SITI FARHAIN BINTI MOHD LUDIN

MASTER OF SCIENCE

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TEMPORAL AND SPATIAL VARIATIONS OF NUTRIENTS AND DISSOLVED GREENHOUSE GASES CONCENTRATIONS IN KENYIR LAKE, MALAYSIA

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Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of Science in the Faculty of Science and Marine Environment Universiti Malaysia Terengganu

OCTOBER 2021

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Dedicated this thesis to:

My supportive and kind-hearted supervisor,

Abah, Mama, siblings and friends.

Thank you so much for your great support and continuous care.

1 owe you guys a lot

May Allah bless

Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfilment of the requirements for the degree of Master of Science

TEMPORAL AND SPATIAL VARIATIONS OF NUTRIENTS AND DISSOLVED GREENHOUSE GASES CONCENTRATIONS IN KENYIR LAKE, MALAYSIA

SITI FARHAIN BINTI MOHD LUDIN

OCTOBER 2021

Main Supervisor : Associate Professor Poh Seng Chee, Ph.D
Faculty : Faculty of Science and Marine Environment

Freshwater lakes represent significant sources of greenhouse gas emissions, largely influenced by nutrient enrichment within the water column. This study evaluates the dynamic of dissolved carbon dioxide (CO_2) and methane (CH_4) distribution patterns in Kenyir Lake, aiming for a better understanding of the physical processes controlling internal loading of CO_2, CH_4, and nutrients in one of the largest freshwater lakes in Malaysia. The distribution of CO_2, CH_4, nutrients, and physicochemical parameters in the water column of Lake Kenyir was determined from November 2017 to November 2018. During this period, water samples were collected at different depths to measure CO_2 and CH_4 using headspace gas chromatography, nutrients using the colorimetric method, and basic water quality parameters using a portable water quality meter. The study showed the level of thermal stratification in the Kenyir Lake varied across seasons. The hypolimnion often remains around 3-6 °C cooler than surface water temperature (28-32 °C) throughout the year. During the raining seasons (November 2017, February 2018, and November 2018), both the Schmidt stability index and Lake Number (Ln) decreased significantly. This indicated enhanced mixing of epilimnetic water with deeper hypolimnetic water particularly from the surface down to 40 m. However, complete lake turnover did not occur during the study period. Despite the upper layer mixing, Kenyir Lake remained thermally stratified, leading to the accumulation of CO_2, CH_4, and inorganic nutrients in the bottom layers of the lake. Dissolved CO_2

and CH_4 concentrations in Kenyir Lake ranged from 1.30-925 µM and 0.10-4226 µM, respectively. Spearman's correlation analysis shows addition of nitrogen and phosphorus-based nutrients resulted in an increase in CH_4 production in the lake. A stronger linear relationship between CH_4 and CO_2 concentration was observed during the dry season (r^2=0.85) compared to the raining season (r^2=0.46), suggesting that the methane oxidation may play a prominent role in contributing to CO_2 levels in lake water during the dry season. The significant greenhouse gas emissions observed in Kenyir Lake underscore the need for similar assessments in other major freshwater lakes across Malaysia. These findings contribute to national climate reporting efforts and support evidence-based lake and watershed management policies.

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

VARIASI MASA DAN RUANG KEPEKATAN NUTRIEN DAN GAS RUMAH HIJAU TERLARUT DI DALAM TASIK KENYIR, MALAYSIA

SITI FARHAIN BINTI MOHD LUDIN

OKTOBER 2021

Penyelia Utama : Profesor Madya Poh Seng Chee, Ph.D
Fakulti : Fakulti Sains dan Sekitaran Marin

Tasik air tawar merupakan sumber utama pelepasan gas rumah hijau, sebahagian besarnya dipengaruhi oleh pengayaan nutrien dalam turus air. Kajian ini menilai corak taburan dinamik karbon dioksida (CO_2) dan metana (CH_4) terlarut di Tasik Kenyir dengan tujuan untuk memahami proses fizikal mengawal pemuatan dalaman CO_2, CH_4 dan nutrien dalam salah satu tasik air tawar terbesar di Malaysia. Taburan CO_2, CH_4, nutrien dan parameter fizikokimia dalam lajur air Tasik Kenyir telah ditentukan dari November 2017 hingga November 2018. Sepanjang tempoh ini, sampel air diambil pada pelbagai dalaman untuk mengukur CO_2 dan CH_4 dengan kaedah kromatografi gas secara ruang kepala, nutrien menggunakan kaedah kolorimetrik, dan parameter kualiti air asas menggunakan meter kualiti air mudah alih. Kajian ini menunjukkan stratifikasi terma di Tasik Kenyir berubah mengikut musim. Suhu di hipolimnion didapati kekal sekitar 3-6 °C, lebih sejuk berbanding suhu permukaan air (28-32 °C) sepanjang tahun. Sepanjang musim hujan (November 2017, Februari 2018 dan November 2018), kedua-dua indeks kestabilan *Schmidt* dan *Lake Number* (Ln) menurun dengan ketara. Ini menunjukkan peningkatan pencampuran air epilimnion dengan air hipolimnion yang lebih dalam, khususnya dari permukaan air tasik hingga kedalaman 40 m. Namun, pemutaran penuh air tasik tidak berlaku sepanjang tempoh kajian ini. Walaupun berlaku pencampuran di lapisan atas, Tasik Kenyir kekal mengalami stratifikasi terma, yang mengakibatkan pengumpulan CO_2, CH_4 dan nutrien tak organik di lapisan dasar tasik. Julat

kepekatan CO_2 dan CH_4 terlarut di Tasik Kenyir masing-masing adalah antara 1.30-925 µM dan 0.10-4226 µM. Analisis korelasi Spearman menunjukkan bahawa peningkatan nutrien berasaskan nitrogen dan fosforus boleh meningkatkan CH_4 di dalam tasik. Hubungan linear yang lebih kuat antara kepekatan CH_4 dan CO_2 telah diperhatikan semasa musim kering (r^2=0.85) berbanding musim hujan (r^2=0.46). Ini menunjukkan bahawa proses pengoksidaan metana mungkin memainkan peranan penting dalam menyumbang kepekatan CO_2 dalam air tasik semasa musim kering. Pelepasan gas rumah hijau yang ketara di Tasik Kenyir menyerlahkan keperluan untuk penilaian serupa di tasik air tawar utama lain di seluruh Malaysia. Penemuan ini menyumbang kepada usaha pelaporan iklim negara dan menyokong dasar pengurusan tasik dan kawasan tadahan berasaskan bukti.

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I owe more than thanks to my family members especially my beloved parent Mohd Ludin Muhammad and Raihan Zainal Abidin for the advises, financial support and encouragement throughout my life. Without their support, it is impossible for me to finish this study. Your prayer for me was what sustained me this far.

Finally, I would like to wish thanks for those who involved in this research, directly or indirectly, your help and kindness is truly appreciated. Thank you very much.

APPROVAL

I certify that an Examination Committee has met on 13th October 2021 to conduct the final examination of Siti Farhain binti Mohd Ludin, on her Master of Science thesis entitled **"Temporal and Spatial Variations of Nutrients and Dissolved Greenhouse Gases Concentrations in Kenyir Lake, Malaysia"** in accordance with the regulations approved by the Senate of Universiti Malaysia Terengganu. The Committee recommends that the candidate be awarded the relevant degree. The members of the Examination Committee are as follows:

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_____

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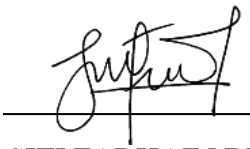
DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UMT or other institutions.



SITI FARHAIN BINTI MOHD LUDIN
Date: 08 October 2025

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SYMBOLS

%	Percentage
°C	Degree Celsius
µL	Micro litre
µg/L	Micro gram per litre
µM	Micro Molar
µmol/L	Micromole per litre
atm	Pressure
C	Carbon
$C_8H_{10}K_2O_{15}Sb_2$	Potassium antimonyl tartrate
CH_4	Methane
cm	Centimetre
CO_2	Carbon dioxide
F	Fugacity
g	Gram
IC	chemical stratification index strength
J/m^2	Joule per square metre
K	Kelvin
km^2	Square kilometre
L_n	Lake number
L	litre
M	Meter
mg	Milligram
mL	Millilitre

mL/min	Millilitre per minute
mm	Millimetre
N	Nitrogen
N_2	Nitrogen gas
$(NH_4)_6Mo_7O_{24}$	Ammonium molybdate
NH_4-N	Ammonium
NH_4^+	Ammonium
N_2O	Nitrous oxide
NO_2-N	Nitrite
NO_3-N	Nitrate
NO_3^-	Nitrate
nm	Nanometre
O_2	Oxygen
P	Phosphorus
p	Partial pressure
PO_4^{3-}	Phosphate
ppm	Part per million
r^2	Coefficient of determination
S ‰	Salinity percentage
SO_2^{-4}	Sulphate
St	Schmidt stability
T	Temperature
VCl_3	Vanadium (III) chloride
w/v	Weight per volume

ABBREVIATIONS

DIC	Dissolve inorganic carbon
DIN	Dissolve inorganic nitrogen
DIP	Dissolve inorganic phosphorus
DOC	Dissolve organic carbon
Feb	February
GC	Gas chromatography
GF/F	Free borosilicate glass microfiber fibre
GHGs	Greenhouse gases
GWh	Giga watt hours
HCL	Hydrochloric acid
HDPE	High Density Poly Ethylene
ICOLD	International Commission on Large Dams
IHA	The International Hydropower Association
Mar	March
May	May
MW	Megawatts
NaOH	Sodium hydroxide
NED	N-(1-napthyl)-ethylenediamine dihydrochloride
Nov	November
OM	Organic matter
Oct	October
PIC	Particulate inorganic carbon

POC	Particulate organic carbon
SPM	Suspended particulate matter
SSI	Schmidt stability index
TNB	Tenaga Nasional Berhad
UNESCO	United Nations Educational, Scientific and Cultural Organization

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CHAPTER 1

INTRODUCTION

1.1 Overview

Climate change and its impact on society is always an important subject of concern globally. In particular, the impacts of global warming become more apparent and greenhouse gases (GHGs) have been discussed as one of the major influencing factors that causing Earth's temperature to increase. Some of the effects of climate change are observed as ocean and atmospheric warming, decreasing snow and ice thickness at Polar Regions, rising of sea levels, and increasing of tropical storms and cyclones frequency (Raj & Singh, 2012).

It is noteworthy to mention that the concentration of atmospheric carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) has been increasing rapidly since the industrial revolution. It is obvious that the increase in atmospheric GHGs is due to human activities such as the burning of fossil fuel for generating energy and rapid land use changes for urbanization (Sujay *et al*., 2017). The increase in atmospheric CO_2 concentration is a major cause of warming of the climate system as it was more dominant compared to CH_4 and N_2O concentration (Tian *et al*., 2016).

Figure 1.1 shows the long-term atmospheric CO_2 and CH_4 concentration trends over the last decades from National Oceanic and Atmospheric Administration's (NOAA) Mauna Loa Observatory at Hawaii. The GHGs data recorded at Mauna Loa laboratory is one of the longest records of direct measurements of CO_2 and CH_4 in the atmosphere. Figure 1.1 also showed that atmospheric CO_2 and CH_4 concentration have been increasing since 1960s and both GHGs concentration keep increasing annually and have no sign to slow down.

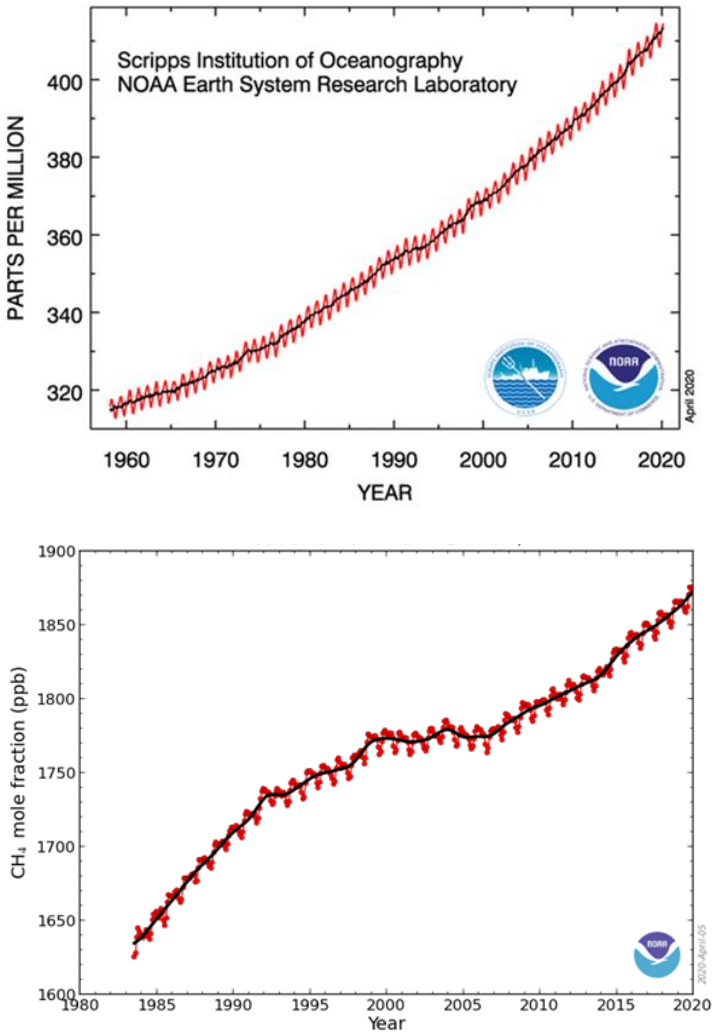

Figure 1.1: Atmospheric CO_2 and CH_4 concentration from Mauna Loa Observatory (NOAA, 2020).

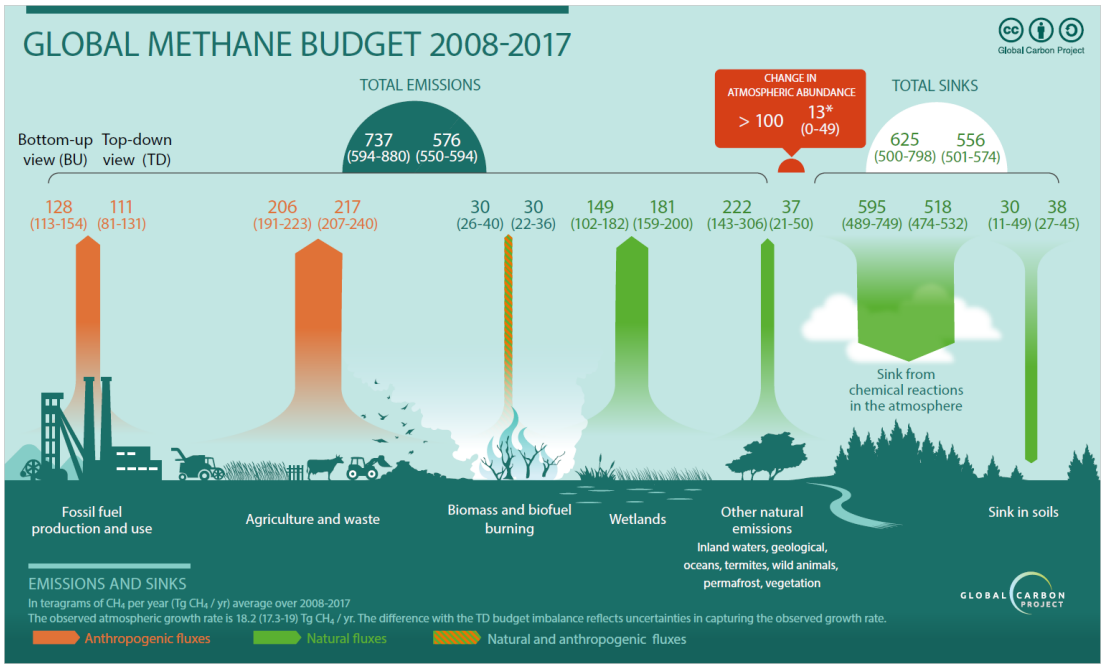

Figure 1.2: Global methane budget 2008-2017 (Adopted from Saunois *et al*., 2020)

Figure 1.2 show that natural and anthropogenic sources contributed 364 and 365 Tg 372 CH_4 to atmosphere annually, respectively. Natural sources include respiration and decomposition of plants, inland water, ocean pool and wetlands release of greenhouse gases to the atmosphere while anthropogenic sources include burning of fossil fuels, biomass burning and activities like deforestation, agriculture, and cement production. Inland waters are considering as one of the major natural GHGs emitter. For example, the total emission of CH_4 from inland waters could reach as high as 27 Tg CH_4/year (Saunois *et al*., 2020).

The influencing factors for production in freshwater ecosystem are complex and often complicated to determine. Nevertheless, the production of CO_2 and CH_4 gases usually interconnected with nutrients enrichment in water column (Painting *et al*., 2013). Especially in man-made environments such as reservoir, burial organic matter (OM) and excessive nutrients production by impending water flow are hotspots for GHGs production and emissions as sediment deposition will increase light penetration and the growth of the phytoplankton community will further fuels GHGs production in reservoir sediments (Ward *et al*., 2017). In freshwater

ecosystem, the carbon cycle is not processed in isolation but being connected with the cycling of nitrogen and phosphorus (Zaehle, 2013).

Big dams are potential GHGs emitter. The International Commission on Large Dams (ICOLD) have registered 45000 large dams worldwide. Most of large dams are for multipurpose use and approximately 36% of the dams are used for electricity generation (Bakıs, 2005). Is it interesting to note that the number of new hydroelectric reservoirs continues to be increased in the tropical or sub-tropical regions due to high demand of energy within the region. Unfortunately, studies also showed that hydroelectric dams emit substantial amounts of greenhouses gases to environment during the construction phase as well as during hydropower operation (Fearnside, 2016).

The terrestrial ecosystem is transformed into an inland water ecosystem during the construction of the hydro power reservoirs. The inundation of large amount of above ground biomass, followed by the decomposition of soil organic matter on the flooded land, accelerating the production of GHG, which is then released into the atmosphere through the reservoir surface emission and downstream emissions of the hydropower dams (St. Louis *et al*., 2000; Tremblay *et al*., 2005). A meta-analysis study conducted by Barros *et al*., (2011) shows that the tropical or subtropical hydro-reservoirs are a more significant contributor to GHG than northern or temperate reservoirs. (Barros *et al*., 2011).

Damming alters river and lake transitioning period. They restricted the natural river flows and turbulent mixing to the slower and lentic condition, these conditions help to suspend more nutrients and particulates, and hence deeper reservoirs with poor mixing would likely sustain oligotrophic conditions. Dams may also cause the flooding of the terrestrial environment of lakes or rivers and change the biogeochemical cycle in water column. Damming has shifted the balance of nutrients and organic substrates, the oxygen and thermal conditions in the water body that favourable to promote GHGs production (Friedl & Wuest, 2002). All these

biogeochemical processes in turn contributing to enhance greenhouse gases emission in hydropower reservoir.

The contribution of hydropower reservoirs to increasing atmospheric greenhouse gas concentrations is receiving increasing attention in Malaysia. While almost 17.1% of energy in this country is generated from renewable energy resources mainly the hydropower (Abdul Latif *et al*., 2021), study the fate and transport of greenhouse gases in large hydro dam has become top priority.

1.2 Problem Statement

Malaysia is rich in hydro powered potential thanks to its high number of fast flowing rivers and high rainfall volume throughout the years. This country has about 104 large dams and more new dams going to be built to fulfil nation energy demands (Yah *et al*., 2017). It is noteworthy to mention that, up to date, there is no report on GHGs data for these man-made reservoirs, the knowledge of the total of GHGs emission from these inland waters remain limited.

To our knowledge, no prior limnology studies in Malaysia have examined the greenhouse production in inland waters. This study had provided baseline data to assess the GHSs emission in Kenyir lake, one of the largest man-made reservoirs in Malaysia. The outcome of this research provided the first baseline data for GHGs in freshwater lake of Malaysia. This research finding also provide a global comparison or benchmarks value of GHGs emission from Malaysia water perspective. This is a necessary step for assessing carbon footprint to fulfil the nation devotion to combat climate change. For the governing agency (Ministry of Energy and Natural Resources) and the energy service provider (TNB), assessing the net greenhouse gas emissions of hydropower plants is increasingly relevant to ensure that energy

production methods are sufficient to support Malaysia's commitment to carbon reduction initiatives and sustainability of the environmental.

1.3 Objectives of the Research

1. To determine spatial and temporal distribution of dissolved nutrients concentration of organic carbon (C), inorganic nitrogen (N), inorganic phosphorus (P) and dissolved concentration of carbon dioxide (CO_2) and methane (CH_4) in Kenyir Lake.

2. To determine the spatial and temporal of physical parameters and their relationship with CO_2 and CH_4 in Kenyir Lake.

CHAPTER 2

LITERATURE REVIEW

2.1 Lake Classification

Lake is a body of water that is geologically surrounded by land, which means it may dry out at some point and fill up again under heavy rain or seasonal conditions. According to Bek (2018), most lakes are of catastrophic origin, formed by volcanic, tectonic, river activity and glacial processes but can also be formed by humans and are called reservoirs.

Every lake is an ecosystem unique to itself. In addition to its origin, each lake has its own characteristics, such as size, drainage basin, features of inflow and outflow, nutrient content, dissolved oxygen content, pH, temperature, and productivity (Akomeah *et al*., 2021). Lake can also be classifying by three criteria which is (i) the depth that determines the water stratification, (ii) thermal structure of the lake and (iii) the trophic state that describes its productivity (Xu & Jiao, 2018).

Lake classification based on depth can be categorised into littoral zone, limnetic zone, profundal zone and benthic zone, respectively (Rachna & Disha, 2016). According to Flim *et al* (2016) and Rachna & Disha (2016), littoral zone refers to shallow water area with slight penetration to the bottom. Limnetic zone refers to the open water area with effective light transmission, corresponding to the upper layer of the lake where photosynthesis occurs, meanwhile profundal zone is referring the bottom and deep-water area beyond the depth of effective light penetration where this region is typically below the thermocline. Lastly is benthic zone which refers to all areas at the bottom, composed of sediment and soil. Due to the composition of organic matter, there is a large demand for dissolved oxygen.

In addition to the depth classification, using the basic of thermal stratification to define a lake is also commonly practice in limnology. Thermal stratification happen is because the density of water varies with temperature at different depth and forming water layers that did not mix to each other's in which a phenomenon where lake is separate into three distinct thermal layers which is epilimnion, metalimnion (or thermocline) and hypolimnion (Ziaie *et al*., 2019) as shown in Figure 2.1

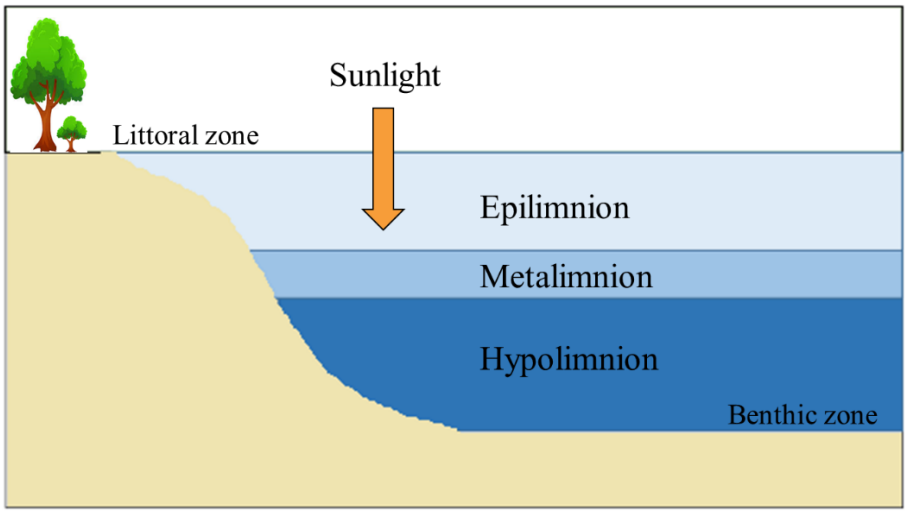

Figure 2.1: General Lake thermal stratification based on depth and light penetration.

According to Ziaie *et al* (2019), epilimnion layer of lake is where the sunlight can reach the surface of the lake, which is usually the warmest layer of water. A thin middle layer called the metalimnion (or thermocline) is generally formed by rapid changes in the temperature of the water, and this separation is usually sufficient to resist the mixing of the layers by the wind. In temperate zone, hypolimnion layer will be formed by the colder, denser water settling at the bottom of the lake. The most extreme thermal stratification occurs within lakes during the warm summer months (Christina *et al*, 2020). During fall turnover, the epilimnion layer will cools, sinks, and falls below the thermocline, causing mixing. Thermal stratification of a lake depends on the lake's depth, shape, and size in which some small, shallow lakes may not experience seasonal thermal stratification because the wind mixes the entire lake (Yang *et al*., 2016).

Lake also can be classify based on trophic state referring to their nutrient contents and vegetation richness in water column. This type of classification consists of three categories namely oligotrophic, mesotrophic, and eutrophic lake (Xu & Fu, 2019). Oligotrophic lake is defined as clear, nutrient poor with few vegetation available in water column. High oxygen contents also commonly found in oligotrophic lake and the low vegetation in water column allow deeper light penetration and less decomposition (Anderson *et al*., 2017)

"Meso" mean middle and mesotrophic lakes tend to have intermediate level of nutrient with some vegetation growth in water column. Mesotrophic lake in temperate region tends to stratify during summer season. The main factor of the stratification is because the present nitrogen and phosphorus nutrients in the lake allow the vegetation to growth at the top layer of the lake and produce oxygen as the by-product of photosynthesis (Liang *et al*., 2019). At the bottom of the lake, the vegetation and other organism die, and anaerobic decomposition occur and forming an anoxic water column (Robert *et al*., 2020).

Lastly are eutrophic lakes which are characterized by water column with high nutrient and chlorophyll levels, turbid, overgrowth macrophyte plant population (Atsushi *et al*., 2015). This type of lake typically surrounded by agricultural lands that received direct discharge from runoff channels. Urban flood retention ponds are another typical eutrophic lake that carried all the type of nutrients from the surrounding landscape (Nicholas *et al*., 2016). Since eutrophic lake carry so much biomass, its turnout becomes a death zone when the decomposition process depleted the oxygen level in the water column.

2.2 Carbon Cycling in A Freshwater Ecosystem

Global carbon storage consists of three main compartments which land, ocean, and atmospheric pools. Large proportion of carbon is found in bedrock or sediments, however the fluxes or transformation from these pools are small compared to the fluxes between the atmosphere, biosphere, and hydrosphere (Battin *et al*., 2009). In carbon cycles, primary producer plays a major role in transforming inorganic carbon into organic carbon, some of which are re-mineralized back into inorganic carbon during decomposition, making them available for primary producers again.

In freshwater ecosystem, carbon cycling is dominated by biological transformations, performed by either autotrophic or heterotrophic organisms (Terrado *et al*., 2017). Autotrophic organisms basically utilising energy of sunlight to turn CO_2 and water into simple organic compound and oxygen through photosynthesis process (Ramon *et al*., 2017). At profundal and benthic zone, chemoautotrophic organisms obtained their energy from the oxidation of inorganic molecules (magnesium, sulphur, iron) and able to synthesize their own organic molecules from the fixation of carbon dioxide (Sabine *et al*., 2019).

While heterotrophic organisms cannot produce their own organic molecules and must depend on external organic compounds as an energy source (Rajta *et al*., 2019). These two groups of organisms play equally important roles in greenhouse production in freshwater ecosystem at surface water autotrophic organisms performing photosynthesis converting CO_2 and water into chemical energy and oxygen. On the other hand, both autotrophic and heterotrophic organism utilising organic matter for energy and converted back to CO_2 through respiration (Dayanidhi & Kazuyuki 2015).

Lake could play a vital role in carbon sequestration, when the lake production is higher than respiration, they can act as carbon sink in the global carbon cycle. Most of the lake function as a natural sink for natural surface water inflow that carrying high loading of dissolved, litter fall, and organic-rich sediments (Fenner *et al*., 2021). The enrichment of organic matter in the water body plays an important role in the mineralization of organic carbon (Zander *et al*., 2020). The increased load of organic matter promotes mineralization, thereby increasing the production of greenhouse gases in the water column (Battin *et al*., 2009). Mineralization, respiration and internal metabolism are the core processes of organic matter decomposition and nutrient circulation (Gudasz *et al*., 2010). Furthermore, these organic matter source also influences organic carbon degradation rate.

The fermentation and respiration processes of the huge quantity of organic matter at the bottom of the lake causes carbon release in the form of CH_4 and CO_2 as well as nutrients to the water column (Cardoso *et al*., 2013). Figure 2.2 shows a General Carbon Dioxide and Methane production and emission pathway in a freshwater lake.

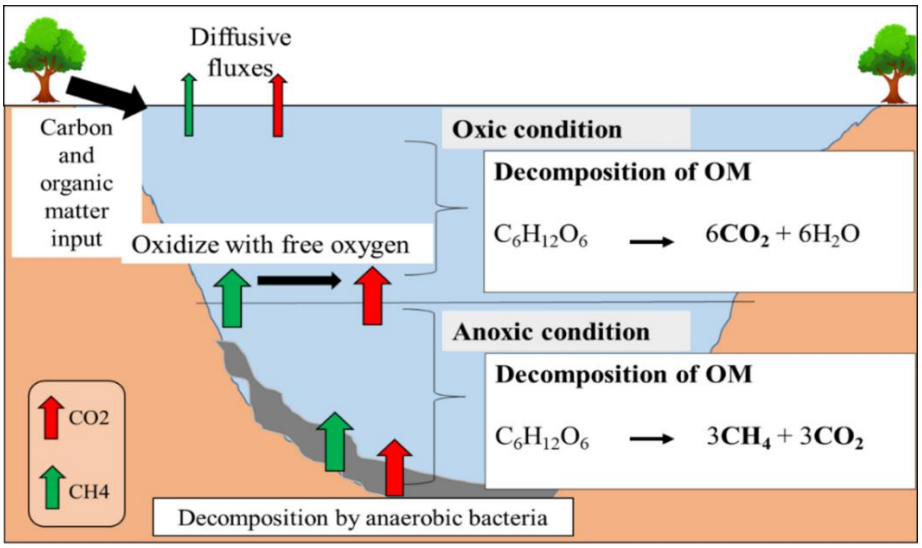

Figure 2.2: Biogeochemical and emission pathway of carbon dioxide and methane in a stratified freshwater lake, red and green arrow represent the natural GHGs emission pathways, equations in the text box represent GHGs productions under different dissolve oxygen level.

The production of GHGs in lakes is subjected to the input of OM from the watershed. Organic matter and specific dissolved organic carbon constitute the basis of mineralization in lakes, which are the sources and main influencing factors of CO_2 and CH_4 that are released directly from sediments into the atmosphere by ebullition and turbulent diffusion. (McGinnis *et al*., 2006).

The production of CH_4 in water column are mainly occur at the bottom layer when methanogenesis took place in the sediment under anoxic condition. However, methanogenesis may also possibly happen within aerobic sediments if other electron acceptors, such as oxygen or sulphate-like electron acceptors is present (Rulík *et al*., 2013). In these processes, a large part of this CH_4 is subsequently consumed by catalytic oxidation of microorganisms directly in the soil and sediment or in the water column. The microbial oxidation of CH_4 to CO_2 in water column can be carried out under aerobic conditions, O_2 as the electron acceptor, or anaerobic (AOM), generally sulphate (SO_4^{2-}) as the electron acceptor (Sturm *et al*., 2018). If the surface water is supersaturated with CO_2 and CH_4, it can be released to the atmosphere (Figure 2.2).

2.3 General Pathway Greenhouse Gases in Lakes

To understand the CH_4 and CO_2 emissions, it is necessary to understand the carbon biogeochemical pathways and understand how its relative contributions differ between aquatic systems (i.e., natural and manmade lake, river, freshwater and coastal wetland, estuary and open ocean). Changes in water column physical parameters and climatic barometric fluctuation, such as changes in hydrostatic pressure (due to climatic barometric fluctuations or changes in water level) can trigger GHGs emission from water column to atmosphere (Varadharajan and Hemond 2012; Wik *et al*. 2013). At shallow lake, winds driven wave action can trigger the release of CH_4 bubbles trapped in the sediment porewater (Joyce and Jewell 2003). Furthermore, the morphometry of a water body also plays a role, as it has been shown that ebullition is strongly effected by water column depth such that its contribution to total CH_4 emissions decrease sharply with depth (DelSontro *et al*. 2018). Figure 2.3 shows a general pathway of carbon dioxide and methane emitted from lakes in littoral and limnetic zone.

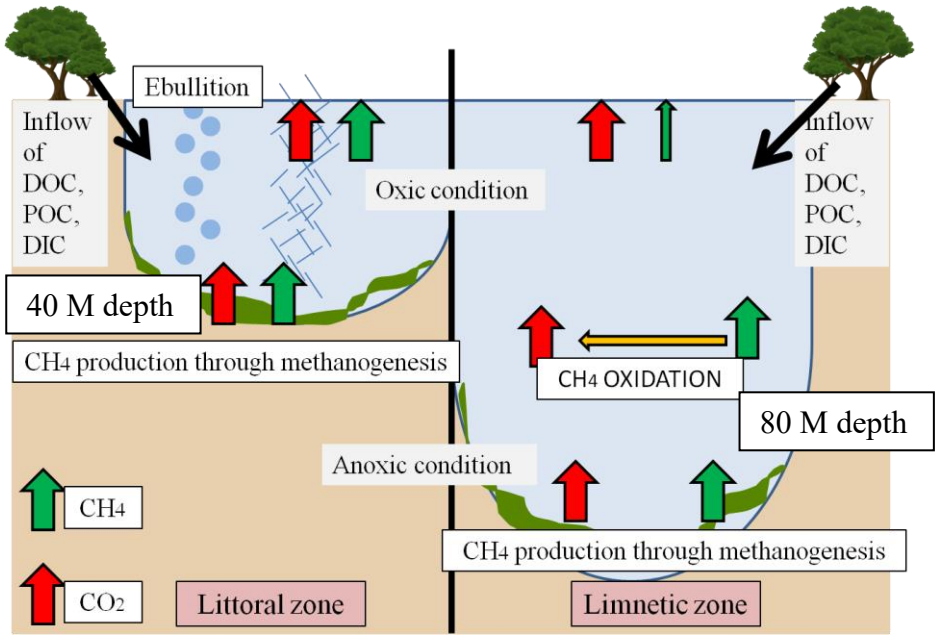

Figure 2.3: General pathway of carbon dioxide and methane emitted from lakes in littoral and limnetic zone.

Based on Figure 2.3, in shallow water (Littoral zone) most of the CH_4 in the bubbles is transferred directly from the lake bed to the atmosphere. Anaerobic mineralization of sediment organic matter, the source of ebullitive CH_4 fluxes, tends to increase exponentially with temperature (Yadav *et al*., 2019). CH_4 consumption mainly takes place in the oxic layer of the water column. Like production, consumption rates also increase with temperature. CH_4 can escape through ebullition when CH_4 was not being consumed 100% or CH_4 oxidation was not fully occurred (Davidson *et al.,* 2018).

In much deeper lakes (limnetic zone), CH_4 diffuses from sediments into oxygenated water bodies can be oxidized to carbon dioxide (CO_2) by methanotrophic bacteria. Therefore, a large amount (but variable) of CH_4 will diffuse out of the sediments may be oxidized before reaching the air-water interface, depending on water column depth and lake thermal structure stability (i.e., well-mixed vs. Stratified) (Kankaala *et al*. 2006). Ultimately, the main CH_4 emissions in lake are likely to originate primarily from anoxic sediments and are driven by anaerobic bacteria, which is controlled by the environment redox conditions, organic matter supply and water temperature.

2.4 Nitrogen and Phosphorus Cycle in A Natural Watershed

In the photosynthesis process, nitrogen is incorporated into organic matter through the assimilation of nitrate (NO_3^-) and ammonium (NH_4^+) by the primary producers. During OM mineralization process, NH_4^+ is produced and it diffused from the anoxic to the oxic zone. NO_3^- is produced by NH_4^+ during the nitrification under aerobic conditions. This process produces N_2O as a by-product. N_2O is a powerful greenhouse gas Nitrification is an aerobic microbial process that converts ammonium (NH_4^+) to nitrate (NO_3^-) in the presence of oxygen. During denitrification process,

nitrates are converted into nitrogen (N_2). The simplest scheme of nitrification is shown in Figure 2.4.

In temperate region, water temperature has a significant impact on nitrification and denitrification processes in the aquatic sediments. There are several major controls on denitrification rates which are NO_3^- concentration, oxygen availability, organic matter availability and temperature which all of which are interconnected with further external controls (Kessler *et al*., 2018).

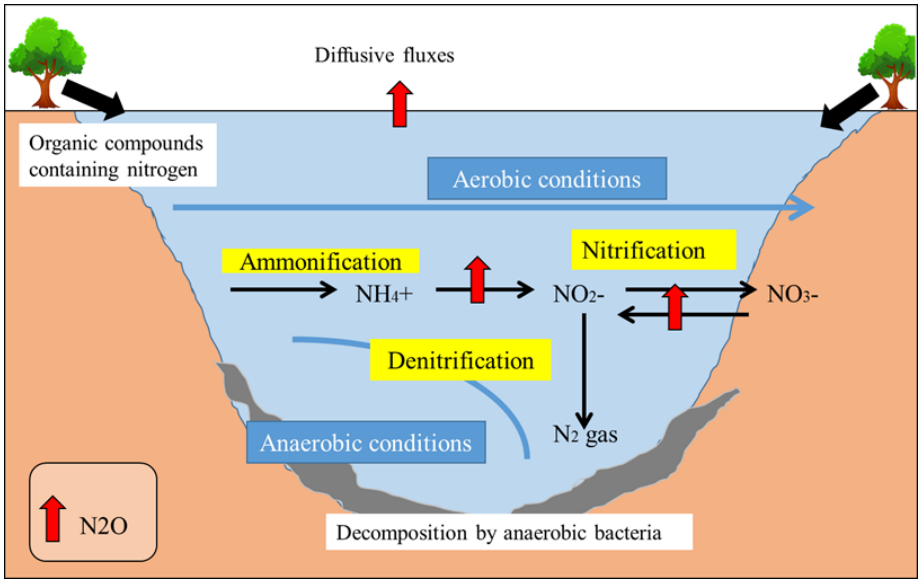

Figure 2.4: General biogeochemical cycle of nitrogen in a natural lake

Meanwhile in tropical region, the higher N_2O emissions was observed under warmer conditions may reflect the effects of temperature on nitrification and denitrification processes, as well availability of nitrogen, which is greater in tropical lakes comparing to boreal and temperate lakes (Kortelainen *et al*., 2019). Intense rainfall can contribute to increase nutrients runoffs and subsequent enhancing N_2O production in the lake, furthermore, the introduction of low temperature water during raining season may also leading to lake turnover and bringing N_2O saturated bottom water to surface (Fenwick *et al*., 2016).

Beside carbon and nitrogen, phosphorus is usually considered the limiting nutrient in many aquatic ecosystems. Phosphorus in aquatic ecosystem usually comes from wastewater effluent from municipal and industrial, leachate from waste disposal sites infiltration from animal feed lots, overflows of combined storm and sanitary sewers. The main driver of eutrophication in freshwater lakes in Malaysia is phosphorus but not nitrogen especially in Aman Lake, Ayer Keroh Lake, Chini Lake and Sembrong Reservoir (Sharip *et al*., 2014). Deoxygenation occurs normally after the eutrophication process, both processes has contributed significant of greenhouses productions in the water column.

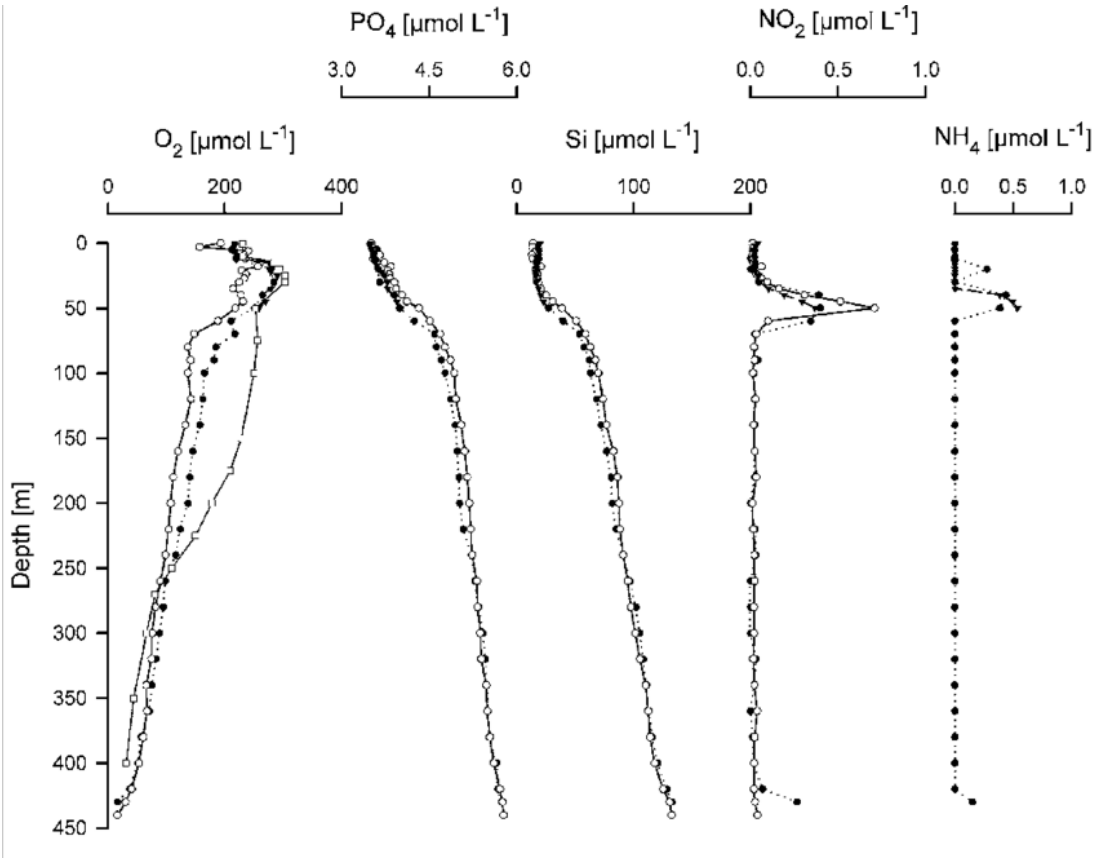

Figure 2.5: Typical nutrients concentration trends in a deep-water lake. (Adopted from Andreas Reimer *et al*., 2009).

Figure 2.5 shows a typical nutrients trend for a deep reservoir in Turkey. As seen in figure 2.5, phosphorus and Si have higher concentration at the bottom of the

lake, while NO_2 and NH_4 concentration have higher concentration at euphotic zone (a layer closer to the surface that receives enough light for photosynthesis to occur). Spikes in nitrite concentration at the bottom of the euphotic zone, known as the main nitrite maximum, are frequently observed features in numerous stratified water body and are believed either by bacterial nitrification or phytoplankton (Andreas Reimer *et al*., 2009).

2.5 GHGs Emitted by Hydroelectric Reservoirs

The UNESCO/IHA Greenhouse Gas Emissions from Freshwater Reservoirs Research Project report indicated that CO_2 accounted for 80% of the total greenhouse gases emissions. Nevertheless, the CO_2 emissions will be affected by the time and space of the creation of a reservoir. For example, new reservoir could have higher CO_2 emissions comparing to the aged reservoir Goldenfum (2010).

The decomposition of organic material in newly inundated reservoir is the main factor led to high CO_2 production in water column (Deemer *et al*., 2016). Once the underlying oxygen-deficient conditions begin to develop at the bottom layer, it is favourable to produce CH_4 under post-inundation conditions.

There is limited comparison study for N_2O emissions for newly build hydropower reservoirs and a few published studies report very low N_2O emissions in boreal aquatic ecosystems, but there are no conclusive results on tropical reservoirs. The summary of concentration of CO_2 and CH_4 in lake and reservoir of worldwide is presented in Table 2.1.

Table 2.1: CO_2 and CH_4 concentration on worldwide freshwater lake and reservoir

Location	Lat, °N	Long, °E	Catchment Size, km^2	Depth, m	purpose	CO_2, µM	CH_4, µM	Reference
Lake Baikal, Siberia	53.5587	108.1650	560,000	1642	Tourism	N/A	0-35	Granin *et al*., 2019
Stortjarn Lake, Québec Canada	63.2148	14.3145	12,046	74	Reservoir	400-1100	0.00-75	Denfeld *et al*., 2018
Lake Erken, Sweden	59.8458	18.5649	141	21	N/A	0.00-400	0.00-10	Ricão canelhas *et al*., 2016
Nam Theun 2 Reservoir, Laos	17.9969	104.9528	4039	7	Hydro electric	6-1118	0.5-275	Chandrashekhar *et al*., 2013
Thermokarst Lake, Qinghai-Tibetan, China	37.0000	100.1333	4186	32.8	N/A	3.6-45.0	0.28-3.0	Mu *et al*., 2016
Everglades Lake, United State	26.0803	80.2201	N/A	1.0	N/A	0.0-8.0	N/A	McDonald *et al*., 2013
Lake Paterno, Central Italy	42.3823	13.0139	N/A	55	N/A	0.0-55	N/A	Tassi *et al*., 2012
Lake Stechlin, Germany	53.1516	13.0261	26	70	N/A	N/A	0.1-1.6	Grossart *et al*., 2011
lake Hallwil, Switzerland	47.2833	8.200	128	46	N/A	N/A	0.01-0.75	Donis *et al*., 2017

Based on Table 2.1, Nam Theun 2 reservoir in Laos has the highest CO_2 concentration in the water column where it can go up to 1118 µM but the depth of the reservoir only 7.0 Meter depth (Chandrashekhar *et al*., 2013). Stortjarn Lake in Québec Canada also recorded more than 1100 µM and the depth of the lake recorded were 74 Meter depth (Denfeld *et al*., 2018). Other than these Lakes and reservoir, carbon dioxide concentration was recorded less than 500 µM.

CH_4 recorded highest in Nam Theun 2 reservoir in Laos with 275 µM and Stortjarn Lake in Québec Canada with 75 µM. Both of this lake also recorded highest CO_2 even though depth and location of these lake and reservoir contrasting. CH_4 concentration in other location recorded not more than 40 µM.

According to Kirillin *et al.* (2012), shallow and small lakes are often well shielded from wind and easily cool which likely to result in incomplete autumn mixing and faster ice development, which could understand why CO_2 and CH_4 concentrations appear to be high in shallow and small lakes compared to deeper lakes. In addition, higher latitude lakes tend to be more oligotrophic, whereas in lower latitudes lakes is higher lake metabolism and carbon processing. Thus, this highlights the difficulty of seasonal carbon dynamics regulation as the interactions was influenced by geographical location, lake morphology, trophic status, and runoff properties (Ducharme-Riel *et al*., 2015)

In this study, Kenyir Lake is classified as large and deep lake situated in a tropical climate region. The reservoir is located at low latitude, surrounded by natural vegetation, and receiving organic materials through the rivers and channels. All the above-mentioned criteria could make Kenyir Lake an important GHGs source to atmosphere.

2.6 GHGs Emission from Hydropower Dam and Reservoir in Malaysia

Over the past decades, Malaysia has built a lot of dams to generate electricity (Table 2.2) to fulfil national energy demands but none of these dams have done environmental assessment on dam operation induced GHGs production and emission. In general, hydropower source is classed as a renewable energy source, yet many global stakeholders also questioned the green credential of hydropower dam due to greenhouse gases emission from the waterbodies and its outlets. In Malaysia, hydropower accounted almost 17% of energy production in this country.

Table 2.2: Methane emission of major hydroelectric dams in Malaysia (Adopted from Ming *et al*., 2018)

No	Location	Catchment Size, km^2	Depth, m	Annual methane Emission ($GgCH_4yr^{-2}$)	Year of Commissioned
1	Chenderoh dam, Perak	25	32	5.75	1930
2	Cameron Highland Scheme, Pahang	182	N/A	0.12	1963
3	Temenggor dam, Perak	153	127	35.18	1972
4	Bersia dam, Perak	5.7	33	1.31	1983
5	Kenering dam, Perak	40.5	48	9.31	1983
6	Kenyir dam, Terengganu	2600	150	85.08	1985
7	Batang Air dam, Sarawak	1200	85	19.55	1985
8	Pergau dam, Kelantan	N/A	75	1.06	2000
9	Bakun dam, Sarawak	14750	205	159.82	2011

Ming *et al* 2018 used an empirical approach to estimate methane emission from Malaysia hydropower dams (Table 2.2). Results show that East Malaysia (Sabah and Sarawak) release approximately 179.37 $GgCH_4yr^{-2}$ with total percentage of 56.55% while peninsular Malaysia release approximately 137.81 $GgCH_4yr^{-2}$ with total percentage of 43.45%. Currently in East Malaysia Bakun dam release the most methane emission with 159.82 $GgCH_4yr^{-2}$ taking 50% of total emission in Malaysia while in Peninsular Malayis, Kenyir dam release the most methane emission with percentage of 26.82% due to large surface area of reservoir.

The number of new hydropower dams expected to be increased as the government plan to introduce more small hydropower systems throughout the country to achieve 20% renewable energy target by 2025. The GHGs emission from hydropower dam are not quantified as there are still gaps in collection data the quantification of their GHGs emission impacts. Developing a strategy for collecting the GHGs baseline data in hydropower dam is essential to the development of a GHG inventory for this industry. As such, Kenyir Lake is chosen as preliminary assessment site.

Figure 3.1 shows location of Kenyir Lake in Terengganu, Malaysia. Kenyir Lake is located at latitude 4°41`N and longitude 102°40`E. It is covered by more than 340 islands with a basin area of 38,000 hectares. This artificial lake was originally submerged in 1986 to generate hydroelectric power and receives water input from two main rivers: Terengganu River and Terenggan River (Kamaruddin, *et al*., 2011).

The main feature of the Kenyir Hydro Electric Project is a rock-filling dam with a 400 MW (megawatts) power plant. Two temporary bypass tunnels were constructed to divert the river during the construction period. The normal capacity of the lake store is 13.6 billion cubic meters of water. On the other hand, the deepest point is 145 meters. The power plant complex can produce 100 MW of electricity that can be supplied throughout Malaysia. Typically, daily operation operates with a

continuous output of 165 MW, with an average annual output of 1600 GWh (gigawatt-hours) (Kenyir Lake, 2020).

CHAPTER 3

METHODOLOGY

3.1 Overview

This study was carried out in Kenyir lake which is man-made lake located in Hulu Terengganu, Malaysia. The dam was built in 1970s to provide water to the Sultan Mahmud Power Station. The purpose of this study was to collect baseline data of physical parameter, dissolved nutrients, and dissolved concentration of carbon dioxide (CO_2) and methane (CH_4) in Kenyir Lake.

Six sampling campaigns were carried within Nov 2017 to Nov 2018 in this study. Seven sampling sites were selected to represent the varies environment setup of the lake. During each sampling campaign, in-situ physical water quality measurement was taken using a pre calibrated YSI 6-Series Multiparameter Water Quality Sondes to measure dissolved oxygen, salinity, conductivity, pH and temperature of the lake water. Water samples were sampled using a niskin water sampler at different depth for the nutrient's analysis (NO_2-N, NO_3-N, NH_4-N and PO_4^{3-}), dissolved organic carbon measurement and methane (CH_4) and carbon dioxide (CO_2) analysis via gas chromatography technique.

3.2 Study Area

The water sampling has been conducted at Kenyir Lake located in Hulu Terengganu, Malaysia. The maximum depth for Kenyir Lake was 145m, and the average depth was 35m (Kamaruddin, *et al*., 2011). The water samples were obtained from seven different sites within the lake. The coordinate and maximum depth of each sampling location was shown in Table 3.1 and Figure 3.1.

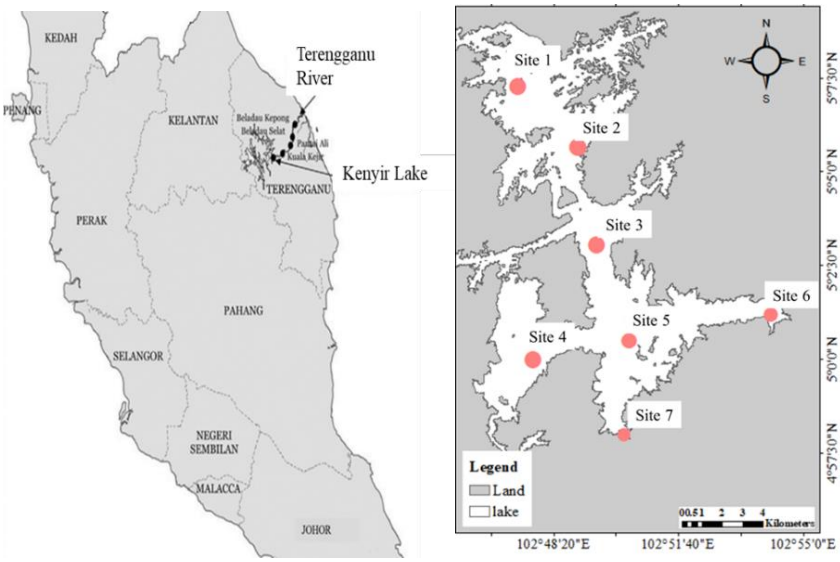

Figure 3.1: Sampling location (red circles) in Kenyir Lake, Terengganu, Malaysia

3.3 Sampling Strategy

Malaysia experiences the northeast monsoon, the southwest monsoon and two shorter monsoon transitions annually. For this study, sampling activities were carried out bimonthly (6 sampling intervals) to cover greenhouse gases changes between wet season (November-February) and dry season (March-August). Wet and dry season were determined by using rainfall dataset taken from Kg Dura (about 10

km to Kenyir Lake) provided by Department of Irrigation and Drainage Terengganu, Malaysia (DID).

Table 3.1: The sampling latitude, longitude, and depth in Kenyir Lake

Station	Latitude	Longitude	Maximum depth (M)
S1	5.121071	102.7899	35
S2	5.09414	102.8169	40
S3	5.050751	102.8248	110
S4	4.999661	102.7965	130
S5	5.007959	102.8397	140
S6	5.020104	102.9027	70
S7	4.966159	102.8371	45

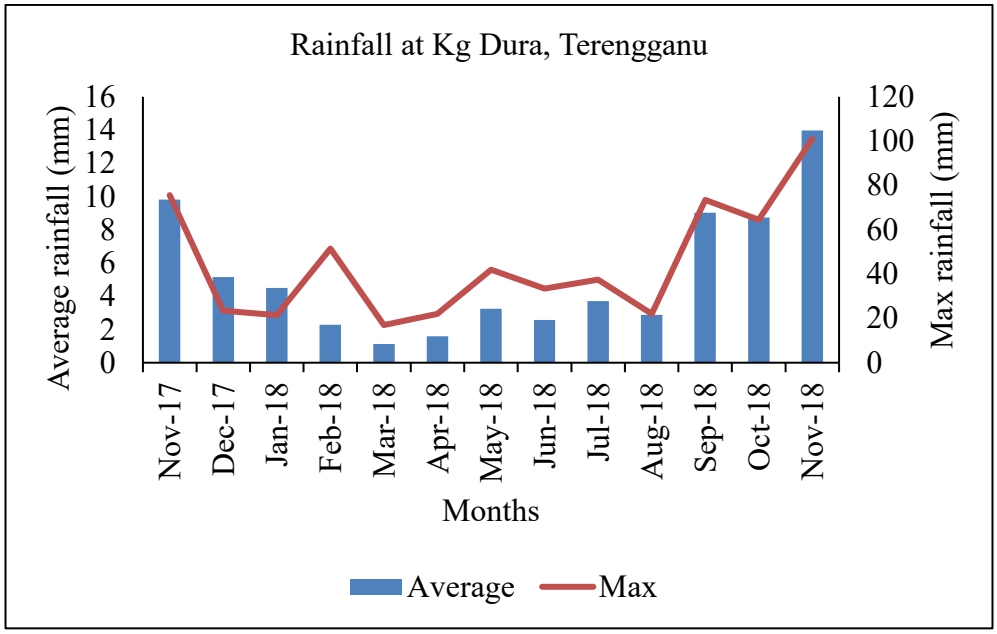

Figure 3.2: 2017-2018 rainfall (mm) at Kg Dura DID station, Terengganu Malaysia

Figure 3.2 shows during wet season the average rainfall in Kenyir Lake was more than 4 mm per month (September to February) and while for dry season, the average rainfall usually less than 4mm per month (March to August). Also, from

March to August, the rainfall clearly lower compared to September to February rainfall. Based on the rainfall data given in Figure 3.2, September to February months were considered as wet season while March to August months would be dry season in this study.

All the water sampling activities were carried out by a research boat (UMT *Discover VII*). The sampling strategy at each station was followed the sampling scheme as shown in Figure 3.3. Figure 3.2 illustrates that the water samples were collected at least at four different depths in each location. First depth was at the 0.5m below surface water of the lake, the second depth was at the point where the photic maxima depth by Secchi Disk reading, third depth was in the middle of the depth between the second depth and the bottom depth, and the final depth was the bottom depth where the dissolved oxygen value reached zero which is anoxia zone by using YSI 6-Series Multiparameter Water Quality Sondes (USA). At each depth of the sampling site, *in situ* dissolved oxygen, salinity, conductivity, pH, and temperature were measured using a calibrated YSI 6-Series Multiparameter Water Quality Sondes. Five-liter Niskin water sampler was used to collect water sample (in duplicate) at different depths.

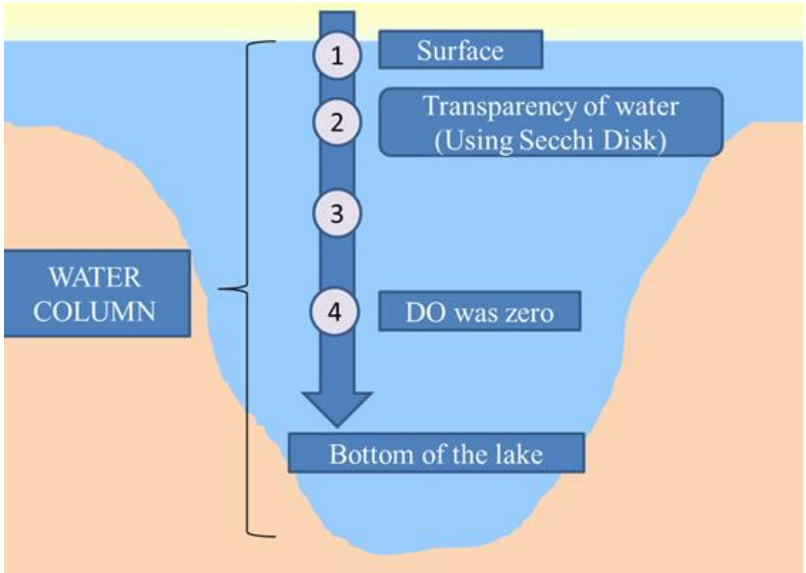

Figure 3.3: The number indicating the sampling depths

3.4 Sampling Procedure

3.4.1 Physical Water Quality Measurement

In this study, *in situ* physical water quality measurement was recorded using a pre calibrated YSI 6-Series Multiparameter Water Quality Sondes (YSI 6600, USA) as show in Figure 3.4. Multiparameter Water Quality Sondes was submerged into the lake at each sampling site and this underwater meter continuously measured the dissolved oxygen, salinity, conductivity, pH and temperature at 10 seconds interval during depth profile casting. Physical water quality measurement was taken directly in Kenyir lake in each location during sampling.

Figure 3.4: YSI 6-Series Multiparameter Water Quality Sondes (YSI 6600, USA)

Measurement of the transparency of the water was measured by using an 8 inch-diameters Secchi Disk with alternating black and white quadrant. The depth is measured at the point where the Secchi disk cannot be seen anymore.

3.4.2 Nutrients Samples sampling

Water samples for the nutrients analysis ($N\text{-}NO_2$, $N\text{-}NO_3$, $N\text{-}NH_4$ and $P\text{-}PO_4$) were collected using a 5 L Niskin water sampler before transferring into the pre-cleaned 250 ml high-density polyethylene (HDPE) bottle. The bottles were cleaned by soaking in 5% HCl for 24 hours, then further cleans with distilled water before dry. During sampling, bottle samples was rinsed with water samples 3 times before filled with the same water collected from Niskin water sampler. The samples then were filtered through 0.2 µM polyethersulfone (PES) syringe filter and filled into a 50ml centrifuge tube. By using 0.2 µM PES membrane filter, this would reduce any impurities and microorganism that depleted nutrients concentration in samples. All the samples have been chilling at 4 ^{o}C throughout the sampling.

Upon arrived at the lab, all the filtered samples were stored in the fridge at -20 ^{o}C until further analysis. The following 3.4.1- 3.4.3 section illustrated the detail sample preparation for nitrate+nitrite, ammonium, and orto-phosphate analysis using a Varian Cary 50 UV Visible Spectrophotometer. All the nutrients analysis was completed within a week after sample collection.

3.4.3 Particulate and Dissolved Organic Carbon (POC & DOC) Sampling

The DOC samples were collected using pre cleaned 250 ml HDPE bottles. The bottles were cleaned by soaking in 5 % HCl for 24 hours, then further cleans with distilled water before dry. During sampling, the samples then were filter through GF/F filter (0.7 µM, Whatman, USA). The filtrate was acidified with hydrochloric acid 37 % until pH 2 was reached to remove all the dissolved inorganic carbon (DIC). The POC sample was retained in the GF/F filter. Both dissolved and particulate samples were kept in ice box (5-10 ^{o}C) during the transportation to lab.

Upon arrived at the lab, all the filtered samples and filter membrane were stored in the fridge at 4.0 ºC until further analysis. The following 3.4.3 section illustrated the detail sample preparation for DOC analysis using a TOC analyzer. All samples analysis was completed within a week after sample collection.

3.4.4 Greenhouse Gases Sampling

The dissolved greenhouse gases samples were sampled based on Beaulieu *et al*. (2014) method. All GHGs sampling was conducted using 60 ml glass serum bottles. Prior sampling the bottles was cleaned by soaking in 5 % HCl for 24 hours, then further cleaned with distilled water. Later the bottles were heated at 450 °C for 4 hours to remove remaining organic residue inside the bottle. In brief, Niskin water sampler was used to collect water samples from different depths.

The water samples were transferred carefully into serum bottles without any agitation or creation of air bubble. The samples were preserved with 30 µL of 1.0 % (w/v) mercuric (II) chloride before seal the serum bottles using rubber septum and aluminum cap. The serum bottled were turned upside down during the transport to prevent any atmospheric contamination or diffusion. The collected samples were kept in room temperature until further laboratory analysis.

3.5 Analytical Chemistry Analysis

3.5.1 Nitrate and Nitrite Analysis

The reduction of the NO_3^- to NO_2^- allowed both NO_3^- and NO_2^- to be detected using Griess reaction technique as mentioned in García-robledo *et al*. (2014). Briefly, the nitrate reduction step was completed using vanadium (III) chloride (VCl_3) as reduction reagent. The addition of Griess reagent to samples will form red color azo solution and measured using a Cary 50 spectrophotometer (Varian, USA). The absorbance is measure at 540 nm with a light path of 1 cm. The detail of reagent preparation was described as below.

The reagents were prepared in which, 0.1 g of sulfanilamide (0.01% w/v) was dissolved into 1 ml of 12 N hydrochloric acid (HCl) and made up to 10 ml with DI water and cool to room temperature. 0.1 g of N-(1-napthyl)-ethylenediamine dihydrochloride (NED) was prepared in 10 ml of deionized water. Combine Griess reagent was prepared by mixing 0.01 % sulfanilamide and NED solution with 1:1 ratio. The reduction reagent 2.0 % Vanadium (III) chloride solution was prepared by dissolving 5 g of VCl_3 in 250 ml of 6 N HCl. The time needed for VCl_3 to complete dissolution take about 1 hour (from turbid to transparent solution) and then it was filtered through 0.7 µM glassfiber filter and the solution was stored in a dark bottle and can last for 6 months at 4 °C. Calibration standards (0.05, 0.1, 0.2, 0.4, 0.8, 1.0, 1.5, 2.0 ppm), blank and quality control standards (0.8 ppm) were prepared using distilled water and 50 ppm NO_3 and NO_2 stock standard solution, respectively.

For sample, blank and quality control standards analysis, 10 ml sample, 0.5 ml Griess-reagent and 1 ml 2 % VCl_3 was mixed into a 50 ml centrifuge tube. The sample was then heat at 60 °C for 25 min inside a thermostat-controlled water bath to speed up the reduction processes and Griess reaction. The García-robledo *et al.* (2014) described protocol is a two-step NO_3 and NO_2 measurement method. The first step involved the direct NO_2 measurement by adding Griess reagent without the VCl_3 reagent. The second step was NOx measurement which consists of NO_2 and NO_3 (it reduced to NO_2) by adding VCl_3-reagent. All the calibration standards, blanks,

samples, and quality control standards were cold down to the room temperature and the complete reaction can generated a red color azo with a maximum absorption at 504 nm. In this study, values of $R^2 > 0.95$ was used to indicate the linearity of calibration by itself yields a 5 % variability error in final measurement. The quality control standard recovery yield typically within the range of 90-110 %.

3.5.2 Ammonium (NH_4)

The measurement of ammonium in calibration standards, blank, quality control samples and water samples were analyses followed the APHA-4500-NH_3-F method. The required reagents were (i) alkaline citrate solution (200g trisodium citrate + 10 g sodium hydroxide (NaOH) in 1 L fresh distilled water), (ii) an oxidizing solution (100 ml alkaline citrate solution was added with 25 ml 5% sodium hypochlorite (Prepare daily using fresh bleach, 5% sodium hypochlorite), (iii) phenol solution (11.1 ml > 89% liquefied phenol was added to 95% v/v ethanol until reached 100 ml last for a week) and lastly, (iv) 0.5% w/v sodium nitroprusside (0.5g sodium nitroprusside in 100ml fresh distilled water and keep in amber bottle last for 30 days).

For each 20 ml samples, 0.8 ml phenol solution, 0.8 ml sodium nitroprusside solution, 2 ml oxidizing solution was added, and the samples will turn to blue color where it was formed by the reaction of ammonia in the samples, hypochlorite, and phenol catalyzed by sodium nitroprusside that was added into it (APHA, 2005). Both calibration (0.05, 0.1, 0.2, 0.4, 0.8, 1, 1.5, 2 ppm) and quality control standard (0.8 ppm) were prepared by dissolve 0.3819 g anhydrous ammonium chloride (dried at 105 °C) in distilled water and diluted to 1 L (100 ppm NH_3-N).

The absorbance wavelength of calibration standards, blank (deionized water), quality control standards (1ppm) was measure at 640nm with a light path of 1cm or greater by with a Varian Cary 50 UV Visible Spectrophotometer. The slope of calibration curve was greater than R>0.95 and the recovery of quality control standards were within 10% error.

3.5.3 Ortho-phosphate (PO_4^{3-})

The water samples for ortho-phosphate were analyses according to an ascorbic acid method as described in Parson *et al.*, (1984). The reagents have been prepared in the following manner. Prepared 5 N sulfuric acid by dilute 14ml concentrated sulfuric acid to 90 mL with DI water. The 5 N sulfuric acid must be cool down to room temperature before mixing. For potassium antimonyl tartrate reagent, dissolved 0.034 g $C_8H_{10}K_2O_{15}Sb_2$ salt in 25 mL DI water and store in glass-stopper bottle. For ammonium molybdate solution, dissolved 0.6 g $(NH_4)_6Mo_7O_{24}$ in 20 mL DI water and store in glass-stopper bottle. Lastly to prepare 0.01 M ascorbic, dissolved 1.08 g ascorbic acid in 20 mL DI water and it must freshly prepared prior use.

The mixture of the reagents of 50 ml 5 N sulfuric acid, 20 ml of ammonium molybdate solution, 20 ml of ascorbic acid, and 10ml potassium antimonyl tartrate solution was mixed to form 100 mL mix reagents. For every 20 mL sample, 2 mL of mix reagents was added and wait at least 10 minutes in which resulting a blue solution. The calibration (0.05, 0.1, 0.2, 0.4, 0.8, 1, 1.5, 2 ppm) and quality control standard (0.8 ppm) were prepared by dissolve 0.4396 g potassium dihydrogen phosphate (predried KH_2PO_4 at 105 °C for one hour) in distilled water and diluted to 1 L (100 ppm PO_4-P).

All calibration standards, blank (deionized water), quality control standard and samples were measured at 885 nm with a light path of 5 cm using a with a Varian Cary 50 UV Visible Spectrophotometer. The obtained recoveries result for quality control standards ranged within 90-110%. The linearity of the calibration curves expressed in R always greater than 0.95.

3.5.4 Dissolved Organic Carbon (DOC)

Determination of the dissolved organic carbon was done using a total organic carbon analyzer (SHIMADZU TOC-L) as shown in Figure 3.5. The organic carbon stock solution is prepared by using reagent grade potassium hydrogen phthalate. Based on Standard Method, 21st edition, 1000 ppm organic carbon stock solution was prepared from reagent grade potassium hydrogen phthalate, which 2.125 g was predried at 105 °C in an oven for hour and dissolved in 1 L of deionized water. The calibration standards were prepared from the 1000 mg C/L stock solution, while the 100 mg C/L concentration quality control standard was measured on weekly basic to assured quality data.

Figure 3.5: Total Organic Carbon Analyzer (SHIMADZU TOC-L & autosampler)

3.5.5 Particulate Organic Matter (POC)

Prior to sampling, the blank filters were prepared in lab by heated in a muffle furnace at 450 °C for 4 hours to remove organic residue (Pettine *et al*., 2001). The filter paper was pre-weighed and kept in a glass desiccator (each of the filter paper was placed in a labeled stainless steel round plate cover with aluminum foil) until sampling. Once the filtration was done, the filter papers were oven-dried at 105 ºC for 2 hours and cooled down to room temperature inside a desiccator. The filter papers were weighed on analytical balance to four decimal places to get more accurate results. The concentration of Suspended solid (SS) of the sample was calculated by the weight difference of filter paper before and after filtration divided by the filtrate volume.

The SPM can be divided into particulate organic carbon (POC) and particulate inorganic carbon (PIC). By combusting the filter samples at 450°C for 4 hours, the organic fraction of SPM is burnt off during the combustion and the weight loss of filters represents the organic fraction of SPM which is POC, while the weight of the samples in the filter paper represents the PIC results. The filter papers were then cooled down to room temperature in glass desiccators before weighing for final weight. Blank sample was also measured by using distilled water.

3.5.6 Headspace Preparation and GHGs Analysis Using GC

The headspace technique was introduced to obtain the gas phase of CH_4 and CO_2 in water samples bottle (Figure 3.6). To created headspace, helium gas was supplied at the rate of 15 mL/min (monitored by using Dwyer Flowmeter) into serum bottle by using a short needle (22 G,2 5.4 mm length). Another long needle (22 G, 40 mm length) was insert into serum bottle and connected to waste beaker. When the

helium tank was turn on, the water inside the serum bottles was displaced by helium gas with the ratio of 2:1 (liquid phase: gas phase) as in Figure 3.6.

The serum bottles were vigorously shaken for one minute at room temperature prior to gas chromatography (GC) injection. A 50 mL syringe coupled with a 3-way valve was used to transfer the gas samples in headspace (serum bottle) to GC's injector port (Figure 3.7). In this case 5 mL of gas sample was withdrawn and injected with a gas chromatograph Agilent 6890A (Figure 3.8). The CO_2 and CH_4 were measured using thermal conductivity detector (GC-TCD) and flame ionization detector (GC-FID), respectively. The measurement was done using different detector as GC-FID more reliable to measure low concentration CO_2 and CH_4 while GC-TCD can be used to measure high concentration CO_2. A series of calibration gases were prepared based on standard gas (3027 ppm CO_2 and 2010 ppm CH_4) purchased from Linde Malaysia. High purity helium gas was used as makeup gas for the calibration gas standards preparation. Ultra-pure nitrogen and Certified Reference Material gas cylinder served as blank and quality control standard was obtained from Linde Malaysia. The recovery percentage for both CO_2 and CH_4 was within 80-120 %, respectively.

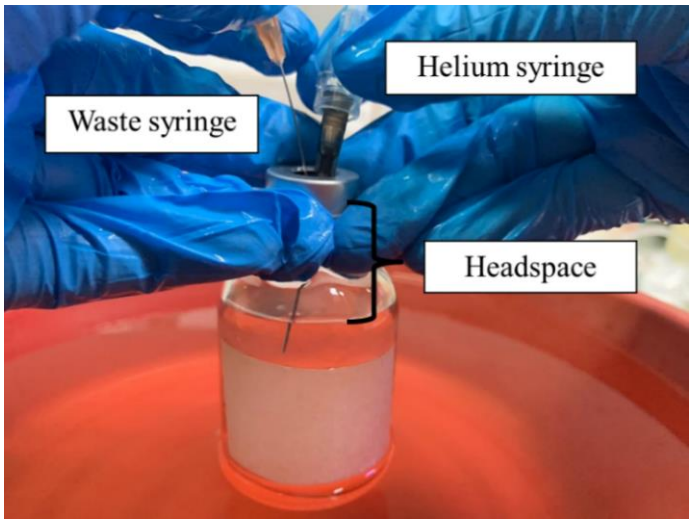

Figure 3.6: Created headspace with the ratio of 2:1 (liquid phase: gas phase).

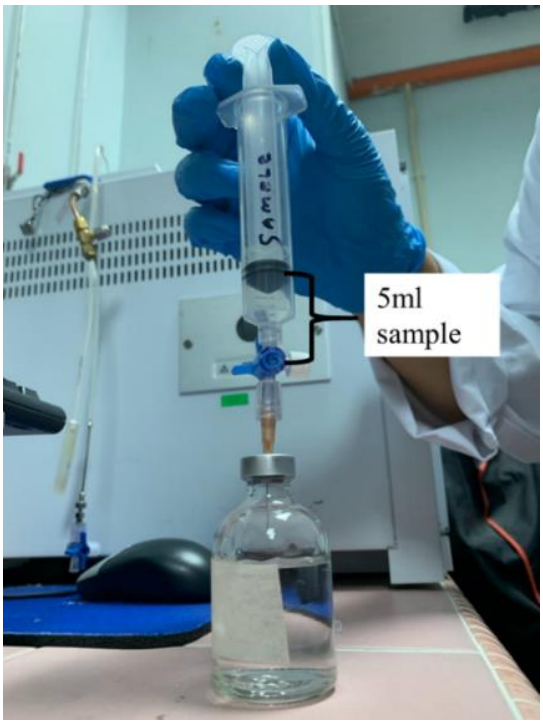

Figure 3.7: 5ml of sample taken from headspace.

Figure 3.8: Gas chromatograph Agilent 6890A (Agilent, USA).

3.5.7 Greenhouse Gases Concentration Calculation

The dissolved concentration of CO_2 and CH_4 were determine by using calculated equation according to Weiss (1970) and Yamamoto *et al.,* (1976)

methods. Using both the Henry's law equation and the Bunsen coefficient, the partial pressure CO_2 and CH_4 in headspace were calculated by taking account the volume of gases absorbed per unit volume of the solution, at the temperature of the measurement, total pressure and the fugacity. Fugacity (thermodynamic property of a real gas which is, the pressure or partial pressure in the equations is substitute for an ideal gas equation applicable to the real gas) of the CO_2 and CH_4 were then calculated back based equations below:

$$pH_2O = \mathrm{EXP}\left[24.4543 - 67.4509\left(\frac{100}{T}\right) - 4.8489\ \ln\left(\frac{T}{100}\right) - 0.000544(S\ ‰)\right] \text{ (i)}$$

where,

pH_2O : Partial pressure (atm)

T : Temperature of the sample

S ‰ : Salinity of the sample

A modified Henry's law equation was obtained to expressing the activity of a thermodynamic correction for the expansion of the solution by dissolved gases and the solute in the gases phase by its fugacity.

The modified Henry's law equation was shown below:

$$F_{CO2} = EXP\ \left[A_1 + A_2\left(\frac{100}{T}\right) + A_3\ \ln\left(\frac{T}{100}\right) + S\ ‰\left[B_1 + B_2\ \frac{T}{100} + B_3\left(\frac{T}{100}\right)^2\right]\right] \text{ (ii)}$$

where,

F: Fugacity in the gas phase (moles/L• atm)

A_1: -160.7333

A_2: 215.4152

A_3: 89.892

B_1: 0.02994

B_2: -0.02746

B_3: 0.00534

T: Temperature of the sample (K)

S: Salinity of the sample (‰)

$$F_{CH4} = EXP\left[A_1 + A_2\frac{100}{T} + A_3 \ln\frac{T}{100} + S\left[B_1 + B_2\frac{T}{100} + B_3\left(\frac{T}{100}\right)^2\right]\right] \text{(iii)}$$

where,

F: Fugacity in the gas phase (moles/L• atm)

A_1 : -67.1962

A_2 : 99.1624

A_3 : 27.9015

B_1 : -0.0729

B_2 : 0.0417

B_3 : -0.00646

T : Temperature of the sample (K)

S : Salinity of the sample (‰)

From the partial pressure and fugacity calculation, dissolved CO_2 and CH_4 can be calculated based the equation below:

$$[Liquid] = \left([Headspace]\left(1 - \left(\frac{pH_2O}{p\ Headspace}\right)\right)\right)F \qquad \text{(iv)}$$

$[Liquid]$: concentration of CO_2/CH_4 in water

Headspace: Concentration of CO_2/CH_4 from headspace (ppm)

pH_2O: Partial pressure (atm)

p Headspace: 1.00 atm

F: Fugacity in the gas phase (moles/L• atm)

3.6 Statistical Analysis

All dataset obtain (n=28) were analysis by using Shapiro-Wilk test to identify normality behaviour of the samples. The test indicated non-normal behaviour of GHGs and nutrients in Kenyir Lake, hence, non-parametric Spearman rank correlation coefficients were calculated between in physicochemical, nutrients and greenhouse gases concentrations. All the data analysis was conducted either on SPSS, Office Excel Data Analysis ToolPak (Microsoft), and/or R Stat.

3.7 Lake Internal Dynamic Analysis

Lake temperature profiles were measured with YSI multiparameter sonde 6600. The surface and hypolimnion temperatures were measured based on average top 2 m-depth temperature and water temperature below thermocline, respectively. Here, thermocline depth was defined at which the rate of temperature decreased at least 1°C per metre. The metalimnion is defined as the water stratum in a stratified lake with the steepest thermal gradient and is demarcated by the bottom of the epilimnion and top of the hypolimnion. The Schmidt stability index (SSI) is a proxy to quantify the energy required to fully mix a thermally stratified lake (express in the unit of J/m^2), equation v.

$$SSI = \frac{g}{A_0}\sum_{Z_0}^{Z_m}\left(z - z_{\bar{p}}\right)\left(p_z - \bar{p}\right) A_z \Delta_z \ \cdots\cdots \left(\frac{J}{m^2}\right) \quad \text{(v)}$$

A_0 is the lake surface area, $\bar{p}$ is the mean density, $z_{\bar{p}}$ is the depth to the center of gravity of the water column, A_z is the area at depth z, z_0 is the water surface depth, z_m is the maximum depth, Δ_z is the layer thickness, $A_z \times \Delta_z$ is the volume of the layer.

The lake number (L_n) can be used to predict lake stability if water column is mixing due to wind forcing (equation vi). A L_n = 1 indicated that the wind is sufficient to force the thermocline to be deflected to the surface at the upwind end of the lake. For $L_n \geq 1$ and $L_n \leq 1$, the stratification will be expected to be strong and weak, respectively with respect to the force by wind stress.

$$L_n = \frac{g\, S_t\left(1-\frac{Z_t}{Z_m}\right)}{\rho_0 u^2 A_0 3/2\left(1-\frac{Z_g}{Z_m}\right)} \qquad \text{(vi)}$$

Where g id the acceleration of gravity, S_t is the Schmidt stability (equation vi), Z_t is the thermocline height (m) from the bottom. Z_m is the maximum depth of the water body, ρ_o is the water density at the surface, u^2 is the water friction velocity due to wind speed, A_o and Z_f is the surface are and the height to centre of volume of the lake in meter off the bottom, respectively (Robertson and Imberger; 1994).

All parameters mentioned above: thermocline depth, hypolimnion temperature, SSI and L_n was calculated using the statistical R software package (rLakeAnalyzer). Details of rLakeAnalyzer software illustration and operation manual can be obtained from Winslow *et al* (2019).

CHAPTER 4

RESULT AND DISCUSSION

4.1 Thermal Structure in Kenyir Lake

Table 4.1 summarised the physical features of Kenyir Lake. The difference for the surface temperature and hypolimnion temperature between littoral zone and limnetic zone within dry and wet season can be seen. In littoral zone, hypolimnion was range between 26-28 °C while in limnetic zone was between 24-26 °C. The differences between this zone were about 2 °C and this will likely influence thermocline depth. In limnetic, the bottom water was much cooler, leading to a highly pronounced thermocline.

In littoral zone, thermocline depth only can be observed in average of 14 m depth while for the limnetic zone, average of the thermocline to happen was in 35 m. Despite the complexity of mixing processes in lakes, one fundamental mechanism for the vertical mixing in stratified waters is turbulent vertical diffusivity, which is primarily controlled by kinetic energy input such as wind and water column stability thus constrained by high water column stratification between the hypolimnion and epilimnion (Vachon *et al*., 2019).

All deep-water bodies including lakes, rivers, and oceans, show characteristic thermal structures in which a well-mixed warm upper layer separates from a relatively cold bottom during part of the annual cycle (Robert et al., 2020). If a body of water exhibits the thermal gradient in water column, it is said to be stratified, and the layer of intense temperature gradient separating the almost homogeneous upper layer from the colder bottom waters is termed the thermocline. However, Table 4.1 also indicated that Kenyir Lake thermal features are not uniform throughout the system.

The thermal profile in both littoral and limnetic zone in Kenyir Lake was found different. The depth for these two thermocline zones also differs more than 10m as thermocline in littoral zone ranges from 10-20 m depth while limnetic zone ranges from 20-40m depth depending on the season (Table 4.1). The surface wind stress, inflow and outflow of runoff, and atmospheric temperature gradients are the main factors that affect the structure in lakes (Yang *et al*., 2019).

Based on Table 4.1, center of buoyancy at Kenyir Lake in littoral zone during dry and wet season was 12.6±1.2 and 12.6±3.3 respectively, meanwhile in limnetic zone were 17.6±1.3 and 18.2±1.7 during dry and wet season respectively. Center of buoyancy depth was calculated by using buoyancy frequency. The buoyancy frequency is the maximum frequency that internal wave propagation can be supported by density stratification, which is the same frequency that the water mass vibrates as it moves vertically from the equilibrium position. (MacIntyre *et al*. 2010).

The effect of the center of buoyancy depth in Kenyir Lake can be seen shifted not more than 2m in both seasons at limnetic zone. This indicated that in limnetic zone, there is little water mixing happens throughout the water column, thus promote total nutrient deposition and contributing to net sedimentation. In the littoral zone, the effect of the center of buoyancy depth were shifted more than 3 m especially during wet season. As littoral zone has an average depth of about 40 m, the 3 m vertical shift of the center of buoyancy depth could promote water mixing between

epilimnion and hypolimnion. This could trigger another cycle of biogeochemical processes like nutrient remineralization and new production in water column (Brahney et al; 2014).

Table 4.1: Statistical summary physical features of Kenyir Lake between littoral and limnetic zone.

	Littoral Zone		**Limnetic Zone[ŧ]**	
	Dry	Wet	Dry	Wet
Surface temperature, °C	(30.8) ±2.0	(28.3) ±1.0	(30.7) ±1	(28.7) ±1
Hypolimnion temperature, °C	25.8±0.5	26.7±1.1	23.8±0.2	24.6±0.7
Thermocline depth, m	16.1±4.7	12.6±5.8	42±17	26.6±11
Thickness of metalimnion, m	1.7±2.6	1.4±0.9	2.4±1.7	1.5±1.0
Secchi depth, m	3.5±1.0	3.1±1.1	4.0±0.8	2.7±1.8
Schmidt stability, (J/m^2)	745±532	289±367	5494±1997	2225±2404
^Center of buoyancy depth	12.6±1.2	12.6±3.3	17.6±1.3	18.2±1.7
Lake number	154±85	19±21	1226±700	217±223

[ŧ]Site 6 data was excluded (missing data).
^ calculates based on Buoyancy Frequency function in "rLakeAnalyzer" parkage described in Winslow et al (2019).

The calculated Schmidt stability (St) is a measure of the energy required to completely mix a thermally stratified lake (Winslow et al., 2019). In littoral zone, dry season required more energy compared to wet season to fully mix Kenyir Lake as dry zone required 745 J/m^2 while wet season required 289 J/m^2 to fully mix the lake. In limnetic zone, dry season required 5494 J/m^2 while wet season required 2225 J/m^2 energy for Kenyir Lake to achieved well mix conditions. In comparison with these two zones, it is very clear that limnetic zone needs more energy to achieve lake full turnover.

Based on Table 4.1, lake number for littoral zone in dry season was 154±85 and wet season was 19±21 meanwhile in limnetic zone, lake number L_N, in dry season was 1226±700 and wet season was 217±223. Lake Number values are shown to be quantitative indicators of deep mixing in lakes and reservoirs that can be used to estimate changes in deep water dissolved oxygen (DO) concentrations (Robertston, 1990). Higher L_N value means that it required more energy to fully mixing throughout the water column. In Littoral zone it required less than 200 L_N value in both seasons to fully mixed while in limnetic zone it is required more than 1000 L_N value to fully mixed especially in dry season. This indicated that the probability limnetic zone to mixing is almost impossible.

Typical temporal variation of water column temperature and dissolved oxygen in both littoral zone and limnetic zone were presented in Figure 4.1 and Figure 4.2 respectively. Littoral zones in Kenyir Lake are also represented by Site 1, 2 and 7 while Site 3, Site 4, Site 5, and Site 6 represented limnetic zone (see appendix). The following temporal discussion were further classified into dry and wet seasons based on rainfall dataset taken from Kg Dura (about 10 km to Kenyir Lake) provided by Department of Irrigation and Drainage Terengganu, Malaysia. The dry periods were represented by March, May, and July 2018 samplings, while sampling during November 2017, February 2018 and November 2018 were considered as wet season.

Figure 4.1 shows that the shallow part of Kenyir Lake was thermally stratified (24 °C to 32 °C) during dry periods (March to July 2018) where thermocline can be clearly observed at 8 m to 20 m depth, while the water column temperature was found relatively lower (24 °C to 29 °C) during wet periods and the thermocline less pronounced in the wet period compared to dry period. The thermocline is the transition mixed water layer between the warmer water at the surface and the cooler deep water. During the Feb 2018 sampling, the average surface water temperature in Kenyir Lake were 1.5 °C less compared to other sampling months. This 1.5 °C difference does shift the thermocline from the 18m to 8m within the period of Nov 2017 to March 2018. Figure 4.1 also showed the

shallow part of the lake become less stratified and the upward migration of low DO% bottom water was observed in Feb 2018. The range of dissolved oxygen (DO) % during dry season was from 100 % at the surface to 20 % to the bottom of the lake while the range of DO % during wet season was from 100 % at the surface to 50% to the bottom of Kenyir Lake in Littoral Zone.

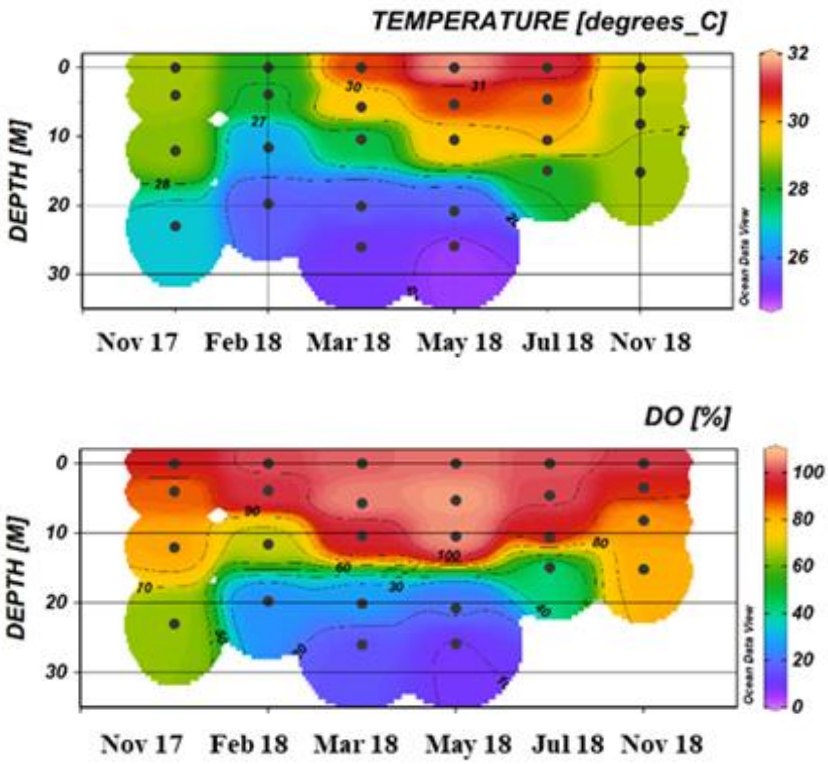

Figure 4.1: Temperature (°C) and dissolved oxygen (%) profile in littoral zone of Site 2.

The thermal structure in limnetic zone of Kenyir Lake shared almost same feature as littoral zone (Figure 4.2). Strong lake thermal stratification occurred during dry season (31 °C at the surface to 24 °C at the bottom of the lake) while during wet season the lake surface temperature was 2 °C cooler (29 °C) and the bottom temperature of the lake remain same 24° C. Dissolved oxygen on the other hand, remain 100% air saturation at surface water throughout the sampling campaign. However, the DO was found to diminish significantly with depth. In general, water

column at the depth beyond 45m in Kenyir Lake is complete absence of dissolve oxygen, this condition is called hypoxia.

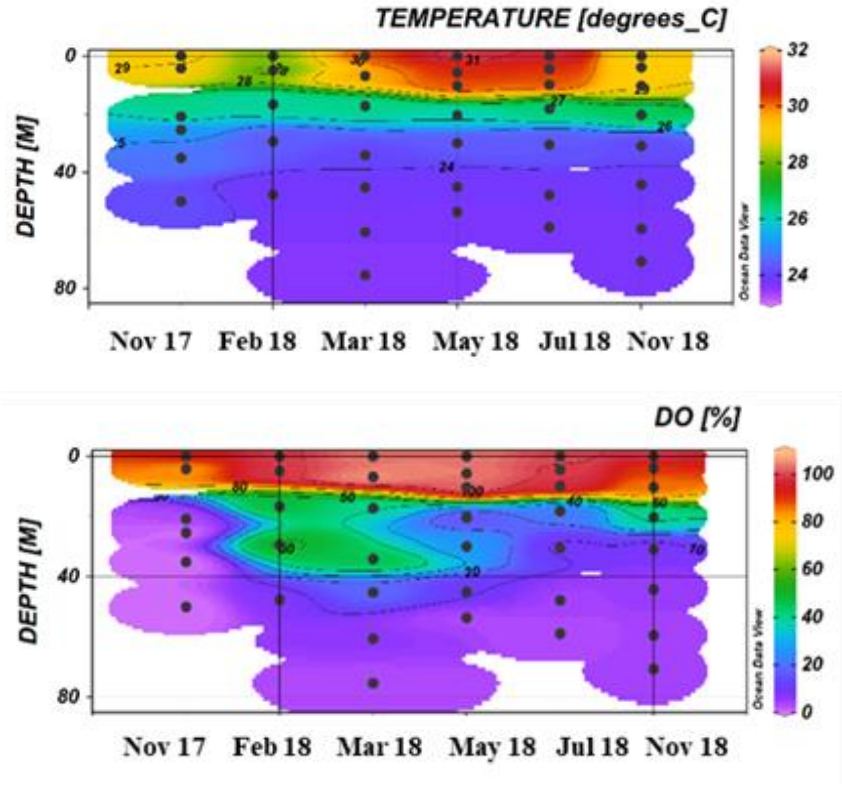

Figure 4.2: Temperature (°C) and dissolved oxygen (%) profile in limnetic zone of Site 3.

In Kenyir, about 50% oxygenated water was discovered at the middle depth during February and March 2018 samplings. The lake is strongly thermal stratified to prevent the any lake turnover event, thus another logical source of oxygen could be coming from runoff. During wet season, runoff could promote the penetration of oxygenated water to the deeper depth (40 m) of the lake.

The vertical temperature distributions pattern of Kenyir Lake from November 2017 to November 2018, which shows a complete cycle of thermal stratification Lake throughout the year. In Kenyir Lake all parameters can be seen were more stratified in the limnetic zone compared to littoral zone. It is interesting that these

phenomena have different impacts on nutrients and greenhouse gases as discussed in the following chapter.

4.2 Seasonal, Temporal and Vertical Variation of Dissolve Nutrients, CH_4 and CO_2 in Kenyir Lake

The temporal pattern and dissolved concentration of carbon dioxide (CO_2), methane (CH_4), dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus DIP, dissolved organic carbon (DOC) and particulate organic carbon (POC) in littoral (site 2) and limnetic zone (site 3) was shown in Figure 4.3 to 4.9, respectively. Other sites data are provided in Appendix. The concentration gradient was represented in color gradient. Both red and violet blue color represent high and low concentration unit, respectively.

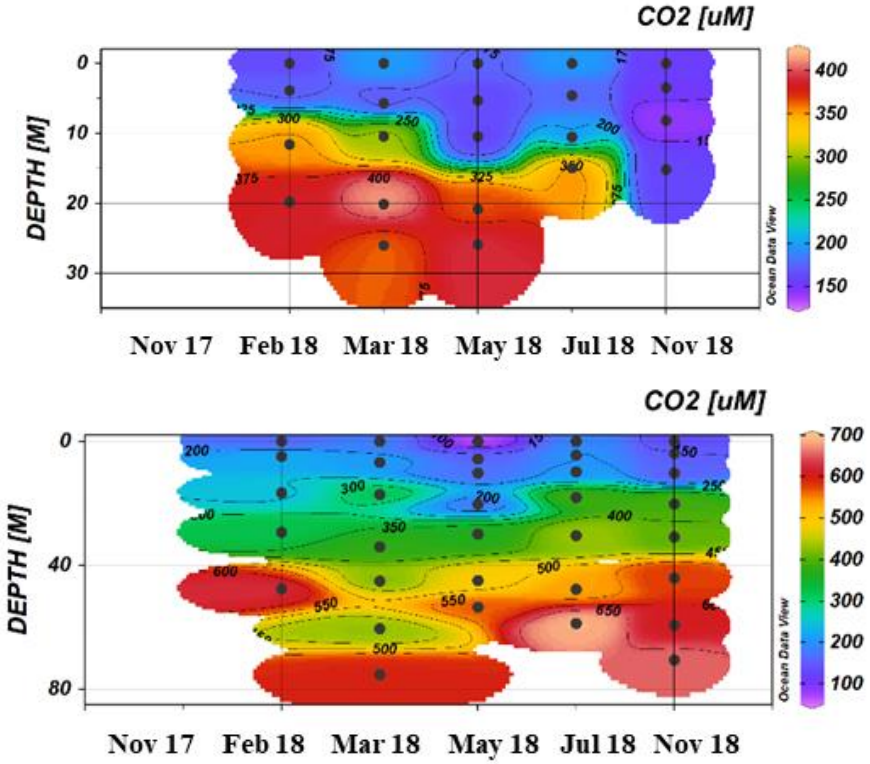

Figure 4.3: CO_2 profile in littoral (top panel, site 2) and Limnetic zone (bottom panel, site 3).

Figure 4.3 illustrates the surface CO_2 concentration in littoral zone was relatively lower (<200 µM) throughout sampling periods, but CO_2 concentration begins to increase with depth until it stabilized around 350 µM at 10-15m depth. Similar like littoral, the average CO_2 concentration at upper 20m in limnetic was about 200 µM. The CO_2 concentrations in water column were gradually increase with depth to reach >700 µM at the depth of more than 50 m. CO_2 concentration at bottom water of limnetic almost double compared with littoral. Strong thermal stratified water in limnetic zone has created a barrier for gas exchange between water column, thus higher CO_2 are anticipated in deeper water. The vertical stratification of CO_2 in the lake was found more prevalence during the dry periods compared to the wet periods. It is interesting to point out vertical CO_2 profile at littoral zone during Nov 2018 showed uniform distribution within top 20 m depth (150-200 µM). Lower CO_2 concentration was recorded (<100 µM) in water column during Nov 2018 could be contributed by the runoff. The increase of runoff near shallow water could promote CO_2 degassing from water column.

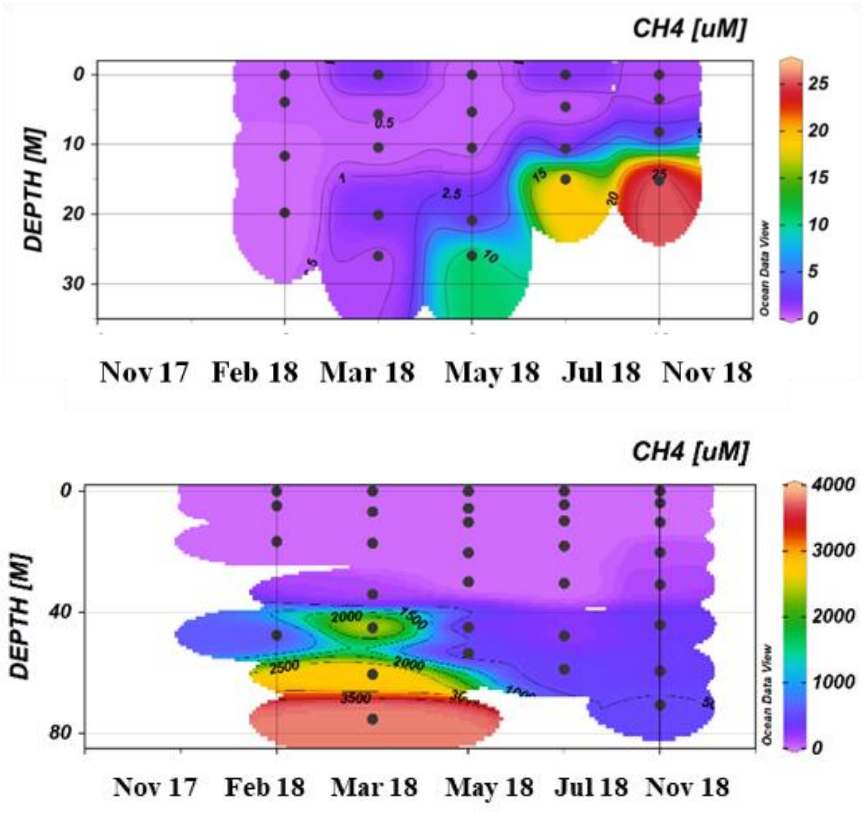

Figure 4.4: CH_4 profile in littoral (top panel, site 2) and Limnetic zone (bottom panel, site 3)

Figure 4.4 illustrates CH_4 profile in Kenyir Lake. In general, the surface water CH_4 concentration was very low (<5 µM). At bottom water, the CH_4 concentration at littoral and limnetic zone were range from 0.5 to 50 and 0.2 to 3800 µM, respectively. Hypoxia condition at bottom layer of Kenyir Lake explained the higher concentration of CH_4 found in this depth. Water column CH_4 concentration remained unchanged throughout the year with the exception during March 2018 at limnetic and May to Nov 2018. At shallow water depth, bubbles released from bottom sediments that reach water column explained the present of high CH_4 level in littoral zone (Figure 4.10). At limnetic, elevated CH_4 level was detected near water column (40-85 m depth). Strong stratification was observed during March 2018 (Figure 4.2), such phenomena decreased the vertical mixing between surface and bottom water, in turn, caused high CH_4 accumulation at site 3 bottom water.

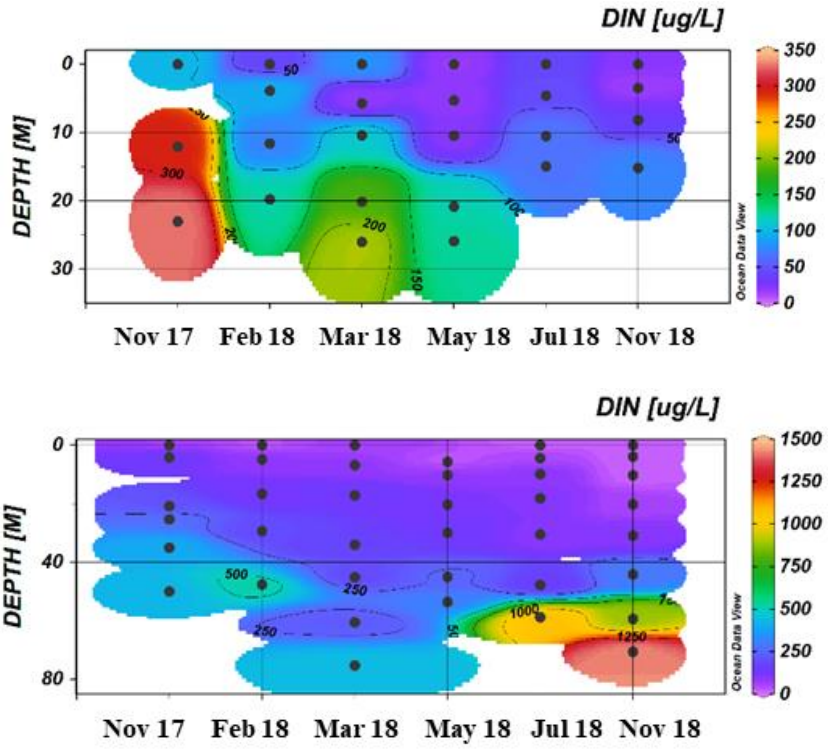

Figure 4.5: DIN profile in littoral (top panel, site 2) and Limnetic zone (bottom panel, site 3)

All surface water DIN concentration was uniformly distributed with the range of 40 µg/L to 150 µg/L (Figure 4.5). In littoral zone, concentration of DIN in November 2017 was found higher compared with other sampling. The concentration ranging from 200 µg/L -300 µg/L throughout the water column. An anomaly was spotted in March 2018, where the DIN concentration at 40m depth was measured as much as 450 µg/L. At limnetic zone, DIN concentration during July and November 2018 sampling were higher compared to other sampling months, especially in November 2018, where the DIN concentration exceeded 1000 µg/L can be observed (Figure 4.5). In general, DIN concentration in Kenyir Lake was more evenly distribute as there is no significant difference from surface to the depth of 20 m. However, the concentration of DIN (>500 µg/L) was found increase with water depth after 40 m. Nutrient levels increase at depth, as they are no longer being consumed by producers after photic zone, and they are being regenerated through the decomposition of organic material by bacteria.

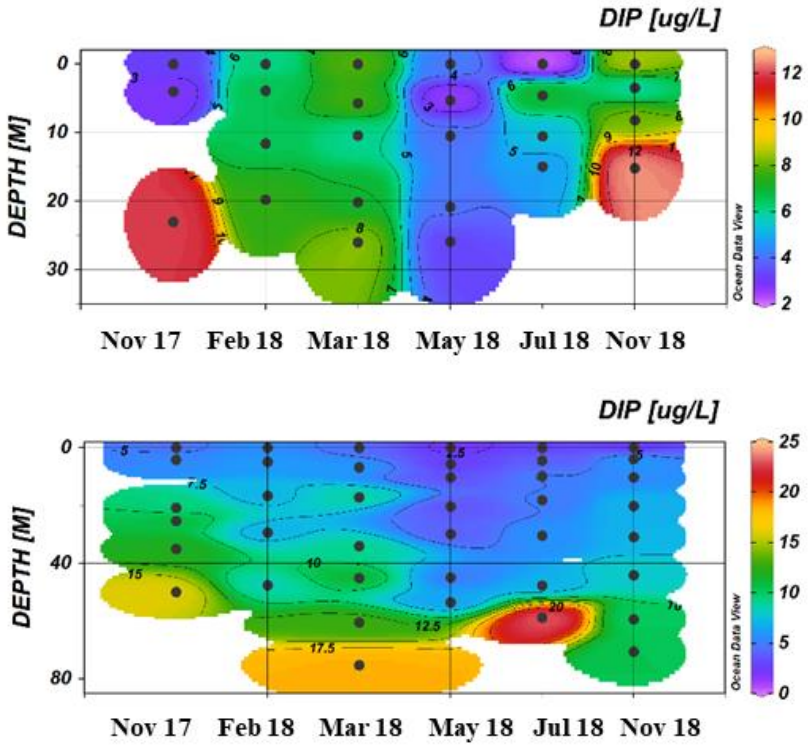

Figure 4.6: DIP profile in littoral (top panel, site 2) and Limnetic zone (bottom panel, site 3)

The concentration of DIP during wet and dry period were ranging from 6 to 18 µg/L, 2 to 10 µg/L, respectively. In littoral zone, DIP concentration was not evenly distributed throughout the lake for both dry and wet periods. The DIP deficiency was more prevalence during May-July 2018. Low DIP level could be attributed to higher productivity during dry season. Runoff could increase the DIP concentration in water column during wet period. In deeper water, the DIP profile showed similar trends like DIN, the concentration increases at depth (Figure 4.6). Higher DIP accumulation at bottom water can be explained the plants die, sink and decay, the nutrients are returned to their dissolved state at deeper levels of the lake.

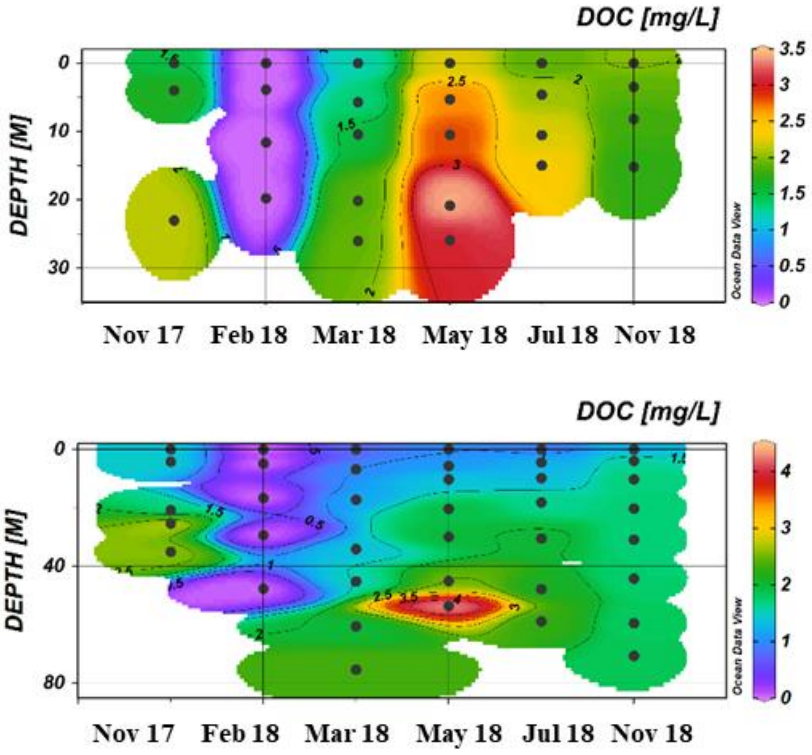

Figure 4.7: DOC profile in littoral (top panel, site 2) and Limnetic zone (bottom panel, site 3)

It noteworthy to mention that the DOC concentration was found uniformly distributed during February 2018 sampling. Lower DOC production in the studied lake could be attributed to lower productivity during wet season. In littoral zone, the averages DOC concentration was relatively lower (around 0.3 µg/L) compared to

limnetic (around 0.9 µg/L). The highest DOC concentration can be observed in May 2018. In Limnetic zone, the average DOC concentration during wet period was much lower compared to the dry period. Strong DOC stratification also observed in November 2017 and May 2018 samplings. Whereas the February 2018 sampling recorded the lowest DOC concentration compared to other sampling periods. The seasonal distribution of DOC in Kenyir Lake reflects the photosynthesis derived carbon source in water column at its maxima happen during the warmer period of the year.

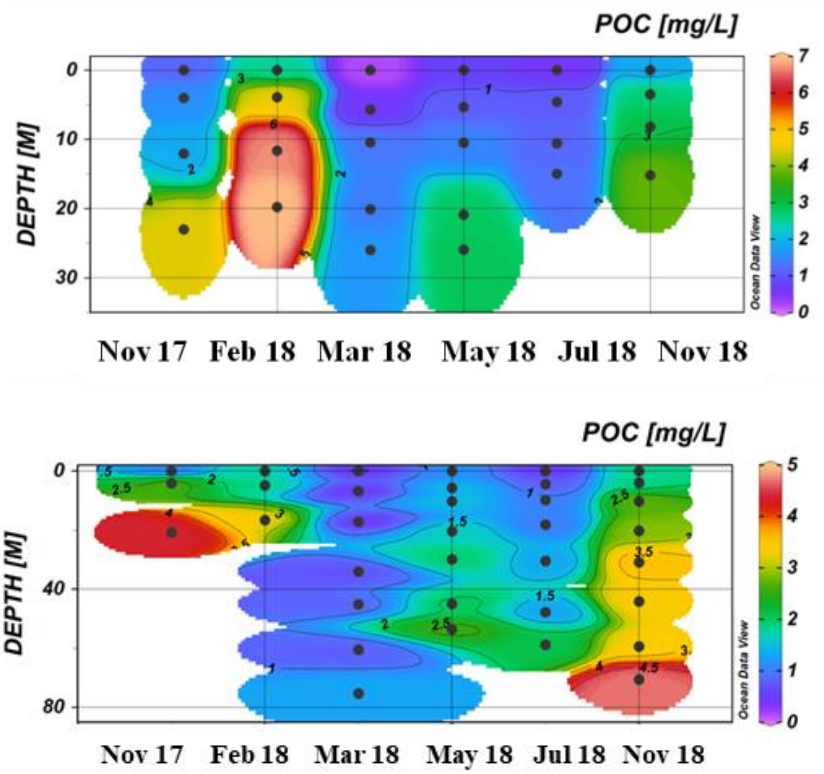

Figure 4.8: POC profile in littoral (top panel, site 2) and Limnetic zone (bottom panel, site 3)

The highest concentration of POC during wet and dry periods was at 3.0 and 2.5 mg/L, respectively (Figure 4.8). POC show similar trends like to DOC. The POC concentration increases with depth. During wet period, POC concentration were found more stratified, as the vertical distribution of POC concentration downward to lake bottom meanwhile POC concentration were more evenly distributed during dry

period. Higher POC concentration during Nov 2017 and Feb 2018 was attributed by the runoff. The flow of stormwater runoff from impervious surfaces rapidly increases stream velocity, which increases the erosion rates of streambanks and channels that increase the POC loading in the receiving water.

4.3 Effects of Lake Stratification on Dissolve nutrients, CH_4 and CO_2

Figure 4.9 shows an index about chemical stratification strength IC-x, where x is representing water quality parameter such as dissolved oxygen (DO), particulate organic carbon (POC), dissolved inorganic nitrogen (DIN), methane (CH_4), dissolved inorganic phosphorus (DIP), dissolved organic carbon (DOC) and carbon dioxide (CO_2).

Each regression coefficient in Figure 4.9 represents a change in the chemical stratification of x relative to the strength of the lake thermal stratification (Schmidt's stability index). Figure 4.9 shows that except for for $IC\text{-}DO_{littoral}$, $IC\text{-}DIN_{limnetic}$, and $IC\text{-}DIP_{limnetic}$, the effect of thermal stratification on water quality gradient is practically negligible ($p>0.05$). Figure 4.9A shows dissolve oxygen stratification was getting stronger (indicated by IC-DO values increasing) when thermal stratification was getting stronger at littoral zone.

As indicated by the coefficient of determination (r^2) in regression in Figure 4.10A, SSI explains 41.6% of IC-DO variation in littoral zone. The remainder ($1\text{-}r^2$) which cannot be explained by SSI, were the variation of dissolve oxygen likely caused by different biogeochemical processes in the lake.

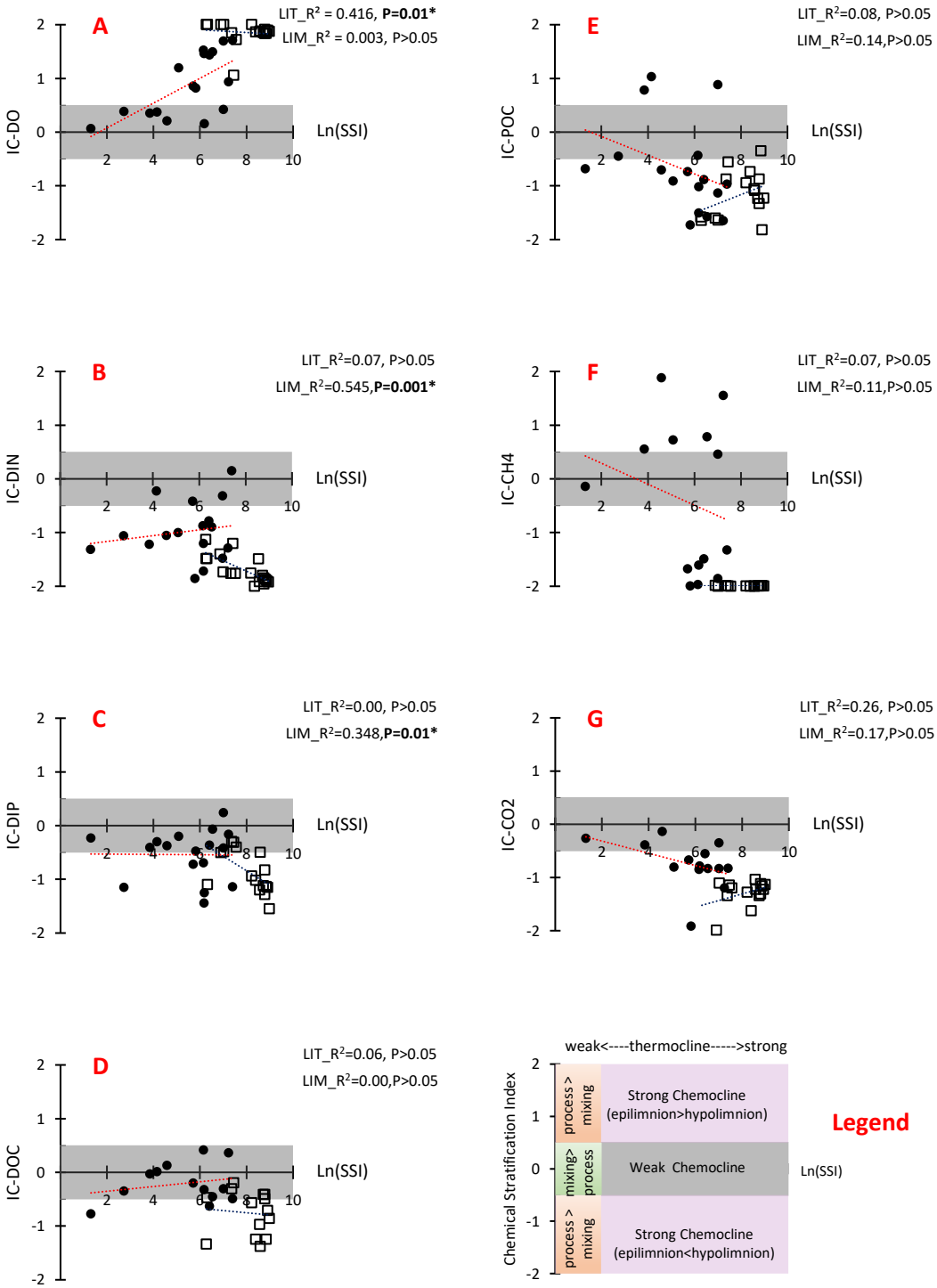

Figure 4.9: Relationship between Schmidt stability (SSI) index and chemical stratification index strength (IC); (□) Limnetic zone and (●) Littoral zone. The regression coefficients for each pair were calculated with a 95% confidence interval.

Both IC-DIN (Figure 4.9B) and IC-DIP (Figure 4.9C) tends to decrease from around 0 to near -2, which mean chemical stratification was getting stronger (indicated by IC-DIP and IC-DIN values decreasing) when the thermal stratification getting stronger at limnetic zone. DIN and DIP assimilate by phytoplankton growth at epilimnion can be responsible for these chemoclines in the Kenyir Lake. In addition, release of phosphorus and nitrogen compounds from deep-water sediment could enhance the chemical stratification in the lake (Su *et al.*, 2019).

Association between SSI and IC-DOC (Figure 4.9D) and IC-POC (Figure 4.9E) are not clear, and it seems that both DOC and POC were affected by other factors such as biogeochemical processes rather than mixing from different water sources (epilimnion vs hypolimnion). Figure 4.9F and Figure 4.9G show most of IC - CH_4 and IC-CO_2 fall under -0.5 – 2.0 range except for IC-CH_4 at littoral site. IC-CH_4 value at littoral was found scatted from 0.5 to 2 indicates the CH_4 profile in water column was strongly control by processes rather than mixing between surface and bottom water. High dissolved CH_4 concentration at surface water could be due to ebullition from shallow anoxic methane-rich sediments. At Site 7, gas transfer and ebullition (i.e., bubbling) across the air-lake interface was observed during field sampling (Figure 4.10).

Figure 4.10: “Methane bubble” at N4.966159°, E102.8371°, Kenyir Lake.

The events of ebullition were observed at Site 7 during sampling. This phenomenon had contributed elevated CH_4 concentration in surface water. Ebullition is typically observed at water depths shallower than 20m.

4.4 Spearman Rank Correlation Analysis

Figure 4.11 shows the overall correlation between GHGs with measured environmental during wet and dry periods in Kenyir Lake. Spearman's correlation was used to determine the relationships among the measured variables. Positive correlation between CH_4 and nutrients (DIN, DIP, DOC and POC) were significant during wet period ($p<0.05$).

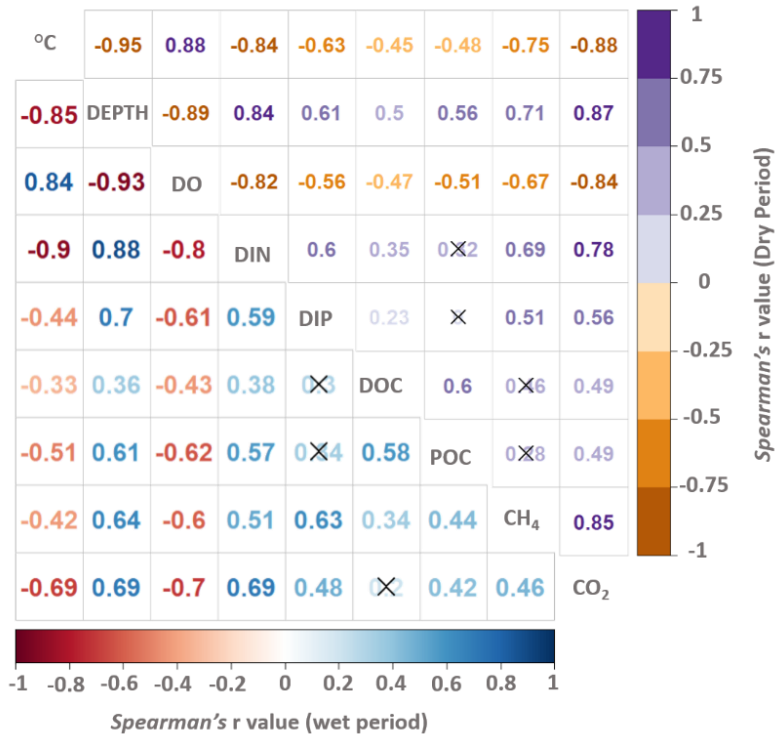

Figure 4.11: Relationship between CO_2/CH_4 concentration and water quality in the Kenyir Lake during dry/wet period. The regression coefficients for each pair were calculated with a 95% confidence interval; the (x) represent $p>0.0$.

Their Spearman's r^2 values ranged from 0.34-0.63. Therefore nutrients (C, N and P) addition from hydrological inputs into the lake could resulted in increasing production of dissolved CH_4 in Kenyir Lake. During dry period, CH_4 has significant positive correlation with DIN (r^2=0.69) and DIP (r^2=0.51) but less with DOC and POC. The result indicates that both DIN and DIP are potential factors controlling the methanogenesis process that strongly affect dissolve CH_4. Stronger linear effect of CH_4 on the CO_2 during dry period (r^2=0.85) compared to wet period (r^2=0.46) was also evident, suggesting that methane oxidation process could induced almost 85% CO_2 production in lake water during the dry period. The remainder (1-r^2) value of 15% can be explained by respiration.

Figure 4.12 and shows overall GHGs correlation with other environmental parameters at both littoral and limnetic zone in Kenyir Lake. It is interesting to note that there is no evidence of a statistically significant interaction between CO_2 and other nutrients (DIN, DIP, POC and DOC). The CO_2 varies in shallow part of the Kenyir Lake was largely control by the lake temperature dissolved oxygen contents and depth of the lake. DOC was the only environmental parameter that show significant relationship with CH_4 at littoral zone (r^2=0.41).

This study suggested higher DOC loading (Figure 4.7) at lake bottom as direct substrate for methanogenesis process, which may promote CH_4 production in lake water. In Limnetic zone, most of the nutrients showed positive correlation with CH_4 except for POC. CH_4 explained 87% of CO_2 variations suggesting methanogenesis process at deeper part of the lake might induced CH_4 oxidized to CO_2 concentration in water column. In Limnetic zone, nutrients play control the production of CH_4 except for POC. CH_4 explained 87% of CO_2 variations suggesting methanogenesis process at deeper part of the lake might induced CH_4 oxidized to CO_2 concentration in water column.

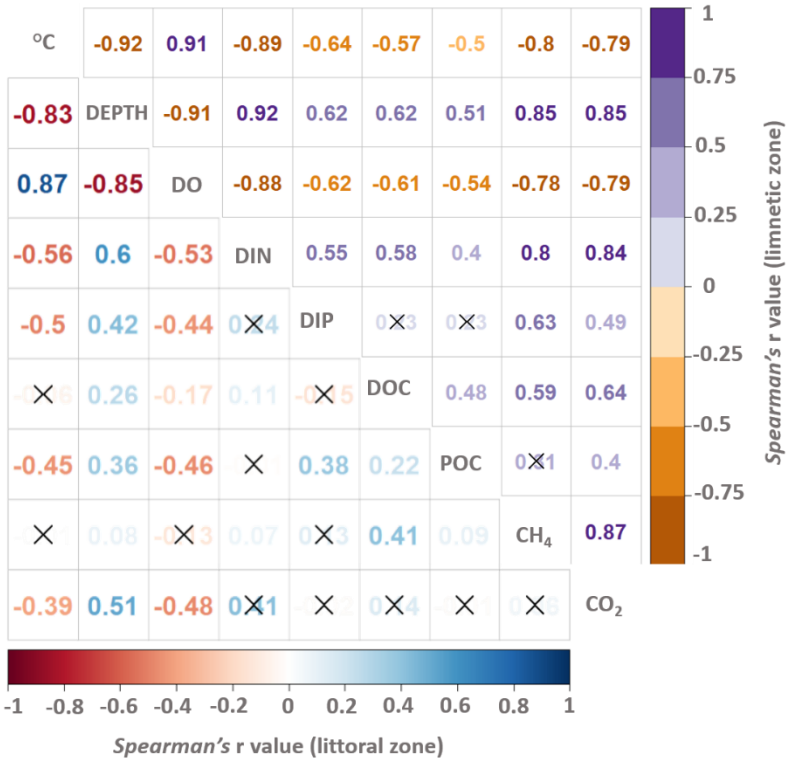

Figure 4.12: Relationship between CO_2/CH_4 concentration and water quality in the littoral and limnetic zone. The regression coefficients for each pair were calculated with a 95% confidence interval; the (x) represent p>0.05.

Overall, based on temperature profile plots, Schmidt stability and L_N calculation and correlation analysis, Kenyir Lake most likely stratified throughout the years and the lake turnover condition is very unlikely to be happen. Lake turnover is a phenomenon whereby the entire water column in a lake is well mixed and this can only happen when the entire lake water column is within the same temperature. As Kenyir Lake is always thermal stratified, this situation will lead to the CO_2, CH_4 and inorganic nutrients accumulation at the bottom of the lake. Minimum hydrological input and large water bodies of the Kenyir Lake could resulted the lake remains as thermal stratified for a long period. However, accumulation of high concentration GHGs at the bottom of the lake can lead to catastrophic event (hypoxia at surface water), if the turnover of the lake happens.

4.5 Comparison of Kenyir Lake CO_2 and CH_4 with worldwide freshwater lake and reservoir

Table 4.2 show comparison study of Kenyir Lake CO_2 and CH_4 against other freshwater lake system. The CO_2 and CH_4 concentration level in Kenyir Lake was ranked at middle and high range respectively compared with other studies. The highest concentration of CO_2 can be observed at Nam Theun 2 Reservoir, Laos with 1118 µM while Kenyir Lake was the second highest (925 µM) but Kenyir Lake recorded the highest CH_4 concentration compared to other freshwater lake system with 4226 µM, almost 5-folds higher than Nam Theun 2 Reservoir, Laos. High organic material accumulation due to unclear vegetation during dam construction and hypoxia condition at the bottom of the lake which favourable the methanogenesis process could be responsible for high CH_4 accumulation in water column.

Table 4.2: Comparison of Kenyir Lake CO_2 and CH_4 with worldwide freshwater lake and reservoir

Location	CO_2, µM	CH_4, µM	Reference
Kenyir Lake, Malaysia	1.3-925	0.10-4226	This Study
Lake Baikal, Siberia	N/A	0-35	Granin *et al*., 2019
Stortjarn Lake, Québec Canada	400-1100	0.00-75	Denfeld *et al*., 2018
Lake Erken, Sweden	0.00-400	0.00-10	Ricão canelhas *et al*., 2016
Nam Theun 2 Reservoir, Laos	6-1118	0.5-275	Chandrashekhar *et al*., 2013
Thermokarst Lake, Qinghai-Tibetan, China	25-200	0.01-5.0	Mu *et al*., 2016
Everglades Lake, United State	0.0-8.0	N/A	McDonald *et al*., 2013
Lake Paterno, Central Italy	0.0-55	N/A	Tassi *et al*., 2012
Lake Stechlin, Germany	N/A	0.1-1.6	Grossart *et al*., 2011

CHAPTER 5

CONCLUSION

5.1 Conclusion

The temporal and spatial variability of CO_2, CH_4, dissolve inorganic nitrogen, dissolve inorganic phosphorus, dissolve organic carbon and particulate organic carbon were mainly controlled by the water mixing and biogeochemical processes in the water column, particular in limnetic zone. Strong thermal stratification was observed in Kenyir Lake.

Temperature and DO% were strongly stratified in Kenyir Lake. Both temperature and DO% showed strong correlation with CO_2, CH_4 and other parameters. Lower the DO% in water column will trigger CH_4 and CO_2 production especially at depth below 40 m depth to the bottom of Kenyir Lake. Higher concentration of the CO_2, CH_4 and inorganic nutrients is likely contributed from the decay of organic matter at hypolimnion depth (anoxic level reach) in which DO% and temperature play very important role in producing CH_4 (methanogenesis), CO_2 (respiration and organic matter degradation) and inorganic nutrients concentration through organic matter remineralization in Kenyir Lake.

In littoral zone, inorganic nutrients can be observed more uniformly distribute throughout the water column while in limnetic zone, concentration of inorganic nutrients only uniformly distribute during wet season but strongly stratified during dry season. Epilimnion CO_2 and CH_4 concentrations were found relatively consistent throughout the sampling period (Nov 2017- Nov 2018), meanwhile both GHGs have different maximum concentration at hypolimnion depth.

The events of ebullition were observed at shallow water during sampling. This phenomenon had contributed elevated CH_4 concentration in surface water. Ebullition is typically observed at water depths shallower than 20m. Table 4.2 show comparison study of Kenyir Lake CO_2 and CH_4 against other freshwater lake system. The CO_2 concentration level in Kenyir Lake was found at the high side compared with other studies.

Kenyir Lake turnover is very unlikely to be happen as the lake experienced strong thermal stratification throughout whole year. However, this situation will lead to strong CO_2, CH_4 and inorganic nutrients accumulation at the bottom of the lake (limnetic zone) as showed in Pearson correlation analysis. High CO_2 and CH_4 concentrations accumulate in bottom water can lead to catastrophic event when turnover of the lake happens in the future. Another possible CO_2 and CH_4 degassing from the lake could be occurred at the outlets of dam when the CO_2 and CH_4 enriched lake bottom water discharging. Together these results highlight a critical need both better understand the emissions pathways of these GHGs and the relationship between the dam operations, biogeochemical drivers, and nutrient inputs which likely to be strongly influenced by climate change in coming decades.

5.2 Recommendation

This study is just the beginning to study the role of Malaysia's freshwater lakes in the global GHG budget. Furthermore, freshwater CO_2 and CH_4 data sets is remain scare in Malaysia. For the future work, it is recommend extending the similar study for the major freshwater reservoirs listed in Table 2.2. Future studies need to integrate large-scale geomorphological and land-use variation, diffuse eruption control systems, and the functional diversity of lakes found in Malaysian freshwater ecosystems GHGs studies shall also cover the sites immediately below the dam outlets and downstream.

This study briefly mentioned about the important of biogeochemical processes in controlling GHGs production in Kenyir Lake. Future studies in Kenyir Lake can focus on utilising the stable isotope technique (both N15 and C13) and *in-situ* mesocosm techniques to identify key biogeochemical process that responsible for CH_4 and CO_2 production in the lake interior.

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APPENDIX A1

Concentration of DIN and DIP in Site 1

Date	Depth (m)	Nitrate (ug/l)	Nitrite (ug/l)	Ammonia (ug/l)	Orthophos-phate (ug/l)
Nov 2017	0.0	52.61	5.69	180.62	12.38
Nov 2017	2.9	179.24	5.91	76.15	11.22
Nov 2017	12.2	159.08	10.96	130.81	16.77
Nov 2017	0.0	76.24	1.70	31.44	6.54
Feb 2018	4.5	61.43	1.21	N/A	5.76
Feb 2018	17.9	110.73	1.06	27.15	6.78
Feb 2018	19.3	117.48	1.38	2.37	N/A
Feb 2018	36.1	125.99	2.63	22.57	9.98
Feb 2018	0.0	47.44	2.68	53.77	6.91
Mar 2018	4.5	48.32	4.06	52.18	7.81
Mar 2018	16.3	125.86	3.41	55.69	7.17
Mar 2018	20.1	123.90	2.38	29.30	7.87
Mar 2018	32.3	346.28	2.28	133.81	8.15
Mar 2018	0.0	N/A	3.65	34.01	2.68
May 2018	2.8	40.92	1.61	27.74	3.14
May 2018	16.8	86.48	1.67	50.35	4.56
May 2018	20.0	N/A	1.26	25.67	5.31
May 2018	31.2	N/A	1.67	30.78	9.82
May 2018	0.0	30.98	1.91	44.21	3.16
Jul 2018	3.6	0.47	3.25	147.92	2.40
Jul 2018	9.7	8.87	1.39	89.54	3.62
Jul 2018	15.6	5.40	0.93	45.00	5.20
Jul 2018	20.6	5.34	0.69	190.68	6.53
Nov 2018	0.0	15.44	1.47	5.50	6.93
Nov 2018	3.8	10.73	2.38	5.89	8.82
Nov 2018	10.6	53.20	2.46	1.64	9.84
Nov 2018	16.4	42.52	1.80	48.29	10.48

*N/A: No data available.

APPENDIX A2

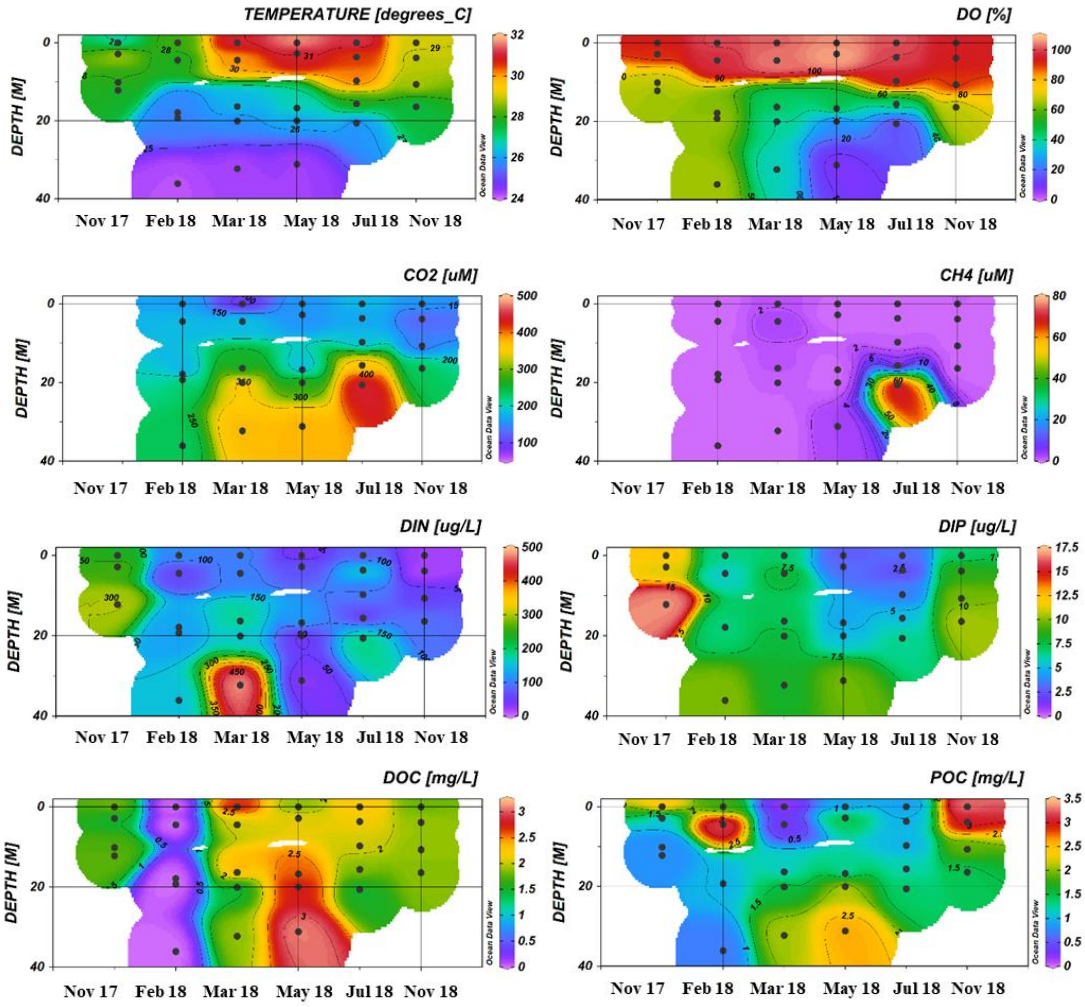
Spearman correlation in Site 1

	Temp	Depth	DO	DIN	DIP	DOC	POC	CH4	CO2
Temp	1.000								
Depth	-.926**	1.000							
DO	.846**	-.859**	1.000						
DIN	-.418*	.421*	-.246	1.000					
DIP	-.560**	.470*	-.396	.051	1.000				
DOC	.282	-.096	-.032	-.208	-.188	1.000			
POC	-.311	.148	-.382	-.403	.285	-.151	1.000		
CH4	.317	-.252	.128	-.041	.107	.309	-.100	1.000	
CO2	-.659**	.693**	-.696**	.323	.201	-.041	.117	0.000	1.000

**Correlation is significant at the 0.01 level (2-tailed).
*Correlation is significant at the 0.05 level (2-tailed).

APPENDIX A3

The temporal pattern and dissolved concentration of CO_2, CH_4, DO, DIN, DIP, DOC, POC and temperature in Site 1



APPENDIX B1

Concentration of DIN and DIP in Site 2

Date	Depth (m)	Nitrate (ug/l)	Nitrite (ug/l)	Ammonia (ug/l)	Orthophos-phate (ug/l)
Nov 2017	0.0	96.54	4.50	N/A	3.21
Nov 2017	4.0	N/A	N/A	N/A	2.85
Nov 2017	12.1	132.13	5.99	155.95	N/A
Nov 2017	23.0	209.24	5.67	114.31	11.91
Feb 2018	0.0	40.01	0.84	N/A	6.15
Feb 2018	3.9	82.61	0.57	13.14	6.59
Feb 2018	11.6	51.27	0.58	22.28	6.58
Feb 2018	19.8	67.64	0.26	55.44	7.51
Mar 2018	0.0	52.51	3.11	25.09	7.83
Mar 2018	5.7	20.67	3.68	N/A	7.70
Mar 2018	10.5	52.78	2.85	58.23	6.05
Mar 2018	20.1	146.67	3.06	34.42	6.99
Mar 2018	26.0	150.19	2.74	58.69	8.38
May 2018	0.0	N/A	1.34	17.40	4.16
May 2018	5.3	N/A	2.29	17.79	2.61
May 2018	10.5	N/A	1.82	20.83	4.09
May 2018	20.9	N/A	1.15	30.62	4.14
May 2018	25.9	28.48	1.55	96.30	3.28
Jul 2018	0.0	1.72	1.04	40.92	2.24
Jul 2018	4.6	3.69	2.06	40.98	6.97
Jul 2018	10.6	4.11	1.11	61.05	5.36
Jul 2018	15.0	13.96	0.92	51.96	4.78
Nov 2018	0.0	11.54	1.86	9.81	8.55
Nov 2018	3.5	3.63	2.50	10.18	5.93
Nov 2018	8.2	27.75	2.34	5.51	8.18
Nov 2018	15.2	65.88	2.36	7.17	12.55

*N/A: No data available

APPENDIX B2

Spearman correlation in Site 2

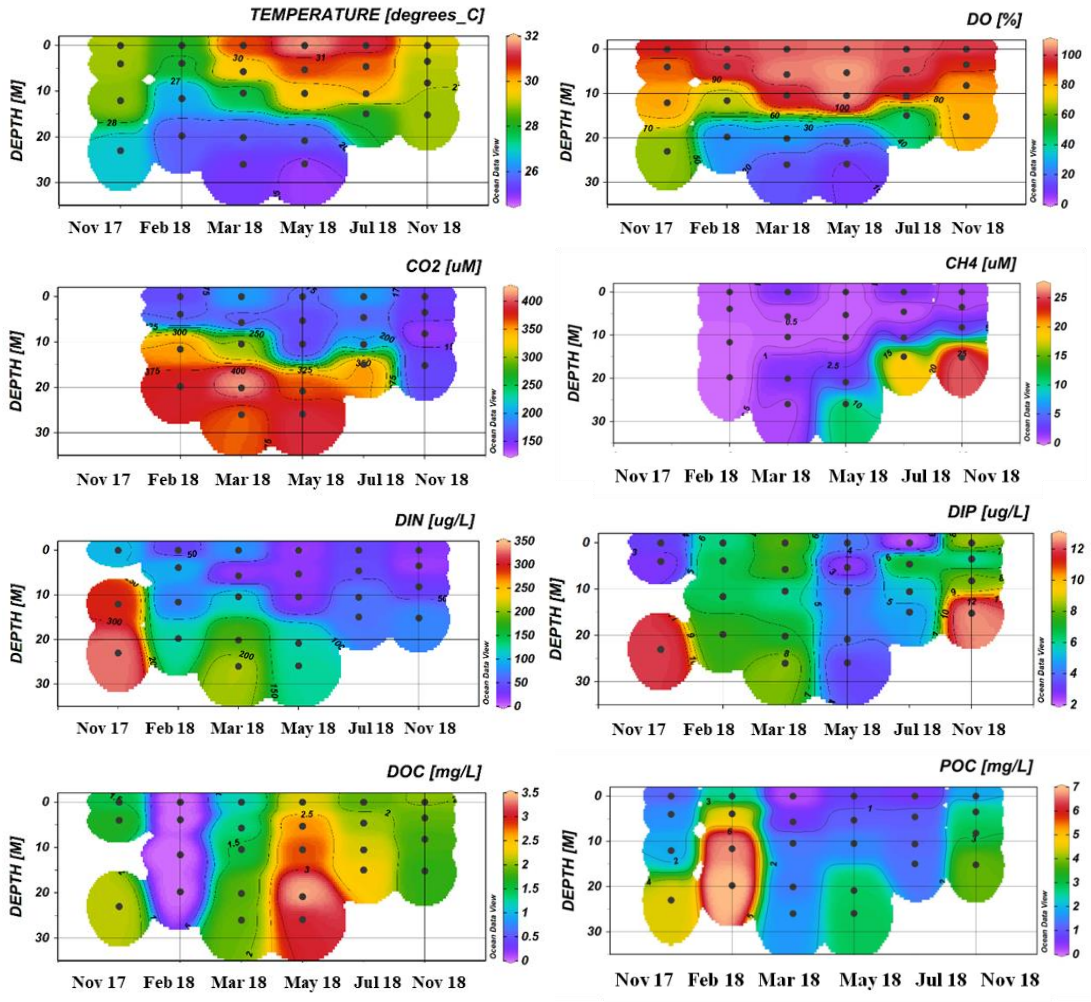
	Temp	Depth	DO	DIN	DIP	DOC	POC	CH4	CO2
Temp	1.000								
Depth	-.771**	1.000							
DO	.868**	-.782**	1.000						
DIN	-.757**	.679**	-.743**	1.000					
DIP	-.194	.047	-.193	.190	1.000				
DOC	.117	.265	-.052	-.109	-.553**	1.000			
POC	-.640**	.273	-.576**	.287	.213	-.108	1.000		
CH4	-.077	.091	-.277	.025	.050	.461*	.040	1.000	
CO2	-.571**	.606**	-.585**	.791**	-.186	.111	-.081	.034	1.000

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

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

APPENDIX B3

The temporal pattern and dissolved concentration of CO_2, CH_4, DO, DIN, DIP, DOC, POC and temperature in Site 2



APPENDIX C1

Concentration of DIN and DIP in Site 3

Date	Depth (m)	Nitrate (ug/l)	Nitrite (ug/l)	Ammonia(ug/l)	Orthophos-phate (ug/l)
Nov 2017	0.0	56.71	6.22	N/A	4.69
Nov 2017	4.2	69.79	5.76	77.75	5.53
Nov 2017	20.7	98.62	12.11	95.77	9.44
Nov 2017	25.3	138.55	7.61	134.19	10.94
Nov 2017	35.0	166.62	5.90	234.04	12.09
Nov 2017	50.0	93.44	15.07	320.90	16.07
Feb 2018	0.0	33.51	0.17	N/A	5.61
Feb 2018	4.9	42.90	0.15	44.91	6.19
Feb 2018	16.6	60.69	N/A	64.52	7.13
Feb 2018	29.3	193.32	N/A	N/A	7.09
Feb 2018	47.6	95.20	1.90	436.44	8.42
Mar 2018	0.0	21.98	2.80	39.54	4.61
Mar 2018	6.7	65.28	4.38	18.84	6.16
Mar 2018	17.2	4.57	5.71	141.92	8.98
Mar 2018	34.1	N/A	11.34	172.54	9.26
Mar 2018	45.1	142.55	2.93	33.33	11.42
Mar 2018	60.4	24.99	4.30	200.77	12.91
Mar 2018	75.3	153.65	2.57	287.53	18.42
May 2018	0.0	0.00	0.00	0.00	2.06
May 2018	5.7	N/A	0.35	30.51	2.64
May 2018	10.2	N/A	2.68	84.09	3.55
May 2018	20.3	120.37	1.22	N/A	3.53
May 2018	29.9	111.51	1.71	30.10	3.92
May 2018	45.0	N/A	10.18	249.00	4.87
May 2018	53.6	N/A	8.11	297.91	6.32
Jul 2018	0.0	1.20	0.92	19.67	2.94
Jul 2018	4.4	4.98	0.63	45.10	4.01
Jul 2018	9.9	21.64	0.75	70.86	5.10
Jul 2018	18.2	N/A	10.36	89.73	5.09
Jul 2018	30.5	23.79	0.94	76.11	5.86
Jul 2018	47.7	110.91	6.59	34.87	7.03
Jul 2018	58.8	0.67	0.71	1079.76	23.19
Nov 2018	0.0	7.82	1.76	5.25	2.28
Nov 2018	3.9	2.78	2.53	9.98	6.13
Nov 2018	10.2	1.22	3.82	17.13	5.65
Nov 2018	20.2	47.06	1.81	9.75	7.04
Nov 2018	30.9	N/A	2.48	99.17	7.07
Nov 2018	44.1	N/A	9.62	286.47	8.14
Nov 2018	59.3	N/A	8.56	875.25	10.15
Nov 2018	70.6	N/A	6.66	1425.84	10.46

*N/A: No data available

APPENDIX C2

Spearman correlation in Site 3

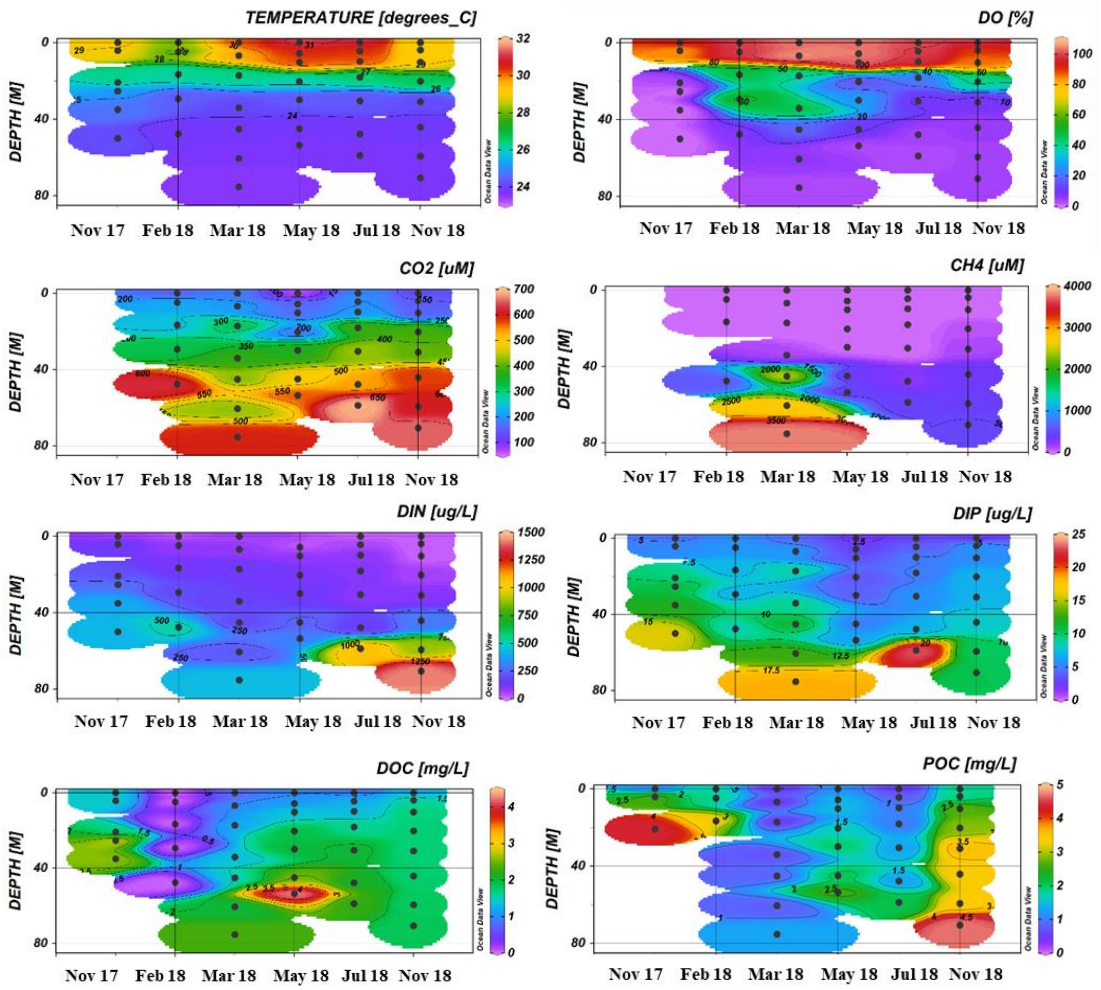
	Temp	Depth	DO	DIN	DIP	DOC	POC	CH4	CO2
Temp	1.000								
Depth	-.947**	1.000							
DO	.939**	-.916**	1.000						
DIN	-.899**	.914**	-.839**	1.000					
DIP	-.783**	.751**	-.693**	.743**	1.000				
DOC	-.654**	.712**	-.747**	.496**	.266	1.000			
POC	-.367*	.323	-.443*	.245	.201	.355*	1.000		
CH4	-.868**	.901**	-.811**	.812**	.738**	.675**	.172	1.000	
CO2	-.889**	.906**	-.882**	.898**	.756**	.578**	.304	.845**	1.000

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

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

APPENDIX C3

The temporal pattern and dissolved concentration of CO2, CH4, DO, DIN, DIP, DOC, POC and temperature in Site 3



APPENDIX D1

Concentration of DIN and DIP in Site 4

Date	Depth (m)	Nitrate (ug/l)	Nitrite (ug/l)	Ammonia(ug/l)	Orthophosphate (ug/l)
Nov 2017	0.0	28.70	5.85	102.26	6.54
Nov 2017	5.3	22.13	6.17	113.18	6.59
Nov 2017	12.0	168.18	11.78	92.70	0.00
Nov 2017	20.7	25.26	11.71	257.61	9.11
Nov 2017	40.0	58.38	21.46	241.41	0.00
Nov 2017	60.0	87.63	18.07	217.88	0.00
Nov 2017	80.0	155.30	10.76	328.50	0.00
Feb 2018	0.0	39.58	N/A	N/A	5.71
Feb 2018	3.4	39.96	N/A	15.63	5.83
Feb 2018	11.6	74.04	N/A	N/A	6.23
Feb 2018	20.2	85.38	N/A	42.65	6.58
Feb 2018	40.0	N/A	2.40	543.28	6.65
Feb 2018	60.0	N/A	2.45	547.64	9.00
Feb 2018	77.0	N/A	2.16	557.50	9.42
Mar 2018	0.0	22.73	2.71	0.00	5.36
Mar 2018	3.7	19.83	2.32	15.79	6.45
Mar 2018	9.6	24.60	2.96	54.48	6.74
Mar 2018	20.1	11.77	10.11	206.99	8.30
Mar 2018	33.9	3.38	6.68	294.43	10.89
Mar 2018	48.5	24.48	10.00	367.00	11.55
Mar 2018	65.9	6.16	13.45	391.04	12.93
May 2018	0.0	N/A	1.21	13.24	2.61
May 2018	4.5	N/A	1.44	16.69	3.57
May 2018	10.6	N/A	10.47	31.60	3.59
May 2018	20.7	N/A	1.06	214.85	3.97
May 2018	35.3	N/A	6.43	217.04	5.62
May 2018	44.9	N/A	5.69	351.57	8.77
May 2018	64.3	N/A	11.32	437.32	9.44
Jul 2018	0.0	13.08	1.17	18.58	5.10
Jul 2018	4.1	10.02	0.93	22.59	5.65
Jul 2018	10.3	8.79	1.08	35.57	5.90
Jul 2018	13.9	0.00	0.00	0.00	6.97
Jul 2018	21.5	32.52	1.41	98.18	7.01
Nov 2018	0.0	12.15	2.57	0.83	7.43
Nov 2018	4.3	11.90	2.49	8.82	8.02
Nov 2018	11.2	31.56	2.73	N/A	8.70
Nov 2018	20.7	N/A	N/A	N/A	9.35
Nov 2018	34.0	15.80	12.22	215.83	10.03

*N/A: No data available

APPENDIX D2

Spearman correlation in Site 4

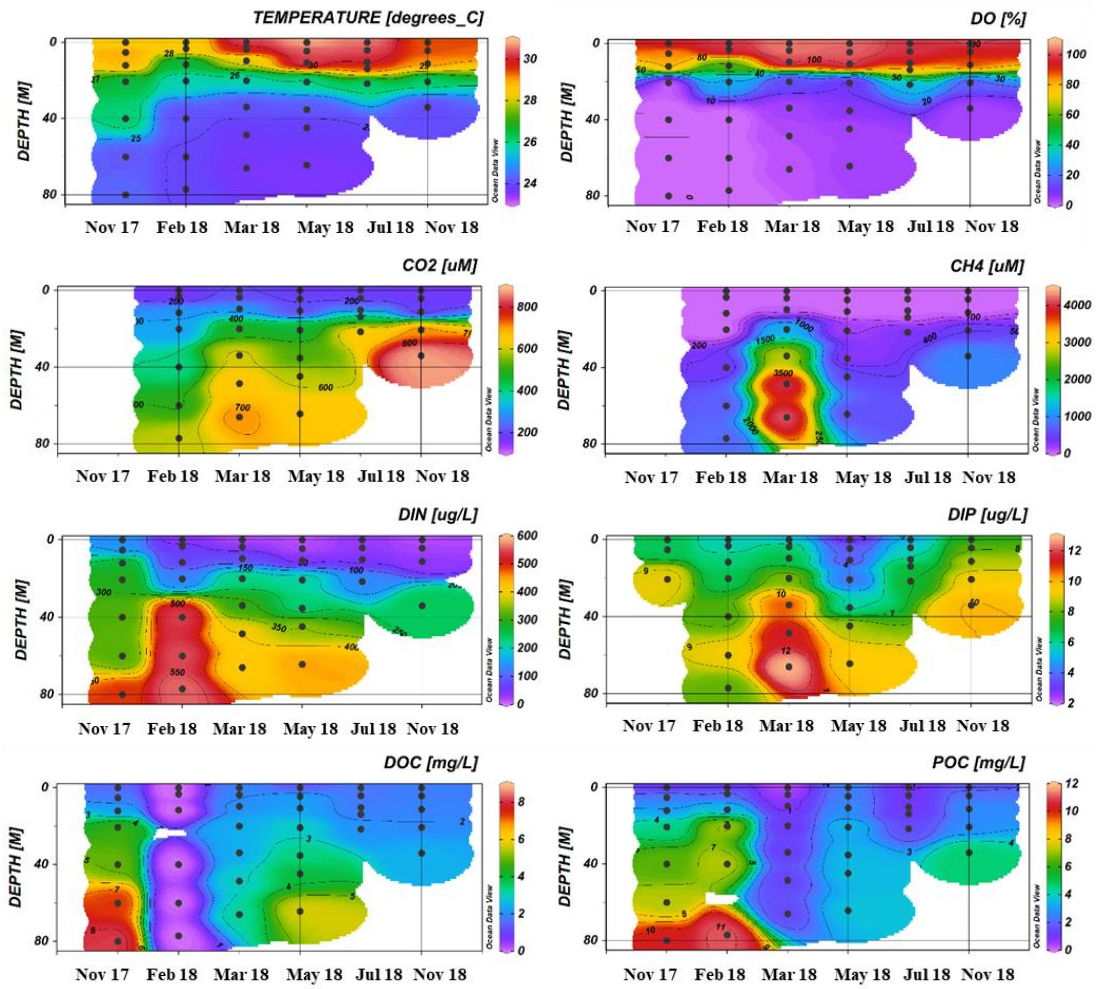
	Temp	Depth	DO	DIN	DIP	DOC	POC	CH4	CO2
Temp	1.000								
Depth	-.888**	1.000							
DO	.898**	-.918**	1.000						
DIN	-.921**	.928**	-.909**	1.000					
DIP	-.768**	.676**	-.703**	.667**	1.000				
DOC	-.434*	.482**	-.258	.305	.325	1.000			
POC	-.486**	.576**	-.568**	.457*	.166	.162	1.000		
CH4	-.790**	.833**	-.761**	.766**	.785**	.623**	.236	1.000	
CO2	-.771**	.868**	-.756**	.837**	.660**	.618**	.315	.858**	1.000

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

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

APPENDIX D3

The temporal pattern and dissolved concentration of CO2, CH4, DO, DIN, DIP, DOC, POC and temperature in Site 4



APPENDIX E1

Concentration of DIN and DIP in Site 5

Date	Depth (m)	Nitrate (ug/l)	Nitrite (ug/l)	Ammonia (ug/l)	Orthophos-phate (ug/l)
Nov 2017	0.0	67.36	9.05	N/A	0.83
Nov 2017	5.6	32.69	5.18	69.11	1.34
Nov 2017	15.2	29.22	6.88	70.88	N/A
Nov 2017	19.0	60.67	8.92	299.26	10.41
Nov 2017	30.0	131.85	8.22	329.96	N/A
Nov 2017	45.0	138.73	8.45	371.21	N/A
Feb 2018	0.0	33.61	N/A	N/A	5.23
Feb 2018	3.8	27.41	2.80	13.06	6.63
Feb 2018	11.4	56.49	N/A	N/A	8.17
Feb 2018	19.6	181.22	N/A	N/A	8.41
Feb 2018	30.8	17.05	N/A	174.84	8.74
Mar 2018	0.0	9.83	2.74	16.82	4.31
Mar 2018	4.9	27.69	2.44	17.29	4.68
Mar 2018	10.8	47.24	3.27	52.89	6.16
Mar 2018	20.5	46.10	3.92	151.61	7.17
Mar 2018	41.3	8.27	12.54	365.76	8.55
Mar 2018	60.0	N/A	10.78	440.02	9.15
Mar 2018	70.0	N/A	15.00	437.45	11.98
May 2018	0.0	N/A	1.17	9.41	1.82
May 2018	5.4	N/A	1.99	36.23	2.25
May 2018	10.1	N/A	10.55	50.12	2.95
May 2018	19.4	N/A	1.48	123.83	2.97
May 2018	34.0	N/A	1.80	165.61	3.54
May 2018	48.2	N/A	14.60	302.22	6.45
May 2018	66.3	N/A	7.34	381.08	6.76
Jul 2018	0.0	6.18	0.81	13.03	4.00
Jul 2018	4.5	4.97	0.76	41.07	4.40
Jul 2018	10.8	22.72	4.09	50.33	5.08
Jul 2018	20.8	N/A	N/A	N/A	5.46
Jul 2018	35.7	N/A	2.91	676.96	5.56
Jul 2018	51.1	N/A	3.87	709.05	5.93
Jul 2018	61.5	N/A	4.71	908.84	6.64
Nov 2018	0.0	9.02	0.73	5.76	6.76
Nov 2018	3.9	1.23	3.31	12.10	7.23
Nov 2018	10.2	53.71	1.29	12.83	8.28
Nov 2018	19.8	58.90	8.46	100.47	9.63
Nov 2018	36.3	109.13	7.99	91.74	18.06
Nov 2018	49.4	21.88	8.28	238.71	20.03
Nov 2018	60.4	0.06	4.06	312.89	24.03

*N/A: No data available

APPENDIX E2

Spearman correlation in Site 5

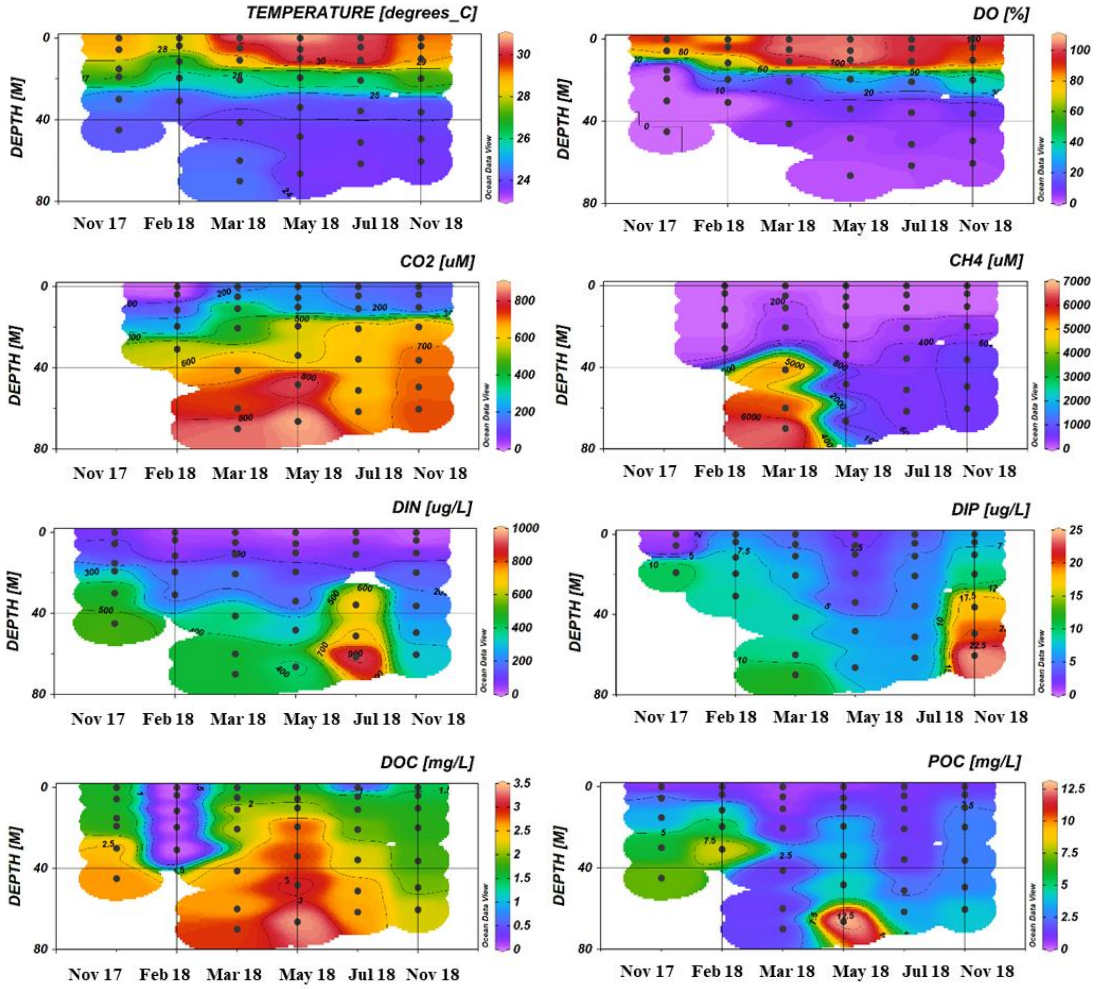
	Temp	Depth	DO	DIN	DIP	DOC	POC	CH4	CO2
Temp	1.000								
Depth	-.898**	1.000							
DO	.945**	-.874**	1.000						
DIN	-.879**	.956**	-.842**	1.000					
DIP	-.574**	.561**	-.591**	.501**	1.000				
DOC	-.590**	.755**	-.462**	.722**	.051	1.000			
POC	-.647**	.591**	-.699**	.483**	.434*	.252	1.000		
CH4	-.771**	.888**	-.698**	.850**	.533**	.755**	.321	1.000	
CO2	-.759**	.903**	-.715**	.848**	.436*	.815**	.420*	.936**	1.000

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

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

APPENDIX E3

The temporal pattern and dissolved concentration of CO2, CH4, DO, DIN, DIP, DOC, POC and temperature in Site 5



APPENDIX F1

Concentration of DIN and DIP in Site 6

Date	Depth (m)	Nitrate (ug/l)	Nitrite (ug/l)	Ammonia (ug/l)	Orthophos-phate (ug/l)
Nov 2017	0.0	60.01	7.24	167.09	N/A
Nov 2017	4.4	N/A	15.95	376.77	7.11
Nov 2017	17.5	73.07	13.85	348.33	7.63
Nov 2017	24.2	78.06	11.99	367.21	N/A
Nov 2017	40.0	281.23	6.42	235.46	N/A
Nov 2017	55.0	15.94	5.39	516.06	18.58
Feb 2018	N/A	N/A	N/A	N/A	N/A
Mar 2018	0.0	34.03	2.82	43.69	3.76
Mar 2018	4.7	54.68	2.93	46.10	4.89
Mar 2018	14.8	108.50	2.81	50.99	6.22
Mar 2018	27.5	145.64	2.33	39.30	9.27
Mar 2018	50.3	4.21	11.73	432.42	9.63
May 2018	0.0	N/A	10.43	8.64	2.12
May 2018	5.5	N/A	1.18	18.07	3.44
May 2018	14.3	N/A	1.00	45.18	3.59
May 2018	25.0	N/A	N/A	182.30	3.92
May 2018	46.1	N/A	6.22	319.87	3.92
Jul 2018	0.0	10.05	1.03	14.16	3.07
Jul 2018	6.2	3.15	1.41	25.25	3.12
Jul 2018	14.8	3.89	1.16	99.14	5.06
Jul 2018	25.9	0.13	6.40	843.80	5.30
Jul 2018	36.0	N/A	5.35	908.75	5.85
Jul 2018	44.7	23.71	5.77	899.25	6.04
Nov 2018	0.0	22.57	1.94	9.41	6.37
Nov 2018	4.5	25.97	2.34	10.39	7.47
Nov 2018	11.9	62.40	2.45	13.77	7.87
Nov 2018	15.3	N/A	6.18	80.49	8.49
Nov 2018	23.7	103.70	1.77	10.48	9.07
Nov 2018	35.6	39.17	9.17	119.78	10.91
Nov 2018	49.6	27.21	7.26	180.56	13.04

*N/A: No data available

APPENDIX F2

Spearman correlation in Site 6

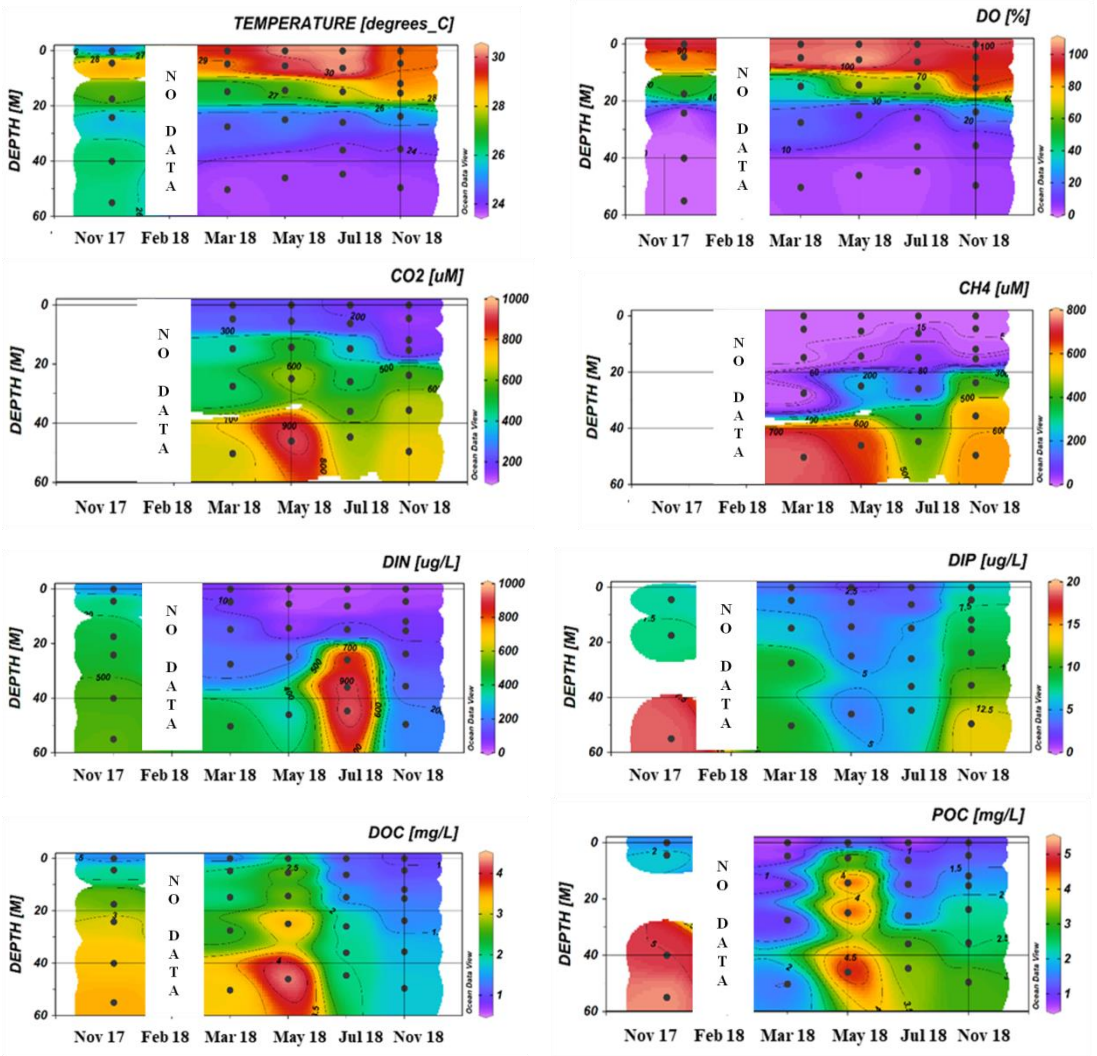
	Temp	Depth	DO	DIN	DIP	DOC	POC	CH4	CO2
Temp	1.000								
Depth	-.954**	1.000							
DO	.949**	-.942**	1.000						
DIN	-.944**	.889**	-.914**	1.000					
DIP	-.590**	.572**	-.511*	.509*	1.000				
DOC	-.494*	.486*	-.377	.403	-.148	1.000			
POC	-.522*	.576**	-.536**	.358	.069	.467*	1.000		
CH4	-.828**	.898**	-.849**	.710**	.456*	.381	.718**	1.000	
CO2	-.857**	.835**	-.805**	.768**	.284	.664**	.573**	.788**	1.000

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

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

APPENDIX F3

The temporal pattern and dissolved concentration of CO2, CH4, DO, DIN, DIP, DOC, POC and temperature in Site 6



APPENDIX G1

Concentration of DIN and DIP in Site 7

Date	Depth (m)	Nitrate (ug/l)	Nitrite (ug/l)	Ammonia (ug/l)	Orthophos-phate (ug/l)
Nov 2017	0.0	34.22	6.01	74.86	2.65
Nov 2017	3.6	94.89	8.21	119.64	N/A
Nov 2017	11.7	231.41	5.42	3.69	10.59
Nov 2017	19.9	72.90	4.47	386.52	11.51
Nov 2017	30.0	46.70	14.28	622.64	14.27
Feb 2018	0.0	31.37	N/A	N/A	5.89
Feb 2018	3.5	46.46	N/A	N/A	5.97
Feb 2018	12.8	48.10	N/A	N/A	6.76
Feb 2018	17.6	62.85	N/A	N/A	6.82
Feb 2018	27.0	9.92	0.44	399.92	9.14
Feb 2018	40.0	49.31	0.44	817.53	9.61
Mar 2018	0.0	45.83	2.71	30.31	4.74
Mar 2018	5.2	41.62	4.12	18.30	5.63
Mar 2018	13.2	131.54	4.04	45.74	6.14
Mar 2018	22.9	113.18	3.84	64.22	6.86
May 2018	0.0	2.82	1.37	4.90	2.97
May 2018	4.8	N/A	1.06	16.49	3.39
May 2018	12.8	N/A	1.39	61.16	13.37
May 2018	19.8	64.98	0.76	55.82	18.35
Jul 2018	0.0	5.91	0.94	32.84	3.38
Jul 2018	4.3	10.41	0.95	40.35	3.89
Jul 2018	6.1	5.74	0.86	50.37	5.49
Jul 2018	8.2	9.86	1.19	49.62	6.55
Nov 2018	0.0	1.04	2.43	19.08	6.65
Nov 2018	4.9	12.37	2.47	11.74	6.79
Nov 2018	6.7	20.09	3.96	6.43	7.93
Nov 2018	8.9	26.19	2.29	7.44	8.40
Nov 2018	11.5	89.50	2.87	17.46	8.42

*N/A: No data available

APPENDIX G2

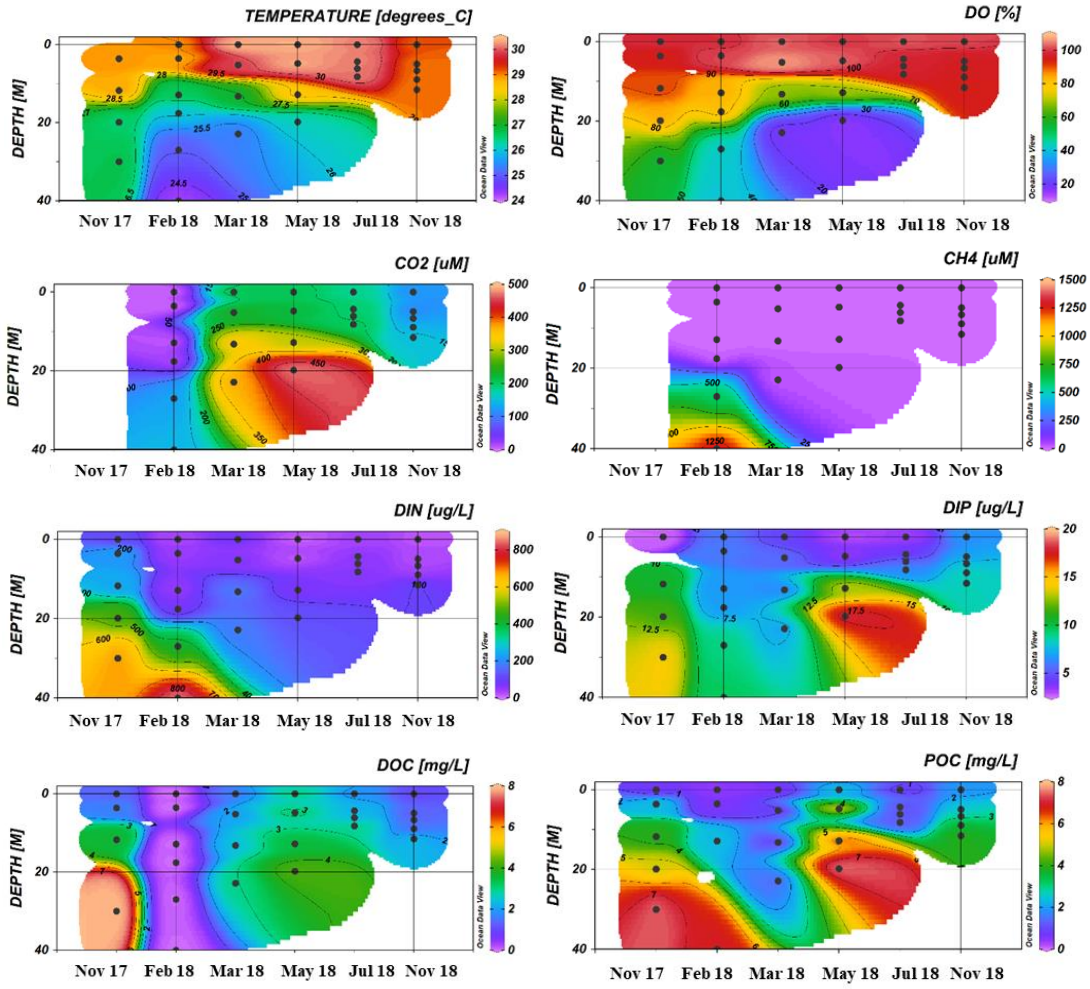
Spearman correlation in Site 7

	Temp	Depth	DO	DIN	DIP	DOC	POC	CH4	CO2
Temp	1.000								
Depth	-.819**	1.000							
DO	.833**	-.896**	1.000						
DIN	-.618**	.730**	-.617**	1.000					
DIP	-.792**	.776**	-.813**	.488*	1.000				
DOC	.314	.090	-.083	.099	-.049	1.000			
POC	-.298	.549**	-.542*	.014	.624**	.383	1.000		
CH4	-.447*	.707**	-.533**	.701**	.401	.366	.386	1.000	
CO2	.162	.202	-.125	.382	-.041	.893**	.170	.609**	1.000

**Correlation is significant at the 0.01 level (2-tailed).
*Correlation is significant at the 0.05 level (2-tailed).

APPENDIX G3

The temporal pattern and dissolved concentration of CO2, CH4, DO, DIN, DIP, DOC, POC and temperature in Site 7



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PUBLICATION

Mohd, L.S.F., Poh, S.C., Lee, D.J.J., Wong, W.W. (2025). The Impact of Thermal Stratification on Nutrients and Greenhouse Gases Distribution in a Deep Tropical Reservoir. Journal of Sustainability Science and Management. (Accepted)

CONFERENCE AND WORKSHOP ATTENDED

CONFERENCES

Spatial, Seasonal and Vertical Variations of Inorganic Nutrients in Kenyir Lake, Terengganu (Oral), 2nd PSU-UMT Postgraduates Colloquium, Prince Songkla University (PSU), Thailand, 24th July- 25th July 2018, organized by Universiti Malaysia Terengganu.

WORKSHOP

Basic Occupational Safety and Health Course, Auditorium INOS, Universiti Malaysia Tereengganu, 31st -1st April 2017, organized by Faculty of Science and Environmental Marine (FSSM), Universiti Malaysia Terengganu.

Workshop on operational training for SKALAR SAN++ CFA Analyzer, Universiti Malaysia Tereengganu, 32th October- 1st November 2017, organized by Institute of Oceanography (INOS), Universiti Malaysia Terengganu.

Third Institute of Oceanography China- Kasetsart University International Collaboration Workshop, 9th august 2018, organized by School of Marine and Environmental Sciences (PPSMS), Universiti Malaysia Terengganu.

Colloquium National Research and Development of Water, 2020, 25th – 26th February 2020, organized by Malaysian National Hydraulic Research Institute (NAHRIM).