

MONITORING LEVEL OF POLLUTANTS IN NUST LAKES



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**A thesis submitted in partial fulfillment of the requirement for the degree of Master
of Science in Environmental Sciences**

Institute of Environmental Sciences & Engineering

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Islamabad, Pakistan

2022

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Dedication

This research is dedicated to my loving, caring, and industrious parents and my friends. Their efforts and sacrifices have made my dream of having this degree a reality. Words cannot adequately express my deep gratitude to them.

“O My Sustainer, Bestow on my parents your mercy even as they cherished me in my childhood”.

Acknowledgements

To the highest God be glory great things He has done. I acknowledge your great provisions, protections, and support throughout this course. I am thankful to my supervisor Dr. Hira Amjad (IESE) for her appreciation, constructive suggestions, criticisms, and encouragement. My deep gratitude goes to her for giving her valuable time in department discussion and concrete suggestions to improve the research work and thesis write-up.

I remain indebted to my respected co-supervisor, Dr. Imran Hashmi (IESE) and committee members, Dr. Hamza Farooq Gabriel (NICE) and Dr. Muhammad Ali Inam (IESE) for sparing time from their busy schedule for attending progress reviews and providing their beneficial suggestions and comments in the context of research and thesis. My appreciation goes to the entire faculty, the staff of IESE, and all my classmates for the support and guidance, they provided me during research. My appreciation also goes to my parents, family, and batch mates especially for their efforts, moral support, and suggestions towards my progress in life.

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LIST OF ABBREVIATIONS

COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EC	Electrical Conductivity
mg/L	Milligram per Liter
mg/m³	Milligrams per Cubic Meter
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
WHO	World Heal Organization
μS/cm	Micro Siemens /Centimeter
CCI	Chlorophyll Content Index
TSS	Total Suspended Solids
WAPDA	Water and Power Development Authority
Chl- a	Chlorophyll a
Chl- b	Chlorophyll b
Chl- c	Chlorophyll c
AAS	Atomic Absorption Spectrophotometer

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ABSTRACT

Water is a very important resource for life. It affects our public and environmental health. Water occupies approximately 71 % of the earth's surface in the shape of rivers, lakes, seas, oceans, glaciers, and ice caps. Both natural and anthropogenic activities have endangered this natural and precious resource. Pakistan is already a water stress country and now it has moved to a water scarce country. The three NUST lakes were constructed to store water and cope with water shortage but due to internal (NUST apartments, sports complex, hostels, cafes, sports complex, saddle club and workshop) and external sources (wastewater from G-13 and H-13), the quality of water present in lakes is deteriorating with each passing day. The current study aimed to determine physicochemical parameters such as pH, total dissolved solids, turbidity, electrical conductivity, temperature, chemical oxygen demand, nitrate, nitrite, phosphate, total kjeldahl nitrogen, chlorophyll-a, b and c, chlorophyll content index and heavy metals in water, sediments and flora at NUST lakes. Samples were collected and analyzed according to the standard protocols. Algal species were also detected under compound microscope. Maximum chlorophyll content was observed in *Stellaria graminea*. Study revealed that contamination level at all sites was significantly high. Concentrations of four heavy metals (Cd, Cr, Zn and Pb) were observed. Higher concentration of Zn was found in water, sediments and plants of all lakes. The eutrophication levels were low making NUST lakes oligotrophic. Pearson correlation was used to identify the relationship among different parameters. Further studies should be conducted for better assessment of waste intrusion sources, nutrient release in lakes and dominant algal species.

CHAPTER 1

1. INTRODUCTION

Clean and safe drinking water is necessary for the survival of planet Earth. Water is very important for development and livelihood. According to United Nations, 1.2 billion people do not consume water that is safe for drinking purpose and atleast 746 million people do not have access to clean water. Rivers, dams and lakes are major sources of fresh water (Bhateria and Jain, 2016).

Lakes are inland water bodies which do not exchange water with an ocean directly. They contain ~0.8% of total water resources around the world and play an important role in developing sustainable ecosystems (Harrison et al., 2016). In arid regions, lakes may be having fresh and salty water. Lake water has physical, chemical and biological parameters. They can be deep or shallow, temporary or permanent. The study of lakes falls under limnology. We can study ecosystems by monitoring and analyzing lake conditions and parameters. Biological, physical and chemical parameters are interlinked and they are different in different media (land, air) either quantitatively or qualitatively. Although they contribute to 50.01% of total water on Earth, they contain 49.8% of liquid surface fresh water. Many organisms depend on lake water for their survival. Lakes provide humans with many goods and services such as they can be used for drinking purpose, removing waste, provision of food and livelihood by fisheries, irrigation purpose, many industrial activities and recreation due to their aesthetic value. Due to increase in population and technological advancement, many human activities are taking place which are causing problems in the management of waste water and contaminating surface water. Weathering of rocks, mining and soil leaching is contaminating natural water. There are various reasons for nutrient enrichment in lakes. Seasonal variations and changes in land use can affect the nutrient concentration in lakes because more fertilizer use adds them to lakes and rivers increasing eutrophication levels and causing biodiversity loss. Plastic debris is also affecting lakewater quality. It affects shoreline, open water and benthic zone. Lakes generally contain four major zones supporting biodiversity. They are: littoral zone, which is shallow water near the shore, contains aquatic plants and other types of aquatic life (Carmignani and Roy, 2017).

The second zone is limnetic zone. It receives light for photosynthesis and contains phytoplankton, zooplankton and fish species. Their amount depends upon the nutrient availability. The deep water zone containing fish species mostly trout and bass is a darker zone with low dissolved oxygen levels called profundal zone. Benthic zone is the deepest present at the lake bottom and contains bacteria, blood worms and decomposers that thrive on dead plants, remains of animal waste and fungi in large number (Bhateria and Jain, 2016).

1.1. Healthy vs Non Healthy Lakes

Healthy lakes have greater water clarity, biodiversity, sun light penetration and chlorophyll a concentrations are in equilibrium with the grazer biota due to less waste intrusion from urbanization, agricultural runoff and industrial activities etc. The chlorophyll value of 10ppb is when algae can be visually noticed in water but surface scums are formed when the value is greater than 30ppb. This layer covers all the aquatic vegetation, increases the biological oxygen demand, affects fish and other aquatic animals and makes water unfit for consumption. Moreover, they decrease the lake aesthetic value. Cyanobacteria produce natural toxins damaging liver, digestive system, neurons and skin. They are even more toxic than the insecticides (Jones and Brett, 2014).

The lake water analysis should focus not only on the lakes but also the sources of waste intrusion, surrounding activities and vegetation. Physicochemical parameters for water quality include pH, electrical conductivity, turbidity, temperature, dissolved oxygen, total dissolved solids, nitrate, nitrite, phosphate, total alkalinity and total hardness.

Eutrophication is another problem caused due to overabundance of nutrients such as nitrogen and phosphorus. When algae die, this leads to overconsumption of oxygen dissolved in water. Therefore, moderate levels of algae are healthy for the lakes, however, excessive algal blooms are undesirable. This makes eutrophication assessment and identification of dominant algal species necessary. For this purpose, chlorophyll (a, b and c) are essential to be determined. chlorophyll 'a' is a blue green micro crystalline solid and is present in all green plants with highest concentration in summer whereas, higher plants and green algae contain chlorophyll 'b'. Chlorophyll 'c' is another form occurring mainly in diatoms, dinoflagellates and brown algae. The microbiological parameters cannot be ignored and are essential to be determined especially the bacterial strains affecting the water quality. All these parameters shall be monitored keeping in mind the seasonal variations and uncertainties due to changes in the environment (Bhateria and Jain, 2016). Pakistan is facing problems regarding shortage of water due to improper management, lack of trained professionals and financial issues. (Khuawar *et al.*, 2018). Almost 80% fresh water ecosystems are affected by scarcity of water due to anthropogenic activities (Bunn, 2016). Therefore, there is a great need to characterize the ecosystems efficiently and ensure its sustainability.

Protection and conservation of lakes falls under Sustainable Development Goal 6. It is about Clean Water and Sanitation for all and established by United Nations General Assembly (2015).

1.2. Lakes in Pakistan

There are many freshwater lakes in Pakistan, situated at various altitudes and latitudes, which are shown in Figure 1.1.

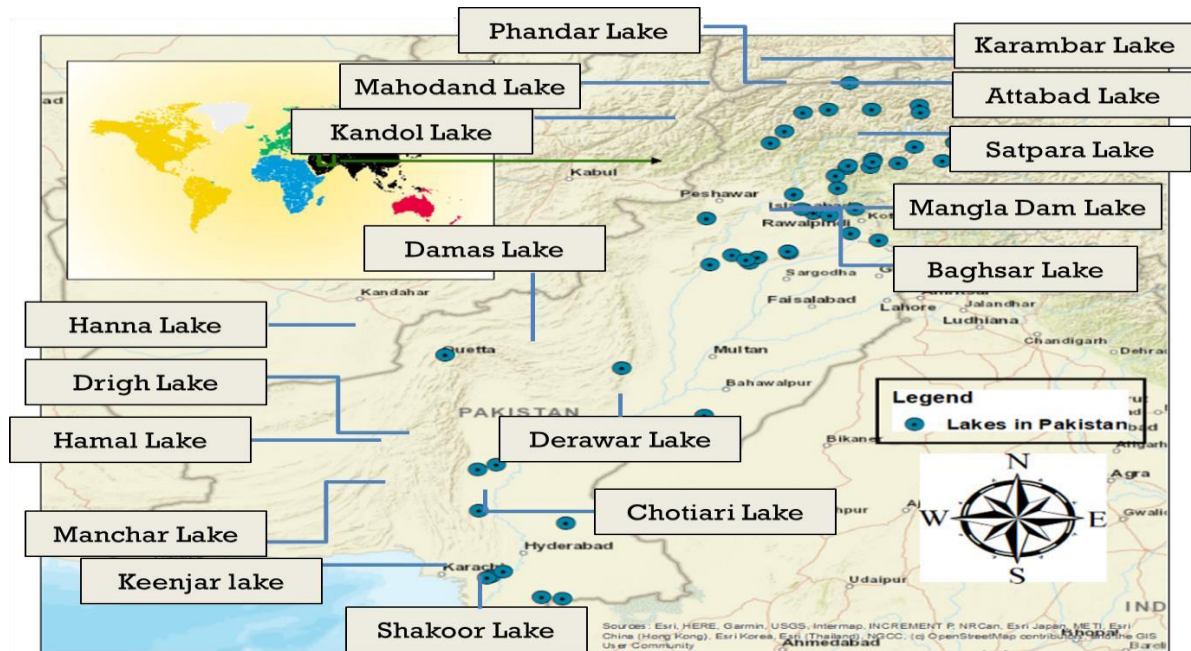


Figure 1.1: Map of Lakes in Pakistan

1.3. Present Study

NUST main campus contains structures having ability to absorb water during rainfall such as footpaths. Three NUST lakes were constructed in 2011. They have been developed at the H-12 campus in order to maintain the water table by damming natural streams/nullahs passing through the campus. However, limited data is available on NUST lakes. The research on NUST lakes that has been carried out is regarding improving harvested rain water quality by three stage portable water filter (Nawaz, 2017). Another study was conducted on water quality assessment (Momina, 2018). This study is designed to assess the current eutrophication, identification of dominant algal species and physicochemical parameters including heavy metal analysis of water, sediments and plants at NUST lakes to propose the lake's restoration and preservation measures.

1.4. Waste Water Intrusion Sources

The major internal waste intrusion sources for the three NUST lakes are hostels, NUST apartments, cafeteria, sports complex, workshop and saddle club while the external waste intrusion is from G-13 and H-13, Islamabad. Waste from G-13 is being poured directly into the Lake-1. This polluted water enters from Lake-1 to Lake-2 followed by H-13 waste being intruded directly into Lake-2. The water containing waste from both these external and internal sources gets poured into the Lake-3. According to the data acquired from Works Directorate, NUST, the area of Lake 1, Lake 2 and Lake 3 is 1.5 acres, 2.2 acres and 2.25 acres respectively. Lake 1 and 3 have almost equal depths i.e., 25ft while Lake 2 is 16-20ft deep. Lake 3 has the largest volume i.e., 0.74 GL while Lake 1 and 2 has volume, 0.17 GL and 0.16 GL respectively. Therefore, this study aims to analyze several pollution parameters and help in devising ways to

reduce waste intrusion by anthropogenic activities. This will fulfill the purpose of development of NUST lakes as they were created for rain water harvesting recreational purpose. In addition to this, their treatment will help in conduction of sports activities for students in future.

1.5. Objectives

1. Estimation of physicochemical parameters and determination of algal growth in NUST lakes.
2. Identification of heavy metals in water, sediments and plant species of NUST lakes.
3. Estimation of health status of lakes through meteorological parameters.

The current research will have pragmatic applications in areas including amelioration of water quality, enhancement of public health status, and implementation of policy measures indispensable to meet the said goals.

CHAPTER 2

2. LITERATURE REVIEW

Pakistan contains a number of natural and artificial lakes. Lakes Keenjhar, Rawal and Saif-ul-Muluk are major lakes of Pakistan. The first two are very important water reservoirs for three cities of Pakistan, while Lake Saif-ul-Muluk is present at a high altitude in a clean and fresh environment at a point where Himalayan and Karakoram ranges connect with each other. These lakes play a very pivotal role in maintaining the ecosystem sustainability and they favour the communities in their proximity. Keenjhar Lake is present in southern region of Pakistan. It is recognized globally as 'Ramsar site'. Indus River is the main water reservoir for Karachi. In the North of Pakistan, Rawal Lake is located in the Potohar plateau close to the foot of Margalla hills. This lake is a major freshwater source for twin cities i.e., Islamabad and Rawalpindi. Precipitation helps in the replenishment of Rawal. Lake while Lake Saif-ul-Muluk is replenished by glacial water as it is situated at a great height in the North (Saleem et al., 2019).

Studies carried out on lakes in Pakistan are based on the physicochemical parameters, biological analysis, heavy metal determination, eutrophication and inhabitant species. A recent study on metagenomic profiling, physicochemical parameters and nutrients indicating eutrophication has been carried out for fresh water lakes i.e., Keenjhar Lake, Rawal Lake and Saif ul Maluk Lake (Saleem et al., 2019). Effects of pollutants on Keenjhar Lake were determined by physiochemical analysis and the results showed that TDS (813 mg/L), chlorides (265mg/L) were high in Kotri effluent and WAPDA colony. Human activities released toxic ions and metals in KB feeder.

A study was conducted by (Awais *et al.*, 2016) on the effect of urbanization on Rawal Lake water quality. It showed that population has been increased from last 11 years in the catchment area. Changes in land use patterns were also observed, forest area decreased from 54 to 48% while built up land has increased from 14.7-23.12%. No major change in the precipitation pattern was observed but water inflow also decreased. This proves that urbanization affects the inflows. Seasonal variations are important to be monitored because they impact the water quality causing fluctuation in the water flow and parameters. Results of another study by (Firdous *et al.*, 2016) showed that land use pattern and seasonal variations had strong impact on soil and water quality.

Studies show that eutrophication causes cyanobacterial bloom in freshwater lakes and this varies in different seasons (Stress *et al.*, 2013).

Chlorophyll analysis in Rawal Lake was conducted to determine the eutrophic category of lake to assess the quality of water for drinking purpose (Butt and Nazir, 2015).

Studies on sediment sample analysis of twenty one sites at Kurang Nullah, Rawal Lake were conducted during monitoring for two years before and after monsoon (2007–2008). Sediment

Quality Guidelines (SQGs) were used to determine the risk of toxicity by heavy metals. According to the results, in pre monsoon, greater mean concentrations of Ni, Mn and Pb were found while Zn, Ni and Mn were higher post monsoon season (Zahra *et al.*, 2014).

Phytoplankton and play dominant roles in aquatic ecosystem. The bacterial activity affects the growth of phytoplankton depending upon the biogeochemical processes. Based on gene sequencing (16S rRNA), a lot of research has been done focused on phytoplankton colonies. Studies have shown that there is a close relationship of algae and bacteria. The results showed that seasonal changes of *Microcystis*, *Synechococcus* (picocyanobacteria) and other bacteria (Actinomycetales, Pirellulaceae and Sphingobacteriaceae) were greater than the spatial change. The spatial distribution of bacterial communities indicated that different phyla were dominant in different areas. The density of phytoplankton, Chl-a, temperature of water, total nitrogen caused variation spatially and temporally in the composition of bacterial communities. This study revealed the distribution of bacteria with respect to space in Lake Taihu and provided information regarding the relationship between algal blooms (cyanobacteria), other bacterial species and their response to different environmental parameters in eutrophic ecosystems containing fresh water (Zhu *et al.*, 2019).

Both ground observations and satellite data can determine water quality and related fluctuations in parameters. A study was conducted on Rawal Lake Landsat sensor data from 2009-2013 along with the ground data in which trophic state index was measured on the basis of chlorophyll a and total phosphorus. The results of Mann–Kendall (MK) statistical tests showed that TSI values on the basis of Secchi disc transparency is significant ($s = 0.523$). Rawal Lake is a hypereutrophic lake i.e., very polluted and its water is unfit for drinking. (Butt and Nazir, 2015).

Constructed wetlands can be a very useful way of mitigating the problem of eutrophication as it helps in long term removal of phosphorus. One such wetland was constructed at Lake Apopka, Florida in USA that helps in the treatment of waste water. It treated almost 30% of the lake volume annually. The removal performance varied each season. Greater removal was observed during (September–May) and less removal during warmer months (June–August) (Dunne *et al.*, 2015).

Lake water of Patna Bird Sanctuary has been analyzed for the variation in physicochemical parameters such as depth, pH, temperature, turbidity and light penetration, BOD, COD and DO varied seasonally. The zooplankton and phytoplankton showed lowest and highest population of 0.780 ± 0.014 to 1.518 ± 0.057 lac/lit and 0.192 ± 0.005 to 0.558 ± 0.035 lac/lit respectively in different seasons of 2004-05 and 2005-06. The current investigations showed that the lake water was most suitable for production of fish in winter as well as rainy season (Sharma and Capoor, 2013).

Lake Taihu has also been studied for the climate change effects on the seasonal patterns ultimately affecting the growth of phytoplankton in Lake Taihu, China. The changes in climate and nutrients in Lake Taihu have been observed over past 20 years. Wind speed decreased from 1997 to 2016 in all four seasons whereas, in Spring and Winter season, the global radiation increased significantly. The increasing trend of Phosphorus and Chlorophyll a was observed in Summer and Autumn. Diatoms, Aulacoseira and Asterionella, grew more at the start of spring and late winter. Multiple Regression Analysis showed that the lower wind speed and high global radiation were the main reason for the growth of phytoplankton in Winter and Spring while the Microcystis (cyanobacteria) was dominant in Summer and Autumn due to change in phosphorus (Deng *et al.*, 2020).

2.1. Need to monitor water quality:

Some of the basic concerns that affect the water sector are:

1. Fresh water is hard to obtain because of its increasing demand.
2. In terms of precipitation, surface flow and ground water, various locations in the country are fitted differently with water and there is an increased stress on the distribution of water resources.
3. Lack of equity in allocations of water.
4. Majority of drinking water is obtained from groundwater which is declining.
5. Lack of awareness among the general public about water scarcity.

Thus, the situation demands quick action and a good management system for the country's water resources (National water policy, 2018).

2.2 Physicochemical Parameters

The following section specifies all parameters affecting water quality.

2.2.1. pH

pH is the measurement of water alkalinity. It depends on the CO₂ concentration, nature of pollutants (acidic or basic) and dissolved nutrients and chemicals. The natural, unpolluted water is acidic in nature with pH 5.6 because CO₂ gets absorbed when it passes through the air. The pH may change during day and night depending upon the CO₂ by aquatic plants (Lashari *et al.*, 2022).

2.2.2. Temperature

Metabolism and reproduction rate of aquatic organisms depends upon the water temperature otherwise, species will not be able to survive. Dissolved oxygen levels in water depend upon the temperature. This affects the activities of microorganisms and chemical reactions. The

temperature level may fluctuate according to the environmental conditions, plants, trees and urbanization. Most of the aquatic organisms thrive at a temperature below 30°C (Kraemer *et al.*, 2015).

2.2.3. Dissolved oxygen

The oxygen levels determine whether a lake is healthy. The oxygen levels below 3ppm means that the oxygen levels are not enough for aquatic life. More than 5ppm concentration is healthy. Aquatic plants absorb the atmospheric oxygen. Moreover, oxygen enters the water by algal photosynthesis. The oxygen then gets removed by organic matter decomposition. Seasonal, temporal variations, activities by plants and animals, low and high altitude of water body, bacterial growth rate in sewage effluent and salt concentration etc (Tian *et al.* 2013).

2.2.4. Electrical Conductivity

Electrical conductivity is the water's ability to allow current to pass through it. It measures the number of ions in water. These ions come from sodium, phosphates, nitrates, chloride, calcium and iron etc. These are dissolved inorganic solids and salts and their presence in water increases its conductivity (Upadhyay *et al.* 2012).

2.2.5. Total Dissolved Solids

The particles which are greater than 2 microns are total suspended solids. The total suspended solids are a sum of TDS (Total Dissolved Solids) and TSS (Total Suspended Solids). TSS consist of inorganic materials or remains of dead plants that enter in water column. Total Dissolved Solids comprise of ion particles that are less than 2 microns. They may include salt ions and organic matter that is dissolved in waste water. Higher concentrations of these solids make water more turbid and unfit for consumption (Sharma and Tiwari, 2018).

2.2.6. Turbidity

Turbidity affects the water clarity. It is caused by phytoplankton, microorganisms, organic and inorganic suspended particles. These particles are a source of nutrients for pathogens and protect microorganisms from the effect of chlorination (Dorner *et al.* 2007).

2.2.7. Nitrate

Nitrate is mostly present in the form of N₂ compound (oxidizing state) in raw water. The main nitrate source in water is from chemical and fertilizer factories, domestic and industrial discharge. Nitrate is important for the survival of aquatic life but when its concentration exceeds beyond the normal limit, it can lower the dissolved oxygen level (hypoxia) in water, increase its temperature and affect other indicators which may become toxic to aquatic life (Dohare *et al.*, 2014).

2.2.8. Nitrite

Nitrates are short lived form of nitrogen and can get converted quickly to nitrates by bacteria. The nitrites can cause brown blood disease in fish. They can react directly with the hemoglobin in humans and form met hemoglobin which affects the ability of human blood to transport oxygen. This condition is found mostly in babies under three months of age. When nitrite and iron react in the human body (in blood), this will cause Blue babysyndrome disease which create methemoglobin which stops oxygen level (Gupta *et al.*, 2013).

2.2.9. Phosphate

Phosphorus is found in organic matter and soil. Phosphates in normal concentration in water are beneficial for the ecosystem. However, due to increasing agricultural activities and mismanagement of waste, the equilibrium is disturbed(Kareem *et al.*, 2021).

2.2.10. Chemical Oxygen Demand

Chemical Oxygen Demand is a measure of oxygen equivalent to organic matter content of a sample which is inclined to oxidation by a strong chemical oxidant. Due to the decomposition of microbes, elevated COD level can cause oxygen depletion to a level harmful to aquatic life (Rahman *et al.*, 2021).

2.2.11. Total Kjeldahl Nitrogen

The common sources of ammonia are human, animal wastes, industrial wastes and certain fertilizers. The measure of organic form of nitrogen and ammonia is Total Kjeldahl Nitrogen (Hajjigholizadeh *et al.*, 2017).

2.2.12. Chlorophyll-a, b and c

Chlorophyll-a is the measurement of the algae that grows in a water body. To describe the trophic state of water, a chlorophyll-a level may be used, while algae are naturally present in freshwater ecosystems. Algae can affect the aesthetic quality for instance, bad odors and green scums. It can decrease levels of dissolved oxygen. When algae is present in high concentrations it can produce toxin that can cause concern to public health (US EPA). Green algae and higher plants contain Chlorophyll-b. Chlorophyll-c is present in brown algae, dinoflagellates and diatoms. Both chlorophyll-b and chlorophyll-c assist chlorophyll-a in photosynthesis (Pareek *et al.*, 2017).

2.2.13. Lake Nutrients and Eutrophication

Lake water quality became a matter of concern since 1960s when people started to use detergents, fertilizers and disposing wastes from industrialized activities. Phosphorus is an important limiting nutrient for algal biomass. It was concluded on the basis of N:P effect on

the algal cells in lake water. It binds with iron, carbonates and aluminium readily and has no gas phase. Then it gets buried in sediments. Limitation of phosphorus is related to the nitrogen deposition from agricultural and atmospheric runoff. These sources can increase limitation of phosphorus and supply nitrogen. Carbon from dissolved bicarbonates in water and atmospheric carbon dioxide makes up half of the algal biomass. It does not affect the long term biomass. It limits short term algal growth. The nitrogen limitation and the ability of nitrogen fixers to continuously satisfy their deficiency of nitrogen is a very important research question. In case of low phosphorus levels, gaseous atmospheric nitrogen is used by cyanobacteria to meet the deficiency. High phosphorus input results in low N:P ratios. The waste from anthropogenic activities releases phosphorus and limits nitrogen. Various studies showed that the total lake phosphorus is a function of external intrusion, hydraulic residence time of lake and tendency of phosphorus to settle down from the water column. Deep lakes having intact watershed vegetation are less eutrophic than the shallow ones. They have large and disturbed watersheds. The relationship between chlorophyll-a and phosphorus shows the algal biomass. If the ratio is less, it means the cell density is low due to limiting factors like nutrients, seasonal mixing, turbidity by minerals, too much algal grazing by filter feeders e.g., mussels or zooplankton and when algae cannot completely consume the available nutrients (Jones and Brett, 2014).

2.2.14. Climate Change and Eutrophication

Change in climate affects eutrophication in lakes. The long term seasonal patterns in relationship with eutrophication has been observed. In response to climate warming, the lake quality decreases (Moss *et al.*, 2011). It is expected that increasing temperatures and storms with fasten nutrient mineralization from catchment soils. This results in increased soil erosion. It will increase addition of nutrients to the lakes ultimately increasing eutrophication. Longer growing seasons and warm conditions are favorable for cyanobacterial growth in lakes because it gives advantage to N-fixing cyanobacteria. Furthermore, this causes anoxia at the lake bottom and enhance the recycling of phosphorus from deep sediments. As a result, algal growth increases and greenhouse gasses such as methane, nitrous oxide and carbon dioxide are released from denitrification. Research suggests that lakes should be managed by controlling nutrients to cope up with changing climatic conditions (Nazari *et al.*, 2018).

2.2.15. Trophic State Index

Carlson's Trophic State Index (TSI) determines lake health using Secchi disc transparency, phosphorus and chlorophyll a concentration. The average values of these parameters determines the TSI of lakes. It is calculated as a biological response when nutrients are added to the lake or the total biomass weight at a specific time and location. This effect varies with seasonal fluctuations, depth and how much zooplankton consume phytoplankton. Following figure shows the types of lakes according to their Trophic State Index value (Devi Prasad *et al.* 2015).

Table 2.1: Lake Trophic States

TSI Values	Trophic Status	Attributes
<30	Oligotrophic	Clear water, oxygen throughout the year in the hypolimnion
30-40	Oligotrophic	A lake will still exhibit oligotrophy, but some shallower lakes will become anoxic during the summer
40-50	Mesotrophic	Water moderately clear, but increasing probability of anoxia during the summer
50-60	Eutrophic	Lower boundary of classical eutrophy: Decreased transparency, warm-water fisheries only
60-70	Eutrophic	Dominance of blue-green algae, algal scum probable, extensive macrophyte problems
70-80	Eutrophic	Heavy algal blooms possible throughout the summer, often hypereutrophic
>80	Eutrophic	Algal scum, summer fish kills, few macrophytes

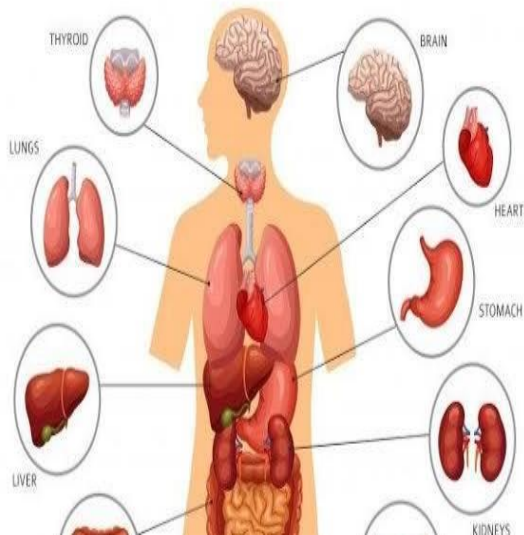
2.3. Heavy Metals

With increasing urbanization and population, heavy metal concentration has increased in past decades (Suman *et al.*, 2018; Ashraf *et al.*, 2019). Heavy metals are dense metallic elements having high atomic numbers and weights. The common heavy metals are cadmium (Cd), mercury (Hg), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), and chromium (Cr). These metals come from anthropogenic and natural sources e.g., generation of water in oil and gas industries (Neff *et al.*, 2011; Pichtel, 2016), use of fertilizers containing phosphate in agricultural sector (Hamzah *et al.*, 2016) sewage sludge (Farahat and Linderholm, 2015), mining and smelting of metals (Chen *et al.*, 2016), application of pesticides (Iqbal *et al.*, 2016), electroplating, and burning of fossil fuels. (Muradoglu *et al.*, 2015).

Heavy metals are non-biodegradable. They can stay in the soil for a long period. They are a threat to the environment (Suman *et al.*, 2018). There are essential and non essential heavy metals on the basis of their role in biological systems.

Table 2.2: Heavy Metals Sources and Impacts

Heavy metals	Sources	Impacts
Cadmium Cd	Weathering of underlying bedrock	Sewage sludge Manure
Chromium Cr	Weathering of Cr-containing rocks	Electroplating, Textile industries
Lead Pb	Forest fires Various erosional processes	Corrosion of materials in the water distribution system
Zinc Zn	–	Discharges of smelter slags Fertilizers



Zinc: Lung failure and diarrhea

Lead: Kidney problems, acute or chronic damage to nervous system

Chromium: Gastrointestinal, kidney or liver damage

Cadmium: Itai Itai disease (Pain in spine and joints), liver damage and abdominal pain

Figure 2.1: Heavy Metals Sources and Impacts

2.4. Dominant algal species

Dominant algal species indicate which algal strain is prominent in eutrophic lakes so that management techniques can be used for their removal. Moreover, some algae can be used for our advantage. Some algal strains have been found in lakes of Pakistan lakes which can be useful for oil production (Manzoor *et al.*, 2016).

Table 2.3: Distribution of Dominant Algal Species in Pakistan

Species	Distribution in Pakistan
1. <i>Chlorella vulgaris</i>	Manghopir eutermal springs, Karachi Lahore, Pasrur, Sialkot, Punjab Keenjhar lake, Thatta, Sindh District Swat, K. P. K
2. <i>Botryococcus braunii</i>	Keenjhar lake, Thatta, Sindh
3. <i>Scenedesmus obliquus</i>	District Swat, K. P. K

4. <i>Scenedesmus quadricauda</i>	Manghopir eothermal springs, Karachi Keenjhar lake, Thatta, Sindh District Swat, K. P. K
5. <i>Scenedesmus dimorphus</i>	Keenjhar lake, Thatta, Sindh District Swat, K.P.K
6. <i>Rhizocolonium hieroglyphicum</i>	Gilgit
7. <i>Scenedesmus acuminatus</i>	Keenjhar lake, Thatta, Sindh
8. <i>Chlorella pyrenoidosa</i>	Haleji lake Keenjhar lake, Thatta, Sindh
9. <i>Scenedesmus bijuga</i>	Keenjhar lake, Thatta, Sindh

2.5. Chlorophyll Content Index

Leaf chlorophyll is an important indicator of green colour in leaves. Greenness in leaves is used to investigate deficiency of nutrients in leaves (Ali *et al.*, 2017). In many agricultural crops, significant correlations have been reported between chlorophyll content and leaf nitrogen. Leaf chlorophyll and dry weight are positively influenced when fertilizers are applied specially nitrogen fertilizer. Chlorophyll can substitute nitrogen content of leaves. It is also an important indicator of deficiency of nitrogen in agriculture. The CCI can be a decisive way for crop N-fertilization. It can also be used to improve biomass estimation and crop yield.

3. METHODOLOGY

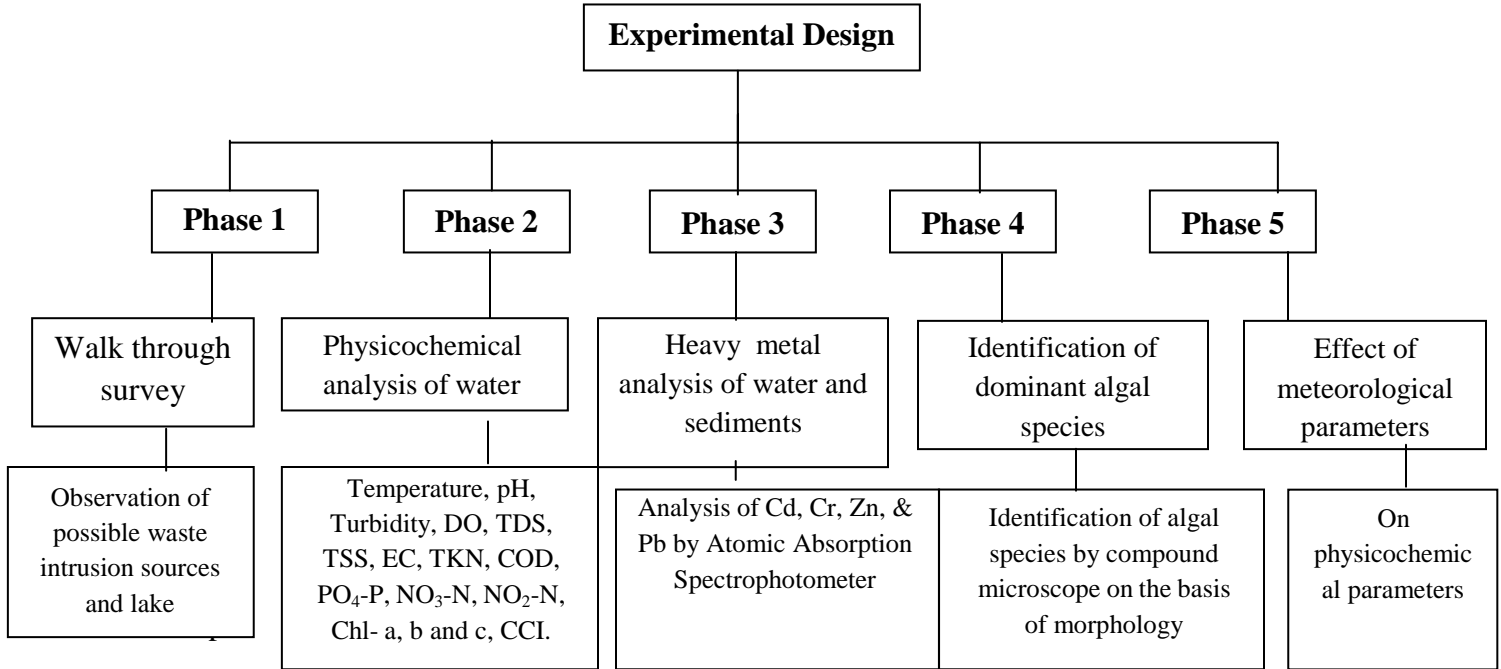


Figure 3.1: Methodology Phases

3.1. Phase 1: Description of Study Area

Three lakes present in National University of Sciences and Technology (NUST), Islamabad Pakistan were studied as research focus area. They were built in 2011 and having a surface area of 1.5, 2 and 2.25 acres, height of 25, 16 – 20 and 25 feet and have storing capacities of 0.17, 0.16 and 0.74 GL, respectively. This data was obtained from (Works Directorate, NUST). The study area is characterized by sub-humid climate and experiences significant changes in seasonal temperatures and precipitation.

Water, sediment and plant samples were collected from shore area of six sampling sites i.e., Inlet and Outlet of lake 1, 2 and 3 as shown in the map (Figure 3.2). A total of 24 samples of surface water were collected from all the sampling locations over the period of four months (September 2021 to December 2021) using sterilized glass sampling bottle. 54 sediment samples and 48 plant samples were collected for analysis. Before collecting water samples, the bottles were rinsed 2-3 times with the sample water. Sampling points and coordinates are shown in Table 3.1.

Table 3.1: Sampling Locations with Coordinates

Sr. No.	Sampling location	Sampling points	No. of samples	Coordinates	Location of sampling points
1	Lake 1	Inlet	15	33°38'31.43"N 72°59'10.48"E	Opposite to NICE Cricket Ground
		Outlet	15	33°38'26.72"N 72°59'20.46"E	Left side of bridge behind Attar Hostel
2	Lake 2	Inlet	15	33°38'26.21"N 72°59'23.08"E	Right side of bridge behind Attar Hostel
		Outlet	15	33°38'22.72"N 72°59'31.29"E	Opposite to Saddle club
3	Lake 3	Inlet	15	33°38'21.56"N 72°59'42.53"E	Opposite NUST Sports Complex
		Outlet	15	33°38'27.58"N 72°59'54.45"E	Opposite NUST Sports Complex

3.2. Phase 2: Water Quality Analysis

3.2.1. Physicochemical Analysis

Physicochemical parameters along with their instruments and methods are shown in Table 3.2

Table 3.2: Methods used for Physicochemical Parameters

Parameters	Units	Instruments/ Method used	Protocol
pH	-	HACH 156 pH meter	APHA, 2017
Temperature	°C	Laboratory Method-HACH	
Electrical Conductivity	µS/cm	Potentiometric Method-Conductivity Meter	
Turbidity	NTU	Turbidity meter(HACH 2100N)	
Dissolved Oxygen	mg/L	DO meter (HACH 156)	
Total Dissolved Solids		Gravimetric method	
Total Suspended Solids		UV-Spectrophotometer (Colorimetric Method)	
Phosphates			
Nitrates			
Nitrites		Kjeldahl Assembly	
Total Kjeldahl Nitrogen		COD Digester	
Chemical Oxygen Demand	mg/m ³	UV-Spectrophotometer	
Chlorophyll- a, b and c	-	Chlorophyll meter ccm-200 plus	
Leaf Chlorophyll Content Index			

On Site Analysis: pH, temperature, turbidity, electrical conductivity, chlorophyll content index and dissolved oxygen were performed on-site using portable measuring instruments/meters.

Laboratory Analysis: Chemical oxygen demand, Total Kjeldahl nitrogen, nitrates, nitrites, phosphates, total dissolved solids, total suspended solids, and chlorophyll a,b and c were analyzed in laboratory using standard methods within 3-5 hours of sample collection. Atomic absorption spectrophotometer was used in laboratory for heavy metal analysis of water, sediments and plants. Moreover, compound microscope was used for identification of algae.

3.3. Phase 3: Heavy Metal Analysis

3.3.1. Sample preparation for AAS Analysis

Water: To remove suspended particles from samples, they were filtered through 0.45 mm pore size filter paper and analytical grade nitric acid (one part) was added in each sample for preservation of metal contamination. Next, prepared samples were stored in pre-cleaned plastic bottles within refrigerator (Saleem *et al.*, 2019).

Sediments and Plants: Sediment samples were collected from sampling sites using grab sampling method. They were dried at 40 °C to remove all the moisture content present. The samples which were dried were finely powdered using a mortar and pestle (Rajeshkumar *et al.*, 2018). About 1–2 g of dried sediment samples were digested using a freshly prepared mixture of acid containing 9 mL of HNO₃ and 3 mL of HCl. After digestion, residue of digested sample was diluted with distilled water up to 25 ml (Javed *et al.*, 2018). In case of flora, 1g of powdered leaves and 15ml of HNO₃ was added and similar process of digestion was repeated.

Atomic Absorption Analysis

Atomic absorption spectrophotometer was used to determine the concentration of selected trace heavy metals water, sediments and plants.

3.4. Phase 4: Identification of Dominant Algal Species

Dominant algal species were observed under the compound microscope on the basis of their morphology.

Phase 5: Meteorological Parameters

Data for meteorological parameters were collected from US-Pak Center for Advanced Studies in Energy (USPak-CASE), NUST for six months i.e. from September 2021 to December, 2022. Data for Global Horizontal Index (W/m²), Ambient Temperature (°C), Wind Speed (m/s) and (%) and Rainfall (mm) were collected and compared with physicochemical parameters.

3.5. Correlation

Pearson correlation matrix was used to determine correlation between the variables.

CHAPTER 4

4. RESULT AND DISCUSSION

The present study addresses the issues related to quality of water. For this purpose, physicochemical and microbiological parameters of water samples collected from NUST Lakes were analyzed using WHO and Pak-EPA Standards as shown in Table 4.1.

Table 4.1: WHO and Pak-EPA Permissible Limits for Physicochemical Parameters

Parameters	Units	Pak-EPA	WHO
Ph		6.5-8.5	6.5-8.5
Temperature	°C	-	-
EC	μS/m		1000
Turbidity	NTU	5	5
DO		-	-
TDS		<1000	<1000
TSS		-	-
Nitrate	mg/L	50	50
Nitrite		<3	3
TKN		-	0.5
Phosphate		-	0.3
COD		-	-
Chlorophyll-a,b and c	mg/m ³	-	-
CCI	-	-	-

Table 4.2: WHO and Pak-EPA Permissible Limits for Heavy Metals

Heavy Metals	Units	Pak-EPA	WHO
Cadmium		0.01	0.003
Chromium		<0.05	0.05
Lead	mg/L (ppm)	<0.05	0.01
Zinc		5	3

4.1. Phase 1: Walk Through Surveys and Water Sample Collection

Through walk through survey of the three lakes, we came to know the difference between lake conditions and possible waste intrusion sources.

4.1.1. Lake Conditions

At L1, the water looked murky, and a significant amount of foam formation was observed because of wastewater intrusion (from surrounding hostels) and excessive nutrients input (Fig 4.1). Algal and excessive vegetative growth was also observed. L1 had unpleasant odor, direct dumping of garbage and wastewater intrusion from surrounding was observed. During sampling at regular time intervals, water from a few inlets feeding water to the L1 was observed.



Inlet

Outlet

Figure 4.1: Lake 1 Sampling points

At L2, foaming was observed, and water intrusion was sensed (likely due to the external water discharge) at the sampling sites (Fig 4.2), however, no apparent source could be seen due to limited mobility, owing to heavy vegetation. Direct discharge from surrounding, plastic bags, massive algal growth and unpleasant odor in water were observed. Water at this lake was more turbid, probably due to the presence of ducks and their fecal material.



Inlet

Outlet

Figure 4.2: Lake 2 Sampling Points

The water quality at L3 looks quite well, compared to two other lakes, but excessive plant growth and moderate algal growth was observed (Fig 4.3). Like the other two lakes, this lake also had an unpleasant odor.



Inlet

Outlet

Figure 4.3: Lake 3 Sampling Points

4.2. Phase 2: Physicochemical Parameters

4.2.1. pH

The value for pH ranged from 7.4-7.8 during the study period. Higher pH values are due to change in physicochemical parameters resulting in carbon dioxide, carbonate and bicarbonate equilibrium (Bhateria and Jain, 2016). Higher pH values were observed at all lake points due to nutrient intrusion and organic load. These values were in accordance with a study where pH ranged from 5.5-7.5 in winter season (Rao *et al.*, 2019).

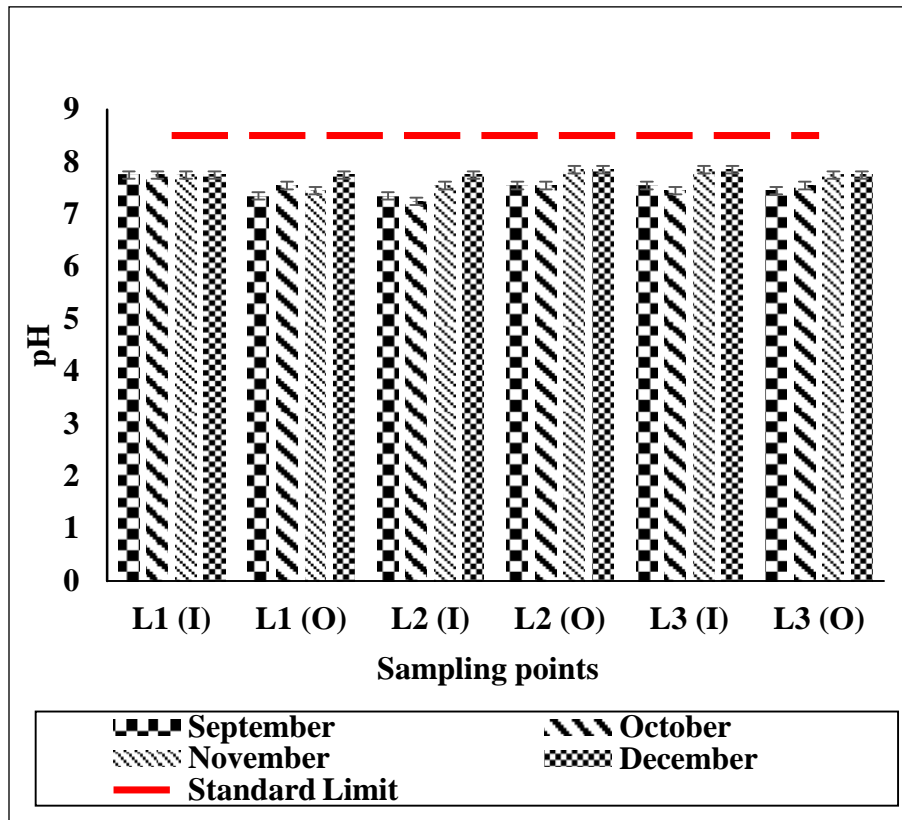


Figure 4.4: Average Profile of pH at all Sampling Sites

4.2.2. Temperature

The temperature of lakes is impacted by many factors including presence of vegetation, season, time of the day and total dissolved solids in water (Tibebe *et al.*, 2019). The temperature profile of all the selected sites showed a decline from 34.7 °C (september) to 13.4 °C (december). L3 (I) had highest temperature and lowest temperature was observed in L3 (O).

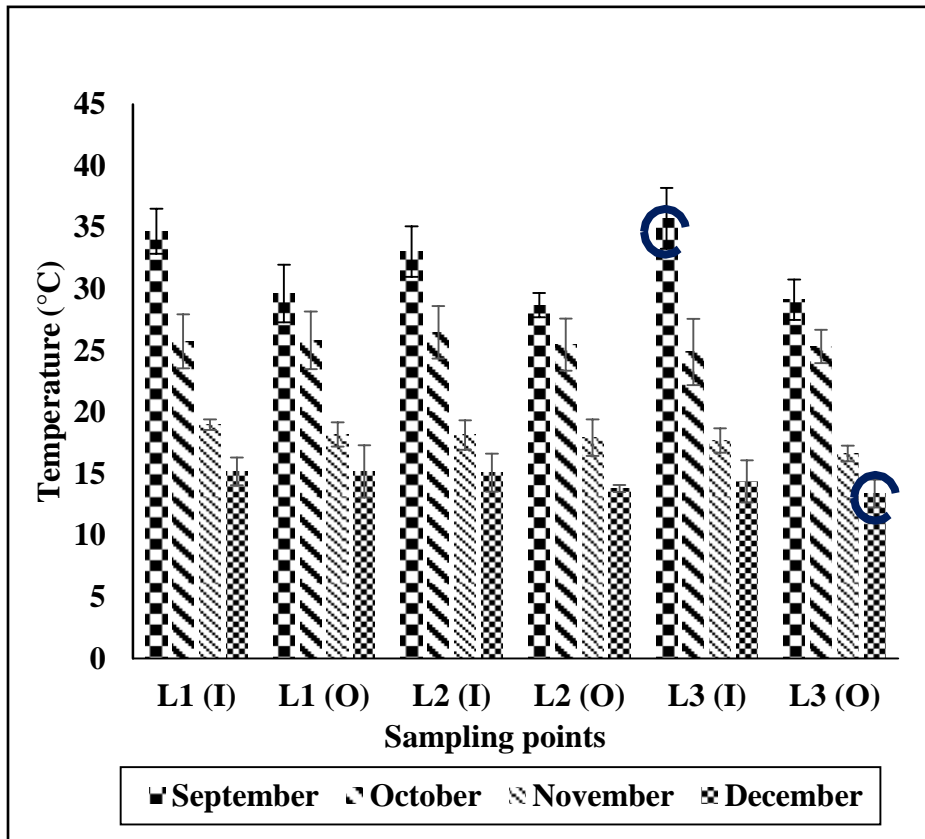


Figure 4.5: Average Profile of Temperature (°C) at all Sampling Sites

4.2.3. Electrical Conductivity

EC ranged from 570-1686 uS/cm. The lowest values were observed in L1 (O) and L2 (I) in the month of September. The values were above the WHO permissible limit i.e., 1000 μ S/cm. The conductivity values showed a high trend at L3, and L1 than at L2. It was probably due to a change in dilution factor resulting in a decrease in conductivity. The highest values were at L2O in December. In L3, EC was high probably due to discharge of wastewater from apartments, saddle club as well as collective waste discharge from L2 and L1. EC shows a direct relation with dissolved solids. High values of EC were indicator of contaminants in surfacewater (Wang *et al.*, 2019).

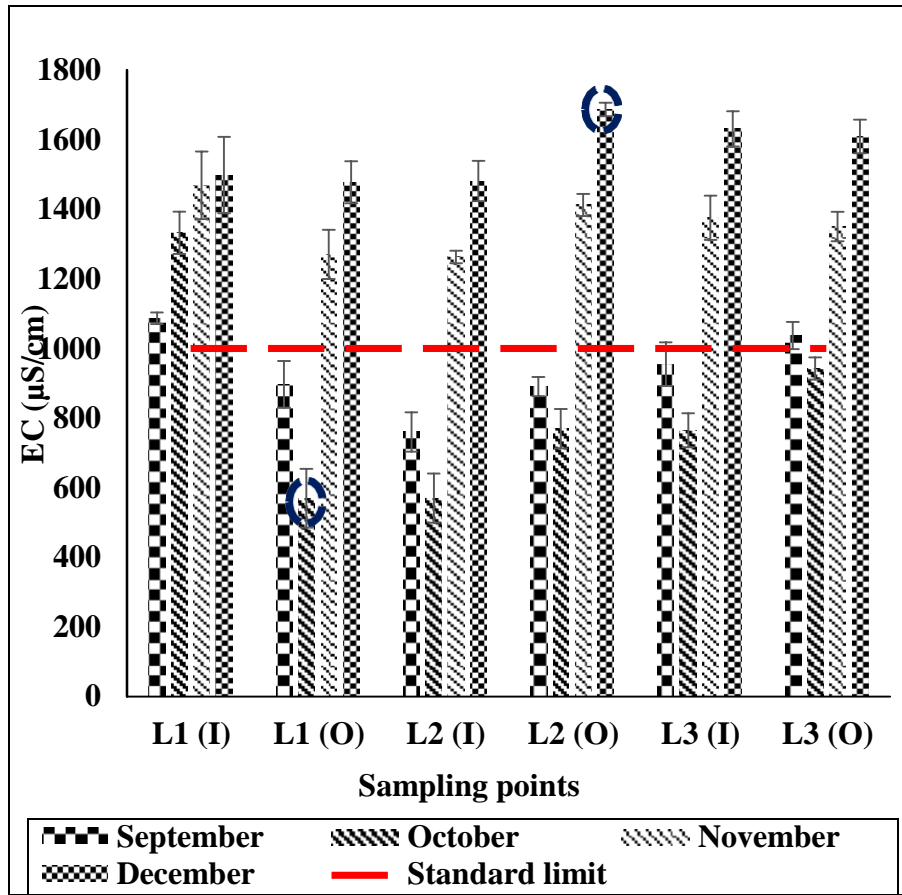


Figure 4.6: Average Profile of Electrical Conductivity (EC- $\mu\text{S}/\text{cm}$) at all Sampling Sites

4.2.4. Dissolved Oxygen

The dissolved oxygen ranged from 1.9-3.2mg/L. It shows inverse relation with temperature. The values increased in winters from september to december. DO is affected by temperature of water and is important for the aerobic respiration and survival of aquatic organisms. During sampling period, all the sites showed almost similar trend with little variation. Low DO values were observed at L3 (I) in september and high values in december at L3 (I). A study was conducted in 2007 on lake water. Low DO values were noted in august (2007) i.e., (2.26 mg/L) and high values were noted in january (6.55 mg/L) (Rao *et al.*, 2019).

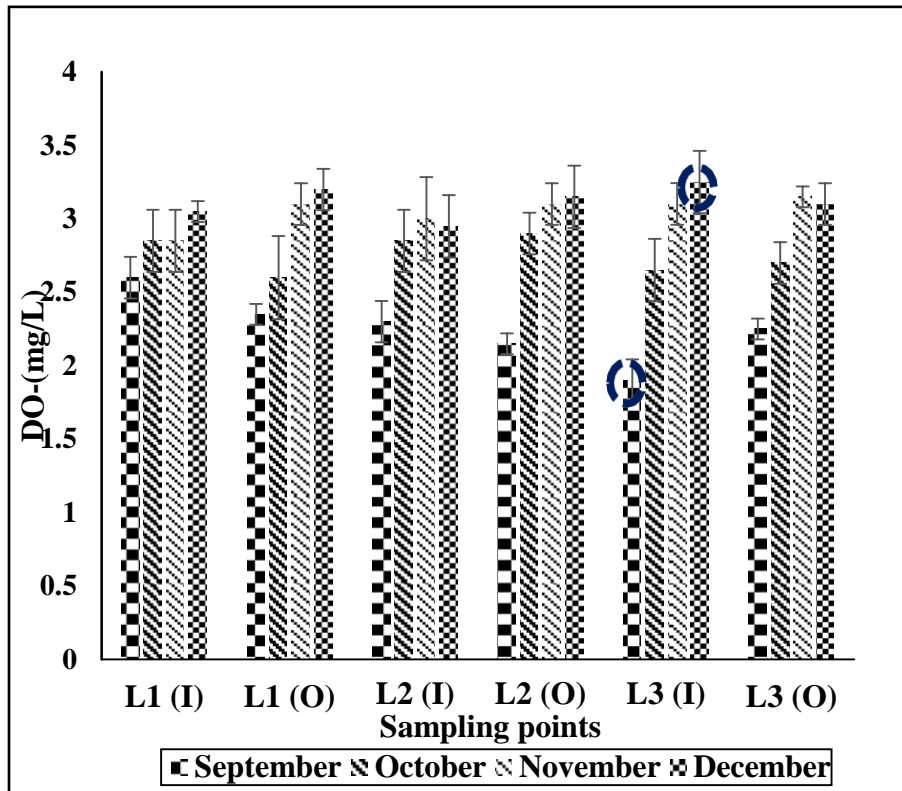


Figure 4.7: Average Profile of Dissolved Oxygen (DO-mg/L) at all Sampling Sites

4.2.5. Turbidity

The turbidity ranged from 24.6-90.2 NTU. Values were high at all points than WHO permissible limits. L3 had greater turbidity as compared to L2 and L1. The probable reason for high turbidity at L3 is excessive vegetation and direct disposal of untreated water. Generally, the reasons for high turbidity can be silt, mud, algae, vegetation, and waste. Ouma *et al.*, 2016 also reported high turbidity in surface water and associated high turbidity with high coliform load.

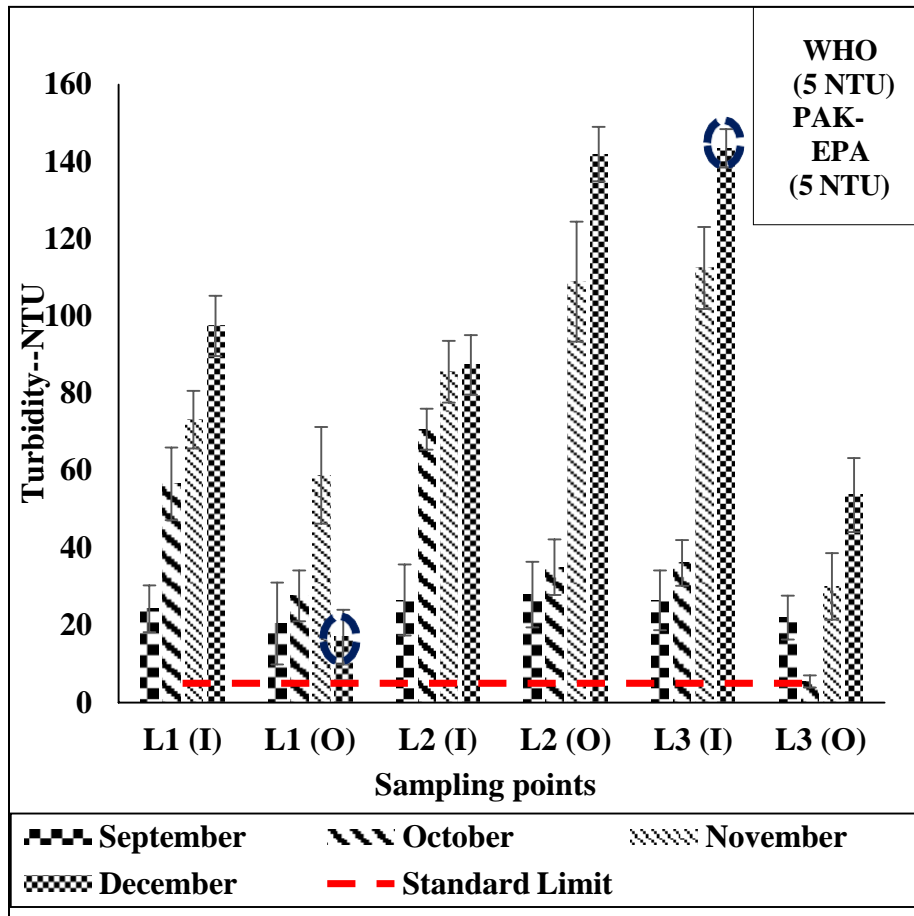


Figure 4.8: Average Profile of Turbidity (NTU) at all Sampling Sites

4.2.6. Total Dissolved Solids

The values of TDS was from 420-905 mg/L. L1 shows high TDS particularly at inlet because of mixing of pollutants from hostels and garbage dumping and lowest concentration was observed at L3(O) in december. TDS values showed variation in all months at all lake points. Presence of organic and inorganic content in water represent the TDS values in water. The values for TDS were within the range but were at the higher end. TDS shows linear relationship with EC. EC and turbidity values were high in winters. Maximum value of TDS was observed in october and november and most of the time decreasing trend of TDS was found from L1>L2>L3. High concentration of TDS enhance the nutrient status of water body resulting in eutrophication. These results were in accordance with a study where TDS values in lake were >800mg/L (Maliki *et al.*, 2020).

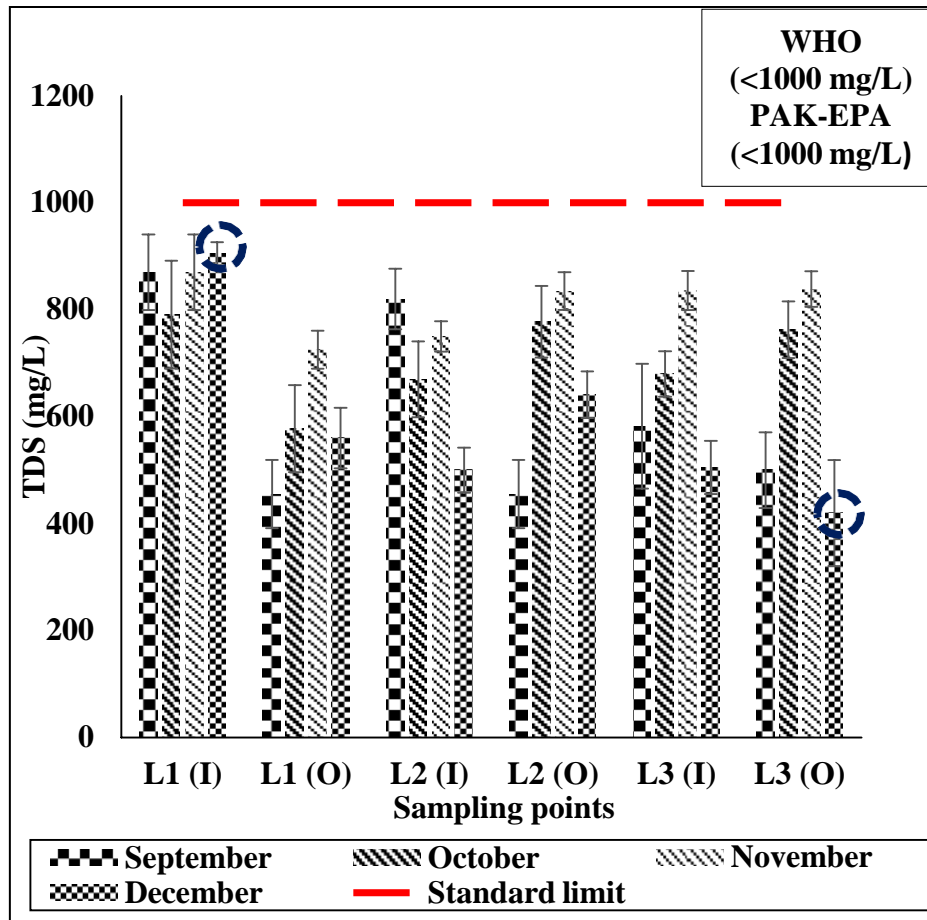


Figure 4.9: Average Profile of Total Dissolved Solids (TDS- mg/L) at all Sampling Sites

4.2.7. Total Suspended Solids

The values of total suspended solids ranged from 25-67.5 mg/L during the study period. In all sampling months, most of the time decreasing trend of TSS was observed from L1>L2>L3. Insignificant variation was observed at L3(I) from september to december. High values were observed at L2(O) depending upon rainfall, waste discharge and landscape features. In a water body, high TSS may often be associated with higher mean concentrations of bacteria, nutrients, clay, silt, plankton, and metals in water. The suspended solids result in the turbid appearance of water and this also depends on seasonal regimes of rainfall, landscape features and discharges in water body. TSS values ranged from 39.3-124.3 mg/L according to a study conducted on estimation of water quality parameters of a lake (Lashari *et al.*, 2022).

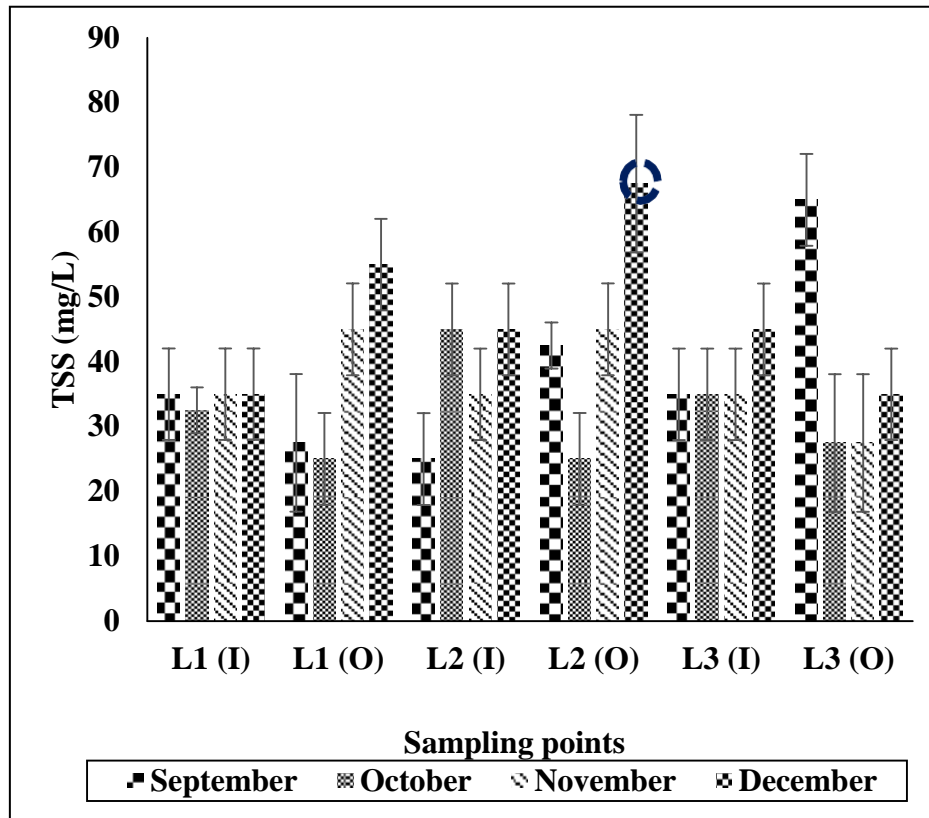


Figure 4.10: Average Profile of Total Suspended Solids (TSS- mg/L) at all Sampling Sites

4.2.8. Nitrate

Nitrate concentration ranged from 0.1-0.35 mg/L. Disposal of untreated wastewater, animal waste, and decaying plant debris adds nitrates to lakes. The values decreased from September to December except L2 (O). High nitrate concentration was observed at L2 (O) in December. L3 (O) had lower nitrate concentration in September. L1 (I) and L3 (I) showed maximum values for nitrates throughout the study period. A decreasing trend was observed from L3, L1, and L2. These values were in accordance with a study where >1 mg/L nitrates were found in winters between June to December. High temperature allows water to mix in summers making it chemically rich (Rao and Azmi., 2019). The nitrate concentration was found to be within the permissible limit.

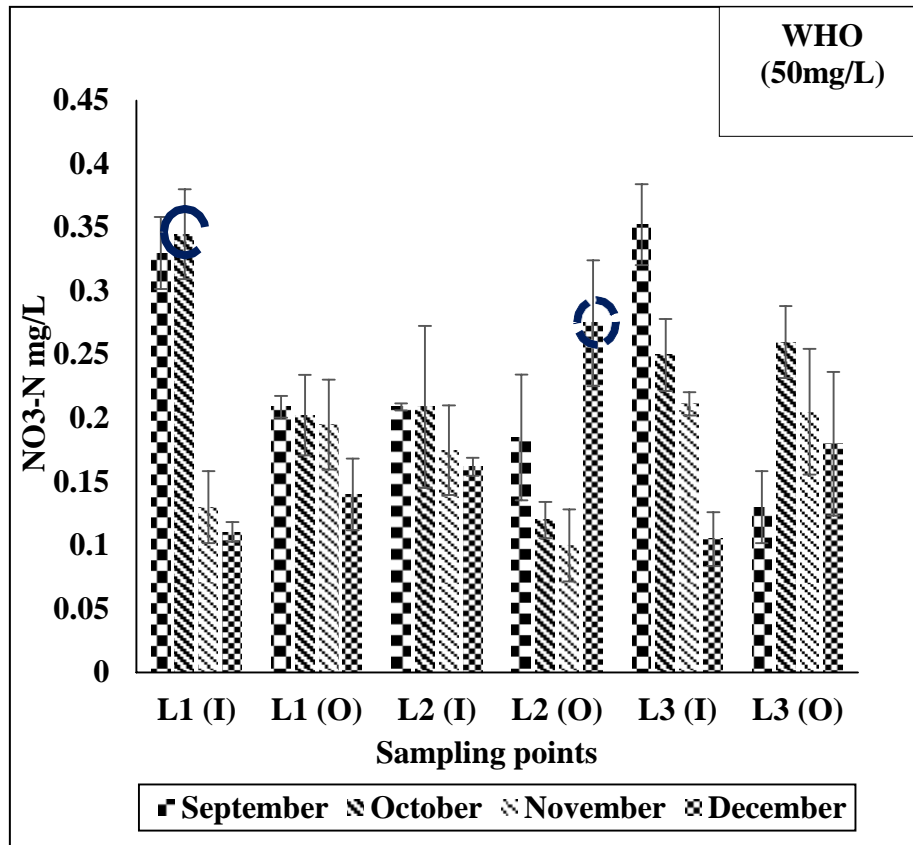


Figure 4.11: Average Profile of Nitrate (NO₃-N- mg/L) at all Sampling Sites

4.2.9. Nitrite

When ammonium is transformed into nitrates by microscopic organisms, nitrite (NO₂) is formed as an intermediate product. It is therefore occasionally raised in water body for a long time. Nitrite is also a transitional product. It transforms to nitrogen gas through denitrification. Values of nitrite ranged from 0.01-0.8 mg/L. Highest values were observed in october at L1. Points having high concentration was due to organic waste discharge. In all lakes, concentration of nitrite was below the permissible limit. Mostly elevated concentration of nitrite was observed at L1 (I) and L3 (O) because of direct discharge of organic wastes or sewage at this point. These results were in accordance with a study in which low nitrite conc. i.e., 0.78-0.84 mg/L in a lake in winters due to low temperature was reported (Kanownik *et al.*, 2019).

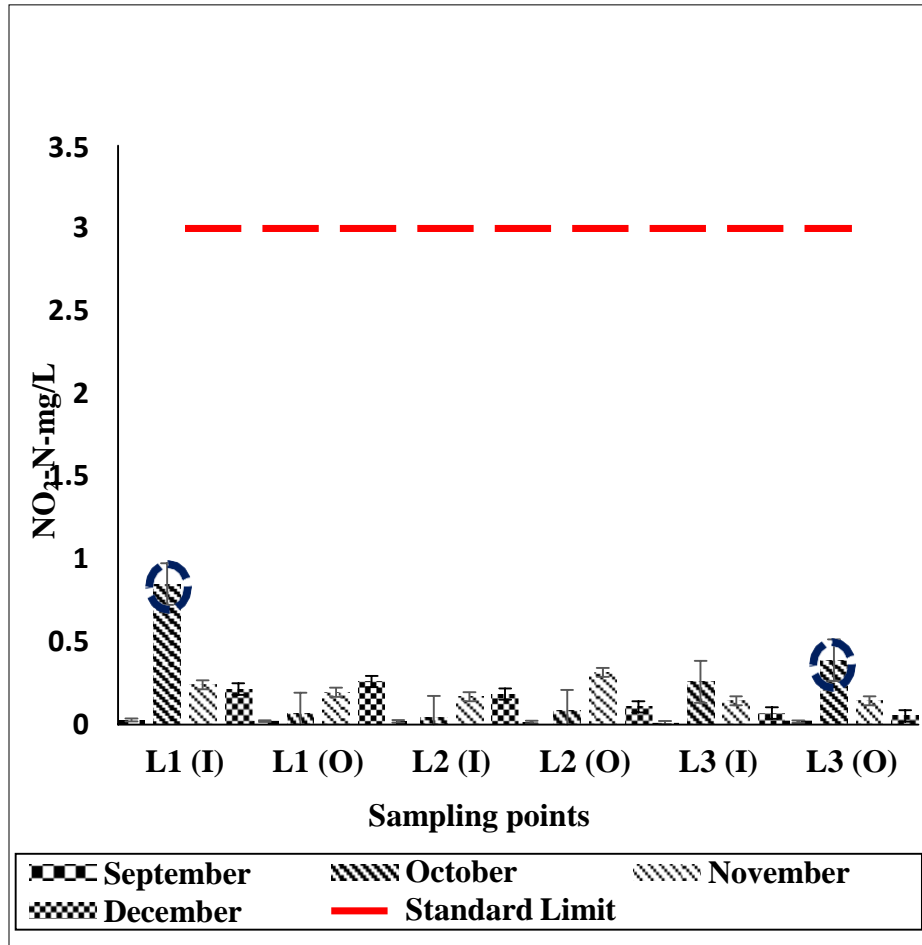


Figure 4.12: Average Profile of Nitrite (NO₂-N-mg/L) at all Sampling Sites

4.2.10. Total Kjeldahl Nitrogen

TKN is a measure of both organic forms of nitrogen and ammonia. TKN values exceeded WHO limits at all sampling sites and ranged from 26.5-97.6 mg/L. In L1 (I) high values were observed due to direct discharge of nutrient rich water. In water with phosphates, algal growth is also high. In surface water, the organic nitrogen of TKN is much higher than the ammonium-nitrogen fraction, and in water with high algal growth and phosphate content, the values for TKN is also elevated. According to a study, high values of total nitrogen were reported in winters in surface water as compared to summers, due to negligible nitrogen uptake and low temperature during this period by Phyto benthos, macrophytes and algae (Kanownik *et al.*, 2019).

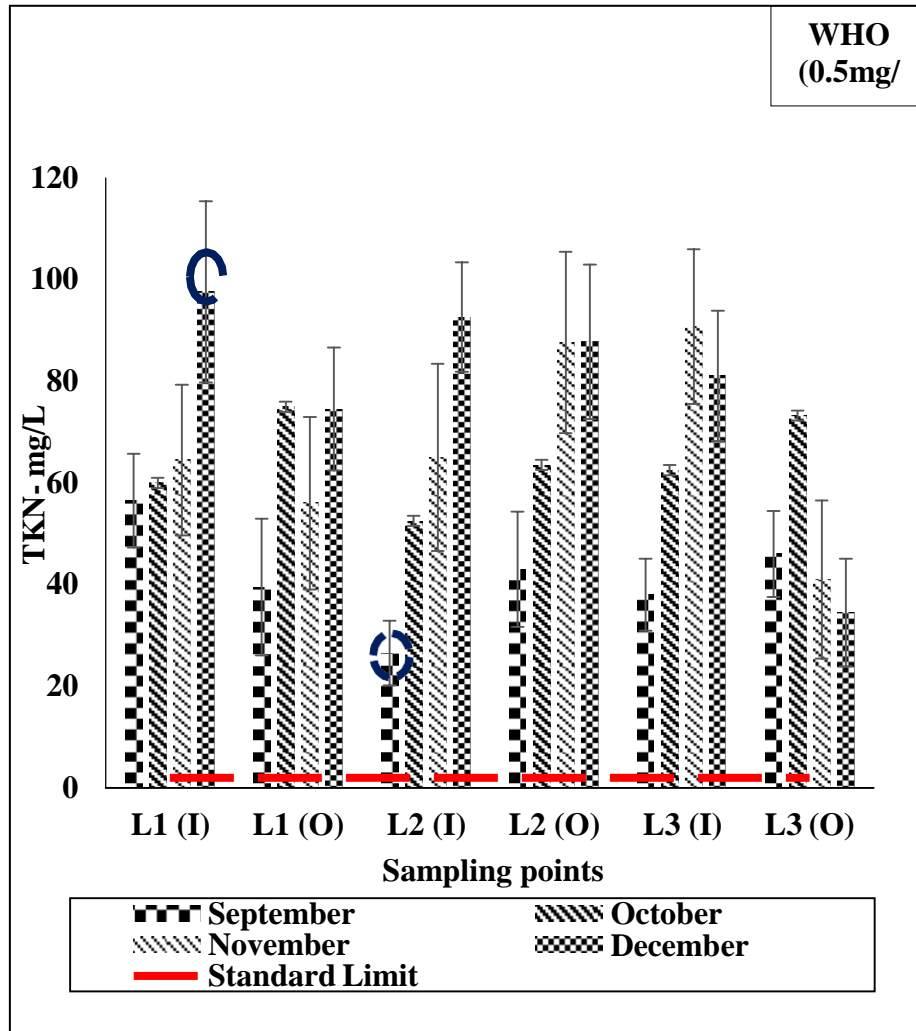


Figure 4.13: Average Profile of Total Kjeldahl Nitrogen (TKN- mg/L) at all Sampling Sites

4.2.11. Phosphate

The phosphate ranged from 0.47-0.75 mg/L. They were above the WHO permissible limits. The trend showed decreasing values from L2 to L1 and L3. In L1 (I), maximum phosphate concentration was observed and at L3 (O), phosphate concentration was high in September. Detergents, human wastes, rain and runoff can be one source of phosphate. Phosphates are also responsible for white foam formation. It acts as a barrier oxygen and light penetration in the water (Ramachandra *et al.*, 2021).

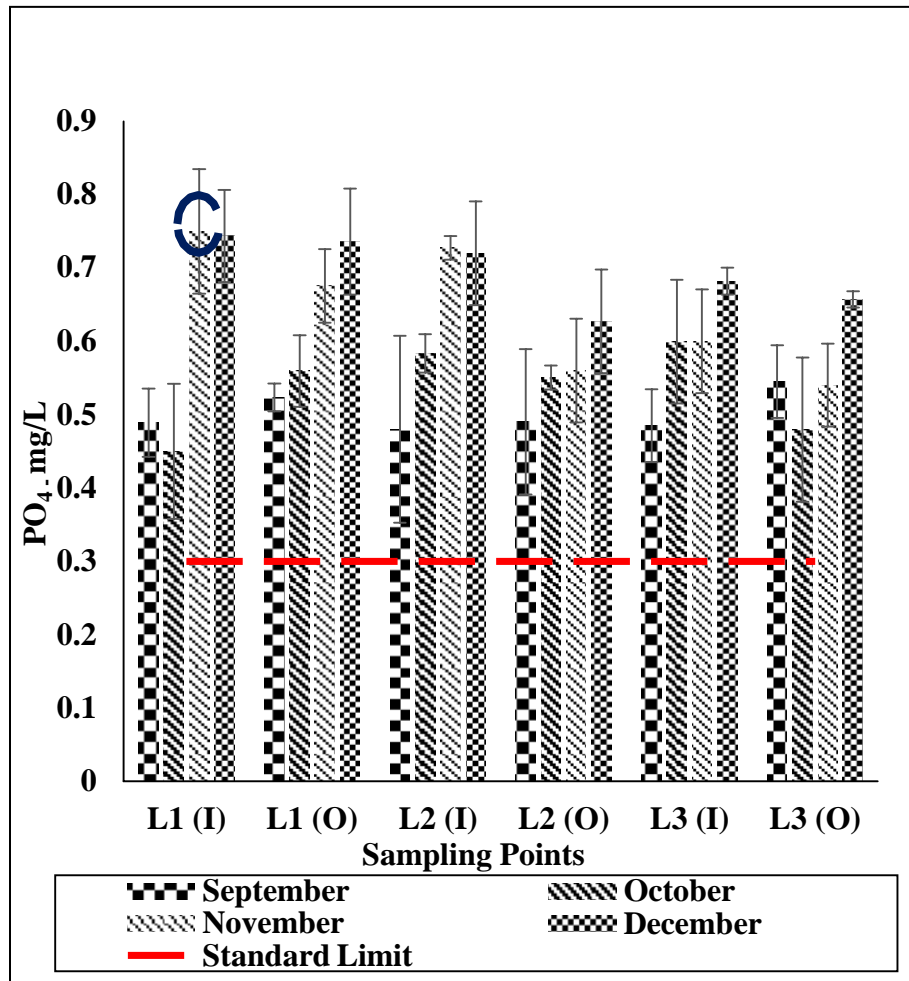


Figure 4.14: Average Profile of Phosphate (PO₄-mg/L) at all Sampling Sites

4.2.12. Chemical Oxygen Demand

Chemical oxygen demand in water shows the presence of all forms of organic matter, both biodegradable and non biodegradable and hence, indicates the level of pollution in water ecosystem. Considerable amount of dissolved solids and algae cells can be a reason behind high values of COD. The values of COD ranged from 187.4-502 mg/L during the study period. Maximum COD values were observed in November at L3 (O) and minimum values at L3 (I) in December. Variation in concentration was observed at all lake points in all months. L1 had highest values as compared to L2 and L3. Almost all sampling sites showed moderate to high value of COD. High values at L3 (I) and L3 (O) is showing pollution load that is caused by the mixing of sewage water from sports complex as well as from other internal and external sources. Overall trend ranged from L1>L2>L3. Considerable amount of suspended solids and algae cells can be a reason behind high values of COD (Weerasinghe *et al.*, 2019).

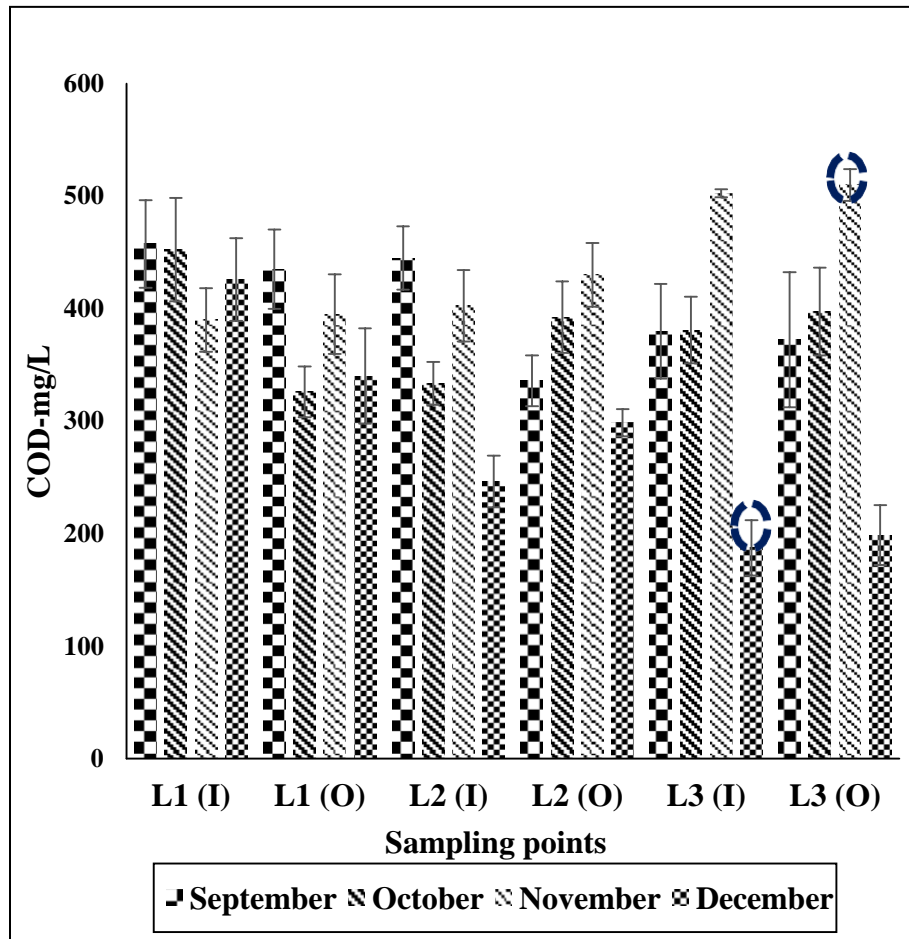


Figure 4.15: Average Profile of Chemical Oxygen Demand (COD- mg/L) at all Sampling Sites

4.3. Chlorophyll-a,b and c

The average chlorophyll ranged from 0.00007-0.0006 mg/L. Maximum concentration was observed in December at L3 (I). A slightly high value was observed at L1 (I) in November due to excessive vegetation and algal growth. The possible causes of fluctuation in lake water are nutrient, turbidity, high wind and rainfall in relation with plenty of plankton in lake. According to a study conducted in Iran in 2018, oligotrophic waters have high depth and clarity as well as little algae contained. When chlorophyll content is less than 0.1 ug/L, water body is oligotrophic (Esfandi *et al.*, 2018).

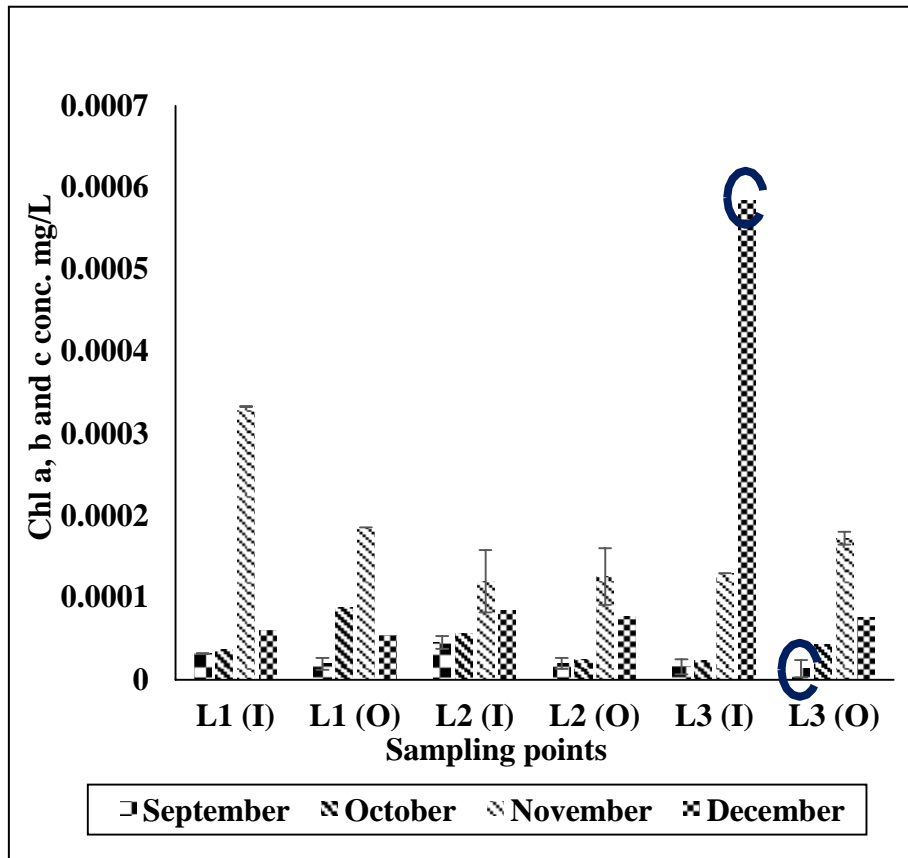


Figure 4.16: Average Profile of Chlorophyll a, b and c (mg/L) at all Sampling Sites

4.4. Chlorophyll Content Index (CCI)

The leaf chlorophyll content index was measured by a chlorophyll meter. The average values ranged from 3.7-165.3. The alphabets on the graph represent the species at lake points. The plant names are mentioned in the box. *Stellaria graminea* is widely spread in lakes. Due to the direct intrusion of wastes and nutrients from L1 and surrounding sources, the highest values of chlorophyll were noted in *Stellaria graminea* at L2 (I) and an insignificant concentration was found in *Sapium sebiferum* at L1 (O). As it was a one-time measurement, repeated analysis of the chlorophyll content in leaves can tell the exact reason behind the variations. Usually, nitrate concentrations affect the plant's photosynthetic process. Temperature and precipitation levels affect the leaf chlorophyll content (Liu *et al.*, 2019).

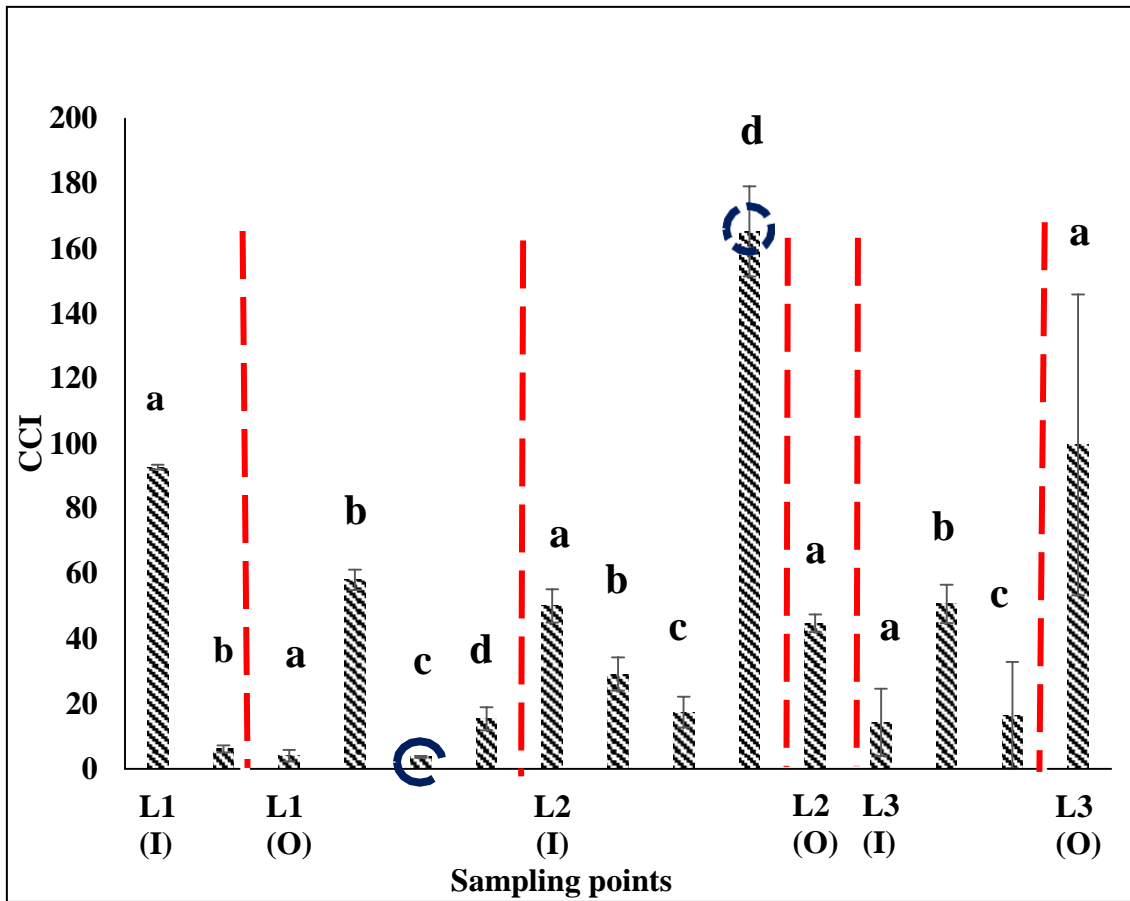


Figure 4.17: Average Profile of Chlorophyll Content Index (CCI) at all Sampling Sites

Table 4.3: Plants at Lake Points

Sampling Points	Species
L1 (I)	a. <i>Bombax ceiba</i> b. <i>Sapindus mukorossi</i>
L1 (O)	a. <i>Bischofia javanica</i> b. <i>Bombax ceiba</i> c. <i>Sapium sebiferum</i> d. <i>Stellaria graminea</i>
L2 (I)	a. <i>Tecoma stans</i> b. <i>Salix babylonica</i> c. <i>Bischofia javanica</i> d. <i>Stellaria graminea</i>
L2 (O)	a. <i>Albizia lebbeck</i>
L3 (I)	a. <i>Eucalyptus camaldulensis</i> b. <i>Bombax ceiba</i> c. <i>Sapium sebiferum</i>
L3 (O)	a. <i>Casia fistula</i>

4.5. Phase 3: Heavy Metals Analysis

An attempt was made to identify the presence of heavy metals (Cd, Cr, Zn and Pb) in plants, water and sediments for the better understanding of pollutants in lake.

4.5.1. Chromium (Cr)

Chromium encourages asthmatic and allergic reactions. It is carcinogenic, and 1000 times more toxic than trivalent chromium. Diarrhea, gastrointestinal, intestinal bleeding, cramps, liver, and kidney damage are all side effects of hexavalent chromium exposure.

4.5.2. Lead (Pb)

Lead contaminates the soils, air, and water as it is emitted into the environment. Lead dust will last forever in the atmosphere. Adults who are exposed to lead can experience high blood pressure, cardiovascular symptoms, hypertension, and reduced kidney functioning.

4.5.3. Zinc (Zn)

Most zinc in lakes settles at the bottom and does not dissolve there. Fish in these lakes may have high zinc concentration. High levels of zinc are often found in air, water and soil with high concentration of other metals such as lead and cadmium.

4.5.4. Cadmium (Cd)

Cadmium is extremely toxic, even at a low concentration, and can damage organs like the kidneys, liver, and lungs. As a result, trace and ultra-trace Cd determinations in environmental and biological samples are now more common.

4.6. Heavy Metal Concentration in Water and Sediments of NUST Lakes

Heavy metal concentration in lake water was maximum at L2 (I) and minimum at L1 (O). Lowest concentration of Cr was observed at L1 (O) i.e, 0.00076 mg/L. In water, Pb was below detection limit and Cd was only detected at L3.

Sediment analysis for water samples showed maximum concentration of Zn at L3 (O) and minimum concentration of Cr at L2 (O). In sediments, Pb and Cd were below detection limit. The metals are transported by precipitation, sorption and dissolution processes, which affect their bioavailability. After some time, precipitation of metals to the sediments takes place by (sedimentation, complexation and adsorption of clay particles) and they accumulate there. After that they reach to a higher level in the food chain (Gunes *et al.*, 2021)

As a result, more heavy metals are found in the sediments than water. Metals present in sediments again get mixed with water by resuspension, desorption and can be dangerous for aquatic organisms. Therefore, we can measure metal pollution in lakes by sediments. High concentrations are a threat to the ecosystem. Therefore, the water and sediment concentrations

can evaluate risks by human activities, effects of industries e.g., impact caused by discharge of wastewater in the rivers.

Relatively high concentrations of Zn was found in water and sediments as compared to other metals but concentration might fluctuate due to change in weather conditions and levels of waste intrusion.

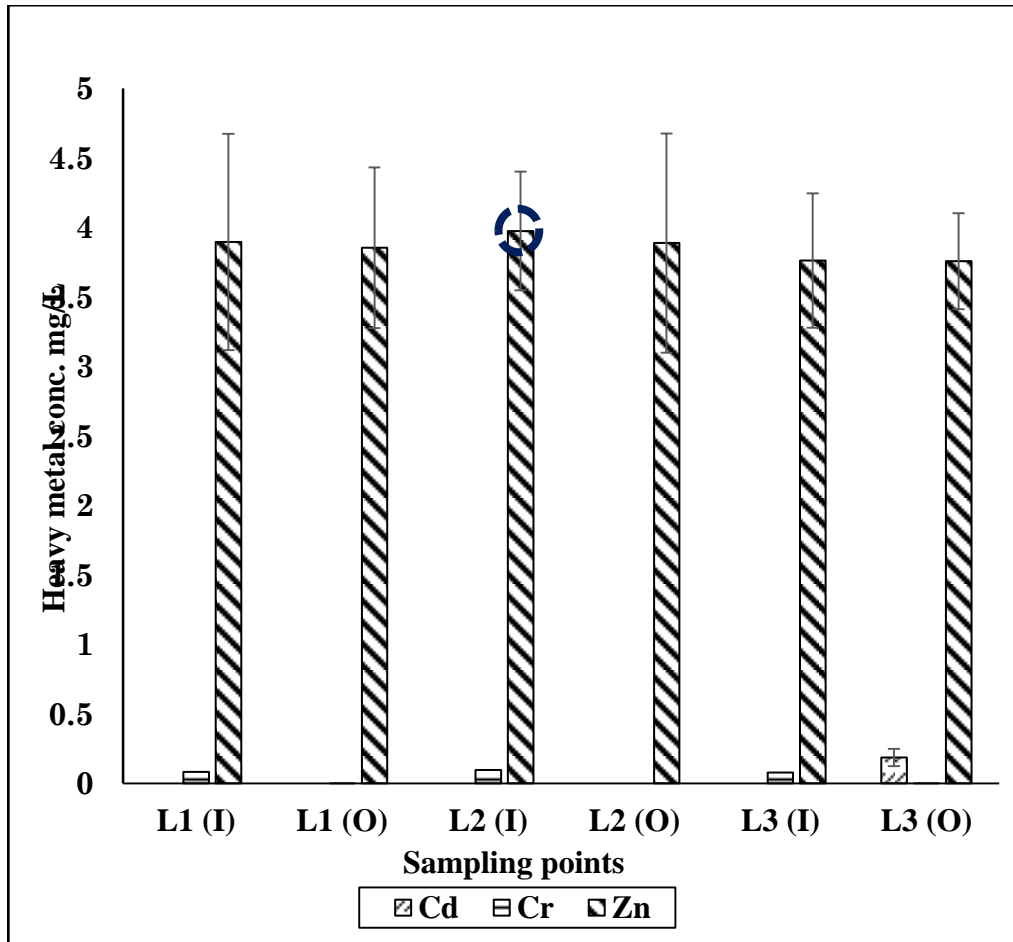


Figure 4.15: Average Profile of Heavy Metals in Water at all Sampling Sites

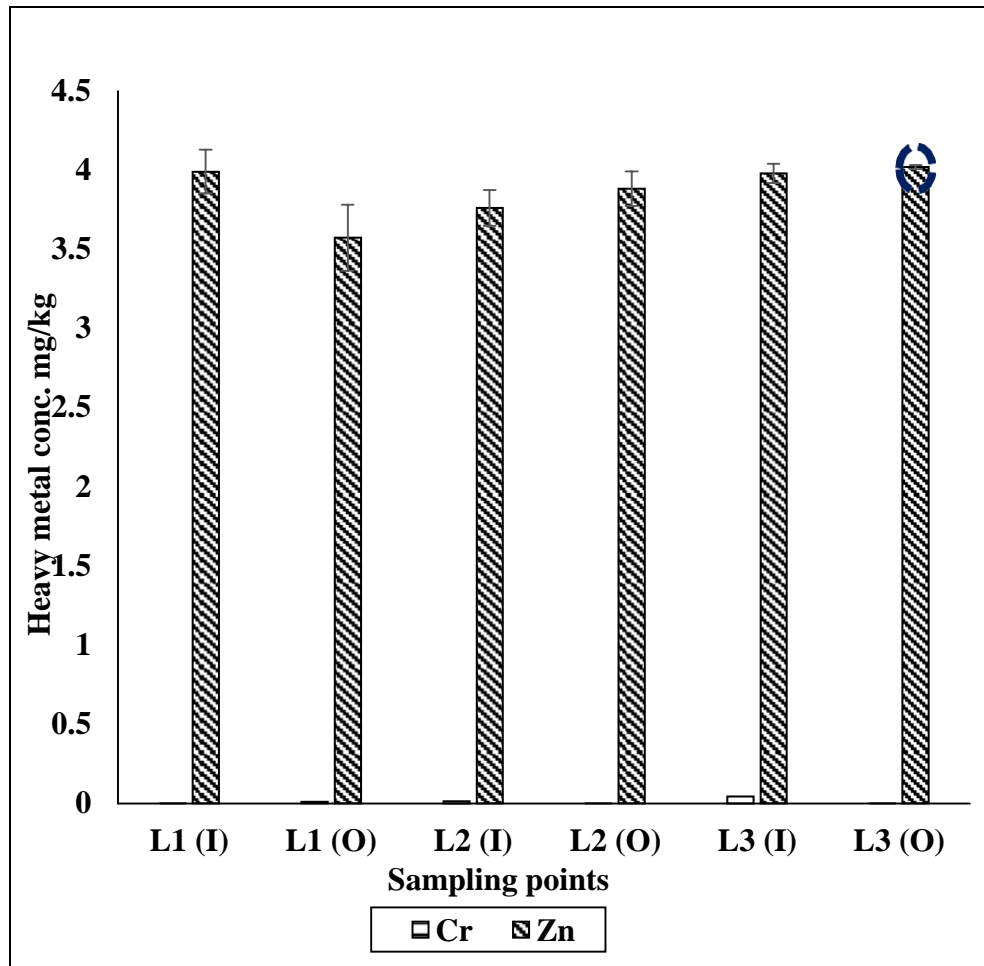


Figure 4.16: Average Profile of Heavy Metals in Sediments at all Sampling Sites

4.7. Heavy Metal Absorption in Plants

Heavy metals in soils have increased rapidly due to anthropogenic and natural activities. Heavy metals persist in environment because they are non-biodegradable. They become part of food chain through crop plants. They accumulate in human bodies through biomagnification. **Phytoremediation** is an approach that is environment friendly. It may be a great way to grow vegetation in soil affected by metals in a cost-effective way and remediate contamination.

There are two types of heavy metals.

Essential heavy metals (Cu, Fe, Mn, Ni and Zn)

Non essential heavy metals (Pb, Cd, As, and Hg)

Essential heavy metals are important for running physiological and biochemical processes during life cycle of plants. They can become very toxic when they exceed the limit. These metals affect biochemical and physiological processes in crop plants and decrease productivity in agriculture. They accumulate in human body through biomagnification (Fasani *et al.*, 2018).

4.8. Uptake Mechanism and Translocation of Heavy Metals in Plants

Different processes are involved in the accumulation of heavy metals in plants including their mobilization, xylem loading and uptake by roots, transport from root to shoot, compartmentation of cells and sequestration. Heavy metals are present in soil in insoluble state. They are not easily bioavailable. Plants release different root exudates which affect the pH in root zone and increase solubility of metals (Dalvi and Bhalerao, 2013). After entering the root cells, heavy metal ions can create complexes with organic acids.

4.9. Phytoremediation

There are different phytoremediation strategies to remediate soils contaminated with heavy metals.

Phytostabilization— involves usage of plants for reducing bioavailability of heavy metals.

Phytoextraction— involves plants for removal of heavy metals.

Phytovolatilization— involves using plants for the absorption of heavy metals from soil and their release in the atmosphere as volatile compounds, and

Phytofiltration— uses plants cultured in a hydroponic environment for absorption or adsorption of heavy metal ions from aqueous waste and groundwater. There are other strategies for phytodegradation and rhizodegradation. Phytostabilization, phytoextraction, phytovolatilization and phytofiltration are the most widely used methods of phytoremediation to remediate the contaminated soil.

Table 4.4: Table Showing Advantages and Limitations of Phytoremediation Technology

Advantages of Phytoremediation Technology	Limitations of Phytoremediation Technology
<ul style="list-style-type: none"> • Aesthetically pleasing • Less disruptive than current methods • The effectiveness in contamination reduction • Low cost • Applicable for a wide range of contaminants • Environment friendly method 	<ul style="list-style-type: none"> • Time consuming • Root depth • The amount of produced biomass • Soil chemistry • Level of contamination • Age of plant • Contaminant concentration • The impacts of contaminated vegetation • Climatic condition

4.10. Heavy Metal Concentration in Plants at NUST Lakes

Analysis of heavy metals in flora at NUST lakes showed variation in metal concentration at all lake points. The alphabets on graph represent the species at lake points. Pb, Cr and Zn were detected at each point. Pb and Cd were present in low concentrations. This information shows that Pb was detected in following 5 species *Bombax ceiba* (L1 (I) 0.202 mg/kg), *Stellaria graminea* (L1 (O) 0.142 mg/kg), *Tecoma stans* (L2 (I) 0.002 mg/kg), *Salix babylonica* (L2 (I) 0.088 mg/kg), *Eucalyptus camaldulensis* (L3 (I) 0.134 mg/kg). Cadmium was detected in 3 species (*Bombax ceiba* L1 (I) 0.023 mg/kg), *Bischofia javanica* (L1 (O) 0.001 mg/kg) and *Sapium sebiferum* (L1 (O) 0.047 mg/kg). Cr was present in *Sapium sebiferum* (L1 (O) 0.009 mg/kg) and *Bombax ceiba* (L3 (I) 0.001 mg/kg). Lastly, Zn was detected in *Sapium sebiferum* (L1 (O) 5.302 mg/kg) and *Stellaria graminea* (L2 (I) 1.311 mg/kg).

Highest metal concentration particularly Cr and Cd was found at L1 (O) and lowest at L3 (I). Cd and Cr are released by fertilizer use or industrial activities. Their higher concentration can affect plant health. A study was conducted in Islamabad on analyzing industrial effluents. In Islamabad, dominant tree-species (*Cassia fistula* and *Albizia lebbeck*) were selected to examine their tolerance against industrial effluents. Results showed a presence of high level of heavy metals (Pb, Cr, Zn, Cd) in the industrial effluents. Data analysis showed that growth of trees species which were irrigated with treatments that are effluent based got affected. However, *Albizia lebbeck*, showed a relatively better tolerance against industrial effluents (Bhatti *et al.*, 2017). Heavy metal concentration in flora at NUST lakes may fluctuate depending upon change in weather conditions and level of incoming waste from different sources.

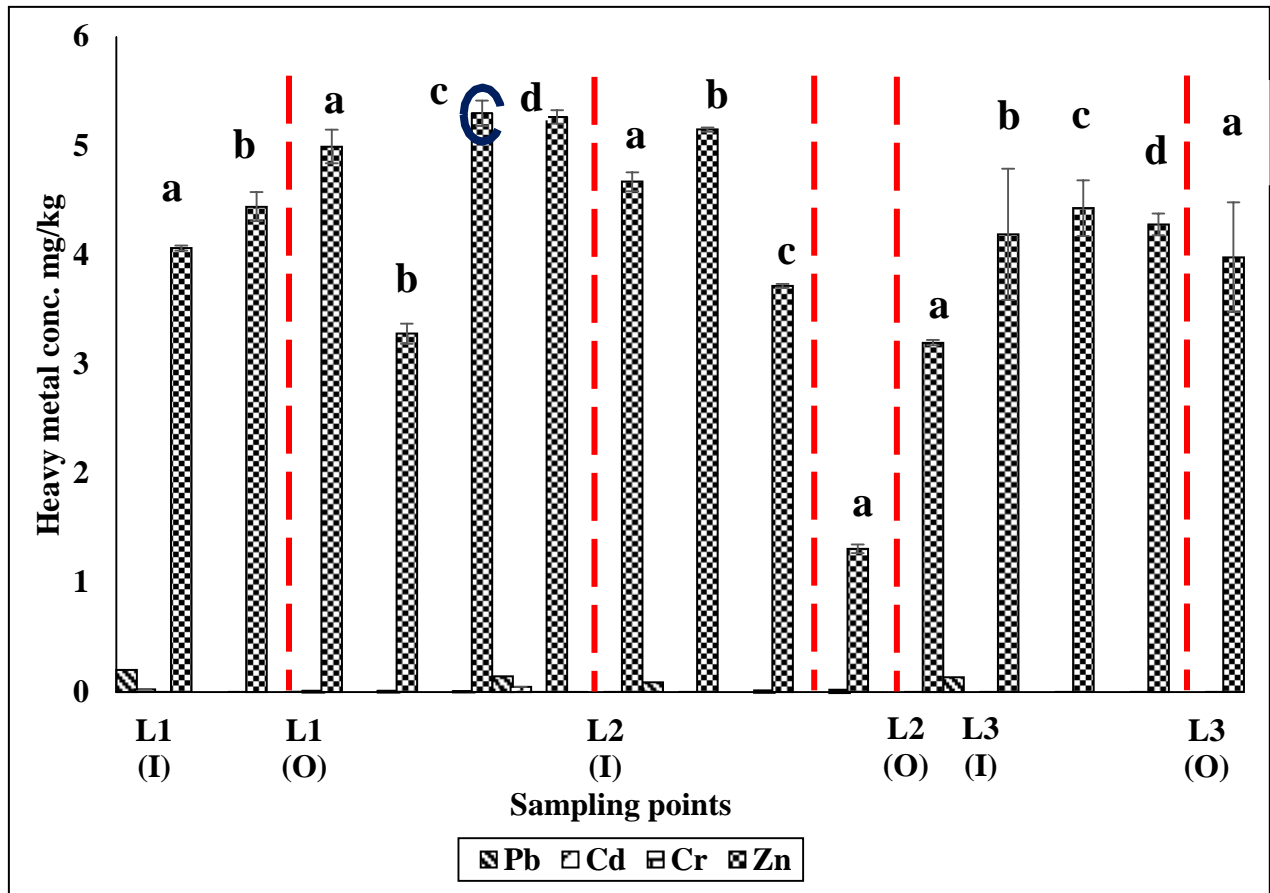


Figure 4.17: Average Profile of Heavy Metals in Plants at all Sampling Sites

Table 4.5: Plants at Lake Points

Sampling Points	Species
L1 (I)	<i>a. Bombax ceiba</i> <i>b. Sapindus mukorossi</i>
L1 (O)	<i>a. Bischofia javanica</i> <i>b. Bombax ceiba</i> <i>c. Sapium sebiferum</i> <i>d. Stellaria graminea</i>
L2 (I)	<i>a. Tecoma stans</i> <i>b. Salix babylonica</i> <i>c. Bischofia javanica</i> <i>d. Stellaria graminea</i>
L2 (O)	<i>a. Albizzia lebbek</i>
L3 (I)	<i>a. Eucalyptus camaldulensis</i> <i>b. Bombax ceiba</i> <i>c. Sapium sebiferum</i>
L3 (O)	<i>a. Casia fistula</i>

Table 4.6: Showing Heavy Metal Concentrations in Water, Sediments and Plants

The following table shows concentration of heavy metals in water, sediments and plants at NUST lakes.

Sr No.	HM (ppm)	WHO Permissible Limit		Samples/ Sampling sites								
				Lake 1			Lake 2			Lake 3		
		W & S (mg/L, mg/kg)	P (mg/kg)	W	S	P	W	S	P	W	S	P
1	Cd	0.003	0.005	BDL	BDL	0.0236	BDL	BDL	BDL	0.1849	BDL	BDL
2	Cr	0.05	0.01	0.0419	0.0058	0.0078	0.0265	0.0074	0.0083	0.0397	0.0228	0.0024
3	Pb	0.01	0.05	BDL	BDL	0.1722	BDL	BDL	0.0449	BDL	BDL	0.1339
4	Zn	3	5	3.8735	3.7835	4.56	3.9305	3.8235	3.6113	3.759	4.001	4.2225

Table 4.7: Dominant Algae and Their Sampling Locations

Species (Botanical name)	Common name	Uses	Sampling locations
<i>Bombax ceiba</i>	Simbal	Used as herbal tea in China. Bombax has phytochemicals which act as anti-cancer agents	L1 (I), L3 (I)
<i>Sapium sebiferum</i>	Chinese tallow tree	Seeds used in soap making	L3 (I)
<i>Stellaria graminea</i>	Common starwort	Water starwort provides habitat for aquatic insects. Birds feed on the leaves and seeds	L1 (I), L1 (O), L2 (I)
<i>Tecoma stans</i>	Tecoma tree	The plant is desirable fodder when it grows in field, grazed by livestock	L1 (O), L2 (I)
<i>Salix babylonica</i>	Weeping willow	Used for matchstick and paper pulp. The leaves and bark are used as a remedy for aches and fever	L1 (O), L2 (I)
<i>Albizia lebeck</i>	Sirin	It is an astringent, also used by some cultures to treat boils, cough. The bark is used medicinally to treat inflammation	L2 (O)
<i>Eucalyptus camaldulensis</i>	Sufaida	Wood is used in pulp production and leaf is used for treatment of infection, fever, upset stomach and to help loosen coughs.	L3 (O)
<i>Bischofia javanica</i>	Bishop tree	The fresh bark is used to treat aching stomach. The sap of bark, mixed with lime is used to treat sore feet	L1 (I), L1 (O), L2 (I)
<i>Sapindus mukorossi</i>	Ritha	Cleansing properties for skin and hair. The soapnut is used as natural remedy for treating migraine	L1 (I)



Bombax ceiba



Tecoma stans



Salix babylonica



Sapindus mukorossi



Bischofia javanica



Sapium sebiferum



Albizia lebbek



Eucalyptus camaldulensis



Stellaria graminea

Figure 4.18: Pictures Showing Flora at NUST Lakes

4.11. Phase 4: Dominant Algal Species

The algal blooms can have different impacts on social, environmental, economic and cultural system. The algal blooms can affect cultural, environmental, social and economic environments. Although we are aware of the physiological, ecological and functional conditions of eutrophication, more information on algal blooms is required. All algae are not green in colour. They exist in different colours. It depends on the dominant pigment in their cells. The dominance of green algae indicates oligotrophic conditions. They purify water bodies by absorbing heavy metals, pollutants that are organic and inorganic and radioactive substances. Microalgae indicate eutrophication levels and determine water quality (Khalil *et al.*, 2021). During the winters, algae can survive mostly at low concentrations due to lower sunlight and less water temperature (Beiras *et al.*, 2018). According to a study, 41 phytoplankton taxa belonging to 5 classes (Cyanobacteria, Chlorophyceae, Euglenophyceae, Bacillariophyceae and Dinophyceae) were quantified in 4 seasons. Minimum values were found in post monsoon and winters (Devi and Gupta, 2015).

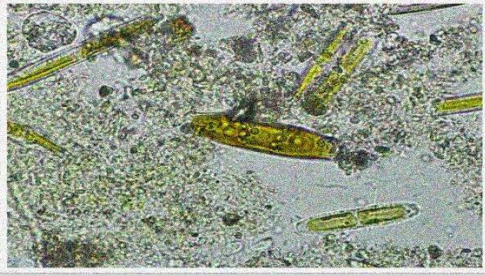


Dominant Algal Species	
<i>Nitzschia sp.</i>	
<i>Navicula gregaria sp</i>	
<i>Euglena sp.</i>	

Figure 4.19: Microscopic Images of Algal Species

Table 4.8: Classification of Algal Species and Their Characteristics

Phylum	Class	Order	Family	Genus	Characteristics
<i>Ochrophyta</i>	<i>Bacillariophyceae</i>	<i>Naviculales</i>	<i>Naviculaceae</i>	<i>Navicula</i>	Boat shaped diatom algae, comprising over 12,000 species
<i>Ochrophyta</i>	<i>Bacillariophyceae</i>	<i>Bacillariales</i>	<i>Bacillariaceae</i>	<i>Nitzschia</i>	Common marine diatom. It has a longitudinal symmetry with valves that are linear or oval shaped.
<i>Euglenozoa</i>	<i>Euglenoidea</i>	<i>Euglena</i>	<i>Euglenaceae</i>	<i>Euglena</i>	Genus of more than 1000 species of single celled, photosynthetic, eukaryotic and flagellated organisms i.e., having a whiplike appendage) microorganisms that feature both plant and animal like characteristics.

4.12. Phase 5: Correlation with Meteorological Parameters

Meteorological variables such as changes in GHI (Global Horizontal Index), ambient temperature, wind speed and rainfall patterns will affect the water quality. The effects of parameters vary according to regions and types of water bodies. During sampling period maximum GHI (211 W/m^2) was observed in the month of September due to maximum ambient temperature which was (27°C) while wind speed remained constant with little variation throughout the sampling period which ranged from (1.3 to 0.9 m/s) during sampling period. Maximum rainfall was (21.4 mm) observed in the month of September whereas minimum rainfall was observed in the month of december (4.5mm). Throughout the sampling period changes in meteorological parameters were observed which in turn impact the water quality. According to (Zhang et al., 2017), water quality in lakes with high eutrophic levels can be sensitive to meteorological parameters, whereas water quality in oligotrophic lakes was not influenced by meteorological changes due to improved buffer capacity and the regulation effect of algae production. The figure below depicts the decreasing trend of parameters.

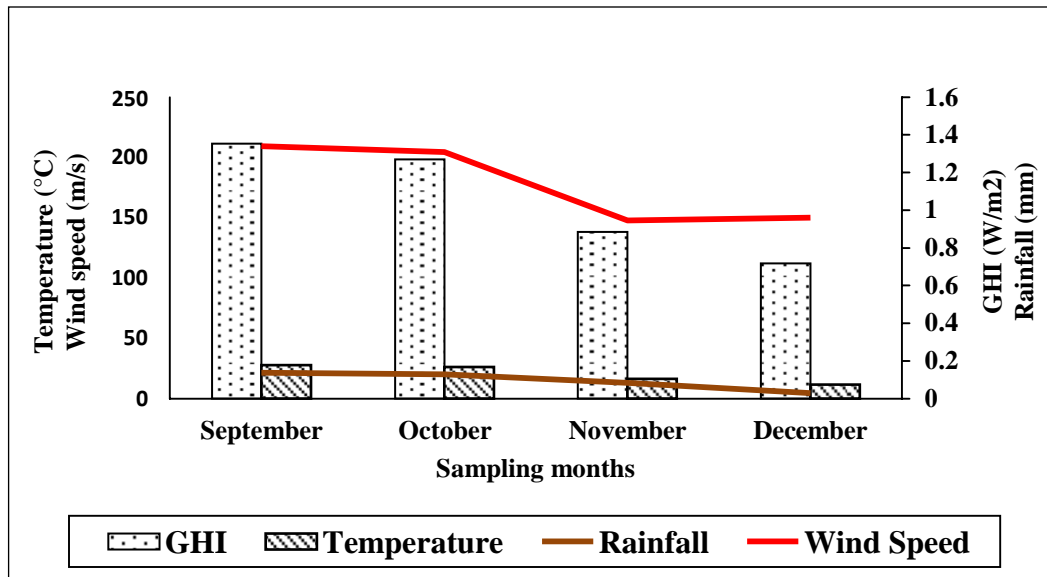


Figure 4.20: Meteorological Parameters

Table 4.9. Correlation of Physicochemical Parameters

	Temp	pH	EC	Turbidity	TSS	TDS	COD	DO	NO ₃ -N	NO ₂ -N	TKN	PO ₄ -P	Avg Chl a, b and c	CCI
Temp	1													
pH	0.09	1												
EC	0.17	0.85	1											
Turbidity	0.51	0.42	0.01	1										
TSS	-0.80	-0.01	-0.33	-0.08	1									
TDS	0.68	0.58	0.72	0.38	-0.64	1								
COD	0.45	0.43	0.77	-0.15	-0.53	0.82	1							
DO	0.35	-0.10	0.13	0.02	-0.19	0.58	0.62	1						
NO ₃ - N	0.80	0.09	0.26	0.28	-0.94	0.53	0.31	-0.08	1					
NO ₂ - N	0.47	0.42	0.81	-0.19	-0.68	0.81	0.96	0.45	0.49	1				
TKN	0.49	0.39	0.18	0.60	0.08	0.47	0.35	0.50	-0.07	0.14	1			
PO ₄ - P	0.68	-0.50	-0.32	0.02	-0.46	0.26	0.32	0.63	0.31	0.23	0.38	1		
Avg Chl a, b and c	-0.40	-0.30	-0.07	-0.80	0.19	-0.53	0.01	-0.34	-0.24	0.02	-0.30	-0.02	1	
CCI	0.77	0.46	0.59	0.45	-0.82	0.92	0.63	0.36	0.79	0.71	0.25	0.23	-0.60	1

1. Pearson's correlation matrix between physicochemical parameters shows that the relationship between temperature and DO was not significant. When temperature increases, DO decreases. Cold water can hold more DO than warm water. NUST lakes are experiencing waste intrusion. Therefore, DO is low even in winters.
2. COD and nitrite showed a significant correlation. COD quantifies amount of oxidizable pollutants found in water. It is an indicator of the contents of reducing substances in water such as nitrite. Greater nitrite concentration means greater COD.
3. TDS provides mineral content for plant growth. A weak positive correlation between TDS and CCI showed that although, greater TDS can negatively affect the growth of plants when they are unable to suck nutrients.
4. Phosphate is essential for growth of plants but plants don't easily uptake macronutrients. Therefore, there is a negative correlation between phosphate and CCI.
5. CCI is positively correlated with nitrates because nitrate is an important nutrient which plants use for photosynthesis.

4.13. Metal Correlation

Table 4.10: Heavy Metal Correlation

	Cr	Zn	As	Pb	Cd
Cr	1				
Zn	-0.17	1			
As	-0.832	-0.29	1		
Pb	0.629	0.768	-0.579	1	
Cd	1	1	-1	1	1

A positive correlation was observed between Cr & Cd, Pb & Cd and Zn and Cd. More metals are absorbed in summers than in winters due to transpiration (Kumar *et al.*, 2019).

According to a study, natural and anthropogenic sources such as (soil erosion or riverbank runoff, geological interaction) and (surface runoff from urban and agricultural areas) were effective in the rainy season on heavy metals respectively while discharge of wastewater and natural processes for weathering were effective in the dry season.

According to a study, lake characteristics and water depth affected concentration of metals. Accumulation of metals was less at shallow water (≈ 2 m depth). Metals were

transported in lakes during rainy season. Anthropogenic sources affect Pb and Zn while natural weathering processes and earth's crust affect Cr. (Gunes *et al.*, 2021).

CHAPTER 5

5. CONCLUSION

Only pH, TDS, nitrate and nitrite were found within the permissible limit of WHO and remaining all the physico-chemical parameters examined in this study exceeded the threshold established by WHO which shows an excessive and persistent level of pollution in lakes. The CCI of leaves depends on nitrate intrusion in water bodies. Nitrate concentration was below the permissible limit in all lakes. Therefore, decrease in photosynthetic activity with temperature and nitrate concentrations, CCI kept fluctuating. Algae are most sensitive species and therefore can be an indicator for water quality. As nutrient concentration was low in lakes, chl a, b and c concentration was also low. Dominant algal species were identified under the compound microscope.

1. Most physico-chemical parameters exceeded WHO limits. pH, TDS, $\text{NO}_3 - \text{N}$, $\text{NO}_2 - \text{N}$ were within WHO limits. TKN, EC, turbidity, $\text{PO}_4\text{-P}$ and DO exceeded the limits.
2. Heavy metal accumulation in plants was higher than sediments and water. Zn was detected in high conc. in all three lakes while Pb was only detected in plants of lakes.
3. Meteorological parameters (Temperature, Wind Speed, Rainfall & Global Horizontal Index) showed insignificant impact on physicochemical parameters.
4. High conc. of turbidity, nitrates, phosphates, and chl-a showed that the lake is subjected to eutrophication. Dominant algae were determined on the basis of morphology. High CCI in plants was observed in *Stellaria graminea* at L2 (I).

5. RECOMMENDATIONS

Following recommendations might help the authorities to monitor health status of NUST lakes and devise ways to control pollution.

1. Identification and characterization of dominant algal species through PCR may be conducted.
2. Impact of weather and seasonal patterns may be studied in detail for determination of pollution status.
3. Regular management of lakes is needed to prevent further degradation. Plantation must be done to restore the affected environment. Phytoremediation is an effective method for mitigation of pollution. Hyper-accumulators such as *Stellaria graminea* and *Albizia lebbek* can be used for phytoremediation.

CHAPTER 7

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