstruction of paleo-environment from lake sediments thereby resulting in non-linear relationship between the magnitudes of lake response and climate change (Fritz 2007).

1.3 Amino Acids Characterization:

The basic structure of Amino Acid is $NH_2CH(R)\text{-}COOH$, with one amine group ($-NH_2$), a carboxylic group (-COOH) and an R-group or side chain. Amino acid can be classified as acidic, basic, neutral, aromatic, proteineous, non-proteineous, hydroxyl and Sulphur containing AA based on the nature of the side chain (R group). Various Amino acids (AA quantified in the present study) their molecular formulas and molecular weight are shown in Table 1.1.

Table 1.1 List of Amino Acids (investigated in the present study), their molecular formulas and molecular weight.

Amino acid	**Abbreviations**		**Molecular formula**	**Molecular weight**
Alanine	Ala	A	$C_3H_7NO_2$	89.09
Arginine	Arg	R	$C_6H_{14}N_4O_2$	174.2
Aspartic acid	Asp	D	$C_4H_7NO_4$	133.1
Cysteine	Cys	C	$C_3H_7NO_2S$	240.3
Glutamic acid	Glu	E	$C_5H_9NO_4$	147.1
Glycine	Gly	G	$C_2H_5NO_2$	75.07
Histidine	His	H	$C_6H_9N_3O_2$	155.2
Isoleucine	Ile	I	$C_6H_{13}NO_2$	131.2
Leucine	Leu	L	$C_6H_{13}NO_2$	131.2
Lysine	Lys	K	$C_6H_{14}N_2O_2$	146.2
Methionine	Met	M	$C_5H_{11}NO_2S$	149.2
Phenylalanine	Phe	F	$C_9H_{11}NO_2$	165.2
Proline	Pro	P	$C_5H_9NO_2$	115.1
Serine	Ser	S	$C_3H_7NO_3$	105.1
Threonine	Thr	T	$C_4H_9NO_3$	119.1
Tryptophan	Try	W	$C_{11}H_{12}N_2O_2$	204.2
Tyrosine	Tyr	Y	$C_9H_{11}NO_3$	181.2
Valine	Val	V	$C_5H_{11}NO_2$	117.2
βAlanine	βAla	-	$C_3H_7NO_2$	89.09
γAminonbutyric acid	GABA	-	$C_4H_9NO_2$	103.12

Amino acids form the major N constituents and important organic carbon composition of the aquatic organism (Parsons et al., 1977). They are the structural composition of protein and a ubiquitous component of all source organisms and degradation mixtures (Cowie and Hedges, 1992). Although bulk organic matter source indicators play crucial role in identifying the origin of organic matter, molecular constituents provide details of production, delivery and preservation of sedimentary organic matter (Meyers, 1997). AA plays a significant role in biogeochemical cycles that occur in lake environments (Bourgoin and Tremblay, 2010). The lake sediments are the major storehouse of AA and act as an important sink, they are absorbed on suspended particulates that eventually reach the lake floor and preserved by successive sediment layer (Ni and Wang, 2015). The temporal variations in AA recorded in sediments reveals the natural procedures happening over time. The non- protein amino acids, β-Ala, γ-Aba, do not occur in living organisms but are the product of decarboxylation of aromatic Aspartic and Glutamic acids respectively, which on the other hand, are a part of living things. Thus, these non-proteins AA are not further metabolized in the presence of other easily available AA. Their relative abundance in the sediments provides the extent of OM degradation (Cowie and Hedges, 1994; Keil, et al., 2000).

Moreover, Amino acids analyses provide information about the specific sources of OM in various paleo-sediments including lake sediments (Cowie and Hedges, 1994; Dauwe et al., 1999; Menzel et al., 2015). Previous investigations have successfully used various amino acids based indices to explore their applicability in various lacustrine environment (Menzel, 2015). Understanding the degradation mechanism of organic matter in sediment is essential for investigating the dynamics of OM in lake. The AA assemblage of OM in sediment is affected by various aerobic and anaerobic decomposition during degradation processes (Cowie et al., 1995; Menzel et al., 2013). The Redox Index (Menzel et al., 2013) provide information about the condition of the sediment at the time of OM deposition. Reactivity index (RI) and Lake Degradation Index (LI) further provide an insightful information on degradation state or freshness of OM in lake sediments (Menzel et al., 2015).

1.4 Literature Review

The study of pollen grains in the Chandratal peat trench, Lahaul Western Himalaya, has unfolded the paleovegetation for the past 12,889 cal yr BP (Rawat et al., 2015). The palynological studies reveal four sequential changes in paleofloristics, corresponding to the changing climate. The paleoclimate of Chandratal peat trench was characterized by alternate fluctuations of climate between wet warm to cold dry. The changes of past climate from wet and warm climatic condition, through stressed moisture condition, to warm and moist climate condition accompanied by the prevalence of cold and dry condition in the region around ~4808-4327 cal yr BP, to warm and wet climate favourable for growth of diverse vegetation and to the present climate condition. For correlating the past vegetation, it is important to develop 'modern analogues' through the palynological analysis of surface sediments. Palynological studies of surface samples from the Lahaul Valley have shown a predominance of extralocal elements (mainly *Pinus*) over the local ground vegetation and it is not compatible to the surrounding vegetation (Kar et al., 2015) nevertheless, their abundance reflected long distance transportation from low altitude region due to phenomenon of upslope wind breeze (Rawat et al., 2012). The study reveals the strengthening of summer monsoon from around 90 cal yr to the present time.

An increasing number of studies in various lake sediments in the Northwest (NW) Himalaya, Central Himalaya and Eastern Himalaya has found a general ameliorating trend of climate in these regions at the present scenerio (Prasad, 2006; Bhattacharyya, 2007; Chauhan, 2006; Trivedi, 2009; Rawat et al., 2012, 2015). The increasing grasses and *Pinus* concentrations in the Chandra bog (Rawat et al. 2015) support the prevalence of moisture and increased temperature in the region and the fair presence of broad-leaved thermophillous taxa and grasses to the present indicate an improved climatic condition in this area. Study in the Surinsar Lake, Jammu, NW Himalaya (Trivedi, 2009) also reveal the slight advance in the oak and aquatic flora which implies the enhanced moonsoonal trend of climate, despite the existing cool and dry climate in this region. Phadtare (1999) in his study from the Gharwal Higher Himalaya also found similar result of ameliorating climate in the region since after the cooling episode of ca 800 yr BP which was marked by an increase in Quercus to Pinus ratio. From the Gangotri Glacier region, the vegetation vis-a-vis climatic changes have been recorded for the past ~2000 yrs BP through palynological studies, whereby Medieval Warming and Little Ice Age events have been recorded (Kar et al., 2002).

Studies in the Kumaon Himalayan Lakes have shown that the TOC in the recent sediments has been increased due to increase input of nutrients in the Lakes (Chakrapani, 2002; Das, 2005; Choudhary et al., 2009), impacting the productivity of the lake and consequently higher TOC in the sediments. The studies in the lakes in the Kumaon region viz. Nainital, Bhimtal, Sattal and Nakuchiatal reveals that algal derived OM is the primary source of organic carbon in these sediments and has limited contribution from terrestrial inputs. However, the recent increased in TOC content in these lakes, compare to the bottom sediments are rather related to the recent increased in anthropogenic activities around the lakes. The enrichments of nutrients in the lakes has steadily increased the primary productivity modifying the trophic state of the lakes from oligotrophic/mesotrophic to eutrophic (Choudhary, 2008, 2009a, 2009b, 2012). The studies in these lakes concluded the vulnerability of these water bodies to external inputs of nutrients.

The hydrogeochemistry studies of Chandratal reveals the predominance of weathering such as carbonate and silicate weathering, oxidation of pyrite, dissolution of sulphate minerals as the main controlling dynamic of the lake water chemistry with minor atmospheric precipitation and anthropogenic activities (Singh et al., 2016). The study successfully infer about the dynamic of the lake in the present period however, the study could not trace the climate change imprints on this lake and the long-term influence of climate variations in the major ions studied.

The Western Himalaya in Indian Himalayan Region (IHR) is spreading on three states namely, Jammu and Kashmir, Himachal Pradesh and part of Uttarkhand. Major Western Himalayan Region viz., Ladhak, Lahaul and Spiti has been studied for hydrogeochemistry (Singh et al., 2014), paleoclimate reconstruction (Rawat et. al., 2015), sediment accumulation (Fort, 1989), summer monsoon variability (Bhutiyani et al., 2009), paleoseismicity (Bookhagen, 2005; Phartiyal, 2009) etc. However, study on the biogeochemistry of the lake sediment deposition and degradation processes are still limited in this region. Organic matter preservation, degradation state and diagenetic changes, especially in High Altitude Lakes, are climate dependent processes and studying these facets of environment can infer about the paleo climate variability in the region. Understanding the factors which control the decadal, multi-decadal and century scale climate variability is essential for many aspects of climate predictability, which on the other hand, there is very limited observational records from the Himalayas for understanding and validating the existing dynamics recorded through instruments (Bakke et al., 2016).

1.6 Aim and Scope of the Present Study

Ever increasing indiscriminate anthropogenic activities during the past decades have delivered bulk quantities of nutrients, and organic constituents to the various Himalayan lakes. The evidence of nutrient enrichment, increase in lake productivity associated with increase plankton productivity has been reported in many Himalayan Lakes and other High mountain lakes in the recent past studies (Chakrapani, 2002; Grimalt, 2004; Das, 2005; Choudhary, 2008, 2009a, 2009b, 2012).

However, study on organic matter preservation, degradation state and diagenetic changes in sediments of Himalayan Lakes is still limited, especially in the High altitude North Western Himalayan region. The present study aim to evaluate the regional paleo environmental conditions and to evaluate the quantity, quality and degradation state of the organic matter in the core sediment of Chandratal Lake. Bulk parameter approaches such as TOC, TN and Biogenic silica are used to estimate the source of organic matter. Amino Acids is used as molecular level tool to evaluate the degradation state and diagenetic processes in the sediment core of Chandratal Lake.

1.7 Objectives of the Study

1. Evaluation of the regional paleo-environmental condition of a highly sensitive high altitude Chandratal lake through study of pollen grains.

2. Reconstruction of organic geochemical record to assess the variations, nature and quality of bulk sedimentary organic matter in the core sediment of Chandratal Lake.

3. To study the distribution pattern and digenetic changes of amino acids in sediment organic matter.

Chapter 2

MATERIALS AND METHOD

2.1 Study Area

Chandratal Lake (32°28′30.65″ N 77°37′1.42″ E) is located in the Lahaul-Spiti district of Himachal Pradesh, which is a part of Indian Cold Desert in the North Western Himalayas Fig 2.1. The Lake is situated at an altitudinal range of about 4300m above mean sea level. The climatic conditions in this region is typically dry temperate and alpine zones (Singh et al., 2014). The lake is formed by damming of glaciers (GSI, 2012). It is situated in the rain shadow side in north of the east-west-oriented Rohtang range (Rawat et al., 2012). The rainfall in this region is scanty and throughout the year it is covered mostly by ice (Singh et al., 2014). The record of the nearest weather station at Koksar shows that it receives ~1000 mm annual precipitation mainly as winter snow (Rawat et al., 2015). The mean air temperature in Chandratal Lake falls nearly –9.4 °C in winter and and during summer season, it is 2.4 °C (Ramanathan, 2011; Azam et al., 2016). Strong winds and dry air blown in most part of the year except for periods of rain and snowfall (Singh et al., 2014). In the recent study of physico-chemical characteristics and nutrients study of various high altitudes lakes in the cold desert region of Himachal Pradesh by Singh et al (2014), the nutrients contents reported in Chandratal Lake water are extremely low and it has been revealed as an ultra-oligotrophic lake. Table 2.1 shows some of the general and environmental properties of Chandratal lake.

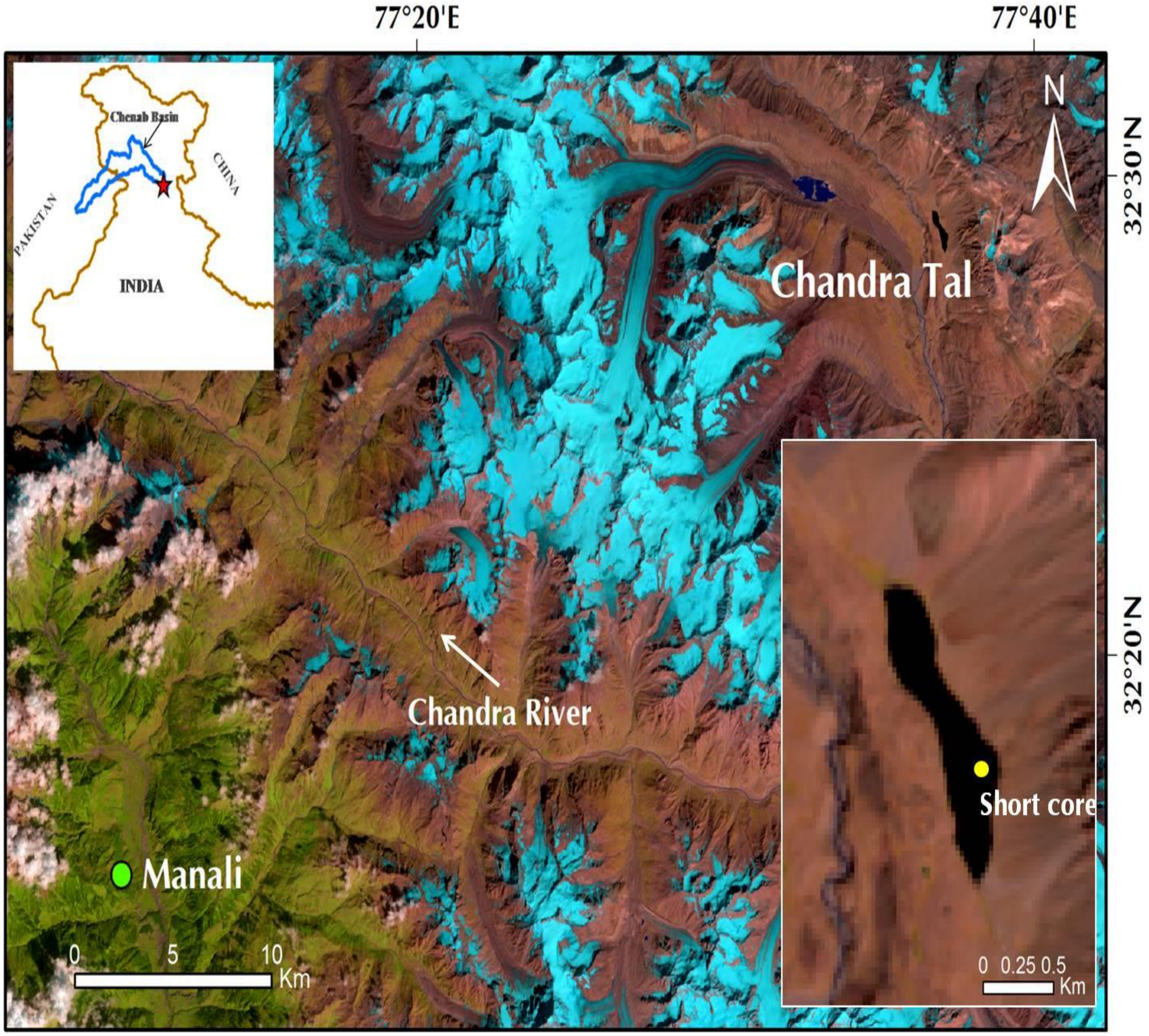


Fig. 2.1: Location map of Chandratal in Himachal Pradesh. The upper left inset shows a map of the Indian boundary, entire Chenab River basin (blue polygon, obtained from *ICIMOD*, Nepal). The lower right inset shows the closer view of Chadra Tal with short core location (yellow). Background is based on Landsat-8, 28 September 2014, band combination 5-4-3 downloaded from *United States Geological Survey (USGS)*. The map coordinates are in the Lat/Long, World Geodetic System 1984 (WGS84) reference system, map is prepared using ArcGIS 10.1.

Table 2.1

The location, hydrological and meteorological properties of Chandratal Lake.

	Chandratal Lake
Latitude	32°28′30.65″ N
Longitude	77°37′1.42″ E
Elevation (m a.s.l)	4300
Surface area (km^2)	2.5[a]
Max. depth (m)	29 m
pH	8.1[b]
Conductivity (µS/cm)	212[b]
Annual precipitation (mm)	1000[c]
Min. annual air Temp. (°C)	-5.8[d]
Max. annual air Temp.	+20

[a] Dwivedi (2012)

[b] Singh et al. (2016)

[c] Rawat (2015)

[d] (Ramanathan, 2011; Azam et al., 2016)

2.2 Methodology:

Coring was done in Chandratal with a sediment core retrieved up to a depth of 1.3 m. The sediment core was stored in cold storage maintaining temperature at 4°C until analysis was done.

2.2.1 Grain size analysis

The grain analysis was done using Laser Particle Analyser (Microtrac S3500) following the method of Konert and Vandenberghe (1997). Prior to the analysis, 1 g of the air-dried samples were taken in long tubes and added with hydrogen peroxide until the effervescence ceased. After the oxidization of organic carbon is completed, 5ml of 10% HCl were added to remove the inorganic carbon. The samples were boiled for 15-20 minutes in a hot plate. 3 g of tetrasodium pyrophosphate were added on the samples and mixed well. The samples were left to settle until layers formation. The supernatants were removed using a glass pipettes and

5 ml of distilled water were added to it. The samples were sonicated for 15 minutes and the samples were ready for analysis in the Laser Particle Analyser.

2.2.2 Analysis of Pollens in Sediments:

Total 26 samples were collected at an interval of 5 cm each. Palynological studies were thereby undertaken to decipher the vegetational and corresponding climatic changes through time. The analysis of pollen grain followed the standard laboratory process described by Moore et al. (1991). The procedure for preparation of the pollen analysis starts with de-flocculation. For this, the samples were first treated with aqueous KOH and simmered at 150°C. This treatment was to remove the humic acids and de-flocculation of the pollens at the same time. After de-flocculation, coarse particles from the samples were removed by sieving with a 150 mesh. The residue were discarded and the filtrate were diluted with water. Decantation of the filtrate was done twice for every 5 hours. The material were then treated with 48% HF to remove the siliceous matter and left for 2-3 days or more and stirred occasionally until the silica contents are completely dissolved. After the HF treatment, the materials were washed thoroughly until no traces of HF were left behind. Again, the samples were sieved through a 600 mesh. The filtrates were discarded and only the residues were taken and centrifuged at 2000 rpm. The HF treatment were then followed by acetolysis process, in which the residue were treated with glacial acetic acid (Acetic acid:Sulphuric acid, 9:1 v/v) to dehydrate the materials and centrifuged again. The mixtures were heated gently to the boiling point using a water bath and centrifuged. Finally the mixture were washed thoroughly with distilled water and then centrifuged. The samples were transferred in a vial tubes with 50% glycerol for preservation until counting of pollens grain was done.

2.2.3 Analysis for Total Organic Carbon

For organic matter determination, the modified wet oxidation method of Walkley and Black titration method (Walkley, 1934) was used. Air dried samples were grind with mortar and pestle and sieved through 600 µm sieve. 0.5 g of sediment was digested with 10 ml of 1.0 N $K_2Cr_2O_7$ and 20 ml of conc. H_2SO_4 (2:1 v/v) and left for 30 minute in an asbestos sheet. 100ml of distilled water, 10 ml H_3PO_4 and 1 ml of Bariumdiphenylaminesulphonate indicator were added. The solution is titrated rapidly with 0.5 N $FeSO_4$ until the solution turned to purple or blue and then more slowly until the color flashed to green. The end point is noted for the TOC calculation.

2.2.4 Analysis of Total Nitrogen

The standard Kjaldahl Method (Jackson, 1958) was used to determine the total Nitrogen. 1 g of air dried soil were mixed with 3 g mixture of $CuSO_4$ and K_2SO_4 (in 1:5 wt. /wt. ratio) and hydrolysed with 10 ml of 98% H_2SO_4. The samples were digested for 2 hours at 390°C. After the digestion, 30 ml of distilled water were added to each samples and transferred to the distillation unit. Approximately 50ml of 40% NaOH were added until the solution turned brown. The distillation unit was run for 9 minutes and the distillates were collected in a conical flask containing 40% boric acid and a mix indicator (Bromocresol green and Methyl red dissolved in Ethanol). The solutions were then titrated against 0.1 N H_2SO_4. The end-point of the titration is from green to pink. Back titration of H_2SO_4 was done to confirm the normality of the titrant.

2.2.5 Analysis of Biogenic Silica

Modified alkaline leaching method (DeMaster, 1981) was used for the analysis of Biogenic Silica (BSi). 0.03 g of dry sediment was extracted with 40 mL of 1% sodium bicarbonate (Na2CO3) solution maintained at pH 11.2 in 85 °C in a water bath shaker for 5 hours. At 3h, 1 mL of each sample were transferred to a separate centrifuge tubes containing 9 mL of 0.021 N HCl. The sub sampling procedure was repeated at 4h and 5h interval. Dissolved silica in the extractions was measured by the molybdate blue spectrophotometric method (Stickland and Parsons, 1972). The intercept of a least-squares regression of Si at 3, 4 and 5 h provides an estimate of BSi value.

2.2.6 Analysis of Amino Acids in Sediments

The amino acid extractions was done in accordance with the method followed by Moilleron et al. (1996). The sediment samples were dried in an oven at 80°C for 24 hours before being ground with pestle and mortar. Samples were then sieved through a 600μm sieve. 10 g of each sample were taken in a 50ml reagent bottle and hydrolyzed with 30 ml 3N HCl for 24 hours at room temperature. The aliquot were then filtered with 0.2µm syringe filter disc. The samples were then analysed using UHPLC thermos Fisher Scientific Reverse, the detector used was DAD-UV, column is C18X 4.67mm with diameter 150 x 4.67mm, with the flow rate at maintained at 1ml/min at 30°C. The sample injection was 10µL/min with run time 30mins. Standard mixture of 0.5µmol/ml amino acid acquired from Sigma Aldrich was used. Calibration standard of 250ppb, 500ppb, 1ppm, 5ppm, 10ppm, 15ppm and 20ppm were made in acetonitrile and water solution (50:50 v/v) for quantification of the amino acids.

2.2.5 Age Estimation of the Sediment Core

Due to the absence of a valid isotope dating for the present study, an estimation of the sediment core was made based on the sedimentation rate recorded by Rawat et al. (2015) from their study in the Chandra Peat trench, located in the Lahaul Spiti, Himachal Pradesh. Approximation of the upper 19 cm were based on the assumption of 0.03cm/yr while below this depth up to the bottom core was assumed 0.005cm/yr. The sediment core age was estimated to be around ~1700 year BP. The estimated sediment age is only an approximation for the present study and its validation is needed through isotope dating.

Chapter **3**

EVALUATION OF THE REGIONAL PALEO ENVIRONMENTAL CONDITIONS OF CHANDRATAL LAKE USING POLLEN ANALYSIS

3.1 Introduction

Palynology is the study of pollens and spores to investigate the past vegetation. In the study of the pollen analysis, investigation of the type of former vegetation is the central object and from this, further conclusions of various ecologic relations are derived. The direct ecological relationship of the vegetation to the climate is the key in constructing the past vegetation and consecutively infer the paleoclimate of the region. Pollens are extremely resilient and do not degrade in environments where other type of fossils can diagenitically degrade, they are present in enormous quantity and are widely available. The stability and the resistance of pollen grains to extreme climate and diagenesis make it a reliable tools in reconstructing past vegetation (Faegri and Iversen, 1950).

3.2 Result

The data is represented in the pollen diagram encompassing the records of past environmental responses (Fig.3.1). The pollen diagram constructed from this profile has been described below along with their interpretations towards the reconstruction of vegetation vis-à-vis climate of this region. The zonation of the pollen diagram has been made based on the frequency distribution of palynological assemblages and the changing frequencies of the arboreal pollen (from trees) and non-arboreal pollen (from herbaceous taxa) ratio (AP/NAP).

In general, the qualitative representation of spore-pollen taxa is not that good, which is normal as it is an arid region with sparse vegetation. Nonetheless, pollen-spores are present in the sediments that bring out the changing vegetation in response to climatic fluctuations. Throughout the sequence an overall dominance of arboreal pollen is observed over the non-arboreal pollen. However, changes in the AP/NAP ratio can be observed across the profile. For a better understanding of pollen-vegetation relationship as well as vegetational succession through time, four pollen zones - CT I, CT II, CT III and CT IV with the prefix ‘CT’ representing Chandratal have been demarcated in the pollen assemblage from bottom to top. These pollen zones have been demarcated on the basis of changing frequencies of AP/NAP ratio, with respect to increase or decrease in the percentages of arboreal/non-arboreal pollen.

Pollen Zone CT I (1-19cm depth): This zone represents the top most part of the profile which demarcates the increased values of AP/NAP ratio. The dominance of arboreals with an average value of 91.35% over non-arboreals (10.89%) is the characteristic feature of this phase. Among arboreals, conifers constituting *Pinus* (75-82%) along with *Picea* (1-4%) and *Abies* (1-4%) predominates over others. The broad-leaved taxa is represented by *Alnus* (1-5%) and *Betula* (0.6-1.7%). Among non-arboreals, Poaceae (0.7-2.8%), followed by Lamiaceae (0.7-2.78%), Ranunculaceae (2.1-3.4%) and Rosaceae (1.3-2.8%) are present in good frequencies. Other taxa, such as, Caryophyllaceae (~1%), Rutaceae (~1%), and Polygonaceae (~0.67%) are present in low abundance in the assemblage. Among steppe elements, *Artemisia* (1-2%) and Cheno/Ams (1-2%) are present in good numbers, with Liguliflorae (0.7-1.4%). The aquatic or marshy taxa present in this zone is Ephedraceae (1.3-1.7%). Ferns (1-5%) along with fungal and algal remains have marked their presence consistently.

Pollen Zone CT II (21-44 cm depth): The zone is marked by the dominance of arboreal taxa (76.67%) over non-arboreal taxa (23.31%) as usual. This zone is however, demarcated by a sharp decreasing trend in the AP/NAP ratio followed by changing frequencies of AP/NAP ratio in the pattern from the previous zone. *Pinus* maintains its predominance and ranges from 55-78%. *Abies* (1-6%), *Picea* (~1%) and *Abies* (~1%) are also well present in good amounts. In the broad-leaved category, *Alnus* (3-5%) and *Betula* (3-5%) represent moderate frequencies, while that of *Juglans* has marked its presence only in one sample. Amongst the non-arboreals, the prominent taxa are *Artemisia* (3-9%), Poaceae (7-15%), Rosaceae (1-9%), Tubuliflorae (1-3%), Liguliflorae (1-2%), Lamiaceae (1-9%), Caryophyllaceae (1-3%), Brassicaceae (~3%), Convolvulaceae (~2%) and Cheno/Ams (0.6-3%). Other taxa, such as Ephedraceae (~1%) and Ranunculaceae (~1%) are recorded in low values. Ferns (1-7%) are present in fair amounts along with algal and fungal spores.

Pollen Zone CT III (46-108 cm depth): This zone is initiated by a distinct increase in the AP/NAP ratio compared to the previous zone, thereafter it has a changing AP/NAP pattern having minor fluctuations in the middle, followed by a sharp decrease in the ratio at the end. The average frequency of arboreals is 85.57% while that of non-arboreals is 14.41%. The conifers predominate and are represented by high values of *Pinus* (51-90%). Other conifers, such as *Picea* (0.8-6%) and *Abies* (0.5-2%) are also present in fair amounts. Among broad-leaved taxa, *Alnus* (0.6-3%), *Betula* (0.9-5%) and *Juglans* (0.6-2%) are represented in moderate frequencies. Among non-arboreals, *Artemisia* (0.5-12%), Poaceae (0.5-19.6%), Rosaceae (0.6-5%), Ranunculaceae (0.9-3.6%), Brassicaceae (0.6-3.6%), Cheno/Ams (0.5-2.4%) are the dominant taxa. Other than these, Tubuliflorae (0.3-1.1%), Liguliflorae (0.3-1.7%) and Caryophyllaceae (0.3-2.1%) are represented in fair amounts. Occurrence of *Salix*, Lamiaceae and Euphorbiaceae are low and sporadic. Ferns along with algal and fungal spores maintain their common presence persistently.

Pollen Zone HO-A IV (109-134 cm depth): This zone is marked by a gradual decrease in the AP/NAP ratio from the preceding zone having a sharp peak in the middle of the trend. Arboreal taxa (81.46%) dominate over non-arboreal taxa (18.52%). *Pinus* (74-83%) continues to dominate. Other taxa, such as *Picea* (~1%) and *Abies* (~1%) are represented in fair amounts. Among broad-leaved elements, *Betula* (1-4%) is present in moderate amount, while *Alnus* (~1%) is occasionally present. The prominent taxa amongst non-arboreals are Poaceae (~6%), *Artemisia* (1-4%), Lamiaceae (0.9-3.6%), Rosaceae (1-3%), which are present in good amounts. Ferns are represented in fair amount along with algal and fungal elements. However, quantitatively, very few taxa have been recorded in this pollen zone.

3.3 Discussion

Vegetation and climatic reconstruction

To reconstruct the vegetational scenario in the study area, records of palynomorphs in the sediment profile of CT have been used. Corresponding changes in the vegetation are marked by the qualitative and quantitative changes in the frequencies of different pollen taxa and the changing trend of the AP/NAP ratios. Since the climate of any particular region primarily governs the vegetation of the area, the vegetational changes have thereby been used to interpret the climatic fluctuations through time. It must be noted that the region has a general arid climate, and the changing vegetation pattern reflect the relative climatic fluctuations within the overall dry regime.

Across the profile an overall dominance of extra-local conifers is observed, led by an overwhelming abundance of *Pinus*, which is attributed to their much higher pollen production (especially *Pinus*) and transport by upthermic winds to the depositional site. The tree-line is characterized by the remnants of *Betula* trees, whereas, Poaceae, *Artemisia*, Cheno/Ams, Asteraceae, Lamiaceae and Rosaceae mainly form the ground vegetation. The palynological results from CT profile has revealed four climatic phases which are summarised below:

Pollen Zone CT I is characterized by an AP/NAP ratio of 91.3/10.8%. The vegetation composition represents higher values of conifers - *Pinus*, *Abies* and *Picea*, amongst which *Pinus* is having the highest frequency range (75-82%). The broad-leaved taxa comprising of *Alnus* and *Betula*, however, have low values. Further, there is poor representation of steppe elements, such as *Artemisia* and other taxa like Rosacae, Cheno/Ams and Liguliflorae. Moisture loving elements like pteridophytic spores are present in good amounts. This type of vegetation suggests that comparatively warm and moist climatic conditions prevailed in the area during this phase.

During the subsequent period, the AP/NAP ratio decreases (76.6/23.3). On an average, there is a decrease in the pollen frequencies of coniferous taxa, especially *Pinus*, along with *Picea* and *Abies*. This zone is demarcated by a decrease in broad-leaved taxa, especially *Alnus* and *Betula* which record an appreciable fall in the pollen spectra. This indicates that the climate turned comparatively cold and arid than the earlier phase. Steppe elements constituting of

Artemisia, Tubuliflorae and Liguliflorae shows a considerable increase in its values. The vegetational picture during this phase suggests deterioration in the climatic conditions towards a colder and more arid regime.

Later, a steady increase in the arboreal/non-arboreal ratio is recorded (85.5/14.4%). *Pinus* is abundant as usual, followed by *Picea* and *Abies*. In the broad-leaved category, *Alnus* and *Betula* show an increase in their numbers as compared to the earlier phase. Non-arboreal elements such as Rosaceae, *Artemisia* and Cheno/Ams are recorded in poor frequencies. Fern spores have marked their presence in good amounts than the preceding zone. The conditions were not favorable for the growth of steppe/herbaceous elements. The overall palynological assemblage suggests the recurrence of a moister environment

During the successive period there is a decrease in the AP/NAP ratio (81.4.2/18.5%). The values of conifers are lesser than the previous zone, *Pinus* however, still being the dominant taxa; but the values represented are decreasing from the earlier zone. Broad-leaved taxa maintain their good frequencies, especially *Betula* is recorded in better frequencies though lesser than the previous zone. Among the steppe elements, *Artemisia* is present in high frequencies. Ferns are also present in lower frequencies than the preceding phase. This suggests that cold and arid climate was present during that phase.

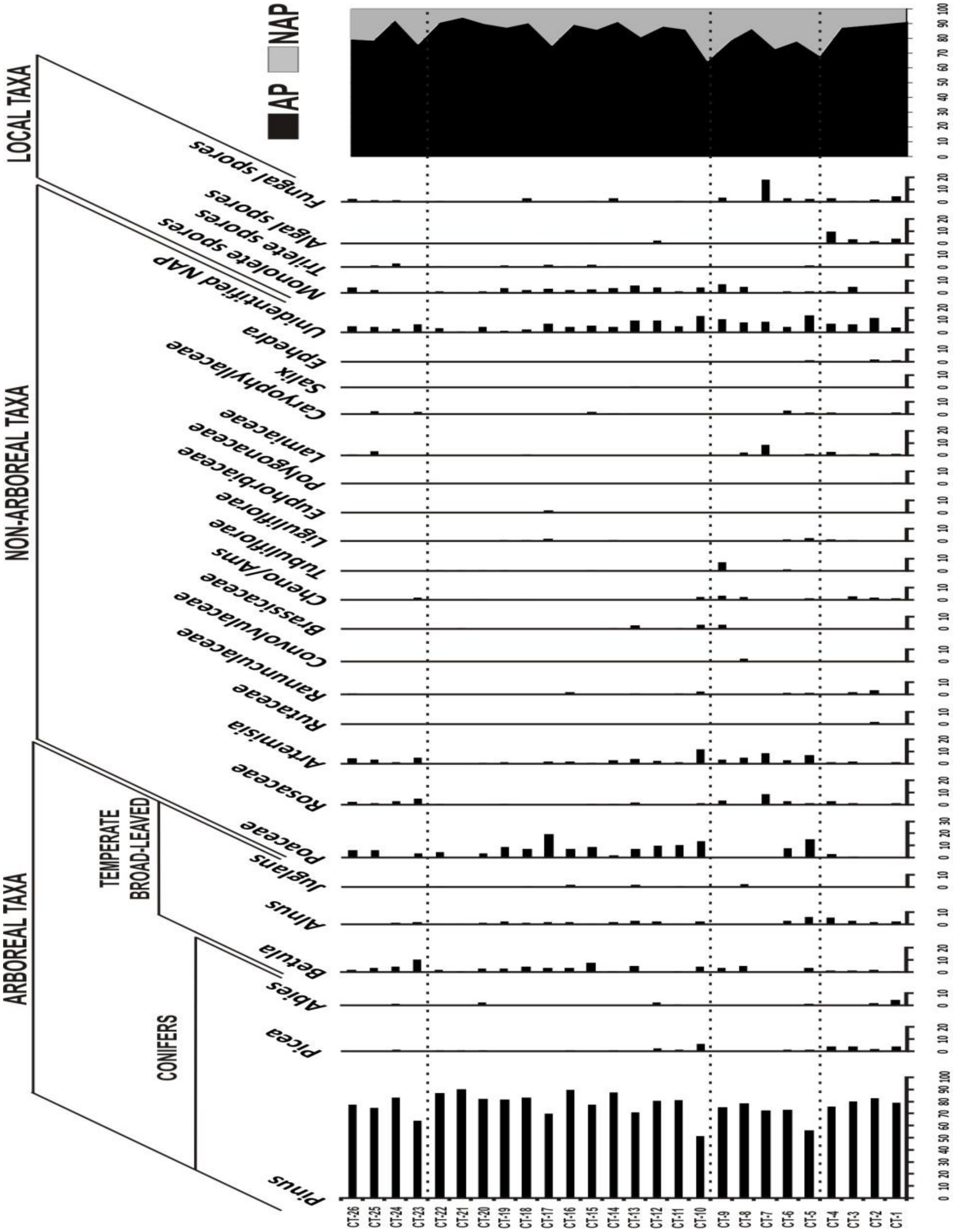


Fig. 3.1 Pollen diagram showing the frequency distribution of pollen-spores from a core (CT) in Chandratal, Lahaul-Spiti, Himachal Pradesh.

3.4 Summary:

In the present study of depth wise investigations of pollen record from the Chandratal Lake core sediment it was able to reconstruct the vegetation vis-à-vis climate record of the region. The arboreal pollen dominate over the non-arboreal pollen throughout the sequence. The zonation of the pollen diagram, based on the changing frequency of different pollen taxa and the AP/NAP ratio, had able to classify it into four palynologically important zones viz., CT I, CT II, CT III and CT IV. The climate of the region oscillates within the overall dry regime from cold and arid climate to comparatively warmer and moist climate. The findings of this study of Chandratal Lake concluded that the overall climate pattern of the region has not changed much within the retrieved sediment core depth. A plausible inference of the climate record was limited by the absence of an isotope dating in the present study.

Chapter **4**

BULK PARAMETER APPROACH TO IDENTIFY SOURCE CHARACTERISTICS

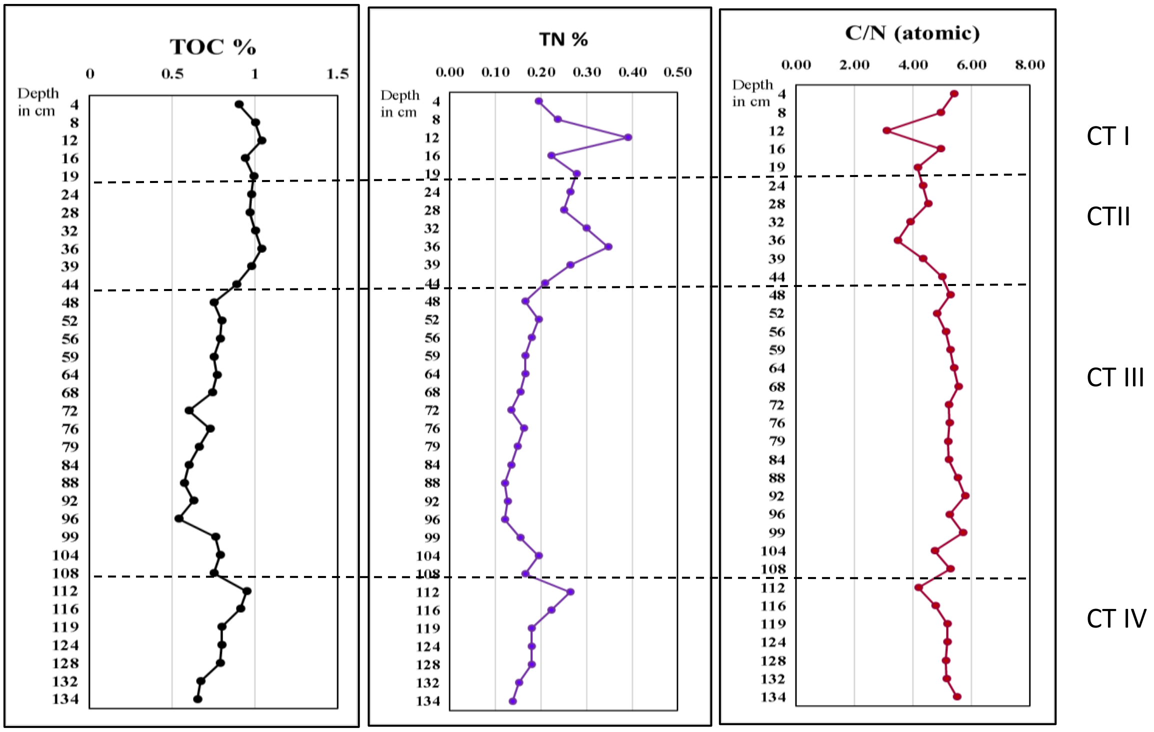
4.1 Introduction

Organic carbon source in lacustrine environment are derived from autochthonous and allochthonous sources. Autochthonous source of lake comprises the non-vascular phytoplankton and algae that contains no carbon rich cellulose and lignin, whereas allochthonous source includes those from cellulose and lignin rich land derived vascular plants such as grasses, shrubs and trees. Although the sources and alterations of organic matters are diverse for different lake's geography and microclimate conditions, the organic matters from these two distinctive sources retained there source peculiarity in their sediments (Meyers, 2003). Understanding the nature, quality and the relative contribution of potential sources is important in understanding the organic carbon dynamics in High altitude Lakes.

The preservation of the organic matter depends on the bulk organic composition, the type of source, the physical environment condition (Meyers, 1993), and on the burial rate and the oxygen content of the overlying bottom and that of the pore water (Hodell and Schelske, 1998). Moreover, the availability and distribution pattern of geochemical parameters in sediments is strongly influenced by the grain size composition of the sediment (Prasad and Ramanathan, 2008; Wen et al., 2008; Renjith et al., 2011). The degree of the degradation of the organic matter infer about the past environmental conditions and the nature of the source (Meyers, 1997). Understanding the bulk chemical composition of the organic matter preserved can help identify the productivity and the nature of the past alterations processes.

Literature review of various proxies have suggested the ameliorating climates in last few decades resulting in the change in productivity in high altitude and latitude lake ecosystem. Few other research have reported the increase in anthropogenic activities in Himalayan Lake due to increase tourism activities and long range transportation of pollutants subsequently affecting the fragile ecosystem and hence the bulk organic inputs in the High altitude lakes. This chapter therefore intends to concentrate on the nature and quality of OM, factors controlling the OM distribution in High Altitude Chandratal Lake and to unfold the sedimentary organic matter source using the bulk parameter as a tool.

4.2 Results:



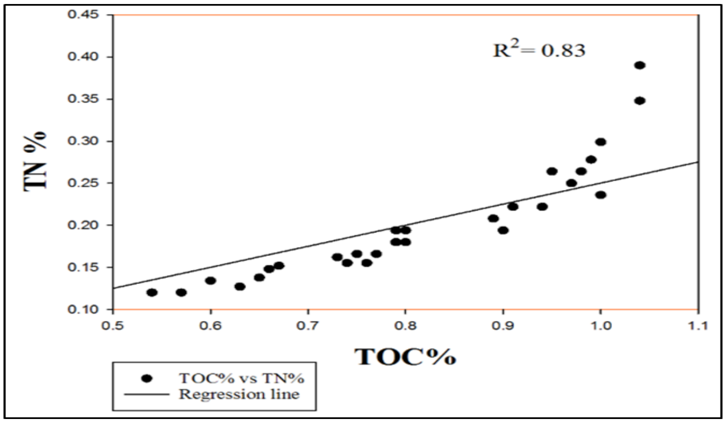
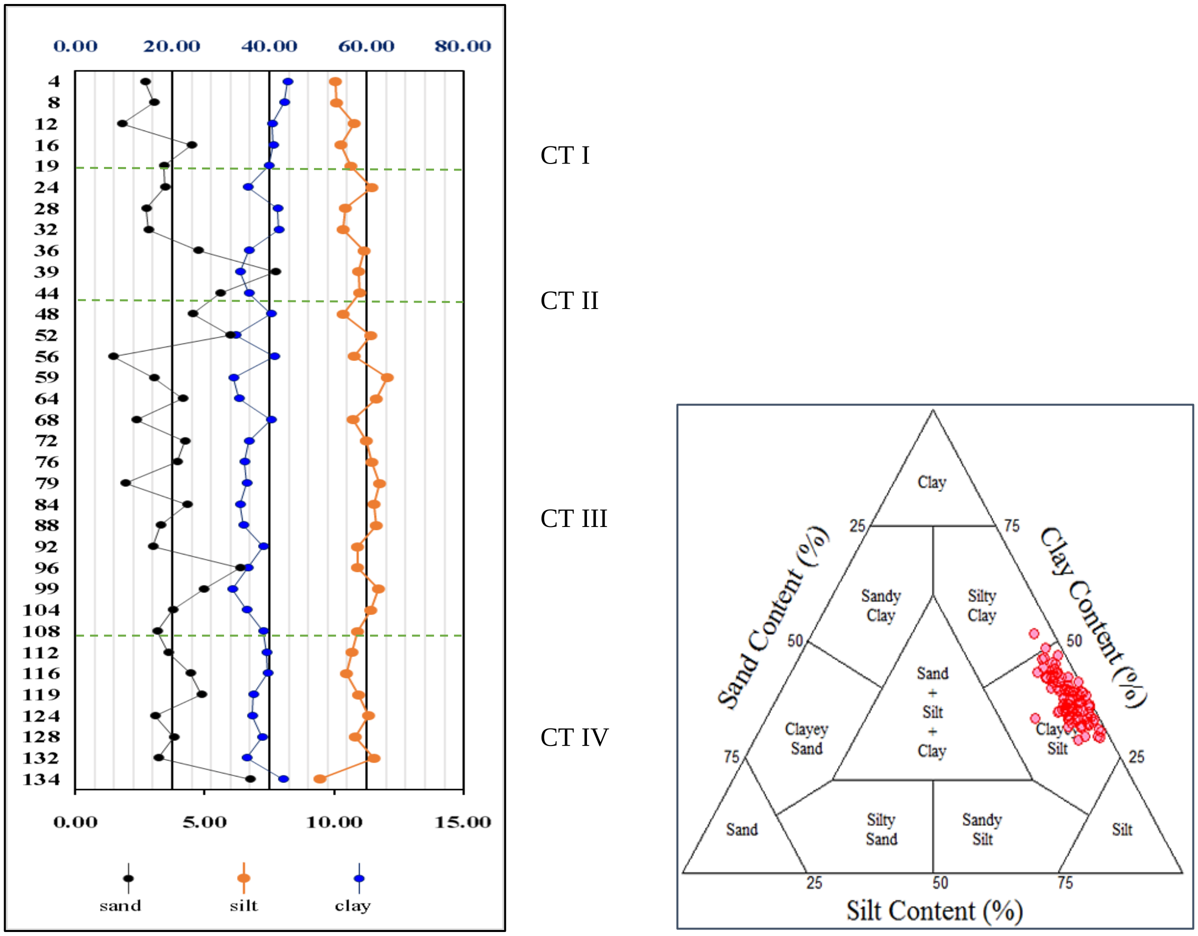


Fig 4.1. Vertical distribution of TOC, TN and atomic C/N atomic ratio in the core sediment of Chandratal Lake and correlation between TOC and TN.

The total organic carbon (TOC) percentage in the core sediment of Chandratal Lake are low with value ranging from 0.54- 1.04% that comparatively decreases from the upper sediment to down the core. Average value of TOC in CT I, II, III and IV are 0.97, 0.98, 0.70, 0.80 percentages respectively. TN values is highest in CT I (0.26%) followed by CT II and CT IV (0.19%). The lowest TN values was observed in CT III with 0.16 %. Fig 4.1. The total nitrogen percentage range from 0.39- 0.12% in the core sediment with 0.19% at the upper core and highest TN percentage at the depth of 12 cm. The total nitrogen distribution showed a strong correlation to that of the total organic content (R^2=0.83). The C/N atomic ratios is lays between 3.11- 5.78. The depth wise percentage of the various bulk parameters studied are presented in Appendix I.

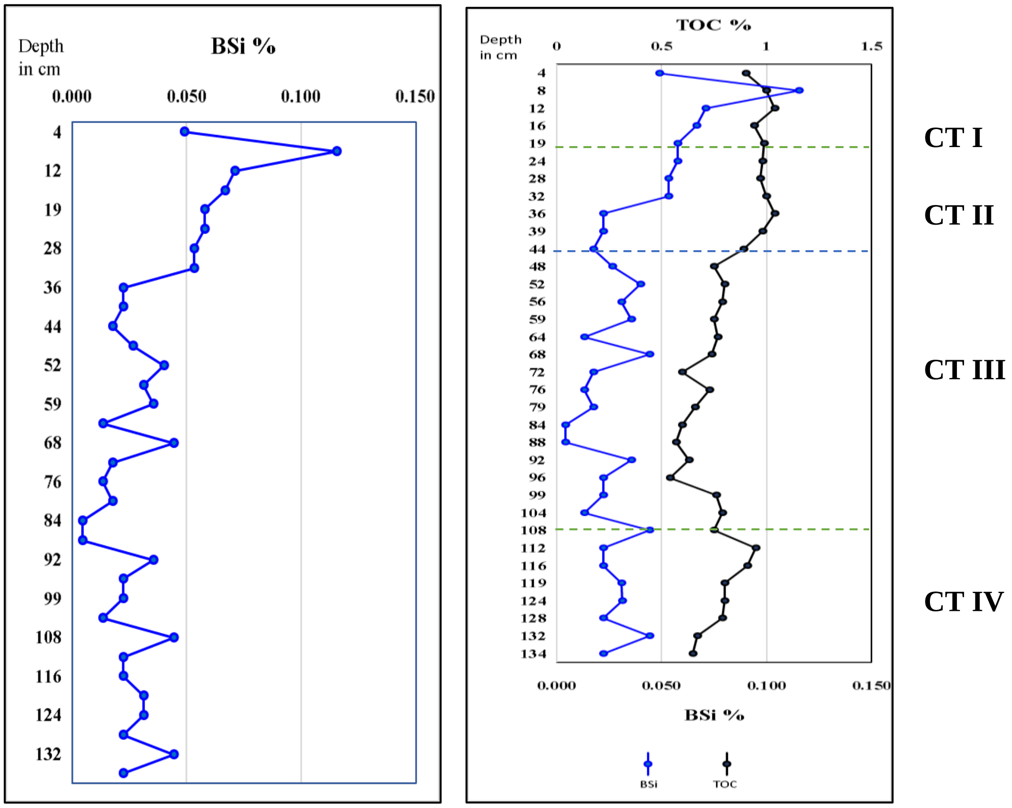


(A)

(B)

Fig. 4.2 (A) Variations in Grain Size Particles with depth in the study region (B) Ternary diagram showing Clay, Silt and Sand percentage in the Chandratal Core sediment.

Grain size is the fundamental property of sediment particles that affect the particle size entrainment, transportation and deposition (Simon et al., 2001) and therefore delivers information to the sediment origin, transport history and depositional conditions (Folk and Ward, 1957; Friedman, 1979; Bui et al., 1990). The composition of the grain size of Chandratal Lake sediment core is primarily silty clay (Fig. 4.2) with 3.91 % sand, 58.49 % silt and 37.59 % clay Fig. 4.2 (A). The overall composition of clay, silt and sand did not showed variations in all the CT zones. The Biogenic Silica (BSi) concentration in the core sediment is very low. BSi concentration ranges from 4.44 – 115.56 µg SiO_2 g^{-1} dry sediment (Fig. 4.3). Biogenic silica showed a constant fluctuation between the concentrations range of 0.004 – 0.04% in the up core until the depth of 32 cm. However, it showed a relative increase in its concentration (0.06-0.11 %) from ~32 cm toward the surface of the core sediment.



(A) (B)

Fig. 4.3. (A) Illustration of depth wise variations of BSi % in the core sediment of Chandratal Lake. (B) Variations of BSi with respect to TOC.

4.3 Discussion

Total Organic Carbon and Total Nitrogen content

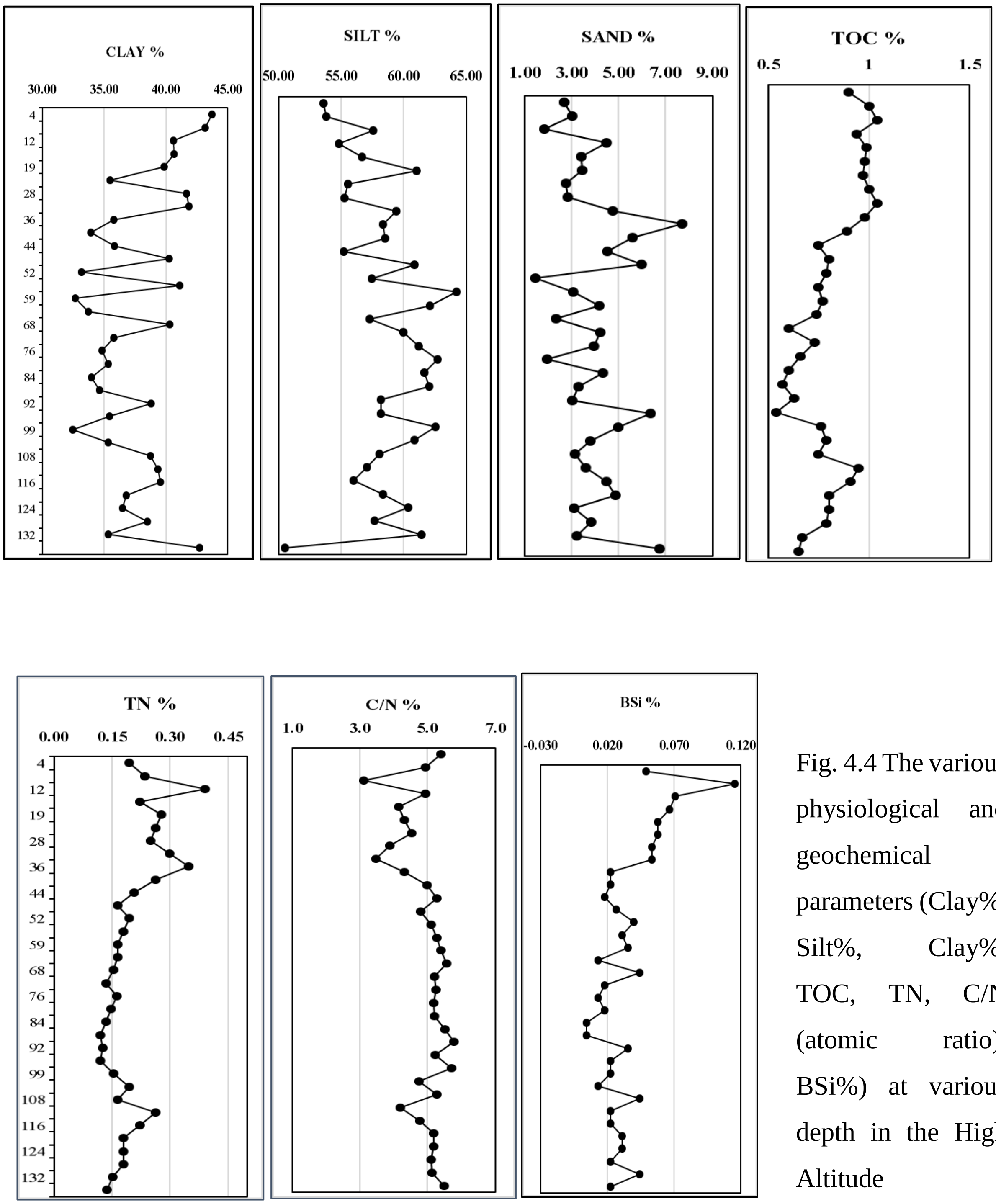


Fig. 4.4 The various physiological and geochemical parameters (Clay%, Silt%, Clay%, TOC, TN, C/N (atomic ratio), BSi%) at various depth in the High Altitude

The various physiological and biochemical parameters are presented in Fig.4.4.

TOC is a bulk representation of the fraction of OM that escaped remineralization during sedimentation and its value is dependent on the initial productivity of materials and the extent of degradation (Meyers, 1995). The low organic carbon content of the Chandratal lake sediment (1.04%- 0.54%) might be attributed to the low paleoproductivity of the lake (Emerson and Hedges, 1988; Meyers, 1994). Allochthonous OM from terrestrial inputs are comparatively less labile than in situ phytoplankton and algae OM source and this was reflected in C/N value. The low C/N ratio (3.11-5.78) suggested the lake primary productivity as the main source of organic matter in Chandratal Lake. Since, Chandratal Lake is a glacial fed with scarce vegetation around the lake area, this was quite apparent for the lower terrestrial inputs in this lake. In addition, lakes in high altitude situated above tree-line has lower value of C/N ratio (Gąsiorowski, 2013) compare to low lying lakes, which are dominated by terrestrial inputs.

The lower TOC (1.04%- 0.54) and TN (0.39- 0.12%) in Chandratal Lake suggested the autochthonous organic matter productivity and allochthonous inputs from the lake surrounding was quite limited. However post depositional processes might also alter the value of TOC/TN and exhibited lower value due to absorption of OM on fine clay particles.

It is quite substantial that different lakes in different environment exhibit different TOC and TN values because many aspects like transportation, deposition condition, post degradation, initial bulk productivity and preservation of the OM affect these values and all these dynamics rather act in an intricate manner (Meyers, 1993). Table 4.1 represented some of the value of TOC, TN and C/N ratio in different lake environments.

Bulk parameters indicator can only give information about the origin of OM but it cannot infer about the mechanisms and changes in the OM after its deposition in the sediment. Therefore, molecular level tools are required to study the depositional and degradation processes.

Table 4.1. Bulk parameters (TOC, TN, C/N) in different climate region lakes sediment.

	Trophic status	Altitude a m.s.l	Annual mean air Temp.(°C)	Precipitation mm yr^{-}	Core length	TOC	TN	C/N	Studied by
Lake Brienz (Switzerland)	Ultra-oligotrophic	564	-	-	65 cm	0.4 – 1%	0.02 - 0.14 %	5- 20	Bechtel and Schubert, 2009
Lake Lugano (Switzerland)	Eutrophic	271	11.9[a]	1709[a]	57 cm	1.1-3.2 %	0.10 - 0.35 %	8-11	-do-
Tso Mori Lake (India)	Oligotrophic	4500	0° to +30 °C (summer) and –40° to –10 °C (winter)	100-300	7.24 m	1.2-0.4 %	0.04 - 0.13 %	9 – 11	Menzel et al., 2015
Naukuchiyatal (India)	Eutrophic	1,320	Max. 29°C to a min. 1.8°C.	2,420	45 cm	3.3-6.0 %	0.33 - 0.63 %	9-12	Choudhary et al., 2009
Lake Biwa (Japan)	Oligotrophic-mesotrophic	84.4	14.3	1570	15 m	1% - 2%	0.02 - 0.23 %	4 – 10	Ishiwatari et al., 2009
Chandratal Lake (India)	Ultra-Oligotrophic	~4300	-5.8	1000	1.3 m	0.54 - 1.04 %	0.39 - 0.12 %	3- 6	Present study

[a] Barbieri and Polli (1992)

4.4 Grain Size Distribution

Grain size variations in lake is an indicator of change in lake processes and energy of sediment transportation. Grain-size variabilities in sediment with depth, generally increases in sand sizes, may reflect low-level lake stands related to periods of dryer and warmer climate, on the other hand, decreases in sand content may reflect periods of wet and cold climates (e.g., Alin and Cohen, 2003). In Chandratal Lake sediment core, finer grain size dominated the sediment with average value of Silt, Clay and Sand of 58.49%, 37.59% and 3.91% respectively. The dominance of finer grain size in the core sediment suggested the lower energies of the lake. The grain size followed a polymodal distribution in the core sediment; this could be due to variations in the sediment transportations, such as hydraulic transport representing different transport and depositional processes in arid region (Sun et al., 2002).

4.5 Biogenic Silica

BSi is a direct measurement of paleo-production of siliceous organism, and this proxy is a pure aquatic origin (Conley, 1988). The steady increased in BSi from the depth of around 32 cm to the top and the prompt upsurge of BSi from around 19 cm toward the surface, occurs more rapidly than any other depth in the current sediment core. This could be due to the Medieval Warm Period (1250- 950 year BP) prevailed from around the depth of 24cm, from the approximate estimation of the age of the sediment considering the sediment rate study by Rawat et al. (2015) as constant. The depth from surface to 19cm falls under the CT I, which was characterized by comparative warmer phase in the CT zone, therefore the increased in BSi concentration coincided with the relative warmer period in this depth. The relative increased in BSi in the CT II could be due to increase salinity in the region which reduced the freezing temperature of the lake thereby inducing sufficient incident light for the phytoplanktons photosynthesis (Wagner et al., 2004). The BSi concentration in the zone CT III and CT IV is quite low (Fig.4.3). From around the depth of 108 – 84 might fall under the younger dryas (12.9-11.5 k yr BP) cold period, according to the estimation made, which is marked by weakening of ISM and low production of carbon as in recorded in other study during this period (Rawat et al., 2015). The CT IV fall under the Post Glacial Maxima of

~17k to ~13k BP this could be the reason for the low bioproductivity and the very low TOC in this depth during this period. The overall BSi content in the core sediment, however, was low (4.44 – 115.56 µg SiO_2 g^{-1} dry sediment) suggesting that the general amelioration in climate was not in a greater extent. This was also quite consistent with the general cold climate condition of Chandratal Lake proposed by the pollen grains record in the present study.

4.6 Pearson Correlation

Pearson correlations were determined to find out the inter relations between different parameters.

Table. 4.2. Correlation between bulk sedimentary parameters in the study region (n=34)

	Clay	Silt	Sand	TOC	TN	C/N	BSi
Clay	1	**-.90****	-*.35*	*.38*	.30	-.167	**.57****
Silt		1	-.08	-*.36*	-.26	.147	**-.45****
Sand			1	-.10	-.12	.067	-*.35*
TOC				1	**.91****	**-.77****	**.57****
TN					1	**-.95****	**.47****
C/N						1	-.32
BSi							1

****. Correlation is significant at the 0.01 level.**

Grain size was found to be one of the controlling factor of TOC and BSi accumulation in the core sediment of Chandratal lake (95% significant level for TOC (written in italic letter and 99% significant level for BSi) Table 4.2. The study found a positive correlation of TOC with clay (<0.002 mm) and a significant negative correlation with silt (0.002-0.06 mm) which could be attributed to the relatively high adsorptive capacity of fine particles for organic matter (Cotano and Villate, 2006; Ramaswamy et al., 2008). Biogenic silica also exhibited highly significant correlation with finer grain size (clay; 0.002 mm), which reflected the influence of granulometry on its distribution. Strong correlation between BSi with TOC, TN and C/N indicated the major contribution of diatoms and phytoplanktons to the bulk organic matter Table 4.2. The interrelationship between TOC and BSi indicated the common source of organic matter and the similar behavior in the core sediment of Chandratal Lake. The negative relationship between BSi and sand percentage suggest that sand percentage as an effective proxy for the study of climate variation in the lake core of Chandratal. For example, low percentage of sand is accompanied by high BSi production which reflected the ameliorating climate in the region, as general decreases in sand content may reflect periods of wet climates (e.g., Alin and Cohen, 2003).

4.7 Summary

The low C/N ratio (3.11- 5.78) suggested that phytoplaktons and microalgae might be the main contributors of OM in the sediment of Chandratal Lake. A slight increase in C/N ratio, TOC and TN at the bottom of the sediment core may suggest a change in OM source or degradation processes. Grain size was found to be one of the factor controlling of TOC accumulation in the sediment, with TOC greater association with finer grain size (<0.002 mm). BSi was also strongly associated with clay fractions. The strong correlation between BSi and TOC reflected the common source of organic matter in sediment and suggested climate as one of the driving force for the productivity of the lake. The increase in BSi burial rate at the upper part of the core proposed the relative warmer climate in Chandratal Lake, however the amount of change is not in a larger extent.

Chapter 5

DISTRIBUTION AND DEGRADATION STATUS OF AMINO ACIDS IN THE CORE SEDIMENT OF CHANDRATAL LAKE

5.1 Introduction

Specific amino acid (AA) accumulate because of differentiation in production during degradation processes or due to resistance to further degradation (Lee and Cronin, 1984; Lee, 1988). Therefore, they are used as a reliable proxy to infer the state of organic matter and source identification in modern as well as paleo- sediments particularly from the marine environment (Lee, 1988; Cowie and Hedges, 1994; Wakeham et al., 1997; Dauwe et al., 1999; Keil et al., 2000). However, application of AA in terrestrial lake is influenced by large variations in AA having stronger imprint on AA composition and obscuring their interpretation (Mecker et al., 2004; Gaye et al., 2007; Unger et al., 2013; Menzel et al., 2015). Nevertheless, recent studies in various lakes under different climate regimes were successfully tested for the applicability of AA indices (Menzel et al., 2015).

This study is an attempt for using the AA indices tested by Menzel et al. (2015) in the paleolimnological studies in different climate systems. Chandratal Lake is located in the North Western part of Himalayas and no studies related to organic geochemistry have been done in this region to the best of my knowledge. Therefore, this study focused on the depth wise distribution pattern of AA and degradation state of the OM and deliberated the diagenetic processes in the sediment sample.

5.2 Results

Distribution Pattern of AA in the Core Sediment of Chandratal Lake

Twenty amino acids are identified from the core sediment extracts of the study area. The detected amino acids include Alanine (Ala), Arginine (Arg), Aspartic acid (Asp), Cysteine (Cys), Glutamic acid (Glu), Glycine (Gly), Histidine (His), Isoleucine (Ile), Leucine (Leu), Lysine (Lys), Methionine (Met), Phenylalanine (Phe), Proline (Pro), Serine (Ser), Threonine (Thr), Tryptophan (Try), Tyrosine (Tyr), Valine (Val), β-Alanine (βAla) and γ-Aminonbutyric acid (GABA). The depth wise mol % of different AA recovered are presented in Appendix II.

For simplicity, the relative abundance of individual amino acids of all the identified amino acids, expressed as mol% of total hydrolysable amino acids (THAA) are presented in the four palynological zones of the core Table 5.1.

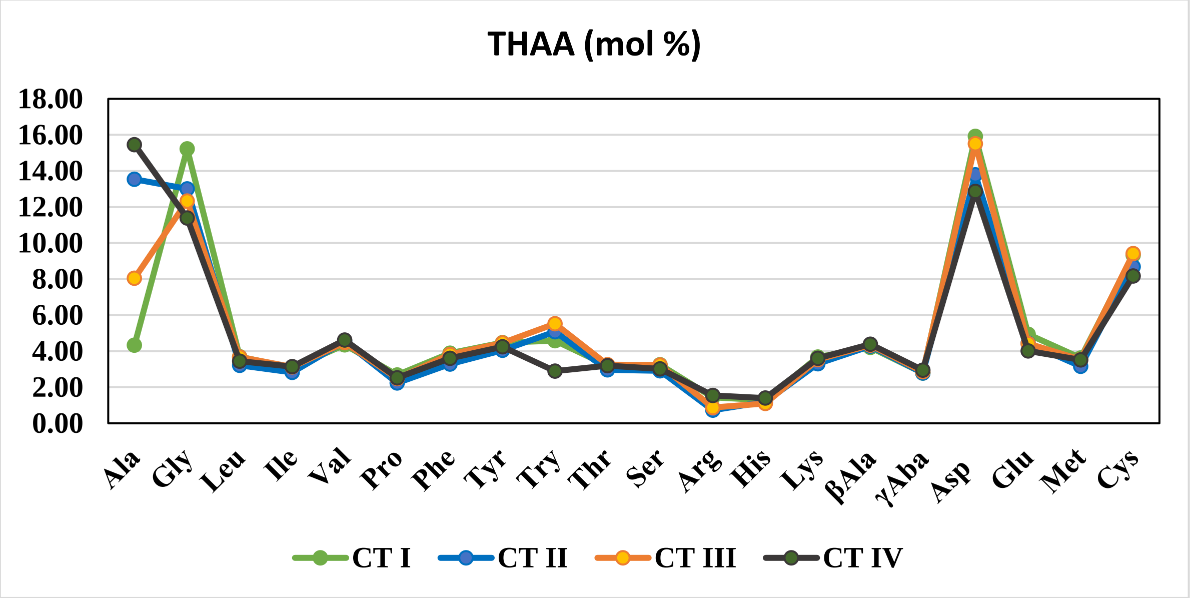


Fig. 5.1 Showing the trend of amino acid distribution (mol %) in different palynological zones of Chandratal Lake core sediment.

Table 5.1 Amino acid distribution in molar % in the sediment core of Chandratal Lake in the palynological zones.

		CT I	**CT II**	**CT III**	**CT IV**
	Aspartic acid	15.92	13.79	15.51	12.86
	Glutamic acid	4.94	4.43	4.42	4.01
Acidic		20.86	18.23	19.93	16.87
	Arginine	1.44	0.73	0.87	1.54
	Histidine	1.29	1.20	1.10	1.40
	Lysine	3.68	3.31	3.53	3.61
Basic		6.41	5.23	5.51	6.55
	Threonine	3.20	2.97	3.26	3.20
	Serine	3.26	2.91	3.23	3.02
Hydroxyl		6.46	5.87	6.49	6.21
	Alanine	4.33	13.54	8.05	15.46
	Glycine	15.23	13.01	12.34	11.39
	Leucine	3.70	3.21	3.67	3.45
	Isoleucine	3.08	2.82	3.12	3.14
	Valine	4.35	4.52	4.48	4.61
Neutral		30.69	37.11	31.66	38.06
	Proline	2.67	2.24	2.49	2.53
Aliphatic		33.36	39.35	34.15	40.59
	Phenylalanine	3.90	3.28	3.81	3.61
	Tyrosine	4.48	4.05	4.46	4.24
	Tryptophan	4.58	5.09	5.53	2.90
Aromatic		12.96	12.42	13.80	10.75
	βAlanine	4.21	4.27	4.33	4.39
	γAminonbutyric acid	2.79	2.78	2.85	2.94
non-protein		7.00	7.06	7.18	7.34
	Methionine	3.63	3.16	3.54	3.52
	Cystine	9.33	8.68	9.41	8.17
S-containing		12.95	11.84	12.95	11.69

Acidic Amino acids were the second most abundant AA in the core Sediment. The maximum concentration of Aspartic acids were found in CT I and II with mole % of 15.92 and 15.51 for Asp, and Glutamic acid maintain its consistency throughout the zone with 4.94, 4.43, 4.42 and 4.01 in CT I, CT II, CT III and CT IV respectively.

Among the basic amino acids, Lysine was the most abundant in all the zones. The maximum abundant was observed in CT I with mol % 3.68. Arginine shows highest mol % at CT IV with mol % 1.54. Histidine showed consistency in its concentration throughout the sediment core with mol % 1.29, 1.20, 1.10 and 1.40 in CT I, CT II, CT III and CT IV respectively.

The Hydroxyl AA, Threonine and Serine maintained their consistency in all the four zones. With values of Thr showing 3.20, 2.97, 3.26 and 3.20 respectively in CT I, II, III and IV respectively while Ser was showing mol % of 3.26, 2.91, 3.23 and 3.02 respectively.

The Neutral Aliphatic amino acids were the most abundant amino acids in the sediment core of Chandratal Lake. Alanine, Glycine, Leucine, Isoleucine, Valine and Proline were recorded in all the zones with maximum abundance of Glycine and Alanine (Glycine 15.23, 13.01, 12.34, 11.39 mole % and Alanine 4.33, 13.54, 8.05, 15.46 mole % in CT I, CT II, CT III and CT IV zone respectively). Maximum relative abundance of glycine was noted at CT I (15.51 mole %) and its abundance decreased down the core. Alanine showed highest relative abundance in CT II and IV (13.54 and 15.46 mole % respectively). The highest abundance of Leucine was recorded as 3.70 mole % (CT I) and 3.67 mole % (CT III) respectively. Isoleucine, Valine and Proline showed relative abundance of 2.82-3.14 mole %, 4.35- 4.61 mole % and 2.24- 2.67 mole % respectively and did not exhibit much variation in all the zones of the core.

Aromatic Amino acids Phe, Tyr and Try abundance in all the zones were low. The total Aromatic AA maintained a relative uniformity in all the four zones. Phe showed mol% 3.90, 3.38, 3.81 and 3.61, Tyr exhibited 4.48, 4.05, 4.46 and 4.24, Try displayed mol % values of 4.58, 5.09, 5.53 and 2.90 in the CT I, CT II, CT III and CT IV zone respectively.

β-Alanine and γ-Aminobutyric acid showed mol % of 4.21, 4.27, 4.33 , 4.39 and 2.79, 2.78, 2.85, 2.94 correspondingly in CT I, CT II, CT III and CT IV respectively.

The Sulphur containing AA are relatively abundant in the core sediment. The Cysteine showed highest abundance at CT III (9.41 mol %) followed by CT I (9.33 mol %) lowest concentration was found in deeper core i.e., CT IV (8.17 mol %). Methionine showed maximum mole % of 3.63 at CT I. Its concentration does not shows much variation with depth.

Table 5.2 Average TOC, C/N, AA, AA-C AND AA-N values in the zones of Chandratal Lake core sediment.

	TOC %	**TOC/TN (ATOMIC)**	**AMINO ACID CONTENT µg/g**	**AA-C%**	**AA-N%**
CT I	1.0	4.5	751.7	34.96	42.45
CT II	1.0	4.3	809.0	37.46	43.23
CT III	0.7	5.3	735.0	32.99	67.86
CT IV	0.8	5.0	814.3	19.09	62.78

The total AA content in all the four zones of Chandratal Sediment core are given in Table 5.2. In CT I the average AA is 751 µg/g, CT II 809 µg/g, CT III 735 µg/g and CT IV with 814µg/g. The average concentration of amino acid did not change within the four zones. The AA-C% and AA-N% are the AA bound Carbon and AA bound Nitrogen to TOC and TN % (wt/wt %) respectively. AA-C% and AA-N% values showed varying percentage in the depth. In CT I and CT II the AA-C and AA-N values were quite comparable with values 34.96, 37.46 and 42.45 and 43.23 respectively. However, at CT III and CT IV the relative values between AA-C and AA-N are wide variance with AA-C and AA-N values of 32.99, 19.09 and 67.86, 62.78 respectively. The change in relative abundance of AA-C to AA-N may attributed to the change in source in OM in the lake sediment (Menzel et al., 2015).

5.3 Discussion

5.3.1 Distribution pattern of AA in the sediment core

The distribution of amino acids in all the four zones of the sediment core of Chandratal Lake were showing similar in AA composition but slight differ in their abundance Fig. 5.1. This might be attributed to the heterogeneous source materials and/ or diversity in degradation processes in the core sediment of the Chandratal Lake. Abundance of Glycine in all the zones could be due to the fact that it is a short chain AA having minor nutrient value and simplicity in its synthesis compare to other AAs during heterotrophic metabolism (Fernandes et al., 2014). Glycine, serine and threonine are components of cell walls of diatoms (Hecky et al.,1973) and their association with cell walls makes them less decomposability compare to other AA (Sigleo and Shultz, 1993) and hence their enrichment in degraded OM (Dauwe and Middelburg, 1998; Keil et al., 2000). Glycine and serine are also a byproduct of photorespiration of growing algae (Ogren and Chollet, 1982). Amino acids such as glutamic acid, aspartic, isoleucine, valine, tyrosine and phenylalanine are generally enriched in the cell plasma of diatoms (Hecky et al., 1973; Dauwe and Middelburg, 1998). The elevation of glycine and alanine in sediment might be subjected to degraded state of OM (Dauwe, 1999). The relative elevation of glycine and alanine in CT II and CT IV compare to CT I and CT III might be due to the presence of more degraded OM in these zones. Aspartic acid are favorably enriched during anaerobic degradation (Cowie et al., 1995). The relative abundance of aspartic acid, serine, glycine, histidine, and proline suggested the contributions of both heterotrophic and microorganism (Dauwe and Middelburg, 1998). Valine was relatively abundant in the core sediment, which might be due to it being a significance component in aquatic organisms (Dauwe and Middleburg, 1998). Other amino acids such as aspartic acid, lysine, glutamic acid, isoleucine, tyrosine are known to be occurred in significant amounts in the cells of aquatic organisms (Dauwe and Middleburg, 1998).

5.3.2 Degradation state of Organic Matter in Sediment of Chandratal Lake

The production and degradation processes of OM in sediment are a fundamental part of lake ecosystem dynamics (Cowie and Hedges, 1994). Sedimentary OM derived from primary production is oxidised to CO_2 and a substantial fractions of them ultimately are preserved in the sediments (Cowie and Hedges, 1994). Amino acids on the other hand are more labile than the bulk sedimentary OM and undergo degradation more rapidly (Cowie and Hedges, 1992; 1994; Wakeham and Lee, 1993). AA are consumed preferentially during sedimentary OM dynamics in lake, resulting in the significant contributions of AA nitrogen to the total nitrogen in the sedimentary OM (Lee, 1988). The discrimination in utilisation of Amino acids by microbial activities affect the AA contents in sediments (Burdige and Martens, 1988). For instance, the more labile AA undergo degradation and the least labile remain in the system. To know the degradation state of OM in sediments, Menzel et al. (2015) have calculated a new lake index (LI) whose applicability were positively tested in different lake environments.

Table. 5.3 The mean (mol%), Standard Deviation (mol%) and Factor Coefficient used in Lake Index (LI) calculation (n=34).

	Mean (mol%)	SD (mol%)	Fac. coeff.
Ala	10.00	11.90	-.287
Gly	12.68	3.90	.165
Leu	3.55	.84	.044
Ile	3.07	.80	.002
Thr	3.19	.86	-.003
Ser	3.13	.83	.014
Val	4.49	1.38	.074
Arg	1.07	.90	.118
His	1.21	.79	.087
Lys	3.53	.98	-.011
Asp	14.72	7.65	.218
Glu	4.41	.86	.216
Phe	3.69	1.07	-.002
Tyr	4.35	1.06	.030
Try	4.77	2.84	-.027
Pro	2.48	.81	-.018
β-Ala	4.32	1.29	.074
γ-Aba	2.85	.99	.052
Met	3.48	.98	-.006
Cys	9.01	1.99	.264

The Degradation Index (DI) (Dauwe and Middleburg, 1998;Dauwe et al., 1999) have proved to be not suitable to decipher degradation state in various terrestrial lake ecosystem (Menzel et al., 2015). The LI was calculated with the same calculation as the DI but based on factor loading of the second axis of the PCA (Menzel et al., 2015). The mean, standard deviations and factor coefficient used for the LI calculation are presented in Table 5.3.

The LI was calculated using the formula:

$$\mathrm{LI} = \sum_i \frac{var_i - AVG_{var_i}}{STD_{var_i}} \times fac.coef._i$$

Where $\mathrm{var_i}$ is the original mole percentage of each AA in the sample, $\mathrm{AVGvar_i}$ and $\mathrm{STDvar_i}$ are the mean and the standard deviation and $\mathrm{fac.coef._i}$ the factor coefficient of the second axis of the PCA of the individual amino acids in the data set (Menzel et al., 2015).

To infer the degradation state of sedimentary OM, the relationship between the Lake Index (LI) and the total hydrolysable amino acids (THAA %) was studied Fig. 5.2.

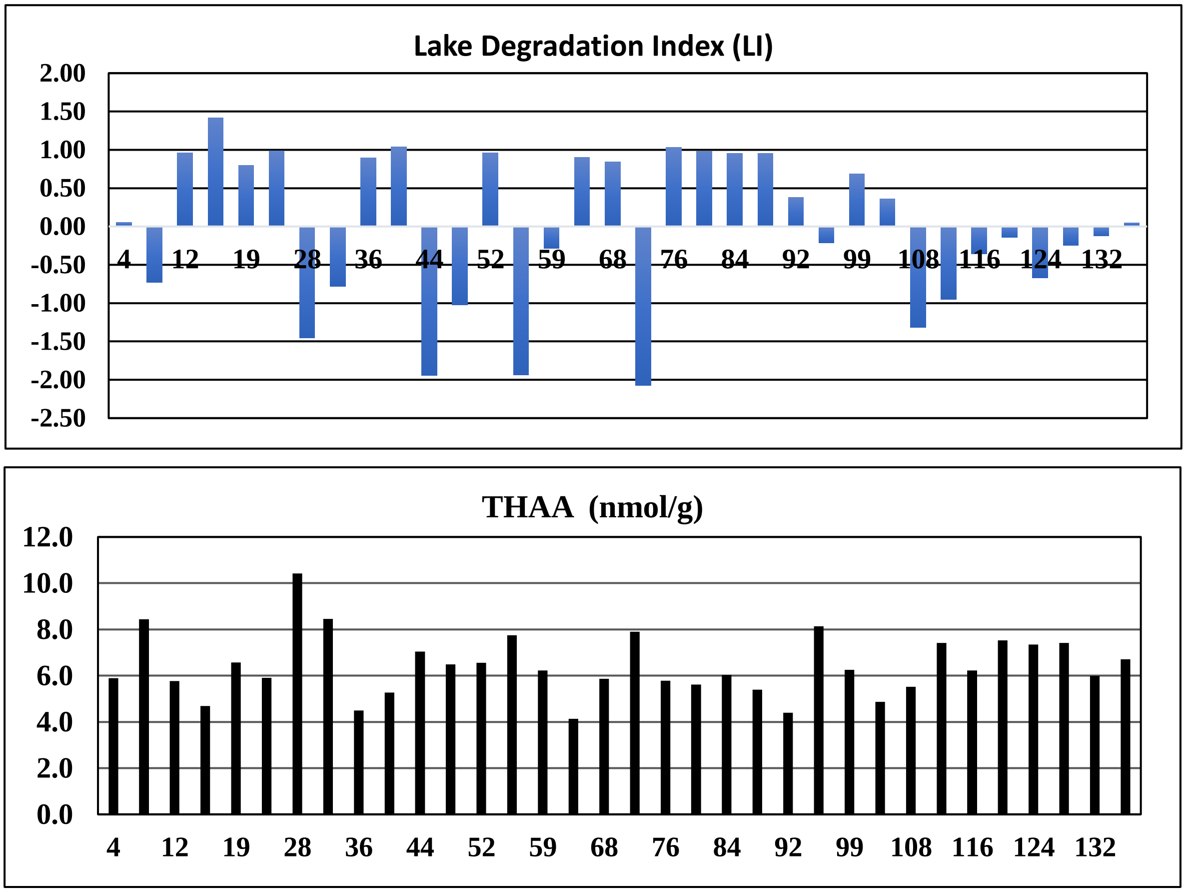


Fig. 5.2 Lake Degradation Index and Total Hydrolysable Amino Acids in the study area.

Previous studies of amino acids in sediments (Henrichs et al., 1984; Cowie and Hedges, 1992; Sugai and Henrichs, 1992; Boski et al., 1998; Dauwe and Middelburg, 1998) have suggested that the relative contribution of individual amino acids to total hydrolysable amino acids (THAA) changes during OM mineralisation. The LI values of -1 to -3 indicates for relatively fresh samples such as plankton and aquatic sediment trap whereas LI values of highly degraded samples shows 8-12 has been reported in previous lake studies (Menzel et al., 2015). In the present study, LI showed values between -2.07 to 1.42, with more negative value in the bottommost part of the core sediment indicating the presence of incomplete degraded OM. Overall the core sediment was a combination of both degraded and partial degraded OM, which is quite superficial for the climate condition prevailing there.

In addition, the Amino acid Nitrogen (AA-N) contribution to total nitrogen (TN) is also considered as a proxy for deciphering the state of OM degradation (after Menzel et al., 2015). Amino acid carbon contribution to total organic carbon shows high potential in deciphering the organic matter sources. As there value is highly depended on the percentage of terrestrial OM and aquatic OM (Menzel et al., 2015). AA-N In lakes are used as degradation proxy of OM with fresh organic matter dominantly shows AA-N values of ≥50% and decreases with advancing degradation (Menzel et al., 2015). The AA-N values in the Chandratal were ranging between 22.70 – 114.85% Fig. 5.3. The fluctuations in the THAA-N in the sediment might be due to the selective removal of amino acids relative to the other organic nitrogen.

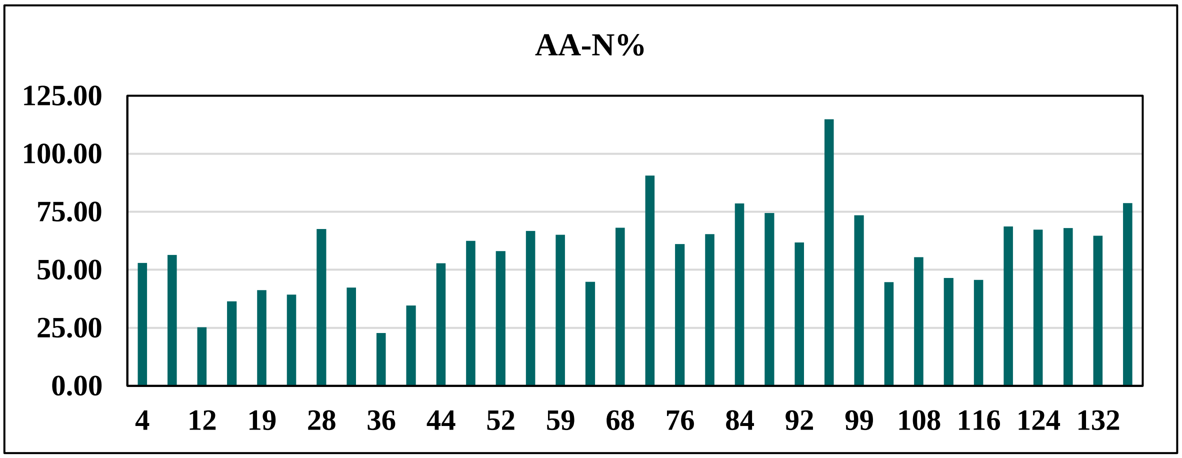


Fig. 5.3 AA-N distribution in the core sediment of Chandratal Lake.

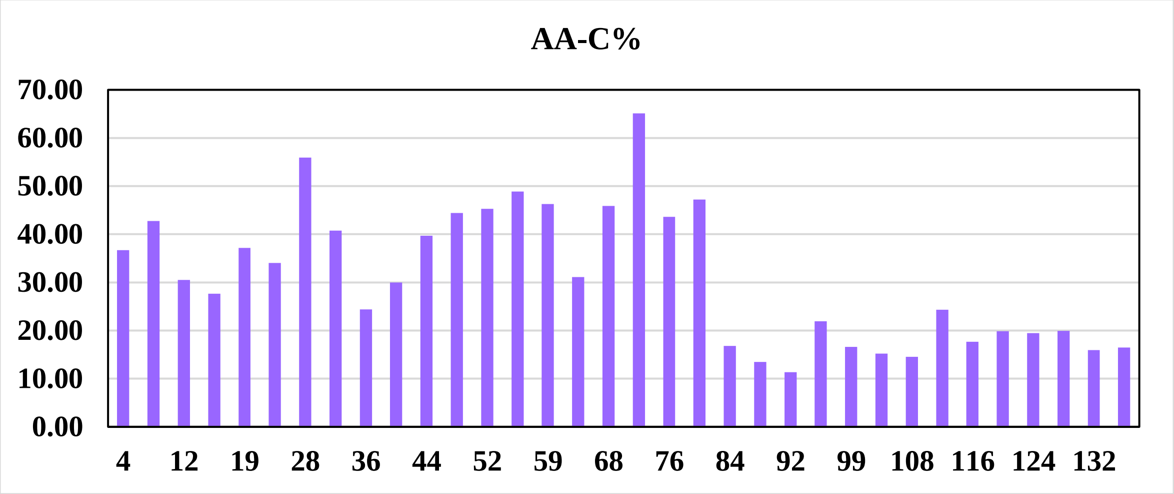


Fig. 5.4 AA-C distribution in the sediment core of Chandratal Lake.

Low AA-C are indicator of terrestrial vascular plant that consists of high lignin than aquatic OM (Verma and Subramanian, 2002). Therefore, AA-C is a useful proxy for identifying the source of OM, with ≥30% in aquatic and values of ≤15 % indicating terrestrial inputs (Menzel, 2015). The value of AA-C in Chandratal Lake core ranged between 11.34 – 65.13% suggesting the inputs of both aquatic and terrestrial OM Fig.5.4. According to the AA-C values observed the aquatic OM is dominant in the upper core while at the deeper core, it is dominated by terrestrial inputs OM. However, this observation might be due to the selective removal of amino acids relative to TOC and hence decreased in AA-C% (Cowie and Hedges, 1992). The fluctuation in the AA-C and AA-N in the sediment core may suggest the partial degradation of OM in the sediments (Alkhatib et al., 2012a).

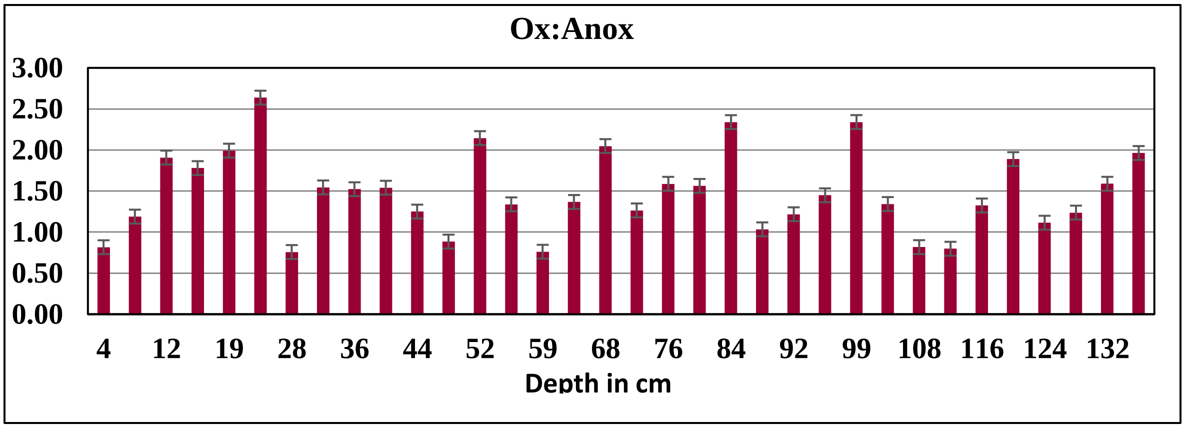


Fig. 5.5 Ratio of oxic and anoxic at different depth of Chandratal Lake.

The redox index (Menzel et al., 2013) is a ratio of AA assemblages' forms in different redox conditions. Monomeric AA assemblage of OM are potentially affected by different in degradation processes, for instance, Asp, Glu, β-Ala, γ-Aba and Lys are relatively enriched in aerobic degradation whereas Ser, Met, Ile, Leu, Tyr and Phe are enriched in anaerobic degradation (Cowie et al., 1995, Menzel et al., 2013). The oxic and anoxic sequences show values of ≥1.5 and ≤1 respectively (Menzel et al., 2015). The Redox Index in the core of Chandratal (Fig.5.5) showed values between 0.76- 2.64 at different depth. This suggested that the sediments were deposited under both aerobic and aerobic phases. The oxic:anoxic followed a polymodal sequences in its distribution.

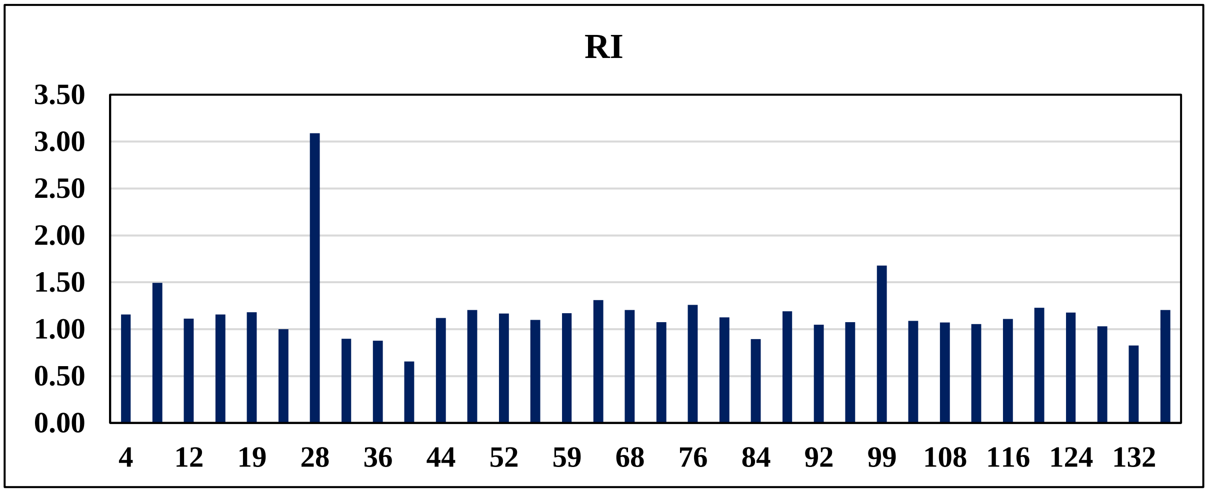
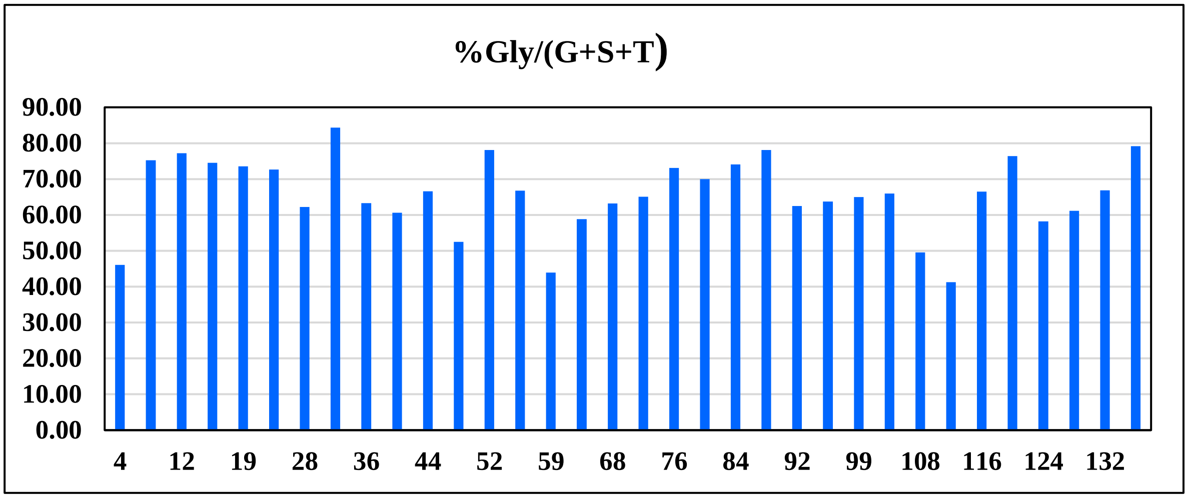


Fig. 5.6 Reactivity index at various depth of the Chandratal Lake core.

The Reactivity Index (RI) (Jennerjahn and Ittekkot, 1997) value indicate the reactivity of sedimentary OM. It is a ratio between most labile aromatic AA monomers to the non-protein AA monomers (Menzel et al., 2015). The more the aromatic AA monomers presence the higher the RI and hence, higher the freshness of OM. RI (Jennerjahn and Ittekkot, 1997) was calculated using the formula:

$$RI = \frac{Tyr + Phe}{\beta - Ala + \ \gamma - Aba}$$

The value of RI in Chandratal lake sediment core ranges from 0.66- 3.09 with maximum values fall in the range of 1.03-1.116 suggesting the overall least reactivity of the OM in the sediment Fig.5.6.



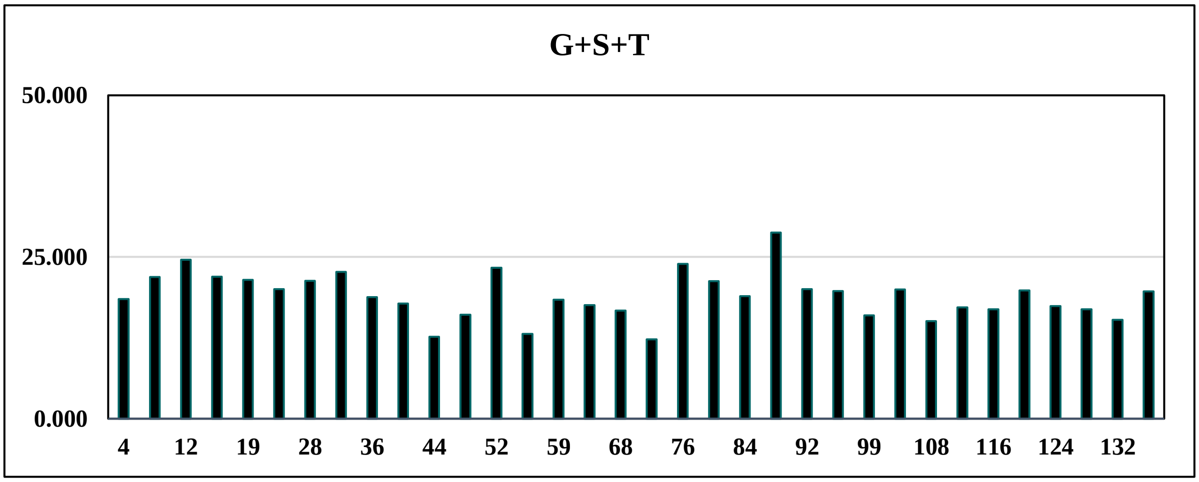
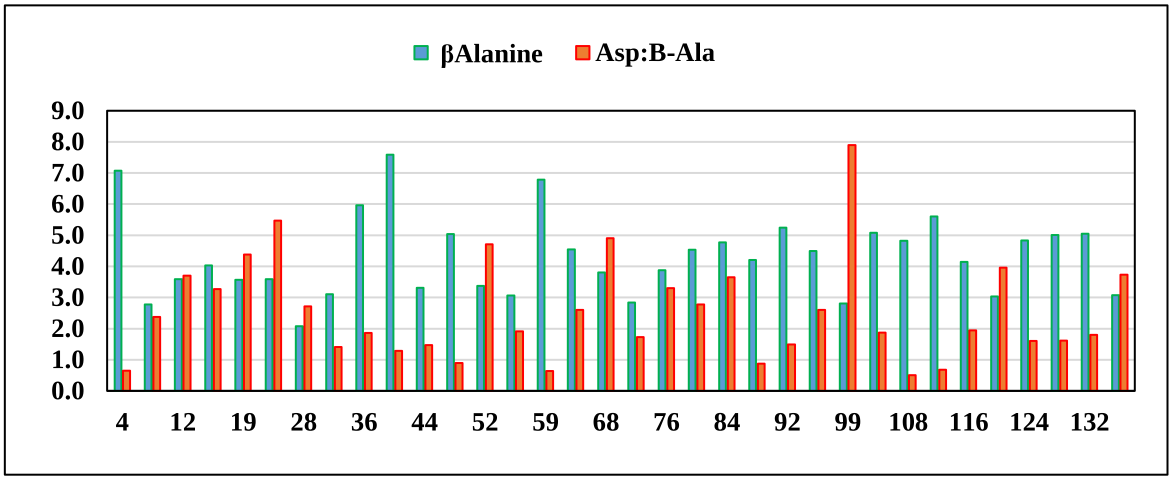


Fig. 5.7 Percentage Gly/(Gly+Ser+Thr) and (Gly+Ser+ Thr) distribution in the core sediment of Chandratal Lake.

Gly, Ser and Thr are enriched in OM with high contribution from siliceous OM (Hecky et al., 1973; King, 1977). Percentage of Glycine to the sum of AA monomers, Gly, Ser and Thr may infer about the relative contributions of the siliceous OM to the degraded sediment (Lomstein et al., 2008). High contribution from siliceous OM shows Gly+Ser+Thr of >27mol% (Menzel et al., 2015), however strong contribution from microbial originated or degradation related enrichment (Keil et al., 2000) of Gly may misinterpret with the result.

The (G+S+T) in the Chandratal Lake sediment showed ca <25 mol % showing low value of these AA monomers which might be attributed to the low contribution of siliceous OM to the sedimentary OM. Most of the %Gly/(G+S+T) showed above 60%, except at some few depth and this was consistent with the relative high abundance of β-Ala in the sedimentary OM (Fig.5.7). The relative high percentage of Gly/G+S+T along with the abundance of β-Ala may indicate the relative enrichment of Gly due to enhance microbial (Menzel et al., 2015) and may imply the minor contribution of siliceous OM in the core sediment of the Chandratal Lake.



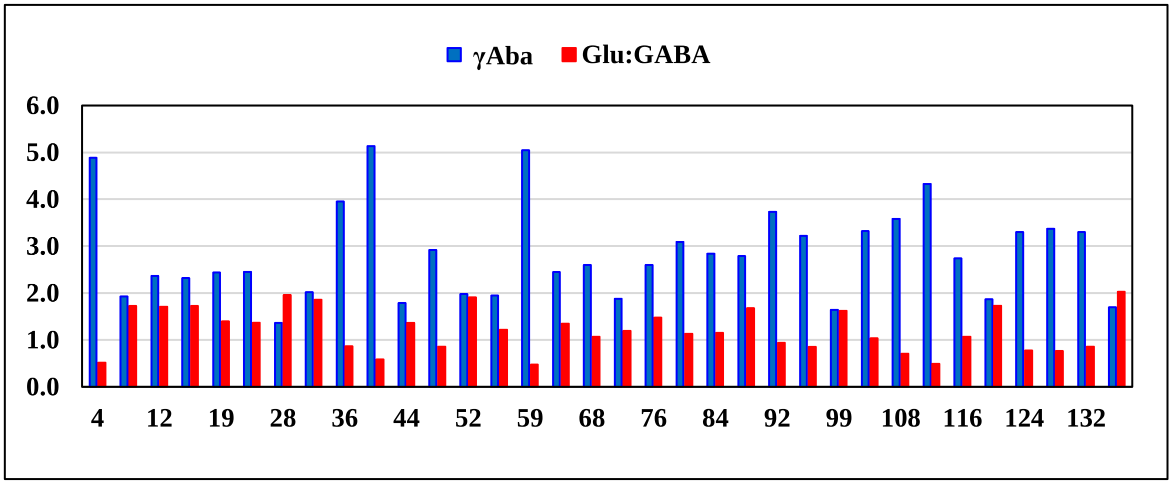


Fig. 5.8 Distribution of β-Ala and GABA AA with the Asp:βAla and the Glu:GABA.

The extent of degradation of OM in sedimentary setting determines the relative distribution of proteins AA such as Asp, Glu and their decarboxylation products β-Ala and GABA. β-Ala and GABA increases with progressing degradation and age of sediment and this carboxylation reaction is a microbial oriented process (Wang and Lee, 1993). Ratios of Asp/β-Ala and Glu/GABA are used as indicators to determine the extent of microbial reworking of OM in the sediments. Increasing mol % of β-Ala and GABA with decreasing Asp/β-Ala and Glu/GABA indicates the presence of degraded OM in the sediments and vice-versa. The ratios of Asp/β-Ala and Glu/GABA in Chandratal Lake range between 0.50- 7.90 and 0.48 – 2.01 respectively. The dominance of the β-Ala and GABA than Asp/β-Ala and Glu/GABA in the bottom suggested the more degraded sedimentary in the bottom of the core compare to the upper core (Fig. 5.8). However, the degree of microbial degradation varied throughout the core and might suggest the varying degradation of Asp and Glu to different extent along the core sediment.

5.3.3 Pearson Correlation

To find out the relationship among the geochemical variables, Pearson correlation was carried out. The Pearson correlation table is presented in Table 5.4.

Accumulation of THAA in the sediment is independent of the grain size particle. Contribution of biogenic silica to sedimentary amino acid was either absent or were demineralized at faster rate. The THAA-N showed strong negative correlation with the TOC and TN supporting it as an indicator of degradation state of OM in sediment (Menzel et al., 2015). The strong positive correlation between degradation proxy, THAA-N and source indicator, C:N suggested the labile inputs of OM in the sediments. Glu/GABA and Asp/β-Ala showed a high positive correlation suggesting their synthesis and by products from the same diagenetic processes and the abundance of microbial derived OM. The high positive correlation between Ox:Anox with Asp/β-Ala, Glu/GABA, Gly/(G+S+T) indicated the increased in degradation in oxic environment in the Chandratal Lake and also suggested the enhance microbial degradation of OM under oxic conditions. Gly/(G+S+T) and THAA showed a high negative correlation with the Lake Degradation Index (LI) suggesting the decreased in AA contents with advancing degradation and the relative contribution of individual AA to the total hydrolysable amino acid contents during degradation process. LI showed strong negative correlation with microbial degradation index Asp:β-Ala and (Gly+Ser+Thr). Bsi did not show any correlation with THAA.

Table. 5.4 The Pearson Correlation of the various biogeochemical and physiological parameters (n=34).

	Clay	Silt	Sand	TOC	TN	CN	BSi	THAA	THAAC	THAAN	β-Ala	Asp:BAla	GAba	Glu: GABA	G+S+T	Gly: GST	RI	LI	ox:anox
clay	1																		
Silt	**-.90****	1																	
Sand	*-.35*	-0.08	1																
TOC	*.38*	*-.36*	-0.10	1															
TN	0.30	-0.26	-0.12	**.91****	1														
CN	-0.17	0.15	0.07	**-.77****	**-.95****	1													
BSi	**.57****	**-.45****	*-.35*	**.57****	**.47****	-0.32	1												
THAA	0.27	-0.27	-0.05	0.08	0.02	-0.04	0.25	1											
THAAC	0.15	-0.05	-0.24	0.19	0.13	-0.12	0.25	*.41*	1										
THAAN	-0.16	0.11	0.14	**-.82****	**-.80****	**.68****	-0.33	**.47****	0.03	1									
βAla	-0.22	0.18	0.12	-0.01	-0.001	-0.005	-0.26	**-.49****	-0.28	-0.23	1								
Asp:BAla	-0.19	0.14	0.14	0.03	0.03	0.02	0.13	0.12	0.005	0.06	**-.54****	1							
GAba	-0.17	0.18	0.02	0.007	0.02	-0.04	-0.18	-.40*	-0.25	-0.19	**.97****	**-.56****	1						
Glu:GABA	0.17	-0.21	0.06	0.12	0.14	-0.11	0.28	0.26	0.17	-0.005	**-.83****	**.55****	**-.86****	1					
G+S+T	0.04	0.003	-0.10	0.12	0.23	-0.25	0.23	-0.06	-0.1	-0.17	-0.12	0.16	-0.09	**.50****	1				
Gly:GST	0.03	-0.08	0.1	0.02	0.13	-0.19	0.18	0.07	-0.02	-0.02	**-.63****	**.49****	**-.68****	**.82****	**.53****	1			
RI	0.23	-0.16	-0.19	0.13	0.004	0.09	0.22	**.58****	0.32	0.18	**-.49****	0.22	**-.45****	*.43*	0.15	-0.03	1		
LI	-0.33	0.28	0.14	0.02	0.10	-0.09	-0.04	**-.54****	-0.32	-0.30	0.24	**.47****	0.17	0.14	**.59****	0.33	-0.23	1	
ox:anox	-0.25	0.16	0.24	0.02	0.10	-0.13	0.05	-0.11	-0.12	-0.07	*-.36*	**.86****	*-.41*	**.45****	0.18	**.64****	-0.21	**.59****	1

** Correlation is significant at the 0.01 level.

5.3.4 Principal component analysis

Principal component analysis (PCA) of the geochemical parameters were carried out, using SPSS statistics 21, to identify and interpret the primary variables governing the major biogeochemical processes in the lake.

The PCA generated four components as shown in the table below (Table 5.5). The first component showed the highest total variance of 26.40%, the second, third and fourth components showed 20.94%, 18.29% and 7.52% respectively.

Table 5.5 Results of Principal Component Analysis

	Component			
	1	2	3	4
Clay	**.413**	-.440	-.517	-.535
Silt	-.385	.356	.424	**.640**
Sand	-.118	.246	.278	-.154
TOC	**.477**	-.795	.084	.182
TN	**.475**	-.786	.227	.213
CN	-.411	**.697**	-.273	-.266
BSi	**.581**	-.438	-.175	-.132
THAA	**.410**	.172	-.647	.221
THAAC	.296	-.064	-.430	**.517**
THAAN	-.213	**.781**	-.433	-.089
β-Ala	-.801	-.448	.248	-.074
Asp:BAla	**.567**	.455	.403	.174
GABA	-.785	-.485	.165	-.040
Glu:GABA	**.867**	.343	.084	-.103
G+S+T	.413	-.031	.409	-.240
Gly:G+S+T	**.711**	.331	.378	-.204
RI	**.446**	.158	-.496	.225
LI	.070	.054	**.868**	-.133
Ox:anox	.462	.354	**.654**	.043
% of Variance	26.40	20.94	18.29	7.52
Cumulative %	26.40	47.346	65.63	73.15

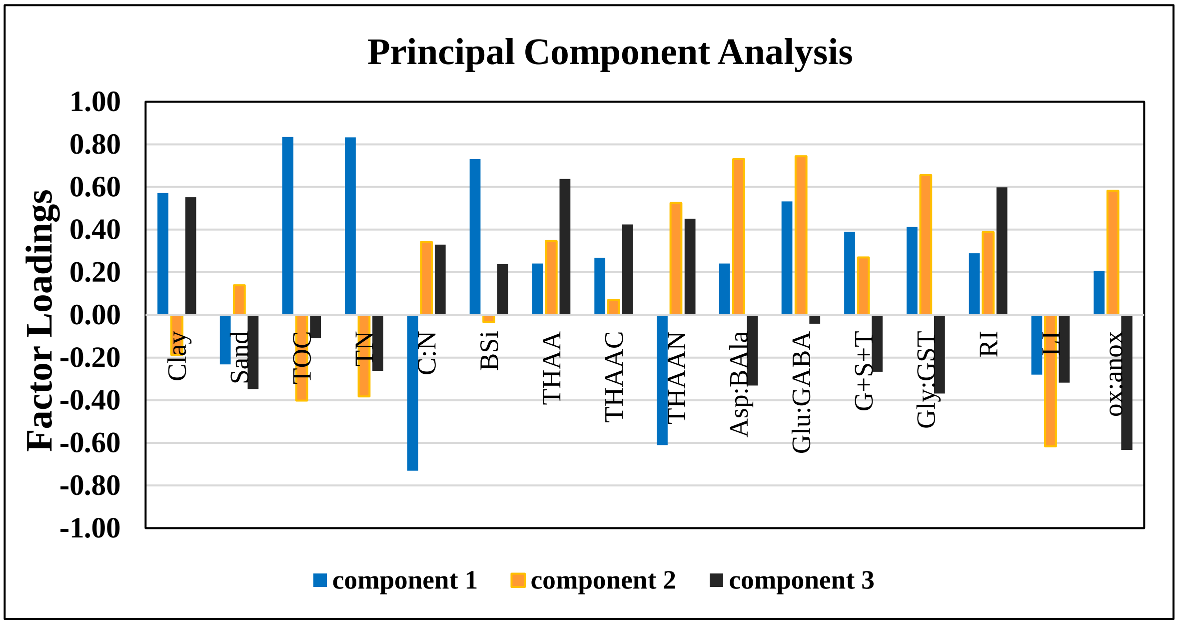


Fig. 5.9 Illustration of the first, second and third component of PCA.

The representation of the first three components is represented in Fig. 5.9. The component 1 explained 26.40% of the total variance and it includes strong positive loading of clay, TOC, TN, BSi, Asp:βAla, Glu-GABA, Gly/(G+S+T) and RI. This indicate the role of grain size as the controlling factor of the organic geochemical variables such as TOC and BSi and its role in the microbial oriented diagenetic processes. The second component of PCA defined 20.94% of the total variance. Strong positive loading of source indicator TN and degradation state proxy THAA-N, indicate the source dependence of the state of OM freshness. The third component of PCA explaining 18.29% of the total variance showed significant positive loading for LI and ox:anox indicating the rate of degradation process under different redox potential. The fourth component of PCA showed 7.52 % of the total variance and exhibited positive loadings of silt and THAA-C indicating the organic matter inputs through denudation and erosional processes.

5.5 Summary

Based on the palynological zones of the study area the relative abundance of the AA followed the following order:

CT I Asp> Gly> Cys> Glu> Tyr> Try> Val> Ala> βAla> Phe> Lys> Leu> Met> Ser> Thr> Ile> GABA> Pro> Arg> His.

CT II Asp> Ala> Gly> Cys> Try> Val> Glu> β-Ala> Tyr> Lys> Phe> Leu> Met> Thr> Ser> Ile> GABA> Pro> His> Arg.

CT III Asp> Gly> Cys> Ala> Try> Val> Tyr> Glu> β-Ala> Phe> Leu> Met > Lys> Thr> Ser> Ile> GABA> Pro> His> Arg.

CT IV Ala> Asp> Gly> Cys> Val> βAla> Tyr> Phe, Lys> Met> Leu> Thr> Ile> Ser> GABA> Try> Phe> Arg> His> Arg.

Glutamic acid, aspartic acid, isoleucine, valine, tyrosine, and phenylalanine are enriched in diatom cell plasma and are easily subjected to degradation. Therefore, their abundance in sediments indicated freshly derived organic matter. The fluctuations in the mol % of glutamic acid and aspartic acid within the sediment core depth suggests the selective utilization of these amino acid by in-situ heterotrophic organisms. The composition of the amino acids and distribution pattern were same in the core sediments except for some AA monomers such as Ala, Gly, Asp Cys Tyr whose distribution were differ with depth which might be attributed to their selective utilization in sedimentary OM and/or differ in redox potential. However, the relative abundance of AA in different climatic phases indicated the unbiased degradation and synthesis of AA to climate variability in the Chandratal Lake core sediment.

From the RI, LI and ratios of protein and non-protein amino acids monomers, the core sediment of Chandratal is composed of a combination of both degraded and fresh OM.

In the present study of Chandratal core sediment, four significant components were identified using the statistic tool PCA. In the first component, the grain size distribution and the organic matter contents showed a close association suggesting the granulometry as the dominant factor in OM content in sediment. In addition, microbial activities were also intense along with it the close association of BSi and TOC indicating the climate driven productivity in the sediment. The second component showed the source dependent OM freshness in the sediment. The third component described the importance of redox potential condition in the degradation and preservation of OM. The fourth component ascribed the OM inputs in the Lake through denudation and erosional responses. The absence of correlation between BSi and AA suggested the independent of amino acids synthesis and degradation to the climate in the sediment core.

SUMMARY

High Altitude Lakes have a unique ecosystem that are particularly sensitive to climates. The food chain is shorter and less complex compare to the low-lying lakes. Moreover, being far from direct influences of Human activities they are considered a pristine environment. They are therefore, valuable for archiving paleo-environment processes. The present study used pollen grain analysis, bulk parameter approach and molecular level tool and attempted to reconstruct the organic matter dynamics in the core sediment of High Altitude Chandratal Lake.

The pollen analysis could identified four important climate phases based on the vegetation implication, viz., CT I, CT II, CT III and CT IV. CT IV represent the deepest part of the core and was represented by the presence of low AP/NAP ratio and the pollen recovered from this was relatively low and represented the cold and arid climate in this phase. CT III was characterized by increase in AP/NAP, presence of fair amount of fern than the preceding one and the condition not suitable for steppe and herbaceous elements, represented the occurrence of moist climate in this phase. CT II zone the overall pollen frequency decreases along with decrease in AP/NAP representing the reoccurrence of cold and arid phase in this zone. CT I represent the most recent zones and was characterized by the presence of pteriodophytes spores and relative high of AP/NAP suggesting the improvement of the climate than the previous zone. However, the general change in climate in the Chandratal Lake sediment core occurred within the overall cold and arid climate regimes.

The bulk sedimentary organic matter in the core sediment of Chandratal Lake study revealed the phytoplanktons and micro algae might be the main contributors of OM in the sediment. The C/N ratios values showed 3.11-5.78, indicating the dominance of in-situ lake production. TOC and BSi concentration was strongly influenced by the grain size. As Chandratal Lake is devoid from direct human activities, the strong correlation between TOC contents of sedimentary OM and the biogenic silica study suggested the climate dependence productivity of the lake. The relative increased in sedimentary BSi concentration in the upper part of the

core from around the depth 28cm could be subjected to the warmer climate and coincided with the projected Medieval Warm Period.

Total hydrolysable amino acid (THAA) in the core sediment of Chandratal Lake had similar AA composition and distribution pattern except for some few AA like aspartic acid, glutamic acid, alanine, glycine and cysteine. The difference in distribution pattern of these AA monomers might be attributed to the selective degradation of AA and change in diagenetic processes. Asp, Glu, Ala, Gly, Val, Tyr, Phe are relatively abundance in cell plasma and easily subjected to degradation. Their relative abundance in the sedimentary THAA suggested the presence of fresh OM. The non- protein β-Ala and GABA were relatively abundant at the bottom core. The ratio of Asp/β-Ala and Glu/GABA indicated the overall active microbial activities in the bottommost part of the core relative to the upper sediment core. RI value (0.66- 3.09) showed the overall least reactivity and the slow rate of remineralization of OM in the sediment core. The LI value showed values between -2.07 to 1.42 indicating the presence of fresh and undegraded state OM. The bottommost core of the sediment had relatively more fresh OM with LI values of -0.12 to -1.32. The value of LI is highly associated with the oxic:anox indicating the more degradation rate with high oxic:anoxic. The absence of relationship between THAA and BSi suggested that THAA degradation was least dependent on climate change within the core sediment. The PCA study to delineate the major processes controlling the OM dynamic in the core sediment identified the granulometric controlled of the clay rich OM and microbial oriented diagenetic processes as the major process. The source dependence of OM degradation state as the second major process. The third process indicated the dependent of the degradation processes to the redox potential. The fourth process explained the denundational and erosional contributions of OM in the sediment.

APPENDIX I

	1 to 4	5 to 8	9 to 12	13 to 16	17 to 19	21 to 24	26 to 28	29 to 32	33 to 36	37 to 39	41 to 44	46 to 48	48 to 52	53 to 56	57 to 59	61 to 64	66 to 68
clay	43.74	43.15	40.60	40.68	39.88	35.51	41.68	41.89	35.81	33.94	35.87	40.25	33.16	41.09	32.69	33.72	40.33
silt	53.58	53.81	57.58	54.82	56.70	61.04	55.58	55.27	59.44	58.33	58.55	55.22	60.87	57.44	64.25	62.11	57.31
sand	2.69	3.03	1.83	4.50	3.43	3.46	2.75	2.84	4.75	7.73	5.59	4.53	5.97	1.46	3.06	4.17	2.35
toc	0.9	1	1.04	0.94	0.99	0.98	0.97	1	1.04	0.98	0.89	0.75	0.8	0.79	0.75	0.77	0.74
TN	0.19	0.24	0.39	0.22	0.28	0.26	0.25	0.30	0.35	0.26	0.21	0.17	0.19	0.18	0.17	0.17	0.16
C/N	5.4	4.9	3.1	4.9	4.2	4.3	4.5	3.9	3.5	4.3	5.0	5.3	4.8	5.1	5.3	5.4	5.6
Bsi	0.049	0.116	0.071	0.067	0.058	0.058	0.053	0.053	0.022	0.022	0.018	0.027	0.040	0.031	0.036	0.013	0.044

	69 to 72	73 to 76	77 to 79	81 to 84	86 to 88	89 to 92	93 to 96	97 to 99	101 to 104	106 to 108	109 to 112	113 to 116	117 to 119	121 to 124	126 to 128	129 to 132	133 to 134
clay	35.78	34.83	35.35	34.01	34.62	38.82	35.45	32.49	35.32	38.78	39.36	39.55	36.78	36.51	38.52	35.32	42.74
silt	59.98	61.22	62.72	61.68	62.08	58.16	58.19	62.53	60.88	58.07	57.04	55.98	58.35	60.39	57.66	61.46	50.52
sand	4.24	3.95	1.93	4.32	3.30	3.02	6.36	4.98	3.79	3.16	3.60	4.47	4.87	3.11	3.83	3.22	6.74
toc	0.6	0.73	0.66	0.6	0.57	0.63	0.54	0.76	0.79	0.75	0.95	0.91	0.8	0.8	0.79	0.67	0.65
TN	0.13	0.16	0.15	0.13	0.12	0.13	0.12	0.16	0.19	0.17	0.26	0.22	0.18	0.18	0.18	0.15	0.14
C/N	5.2	5.3	5.2	5.2	5.5	5.8	5.2	5.7	4.8	5.3	4.2	4.8	5.2	5.2	5.1	5.1	5.5
Bsi	0.018	0.013	0.018	0.004	0.004	0.036	0.022	0.022	0.013	0.044	0.022	0.022	0.031	0.031	0.022	0.044	0.022

APPENDIX II

	1 to 4	5 to 8	9 to 12	13 to 16	17 to 19	21 to 24	26 to 28	29 to 32	33 to 36	37 to 39	41 to 44	46 to 48	48 to 52	53 to 56	57 to 59	61 to 64	66 to 68
Ala	0.47	19.9	0.28	0.79	0.23	0.21	18.07	27.26	0.22	0.4	35.1	22.53	0.53	35.48	1.97	1.08	0.47
Gly	8.53	16.47	18.98	16.38	15.8	14.55	13.26	19.15	11.9	10.78	8.43	8.44	18.24	8.75	8.08	10.34	10.55
Leu	5.6	3.3	3.21	3.28	3.1	2.63	4.15	2.09	3.79	4.25	2.36	4.12	3.44	2.45	5.9	4.19	3.54
Ile	4.7	2.64	2.43	2.99	2.65	2.46	3.85	1.87	3.56	3	2.18	3.74	2.38	2.06	5.14	3.76	2.8
Thr	4.93	2.64	2.67	2.95	2.81	2.87	4.2	1.83	3.59	3.16	2.17	3.78	2.48	2.19	5.3	3.79	3.12
Ser	5.05	2.78	2.92	2.65	2.88	2.6	3.86	1.74	3.32	3.84	2.06	3.86	2.63	2.17	5.01	3.44	3.03
Val	7.25	3.05	3.7	4.01	3.72	3.77	2.31	3.26	6.05	8.56	3.18	5.21	3.28	3.17	6.79	4.67	3.91
Arg	2.12	0.37	0.66	3.31	0.72	1.1	0.27	0.32	0.9	1.42	0.34	1.26	0.48	0.27	0.36	2.24	1.92
His	0.47	1.57	1.15	1.16	2.08	0.24	0.53	2.3	0.99	2.54	0.57	0.44	1.83	0.55	1.2	1.38	1.43
Lys	6.01	3.07	2.82	3.4	3.12	2.77	4.79	2.13	4.05	3.35	2.78	4.16	2.36	2.3	5.87	4.08	3.08
Asp	6.86	9.84	19.84	19.68	23.36	29.31	8.43	6.54	16.56	14.62	7.3	6.76	23.74	8.75	6.44	17.69	27.93
Glu	3.62	4.75	5.77	5.7	4.86	4.8	3.8	5.36	4.87	4.31	3.47	3.58	5.37	3.38	3.44	4.71	3.97
Phe	6.58	3.22	3	3.42	3.25	2.63	4.93	2.16	3.73	3.61	2.62	4.5	2.75	2.55	6.91	4.07	3.4
Tyr	7.24	3.82	3.62	3.91	3.83	3.4	5.71	2.43	4.97	4.74	3.07	5.07	3.5	2.96	6.94	5.1	4.31
Try	0.7	6.12	7.79	2.28	6.02	4.31	4.86	6.59	3.8	3.34	7.64	0.13	7.18	7.02	0.74	3.72	3.16
Pro	4.74	1.97	1.93	2.48	2.26	1.7	3.58	1.48	2.6	2.26	1.83	2.93	1.54	1.6	4.63	2.78	2.18
βAla	7.07	2.78	3.59	4.03	3.57	3.58	2.08	3.11	5.96	7.59	3.31	5.04	3.37	3.06	6.79	4.55	3.81
γAba	4.88	1.93	2.36	2.32	2.44	2.45	1.36	2.02	3.95	5.13	1.79	2.92	1.98	1.95	5.05	2.45	2.6
Met	5.7	3.07	2.84	3.49	3.03	2.55	4.52	2.11	3.87	3.28	2.62	4.12	2.48	2.35	6.35	3.94	3.13
Cys	7.47	6.72	10.42	11.77	10.27	12.06	5.43	6.27	11.31	9.84	7.17	7.41	10.43	6.99	7.1	12.02	11.67

APPENDIX II (contd.)

	69 to 72	73 to 76	77 to 79	81 to 84	86 to 88	89 to 92	93 to 96	97 to 99	101 to 104	106 to 108	109 to 112	113 to 116	117 to 119	121 to 124	126 to 128	129 to 132	133 to 134
Ala	38.39	0	0.55	0.22	0.75	0	6.58	0.38	0	19.91	14.11	18.21	13.98	14.24	14.32	17.28	16.1
Gly	7.99	17.49	14.87	14.02	22.47	12.52	12.58	10.37	13.17	7.49	7.1	11.23	15.14	10.14	10.34	10.21	15.56
Leu	2.42	4.14	3.5	3.09	3.72	3.77	3.93	2.98	3.71	3.85	4.7	3.24	2.74	3.98	3.46	3.58	2.47
Ile	2.09	2.68	3.42	2.5	3.43	3.43	3.1	2.57	3.41	3.45	4.93	2.96	2.32	3.56	3.35	2.57	2.31
Thr	2.18	2.98	3.24	2.58	3.2	3.82	3.37	2.74	3.46	3.85	5.4	2.82	2.49	3.61	3.31	2.69	2.07
Ser	2.11	3.44	3.15	2.32	3.11	3.71	3.79	2.86	3.33	3.76	4.73	2.85	2.19	3.67	3.26	2.37	2.03
Val	3.02	4.13	4.78	5.08	4.47	5.58	4.54	2.91	5.06	5	5.95	4.19	3.31	5.24	5.23	5.32	3.05
Arg	0.24	0.99	2.34	1.12	0.64	0.32	0.15	1.33	0.15	0.18	2.1	2.1	0.56	0.45	3.53	1.11	0.94
His	1.7	1.59	1.22	0.65	3.36	0.13	0.69	0.92	0.27	0.26	0.36	1.1	1.81	0.85	0.84	2.36	2.45
Lys	2.27	2.92	3.86	3.06	4.03	3.82	3.54	3.15	3.96	4.02	5.62	3.59	2.65	4.41	3.59	2.78	2.61
Asp	7.33	19.12	18.8	26.06	5.5	11.67	17.45	33.12	14.18	3.61	5.64	12.05	17.98	11.54	12.06	13.59	17.17
Glu	3.21	5.47	4.99	4.66	6.67	5	3.93	3.79	4.9	3.64	3.02	4.18	4.6	3.65	3.67	4.04	4.91
Phe	2.24	3.41	4.06	3.27	3.9	4.33	3.87	3.42	4.05	4.28	5.04	3.5	2.65	4.51	4.05	3.02	2.5
Tyr	2.83	4.74	4.52	3.53	4.43	5.08	4.42	4.05	5.11	4.72	5.44	4.14	3.37	5.05	4.6	3.87	3.24
Try	6.94	5.08	2.15	4.07	8.82	10.78	6.18	3.17	10.1	9.27	0.16	2.28	6.04	2.12	2.08	3.18	4.4
Pro	1.48	2.12	2.69	1.88	2.56	2.84	2.63	2.36	2.82	2.75	3.95	2.57	1.8	3.2	2.68	1.82	1.66
βAla	2.84	3.88	4.53	4.77	4.21	5.25	4.49	2.81	5.08	4.82	5.6	4.15	3.04	4.83	5.01	5.05	3.08
γAba	1.88	2.6	3.1	2.84	2.79	3.74	3.23	1.64	3.32	3.59	4.33	2.74	1.86	3.3	3.37	3.3	1.7
Met	2.18	2.98	3.91	2.98	3.85	3.88	3.43	3.14	3.82	4.03	5.54	3.48	2.68	4.12	3.68	2.69	2.47
Cys	6.64	10.24	10.31	11.29	8.1	10.33	8.12	12.31	10.12	7.51	6.25	8.64	8.76	7.53	7.58	9.15	9.28

REFERENCES

Alin, S. R., & Cohen, A. S. (2003). Lake-level history of Lake Tanganyika, East Africa, for the past 2500 years based on ostracode-inferred water-depth reconstruction. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *199*(1), 31-49.

Alkhatib, M., Lehmann, M. F., & Del Giorgio, P. A. (2012). The nitrogen isotope effect of benthic remineralization-nitrification-denitrification coupling in an estuarine environment. *Biogeosciences*, *9*, 1633-1646.

Azam, M.F., Ramanathan, AL., Wagnon, P., Vincent, C., Linda, A., Berthier, E., Sharma, P., Mandal, A., Angchuk, T., Singh, V.B. and Pottakkal, J.G., 2016. Meteorological conditions, seasonal and annual mass balances of Chhota Shigri Glacier, western Himalaya, India. Annals of Glaciology, in press.

Bakke, J., Vasskog, K., Ramanathan, A. L., Mandal, A., Kumar, O., & Nesje, A. (2016). The Water Tower of India in a Long-term Perspective–A Way to Reconstruct Glaciers and Climate in Himachal Pradesh during the last 13,000 Years. *Journal of Climate Change*, *2*(1), 103-112.

Bernasconi, S. M., Barbieri, A., & Simona, M. (1997). Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. *Limnology and Oceanography*, *42*(8), 1755-1765.

Bhattacharyya, A., Sharma, J., Shah, S. K., & Chaudhary, V. (2007). Climatic changes during the last 1800 yrs BP from paradise lake, Sela Pass, Arunachal Pradesh, Northeast Himalaya. *Current Science*, 983-987.

Bhutiyani, M. R., Kale, V. S., & Pawar, N. J. (2010). Climate change and the precipitation variations in the northwestern Himalaya: 1866–2006. *International Journal of Climatology*, *30*(4), 535-548.

Bookhagen, B., Thiede, R. C., & Strecker, M. R. (2005). Late Quaternary intensified monsoon phases control landscape evolution in the northwest Himalaya. *Geology*, *33*(2), 149-152.

Boski, T., Pessoa, J., Pedro, P., Thorez, J., Dias, J. M. A., & Hall, I. R. (1998). Factors governing abundance of hydrolyzable amino acids in the sediments from the NW European Continental Margin (47–50 N). *Progress in Oceanography*, *42*(1), 145-164.

Bourgoin, L. H., & Tremblay, L. (2010). Bacterial reworking of terrigenous and marine organic matter in estuarine water columns and sediments. *Geochimica et Cosmochimica Acta*, *74*(19), 5593-5609.

Bui EN, Mazullo J, Wilding LP. 1990. Using quartz grain size and shape analysis to distinguish between aeolian and fluvial deposits in the Dallol Bosso of Niger (West Africa). *Earth Surface Processes and Landforms*14: 157–166.

Burdige, D. J., & Martens, C. S. (1988). Biogeochemical cycling in an organic-rich coastal marine basin: 10. The role of amino acids in sedimentary carbon and nitrogen cycling. *Geochimica et Cosmochimica Acta*, *52*(6), 1571-1584.

Chakrapani, G. (2002). Water and sediment geochemistry of major Kumaun Himalayan lakes, India. *Environmental Geology*, *43*(1), 99-107.

Chauhan, M. S. (2006). Late Holocene vegetation and climate change in the alpine belt of Himachal Pradesh. *Current Science*, 1562-1567.

Choudhary P, Routh J, Chakrapani GJ (2009b) An environmental record of changes in sedimentary organic matter from Lake Sattal in Kumaun Himalayas, India. Sci Total Environ 407:2783–2795

Choudhary P, Routh J, Chakrapani GJ, Kumar B (2009a) Organic matter and stable isotopic record of paleoenvironmental changes in sediments from Nainital Lake in Kumaun Himalayas, India. J Paleolimnol 42:571–586

Choudhary, P. (2008). *Characterisation of organic matter in sediments of Kumaun Himalayan Lakes,(p. 110)* (Doctoral dissertation, Ph. D Thesis, Indian Institute of Technology, Roorkee, India).

Choudhary, P., Routh, J., & Chakrapani, G. J. (2013). A 100-year record of changes in organic matter characteristics and productivity in Lake Bhimtal in the Kumaon Himalaya, NW India. *Journal of paleolimnology*, *49*(2), 129-143.

Choudhary, P., Routh, J., Chakrapani, G. J., & Kumar, B. (2009). Biogeochemical records of paleoenvironmental changes in Nainital Lake, Kumaun Himalayas, India. *Journal of Paleolimnology*, *42*(4), 571-586.

Conley, D. J. (1988). Biogenic silica as an estimate of siliceous microfossil abundance in Great Lakes sediments. *Biogeochemistry*, *6*(3), 161-179.

Conley, D. J., & Schelske, C. L. (2002). Biogenic silica. *Tracking environmental change using lake sediments*, 281-293.

Cotano, U., & Villate, F. (2006). Anthropogenic influence on the organic fraction of sediments in two contrasting estuaries: a biochemical approach. *Marine Pollution Bulletin*, *52*(4), 404-414.

Cowie, G. L., & Hedges, J. I. (1992). Sources and reactivities of amino acids in a coastal marine environment. *Limnology and Oceanography*, *37*(4), 703-724.

Cowie, G. L., & Hedges, J. I. (1994). Biochemical indicators of diagenetic alteration in natural organic matter mixtures. *Nature*, *369*(6478), 304-307.

Cowie, G. L., Hedges, J. I., Prahl, F. G., & De Lange, G. J. (1995). Elemental and major biochemical changes across an oxidation front in a relict turbidite: an oxygen effect. *Geochimica et Cosmochimica Acta*, *59*(1), 33-46.

D.J. DeMaster.The supply and accumulation of silica in the marine environment Geochem. Cosmochim. Acta, 45 (1981), pp. 1715-1732

Das, B. K. (2005). Environmental pollution impact on water and sediments of Kumaun lakes, Lesser Himalaya, India: a comparative study. *Environmental Geology*, *49*(2), 230-239.

Dauwe, B., & Middelburg, J. J. (1998). Amino acids and hexosamines as indicators of organic matter degradation state in North Sea sediments. *Limnology and Oceanography*, *43*(5), 782-798.

Dauwe, B., Middelburg, J. J., Herman, P. M., & Heip, C. H. (1999). Linking diagenetic alteration of amino acids and bulk organic matter reactivity. *Limnology and Oceanography*, *44*(7), 1809-1814.

Douglas, MSV , and JP. Smol . 1999. Freshwater diatoms as indicators of environmental change in the High Arctic. In Stoermer, E. , and JP. Smol . (Eds) The diatoms: applications for the environment and Earth sciencesCambridge, UK Cambridge University Press

Emerson, S., & Hedges, J. I. (1988). Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography*, *3*(5), 621-634.

Emerson, S., & Hedges, J. I. (1988). Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography*, *3*(5), 621-634.

Faegri, K., & Iversen, J. (1950). Text-book of modern pollen analysis. *GFF*, *72*(3), 363-364.

Fernandes, L., Garg, A., & Borole, D. V. (2014). Amino acid biogeochemistry and bacterial contribution to sediment organic matter along the western margin of the Bay of Bengal. *Deep Sea Research Part I: Oceanographic Research Papers*, *83*, 81-92.

Folk, R. L., & Ward, W. C. (1957). Brazos River bar: a study in the significance of grain size parameters. *Journal of Sedimentary Research*, *27*(1).

Friedman, G. M. (1979). Differences in size distributions of populations of particles among sands of various origins: addendum to IAS Presidential Address. *Sedimentology*, *26*(6), 859-862.

Fritz, S. C. (2008). Deciphering climatic history from lake sediments. *Journal of Paleolimnology*, *39*(1), 5-16.

Fritz, S. C., Baker, P. A., Seltzer, G. O., Ballantyne, A., Tapia, P., Cheng, H., & Edwards, R. L. (2007). Quaternary glaciation and hydrologic variation in the South American tropics as reconstructed from the Lake Titicaca drilling project. *Quaternary Research*, *68*(3), 410-420.

GĄSIOROWSKI M. 2013. Cladocera record from Budzewo (Skaliska Basin, north-eastern Poland). Acta Palaeobot. 53(1): 93-98.

Gaye, B., Fahl, K., Kodina, L. A., Lahajnar, N., Nagel, B., Unger, D., & Gebhardt, A. C. (2007). Particulate matter fluxes in the southern and central Kara Sea compared to sediments: Bulk fluxes, amino acids, stable carbon and nitrogen isotopes, sterols and fatty acids. *Continental Shelf Research*, *27*(20), 2570-2594.

Grimalt, J. O., van Drooge, B. L., Ribes, A., Fernandez, P., & Appleby, P. (2004). Polycyclic aromatic hydrocarbon composition in soils and sediments of high altitude lakes. *Environmental Pollution, 131*(1), 13–24.

GSI (2012) Geology and mineral resources of the states of India. Geology and mineral resources of Himachal Pradesh, miscellaneous publication number 30(XVII), Geological Survey of India.

Hecky, R. E., Mopper, K., Kilham, P., & Degens, E. T. (1973). The amino acid and sugar composition of diatom cell-walls. *Marine biology*, *19*(4), 323-331.

Henrichs, S. M., Farrington, J. W., & Lee, C. (1984). Peru upwelling region sediments near 15 S. 2. Dissolved free and total hydrolyzable amino acids. *Limnology and Oceanography*, *29*(1), 20-34.

Hodell, D. A., & Schelske, C. L. (1998). Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. *Limnology and Oceanography*, *43*(2), 200-214.

Huston, A. L., & Deming, J. W. (2002). Relationships between microbial extracellular enzymatic activity and suspended and sinking particulate organic matter: seasonal transformations in the North Water. *Deep Sea Research Part II: Topical Studies in Oceanography*, *49*(22), 5211-5225.

Ishiwatari, R., & Uzaki, M. (1987). Diagenetic changes of lignin compounds in a more than 0.6 million-year-old lacustrine sediment (Lake Biwa, Japan). *Geochimica et Cosmochimica Acta*, *51*(2), 321-328.

Bremner, J. M. (1960). Determination of nitrogen in soil by the Kjeldahl method. *The Journal of Agricultural Science*, *55*(1), 11-33.

Jackson, M. L. (1958). Nitrogen determinations for soil and plant tissue. *Soil chemical analysis*, 183-204.

J.D.H. Strickland, T.R. Parsons (2nd ed.), A Practical Handbook of Seawater Analysis, vol. 167, Bull. Fish. Res. Board Can. (1972), p. 310

Jennerjahn, T. C., & Ittekkot, V. (1997). Organic matter in sediments in the mangrove areas and adjacent continental margins of Brazil. 1. Amino acids and hexosamines. *Oceanolica Acta*, *20*(2), 359-369.

Kar, R., Bajpai, R., & Singh, A. D. (2015). Modern pollen assemblages from Hamtah and Chhatru glaciers, Lahaul-Spiti, India: Implications for pollen–vegetation relationship in an alpine arid region of western Himalaya. *Quaternary International*, *371*, 102-110.

Kar, R., Ranhotra, P. S., Bhattacharyya, A., & Sekar, B. (2002). Vegetation vis-à-vis climate and glacial fluctuations of the Gangotri Glacier since the last 2000 years. *Current Science*, *82*(3), 347-351.

Keil, R. G., Tsamakis, E., & Hedges, J. I. (2000). Early diagenesis of paniculate amino acids in marine systems. *Perspectives in Amino Acid and Protein Geochemistry, Oxford University Press, Inc., New York*, 69-82.

Keil, R. G., Tsamakis, E., & Hedges, J. I. (2000). Early diagenesis of paniculate amino acids in marine systems. *Perspectives in Amino Acid and Protein Geochemistry, Oxford University Press, Inc., New York*, 69-82.

King Jr, K. (1977). Amino acid survey of recent calcareous and siliceous deep-sea microfossils. *Micropaleontology*, 180-193.

Kotlia, B. S., & Joshi, L. M. (2013). Neotectonic and climatic impressions in the zone of Trans Himadri Fault (THF), Kumaun Tethys Himalaya, India: A case study from palaeolake deposits. *Zeitschrift für Geomorphologie*, *57*(3), 289-303.

Kotlia, B. S., Bhalla, M. S., Sharma, C., Rajagopalan, G., Ramesh, R., Chauhan, M. S., ... & Chacko, S. T. (1997). Palaeoclimatic conditions in the upper Pleistocene and Holocene Bhimtal-Naukuchiatal lake basin in south-central Kumaun, North India. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *130*(1-4), 307-322.

Le Fort, P. (1989). The Himalayan orogenic segment. In *Tectonic evolution of the Tethyan region* (pp. 289-386). Springer Netherlands.

Lee, C. (1988). Amino acid and amine biogeochemistry in marine particulate material and sediments. *Nitrogen cycling in coastal marine environments*, 125-141.

Lee, C., & Cronin, C. (1984). Particulate amino acids in the sea: Effects of primary productivity and biological decomposition. *Journal of Marine Research*, *42*(4), 1075-1097.

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*(20), 3573-3584.

Lomstein, B. A., Jørgensen, B. B., Schubert, C. J., & Niggemann, J. (2006). Amino acid biogeo-and stereochemistry in coastal Chilean sediments. *Geochimica et Cosmochimica Acta*, *70*(12), 2970-2989.

M. Konert, J. VandenbergheComparison of laser grain size analysis with pipette and sieve analysis: a solution for the underestimation of the clay fraction. Sedimentology, 44 (1997), pp. 523-535

Meckler, A. N., Schubert, C. J., Cowie, G. L., Peiffer, S., & Dittrich, M. (2004). New organic matter degradation proxies: Valid in lake systems?. *Limnology and oceanography*, *49*(6), 2023-2033.

Menzel, P., Anupama, K., Basavaiah, N., Das, B. K., Gaye, B., Herrmann, N., & Prasad, S. (2015). The use of amino acid analyses in (palaeo-) limnological investigations: A comparative study of four Indian lakes in different climate regimes. *Geochimica et Cosmochimica Acta*, *160*, 25-37.

Menzel, P., Gaye, B., Mishra, P. K., Anoop, A., Basavaiah, N., Marwan, N., ... & Wiesner, M. G. (2014). Linking Holocene drying trends from Lonar Lake in monsoonal central India to North Atlantic cooling events. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *410*, 164-178.

Menzel, P., Gaye, B., Wiesner, M. G., Prasad, S., Stebich, M., Das, B. K., ... & Basavaiah, N. (2013). Influence of bottom water anoxia on nitrogen isotopic ratios and amino acid contributions of recent sediments from small eutrophic Lonar Lake, central India. *Limnology and Oceanography*, *58*(3), 1061-1074.

Meyers, P. A. (1997). Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Organic geochemistry*, *27*(5), 213-250.

Meyers, P. A. (2003). Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Organic geochemistry*, *34*(2), 261-289.

Meyers, P. A., & Lallier-Vergès, E. (1999). Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. *Journal of Paleolimnology*, *21*(3), 345-372.

Meyers, P. A., Leenheer, M. J., & Bourbonniere, R. A. (1995). Diagenesis of vascular plant organic matter components during burial in lake sediments. *Aquatic Geochemistry*, *1*(1), 35-52.

MEYERS, P.A. (1994) Preservation of elemental and isotopic source identification of sedimentary organic matter. Chemical Geol., v.114, pp.289–302.

Meyers, P.A. and Eadie, B.J., 1993. Sources, degradation and recycling of organic matter associated with sinking panicles in Lake Michigan. Org. Geochem., 20: 47-56.

Mishra, P. K., Anoop, A., Jehangir, A., Prasad, S., Menzel, P., Schettler, G., ... & Gaye, B. (2014). Limnology and modern sedimentation patterns in high altitude Tso Moriri Lake, NW Himalaya–implications for proxy development. *Fundamental and Applied Limnology/Archiv für Hydrobiologie*, *185*(3-4), 329-348.

Moore, P. D., Webb, J. A., & Collison, M. E. (1991). *Pollen analysis*. Blackwell scientific publications.

Moilleron, R., Berrekhis, A., Vidonne, A., & Rémy, F. (1996, September). HPLC and ninhydrin photometric determination of amino acids in CaCO 3 rich lacustrine sediments of the Jura region, France. In *Annales de Limnologie-International Journal of Limnology* (Vol. 32, No. 3, pp. 197-204). EDP Sciences.

Nautiyal, C. M., & Chauhan, M. S. (2009). Late Holocene vegetation and climate change in Loktak Lake region, Manipur, based on pollen and chemical evidence.

Ni, Z., & Wang, S. (2015). Historical accumulation and environmental risk of nitrogen and phosphorus in sediments of Erhai Lake, Southwest China. *Ecological Engineering*, *79*, 42-53.

OGREN, W. L., & CHOLLET, R. (1982). Photorespiration. *Photosynthesis V2*, 191-230.

Ostrom, N. E., Macko, S. A., Deibel, D., & Thompson, R. J. (1997). Seasonal variation in the stable carbon and nitrogen isotope biogeochemistry of a coastal cold ocean environment. *Geochimica et Cosmochimica Acta*, *61*(14), 2929-2942.

Parsons, T. R., Thomas, W. H., Seibert, D., Beers, J. R., Gillespie, P., & Bawden, C. (1977). The effect of nutrient enrichment on the plankton community in enclosed water columns. *International Review of Hydrobiology*, *62*(5), 565-572.

Phadtare NR. 2000. Sharp decrease in summer monsoon strength 4000- 3500 cal yr B.P. in the Central Higher Himalaya of India based on pollen evidence from alpine peat. Quaternary Research 53: 122– 129.

Phartiyal, B., Sharma, A., Srivastava, P., & Ray, Y. (2009). Chronology of relict lake deposits in the Spiti River, NW Trans Himalaya: Implications to Late Pleistocene–Holocene climate-tectonic perturbations. *Geomorphology*, *108*(3), 264-272.

Prasad, M. B. K., & Ramanathan, A. L. (2008). Sedimentary nutrient dynamics in a tropical estuarine mangrove ecosystem. *Estuarine, Coastal and Shelf Science*, *80*(1), 60-66.

Prasad, S., & Enzel, Y. (2006). Holocene paleoclimates of India. *Quaternary Research*, *66*(3), 442-453.

Ramanathan, AL., 2011. Status Report on Chhota Shigri Glacier (Himachal Pradesh). In: Report, H.G.T. (Ed.), Department of Science and Technology, Ministry of Science and Technology, New Delhi.

Ramaswamy, V., Gaye, B., Shirodkar, P. V., Rao, P. S., Chivas, A. R., Wheeler, D., & Thwin, S. (2008). Distribution and sources of organic carbon, nitrogen and their isotopic signatures in sediments from the Ayeyarwady (Irrawaddy) continental shelf, northern Andaman Sea. *Marine Chemistry*, *111*(3), 137-150.

Rawat, S., Gupta, A. K., Sangode, S. J., Srivastava, P., & Nainwal, H. C. (2015). Late Pleistocene–Holocene vegetation and Indian summer monsoon record from the Lahaul, northwest Himalaya, India. *Quaternary Science Reviews*, *114*, 167-181.

Rawat, S., Gupta, A. K., Srivastava, P., Sangode, S. J., & Nainwal, H. C. (2015). A 13,000 year record of environmental magnetic variations in the lake and peat deposits from the Chandra valley, Lahaul: implications to Holocene monsoonal variability in the NW Himalaya. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *440*, 116-127.

Rawat, S., Phadtare, N. R., & Sangode, S. J. (2012). The Younger Dryas cold event in NW Himalaya based on pollen record from the Chandra Tal area in Himachal Pradesh, India. *Current Science*, 1193-1198.

Redfield, A. C. (1963). The influence of organisms on the composition of seawater. *The sea*, *2*, 26-77.

Renjith, K. R., Chandramohanakumar, N., & Joseph, M. M. (2011). Fractionation and bioavailability of phosphorus in a tropical estuary, Southwest India. *Environmental monitoring and assessment*, *174*(1-4), 299-312.

Ritchie, J. C. (1995). Current trends in studies of long-term plant community dynamics. *New Phytologist*, *130*(4), 469-494.

Ruttenberg, K. C., & Goni, M. A. (1997). Phosphorus distribution, C: N: P ratios, and δ13Coc in arctic, temperate, and tropical coastal sediments: tools for characterizing bulk sedimentary organic matter. *Marine Geology*, *139*(1-4), 123-145.

Sigleo, A. C., & Shultz, D. J. (1993). Amino acid composition of suspended particles, sediment-trap material, and benthic sediment in the Potomac Estuary. *Estuaries*, *16*(3), 405-415.

Singh, V. B., Ramanathan, A. L., & Mandal, A. (2016). Hydrogeochemistry of high-altitude lake: a case study of the Chandra Tal, Western Himalaya, India. *Arabian Journal of Geosciences*, *9*(4), 308.

Singh, Y., Khattar, J. I. S., Singh, D. P., Rahi, P., & Gulati, A. (2014). Limnology and cyanobacterial diversity of high altitude lakes of Lahaul-Spiti in Himachal Pradesh, India. *Journal of biosciences*, *39*(4), 643-657.

Smol, J. P. (1988). Paleoclimate proxy data from freshwater arctic diatoms. *Verh. Int. Ver. Limnol*, *23*, 837-844.

Smol, J. P., & Cumming, B. F. (2000). Tracking long-term changes in climate using algal indicators in lake sediments. *Journal of Phycology*, *36*(6), 986-1011.

Sollins, P., Spycher, G., & Glassman, C. A. (1984). Net nitrogen mineralization from light- and heavy-fraction forest soil organic matter. *Soil Biology and Biochemistry*, *16*(1), 31-37.

Sollins, P., Spycher, G., & Glassman, C. A. (1984). Net nitrogen mineralization from light- and heavy-fraction forest soil organic matter. *Soil Biology and Biochemistry*, *16*(1), 31-37.

Sommaruga, R. (2001). The role of solar UV radiation in the ecology of alpine lakes. *Journal of Photochemistry and Photobiology B: Biology*, *62*(1), 35-42.

Sterner, R. W., Elser, J. J., Fee, E. J., Guildford, S. J., & Chrzanowski, T. H. (1997). The light: nutrient ratio in lakes: the balance of energy and materials affects ecosystem structure and process. *The American Naturalist*, *150*(6), 663-684.

Sugai, S. F., & Henrichs, S. M. (1992). Rates of amino acid uptake and mineralization in Resurrection Bay (Alaska) sediments. *Marine Ecology Progress Series*, 129-141.

Sun, D., Bloemendal, J., Rea, D. K., Vandenberghe, J., Jiang, F., An, Z., & Su, R. (2002). Grain-size distribution function of polymodal sediments in hydraulic and aeolian environments, and numerical partitioning of the sedimentary components. *Sedimentary Geology*, *152*(3), 263-277.

Trivedi, A., & Chauhan, M. S. (2009). Holocene vegetation and climate fluctuations in northwest Himalaya, based on pollen evidence from Surinsar Lake, Jammu region, India. *Journal of the Geological Society of India*, *74*(3), 402-412.

Unger, D., Herbeck, L. S., Li, M., Bao, H., Wu, Y., Zhang, J., & Jennerjahn, T. (2013). Sources, transformation and fate of particulate amino acids and hexosamines under varying hydrological regimes in the tropical Wenchang/Wenjiao Rivers and Estuary, Hainan, China. *Continental Shelf Research*, *57*, 44-58.

Ventelä, A. M., Saarikari, V., & Vuorio, K. (1998). Vertical and seasonal distributions of micro-organisms, zooplankton and phytoplankton in a eutrophic lake. In *Eutrophication in Planktonic Ecosystems: Food Web Dynamics and Elemental Cycling* (pp. 229-240). Springer Netherlands.

Verma, A., & Subramanian, V. (2002). Organic matter and amino acid concentrations in surface sediments of Vembanad Lake–a tropical estuary, west coast of India. *Regional Environmental Change*, *2*(4), 143-149.

Wagner, T., Zabel, M., Dupont, L., Holtvoeth, J., & Schubert, C. J. (2004). Terrigenous signals in sediments of the low latitude Atlantic—implications for environmental variations during the Late Quaternary, Part I: organic carbon. *The South Atlantic in the late Quaternary: Reconstruction of material budgets and current systems: Berlin, Springer*, 295-322.

Wakeham, S. G., & Lee, C. (1993). Production, transport, and alteration of particulate organic matter in the marine water column. In *Organic geochemistry* (pp. 145-169). Springer US.

Wakeham, S. G., Lee, C., Hedges, J. I., Hernes, P. J., & Peterson, M. J. (1997). Molecular indicators of diagenetic status in marine organic matter. *Geochimica et Cosmochimica Acta*, *61*(24), 5363-5369.

Walkley, A., & Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil science*, *37*(1), 29-38.

Wang, X. C., & Lee, C. (1993). Adsorption and desorption of aliphatic amines, amino acids and acetate by clay minerals and marine sediments. *Marine Chemistry*, *44*(1), 1-23.

Wen, L. S., Warnken, K. W., & Santschi, P. H. (2008). The role of organic carbon, iron, and aluminium oxyhydroxides as trace metal carriers: Comparison between the Trinity River and the Trinity River Estuary (Galveston Bay, Texas). *Marine Chemistry, 112*, 20–37.

Wetzel, R. G. (2001). *Limnology: lake and river ecosystems*. Gulf Professional Publishing.