Carbon and nitrogen assimilation rates in aquatic ecosystems

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by

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Dedicated to

My beloved family

Declaration

I declare that this thesis report represents my ideas in my own words, and I have included others' ideas with appropriate citations from original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/fact/source/data in my submission. I understand that any violation of the above can cause disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom permission has not been taken when needed.

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CERTIFICATE

It is certified that the research work contained in the thesis entitled "**Carbon and nitrogen assimilation rates in aquatic ecosystems**" by **Ms. Km Ajayeta Rathi** (Roll no. 19330002), has been carried out under my supervision and this work has not been submitted elsewhere for a degree. I have read this dissertation, and I believe it is fully adequate, in scope and quality, for the degree of Doctor of Philosophy.

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Abstract

Aquatic ecosystems play an important role in the carbon and nitrogen biogeochemical cycles and contribute significantly to global carbon and nitrogen budgets. These ecosystems are highly prone to the effects of climate change and anthropogenic activities, which can alter the intensity of biogeochemical processes in these ecosystems. The understanding of carbon and nitrogen cycles is crucial for ecosystem dynamics and predicting responses to environmental changes. Among the different processes involved in biogeochemical cycling, this thesis focuses on the carbon and nitrogen assimilation rates in diverse aquatic ecosystems. These rates are affected by various environmental parameters such as temperature, salinity, flow velocity, nutrients, land cover, land use, water diversion, and extraction. Specifically, this thesis reports the results of experiments performed related to carbon (primary production (PP)) and nitrogen assimilation (dinitrogen (N_2) fixation) rates in the marine, lacustrine, and riverine ecosystems using stable isotopic tracer techniques. The findings of this study elucidate the mechanisms regulating assimilation rates, providing insights into the resilience and adaptability of aquatic ecosystems in the face of ongoing environmental perturbations.

In marine ecosystems, PP and N_2 fixation rates by phytoplankton are often limited by macro- and micronutrient availability, whose distribution is changing due to climate change and anthropogenic impacts. A significant number of studies have been conducted worldwide to decipher the role of nutrient (un)availability on PP and N_2 fixation, leaving the northern Indian Ocean largely unexplored. Nutrient enrichment (addition of macro- and micronutrients alone or in combination) and stoichiometric experiments (addition of macronutrients with varying N:P ratio at different concentration levels) were conducted in the northern Indian Ocean (Bay of Bengal, Andaman Sea, and Arabian Sea) during the fall inter-monsoon to decipher the role of nutrients availability on PP and N_2 fixation. The results of the nutrient enrichment experiments showed that PP in the open Bay of Bengal was not nutrient-limited, however, co-limitation of macro- and micronutrients for PP was observed in the coastal Bay of Bengal and the Andaman Sea. The PP in the Arabian Sea was primarily limited by nitrogen. The co-limitation of macro- and micronutrients for PP was observed in the coastal Arabian Sea. The N_2 fixation in the coastal and open Bay of Bengal showed co-limitation of macro-

and micronutrients. In the southern Arabian Sea, N_2 fixation was not limited or co-limited by nutrients, however, in the northern Arabian Sea, co-limitation of macro- and micronutrients was observed for N_2 fixation. In the stoichiometric experiments, despite the increase in PP, N:P ratio manipulations at different concentrations did not show consistent increase or decrease in PP. This indicated that once the nutrient threshold was reached, changes in nutrient concentrations or their proportions might not have a substantial impact on PP in the northern Indian Ocean.

Compared to marine ecosystems, carbon and nitrogen cycling in inland waters display different interactions due to higher terrestrial influence owing to anthropogenic activities. The inland waters are known as hotspots for carbon and nitrogen and have recently been included in the Intergovernmental Panel for Climate Change carbon budget albeit with high uncertainties due to fewer studies. The inland waters, such as lakes, are facing the issues of salinization, desiccation, and regime shift, whereas rivers suffer from discontinuity in their flow. This study explores the carbon and nitrogen assimilation rates in some of the lakes and rivers located in western India to decipher changes in carbon and nitrogen fixation due to above mentioned stresses. The results indicated that carbon and nitrogen assimilation rates in the inland waters were highly influenced by temperature, salinity, dissolved and particulate pools of carbon and nitrogen, water level changes, and engineering modifications. The study carried out in a closed basin freshwater lake showed decrease in carbon and nitrogen assimilation rates with rising water level from summer to monsoon, which coincided with decrease in temperature, nitrogenous nutrients, salinity, sunlight, and biomass. Contrary to the closed basin lake, an open basin lake that transitioned from saline in the summer to freshwater in the monsoon, showed increase in carbon and nitrogen assimilation rates during monsoon (i.e., with rise in water level), possibly due to input of nutrients from the catchment runoff. This lake also transitioned from clear water (macrophyte-domination) to a turbid water state (phytoplankton-domination) from summer to monsoon. A hyper(saline) lake and associated water bodies (brine reservoir and saltpans) were also studied for carbon and nitrogen assimilation and were found to be completely different from the freshwater lakes, which was due to large dissolved inorganic and organic carbon pools. In this saline system, PP and N_2 fixation rates decreased with increasing salinity, which might be due to changes in community composition. The activity of N_2 fixers was reduced at higher salinity resulting in below detection rates. In general, PP and N_2 fixation rates were higher in the saline lake than in the freshwater lakes. Also, contrary to some studies, N_2 fixation was observed in inland waters even under dissolved inorganic nitrogen replete conditions.

Among the aquatic systems, the rivers (which act as the conduit for transporting materials to the ocean and storing them in their sediments) around the world are experiencing the effect of human interventions (such as damming) in their connectivity. The last part of this thesis explores the role of damming on the PP and N_2 fixation rates along a river continuum. The results showed that PP and biomass increased in the dammed reservoirs compared to flowing water, suggesting that stagnant waters are more favourable for phytoplankton growth. N_2 fixation rates did not show any trend and no significant difference was observed between flowing and reservoir waters. This indicates that the spur in PP or biomass in the reservoirs was largely driven by nitrogenous nutrients derived from the catchment of the rivers, which accumulated over time.

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List of Abbreviations

$\delta^{13}C$	Stable carbon isotopic composition with respect to V-PDB
$\delta^{15}N$	Stable nitrogen isotopic composition with respect to Air-N_2
µM	Micromole per litre
‰	per mil (parts per thousand)
Anammox	Anaerobic Ammonium Oxidation
CA	Carbonic Anhydrase
CCM	Carbon Concentrating Mechanism
CH_4	Methane
Chl a	Chlorophyll a
CIL	Cambridge Isotope Laboratories
CO_2	Carbon Dioxide
CO_3^{2-}	Carbonate
CTD	Conductivity Temperature Depth
DIC	Dissolved Inorganic Carbon
DIN	Dissolved Inorganic Nitrogen
DNRA	Dissimilatory Nitrate Reduction to Ammonium
DO	Dissolved Oxygen
EA	Elemental Analyzer
EC	Electrical Conductivity
E. U.	European Union
Fe	Iron
$g\ L^{-1}$	Gram per Litre
GC	Gas Chromatography
HCO_3^-	Bicarbonate
IAEA	International Atomic Energy Agency
IPCC	Intergovernmental Panel on Climate Change
IRMS	Isotope Ratio Mass Spectrometry
KR	Kadana Dam Reservoir

MBR	Mahi Bajaj Sagar Dam Reservoir
MLD	Mixed Layer Depth
Mo	Molybdenum
mg L^{-1}	Milligram per Litre
mS cm^{-1}	Millisiemens per centimetre
N_2	Dinitrogen
N_2O	Nitrous Oxide
NH_3	Ammonia
NH_4^+	Ammonium
nM	Nanomole per litre
NO_2^-	Nitrite
NO_3^-	Nitrate
OM	Organic Matter
OMZs	Oxygen Minimum Zones
ORV	Oceanographic Research Vessel
Pg	Petagram
PO_4^{3-}	Phosphate
POC	Particulate Organic Carbon
POM	Particulate Organic Matter
PON	Particulate Organic Nitrogen
PP	Phytoplankton Primary Productivity
SiO_4^{4-}	Silicate
SP	Saltpans post-monsoon
SPM	Saltpans pre-monsoon (March)
SSL	Sambhar Salt Lake
SSS	Sea Surface Salinity
SST	Sea Surface Temperature
TSM	Total Suspended Matter
VPDB	Vienna PeeDee Belemnite

Chapter 1

Introduction

Biogeochemical cycles are integral to the Earth's ecosystems, facilitating the movement and transformation of essential elements such as carbon and nitrogen through biotic and abiotic pools. These cycles represent pathways by which elements and compounds move through the atmosphere, hydrosphere (oceans and inland waters), lithosphere (Earth's crust), and biosphere (living organisms) (Schlesinger & Bernhardt, 2013). Carbon and nitrogen are crucial bioavailable elements necessary for the sustenance of life and are required for the structure and functioning of every ecosystem. Their cycles are tightly coupled through various pathways, including microbial-mediated complex reactions, such that modifications to one can influence the other (Burgin et al., 2011). Aquatic ecosystems such as oceans, lakes, and rivers play a crucial role in the carbon and nitrogen biogeochemical cycles. The primary producers (phytoplankton or autotrophs) form the basis o f the aquatic food web, and their growth depends on several environmental parameters such as nutrients and light. These tiny microorganisms are important in aquatic ecosystems as they couple the carbon cycle with the biogeochemical cycles of other elements such as nitrogen, phosphorus, and iron (Litchman et al., 2015).

Over the last century, human-driven climate change has increased greenhouse gases in the atmosphere, influencing the biogeochemical cycling processes in aquatic ecosystems. Additionally, anthropogenic activities have led to increased reactive nitrogen in ecosystems through fertilizer use and fossil fuel burning, causing nutrient disparities with cascading effects on these ecosystems (Galloway et al., 2008). These changes have resulted in the degradation of aquatic ecosystems, leading to issues such as eutrophication, harmful algal blooms, anoxia, fish kills, and nutrient limitations; thereby impacting biodiversity (Ryther & Dunstan, 1971; Baron et al., 2013). Climate change has further impacted aquatic ecosystems through alterations in dust deposition, aerosols, water column stratification, and precipitation patterns, with significant impacts particularly on marine environments (Doney et al., 2012). Inland waters are also affected by major issues such as supersaturation of carbon dioxide (CO_2), lake desiccation, freshwater salinization, damming of rivers, wastewater inputs, and regime shifts (Brothers et al., 2013; Raymond et al., 2013; Cunillera-Montcusí et al., 2022). These are important for irrigation, flood control, hydroelectric power generation, and water supply (Goldman et al., 2013). Biogeochemical cycles of carbon and nitrogen are central to ecosystem productivity, climate regulation, and biogeochemical health. However, the effects of these changes on the magnitude of biogeochemical processes—such as carbon [phytoplankton primary production (PP) or carbon fixation] and nitrogen [biological dinitrogen (N_2) fixation, ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-) uptake] assimilation rates—remain uncertain in aquatic ecosystems. Understanding these processes is crucial for comprehensive ecosystem dynamics, energy flow, predicting and mitigating the impacts on ecosystem health and function, and global carbon and nitrogen budgets, which ultimately affect the Earth's climate through their feedback mechanism. Given the critical role of carbon and nitrogen cycles in supporting life and maintaining ecosystem stability, there is a pressing need to investigate how these cycles are being altered by human activities and climate change. A brief overview of the aquatic carbon and nitrogen cycles is provided below.

1.1 Aquatic carbon cycle

The aquatic carbon cycle is a dynamic system governed by the interplay of biological, chemical, and physical processes that regulate the exchange and storage of carbon within aquatic ecosystems. The main processes in the aquatic carbon cycle include the solubility pump, the carbonate pump, and the biological pump, which remove carbon from the atmosphere and influence the Earth's climate (DeVries, 2022). The solubility pump depends on the physicochemical properties of water columns to transport CO_2 from the atmosphere into aquatic ecosystems (Fig. 1.1). Once CO_2 is dissolved in surface waters, it forms different species of dissolved inorganic carbon (DIC): dissolved CO_2, bicarbonate (HCO_3^-), and carbonate ions (CO_3^{2-}). The distribution of these species is related to the pH of water; at the typical pH of ocean water (8.2), ~ 90 % of DIC is HCO_3^-, 9 % is CO_3^-, and 1 % is dissolved CO_2 (Zeebe & Wolf-Gladrow, 2001). However, this species distribution (%) can vary depending on the type and pH of the aquatic ecosystem. The solubility of CO_2 in water increases with decreasing temperature and increasing pressure, enabling colder waters to dissolve more CO_2 (Takahashi et al., 2009). Additionally, the carbonate pump involves carbonate precipitation and dissolution which play crucial roles in the carbon cycle. Precipitation removes DIC from the water while dissolution increases it. The dominance of these processes depends on the pH of aquatic ecosystems (Ridgwell & Zeebe, 2005). Marine ecosystems, covering 70% of the Earth's surface, are pivotal in long-term carbon storage, holding 50 times more carbon than the atmosphere (Cai & Jiao, 2022).

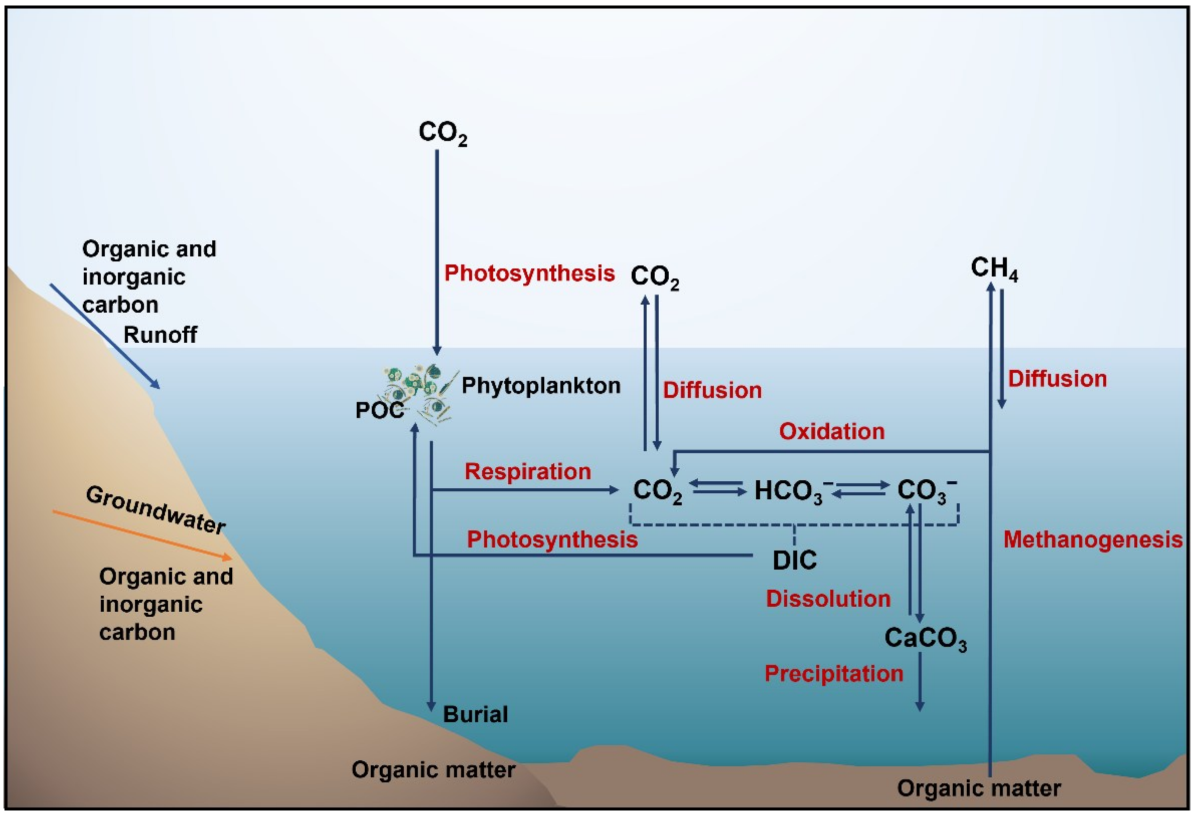


Fig. 1.1 A simplified schematic of the carbon cycle in the aquatic ecosystem.

The biological pump starts with the assimilation of CO_2 or HCO_3^- from the DIC pool by phytoplankton. Despite covering only 0.2 % of autotrophs within the biosphere, phytoplankton contributions to the carbon cycle through PP are significant (Sanders et al., 2014). Phytoplankton PP is a fundamental process that sustains life on the Earth by converting inorganic carbon into organic matter (OM) through photosynthesis in the euphotic zone of aquatic ecosystems. The formation of OM through this process forms the base of the aquatic food web (Ducklow et al., 2001). Several factors such as temperature, nutrients, light, and salinity can influence PP and, ultimately, the efficiency of biological pump in aquatic ecosystems (de La Rocha & Passow, 2014). Phytoplankton can be consumed by zooplankton (primary consumers), which in turn can be consumed by consumers of higher trophic levels. When both phytoplankton and zooplankton die, the OM begins to settle towards the deeper water layers (Eppley & Peterson, 1979). This OM can be remineralized by bacteria in the water column or sediments, converting it back into CO_2 and nutrients that can be utilized by other organisms. During remineralization process, oxygen is consumed, leading to its depletion in the waters. Some of the OM is sequestered in the bottom sediment, effectively removing carbon from the atmosphere. The OM in the sediments can further remineralize to methane (CH_4), a greenhouse gas, through the methanogenesis process (Torres-Alvarado et al., 2005). The biological pump thus facilitates the sequestration of carbon in aquatic ecosystems, where it can remain for varying time scales depending on the specific reservoirs (Hedges & Keil, 1995).

1.2 Aquatic nitrogen cycle

The biogeochemical cycle of nitrogen is driven by microbes involving redox reactions and many enzymes (Pajares & Ramos, 2019). Despite its high abundance in the atmosphere (78 %), nitrogen is limiting for PP in natural ecosystems (Zerkle & Mikhail, 2017). Most of the nitrogen is in the form of N_2 gas containing a triple bond (N≡N) with oxidation state zero. The dissociation of this triple bond requires a large amount of energy (941 kJ mol^{-1}) making it inert at standard temperature and pressure (Jin et al., 2023). The incorporation of nitrogen into biological molecules requires the N_2 gas to be converted to its reactive forms (bioavailable forms) (Canfield et al., 2010). Atmospheric (dissolved) N_2 can be converted to bioavailable nitrogen through the process of biological N_2 fixation, which is performed by certain specialised organisms called diazotrophs (N_2 fixers), providing new nitrogen to aquatic ecosystems (Fig. 1.2). This process is considered crucial in evolutionary terms because it facilitated the development of diverse life forms by increasing nitrogen availability, which is essential for the synthesis of proteins, nucleic acids, and other vital biomolecules (Canfield et al., 2010). Diazotrophs contain a specific enzyme for N_2 fixation called nitrogenase, which converts N_2 gas into OM. The nitrogenase enzyme is extremely sensitive to oxygen and comprises two proteins: dinitrogenase [phosphorus clusters and metal (molybdenum-iron) cofactor] and dinitrogenase reductase (iron-protein) (Postgate, 1998). The OM decomposition by heterotrophic bacteria releases NH_4^+ into the water column through a process called ammonification.

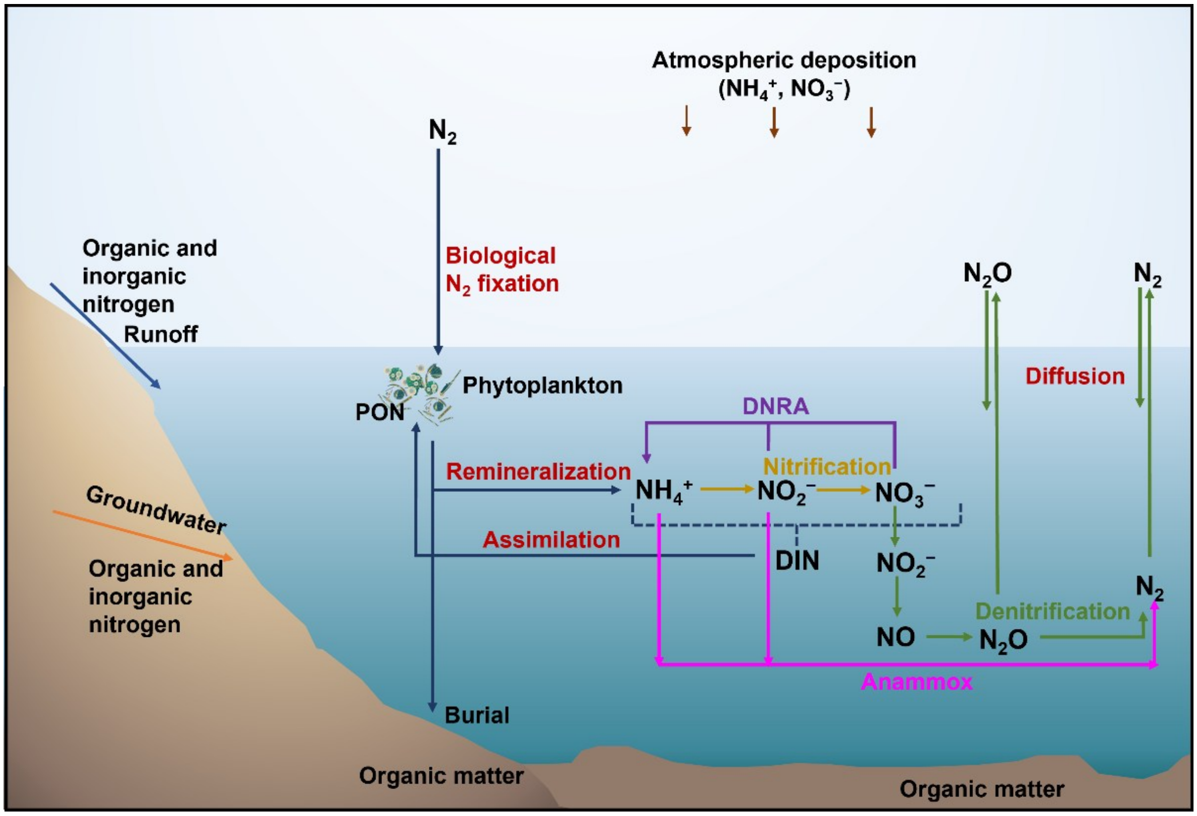


Fig. 1.2 A simplified schematic of the nitrogen cycle in the aquatic ecosystem.

The next step in the nitrogen cycle is the nitrification process, a two-stage microbially mediated process. In this process, first ammonium-oxidizing bacteria (*Nitrosomonas*) convert NH_4^+ into NO_2^-, which is further oxidized to NO_3^- by nitrite-oxidizing bacteria (*Nitrobacter*) (Holland & Weitz, 2003). These forms of nitrogen can only be stable in oxic conditions. Nitrous oxide (N_2O) is the by-product of the nitrification process, which is a potent greenhouse gas that impacts the Earth's radiation budget. The phytoplankton biomass assimilates these reactive dissolved inorganic nitrogen (DIN = NH_4^+ + NO_2^- + NO_3^-) forms for growth, incorporating them into their organic molecules through a process called assimilation. NH_4^+ is considered a preferred form of nitrogen by aquatic organisms because of its reduced form, which makes it energetically favourable (Sanz-Luque et al., 2015). The bioavailable nitrogen present in aquatic ecosystems can be lost via two microbial processes—denitrification and anaerobic ammonium oxidation (anammox)—occurring in oxygen-depleted waters (Codispoti et al., 2000). In denitrification, NO_3^- is reduced to N_2O and ultimately to N_2 gas through a series of steps, releasing these gases into the atmosphere. Additionally, the anammox process which is less understood, converts NH_4^+ into N_2 gas using NO_2^- as an electron acceptor (Mulder et al., 1995). Another important process in this cycle is dissimilatory nitrate reduction to ammonium (DNRA) which is a type of anaerobic respiration performed by specific groups of heterotrophic bacteria. These microorganisms use NO_3^- as an electron acceptor and convert it into NH_4^+. These interconnected processes maintain the nitrogen balance in aquatic ecosystems, supporting diverse life forms (Canfield et al., 2010).

Out of many processes within carbon and nitrogen cycles, this thesis focuses on some less understood aspects of carbon and nitrogen assimilation rates (PP and N_2 fixation) across different aquatic ecosystems ranging from marine to freshwater. Below is a succinct overview of global and Indian perspectives on carbon and nitrogen assimilation in aquatic ecosystems.

1.3 Primary production and N_2 fixation in the marine ecosystems: global and Indian perspectives

Marine PP contributes ~50 Pg of organic carbon globally, playing a crucial role in global climate change studies due to its substantial climatological and ecological impact (Falkowski et al., 1998, 2000). Some of this organic carbon is exported from the surface layers to the deep ocean, making its way to carbon storage (Eppley & Peterson, 1979). Understanding the global marine biogeochemical cycles requires exploring the factors that control PP, with nutrient availability in the surface ocean as one of the important regulating factors (Moore et al., 2013). The complex interaction between biogeochemical and physical factors in the ocean drives global nutrient distribution. Phytoplankton requires naturally occurring bioavailable nutrients such as nitrogen and phosphorus for PP and incorporates them into their cellular components like deoxyribonucleic acid, ribonucleic acid, phospholipids, and proteins after obtaining them from their surroundings (Geider & La Roche, 2002; Liefer et al., 2019). Additionally, trace elements such as iron and molybdenum are essential for their metabolic activities. Nutrients required in higher amounts (µM) by organisms in aquatic systems are termed macronutrients (e.g., nitrogen and phosphorus), while those needed in small amounts (nM) are known as micronutrients (e.g., iron and molybdenum).

N_2 fixation is one of the processes through which nitrogen is made available for photosynthesis and is the largest natural source of fixed nitrogen, especially in the open ocean (Schlesinger & Bernhardt, 2013). The nitrogenase enzyme responsible for N_2 fixation also depends on the availability of these macro- and micronutrients for its base structure (Hoffman et al., 2014). Therefore, low concentrations of these nutrients relative to their demand may limit phytoplankton and diazotroph functionality, ultimately limiting PP and N_2 fixation in marine ecosystems. Diazotrophs are more vulnerable to nutrient limitation than non-diazotrophs due to their higher energy and trace element demands for breaking the N_2 triple bonds (Langlois et al., 2012). Moreover, the phytoplankton community composition may alter due to nutrient limitation, favouring the dominance of physiologically advantageous species (Falkowski & Oliver, 2007). The nutrient limitation refers to the scenario where phytoplankton growth is limited by a single nutrient, whereas co-limitation occurs when growth is constrained by two or more nutrients (Saito et al., 2008; Moore et al., 2013).

The surface ocean is experiencing significant changes due to anthropogenic inputs and rising greenhouse gas levels, affecting ocean stratification, water circulation, phytoplankton composition, and nutrient distributions; which in turn affect biogeochemical processes (Bopp et al., 2001; Khatiwala et al., 2013; Gruber et al., 2019). Therefore, it is important to understand the effect (limitation or co-limitation) of these nutrients on PP and N_2 fixation in oceans to comprehend the feedback between organisms and the environment (Arrigo, 2005). In marine ecosystems, nitrogen is believed to limit PP in the surface layer, which might be related to the limitation of phosphorus and iron for N_2 fixation (Falkowski, 1997; Tyrrell, 1999; Mills et al., 2004). The supply of these nutrients is a critical factor regulating the spatial patterns and overall contributions of PP and N_2 fixation to the global oceanic carbon and nitrogen budgets. Surprisingly, molybdenum has also been identified as a limiting nutrient for N_2 fixation in the ocean, ultimately limiting PP despite having conservative properties in marine ecosystems (Howarth & Cole, 1985).

Globally, numerous studies have been conducted to understand the nutrient limitation and co-limitation on PP and N_2 fixation, mainly in the Atlantic and Pacific Oceans (Mills et al., 2004; Bonnet et al., 2008; Davey et al., 2008; Moore et al., 2013; Browning et al., 2017, 2022; Wen et al., 2022a, 2022b) with limited focus on other oceanic regions, especially the northern Indian Ocean. These studies reported that PP in the Atlantic and Pacific Oceans was limited or co-limited by nitrogen and iron, while N_2 fixation was limited or co-limited by phosphorus and iron. The northern Indian Ocean is unique because of its topography and seasonally reversing monsoon winds, yet less is known about the role of macro- and micronutrients on biogeochemical processes such as PP and N_2 fixation. The northern Indian Ocean is divided into two parts by the Indian subcontinent: the Bay of Bengal in the east and the Arabian Sea in the west. Despite being at the same latitude, both basins show different biogeochemical characteristics (Phillips et al., 2021). The Arabian Sea is highly productive and important for N_2 fixation because it hosts a variety of phytoplankton and diazotrophs (Capone et al., 1998; Wiggert et al., 2005). In contrast, the Bay of Bengal is less productive and has lower N_2 fixation rates (Prasanna Kumar et al., 2002; Löscher et al., 2020). In the northern Indian Ocean, many studies have reported estimates of PP and N_2 fixation (Madhupratap et al., 1996; Prasanna Kumar et al., 2001; Gandhi et al., 2011; Saxena et al., 2020, 2023, 2024). However, few studies have explored the limitation and co-limitation of nutrients for these processes. Despite having higher dust deposition in the Arabian Sea, field studies, remote sensing, and modelling studies have suggested nitrogen and iron limitations for PP in the Arabian Sea (Moore et al., 2004; Wiggert & Murtugudde, 2007; Behrenfeld et al., 2009; Sharada et al., 2020). In contrast, the Bay of Bengal has typically not been considered iron-limited due to its significant supply of iron aerosol inputs from nearby continents and high iron concentrations in these waters (Srinivas & Sarin, 2013; Grand et al., 2015; Chinni et al., 2019). However, nitrogen limitation has been reported here for PP during the spring inter-monsoon (Twining et al., 2019). Takeda et al. (1995) suggested that the phytoplankton growth was limited by macronutrients and iron in the Arabian Sea during the winter monsoon. Iron limitation for PP has been observed in the northwestern part of the Arabian Sea during the summer monsoon (Naqvi et al., 2010; Moffett et al., 2015). Based on atmospheric deposition studies, Srinivas & Sarin (2013) indicated phosphorus and iron limitations for PP in the Arabian Sea. Some studies have also reported increased phytoplankton biomass after the addition of aerosols in the coastal Bay of Bengal (Yadav et al., 2016; Kumari et al., 2022). Inorganic phosphate (PO_4^{3-}) limitation has been observed for N_2 fixation in the Bay of Bengal during the summer monsoon (Sarma et al., 2020). Despite the above mentioned studies, the northern Indian Ocean remains undersampled both spatially and temporally, particularly during the fall inter-monsoon, when weaker winds lead to stratification in the top layer.

Apart from nutrient limitation and co-limitation, the stoichiometric ratio of dissolved inorganic nutrients [nitrate (NO_3^-): phosphate (PO_4^{3-}) = N:P] affects biogeochemical processes such as PP and N_2 fixation rates in marine ecosystems. The elemental stoichiometry in phytoplankton cells determines the interaction between nutrient cycles and the global carbon cycle (Galbraith & Martiny, 2015). Traditionally, the N:P ratio in biological oceanography has been considered constant and is known as the Redfield ratio (16:1), with deviation from this ratio explaining the nutrient limitations in the ocean (Redfield, 1958; Tyrrell, 1999). However, recent studies have revealed variations in the N:P ratio, which have consequences for the carbon cycle and the ocean's response to climate change (Geider & La Roche, 2002; Klausmeier et al., 2004; Deutsch & Weber, 2012; Moreno et al., 2018). Currently, nutrient concentrations and their ratio in marine ecosystems are influenced by anthropogenic activities, stratification due to global warming, circulation patterns, and the intensification of oxygen minimum zones (OMZs) (Czerny et al., 2016; Spilling et al., 2019). Some studies suggest uncertainty about whether the N:P ratio or absolute nutrient concentrations play a more important role in affecting PP and N_2 fixation (Li et al., 2011; Bhavya et al., 2016). It remains unclear how this varying N:P stoichiometry impacts the global cycling of carbon and nutrients (Arrigo, 2005). In addition to experimental studies, incorporating the effects of nutrient concentrations or stoichiometry on PP and N_2 fixation in modelling studies will improve our understanding of carbon export and enhance global climate change predictions.

1.4 Primary production and N_2 fixation in inland waters: global and Indian perspectives

Inland waters encompass rivers, lakes, floodplains, reservoirs, and wetlands, collectively covering 2.7 % of the Earth's surface area, with lakes being the predominant type (Likens, 2009; Raymond et al., 2013). Despite their small surface area, inland waters play a crucial role in the global biogeochemical cycle, acting as hotspots for carbon and nitrogen cycling with broader implications (Cole et al., 2007; Xia et al., 2018). Historically, the focus has been on marine, terrestrial, and atmospheric ecosystems, leaving inland waters relatively under explored. Inland waters were traditionally viewed primarily as conduits between land and ocean, resulting in their relative underrepresentation in scientific studies (Cole et al., 2007). However, their importance is increasingly recognized due to their significant role in processing carbon and nitrogen received from watersheds, exchange with the atmosphere, sequestering in sediments, and transporting laterally to the ocean (Vitousek et al., 1997; Cole et al., 2007; Mendonça et al., 2017; Wang et al., 2021). The Intergovernmental Panel on Climate Change's fifth assessment report also acknowledges inland waters as a significant part of the global carbon cycle. In recent decades, anthropogenic activities and climate change have substantially impacted inland waters, affecting carbon and nitrogen cycling processes; which remains an interesting topic of research (Finlay et al., 2013; Yvon-Durocher et al., 2017).

The CO_2 release from inland waters to the atmosphere is comparable to CO_2 uptake by the ocean, with organic carbon storage in inland water sediments surpassing that of oceans due to higher rates of preservation (Cole et al., 2007; Tranvik et al., 2009). Inland waters receive around ~ 1.9 Pg C yr^{-1} from land areas; however, ~ 0.8 Pg C yr^{-1} of this carbon is returned to the atmosphere after processing in inland waters, ~ 0.85 Pg C yr^{-1} is transported to the ocean, and ~ 0.2 Pg C yr^{-1} stored in sediments (Cole et al., 2007; Bauer et al., 2013; Raymond et al., 2013). The global nitrogen burial rate in lake sediments since the preindustrial era is ~ 9.6 ± 1.1 Tg N yr^{-1}, which is highly correlated with carbon burial rates (Wang et al., 2021). Despite the predominance of riverine ecosystems in tropical and northern boreal regions, most studies of lakes and rivers have been conducted in temperate regions, especially deep lakes (Verpoorter et al., 2014; Allen & Pavelsky, 2018). Consequently, the impacts and major factors influencing carbon and nitrogen cycling processes in inland waters at various spatial and temporal scales remain poorly understood. A comprehensive geographical analysis, particularly in tropical and subtropical regions, is needed to improve the understanding of coupled biogeochemical processes in inland waters.

Freshwater ecosystems such as lakes and rivers are directly impacted by changes in carbon and nitrogen cycling processes, which are crucial for human survival and social development. Therefore, understanding the key variables influencing these processes is essential. Nitrogen cycling processes, such as N_2 fixation, are even less studied in inland waters than carbon cycling processes. While the rates and mechanisms governing N_2 fixation in terrestrial and marine ecosystems are relatively well understood, the same processes in inland waters have received little attention (Marcarelli et al., 2022). N_2 fixation can alter ecological interactions even at low rates due to its effect on the availability of critical limiting nutrients and occurs rapidly enough to influence the nitrogen budget from local to global scales (Vitousek et al., 2010; Marcarelli et al., 2022). Several studies have reported the supersaturation of CO_2 in inland waters (i.e., increased partial pressure relative to the atmosphere in these ecosystems due to higher respiration; Raymond et al., 2013 and references therein); however, its impact on the PP has not been fully understood, particularly from the methodological perspective.

Globally, most of the research related to PP and nitrogen assimilation rates in inland waters was conducted in temperate regions (Gu & Alexander, 1993a,1993b; Nõges & Kangro, 2005; Blindow et al., 2006). In tropical regions, PP and nitrogen assimilation rates related studies in lakes and reservoirs focused primarily on African and Brazilian waters (Barbosa et al., 1980; Robarts, 1984; Petrucio et al., 2006; Feresin et al., 2010). Indian inland waters (lakes, rivers, and reservoirs) remain largely unexplored regarding the carbon and nitrogen assimilation rates. One study has examined the effect of wastewater input and water stagnancy on PP in a riverine ecosystem, reporting significantly higher PP in stagnant water and polluted areas (Sarkar and Kumar, 2024). Other studies have used the light-dark oxygen method to measure gross PP in Indian inland waters, generally finding higher PP in dry seasons compared to wet seasons (Chattopadhyay & Banerjee, 2008; Patel et al., 2012; Sontakke & Mokashe, 2014; Chishty & Choudhary, 2022; Khanam, 2024). To the best of our knowledge, aside from studies on carbon and nitrogen assimilation rates in the Chilika Lagoon (Mukherjee et al., 2019) and Cochin Estuary (Bhavya et al., 2016), no studies have reported nitrogen assimilation rates in the inland waters of India. As elsewhere in the world, India's diverse aquatic ecosystems, varying from ephemeral to perennial riverine systems and freshwater to hypersaline lakes, are facing numerous issues such as lake desiccation, freshwater salinization, water withdrawal, and river damming due to anthropogenic influences and climate change (Hassani et al., 2020; Maavara et al., 2020; Cunillera-Montcusí et al., 2022).

In this thesis, stable isotope techniques have been employed to estimate the assimilation rates of carbon and nitrogen. Below is a brief overview of the application of stable isotopes in the carbon and nitrogen biogeochemical cycles.

1.5 Application of stable isotopes in carbon and nitrogen biogeochemical cycles

Stable isotopes are invaluable tools for studying carbon and nitrogen dynamics in various ecosystems (terrestrial or aquatic) because they help trace the pathways and transformation of these elements from one pool to another (e.g., organic to inorganic or vice versa). These tools provide insights into processes such as PP, nutrient assimilation, N_2 fixation, OM decomposition, nitrification, denitrification, and gas exchange in aquatic ecosystems (Schelske & Hodeli, 1991; Unkovich et al., 2001; Gu et al., 2006; Sun et al., 2011). The stable isotopic composition is typically expressed using δ notation, defined as:

$$\delta\ (‰) = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \qquad \text{……… (1.1)}$$

Where R is the ratio of the abundance of heavier to lighter isotopes (e.g., $^{13}C/^{12}C$ or $^{15}N/^{14}N$). The stable isotopic composition is reported relative to international standards to facilitate global comparisons. Stable isotopic composition of carbon and nitrogen ($\delta^{13}C$ and $\delta^{15}N$, respectively) have been used extensively in biogeochemistry to identify sources, estimate metabolic rates, trace energy transfer through the food web, study trophic interactions, and understand past climatic conditions (Kling et al., 1992; Sun et al., 2011). They also help in estimating the relative contributions of terrestrial and *in situ* sources in aquatic ecosystems due to their distinct isotopic compositions. During chemical reactions or biogeochemical processes, molecules containing lighter isotopes often react or diffuse quickly than those with heavier isotopes. This leads to isotopic fractionation, where the ratio of heavy to light isotopes changes between reactants and products. The microbial processes in carbon and nitrogen biogeochemical cycles favour kinetic fractionation which results in preferential incorporation of lighter isotopes in the products. For example, terrestrial C_3 and C_4 plants take CO_2 from the atmosphere (– 8 ‰), leading to $\delta^{13}C$ values ranging from ~ – 33 to – 22 ‰ and – 20 to – 10 ‰, respectively, in plants (Bender, 1971). Whereas freshwater phytoplankton and algae $\delta^{13}C$ varies from ~ – 42 to – 24 ‰ (Kendall et al., 2001), which can become enriched during periods of higher growth. Similarly, a $\delta^{15}N$ value of 0 ‰ is indicative of N_2 fixation, as fractionation is negligible by diazotrophs during this process. Stable isotope tracer techniques using ^{13}C or ^{15}N enriched salts/gases have the potential to track the assimilation of carbon and nitrogen in aquatic ecosystems, aiding in the estimation of the process rates. In these techniques, atom % of the heavier isotope is used instead of isotopic composition and is expressed as:

$$\text{Atom (\%)} = \left(\frac{R_{sample}}{1+R_{sample}}\right) \times 100 \qquad \text{……… (1.2)}$$

These tracer techniques have been widely employed to estimate rates of carbon and nitrogen assimilation in various aquatic ecosystems, including those studied in this thesis, whose objectives are described below.

1.6 Objective of the thesis

In light of the preceding discussion, it is quite clear that, despite several studies related to PP and N_2 fixation in the northern Indian Ocean, there remains a glaring knowledge gap regarding the role of nutrient enrichment in modulating these processes. Similarly, there is even a broader knowledge gap regarding cycling of carbon and nitrogen in the inland waters of India. This is particularly true for process rates in the lakes and rivers leading to poor understanding of the flow and evasion of these elements and their budgets. Therefore, the present thesis aims to understand the carbon and nitrogen biogeochemistry in the inland waters (lakes, rivers, and reservoirs) of India and adjacent oceanic basins with focus on carbon and nitrogen assimilation rates and their controlling factors.

Specifically, this thesis focuses on understanding:

(i) The effect of macro- and micronutrient addition on PP and N_2 fixation in the northern Indian Ocean.

(ii) Relative importance of nutrient stoichiometry (N:P ratio) and/or absolute concentration on PP and N_2 fixation in the northern Indian Ocean.

(iii) The impact of water volume changes on carbon and nitrogen assimilation rates in a shallow enclosed freshwater lake.

(iv) The changes in carbon and nitrogen assimilation rates during the seasonal salinity transition of an open freshwater lake.

(v) Carbon and nitrogen assimilation rates in a (hyper)saline lake and related water bodies such as the brine reservoir and salt pans.

(vi) The effect of damming or water stagnancy on PP and N_2 fixation along a river continuum.

1.7 Outline of the thesis

The thesis is divided into six chapters. A brief overview of the content in each chapter is mentioned below.

Chapter 1

This chapter provides an outline of the different processes involved in carbon and nitrogen biogeochemical cycles in aquatic ecosystems, emphasizing their significance in both ocean and inland waters. It includes a concise review of studies on carbon and nitrogen assimilation rates in both Indian and global contexts. Additionally, the chapter outlines the broad and specific research objectives of the thesis.

Chapter 2

This chapter briefly introduces the study areas chosen to achieve the thesis objectives, along with details of the sampling campaigns and protocols for sample collections (specific sampling sites for each field campaign and ecosystems covered are detailed in respective chapters). Additionally, this chapter focuses on various analytical techniques and methods used to measure the environmental parameters, biogeochemical parameters, and rates of carbon and nitrogen assimilation.

Chapter 3

This chapter addresses PP and N_2 fixation rates in the surface waters of the northern Indian Ocean. It discusses the effect of nutrient enrichment on these rates. The first section of the chapter describes the macro- and micronutrient limitations and co-limitations of these processes. The second section examines the effect of the changing stoichiometry (N:P ratio) with varying concentrations on PP and N_2 fixation rates.

Chapter 4

This chapter explores the carbon and nitrogen assimilation rates in the lacustrine ecosystems of India. It is divided into four sections: the first section deals with the effect of changes in lake water volume and environmental parameters on carbon and nitrogen assimilation rates in a freshwater shallow lake in a closed basin; the second section describes the effects of freshwater salinization on these rates during a regime shift in a freshwater shallow lake; the third section further investigates these rates in a (hyper)saline lake and associated water bodies; and the last section is related to methodological aspects of PP using ^{13}C tracers in CO_2 supersaturated lacustrine ecosystems.

Chapter 5

This chapter deals with the effect of damming of rivers on PP and N_2 fixation rates along a river continuum. Additionally, the methodological aspects of PP using ^{13}C tracers in the riverine ecosystem are also discussed here.

Chapter 6

This chapter highlights the key findings of the present thesis and suggests directions for future research works.

Chapter 2

Materials and Methods

The thesis covers some of the important aspects of carbon and nitrogen cycling in three types of natural aquatic ecosystems, with a specific emphasis on the marine ecosystem (the northern Indian Ocean), freshwater to saline lacustrine ecosystems [Thol Lake, Nalsarovar Lake, and Sambhar Salt Lake (SSL)], and the riverine ecosystem (Mahi River) (Fig. 2.1). This thesis incorporates findings from two different research expeditions conducted in the northern Indian Ocean (the Bay of Bengal, the Andaman Sea, and the Arabian Sea) during the fall inter-monsoon and field campaigns in the lakes and the Mahi River during distinct seasons (Table 2.1). Detailed descriptions of the sampling locations and study areas are provided in the relevant chapters.

The primary focus of this thesis centres around the results obtained through isotope tracer-based experiments of carbon and nitrogen assimilation rates by phytoplankton. This thesis also includes measurements of the concentration and stable isotopic composition of DIC and particulate organic matter (POM) along with dissolved greenhouse gases and environmental parameters such as temperature, salinity, and nutrients. The parameters measured and experiments conducted varied slightly depending on the objectives and system studied (listed in Table 2.1).

Table 2.1 Aquatic ecosystems and sampling periods with every thesis chapter (and sections).

Thesis Chapter	Aquatic ecosystems	Sampling dates (Seasons)	Parameters and rates measured
3	Northern Indian Ocean (the Bay of Bengal, the Andaman Sea, and the Arabian Sea)	September-November (Fall inter-monsoon) 2021	SST, SSS, NOx, PO_4^{3-}, SiO_4^{4-}, DIC, PP (HCO_3^- uptake), and N_2 fixation rates
4.1	Thol Lake	May (Summer) 2022 September (Monsoon) 2022	Temperature, pH, DO, EC, NOx, NH_4^+, PO_4^{3-}, SiO_4^{4-}, dissolved CO_2, DIC, $\delta^{13}C_{DIC}$, POC, PON, $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$, PP (HCO_3^- uptake), N_2 fixation rates, NH_4^+ assimilation, NO_2^- assimilation, and CO_2 assimilation rates
4.2	Nalsarovar Lake	May (Summer) 2022 September (Monsoon) 2022 January (Winter) 2023	Temperature, pH, DO, EC, NOx, NH_4^+, PO_4^{3-}, SiO_4^{4-}, dissolved CO_2 and CH_4, DIC, $\delta^{13}C_{DIC}$, POC, PON, $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$, PP (HCO_3^- uptake), N_2 fixation rates, NH_4^+ assimilation, NO_2^- assimilation, and CO_2 assimilation rates
4.3	Sambhar Salt Lake	October (Post-monsoon) 2022 March (Pre-monsoon) 2023	Temperature, pH, DO, EC, NOx, NH_4^+, PO_4^{3-}, SiO_4^{4-}, dissolved CO_2, DIC, $\delta^{13}C_{DIC}$, POC, PON, $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$, PP (HCO_3^- uptake), N_2 fixation rates, NH_4^+ assimilation, NO_3^- assimilation, and CO_2 assimilation rates
5	Mahi River	October (Post-monsoon or high flow season) 2023	Temperature, pH, DO, salinity, dissolved CO_2, DIC, $\delta^{13}C_{DIC}$, TSM, POC, PON, $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$, PP (HCO_3^- uptake), N_2 fixation rates, and CO_2 assimilation rates

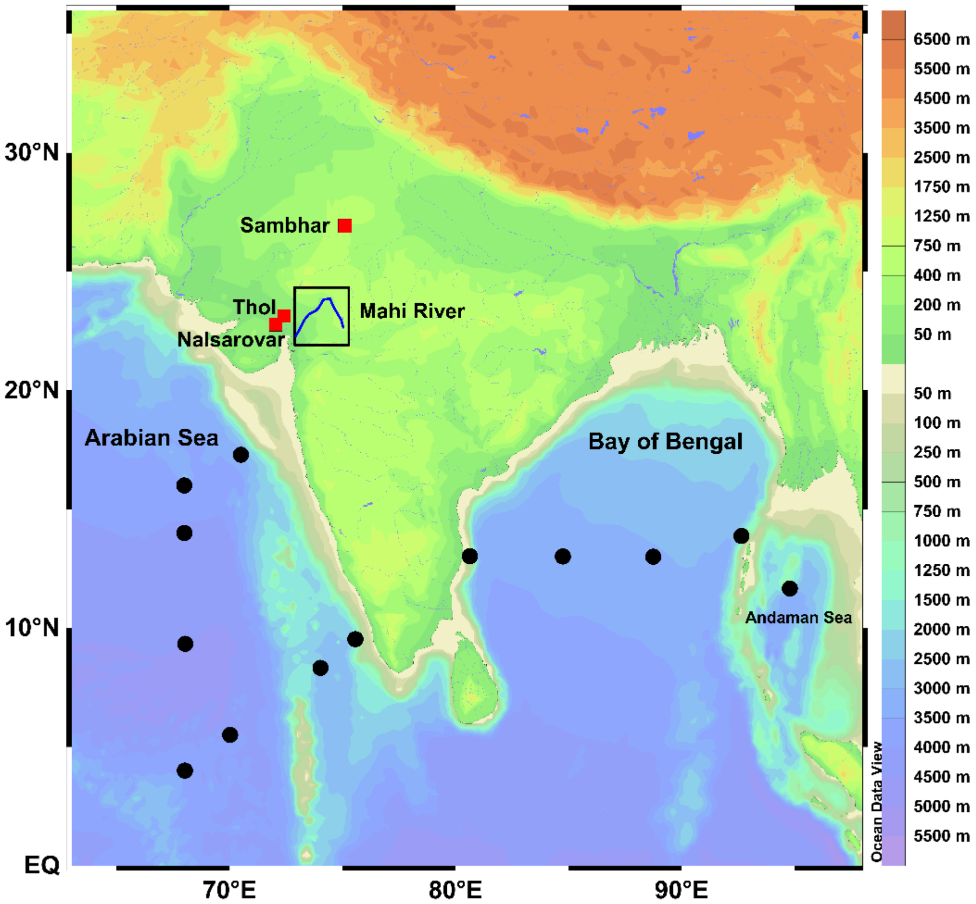


Fig. 2.1 Map showing the study areas (locations). Black dots represent sampling stations in the Arabian Sea, Bay of Bengal, and Andaman Sea. Red squares represent the locations of lakes and the blue line in the black box represents the Mahi River main channel.

2.1 Environmental parameters

In marine ecosystems, sea surface temperature (SST) and sea surface salinity (SSS) data were obtained using a Sea-Bird Scientific conductivity-temperature-depth (CTD) profiler equipped with Niskin bottles. Samples for analyses of inorganic dissolved nutrients [NO_3^-, NO_2^-, PO_4^{3-}, and silicate (SiO_4^{4-})] were collected from Niskin bottles into 60 ml high-density polyethylene (HDPE) bottles after passing through syringe filters (0.45 µm pore size) and kept frozen at −20 °C until measurement. Samples were thawed at room temperature and gently shaken before measurement. Nutrient concentrations, viz. NOx = NO_3^- + NO_2^-, PO_4^{3-}, and SiO_4^{4-} were measured onboard using a continuous flow autoanalyzer (SKALAR, San^{++}) with detection limits of 0.23, 0.02, and 0.5 µM, respectively.

In lacustrine and riverine ecosystems, data for surface water temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) were measured *in situ* using handheld probes (Hanna instruments) with an accuracy of ± 0.05 °C, ± 0.10, ± 2 %, and ± 0.01 mg L^{-1}, respectively. During river water sampling, DO in surface water samples was measured using Winkler's titration method (Hanna DO kit), where samples were fixed using reagents as described by Grasshoff et al. (2009). Samples for dissolved inorganic nutrients in lakes were collected in HDPE bottles after filtering through 0.7 μm pore size filters (GF/F) and kept frozen at −20 °C until further analysis. Dissolved nutrients (NOx, NO_2^-, NH_4^+, PO_4^{3-}, and SiO_4^{4-}) were measured using a continuous segmented flow autoanalyzer (QuAAtro39, Seal Analytical Limited, Germany) with detection limits of 0.01, 0.07, 0.1, 0.03, and 0.13 μM, respectively, at the Physical Research Laboratory (PRL), India (Fig. 2.2). For the SSL, nutrient samples were measured after dilution with ultrapure water (Milli-Q) due to higher salinity. There is a likelihood of blank contribution in SiO_4^{4-} data due to the use of GF/F filters during filtration of samples. Although the blank is expected to be consistent, no significant conclusions have been made using this data. Nutrient analyses could not be performed for samples collected from the studied river system.

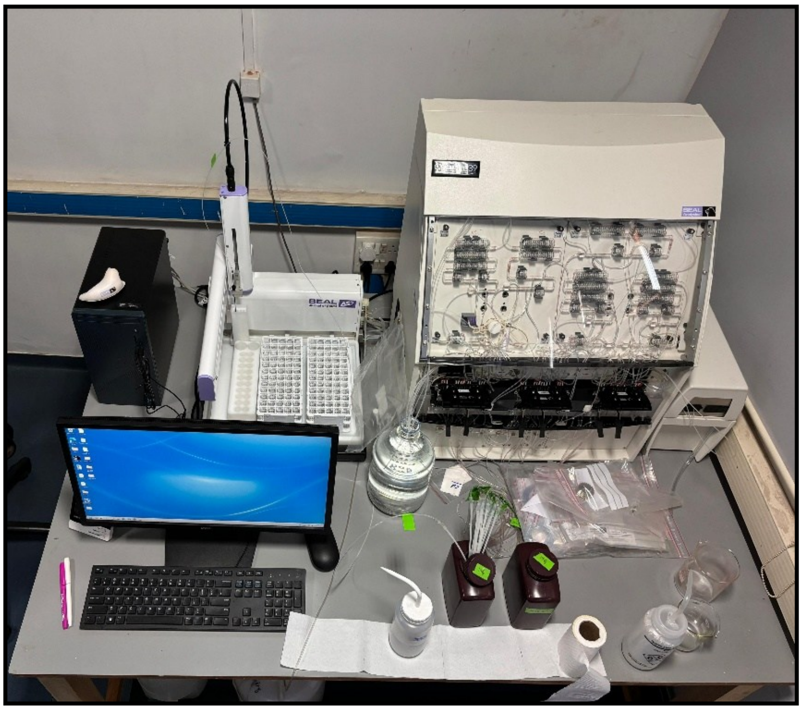


Fig. 2.2 Continuous segmented flow autoanalyzer at PRL (Seal Analytical Limited) used for nutrient analysis in samples collected from lakes.

Briefly, an autoanalyzer consists of an autosampler, chemistry module with pump, and detectors. It works on the principle of segmented flow analysis, a type of continuous flow method in wet chemistry. Samples and reagents are carried in a continuous stream, segmented with bubbles, and pumped through a manifold to facilitate reactions before passing into a flow cell for detection. The chemistry module has different channels for individual nutrients. NO_2^- concentration is measured by the reaction of diazonium compounds in the samples with N-(1-naphthyl) ethylene diamine dihydrochloride, forming a reddish-purple colour complex measured at 540 nm. NO_3^- concentration is measured using the cadmium reduction method, where NO_3^- is reduced to NO_2^- at pH ~ 8.2 in a copper-cadmium granules or copperized cadmium reduction coil. The total NO_2^- (both reduced and originally present) was measured at 540 nm. The NH_4^+ concentration is measured by a method based on the Berthelot reaction, which involves chlorinating NH_4^+ to produce monochloramine. This then reacts with salicylate to form a green-coloured complex measured at 660 nm. The method for PO_4^{3-} concentration measurement relies on a reaction involving the reaction of PO_4^{3-} with a combined reagent of ammonium heptamolybdate and potassium antimony (III) oxide tartrate by reduction with ascorbic acid. The blue-coloured antimony-phospho-molybdate complex is measured at 880 nm. The method for measuring SiO_4^{4-} concentration involves reducing a silico-molybdate complex in an acidic solution to molybdate blue using ascorbic acid, with detection at 820 nm. Oxalic acid is used to minimize interference from PO_4^{3-}.

2.2 Dissolved inorganic carbon concentrations and isotopic composition

Surface water samples for DIC concentration and its carbon isotopic composition ($\delta^{13}C_{DIC}$) were collected from all studied ecosystems in 60 ml serum glass bottles, which were tightly closed with butyl rubber septa and aluminium caps without headspace. These bottles were poisoned with saturated mercury chloride to stop microbial activity and stored for further analysis. DIC concentration and $\delta^{13}C_{DIC}$ were measured using gasbench II (Thermo Fisher Scientific, Germany) connected to the continuous flow isotope ratio mass spectrometer (IRMS; MAT 253; Thermo Fisher Scientific, Germany) (Fig. 2.3). For the measurements, a 12 ml septum vial filled with orthophosphoric acid (100 %) was flushed with high-purity helium gas. Water samples (1 ml) were injected into these vials using a syringe and allowed to react at 25 °C for 18 hours to ensure complete extraction of DIC into CO_2 in the vial's headspace. Subsequently, the CO_2 was transferred to the mass spectrometer for isotopic analysis. The analytical precision, determined by repeated measurements of the standard (Na_2CO_3; $\delta^{13}C = -11.4 \pm 0.1$ ‰), was better than 0.1 ‰.

Fig. 2.3 Gasbench II connected to IRMS (MAT 253) system at PRL.

2.3 Particulate organic carbon and nitrogen: concentrations and isotopic composition

For both marine and inland water ecosystems, surface water samples for POM [particulate organic carbon (POC) and particulate organic nitrogen (PON)] concentrations and their isotopic compositions ($\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$) were collected by filtering the water through pre-combusted (450 °C for 4 hrs) GF/F filters (25 mm and 47 mm, 0.7 µm pore size). After filtration, samples were kept in petri dishes, dried overnight at 50 °C, and stored for laboratory analysis. The filtration volume varied for different aquatic ecosystems depending on the POM concentration. These samples were analysed using an elemental analyzer (EA, Flash 2000, Thermo Fisher Scientific, Germany) connected to an IRMS (Delta V Plus, Thermo Fisher Scientific, Germany) (Fig. 2.4). To determine the POC concentrations and $\delta^{13}C_{POM}$, filters were fumigated using concentrated hydrochloric acid [37 % (v/v) HCl] to eliminate the inorganic carbon fraction. Subsequently, the filters were packed in tin capsules for further analysis. For PON and $\delta^{15}N_{POM}$, filters were directly packed into tin capsules without acid treatment.

Carbon analysis was performed using a laboratory standard (cellulose, $\delta^{13}C$ = −24.62 ± 0.1 ‰ and carbon content = 44.4 %) calibrated against cellulose standard (IAEA-CH-3; $\delta^{13}C$ = −24.72 ± 0.1 ‰ and carbon content = 44.4 %) procured from International Atomic Energy Agency (IAEA). For nitrogen analyses, ammonium sulphate (IAEA-N-2;

$\delta^{15}N$ = 20.3 ± 0.08 ‰ and nitrogen content = 21.2 %) was used as the standard. Additionally, a protein standard (IVA-OAS; $\delta^{15}N$ = 5.94 ± 0.08 ‰ and nitrogen content = 13.3 %) was used regularly to verify the instrument's precision over time. The analytical precisions for carbon and nitrogen isotopic compositions were better than 0.1 ‰ and 0.3 ‰, respectively. The $\delta^{13}C$ and $\delta^{15}N$ are expressed relative to international standards, Vienna Pee Dee Belemnite (V-PDB) and atmospheric nitrogen (Air-N_2), respectively.

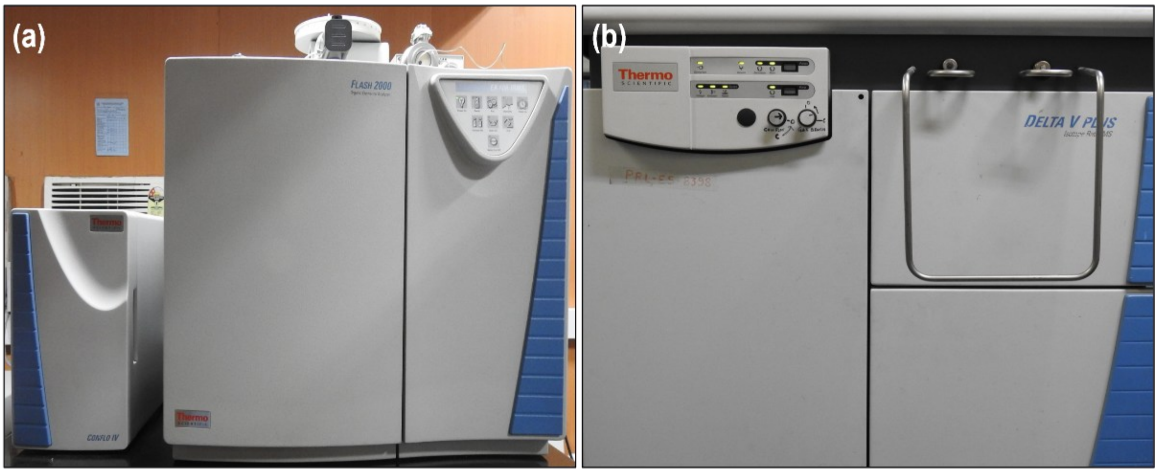


Fig. 2.4 Elemental analyzer (Flash 2000; left) and IRMS (Delta V Plus; right) at PRL.

2.4 Carbon and nitrogen assimilation rates

2.4.1 Principle

Depending on the objectives of the systems studied, carbon (CO_2 and HCO_3^-) and nitrogen (N_2, NO_3^-, NO_2^-, and NH_4^+) assimilation rates were measured based on the incorporation of ^{13}C-labelled and ^{15}N-labelled tracers by the phytoplankton during incubation experiments in different aquatic ecosystems (Slawyk et al., 1977; Dugdale & Wilkerson, 1986; Montoya et al., 1996). To calculate the carbon and nitrogen assimilation rates, the ambient substrate concentrations (DIC, NO_3^-, NO_2^-, NH_4^+, and N_2) along with POC and PON concentrations with their isotopic compositions ($\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$) for both natural (without tracer addition) and incubated (after tracer addition) samples were required.

2.4.2 Sampling and Analyses

Surface water samples for carbon and nitrogen assimilation rates experiments in aquatic ecosystems were collected in transparent polycarbonate bottles (Nalgene) in duplicates (seawater: 2.35 L and lakes: 1.23 L) and triplicates (1.23 L) for the river. In SSL, samples were collected in 130 ml serum glass bottles during pre-monsoon. Samples were spiked with $^{15}NH_4Cl$ (99 atom%), $Na^{15}NO_2$ (98 atom%), $Na^{15}NO_3$ (99 atom%), and $NaH^{13}CO_3$ (99 atom%) procured from Cambridge Isotope Laboratories (CIL) to measure NH_4^+, NO_2^-, NO_3^-, and HCO_3^- assimilation rates (HCO_3^- assimilation rates considered as a measure of PP in this thesis), respectively. For measurements of N_2 and CO_2 assimilation rates, tracer gases $^{15}N_2$ (98 atom%) and $^{13}CO_2$ (98 atom%) procured from CIL were added to the samples using a gas-tight syringe (Hamilton). The added spikes of ^{13}C and ^{15}N were generally less than 10 % of the substrate concentrations in the total sample volume; however, occasionally greater than 10 % additions were observed in the lakes and rivers. After the tracer addition, bottles were gently shaken to ensure proper mixing of tracers and then incubated in flowing water to maintain the temperature. Incubation times were 24 hours for the marine samples and 4 hours (10 AM – 2 PM) for lake and river samples. Post-incubation samples were filtered through pre-combusted (450 °C for 4 hrs) GF/F filters (0.7 µm pore size) and stored in petri dishes after drying at 50 °C overnight for further analysis (Fig. 2.5). Samples were analysed using continuous flow IRMS (Delta V Plus, Thermo Fisher Scientific, Germany) interfaced with an EA (Flash 2000, Thermo Fisher Scientific, Germany) to determine POC and PON concentrations and their isotopic compositions as described previously.

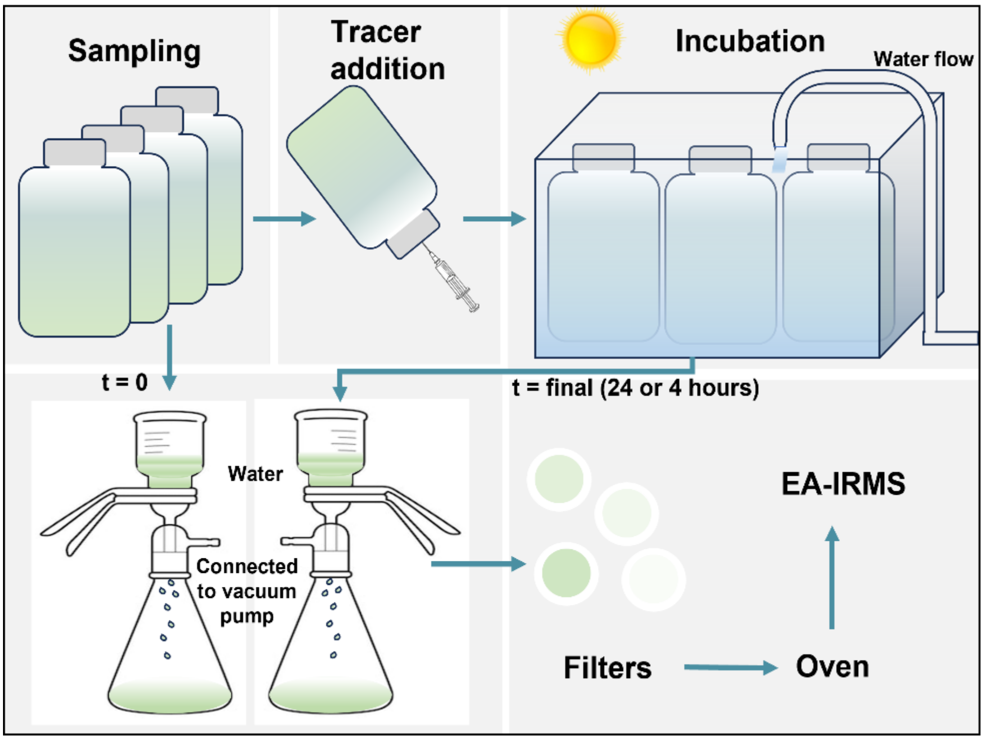


Fig. 2.5 Schematic of measurement protocol for carbon and nitrogen assimilation rates (redrawn after Saxena, 2022).

2.4.3 Estimation of assimilation rates

In nature, two stable isotopes of carbon exist: ^{12}C, which constitutes 98.887 % of the total carbon, and ^{13}C, which contributes 1.113 %. Similarly, nitrogen has two stable isotopes: ^{14}N, making up 99.636 %, and ^{15}N, contributing 0.364 % to the total nitrogen. Isotope labelling techniques utilize the lower abundance of heavier isotopes, such as ^{13}C for carbon and ^{15}N for nitrogen, as tracers (Dugdale & Goering, 1967; Dugdale & Wilkerson, 1986). This concept forms the basis of tracer incubation experiments for the estimation of carbon and nitrogen assimilation rates. This method is based on the following assumptions:

(i) Phytoplankton rely on a single carbon or nitrogen source.

(ii) During the assimilation of carbon and nitrogen, phytoplankton exhibit no discrimination between lighter and heavier isotopes.

(iii) There is no grazing by zooplankton.

(iv) No nutrient formation occurs during incubation.

The concept of carbon and nitrogen assimilation is based on the isotopic mass balance at the end of the incubation experiment, where the number of ^{13}C atoms within the final POC is equal to the sum of the ^{13}C atoms initially present in the POC and the atoms taken up from the ambient DIC.

$$A_{POC_f}[POC_f] = A_{POC_0}[POC_0] + A_C\,\Delta[POC] \quad \text{......... (2.1)}$$

Where A_{POC_f} = ^{13}C atom% in POC at the end of incubation,

A_{POC_0} = ^{13}C atom% in POC at the start of the incubation,

A_C = ^{13}C enrichment in the dissolved phase after tracer addition at the start of the incubation,

$[POC_f]$ = concentration of POC at the end of the incubation,

$[POC_0]$ = concentration of POC at the start of the incubation,

$\Delta[POC]$ = carbon taken up during incubation.

Since,

$$[POC_f] = [POC_0] + \Delta[POC] \quad \text{......... (2.2)}$$

$$[POC_0] = [POC_f] - \Delta[POC] \quad \text{......... (2.3)}$$

Substituting equation (2.3) into (2.1),

$$A_{POC_f}[POC_f] = A_{POC_0}([POC_f] - \Delta[POC]) + A_C\,\Delta[POC] \quad \text{......... (2.4)}$$

$$[POC_f]\,(A_{POC_f} - A_{POC_0}) = \Delta[POC]\,(A_C - A_{POC_0}) \quad \text{......... (2.5)}$$

$$\Delta[POC] = [POC_f]\left(\frac{A_{POC_f} - A_{POC_0}}{A_C - A_{POC_0}}\right) \quad \text{......... (2.6)}$$

In the above equation, A_C was calculated using the following formula:

$$A_C = \frac{^{13}C_{tracer} \times tracer\ conc. + {}^{13}C_{natural} \times natural\ conc.}{tracer\ conc. + natural\ conc.} \quad \text{......... (2.7)}$$

Where tracer conc. = added concentrations of DIC,

natural conc. = ambient concentrations of DIC before tracer addition,

$^{13}C_{natural}$ = ^{13}C atom% of natural in the dissolved phase before tracer addition,

$^{13}C_{tracer}$ = ^{13}C atom% of added tracer.

Volumetric rates of carbon assimilation were calculated as follows:

$$Carbon\ assimilation\ rates\ or\ PP = \left(\frac{POC_f}{t}\right)\left(\frac{A_{POC_f} - A_{POC_0}}{A_C - A_{POC_0}}\right) \quad \text{......... (2.8)}$$

Where t = incubation time.

Similarly, nitrogen assimilation rates were calculated as the carbon assimilation rates.

$$Nitrogen\ assimilation\ rates = \left(\frac{PON_f}{t}\right)\left(\frac{A_{PON_f} - A_{PON_0}}{A_N - A_{PON_0}}\right) \quad \text{......... (2.9)}$$

Where t = incubation time,

A_{PON_f} = ^{15}N atom% in PON at the end of incubation,

A_{PON_0} = ^{15}N atom% in PON at the start of the incubation,

A_N = ^{15}N enrichment in the dissolved phase after tracer addition at the start of the incubation,

$[PON_f]$ = concentration of PON at the end of the incubation.

In the above equation, A_N is defined as,

$$A_N = \frac{^{15}N_{tracer} \times tracer\ conc. + {}^{15}N_{natural} \times natural\ conc.}{tracer\ conc. + natural\ conc.} \qquad \text{......... (2.10)}$$

Where the measured values of dissolved inorganic nutrients (NO_3^-, NO_2^-, and NH_4^+) were used.

The same equations (2.9) and (2.10) were used to estimate the N_2 fixation and CO_2 assimilation rates in the surface water samples. Natural dissolved N_2 was calculated according to the formula given by Weiss (1970), which describes its solubility as a function of *in situ* salinity and temperature. For the calculation of A_C during the CO_2 assimilation rates, the total DIC concentrations were used for natural concentration.

As N_2 fixation rates are generally quite low, the minimal quantifiable rates for N_2 fixation rate were determined using standard error propagation through the observed differences between duplicate samples (Gradoville et al., 2017). Rates exceeding minimum quantifiable rates are reported. The mean of N_2 fixation rates was taken after adjusting below detection limit values to zero, and the rates were reported as below detection limit at sites where duplicates (ocean and lakes) or triplicate samples (river) all showed below detection limit values (Selden et al., 2021).

2.5 Dissolved greenhouse gases concentrations

In lacustrine and riverine ecosystems, surface water samples for dissolved greenhouse gases (CO_2 and CH_4) were collected in 60 ml serum glass bottles sealed with rubber septa and aluminium caps without headspace. The samples were poisoned with saturated mercury chloride to cease the microbial activity and stored for further analysis. The concentrations of these gases were measured using gas chromatography (GC; Agilent Technologies, USA; Fig. 2.6) by employing the headspace equilibrium method as described by McAuliffe (1971). Initially, 5–40 ml of the water sample was drawn into a 60 ml gas-tight syringe (BD company) from the serum bottles, depending on the expected gas concentrations. Helium (99.999%) was then introduced into the syringe, and samples were equilibrated with helium by vigorously shaking for approximately 4-5 minutes at laboratory temperature. A 10 ml subsample from the headspace was injected into the GC for gas analysis. To calibrate and verify instrument accuracy and precision, four standard gas mixtures with varying concentrations of CO_2 and CH_4 were used. These standards, procured from Agilent Technologies, USA, and Deuste Gas Solutions GmbH, Germany, had known concentrations (CO_2: 995.2, 600, 411, and 98.3 ppm; CH_4: 5000, 4993, 2003, and 506.8 ppb). The analytical precision for repeated measurements of these standards was less than 3 % for both gases.

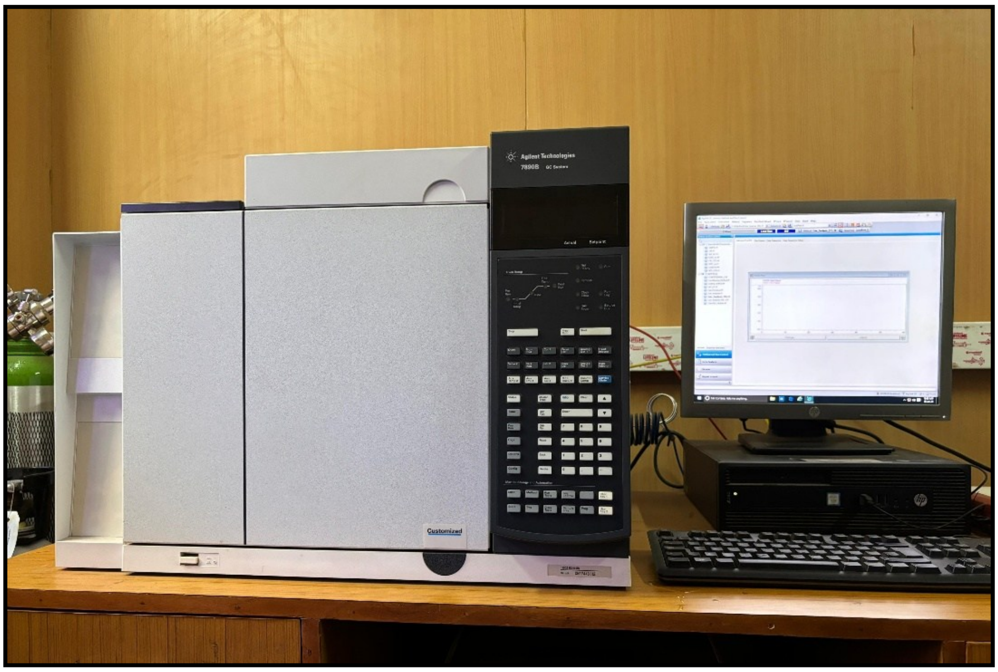


Fig. 2.6 Analyzer (Gas Chromatography) for measurements of greenhouse gas concentrations at PRL.

Concentrations of dissolved greenhouse gases (C_m) in the water were measured following Wilson et al. (2018):

$$C_m = \left(\beta\, x\, P\, V_{wp} + \frac{xP}{RT} V_{hs}\right) / V_{wp} \qquad \text{......... (2.11)}$$

Where β = Bunsen solubility coefficient of gases and is a function of sample temperature (T) and salinity (S),

x = mole fraction of gas measured in headspace (ppb),

P = atmospheric pressure,

V_{wp} = volume of water sample,

V_{hs} = volume of headspace,

R = gas constant (0.08205746 L atm K^{-1} mol^{-1}),

T = equilibrium temperature (K) in the laboratory.

β was calculated following Weiss (1974) for CO_2 and Wiesenburg & Guinasso (1979) for CH_4.

$$ln\beta = A_1 + A_2\left(\frac{100}{T}\right) + A_3 ln\left(\frac{T}{100}\right) + A_4\left(\frac{T}{100}\right)^2 + S\left[B_1 + B_2\left(\frac{T}{100}\right) + B_3\left(\frac{T}{100}\right)^2\right]$$

……(2.12)

Where A_1, A_2, A_3, A_4, B_1, B_2, and B_3 are constants for gases.

2.6 Statistical analysis

Statistical analysis was performed with SigmaPlot 14.0 (Systat, USA). Data distribution was first assessed for normality using the Shapiro-Wilk test. One-way analysis of variance (one-way ANOVA) was then employed to determine statistical differences in measured parameters and assimilation rates across seasons. If the normality test indicated a deviation from normality, Kruskal-Wallis ANOVA on Ranks (one-way ANOVA on ranks) was applied. Subsequently, a pairwise comparison was made using Tukey's or Dunn's test. Pearson's correlation among various parameters was analysed using Origin 2024b (Origin Lab Corporation). A significance level of $p < 0.05$ was employed to identify statistical differences among parameters across different seasons.

Chapter 3

Marine Ecosystems

Phytoplankton form the base of the marine food web and are responsible for nearly half of global PP carried on the Earth's surface (Falkowski et al., 1998; Behrenfeld et al., 2001). They form OM through photosynthesis by assimilating inorganic carbon and nutrients (such as NO_3^-, referred as N and PO_4^{3-}, referred as P in this chapter) and help regulate marine biogeochemical carbon and nitrogen cycles (Dugdale & Goering, 1967; Falkowski & Raven, 2007). Around half of the ocean's bioavailable nitrogen is produced by diazotrophs through N_2 fixation and supports more than 30% of the carbon export from surface to deep waters, which ultimately affects the global climate (Falkowski, 1997; Gruber & Galloway, 2008; Wang et al., 2019). In addition to macronutrients, micronutrients such as iron (Fe) and molybdenum (Mo) are crucial for biological processes in the ocean, acting as metal cofactors in enzymes and structural elements in proteins (Morel & Price, 2003). The availability of these macro- and micronutrients regulate the activities of marine primary producers, yet little is known about the worldwide biogeography of nutrient limitation and co-limitation (Tyrrell, 1999; Browning et al., 2017). The distribution of these nutrients in the ocean is changing due to climate change and human activities, but their impacts on PP and N_2 fixation are not yet fully understood (Bopp et al., 2001; Doney et al., 2012). Moreover, it has been proposed that ratios of macronutrients or stoichiometry (N:P ratio) also play a critical role in controlling marine PP (Tyrrell, 1999). The nutrient stoichiometry in the surface waters may alter due to subsurface water upwelling or addition from other sources, such as riverine inputs or atmospheric deposition, which may subsequently impact the rates of PP and N_2 fixation (Franz et al., 2012). While nutrient limitation and co-limitation experiments for these processes have been performed in many parts of the world's oceans, the northern Indian Ocean has received considerably less attention, despite playing a significant role in regulating the carbon budget and climate (Moore et al., 2013).

In light of the above discussion, the first section of this chapter explores the role of macro- and micronutrients on PP and N_2 fixation rates through nutrient enrichment experiments conducted in the Bay of Bengal and the Arabian Sea during the fall inter-monsoon. The second section discusses the effect of varying N:P with different concentrations on the PP and N_2 fixation rates in these basins during the same season.

3.1 Study Area

The northern Indian Ocean is globally significant due to its unique geographical setting, which greatly affects climate and undergoes changes in wind speed, temperature, stratification due to freshwater input, wind direction, precipitation, and upwelling (Madhupratap et al., 1996). The wind direction is from the southwest during the summer monsoon (June to September) and reverses during the winter monsoon to blow from the northeast (December to February). The periods between these two monsoons are known as spring inter-monsoon (March-May) and fall inter-monsoon (October-November). The northern Indian Ocean is also recognized for having the highest dust deposition, like the Atlantic Ocean and the South China Sea (Xu & Weber, 2021). The Indian Ocean receives 8–32 % of the world's total ocean dust deposition annually, which is ~ 29–154 Mt (Mahowald et al., 2005). The northern Indian Ocean covers less than 5 % of the global ocean and is divided into two basins by the Indian subcontinent: the northwestern Indian Ocean (Arabian Sea) and the northeastern Indian Ocean (Bay of Bengal and Andaman Sea) (Fig. 3.1). The biogeochemistry of these basins differs from each other in many aspects due to the influence of diverse physical processes (Phillips et al., 2021).

3.1.1 Bay of Bengal

The Bay of Bengal region is less productive than its counterpart, the Arabian Sea (Fig. 3.1; Qasim, 1982; Singh et al., 2012). The high freshwater influx from rivers and precipitation (> evaporation) into the Bay of Bengal create a strong surface stratification (Subramanian, 1993; Prasad, 1997). During the summer monsoon, this stratification forms a thick layer at the surface, effectively preventing the upward movement of nutrients. This lack of nutrient movement, combined with reduced sunlight due to cloud cover and high sediment load, significantly limits PP (Prasanna Kumar et al., 2002, 2010). Most of the nutrients carried by rivers are consumed in estuaries and coastal regions (Kumar et al., 2004; Singh & Ramesh, 2011). Despite the stratification, eddies and cyclones have been proposed as potential mechanisms that under favourable conditions can introduce nutrients from the subsurface to surface layers, thereby enhancing PP (Prasanna Kumar et al., 2004; Venkateswrlu & Rao, 2004). Additionally, the Bay of Bengal receives dust inputs from anthropogenic and lithogenic aerosols from the adjacent Indian subcontinent (Srinivas et al., 2012; Srinivas & Sarin, 2013).

3.1.2 Arabian Sea

The Arabian Sea is globally recognized as one of the most biologically productive regions (Fig. 3.1; Qasim, 1982). The intense summer monsoon winds drive upwelling in the northwestern Arabian Sea, transporting nutrients from the deeper to the surface waters, enhancing PP (Bauer et al., 1991; Singh & Ramesh, 2015). Similarly, the cooler winds during the winter monsoon facilitate convective mixing in the northeastern Arabian Sea that increases surface PP by bringing up subsurface nutrients (Madhupratap et al., 1996; Prakash & Ramesh, 2007; Kumar et al., 2010). However, during summer, the eastern part of the Arabian Sea is relatively less productive. The Arabian Sea gets nutrients in the form of mineral dust from the Thar desert, South Asia, Arabia, and the eastern horn of Africa through atmospheric transport (Prospero et al., 2002; Zhu et al., 2007; Ramaswamy, 2014).

3.1.3 Andaman Sea

The Andaman Sea is a part of the northeastern Indian Ocean bounded by the Andaman and Nicobar Islands of India to the west, Myanmar and Thailand to the east, and the Malay Peninsula to the south (Fig. 3.1; Chinni et al., 2019). The main pathways for water exchange between the Andaman Sea and the Bay of Bengal are the Ten-Degree Channel and the Great Channel; otherwise, the horizontal ventilation between them is restricted by the Andaman-Nicobar Islands (Gupta et al., 1981). The biogeochemistry of this basin is likely to be influenced by geological processes like active subduction zones and submarine volcanoes (Khan & Chakraborty, 2005; Sheth et al., 2009).

3.2 Role of macro- and micronutrients on PP and N_2 fixation across the northern Indian Ocean

Phytoplankton play a crucial role in the ocean's biogeochemical cycles, as their biomass directly connects the cycling of macro- and micronutrients with the carbon cycle (Moore et al., 2013). N_2 fixation is a crucial process that provides nitrogen, essential for phytoplankton photosynthesis, influencing PP and the global carbon and nitrogen cycle budgeting (Falkowski, 1997). Besides nitrogen, phytoplankton require other macro- (such as P) and micronutrients (such as Fe and Mo) which impact both PP and N_2 fixation and can limit their growth. Phosphorus is necessary for the storage of genetic information, the structure of cells, and the production of energy in organisms. Fe and Mo are critical micronutrients for various important biological activities, including photosynthesis, respiration, nitrogen metabolism, and especially for N_2 fixation, because of the Fe-Mo protein in nitrogenase enzyme responsible for this process (Cole et al., 1993; Berman-Frank et al., 2001; Marcarelli et al., 2022). Extending Liebig's law to the marine environment, it is assumed that an organism's growth will be constrained by the element in the shortest supply relative to its needs (Martin, 1991). A large part of the oceans exhibits a deficiency in the bioavailable nutrients necessary for sustaining their growth (Moore, 2016). Thus, the availability of macro- and micronutrients is a critical factor in controlling phytoplankton growth, diversity, PP, and N_2 fixation. Apart from Fe, there is little evidence that several other trace elements (such as Mn and Zn) significantly inhibit the growth of marine phytoplankton and bacteria (Moore et al., 2013).

Large-scale ocean circulation and biogeochemical interactions influence the nutrients in marine ecosystems, shaping the regional patterns of nutrient limitation (Brierley & Kingsford, 2009). Therefore, to predict the biogeochemical consequences of global climate change, including human-induced impacts on oceanic biogeochemical cycles, it is imperative to determine the nutrients that limit PP and N_2 fixation in the ocean. The tropical Indian Ocean constitutes the majority of the world's largest warm pool where interaction with the monsoon creates intricate regional and global circulation patterns (Wang et al., 2004). These patterns significantly impact nutrient distribution, yet our understanding of nutrient limitation or co-limitation in this ocean remains inadequate.

There have been few studies of nutrient limitation on PP and N_2 fixation in the Bay of Bengal (Twining et al., 2019; Sarma et al., 2020) and the Arabian Sea (Takeda et al., 1995; Naqvi et al., 2010). However, these studies are limited to summer and winter monsoons with no understanding of nutrient limitation during the fall inter-monsoon. The northern Indian Ocean becomes nearly oligotrophic during the inter-monsoon due to weak winds and strong stratification, especially the Arabian Sea (Brock et al., 1994; Prasanna Kumar et al., 2007). The dust deposition also decreases during the fall inter-monsoon in this region (Morrison et al., 1998; Schott & McCreary, 2001). Studies have reported that atmospheric mineral dust from arid or semiarid regions is a primary source of trace elements, such as Fe, in the ocean surface waters (Jickells et al., 2005; Mahowald et al., 2005). However, the impact of dust on phytoplankton biomass remains uncertain as the soluble fraction of Fe varies widely depending on the source of dust (Siefert et al., 1999; Srinivas et al., 2012). It appears that Fe may be the limiting nutrient in the Arabian Sea as a relationship between dust deposition and diazotrophs has been observed (Capone et al., 1998; Morrison et al., 1998). The case might be different for the Bay of Bengal, which is not considered Fe limited due to its deposition through anthropogenic aerosols (Kumar et al., 2010; Srinivas et al., 2012). Unlike Fe, Mo does not exhibit nutrient like pattern and behaves conservatively in the ocean (Dellwig et al., 2007), including both regions of the northern Indian Ocean (Goswami et al., 2012). Although it has been hypothesized that Mo can limit PP and N_2 fixation in oceans as sulphate inhibits its assimilation (Howarth and Cole 1985), little direct evidence supports this argument.

Taken together, it is quite clear that large gaps in the understanding of nutrient limitation or the role of macro- and micronutrient addition on PP and N_2 fixation exist in the northern Indian Ocean, particularly during the fall inter-monsoon. To address this, nutrient enrichment incubation experiments were conducted in the northern Indian Ocean during the fall inter-monsoon to assess how the addition of nutrients to natural seawater affects PP and N_2 fixation rates. Since these nutrients have been suggested as potentially limiting marine PP and N_2 fixation, evaluation of the possibility of N and P limitation as well as Fe and Mo limitation using short-term nutrient enrichment experiments have been performed in this thesis.

3.2.1 Sampling and Methodology

To conduct the enrichment experiments, surface seawater samples were collected at eight locations (10 m depth) including the Bay of Bengal (two stations), the Andaman Sea (one station), and the Arabian Sea (five stations) during the fall inter-monsoon [21 Sept–15 Oct 2021 (SK373) and 4 Nov–25 Nov 2021 (SK374)] onboard ORV *Sagar Kanya* (Fig. 3.1). For the enrichment experiments and POM contents, samples were collected from 12 L Niskin bottles mounted on a CTD rosette sampler to 2.35 L acid washed (1M HCl) polycarbonate bottles (Nalgene). Details of the methodology for parameters measured for this study are explained in Chapter 2. The details of the nutrient enrichment experiments are described in this section.

The mixed layer depth (MLD) was calculated based on a temperature variation of 0.2 °C from the SST (de Boyer Montégut et al., 2004). Monthly mean surface seawater chlorophyll a (Chl a) data was obtained from the MODIS Aqua satellite, with a resolution of 4 km (https://oceancolor.gsfc.nasa.gov/l3/). Surface seawater dissolved Fe concentrations were sourced from the global ocean biogeochemistry analysis and forecast model product provided by the E.U. Copernicus Marine Service, which offers data at a spatial resolution of 0.25° × 0.25° (https://doi.org/10.48670/moi-00015). SSS was obtained from the multi-observation global ocean 3D temperature salinity height geostrophic current and MLD product provided by the E.U. Copernicus Marine Service, which offers data at a spatial resolution of 0.25° × 0.25° (https://doi.org/10.48670/moi-00052).

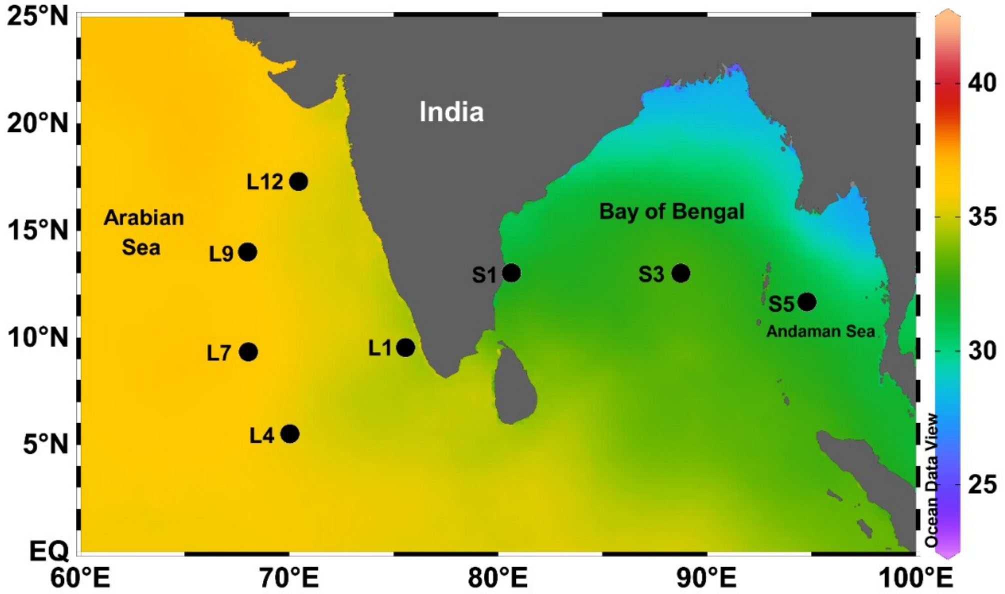


Fig. 3.1 Sampling locations of nutrient enrichment experiments in the northern Indian Ocean. Background colour represents the sea surface salinity for the sampling periods (Sept-Nov 2021). S1 and S3 (Bay of Bengal), S5 (Andaman Sea), and L1 – L12 (Arabian Sea).

3.2.1.1 Nutrients enrichment experiments

Phytoplankton primary production and N_2 fixation rate measurements were performed following the methods of Slawyk et al. (1977) and Montoya et al. (1996), respectively, as described in Chapter 2. Nutrient enrichment experiments were carried out following the methodology described by Mills et al. (2004), which is briefly summarized here. Surface seawater samples for PP and N_2 fixation rate measurements were collected in duplicate in 2.35 L bottles. Incubation was initiated by adding 2 mL of 0.2 M $NaH^{13}CO_3$ (99 atom% ^{13}C enriched, CIL) and 2 mL of $^{15}N_2$ gas (98 atom% ^{15}N enriched, CIL), respectively, followed by gentle shaking to ensure thorough mixing. This experiment acted as the control (unamended) to compare the difference in PP and N_2 fixation rates as a result of nutrient enrichment. For the nutrient enrichment experiments, surface seawater in duplicates was collected in 2.35 L bottles at all stations, where salts containing N, P, Fe, Mo, and their combinations were added leading to total of 20 bottles of 2.35 L at each station (Fig. 3.2).

Specifically, to these bottles, approximately 0.4 µM $NaNO_3$, 0.8 µM NaH_2PO_4, 2 nM $FeCl_3$, and 0.4 µM $NaMoO_4$ were added singly or in combination alongside the ^{13}C (2 mL of 0.2 M $NaH^{13}CO_3$) and ^{15}N (2 mL of $^{15}N_2$ gas) tracers to assess the impact of nutrients on PP and N_2 fixation rates (Table 3.1; Fig. 3.2). These added nutrient concentrations were selected to elevate the natural levels in the seawater, based on reported from previous studies. Apart from this, a part of aerosol filters collected during the same cruise were added to two additional bottles along with ^{13}C (2 mL of 0.2 M $NaH^{13}CO_3$) and ^{15}N (2 mL of $^{15}N_2$ gas) tracers. In all the bottles, the added ^{13}C and ^{15}N tracers were less than 10 % of the total DIC and dissolved N_2 in the samples. The bottles for the nutrient enrichment experiment were processed similar to the unamended (without nutrient addition) bottles. Post incubation sample analysis as well as PP and N_2 fixation rates were calculated in similar manner for all the bottles as discussed in Chapter 2.

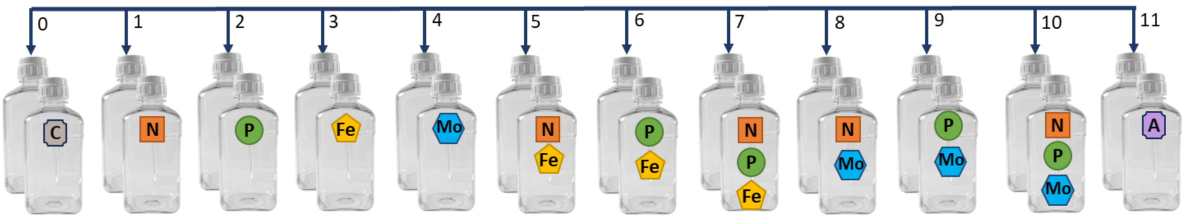


Fig. 3.2 Combinations of nutrients added to each bottle at every station during nutrient enrichment experiments. C = control, N = nitrate, P = phosphate, Fe = iron, Mo = molybdenum, and A = aerosols.

Table 3.1 Combinations and concentrations of nutrients added to sample bottles for enrichment experiments.

Incubation No.	Experiments	Amended Concentrations
1	Control	No amendment
2	$NaNO_3$ (N)	0.4 µM
3	NaH_2PO_4 (P)	0.8 µM
4	$FeCl_3$ (Fe)	2 nM
5	Na_2MoO_4 (Mo)	0.4 µM
6	$NaNO_3$ + $FeCl_3$ (NFe)	0.4 µM + 2 nM
7	NaH_2PO_4 + $FeCl_3$ (PFe)	0.8 µM + 2 nM
8	$NaNO_3$ + NaH_2PO_4 + $FeCl_3$ (NPFe)	0.4 µM + 0.8 µM + 2 nM
9	$NaNO_3$ + Na_2MoO_4 (NMo)	0.4 µM + 0.4 µM
10	NaH_2PO_4 + Na_2MoO_4 (PMo)	0.8 µM + 0.4 µM
11	$NaNO_3$ + NaH_2PO_4 + Na_2MoO_4 (NPMo)	0.4 µM + 0.8 µM + 0.4 µM
12	Aerosols (A)	Aerosol filter (4 × 2 cm^2)

3.2.1.2 Aerosol sample collection and measurement

To collect the total suspended particulate aerosol samples for the enrichment experiment, a high-volume air sampler was used onboard. Samples were collected onto pre-combusted quartz fiber filters at a flow rate of 1.13 m^3/min for 19-21 hours at the beginning of both cruises. A small part (4 × 2 cm^2) of these filters was utilized for total aerosol enrichment incubation experiments in both basins. Water-soluble N and Fe concentrations in the aerosols were determined using ion chromatography (IC, Dionex 500) and inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo-X series), respectively, following methods of Patel & Rastogi (2021). Furthermore, an analysis of several blank quartz fiber filters was conducted, and N and Fe concentrations were corrected using blank filter data.

3.2.2 Results

3.2.2.1 Environmental parameters and nutrients

The SSS at the coastal location in the Bay of Bengal was 33.56, whereas the open Bay of Bengal showed a salinity of 32.79. The SSS in the Andaman Sea was 29.65. In the Arabian Sea, SSS ranged from 34.53 to 36.38 with low values in coastal water and high in open water (Table 3.2). The SST varied from 28.25 to 29.29 °C during the sampling period, where the lowest SST was observed in the Arabian Sea (L9) and the highest in the Bay of Bengal (S1). The MLD varied from 5 to 49 m during the sampling period, with the shallowest depth observed in the Andaman Sea (Table 3.2).

The concentration of NOx ranged from below detection limit to 0.5 µM in the surface waters and was depleted at almost all stations (Table 3.2). The concentrations of PO_4^{3-} and SiO_4^{4-} were above the detection limit except for SiO_4^{4-} at two stations (L1 and L4) of the Arabian Sea. The PO_4^{3-} concentration had a small range in both basins, where it varied from 0.16 to 0.19 µM in the Bay of Bengal and the Andaman Sea and from 0.30 to 0.35 µM in the Arabian Sea. The highest SiO_4^{4-} concentration (6.8 µM) was observed in the Andaman Sea; otherwise, it varied from 0.94 to 4.14 µM. The concentrations of water-soluble Fe in the aerosol samples were 0.02 µg/m^3 and 0.21 µg/m^3 in the Bay of Bengal and the Arabian Sea, respectively. The concentrations of NO_3^- in the aerosol samples were 1.25 µg/m^3 in the Bay of Bengal and 0.80 µg/m^3 in the Arabian Sea. The N:P (NOx/PO_4^{3-}) varied from 0 to 3.19 during the study period (Table 3.2).

Table 3.2 The sampling locations and physical parameters [sea surface temperature (SST), sea surface salinity (SSS), mixed layer depth (MLD), nitrate + nitrite (NOx = NO_3^-+ NO_2^-), phosphate (PO_4^{3-}), silicate (SiO_4^{4-})] along with primary production (PP) and N_2 fixation rates (NFR) in unamended (control) bottles at each station. BD stands for below detection limit. Nutrient enrichment experiments were also performed at these locations.

Cruise Id	Date (2021)	Station Id	Latitude (°N)	Longitude (°E)	SST (°C)	SSS	MLD (m)	NOx (µM)	PO_4^{3-} (µM)	N:P	SiO_4^{4-} (µM)	PP (µM C d^{-1})	NFR (nM N d^{-1})
SK373	24-Sep	S1	13.0172	80.6269	29.29	33.56	49	BD	0.19	-	3.29	0.08 ± 0.02	0.11 ± 0.02
SK373	28-Sep	S3	13.0047	88.7446	29.04	32.79	27	0.45	0.18	2.5	1.56	0.28 ± 0.07	0.26 ± 0.05
SK373	02-Oct	S5	11.6591	94.783	28.92	29.65	5	0.51	0.16	3.19	6.8	0.33 ± 0.02	0.90 ± 0.66
SK374	04-Nov	L1	9.5419	75.5515	29.11	34.53	29	BD	0.33	-	BD	0.45 ± 0.18	0.15 ± 0.07
SK374	08-Nov	L4	5.5021	70.0363	28.74	36.27	43	0.5	0.34	-	BD	0.41 ± 0.04	0.06 ± 0.03
SK374	13-Nov	L7	9.3284	68.0652	28.52	36.38	41	0.48	0.3	1.6	0.94	0.72 ± 0.06	0.06 ± 0.01
SK374	16-Nov	L9	14.0001	68.0031	28.25	36.27	40	BD	0.35	-	2.9	0.43 ± 0.03	0.31 ± 0.07
SK374	20-Nov	L12	17.2879	70.499	28.44	34.89	21	0.31	0.32	0.97	4.14	0.81 ± 0.00	0.06 ± 0.03

3.2.2.2 Phytoplankton primary production and N_2 fixation rates

The results of the unamended (control) experiments are reported as natural PP and N_2 fixation rates. Surface PP was 0.08 ± 0.02 μM C d^{-1} (mean ± stdev) at the coastal and 0.28 ± 0.07 μM C d^{-1} in the open Bay of Bengal (Fig. 3.3). Surface N_2 fixation rates were 0.11 ± 0.02 nM N d^{-1} and 0.26 ± 0.05 nM N d^{-1} in the coastal and open Bay of Bengal, respectively (Fig. 3.4). The measured surface PP in the Andaman Sea was 0.33 ± 0.02 μM C d^{-1} and the N_2 fixation rate was 0.90 ± 0.66 nM N d^{-1}. The PP in the surface waters of the Arabian Sea ranged from 0.41 ± 0.04 to 0.81 ± 0.002 μM C d^{-1} and N_2 fixation rates varied from 0.06 ± 0.01 to 0.31 ± 0.07 nM N d^{-1} (Figs. 3.3 and 3.4, and Table 3.2).

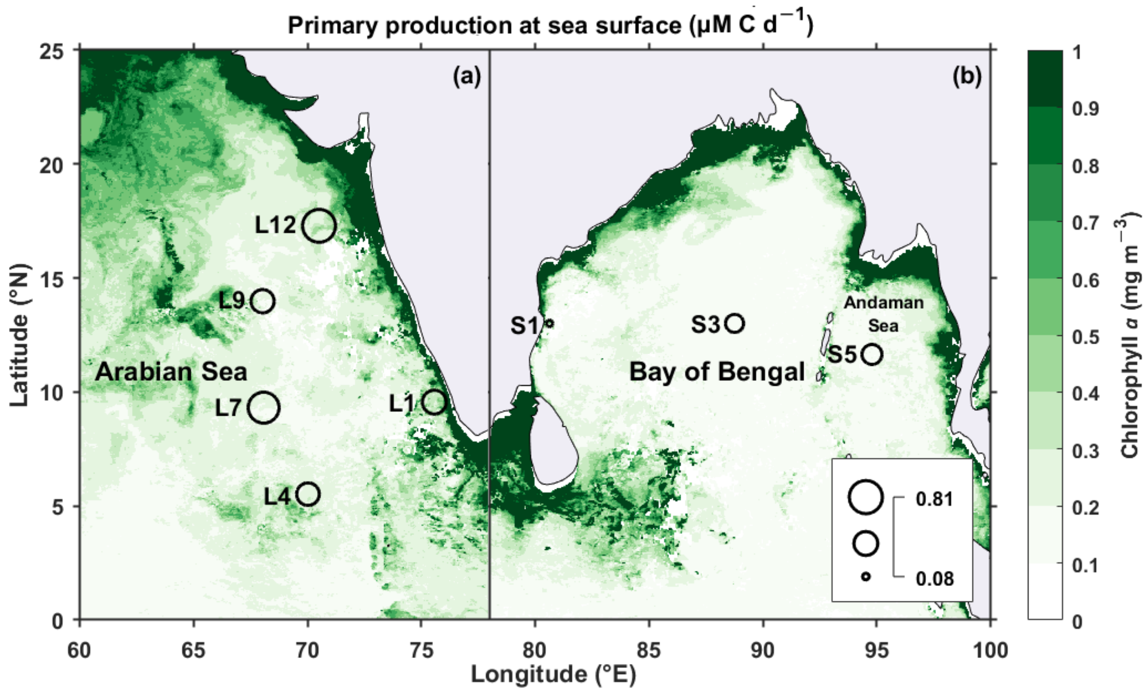


Fig. 3.3 Sampling locations of nutrient enrichment experiments with circles showing primary production (μM C d^{-1}) in control and the background colour representing the surface chlorophyll a concentration (mg m^{-3}) obtained from Aqua MODIS for September (b) and November (a) months.

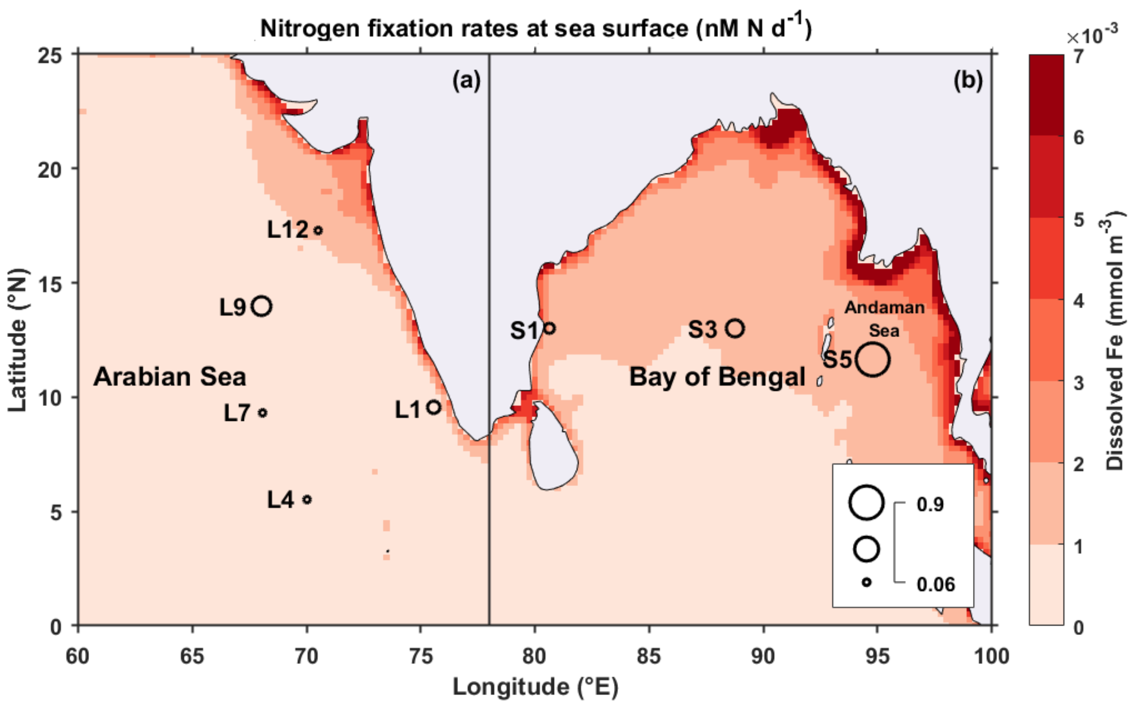


Fig. 3.4 Sampling locations of nutrient enrichment experiments with circles showing N_2 fixation rates (nM N d^{-1}) in control and the background colour representing the dissolved Fe concentration (mmol m^{-3}) in surface waters obtained from the global ocean biogeochemical models for September (b) and November (a) months.

3.2.2.3 Nutrient Enrichment Experiments

The effect of nutrient addition on PP and N_2 fixation rates was compared to the unamended (control) experiments, and it was also interpreted based on relative change [{(enrichment experiments – control)/control} × 100] in mean values.

The Bay of Bengal

The Coastal Bay of Bengal

In the coastal Bay of Bengal (S1), an increase in PP was observed after the addition of Mo, whereas the addition of N, P, and Fe alone did not show any increase. The maximum increase in PP occurred when NMo combination and aerosols were applied. A small increase in PP was also observed when Fe was added with macronutrients (Fig. 3.5a). N_2 fixation rates increased after the addition of N alone. Contrary to expectation, N_2 fixation rates did not stimulate after the addition of Fe and Mo alone. N_2 fixation rates also increased when PMo combination and aerosols were added (Fig. 3.5b).

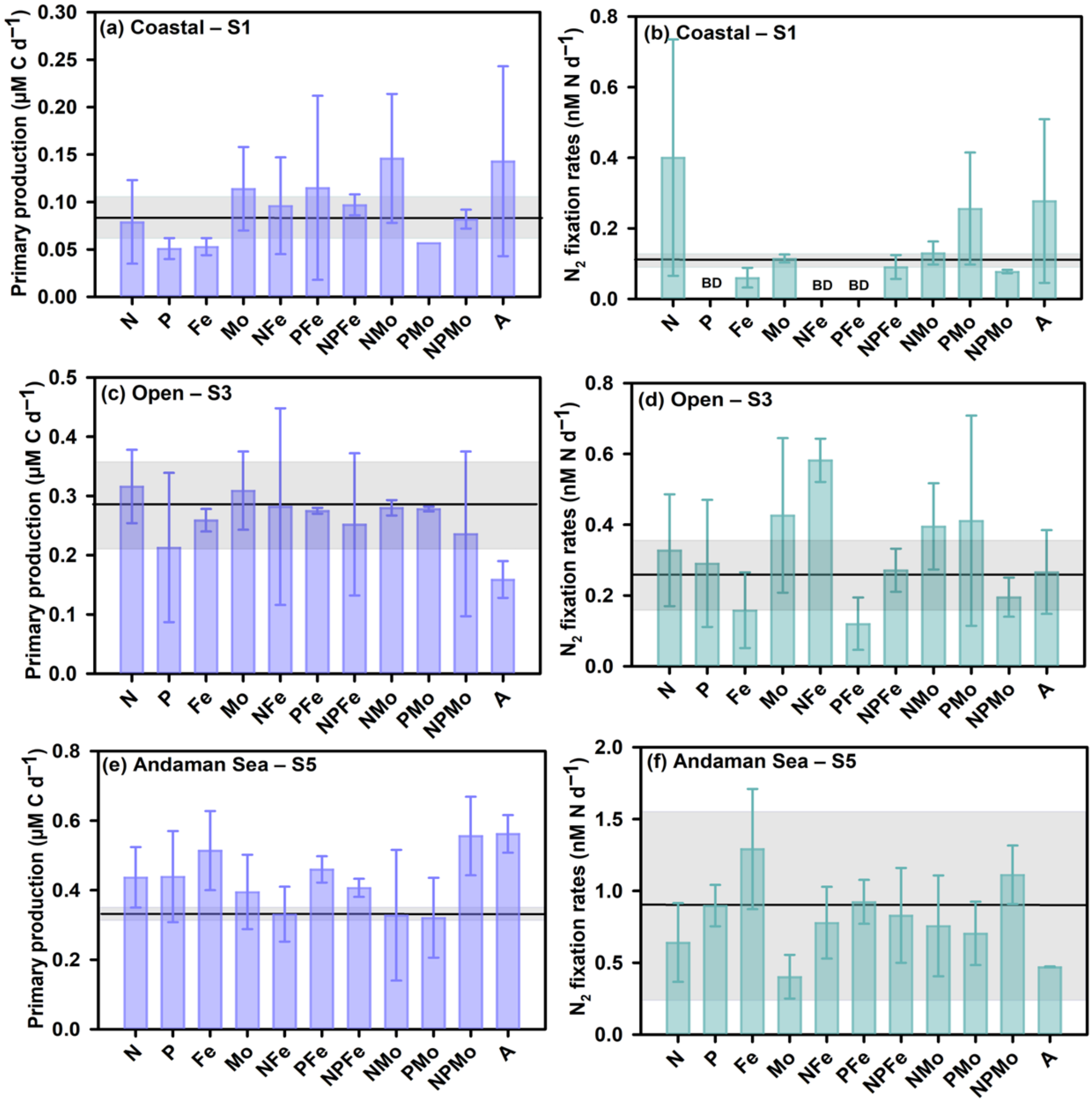


Fig. 3.5 Response of primary production (PP) and N_2 fixation rates to nutrient enrichment experiments. Error bars represent the standard deviation of duplicates (n = 2). The symbol A is for aerosol filter addition. The black line and associated grey horizontal bar represent the mean and standard deviation of control PP and N_2 fixation rates, respectively. Note the difference in the scale of the y-axes.

The Open Bay of Bengal

In the open Bay of Bengal (S3), no increase in PP was observed when nutrients were added alone or in combinations (Fig. 3.5c). The highest increase in N_2 fixation rate was noticed after the addition of NFe combination. N_2 fixation rates increased similarly when Mo was added alone or in combination with N (NMo) and P (PMo) (Fig. 3.5d). A decrease in PP resulted from the addition of aerosols, however, N_2 fixation rates remained unchanged. A small increase was also observed in the N_2 fixation rates after the N addition alone (Figs. 3.5c and d).

The Andaman Sea

In the Andaman Sea (S5), the highest increase in PP was observed after the addition of NPMo combination and aerosols. PP also increased when nutrients were added alone and in combinations of PFe and NPFe (Fig. 3.5e). N_2 fixation rates increased with the addition of Fe alone. No increase in N_2 fixation rates was observed due to the addition of Mo alone or in combination with macronutrients, except NPMo (Fig. 3.5f).

The Arabian Sea

The Coastal Arabian Sea

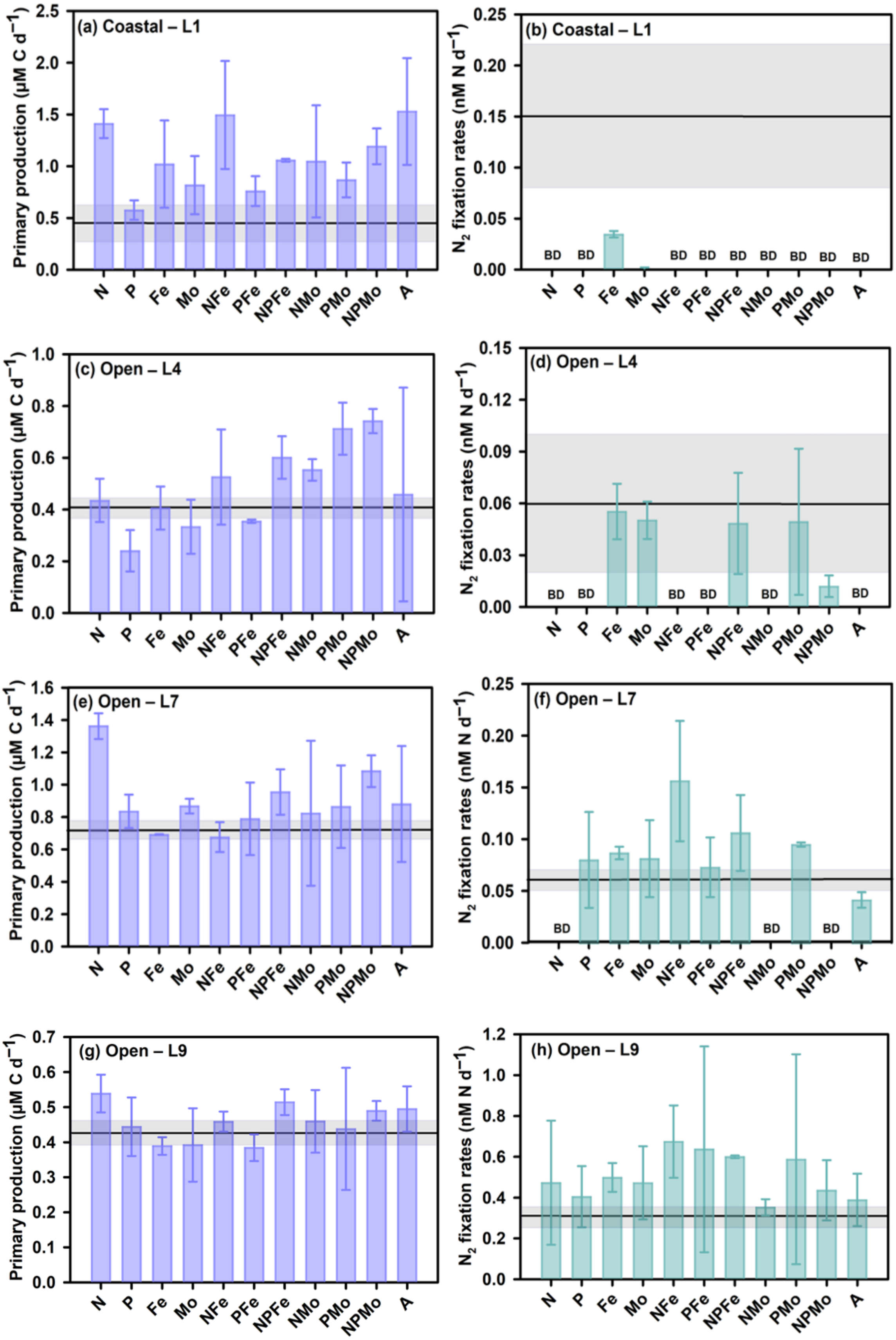
In the coastal Arabian Sea (L1 and L12), PP increased after the addition of N, P, Fe, and Mo alone, except that there was no increase due to Fe addition alone at station L12. At both stations, the smallest increase was observed when P was added alone. In general, PP increased at these two coastal locations when nutrients were added in combinations (Figs. 3.6a and i). No increase in N_2 fixation rates was observed for any addition at L1 (Fig. 3.6b); however, N_2 fixation rates were stimulated in experiments with Fe addition alone and in combinations of NFe and PFe at L12 (Fig. 3.6j). Interestingly, an increase in N_2 fixation rates also resulted after the addition of N alone. No increase in N_2 fixation was observed in combinations of Mo with macronutrients (Figs. 3.6b and j).

The Open Arabian Sea

In the southern open Arabian Sea (L4), no increase in PP was observed when nutrients were added alone (Fig. 3.6c). However, increase in PP was observed when N was added in combination with other nutrients. Similarly, PP increased in the combination of Mo with macronutrients (Fig. 3.6c). N_2 fixation was not stimulated in any of the experiments, either alone or in combinations (Fig. 3.6d).

In the northern part of the open Arabian Sea (L7 and L9), PP increased with the addition of N alone (Figs. 3.6e and g). The increase in PP was also observed due to the addition of the combinations of NPFe and NPMo. N_2 fixation rates increased in all experiments of Fe and in combinations of macronutrients with Fe (Figs. 3.6f and h). N_2 fixation increased due to the addition of Mo and its combination with P (PMo). However, the combination of Mo and N did not stimulate N_2 fixation. The maximum increase in N_2 fixation was observed with the addition of NFe at both stations (Figs. 3.6f and h). In general, N_2 fixation was stimulated in all the experiments at L9 (Fig. 3.6h).

All stations in the Arabian Sea showed an increase in PP after aerosol additions, whereas no increase in N_2 fixation was observed because of this amendment (Fig. 3.6).



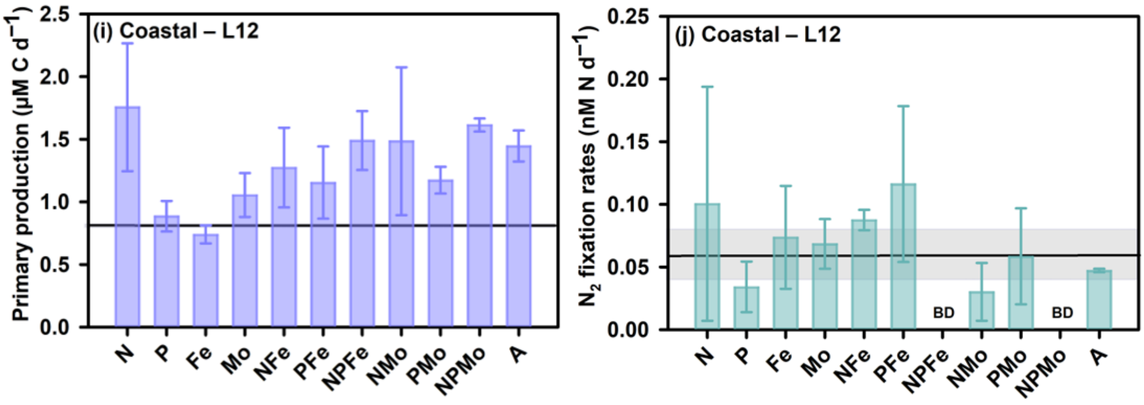


Fig. 3.6 Response of primary production (PP) and N_2 fixation rates to nutrient enrichment experiments in the Arabian Sea. Error bars represent the standard deviation of duplicates (n = 2). The symbol A is for aerosol filter addition. The black line and associated grey horizontal bar represent the mean and standard deviation of control PP and N_2 fixation rates, respectively. Note the difference in the scale of the y-axes.

3.2.3 Discussion

3.2.3.1 Environmental parameters and nutrients

The Bay of Bengal was less saline than the Arabian Sea during the fall inter-monsoon (Fig. 3.1, Table 3.2). This difference in salinity is attributed to the higher freshwater input into the Bay of Bengal, resulting from substantial precipitation and the influx from major river drainage systems (Subramanian, 1993; Varkey et al., 1996). The open Bay of Bengal (S3) was slightly less saline than the coastal region (S1), likely due to precipitation at the time of sampling. The SSS was the lowest in the Andaman Sea (S5) resulting from large freshwater input from the Salween and Irrawaddy rivers (Chapman et al., 2015). The coastal Arabian Sea (L1 and L12) was less saline than the open waters (L4, L7, and L9) due to freshwater influx and intrusion of low salinity water from the Bay of Bengal through East India coastal current (Table 3.2, Zhu et al., 2022).

The ambient nutrient concentrations in the study region were low and within the range reported in previous studies (Table 3.2; Kumar et al., 2004; Singh et al., 2019; Chinni et al., 2019). As riverine nutrients are understood to be largely consumed in the estuaries or coastal waters, the discharged freshwater from the rivers is not supposed to be a significant source of nutrients to the Bay of Bengal and the Arabian Sea (Kumar et al., 2004; Singh & Ramesh, 2011). Also, the riverine freshwater discharge limits the vertical mixing of nutrients from the subsurface to the surface waters (Prasanna Kumar et al., 2002). The dissolved nutrients N:P ratio was always less than the Redfield ratio (N:P = 16:1) during this study indicating nitrogen limitation (Table 3.2; Redfield, 1958).

3.2.3.2 Phytoplankton primary production and N_2 fixation rates

Surface PP in the Arabian Sea was higher than in the Bay of Bengal, while N_2 fixation rates were similar in both basins (Figs. 3.3 and 3.4). The lower PP in the Bay of Bengal was due to strong stratification resulting from precipitation and riverine freshwater input inhibiting mixing with subsurface waters during this season (Prasanna Kumar et al., 2002). In the open Bay of Bengal, PP was within the range of 0.26 to 3.76 µM C d^{-1} reported by Prasanna Kumar et al. (2007) during the same season; however, it was relatively lower for the coastal region during this study. In the Arabian Sea, the surface PP in this study was within the range previously reported for the fall inter-monsoon (0.06–0.99 µM C d^{-1}, Bhattathiri et al., 1996) and the winter monsoon (0.39 to 2.75 µM C d^{-1}, Saxena et al., 2024). PP in the surface waters of the Andaman Sea was also within the range reported in the study carried out during the winter monsoon (0.11 to 5.58 µM C d^{-1}; Devassy & Bhattathiri, 1981).

The N_2 fixation rates reported here are within the range reported from the Bay of Bengal during the spring inter-monsoon [(0.04–0.19 nM N d^{-1}, Wu et al., 2022) and (0.06–0.38 nM N d^{-1}, Saxena et al., 2023)]. In the Arabian Sea, N_2 fixation rates reported here are within the rates reported by Saxena et al. (2024) for the winter monsoon (below detection limit to 17.39 nM N d^{-1}) but much less than the one reported by Gandhi et al. (2011) during the spring inter-monsoon as it was measured in the *Trichodesmium* bloom patch. PP was correlated with the N_2 fixation rates in the Bay of Bengal and the Andaman Sea; however, they did not show any trend in the Arabian Sea. In the Arabian Sea, N_2 fixation was higher at the stations where NOx was below detection limit in the surface waters (Fig. 3.4 and Table 3.2), suggesting that low DIN concentrations are favourable for diazotrophs.

3.2.3.3 Nutrient Enrichment Experiments

Nutrient enrichment experiments have been carried out to understand the effect of macro- and micronutrients on PP and N_2 fixation rates in the northern Indian Ocean. Other than single nutrient limitation, PP and N_2 fixation might be co-limited by more than one nutrient. The co-limitation is defined as either (i) where two or more non-substituted nutrients decrease to the same limiting levels (simultaneous co-limitation) or (ii) where nutrients can be substituted at the community level or biochemically (same enzyme or different enzymes with the same function required distinct nutrients) (independent co-limitation) or (iii) one nutrient is required for the assimilation of others or serial limitation (increased more after second nutrient addition) (Arrigo, 2005; Saito et al., 2008; Moore et al., 2013; Sperfeld et al., 2016).

The Bay of Bengal

The Coastal Bay of Bengal

The NOx concentration was below detection limit in the coastal Bay of Bengal suggesting PP might be limited by N, however, no increase in PP was observed due to the addition of N alone (Fig. 3.5a and Table 3.2). The increase in PP due to the addition of nutrients in combination (NFe, PFe, and NPFe) indicated simultaneous co-limitation, where more than one nutrient was drowned down to the same limiting level and the simultaneous addition of these nutrients increased PP. It has been argued that even if rivers bring nutrients, only a small fraction (< 5%) reaches coastal waters, with most being consumed in the estuaries, leading to co-limitation (Singh & Ramesh, 2011). It appears that PP increased in a combination of N with Mo due to the co-limitation of these nutrients because the enzymes responsible for N reduction to NH_4^+ require Mo (Fig. 3.5a; Timmermans et al., 1994; Schwarz et al., 2000). The highest increase in N_2 fixation rates occurred with the addition of N alone, showing no suppression of N_2 fixation in the presence of N. N_2 fixation rates increased in PMo combination as the nitrogenase enzyme responsible for this process requires P and Mo (Fig. 3.5b). It seems that N was not the primary nutrient limiting PP in the coastal Bay of Bengal, consistent with findings from other studies based on nutrient microcosm experiments as well (Sarma et al., 2013; Kumari et al., 2022). There was no increase in N_2 fixation rates due to the addition of Fe alone and combinations of Fe with macronutrients indicated that diazotrophs at this location were not Fe-limited. It might be due to competition for nutrients between diazotrophs and non-diazotrophs in these waters.

The increased PP and N_2 fixation rates in aerosol experiments also indicated nutrient co-limitation for organisms and suggested that aerosols can provide essential nutrients (N, P, or Fe) for phytoplankton to overcome nutrient limitations in coastal waters (Figs. 3.5a and b; Yadav et al., 2016; Kumari et al., 2022). Siswanto et al. (2023) observed increase in phytoplankton community biomass in the coastal Bay of Bengal confirming that these species are sensitive to atmospheric aerosols.

The Open Bay of Bengal

There was no increase in PP in the open Bay of Bengal in all nutrient addition experiments suggesting that phytoplankton communities are not limited by nutrients and might be acclimatized to these environmental conditions (Bonnet et al., 2008). To cope with these low nutrient conditions and sustain PP, phytoplankton must have evolved their ecophysiological functioning (Geider & La Roche, 1994). Decrease in PP in the aerosol experiment might be due to the dust sensitivity of picophytoplankton (*Prochlorococcus* and *Synechococcus*) (reduced abundance after dust addition), which predominantly inhabit the open waters of the Bay of Bengal, probably due to Cu or Cd toxicity (Fig. 3.5c; Paytan et al., 2009; Mackey et al., 2012; Baer et al., 2019). No increase in N_2 fixation due to aerosol addition indicates no limitation of Fe and P, which are typically supplied by atmospheric deposition. This was also corroborated by no increase in PP due to P and Fe additions alone or in combination (PFe and NPFe). Similar increase in N_2 fixation rates with Mo addition alone and in combination with macronutrients (NMo and PMo) showed Mo limitation for diazotrophs as nitrogenase enzymes found in these organisms require Mo due to metal co-factor (protein) present in them (Fig. 3.5d; Newton, 1997). N limitation for PP using Chl a as a proxy and severe P limitation for N_2 fixation during the spring inter-monsoon and summer monsoons, respectively, have been previously reported from the open Bay of Bengal (Twining et al., 2019; Sarma et al., 2020). Additionally, N limitation in *Synechococcus* and multiple nutrient limitation in picophytoplankton (*Prochlorococcus* and eukaryotes) in the open Bay of Bengal have been documented (Twining et al., 2019; Jiang et al., 2023).

The Andaman Sea

Phytoplankton primary production in the Andaman Sea was found to be co-limited by multiple nutrients as indicated by increase in PP in all experiments except with the addition of NFe, NMo, and PMo (Fig. 3.5e). The enhanced PP after nutrient addition was due to the insufficiency of ambient nutrient concentrations to support the phytoplankton growth. A comparable increase in PP due to additions of N, P, and Fe alone or in combinations (PFe and NPFe) showed independent co-limitation of P and Fe because no increase was observed due to NFe addition. The maximum increase in PP was observed due to NPMo addition suggesting serial colimitation (higher increase than N, P, and Mo). The aerosols addition also showed similar increase in PP possibly due to the supply of multiple nutrients (Fig. 3.5e). The Andaman Sea has been recognized as oligotrophic and known for its nutrient limitations (Qasim & Ansari, 1981; Gomes et al., 1992). Gomes et al. (1992) reported that N availability potentially regulates PP in the Andaman Sea. An increase was observed in N_2 fixation rates after the addition of Fe alone due to Fe limitation for diazotrophs (Fig. 3.5f). *Trichodesmium* species have been reported from this region during the winter monsoon (Devassy & Bhattathiri, 1981) and the fall inter-monsoon (Sarojini & Sarma, 2001). The high demand for nutrients like Fe, and Mo by diazotrophs might have led to the undernourishment of other communities of phytoplankton as there was no co-limitation for N_2 fixation in the Andaman Sea.

The Arabian Sea

The Coastal Arabian Sea

In the coastal Arabian Sea (L1 and L12), increase in PP due to N addition alone or combinations of N with other nutrients suggested PP to be primarily limited by N in this region (Figs. 3.6a and i). The west coast of India experiences seasonal depletion of oxygen in subsurface water during the late summer monsoon and fall inter-monsoon that leads to processes such as denitrification and anammox, which remove N from sediments (Rowe et al., 1975; Naqvi et al., 2006). As a result, the surface waters along the coast can become deficient in N due to the upward movement of these waters resulting in N limitation. The small or negligible increase in P treatments might not be due to limitations on PP as P is more readily recycled from sediments to the water column (Nixon, 1980; Seitzinger et al., 1984). Additionally, an increase in PP was observed with combined macro- and micronutrients due to the co-limitation of nutrients for phytoplankton growth in coastal regions (Figs. 3.6a and i). This increase is higher in the NFe and NMo than PFe and PMo, respectively, suggesting that combined with micronutrients, N plays a more important role than P for phytoplankton in these waters. Because of several nutrient limitations, aerosol deposition alone may not effectively promote PP in the coastal Arabian Sea. Still, it does, however, can contribute a significant quantity of nutrients to ocean waters (Guieu et al., 2019). There was no evidence of co-limitation of nutrients for N_2 fixation at coastal station L1, which suggests that other factors might be controlling the N_2 fixation in this region. However, at coastal station L12, N_2 fixation rates increased in experiments with combinations of Fe with macronutrients indicating PFe co-limitation for diazotrophs. There was no evidence for limitation or co-limitation of Mo for N_2 fixation in the coastal regions (L1 and L12) (Figs. 3.6b and j).

The Open Arabian Sea

In the southern open Arabian Sea (L4), PP did not increase when nutrients were added alone but did increase when added in combinations (NFe and NPFe) suggesting simultaneous co-limitation (Fig. 3.6c). Additionally, simultaneous co-limitation for P and Mo was observed as the addition of these alone failed to stimulate PP. N_2 fixation was neither limited nor co-limited by nutrients in the southern open Arabian Sea (Fig. 3.6d). There was no Mo limitation or co-limitation for diazotrophs as no increase was observed in Mo experiments of N_2 fixation.

In the northern Arabian Sea (L7 and L9), N addition alone increased PP showing N limitation, which was higher at L7 (Figs. 3.6e and g). At these stations, an increase in N_2 fixation was observed when P and Fe were added alone, and Fe was added in combination with macronutrients suggesting PFe independent co-limitation of N_2 fixation. Nutrient enrichment experiments have shown PFe co-limitation for N_2 fixation in the Atlantic Ocean and southern China Sea, where dust deposition is high, similar to the Arabian Sea (Mills et al., 2004; Wen et al., 2022b). All experiments showed an increase in N_2 fixation at L9 with a maximum for NFe addition indicating serial co-limitation of nutrients. Independent co-limitation for N_2 fixation was observed for this location for PMo addition due to the requirement for these elements by nitrogenase enzyme (Figs. 3.6f and h; Newton, 1997).

These findings are consistent with the observations in other parts of the ocean, such as the Atlantic and Pacific (Mills et al., 2004; Moore et al., 2008; Bonnet et al., 2008; Browning et al., 2017; Wen et al., 2022b; Browning et al., 2022). Around 1.3–3.2-fold increase in PP in all experiments and locations (except at L4) indicated that N was the most essential nutrient for PP in the Arabian Sea (Fig. 3.6). The lower N in the Arabian Sea might be due to N-loss from OMZs. The N scarcity in the surface Arabian Sea during inter-monsoon has been reported by many studies (DeSousa et al., 1996; Capone et al., 1998). Coastal stations showed a 1.3–3.4-fold increase in PP in combined nutrient experiments, whereas the northern open Arabian Sea (L7 and L9) showed the highest increase in the N treatment only. In the Arabian Sea, aerosol addition increased PP in the coastal areas with less in the open seas confirming that aerosol deposition can play an important role in stimulating PP in coastal regions (Fig. 3.6).

3.2.3.4 Nutrient limitation in the northern Indian Ocean

Open and coastal waters of the northern Indian Ocean with varying physio-chemical characteristics and phytoplankton communities were explored in this study. Limitation and co-limitation of nutrients for PP and N_2 fixation appear to be widespread in the northern Indian Ocean (Takeda et al., 1995; Twining et al., 2019). Due to varying sources of nutrients, their effect on these processes was not the same in the open waters of both basins. For example, atmospheric Fe studies reported that Fe mass concentrations are the same for both basins, however, fractional solubility differs (Arabian Sea = ~ 0.02–0.4 % and Bay of

Bengal = ~ 1.4–24 %, Srinivas et al., 2012) because of atmospheric processing (Siefert et al., 1999). Even though the Arabian Sea is one of the world's major dust-receiving regions, Fe limitation has been found here during the late southwest monsoon in the northwest region (Naqvi et al., 2010; Moffett et al., 2015). The northern Indian Ocean was predicted to experience PP limitation by N and Fe based on a model study by Wiggert et al. (2006), and the results of this study provide evidence for the same. These findings support that N_2 fixation may be widely co-limited by Fe and P in elevated dust-deposited regions as observed at stations L7-L12 despite having higher Fe at L12 (Figs. 3.4 and 3.6). During the fall inter-monsoon, lower dust deposition in the Arabian Sea impacts the nutrient stoichiometry in the region, leading to co-limitation of nutrients for PP and N_2 fixation (Schott & McCreary, 2001; Léon & Legrand, 2003; Singh & Singh, 2022). It might also be due to stratification caused by weak winds during this season. N limitation of PP in the Arabian Sea was also corroborated by the N:P ratio which was less than the Redfield ratio (16:1) (Table 3.2). This stoichiometry analysis underscores the consistency between these results and the data obtained from oceanographic observations. Despite the studies presented here, there remains considerable space to explore further the interplay of nutrients on PP. The possible factors contributing to the observed impact could be the supply of nutrients and its regulation of N_2 fixation (Falkowski, 1997). The distinctive elemental composition of different constituents present in phytoplankton cells might offer insights into the observed constraints imposed by nutrient availability (Geider & Roche, 2002). The observed discrepancy implies that various factors, including the nutrients, phytoplankton assemblages, the interaction between physical and ecological mechanisms, and the specific experimental setup, are pivotal in determining the changes in PP and N_2 fixation due to nutrient addition.

N_2 fixation has been found to be co-limited by P and Fe in other oceans as well (Mills et al., 2004; Sohm et al., 2011; Langlois et al., 2012; Wen et al., 2022). The effect of aerosols was visible on the PP but not on the N_2 fixation in both basins and was higher in the coastal regions (Figs. 3.5 and 3.6). An increase in N_2 fixation was observed in the experiments, especially with N, NFe, or NPFe in both basins except L1 and L4 in the Arabian Sea and the Andaman Sea which was unexpected as diazotrophs can fulfil their own N requirement by fixing atmospheric N_2 (Figs. 3.5 and 3.6). The reason for this might be specific to diazotroph communities present in water. Langlois et al. (2012) observed an increase in UCYN$_2$-fixer and Gamma A (diazotrophs) after the addition of dissolved N or combinations of NP and NPFe, confirming that diverse diazotrophic communities respond differently. The differences in the roles of these nutrients in cellular processes could explain these limitations. Nucleic acids, adenosine triphosphate, and phospholipids all include P, which cells utilize for growth and division, whereas on the other hand, Fe plays a crucial role in various enzymes such as nitrogenase, and their increased concentrations might contribute to N_2 fixation. N is also important for cell growth and division as it is present in nucleic acids and metabolic compounds. Another study on *Crocosphaera watsonii* (UCYN$_2$-fixer) reported increased rates of N_2 fixation in the presence of N (Dekaezemacker & Bonnet, 2011). There are limited studies available on the diazotroph community level in the northern Indian Ocean. However, some studies reported the presence of UCYN$_2$-fixer and Gamma proteobacteria during different seasons in the Arabian Sea (Mazard et al., 2004; Bird et al., 2005; Jayakumar et al., 2012; Bird & Wyman, 2013). UCYN$_2$-fixer and Gamma proteobacteria have also been reported from the Bay of Bengal (Wu et al., 2019; Li et al., 2021; Chowdhury et al., 2023) during other seasons. The reason for increased N_2 fixation rates in NP and NPFe experiments might be due to the division of diazotrophs (Davey et al., 2008). Dekaezemacker et al. (2013) also noticed an increase in N_2 fixation with N and NFe addition in the eastern tropical South Pacific Ocean. For this, they proposed a hypothesis that the availability of inorganic nutrients may directly limit N_2 fixation or indirectly through stimulating PP and the subsequent excretion of dissolved OM and/or the creation of microenvironments that are conducive to heterotrophic N_2 fixation. The dominance of heterotrophic diazotrophs in the northern Indian Ocean has been highlighted by recent studies (Shiozaki et al., 2014; Wu et al., 2019).

Drivers of molybdenum limitation in the northern Indian Ocean

Mo does not exhibit systematic depletion in surface waters like other algal nutrients and displays conservative behaviour in the open ocean (Morris, 1975). Thus, it would appear that PP and N_2 fixation rates will not be limited by Mo in seawater (Collier, 1985). However, in this study, increases in PP were noted following the addition of Mo alone and in combination with macronutrients at some stations (Figs. 3.5 and 3.6). This increase could be attributed to several factors, including the functioning of Mo at these places, removal kinetics (such as adsorption of Mo onto Mn oxides), proximity to river or shelf sediment inputs, coastal upwelling, and biogenic scavenging (Morford & Emerson, 1999; Dellwig et al., 2007). This can be explained by the hypothesis of Howarth and Cole (1985), which argues that sulphate inhibits phytoplankton's capacity to assimilate Mo, thereby reducing its availability in seawater compared to freshwater. In this study, sulphate-to-molybdate ratio might have decreased compared to natural seawater as a result of Mo addition, which led to an increase in PP and N_2 fixation rates (Figs. 3.5 and 3.6). According to experimental research, a higher sulphate-to-molybdate ratio limits the uptake of Mo, reduces N_2 fixation, and prevents the growth of organisms that rely on N (Howarth & Cole, 1985; Cole et al., 1986). Based on these observations, it was postulated that N limitation in phytoplankton might occur because of low Mo availability (Paerl et al., 1987).

3.2.4 Conclusion

The purpose of this study was to understand the role of nutrients in limiting PP and N_2 fixation rates in the northern Indian Ocean during the fall inter-monsoon. During the study period, the ambient concentrations of inorganic nutrients, particularly N, were depleted in the surface waters. The experiments conducted in the northern Indian Ocean revealed limitation and co-limitation of macro- and micronutrients in regulating PP and N_2 fixation rates. Results of the experiments suggested no nutrient limitation on PP in the open Bay of Bengal, whereas N was the primary limiting nutrient in the Arabian Sea. Depending on the geographical location, multiple nutrient limitations or co-limitations on PP and N_2 fixation were observed indicating a relationship between the biogeochemical setting and the phytoplankton community. This alignment with theoretical expectations holds significant implications for predicting PP and N_2 fixation at ocean basin scales and projecting potential changes under future environmental perturbations.

3.3 Response of nutrient concentrations and stoichiometry (N:P) on PP and N_2 fixation in the northern Indian Ocean

Stoichiometry (N:P ratio) is a fundamental concept in oceanography, linking nutrient availability to PP and carbon sequestration (Redfield, 1958; Arrigo, 2005; Deutsch & Weber, 2012). The classical Redfield ratios (N:P = 16:1) describe the average proportions of these elements needed by phytoplankton for metabolism, reflecting their roles in oceanic biogeochemical cycles (Deutsch & Weber, 2012). Therefore, the changes in phytoplankton stoichiometry will depend on the dissolved inorganic N:P ratio of water (Hagstrom et al., 2024). The Redfield N:P ratio was thought to be constant throughout the global ocean, and the deviation from this ratio explains the nutrient limitation for organisms in ocean waters (Lagus et al., 2004; Moore et al., 2013). Recent studies showed changes in N:P ratios in various parts of the world ocean due to different processes (Weber & Deutsch, 2010; Martiny et al., 2013). The processes through which this global relationship emerges despite the wide range of N:P ratios at the organism level are not known. This will affect the feedback which relies on physiological processes that control N:P, the carbon and nitrogen cycles, the linkage between nutrient availability and export, and how the oceans respond to climate change (Deutsch & Weber, 2012; Moreno et al., 2018). This ratio can be affected by several processes like atmospheric deposition, stratification due to global warming, upwelling of subsurface water, and riverine inputs in coastal areas (Lagus et al., 2004; Doney et al., 2012). Climate change and extreme events will have a substantial impact on nutrient inputs, functional communities, and food webs in many marine ecosystems (Bonachela et al., 2016). In recent decades, anthropogenic activities such as damming on rivers, and enhanced fertilizers used in agriculture have changed the N:P ratios in coastal regions (Beusen et al., 2022). Redox-sensitive nutrient cycles such as nitrogen and phosphorus in the marine environment may be altered by the intensification of OMZs in the ocean due to climate change (Kalvelage et al., 2011). The upwelling of water from the subsurface where the OMZs are present will impact N:P ratios due to N-loss and availability of P, which is released under anaerobic conditions (Spilling et al., 2019). It has been demonstrated that some functional ecotypes of phytoplankton have different nutritional requirements because various cellular units of autotrophs (such as proteins, ribonucleic acid, or chlorophyll) have a different stoichiometric composition from the traditional Redfield stoichiometry (Geider & La Roche, 2002; Liefer et al., 2019). Therefore, a different ratio can be beneficial for certain species of phytoplankton whose growth rates are favoured at these ratios (Cloern, 2001). These changes in stoichiometric ratios introduce significant uncertainty in predicting marine PP and the global carbon cycle by impacting the marine food web (Arrigo, 2005). Even though our understanding of governing mechanisms of elemental ratios in the marine environment has increased, there is still limited knowledge of how global change and anthropogenic activities will affect nutrient stoichiometry and how these changes will affect PP and N_2 fixation. These rates are rarely assessed in stoichiometric investigations, despite the crucial role that uptake plays in the transfer of nutrients from the dissolved pool to the particulate pool. Due to the expansion of OMZs in coastal areas, PP is likely to decrease due to N-limitation, and changes in nutrient supply may further impact PP (Dugdale & Hancock, 1985). Previous studies reported that the N:P ratio regulated phytoplankton dynamics more than the concentration of specific nutrients and can lead to harmful algal blooms in coastal areas (Hodgkiss & Ho, 1997; Spilling et al., 2019). Although there is evidence that variations in the N:P ratio change the phytoplankton community structure, studies of the stoichiometric impact on PP and N_2 fixation rates are rather limited. The northern Indian Ocean contains OMZs and anoxic waters in open and coastal areas and receives nutrients through atmospheric deposition, riverine inputs, and upwelling of subsurface waters leading to likely change in nutrient stoichiometry. Therefore, to understand the effect of the N:P ratio on PP and N_2 fixation rates, experiments to measure these rates (referred to hereafter in this section as stoichiometric experiments) at different stoichiometry (N:P ~ 5:1; 10:1; 16:1; and 20:1) at three concentration levels (low, medium, and high) were conducted in the northern Indian Ocean during the fall inter-monsoon.

3.3.1 Sampling and Methodology

3.3.1.1 Sampling

For stoichiometric experiments, seawater samples were collected at five locations (10 m depth) from the northern Indian Ocean onboard ORV *Sagar Kanya* during the fall inter-monsoon [21 Sept–15 Oct 2021 (SK373) and 4 Nov–25 Nov 2021 (SK374)] using Niskin bottles connected to a CTD rosette sampler. Out of five stations, one was in the open Bay of Bengal (S2), one was in the Bay of Bengal near Andaman Island [hereafter, coastal Andaman (S4)], and three were in the Arabian Sea (L2, L5, and L10) (Fig. 3.7). For the experiments, samples were collected in 2.35 L polycarbonate bottles (Nalgene) from Niskin bottles. The details of the measurements for all parameters required to calculate PP and N_2 fixation rates are already discussed in Chapter 2.

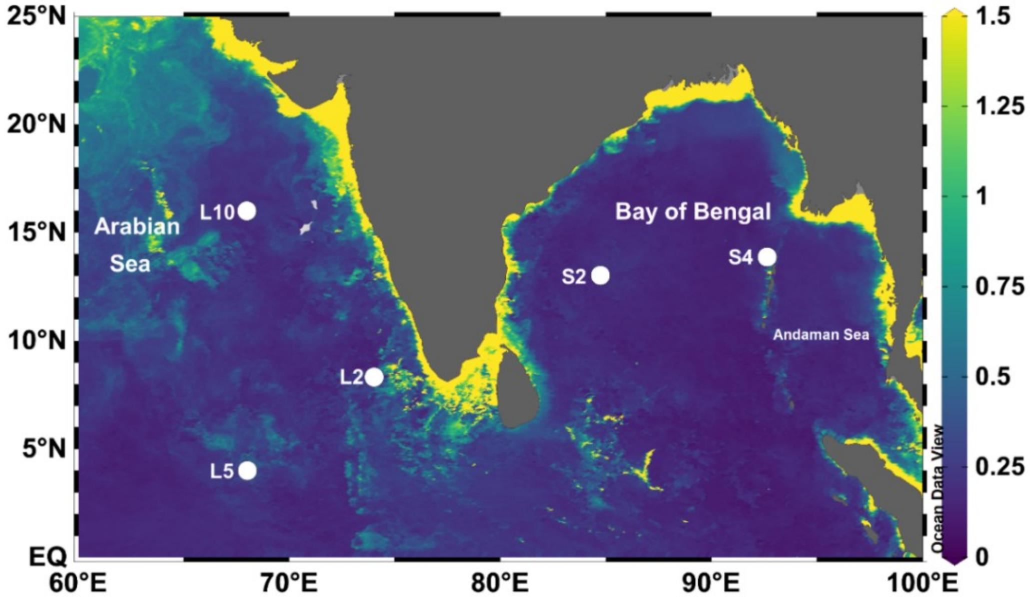


Fig. 3.7 Sampling locations for the stoichiometric experiments in the northern Indian Ocean. The background colour represents the surface chlorophyll a concentration (mg m^{-3}) obtained from Aqua MODIS for November 2021. S2 (Bay of Bengal), S4 (Coastal Andaman), and L2, L5, and L10 (Arabian Sea).

3.3.1.2 Stoichiometric experiments for primary production and N_2 fixation

The methodology for the stoichiometric experiments and measurements is similar to the nutrient enrichment experiments described in Section 3.2.1. For these experiments, surface seawater samples were collected in 2.35 L bottles in duplicate at all stations. At each station, 26 bottles were filled including control (without nutrients addition) bottles. To these bottles, nutrients ($NaNO_3$ and NaH_2PO_4) were added in different N:P ratios (5:1, 10:1, 16:1, and 20:1) with three varying concentrations [low concentrations (LC), medium concentrations (MC), and high concentrations (HC)] along with ^{13}C (2 mL of 0.2 M $NaH^{13}CO_3$) and ^{15}N (2 mL of $^{15}N_2$ gas) tracers to observe the effect of stoichiometry (N:P) on PP and N_2 fixation rates (Table 3.3; Fig. 3.8). The analysis of PP and N_2 fixation rates were similar to the one discussed in Section 3.2.1 and Chapter 2.

Table 3.3 Concentrations of nutrients added for stoichiometric experiments for PP and N_2 fixation to achieve the desired ratios. LC, MC, and HC stand for low concentrations, medium concentrations, and high concentrations, respectively.

Incubation No.	Experiments (N:P)	Amended Concentrations ($NaNO_3 + NaH_2PO_4$) µM
1	Control	No amendment
2	5:1 (LC)	0.05 + 0.01 µM
3	5:1 (MC)	1.0 + 0.2 µM
4	5:1 (HC)	12.5 + 2.5 µM
5	10:1 (LC)	0.1 + 0.01 µM
6	10:1 (MC)	2.0 + 0.2 µM
7	10:1 (HC)	25 + 2.5 µM
8	16:1 (LC)	0.16 + 0.01 µM
9	16:1 (MC)	3.2 + 0.2 µM
10	16:1 (HC)	40 + 2.5 µM
11	20:1 (LC)	0.2 + 0.01 µM
12	20:1 (MC)	4.0 + 0.2 µM
13	20:1 (HC)	50 + 2.5 µM

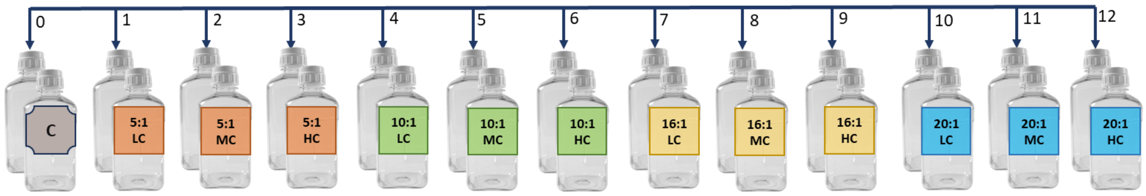


Fig. 3.8 Set up of stoichiometric experiments for primary production and N_2 fixation rate estimation. The ratios are the N:P ratios in the bottles at low concentrations (LC), medium concentrations (MC), and high concentrations (HC). The concentration levels of nutrients (salts) added to achieve the ratios are listed in Table 3.3.

3.3.2 Results

3.3.2.1 Environmental parameters and nutrients

The SST at the studied locations for these experiments did not show much difference in both basins and varied from 28.02 to 29.14 °C. The SSS was 33.15 at the open Bay of Bengal location, 32.11 at the coastal Andaman, and varied from 34.95 to 36.30 at the Arabian Sea locations. The MLD at these locations varied from 7 to 50 m, with the shallowest at the Bay of Bengal location (S4) (Table 3.4).

The concentration of NOx was below detection limit in the open Bay of Bengal (S2) and 0.45 µM in the coastal Andaman (S4). NOx concentrations varied from below detection limit to 0.42 µM at the Arabian Sea locations. The concentrations of PO_4^{3-} varied from 0.31 to 0.36 µM at all experimental locations, except at coastal Andaman (S4), where it was below detection limit. The SiO_4^{4-} concentrations varied from 1.32 to 5.67 µM. The N:P ratio was less than 1.3 at all the stations at the beginning of the experiment (Table 3.4).

3.3.2.2 Phytoplankton primary production and N_2 fixation rates

The control or unamended results are reported as natural PP and N_2 fixation rates. Surface PP and N_2 fixation rates were 0.71 ± 0.16 µM C d^{-1} and 0.31 ± 0.05 nM N d^{-1}, respectively, at the open Bay of Bengal (S2) location. In the coastal Andaman (S4), the PP was 0.10 ± 0.01 µM C d^{-1} and N_2 fixation rate was 0.15 nM N d^{-1}. The measured PP and N_2 fixation rates at the Arabian Sea locations varied from 0.24 ± 0.07 to 0.39 ± 0.03 µM C d^{-1} and 0.03 ± 0.01 to 0.23 ± 0.07 nM N d^{-1}, respectively (Fig. 3.9 and Table 3.4).

Table 3.4 Details of sampling locations, physical parameters [sea surface temperature (SST), sea surface salinity (SSS), mixed layer depth (MLD)] and nutrient concentrations [NOx = nitrate + nitrite, phosphate (PO_4^{3-}), silicate (SiO_4^{4-})] at locations where stoichiometric experiments were performed. Primary production (PP) and N_2 fixation rates (NFR) in unamended (control) bottles at these locations are also shown. BD stands for below detection limit.

Cruise Id	**Date (2021)**	**Sample Id**	**Latitude (°N)**	**Longitude (°E)**	**SST (°C)**	**SSS**	**MLD (m)**	**NOx (µM)**	**PO_4^{3-} (µM)**	**N:P**	**SiO_4^{4-} (µM)**	**PP (µM C d^{-1})**	**NFR (nM N d^{-1})**
SK373	26-Sep	S2	13.0078	84.7396	29.14	33.15	8	BD	0.31	-	3.55	0.71 ± 0.16	0.31 ± 0.05
SK373	30-Sep	S4	13.867	92.6351	28.82	32.11	7	0.45	BD	-	5.67	0.10 ± 0.01	0.15
SK374	05-Nov	L2	8.322	74.0176	28.93	34.95	11	BD	0.36	-	1.32	0.24 ± 0.07	0.12 ± 0.03
SK374	10-Nov	L5	4.0017	68.02	28.85	35.94	50	0.42	0.32	1.31	1.96	0.39 ± 0.03	0.03 ± 0.01
SK374	17-Nov	L10	16.0001	67.9932	28.02	36.3	43	0.32	0.35	0.91	3.27	0.32 ± 0.10	0.23 ± 0.07

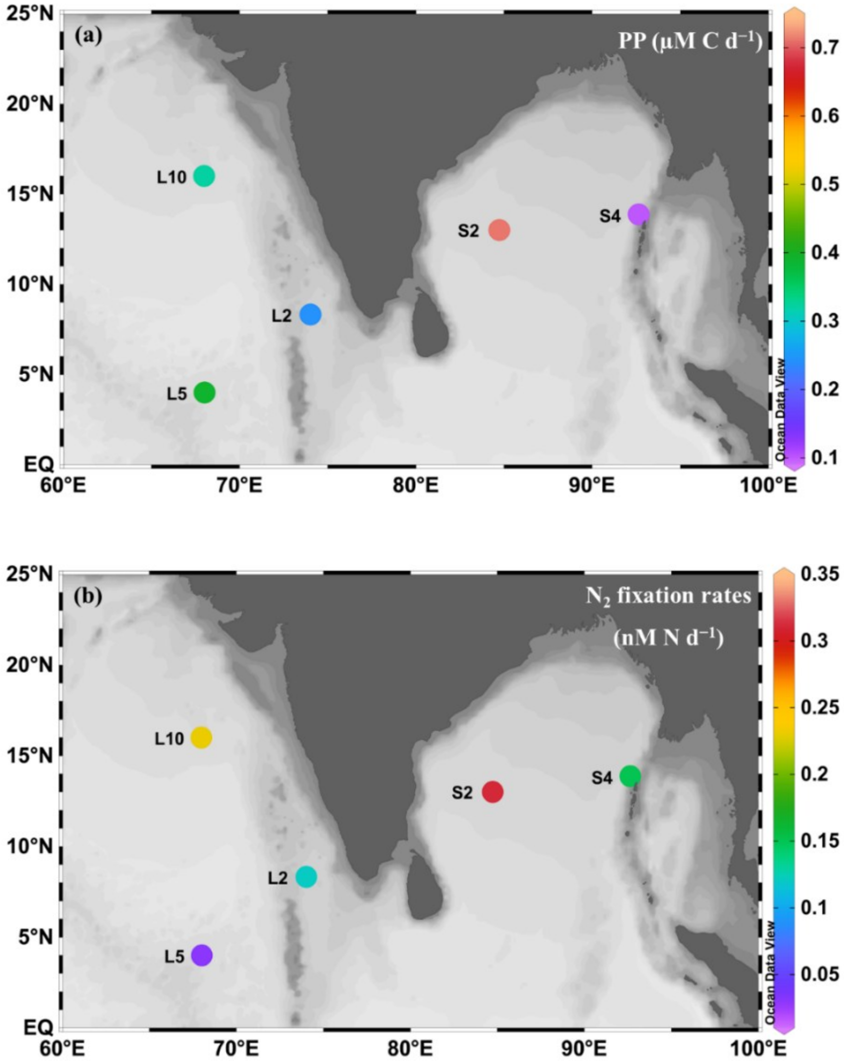


Fig. 3.9 Sampling locations with (a) primary production (PP) (μM C d^{-1}) and (b) N_2 fixation rates (nM N d^{-1}) in the control bottles.

3.3.2.3 Stoichiometric experiments for primary production and N_2 fixation

The Bay of Bengal

In the open Bay of Bengal (S2), except for 5:1 ratio at low and high concentrations, increase in PP was observed for all experiments with changing N:P ratios and concentrations (Fig. 3.10a). Interestingly, increase in PP for 16:1 was similar at all concentrations. Similar increase in PP as observed for 16:1 was also noticed for 10:1 (LC and MC). The highest increase in PP was observed for 5:1 at medium concentration (Fig. 3.10a). N_2 fixation decreased throughout all the experiments, except for small increases for 20:1 at medium concentration (Fig. 3.10b).

In the coastal Andaman (S4), except for 5:1 at low concentration, PP increased in all the combinations of N:P ratio, which was similar to the open Bay of Bengal (Fig. 3.10c).

Except for similarity in PP for 16:1 (MC) and 16:1 (HC), no consistency in PP was observed due to changing N:P or concentrations. N_2 fixation decreased in all experiments except 10:1 (MC) and 20:1 (MC) (Fig. 3.10d).

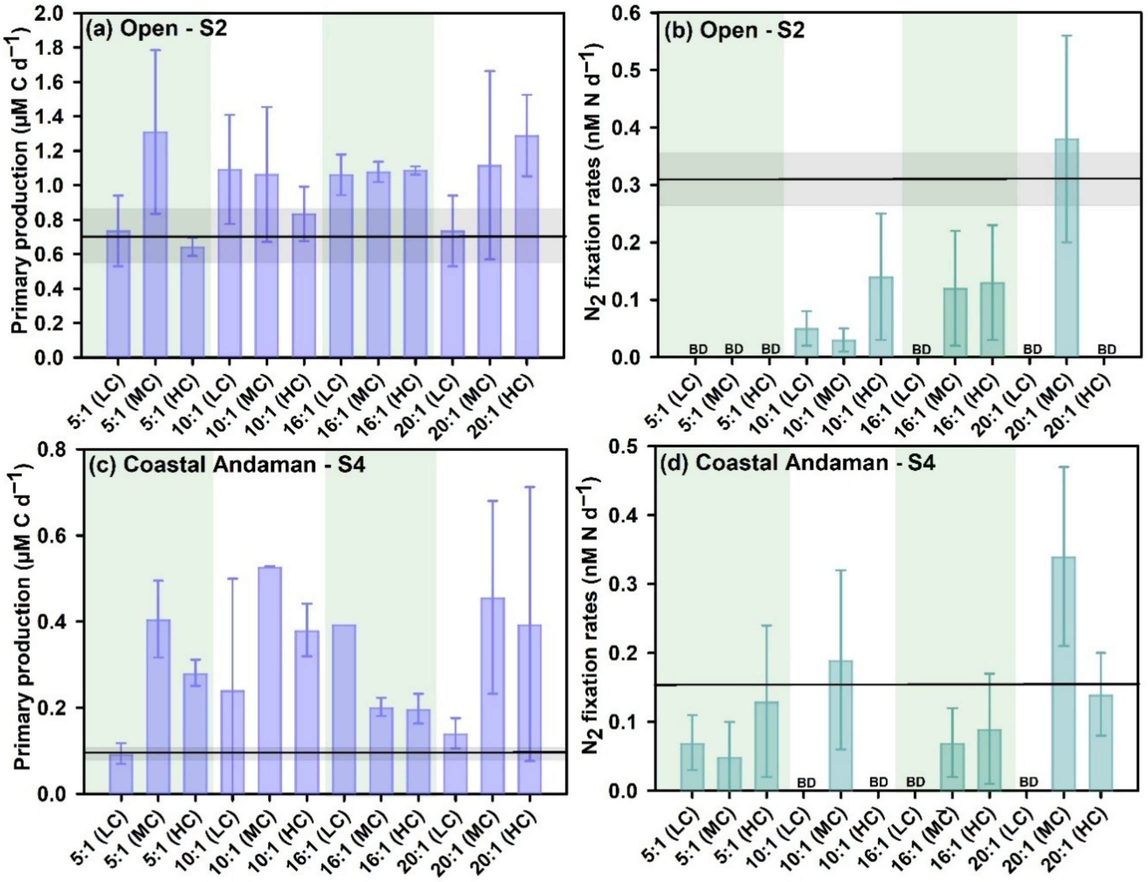


Fig. 3.10 Response of primary production (PP) and N_2 fixation rates to stoichiometric experiments. Error bars represent the standard deviation of duplicates (n = 2). The black line and associated grey horizontal bar represent the mean and standard deviation of control PP and N_2 fixation rates, respectively. Note the difference in the scale of the y-axes. LC, MC, and HC represent low, medium, and high concentrations, respectively. BD stands for below detection limit.

The Arabian Sea

In the southeastern Arabian Sea (L2), PP increased after the addition of different combinations of N:P ratios with varying concentrations, except for 10:1 (MC) and 16:1 (HC). The maximum increase was observed for 20:1 at medium concentrations (Fig. 3.11a). A decrease in N_2 fixation was observed in all experiments at this location (Fig. 3.11b). In the southern Arabian Sea (L5), PP increased in all the experiments (Fig. 3.11c). For 5:1 and 20:1 ratios, enhancement in PP was observed with increasing concentrations (LC < MC < HC). However, the opposite was observed for 16:1 (LC > MC > HC). Except for 10:1 (MC), N_2 fixation rates were below detection limit in all the experiments at this location (Fig.

3.11d). In the northern Arabian Sea (L10), the increase in PP was almost similar for all additions except for 10:1 (LC) and 20:1 (HC), which showed a relatively lower increase (Fig 3.11e). Similar to other stations, decrease in N_2 fixation was observed at this location as well (Fig. 3.11f).

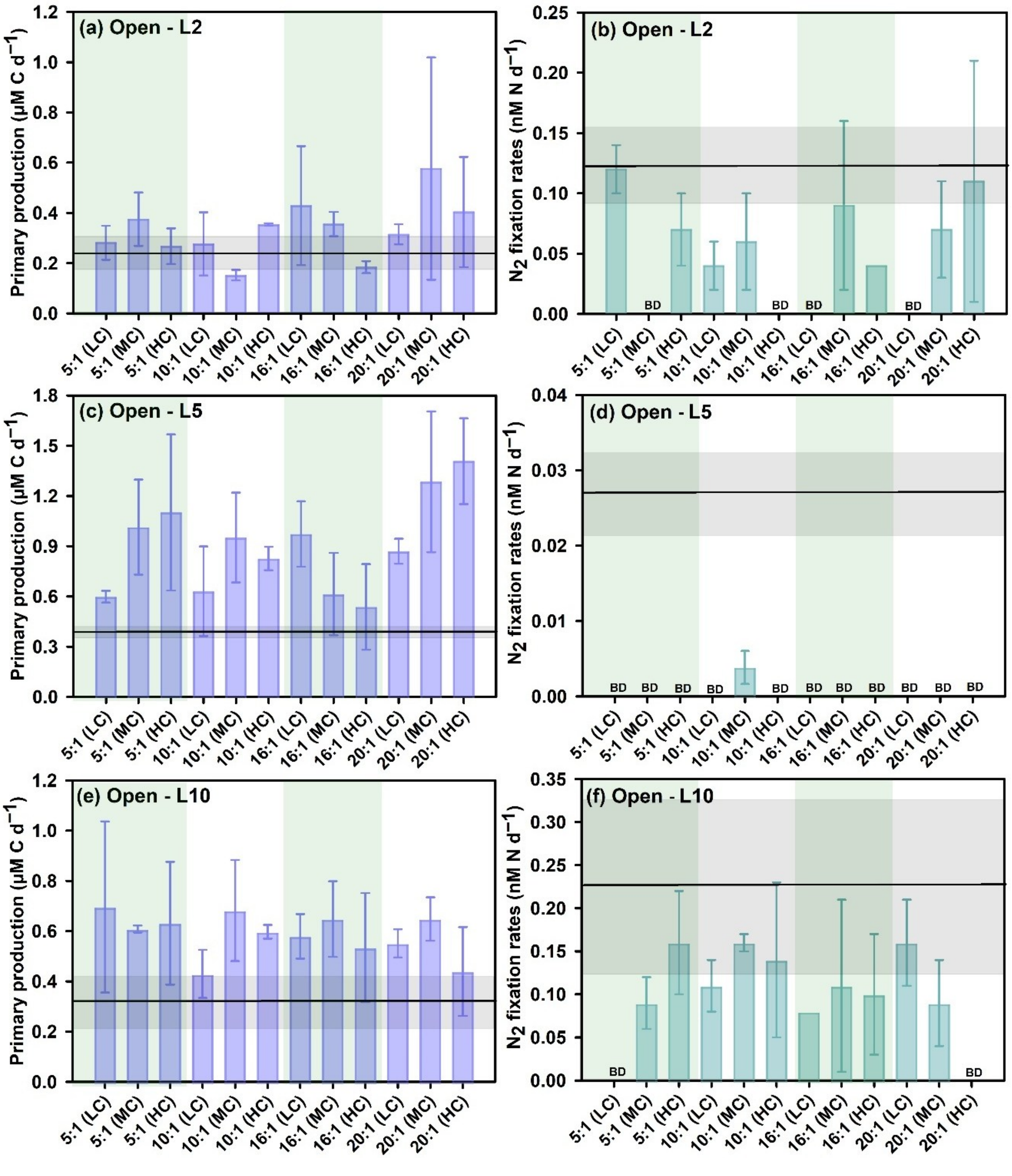


Fig. 3.11 Response of primary production (PP) and N_2 fixation rates to stoichiometric experiments in the Arabian Sea. Error bars represent the standard deviation of duplicates (n = 2). The black line and associated grey horizontal bar represent the mean and standard deviation of control PP and N_2 fixation rates, respectively. Note the difference in the scale of the y-axes. LC, MC, and HC represent low, medium, and high concentrations. BD stands for below detection limit.

3.3.3 Discussion

Despite the importance of the northern Indian Ocean in the carbon and nitrogen budget, it is still not understood how stoichiometric variations impact the PP and N_2 fixation rates. This study was aimed to decipher the effect of stoichiometric (N:P) ratio with varying concentrations on the PP and N_2 fixation in the northern Indian Ocean during the fall inter-monsoon.

In general, the ambient dissolved inorganic N:P ratio was quite low at the five studied locations, with three of them having either N or P levels below detection limit (Table 3.4). There was no specific trend in PP due to different N:P ratios or varying concentrations, however, some results were noticeable. PP increased with respect to control in most experiments after the nutrient addition, whereas no increase was observed in N_2 fixation rates (Figs. 3.10 and 3.11). These results indicate the ability of phytoplankton species to respond rapidly to the supply of nutrients. As in the enrichment experiment discussed earlier, increase in PP due to nutrient addition showed N limitation at these locations, also reported by other studies in the northern Indian Ocean (Takeda et al., 1995; Twining et al., 2019). Interestingly, any modulation in the N:P ratio at low, medium, or high concentrations did not yield considerably different increase in PP with respect to control, which indicated a threshold of nutrients for phytoplankton (Ye et al., 2021; Kwon et al., 2022). Czerny et al. (2016) observed an increase in Chl a with high N than those with low N experiments and reported that phytoplankton biomass is affected by N supply, not by N:P ratio. However, the results of the present study did not indicate such clear observation in the northern Indian Ocean. In this study, no considerable increase in PP was noted when N concentrations were increased while keeping P constant as observed for a particular concentration (LC or MC or HC) at different N:P ratios (Table 3.3; Figs. 3.10 and 3.11). Also, despite a wide range of nutrient concentrations added, PP did not increase in the same proportions. These results point to the fact that phytoplankton starts taking up the nutrients immediately after the addition and once a threshold concentration is reached, which may be the case with the lowest concentration additions in this study, further increase in nutrients or manipulations in stoichiometry does not lead to the proportional increase in assimilation. Contrary to the present study, Franz et al. (2012) and Hauss et al. (2012) conducted a mesocosm experiment off the coast of Perú, with N:P ratio ranging from 2.5 to 16, and reported that phytoplankton biomass was correlated with N addition levels in N depleted conditions. They also observed a positive correlation between the particulate organic N:P ratio and the inorganic N:P ratio.

No pattern in the observed PP and N_2 fixation rates due to concentration and stoichiometric manipulation might also be due to the presence of different species of phytoplankton at different locations which can have distinct nutrient requirements (Spilling et al., 2019; Neri et al., 2023). The cellular characteristics of organisms might have different nutrient requirements leading to different impacts of stoichiometry and concentrations on PP. Although no pattern was observed in this study, some studies from other oceanic basins state a different story. Experiments conducted by Franz et al. (2012) in the eastern tropical North Pacific suggest that while phytoplankton stoichiometry can be somewhat flexible, it doesn't always match variations seen in lab experiments (Hecky et al., 1993) or those predicted by theoretical models (Klausmeier et al., 2004). They have reported that lower biomass accumulation at a lower N:P ratio is due to the availability of N in their experiments. Meyer et al. (2016) conducted a mesocosm experiment to observe the effect of changing N:P ratio (2.67–48) on the PP and N_2 fixation in the eastern tropical North Atlantic and observed N limitation on PP as observed in this study. They further reported that N_2 fixers utilized dissolved organic phosphate in low inorganic PO_4^{3-} conditions and a change in N:P ratio might lead to a shift in the community composition which can influence PP and carbon export. Wan et al. (2011) reported that a non-Redfield N:P ratio (10:1) works better than the Redfield in the Baltic Sea and a change in N:P ratio from 16:1 to 10:1 to 6:1 causes the model results to move closer to Chl a observed value.

A mesocosm experiment was carried out in the northern Adriatic Sea, which received large nutrient loads, to examine the impact of the N:P ratio on PP and suggested P limitation, but only if N additions were high (Granéli et al., 1999). Contrary to the present study, Spackeen et al. (2018) observed a significant increase in DIC uptake rates with an increase in N:P ratio, which could not be enhanced at a very low N:P ratio (2:1). Depending on ecological conditions, a stoichiometric modelling study suggested optimal range for N:P ratios to be 8.2-45 for phytoplankton (Klausmeier et al., 2004). In comparison to the typical load in the Bay of Blanes, average picophytoplankton PP tended to rise with both excess N (at a N:P of 160) and slightly excess P (at a N:P of 10) (Agawin et al., 2004). Spilling et al. (2019) reported high Chl a fluorescence in N:P (10:1) compared to (5:1) and suggested N-limitation for the phytoplankton community.

N_2 fixation rates in this study were measurable in the control treatments suggesting that the northern Indian Ocean has a diazotroph niche (Fig. 3.9b). In all the stoichiometric experiments conducted in this study, the N_2 fixation rates decreased in almost all treatments at every station possibly indicating the effect of N addition, which might have decreased the ability of diazotrophs to fix N_2 (Figs. 3.10 and 3.11). Diazotrophs are thought to be less advantageous than non-diazotrophs, which grow more quickly in an N-replete environment (Tyrrell, 1999; Ward et al., 2013). The N limitation indicated that because diazotrophs can develop without a fixed N source, they have an advantage over their competitors in N depleted conditions. Laboratory culture experiments reported that N compounds do not repress N_2 fixation always (Holl & Montoya, 2005; Dekaezemacker & Bonnet, 2011). N_2 fixation has also been reported in nutrient-rich waters of the Pacific and Atlantic Oceans (Subramaniam et al., 2013; Loescher et al., 2014). Moreover, preferential uptake of dissolved N may cause N_2 fixation to be down-regulated even in the presence of diazotrophs (Holl and Montoya, 2005). Several studies have examined the impact of reduced N:P ratio on diazotrophs and the majority of these investigations show that N_2 fixation is unaffected, at least in the short term (Wasmund et al., 2015); however, in this study clear decrease in N_2 fixation rates due to stoichiometric manipulations were observed.

3.3.4 Conclusion

This study was conducted to understand the effect of changes in nutrient concentrations and varying stoichiometry (N:P) on PP and N_2 fixation in the northern Indian Ocean. Increase in PP in all the experiments suggested N limitation in the region, whereas decreased N_2 fixation indicated suppression due to N addition and stoichiometric manipulations. Contrary to some studies in other oceanic basins, no consistent pattern in PP due to increase in nutrient concentrations or stoichiometry was observed. It may be due to the inability of the phytoplankton to take up excess nutrients once their threshold requirement is reached. This inconsistent PP observed across the northern Indian Ocean may also be due to differences in phytoplankton community structure and their metabolic requirements.

Chapter 4

Lacustrine Ecosystems

Lakes play a significant role in the global carbon and nitrogen cycles, acting as both sinks and sources of these elements, making them a primary focus of current aquatic studies. Despite covering only a small area (2.2 %) of the land surface and once being considered temporary reservoirs for materials, studies have revealed that lakes are hotspots for intense carbon and nitrogen processing (Tranvik et al., 2009; Wang et al., 2021). Most studies on lacustrine ecosystems have focused on large and deep lakes, often neglecting small and shallow lakes, which cover a significant portion (one-third) of inland waters (Wetzel, 2001; Downing et al., 2006). Carbon burial in lakes reaches up to ~ 25–58 % of the annual burial in oceans (Dean & Gorham, 1998; Cole et al., 2007), and as sources, they emit ~ 140 Tg of CO_2 yr^{-1}, nearly half of the carbon transported to the ocean by rivers annually (Cole et al., 1994). The carbon and nitrogen biogeochemical cycles in lakes are tightly coupled through processes such as PP, N_2 fixation, nutrient assimilation, and degradation of OM. These processes are affected by several factors such as light intensity, temperature, grazing by zooplankton, nutrient availability, land use, and lake morphology (Likens, 1973; Peng et al., 2021). While some phytoplankton can directly assimilate nitrogen through N_2 fixation, others assimilate nitrogen that originates from land, and regenerate NH_4^+ to enhance PP and transfer of carbon (Harrison, 1978; Vitousek & Howarth, 1991). Climate change (i.e., precipitation and temperature) and anthropogenic influences (e.g., water diversion and construction) impact water levels in lakes, which in turn can alter the physical environment, nutrient concentrations, and phytoplankton composition and biomass (Hofmann et al., 2008; Adrian et al., 2009). These changes ultimately affect carbon and nitrogen assimilation rates in lacustrine ecosystems. For the functioning and services of aquatic ecosystems, regional investigations of these rates are increasingly vital for water resources (Hanson et al., 2015).

In this chapter, some of the important processes of carbon and nitrogen biogeochemical cycles such as PP, N_2 fixation, and nutrients (nitrogenous nutrients such as NH_4^+, NO_3^-, and NO_2^-) assimilation rates have been explored in the three different lacustrine ecosystems, which comprise a freshwater closed basin lake, a lake in transition from freshwater to saline, and a saline lake with different classes of variable salinity. These three lacustrine ecosystems are recognized as wetlands of international importance (Ramsar sites) and home to various migratory birds that use them as nesting and breeding grounds (Karia, 2012; Solanki & Sharma, 2021). Given the increasing number of shallow and small freshwater lakes under consideration, the first section explores the effect of changes in the lake water volume and environmental parameters on the carbon and nitrogen assimilation rates in a closed basin freshwater lake. The second section of the chapter focuses on a natural freshwater open basin lake, which shifts into a saline lake as the evaporation exceeds precipitation during summer. Freshwater salinization and regime shift (macrophytes to phytoplankton domination) is a major crisis due to natural perturbations (such as temperature increase or shift in precipitation pattern) and human interventions (like water withdrawal or nutrients used for agriculture). In this section, the effect of freshwater salinization with changes in water level on the carbon and nitrogen assimilation rates has been discussed. The third section focuses on a saline lake and associated water bodies, where the effect of salinity on the carbon and nitrogen biogeochemical processes has been discussed. Saline lakes (salinity > 3 g L^{-1}) are an important part of inland water bodies and have the same volume (85,400 km^3) as freshwater lakes (91,000 km^3) (Williams, 1993a). These lakes are mostly found in the arid and semi-arid regions of the world, where hydrological imbalance (evaporation exceeds precipitation) triggers salt accumulation ("Hydrogeologic processes in saline systems," 2002). These lakes have been largely overlooked from a biogeochemical perspective, and most studies carried out focused on the microbial diversity in these saline ecosystems.

4.1 Carbon and nitrogen assimilation rates in a closed basin shallow freshwater lake

Freshwater lakes contain < 1% of global water volume and provide tremendous services of social and economic value such as regulation of floods, clean water, and sustainability (Herdendorf, 1982; Meerhoff & González-Sagrario, 2021). Among freshwater lakes, small shallow lakes harbour abundant biodiversity and cover as much area as deep lakes but remain unexplored despite having very active carbon and nitrogen biogeochemical cycles (Downing et al., 2006; Scheffer et al., 2006). Shallow lakes, due to their frequent mixing and sediment resuspension, differ functionally from deep lakes (Padisak & Reynolds, 2003). Carbon assimilation or PP, OM sequestrations, nutrient processing, and greenhouse gas concentrations are much different in shallow small lakes than in large ones, as these small bodies are heterotrophic and process more carbon and nitrogen (Kelly et al., 2001; Post, 2002; Downing, 2008; Müller et al., 2021). PP forms the basis of energy flow in an aquatic ecosystem and requires nitrogen which can be obtained from catchment runoff or supplied through the N_2 fixation (Vitousek & Howarth, 1991). The specific conditions for N_2 fixation in aquatic ecosystems, especially in closed shallow basins, are still debatable (Howarth et al., 1988; Marcarelli et al., 2022), and it is assumed that this process does not occur in high DIN conditions (Tõnno & Nõges, 2003). However, other studies reported that low DIN does not consistently stimulate the growth of N_2 fixers (Dolman et al., 2012; Gobler et al., 2016), suggesting the role of other variables. Climate change and anthropogenic factors are also affecting the capacity of these lakes to store carbon and nitrogen and release them into the atmosphere. Droughts, floods, and storms are occurring more frequently due to global climate change, which eventually influences the lake water quality, habitat, and biogeochemical processes occurring inside lakes by abrupt changes in water levels and nutrient concentrations especially in tropical areas (Havens et al., 2016). Furthermore, anthropogenic factors like water diversion, extraction, land use, and land cover also impact these processes.

In recent decades, an increasing number of studies have investigated the ecological and socio-economic effects of fluctuating water levels on lacustrine ecosystems and reservoirs (Usmanova, 2003; Wantzen et al., 2008). However, the impact of water level changes, temperature, and salinity on biogeochemical processes such as PP, N_2 fixation, and nitrogen assimilation in small shallow lakes is not well understood. There is a significant amount of literature available on PP in temperate lakes (Nõges & Kangro, 2005; Blindow et al., 2006); however, there are fewer studies on PP in tropical lakes. Most of the tropical lake studies have been conducted in African lakes and Brazilian freshwater reservoirs (Robarts, 1984; Petrucio & Barbosa, 2004; Nishimura et al., 2008), with almost no study in the Indian subcontinent. Therefore, given the significance of carbon and nitrogen related processes in shallow tropical lakes in other regions, it is crucial to understand them in the Indian setting as well. The current study investigates how seasonal changes affect PP along with N_2 fixation, NH_4^+, and NO_2^- assimilation rates in a shallow tropical lake (Thol Lake, India).

4.1.1 Study Area

Thol (23°22.50′N and 72°37.50′E), a man-made shallow freshwater lake, is located in the Indian state of Gujarat (Fig. 4.1). It is a confined basin surrounded by grasslands and marshes. Covering a total area of 6.99 km^2, the lake is found in a semi-arid region with an average annual precipitation of around 600 mm (Vyas & Dabgar, 2012). It experiences fluctuations in water level seasonally, including a decline in summer due to evaporation and a rise during monsoon from precipitation and runoff (Desai et al., 2018). Originally built for irrigation needs and to mitigate flooding and erosion by storing rainwater, this lake was recognized for its significance as a habitat and resting site for migratory avifauna, leading to its designation as a bird sanctuary in 1988 and listed as a 'Ramsar site'. A part of this sanctuary is utilized by local communities for agricultural lands, potentially causing harm to the bird's habitat (Karia, 2012).

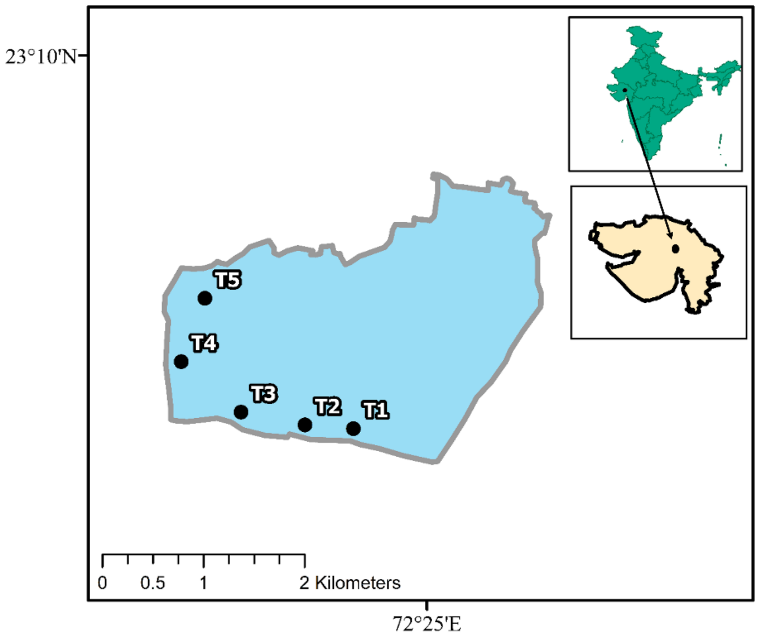


Fig. 4.1 Study area and sampling locations in the Thol Lake (black circles). The sampling was restricted to the region where water is deeper and normally available throughout the year.

4.1.2 Sampling

Water samples from the Thol Lake were collected during summer (May 2022) and monsoon (September 2022) at five locations in both seasons to address the above objectives (Fig 4.1). The water depth was lower in the summer compared to monsoon. Large numbers of migratory birds were observed in the lake during summer (Fig. 4.2). Detailed descriptions of the water sampling protocols for different parameters along with carbon and nitrogen assimilation rates measurements are already described in Chapter 2.

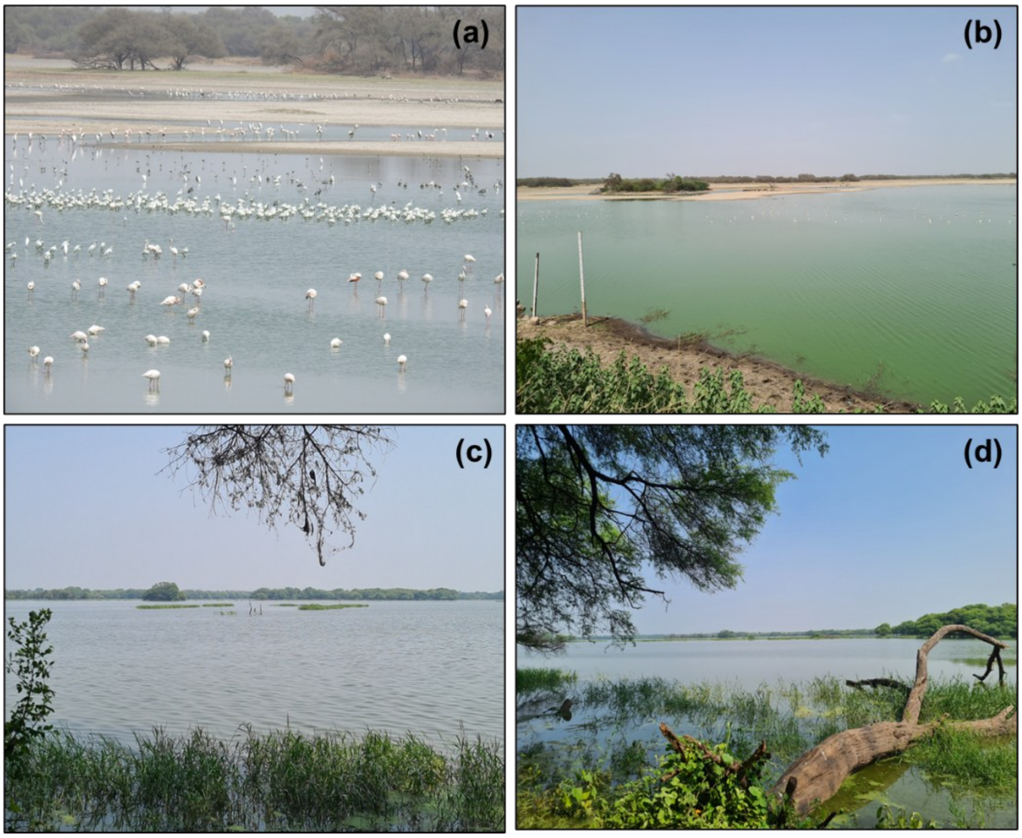


Fig. 4.2 Field photographs of the Thol Lake during summer (a and b) and monsoon (c and d).

4.1.3 Results

4.1.3.1 Environmental parameters

Significant seasonal variation was observed in the environmental parameters of the Thol Lake water. Surface water temperature decreased from summer (mean ± stdev = 37.32 ± 1.02 °C) to monsoon (33.46 ± 0.44 °C) (Fig. 4.3a). EC was four-fold higher during summer (4.22 ± 0.24 mS cm^{-1}) than monsoon (1.10 ± 0.02 mS cm^{-1}) (Fig. 4.3b). A decrease in pH was noticed from summer (9.56 ± 0.15) to monsoon (9.36 ± 0.10) (Fig. 4.3c). Although oxygenated throughout, DO concentrations were higher during summer (18.31 ± 0.96 mg L^{-1}) than monsoon (10.68 ± 1.65 mg L^{-1}) (Fig. 4.3d).

4.1.3.2 Dissolved inorganic carbon and nutrients cycling

Dissolved inorganic carbon concentration decreased along with $\delta^{13}C_{DIC}$ from summer (DIC = 6.15 ± 0.51 mM and $\delta^{13}C_{DIC}$ = 4.74 ± 0.21 ‰) to monsoon (DIC = 3.56 ± 0.69 mM and

$\delta^{13}C_{DIC}$ = −1.49 ± 0.27 ‰) (Fig. 4.4a). Dissolved CO_2 concentration increased from summer (56.12 ± 63.36 μM) to monsoon (440.72 ± 198.79 μM) (Fig. 4.4b).

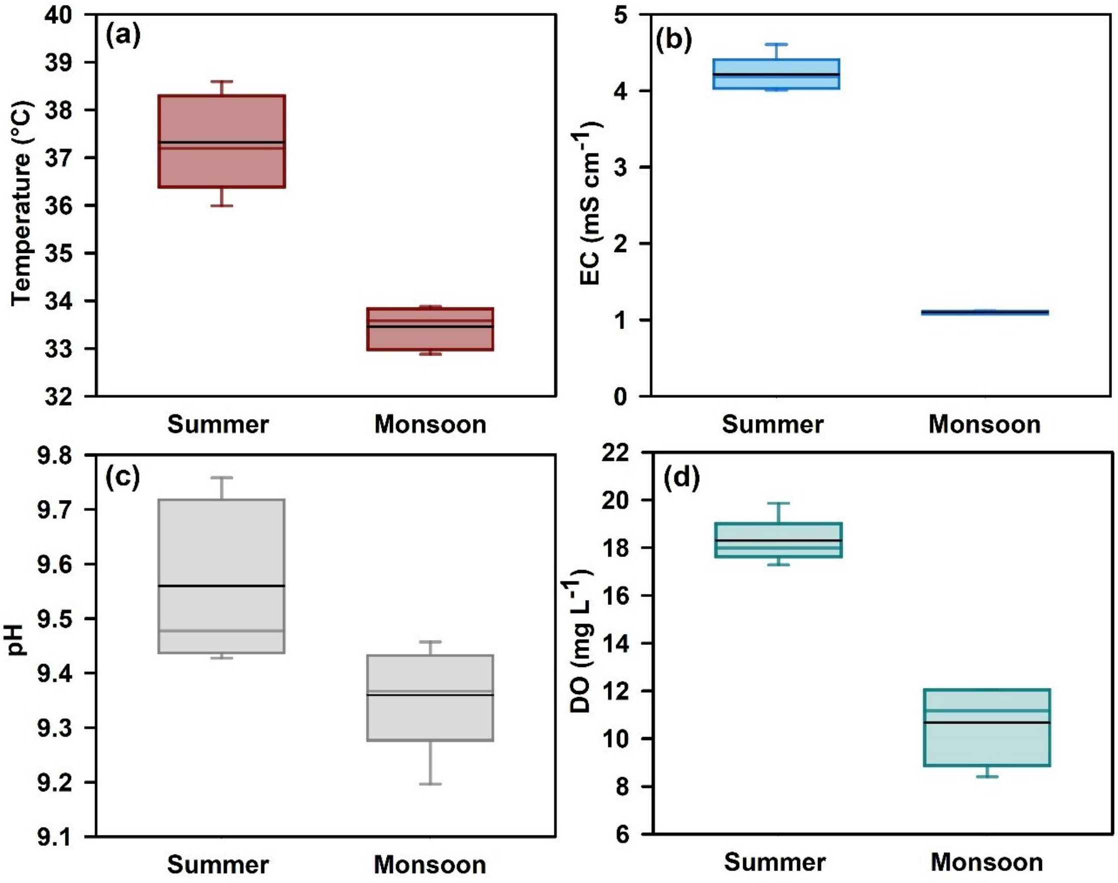


Fig. 4.3 Box whisker plots of (a) temperature, (b) EC, (c) pH, and (d) DO, showing seasonal variation in these environmental parameters of the surface waters of the Thol Lake. The black lines within the box represent the mean values.

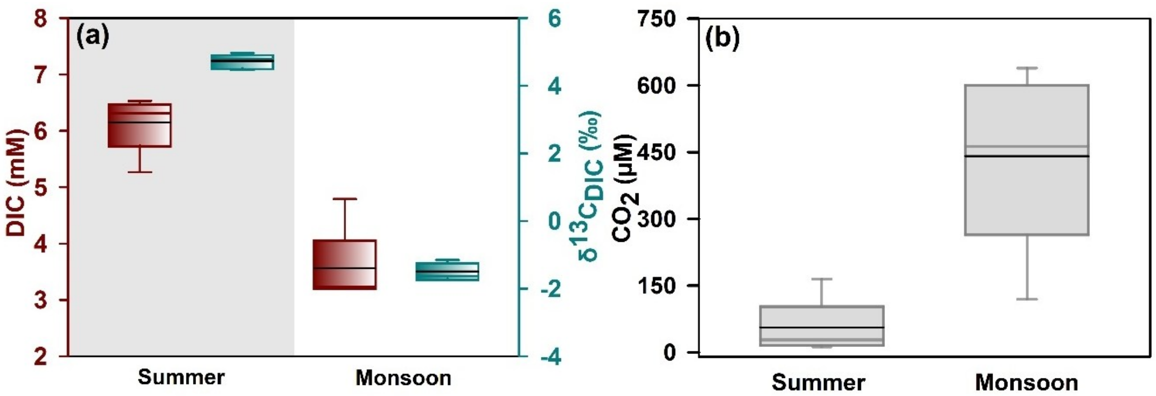


Fig. 4.4 Seasonal variation in (a) concentrations of DIC (reddish) and $\delta^{13}C_{DIC}$ (greenish) and (b) concentrations of CO_2. The black lines within the box represent the mean values.

Dissolved inorganic nitrogen decreased several folds from summer to monsoon, where concentration of NH_4^+ decreased from 18.00 ± 5.79 μM to 2.23 ± 0.09 μM (Fig.

4.5a). There was no significant difference in the NOx concentrations between summer (1.10 ± 0.78 μM) and monsoon (0.83 ± 0.40 μM) (Fig. 4.5a). PO_4^{3-} and SiO_4^{4-} concentrations increased from summer (PO_4^{3-} = 2.39 ± 1.29 μM and SiO_4^{4-} = 153.68 ± 24.11 μM) to monsoon (PO_4^{3-} = 20.50 ± 2.57 μM and SiO_4^{4-} = 188.70 ± 3.76 μM) (Figs. 4.5b and c). The N:P (DIN:DIP) ratio decreased significantly from summer (10.74 ± 7.15) to monsoon (0.15 ± 0.02) (Fig. 4.5d).

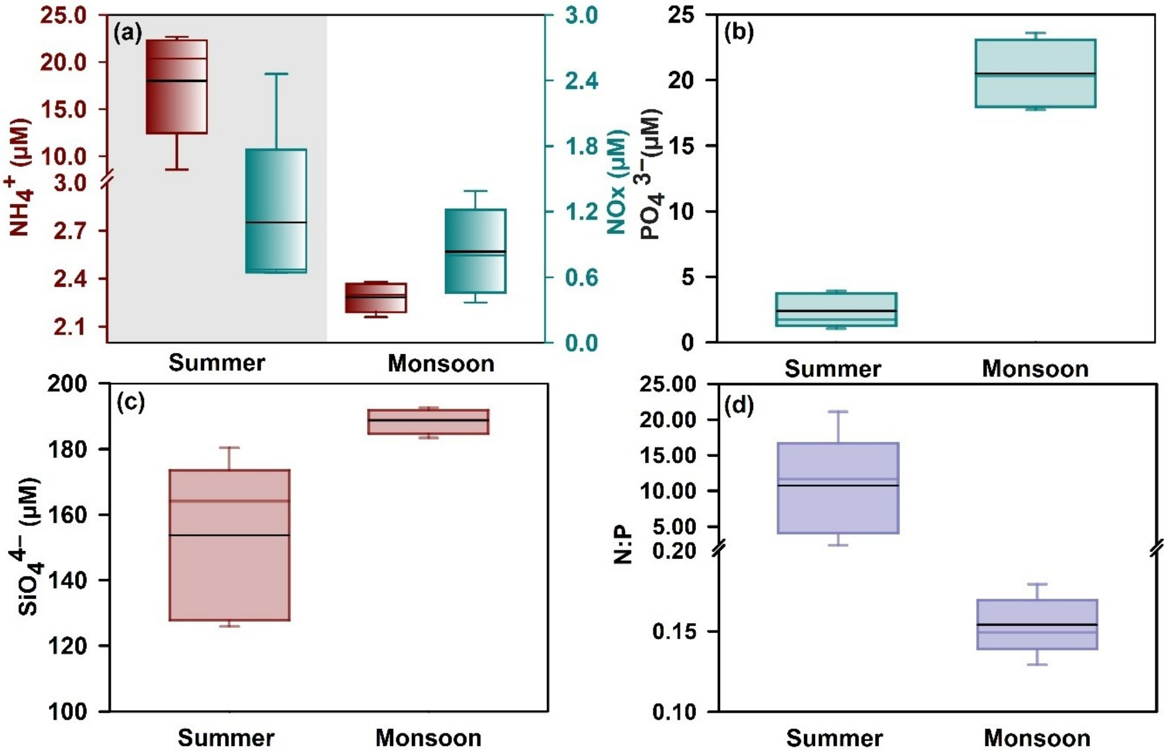


Fig. 4.5 Seasonal variation in concentrations of (a) dissolved inorganic nitrogen (NH_4^+ and NOx), (b) PO_4^{3-}, (c) SiO_4^{4-}, and (d) N:P ratio. The black lines within the box represent the mean values. Note the break in the y-axes in (a and d).

4.1.3.3 Particulate organic matter, primary production, and nitrogen assimilation

The POM concentrations were higher during summer (POC = 4.80 ± 0.25 mM and PON = 0.87 ± 0.13 mM) than monsoon (POC = 0.69 ± 0.06 mM and PON = 0.11 ± 0.01 mM) (Fig. 4.6a). The $\delta^{13}C_{POM}$ decreased from summer (−15.00 ± 0.79 ‰) to monsoon (−23.87 ± 0.71 ‰) in the lake, whereas $\delta^{15}N_{POM}$ showed the opposite trend to increase from summer (6.24 ± 0.36 ‰) to monsoon (12.27 ± 0.27 ‰) (Fig. 4.6b).

On an average, PP in the Thol Lake decreased ~ 4-fold from summer (191.41 ± 37.76 μM C h^{-1}) to monsoon (40.20 ± 8.74 μM C h^{-1}) (Fig. 4.7a). N_2 fixation along with NH_4^+ and NO_2^- assimilation rates were also higher during summer (N_2 fixation rates = 0.30 ± 0.12 μM N h^{-1}, NH_4^+ assimilation rates = 3.36 ± 1.22 μM N h^{-1}, and NO_2^- assimilation rates = 0.16 ± 0.05 μM N h^{-1}) as compared to monsoon (N_2 fixation rates = 0.02 ± 0.01 μM N h^{-1}, NH_4^+ assimilation rates = 0.71 ± 0.08 μM N h^{-1}, and NO_2^- assimilation rates = 0.03 ± 0.01 μM N h^{-1}) (Figs. 4.7b, c, and d). The C:N (POC:PON) ratio was slightly higher during monsoon (6.45 ± 0.48) than in summer (5.56 ± 0.61).

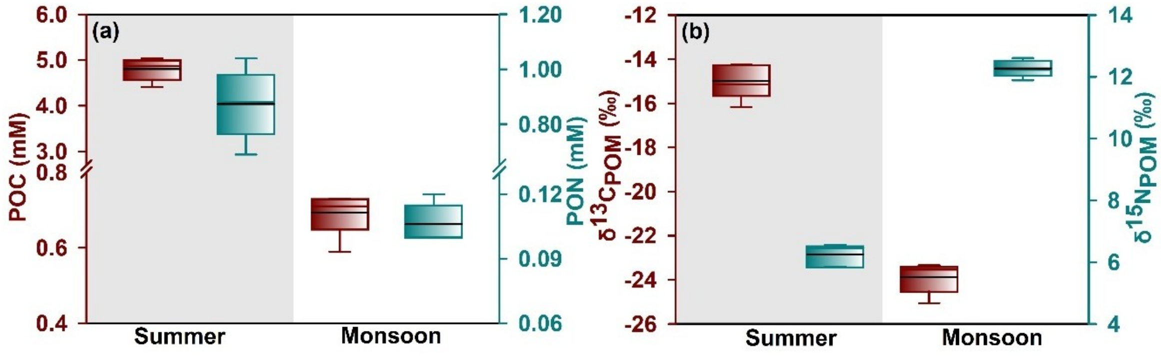


Fig. 4.6 Seasonal variation in (a) concentration and (b) isotopic composition of particulate organic matter [POC (reddish) and PON (greenish)]. The black lines represent the mean values. Note the break in the y-axis in (a).

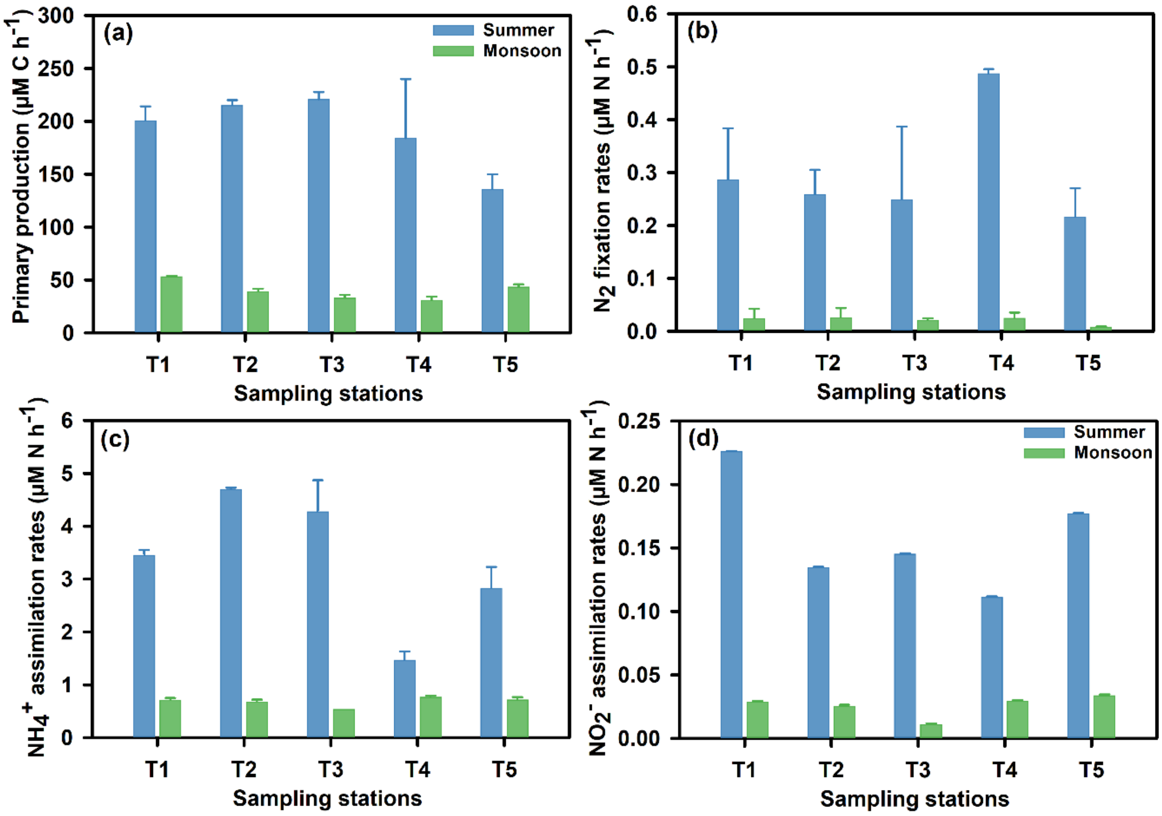


Fig. 4.7 Seasonal variation in the (a) primary production, (b) N_2 fixation rates, (c) NH_4^+ assimilation rates, and (d) NO_2^- assimilation rates in the lake. The error bar represents the standard deviation of duplicate samples.

4.1.4 Discussion

4.1.4.1 Environmental parameters

The surface water temperature was higher during summer due to the shallow water depth, higher solar radiation, and elevated air temperature (Fig. 4.3a). Frequent cloud cover during monsoon reduces incident solar radiation which leads to decreased water temperature in the lake (Chattopadhyay & Banerjee, 2008). The decreased EC from summer to monsoon was due to dilution of ions by the monsoonal precipitation (Fig. 4.3b). The lake remained highly alkaline in both seasons, and the slightly reduced pH during monsoon might be due to changes in CO_2 concentrations in the DIC pool (Fig. 4.3c).

4.1.4.2 Dissolved inorganic carbon and nutrients cycling

Seasonal variation was observed in DIC concentration and $\delta^{13}C_{DIC}$ in the Thol Lake. During summer, reduced lake water volume leads to an increase in DIC concentrations, which might be due to evaporation, sediment resuspension caused by wind activity, or DIC release from pore water at the water-sediment interface (Herczeg, 1987; Song et al., 2013). In contrast, the decreased DIC concentration in the lake during monsoon was due to dilution through precipitation and subsequent runoff from the catchment (Fig. 4.4a). Enhanced pH and increased $\delta^{13}C_{DIC}$ during summer may be due to higher CO_2 outgassing at increased salinity and temperature, as well as higher PP (Figs. 4.3 and 4.4a). It appears that preferential assimilation of ^{12}C during photosynthesis and release of ^{12}C containing CO_2 molecules during outgassing led to the enrichment of ^{13}C in the remaining DIC pool (Herczeg, 1987; Lei et al., 2012). Despite challenges in distinguishing between CO_2 outgassing and PP, the increased biomass (POM) suggests that PP predominantly influenced DIC pool in the lake. Temperature has a significant impact on photosynthetic activities, gas solubility, aquatic metabolism, and PP. As a result, rising temperatures with the increased metabolic activity of phytoplankton cause a drop in CO_2 concentrations during summer (Figs. 4.3a and 4.4b; Engel et al., 2019). Lower $\delta^{13}C_{DIC}$ during monsoon resulted from increased dissolved CO_2 concentration, which might be due to inputs from soil CO_2 via runoff, atmospheric diffusion, aquatic respiration, and the breakdown of external OM (Fig. 4.4; Bade et al., 2004). The observed lower DO concentrations in the lake during monsoon corroborate OM remineralization. A lower $\delta^{13}C_{DIC}$ during monsoon also indicates the influence of land plants from the watershed (Gu et al., 2006). During monsoon, surface water pH declined due to increase in dissolved CO_2 within the DIC pool (summer = 0.88% and monsoon = 12.59%; Fig. 4.3c). The negative correlation between

CO_2 and DO concentrations within the lake further reinforces the inverse relationship between PP and CO_2 concentrations (Sun et al., 2021).

The DIN concentrations decreased from summer to monsoon in the lake showing seasonal fluctuations. The lake water level reduction during summer led to the accumulation of nitrogenous nutrients (NOx and NH_4^+) (Fig. 4.5a). The decrease in DIN concentrations was due to the dilution effect of runoff caused by the higher rainfall during monsoon. Summer water level decline in the lake may change the light and mixing regime, which might foster cyanobacterial blooms and increased nutrient concentrations. A greater number of migratory birds, especially flamingos, were observed in the Thol Lake in summer, and avian overcrowding in a shrinking lake area might have led to guanotrophication (Figs. 4.2a and b). The supply from guano and sediment bioturbation caused by wading and foraging of migratory birds leads to an increase in NH_4^+ concentrations (Dessborn et al., 2016; Batanero et al., 2017), which was observed during this study (Fig. 4.5a). However, no change in NOx concentrations indicated minimal nitrification in the lake (Fig. 4.5a). Studies in saline lakes have reported similar accumulation of NH_4^+ and inhibition of nitrification at high pH as the lake volume reduced (Sarkar et al., 2023). PO_4^{3-} concentration was enhanced during monsoon which was related to inputs from soil erosion and fertilizers from agricultural runoff (Fig. 4.5b; Powers et al., 2016). The higher concentration of SiO_4^{4-} during monsoon was also due to erosion from the catchment area (Fig. 4.5c).

4.1.4.3 Phytoplankton primary production and nitrogen assimilation

The PP decreased from summer to monsoon in the Thol Lake and was higher than reported for most of the freshwater lakes in the world (Fig. 4.7a and Table 4.1). However, similar or higher rates have been reported from some of the hypertrophic lakes in Africa (Table 4.1). The increased PP aligns with higher water temperature, DO, and elevated POM concentrations indicating the correlation between productivity and DO during summer (Figs. 4.3 and 4.6a). With the temperature rise, there appears to be a boost in the enzymatic activity related to photosynthesis, resulting in enhanced growth, metabolism, and rates of carbon and nitrogen assimilation in this closed basin (Cha et al., 2017). Increased nutrient concentrations and light intensity during summer also enhanced PP, which is important for photosynthesis by phytoplankton (Philips et al., 1997). A surge in DO with increased biomass, observed here, has also been reported in other study, where phytoplankton consume inorganic carbon and release O_2 during photosynthesis (Fig. 4.3d; Hilaluddin et al., 2020).

The $\delta^{13}C_{POM}$ showed seasonal variation and was positively correlated with PP, DIC, and $\delta^{13}C_{DIC}$ and negatively with CO_2 concentrations (Figs. 4.6b, 4.7a, and 4.4). The apparent carbon-isotope partitioning ($\Delta\delta^{13}C_{DIC\text{-}POM} \approx \varepsilon_{app} = [(\delta^{13}C_{DIC} + 1000) / (\delta^{13}C_{POM} + 1000) - 1] \times 10^3$; Farquhar et al., 1989) between inorganic and organic carbon pools during summer was around 20.0 ‰. It is likely that enhanced PP under low CO_2 conditions during summer led to reduced ε_{app} due to rise in carbon demand by phytoplankton causing higher $\delta^{13}C_{POM}$ (Lehmann et al., 2004). Previous findings indicated a positive correlation between $\delta^{13}C_{POM}$ with phytoplankton growth rate (Zohary et al., 1994; Gu et al., 2006). In aquatic ecosystems, where HCO_3^- dominates (pH range from 6.35 to 10.33), some species of phytoplankton can rely on HCO_3^- as a carbon source during higher growth rates and showed increased $\delta^{13}C_{POM}$ (Mook et al., 1974); however, PP also depends on CO_2 (Alling et al., 2012). A similar correlation between POM and DIC was also reported from a desiccating hypersaline lake situated in northwestern India (Sarkar et al., 2023). Gu et al. (2006) reported $\delta^{13}C_{POM}$ to be related to phytoplankton production in the surface waters of a eutrophic subtropical lake based on a strong correlation between $\delta^{13}C_{POM}$ and biomass. Several studies reported a positive correlation between $\delta^{13}C_{POM}$ and $\delta^{13}C_{DIC}$ and suggested ^{13}C enrichment in POM due to enhanced PP (Zohary et al., 1994; Gu et al., 2006).

During monsoon, heavy precipitation and runoff from the catchment area increased the lake water level and affected PP in the lake along with DIC and POM concentrations and their isotopic compositions (Figs 4.7a, 4.4a, and 4.6). Lower light intensity and water temperature because of cloud cover might result in decreased PP during monsoon (Philips et al., 1997). This decline in PP also led to decreased DO concentrations, which was due to reduced metabolic activity caused by the lower temperature (Figs. 4.3 and 4.7a). During monsoon, turbidity was visibly high due to increased concentration of suspended sediment through soil erosion in the catchment, which along with water turbulence, can also negatively impact PP by influencing light intensity, phytoplankton biomass, and communities (Philips et al., 1997; Díaz-Torres et al., 2021). Water turbulence and reduced light intensity resulting from rainfall have been reported to have a detrimental impact on PP in shallow lakes (Feresin et al., 2010). Reduction in PP with relatively higher concentrations of CO_2 and decrease in $\delta^{13}C_{POM}$ were observed in the Thol during monsoon (Figs. 4.7a, 4.4b, and 4.6b). This depletion of ^{13}C in POM can be attributed to an increase

ε_{app} (~ 22.9 ‰) and the utilization of ^{13}C depleted DIC sources (Gu et al., 1994). The decline in PP, caused by a decrease in the euphotic zone due to the supply of allochthonous material because of heavy rainfall, is a common occurrence in Brazilian lakes (Henry et al., 2006; Petrucio et al., 2006). Although an increase in the nutrient concentrations by runoff in the lake has been reported (Wei et al., 2022), our observations revealed a surge in nitrogenous nutrient levels during summer attributed to reduced water volume, which concealed the impact of catchment nutrient input on PP during monsoon in this closed basin (Fig. 4.5a). Díaz-Torres et al. (2021) observed an increase in nutrient inputs in Lake Cajititlán due to runoff, leading to alterations in phytoplankton communities. No data related to phytoplankton community structure was collected during this study, which could be addressed in future.

N_2 fixation rates along with NH_4^+ and NO_2^- assimilation rates decreased from summer to monsoon in the Thol and were within the range reported for freshwater lakes in other parts of the world (Figs. 4.7b, c, and d, respectively, and Table 4.2). Increased NH_4^+ and NO_2^- assimilation rates coincided with enhanced PP during summer in this nutrient-replete lake. It is assumed that N_2 fixation occurs mostly in nitrogen-depleted conditions; however, despite the elevated levels of DIN, higher rates of N_2 fixation were observed in this lake during summer, suggesting a thriving niche for diazotrophs even under DIN enriched conditions. Diazotrophs exhibit a preference for high light intensity due to their need for substantial energy to break the N_2 triple bond and calm water for the formation of colonies or filaments (Reynolds & Walsby, 1975; Havens et al., 1998). Increase in N_2 fixation rates in warmer waters was also reported from Lake Malawi, situated in the tropical region (Gondwe et al., 2008). Various studies conducted in lakes have reported enhanced N_2 fixation in high DIN environments, where diazotrophic cyanobacteria often emerge as the predominant phytoplankton species. However, the overall impact of N_2 fixation appears to be somewhat limited, potentially due to increased DIN assimilation (Ferber et al., 2004; McCarthy et al., 2007).

The $\delta^{15}N_{POM}$ increased from summer to monsoon with decrease in PP and nitrogen assimilation rates (Figs. 4.6b and 4.7). Relatively lower $\delta^{15}N_{POM}$ during summer might be due to relatively higher N_2 fixation and assimilation of ^{15}N depleted DIN by phytoplankton compared to monsoon (Gu & Alexander, 1993). Sarkar et al. (2023) speculated the presence of N_2 fixers in a hypersaline environment during the dry season based on decreased $\delta^{15}N_{POM}$.

Table 4.1 Phytoplankton primary production (μM C h^{-1}) rates in freshwater lakes across the world.

Lake Name	System Type	PP	Method	References
Lake Monte Alegre (Brazil)	Shallow, eutrophic, tropical, freshwater	0.56–3.38	^{14}C method	(Feresin et al., 2010)
Lake Carioca (Brazil)	Shallow, tropical	0.002–0.75	^{14}C method	(Barbosa & Tundisi, 1980)
Lake Carioca (Brazil)	Shallow, tropical, meso-oligotrophic	62.28	^{14}C method	(Petrucio & Barbosa, 2004)
Billing reservoir (Brazil)	Shallow, large reservoir, tropical	4.61–9.14	^{14}C method	(Nishimura et al., 2008)
Seven lakes (Rio Doce basin, Brazil)	Shallow, tropical	0.25–43.6	^{14}C method	(Petrucio et al., 2006)
Lakes and reservoirs (Mekong basin)	Shallow, large, tropical	0.01–14.58	^{13}C-labelled method	(Hiroki et al., 2020)
Lake Zeekoevlei (South Africa)	Shallow, hypertrophic, subtropical	43.75–127	Light and dark oxygen method	(Harding, 1997)
Lake Okeechobee (USA)	Large freshwater	5–29	^{14}C light and dark bottle	(Gu et al., 1997)
Lake Apopka (USA)	Shallow, subtropical, hypertrophic	33.3–87.5	Light and dark oxygen method	(Gale & Reddy, 1994)
Lakes (Kenya)	Shallow, tropical	1.58–23.42	Oxygen method	(Melack, 1979)
Hartbeespoort (South Africa)	Hypertrophic reservoir	1.03–493	^{14}C method	(Robarts, 1984)
McIlwaine (Zimbabwe)	Hypertrophic, shallow, tropical	12.92–54.42	^{14}C method	(Robarts, 1979)
Wuras (South Africa)	Shallow, temperate, man-made	3.75–35	^{14}C light and dark method	(Stegmann, 1982)
Waigani Lake (N. Guinea)	Shallow, hypertrophic	136.67–656.25	Oxygen method	(Osborne, 1991)

N_2 fixers exhibit little or no isotopic fractionation when they fix atmospheric N_2 (0 ‰) for their nitrogen requirement (Hoering & Ford, 1960; Gu & Alexander, 1993). The depletion of ^{15}N in the DIN pool could be linked to bird guano, potentially from birds consuming N_2-fixing plants from agricultural areas (such as cornfields), which are ^{15}N-depleted due to the utilization of commercial fertilizers (Kitchell et al., 1999). During monsoon, N_2 fixation, NH_4^+ assimilation, and NO_2^- assimilation rates declined significantly which coincided with the reduced PP and DIN concentrations (Figs 4.7 and 4.5a). A significant decrease in N_2 fixation rates might be due to changes in dominant N_2 fixer communities resulting from water turbulence and decreased light intensity due to clouds (Reynolds & Walsby, 1975). The increase in $\delta^{15}N_{POM}$ during monsoon could be attributed to allochthonous POM and DIN from catchment runoff which exhibit increased $\delta^{15}N$ (i.e., manure) and/or decreased N_2 fixation (McClelland et al., 1997).

In general, C:N ratio was low in the lake, which indicated dominant signature of autochthonous POM, and was within the range for freshwater phytoplankton and algae (Kendall et al., 2001). During both seasons, the N:P ratio was less than 16 (Redfield ratio, Fig. 4.5d), which suggested nitrogen limitation, a condition favourable for N_2 fixation (Vrede et al., 2008). The N:P ratio decreased several folds during monsoon indicating an increase in nitrogen limitation for phytoplankton. This increase in nitrogen limitation during monsoon could be related to a 14-fold decrease in N_2 fixation rates, which provided new nitrogen to the system. The relative unavailability of nitrogen during monsoon could have led to 4-5-fold reduction in NH_4^+ and NO_2^- assimilation rates with a similar decrease in PP (Fig. 4.7). In this closed basin, higher contribution of N_2 fixation to PP during summer as compared to monsoon was observed. The low rates of N_2 fixation in mixing season (~ monsoon) resulting from reduced light intensity and increased turbidity have also been reported from Lake Malawi and Lake Valencia (Levine & Lewis, 1985; Gondwe et al., 2008). The nitrogenase enzyme, which can fix atmospheric N_2, is sensitive and can be negatively impacted by oxygen and turbulent mixing during monsoon. This combination could potentially damage the heterocyst's cyanobacteria filaments, exposing them to oxygen (Paerl & Bland, 1982). The decreased concentrations of DIN, temperature, and biomass during monsoon might have contributed to reduced rates of NH_4^+ and NO_2^- assimilation in the lake (Figs. 4.7c and d).

Table 4.2 Nitrogen assimilation rates in freshwater lakes across the globe. BD stands for below detection limit.

Lake Name	System Type	Rates (μM h^{-1})	References
N_2 fixation rates			
Smith Lake (USA)	Shallow, eutrophic	<0.01–1.29	(Gu & Alexander, 1993b)
Smith Lake (USA)	Shallow, eutrophic	<0.01–0.6	(Gu & Alexander, 1993a)
Lake Okeechobee (USA)	Large freshwater,	0.01–0.38	(Gu et al., 1997)
Lake Okeechobee (USA)	Shallow	0.005–0.09	(Philips et al., 1995)
Lake Vortsjarv (Estonia)	Large, shallow	0.005–0.016	(Tõnno & Nõges, 2003)
Lake Champlain (USA)	Large, shallow	0.100 ± 0.272	(McCarthy et al., 2013)
Utah Lake (USA)	Large, shallow	0–0.0007	(Li et al., 2022)
Lakes, Canada	Prairie lakes	0–0.62	(Boyer, 2021)
Ammonium assimilation rates			
Smith Lake (USA)	Shallow, eutrophic	0.01–3.69	(Gu & Alexander, 1993b)
Smith Lake (USA)	Shallow, eutrophic	1.4–6	(Gu & Alexander, 1993a)
Lake Okeechobee (USA)	Shallow, subtropical	0.54–0.86	(Gu et al., 1997)
Taihu Lake (China)	Shallow, Freshwater	0.02–6.82	(Hampel et al., 2018)
Taihu Lake (China)	Shallow, Freshwater	0.03-4.19	(McCarthy et al., 2007)
Lake Champlain (USA)	Large, shallow	0.205 ± 0.022	(McCarthy et al., 2013)
Lake Maracaibo (Venezuala)	Deep, hypertrophic, tropical	1.00–8.00	(Gardner et al., 1998)
Lake Okeechobee (USA)	Shallow, subtropical,	0.6	(James et al., 2011)
Lake Michigan (USA)	Deep, large lake	BD–0.16	(Gardner et al., 2004)
Lake Erie (USA)	Deep, large lake	0.07–0.12	(McCarthy et al., 2007)
Lake Buffalo, Canada	Shallow, prairie	0.05–0.46	(Boyer, 2021)
Lake Superior (USA)	Largest freshwater lake	0.0003- 0.0052	(Kumar et al., 2008)

4.1.5 Conclusion

Seasonal variation in PP of a tropical shallow lake (Thol Lake) with nitrogen assimilation and N_2 fixation rates were investigated as the lake water level changed due to evaporation and monsoonal precipitation. During low water level conditions in the summer, extensive phytoplankton bloom occurred due to high water temperature, enhanced light, and abundant nutrients leading to increased PP. The high photosynthetic activity and PP in the lake during summer enhanced DO and nitrogenous nutrient assimilation, as evidenced by higher rates of NH_4^+ and NO_2^- assimilation along with N_2 fixation. In contrast, during monsoon, the decline in PP correlated with decreased rates of N_2 fixation, NH_4^+ assimilation, and NO_2^- assimilation, which was due to reduced light intensity, nutrients, and temperature as well as increase in water turbulence mixing. Evidence for N_2 fixation in high DIN conditions was also observed in the studied closed basin.

4.2 Lake in transition: effect of lake water volume and salinity changes on carbon and nitrogen assimilation rates

In shallow lakes, the exchange of matter and energy is extensive, influenced by the complexity within each habitat (Schindler & Scheuerell, 2002). The significance of habitat complexity is captured in the alternative stable state hypothesis for shallow lakes (Scheffer et al., 1993). These lakes not only support a disproportionate share of biodiversity but offer numerous critical services to humanity, including flood control, food and water provision, water filtration, and carbon and nitrogen sequestration. Freshwater salinization due to natural perturbations and anthropogenic activities is a significant global environmental issue in aquatic ecosystems, harming aquatic life and affecting carbon and nitrogen biogeochemical processes (Cunillera-Montcusí et al., 2022). Excess precipitation causes lake levels to rise, increasing surface area until evaporation balances it. In contrast, insufficient precipitation leads to lake shrinkage with increasing salinity, potentially culminating in complete desiccation (Deocampo & Jones, 2014). Increasing amounts of salts and ions are entering aquatic systems, leading to widespread salinization of freshwater bodies (Jeppesen et al., 2020). These environmental issues lead to greater instability of lacustrine ecosystems and higher chances of regime shifts from a clear state (macrophytes-dominated) to a turbid state (phytoplankton-dominated) (Gilarranz et al., 2022). Additionally, seasonality significantly affects lake biogeochemistry, especially in highly seasonal or monsoonal systems that experience dramatic hydrologic fluctuations. While most freshwater salinization research has focused on OM decomposition, less is known about its effects on carbon and nitrogen assimilation, especially in shallow lakes, that are more vulnerable to these effects (Macêdo et al., 2019; Canhoto et al., 2021). This knowledge gap hampers the development of accurate ecohydrological models to predict the impact of freshwater salinization under various future scenarios. A more comprehensive perspective on the impacts of salinization is essential for addressing ecosystem functioning (Cañedo-Argüelles, 2020). Identifying key predictors of phytoplankton community biomass in shallow lakes is challenging due to the interrelated factors involved. The connection of ecological regime shifts with carbon and nitrogen cycles in aquatic ecosystems is poorly understood, despite recent attention. Regime shifts in shallow lakes may significantly change their role in the global carbon and nitrogen cycles by changing their contribution towards sources and sinks. An increase in sedimentation rates has been observed, which coincided with the regime shifts in lakes from macrophyte-dominated (40 %) to phytoplankton-dominated state (80 %), probably due to higher carbon burial and lower mineralization rates during the latter state (Brothers et al., 2013). Despite the importance of N_2 fixation for phytoplankton in aquatic systems, the factors that affect this process in freshwater and saline ecosystems are poorly understood (Vitousek et al., 2002). Addressing gaps in understanding the key factors driving phytoplankton productivity is crucial for supporting various aquatic organisms. This research investigates the interactive effect of changes in salinity, nutrients, and lake water levels on PP, N_2 fixation, and nutrient assimilation rates in the Nalsarovar Lake, India, as an example of an open basin freshwater shallow lake.

4.2.1 Study Area

The Nalsarovar Lake (22°46′33″N and 72°02′21″E) is the largest freshwater lake located in the Thar desert biogeographic area of the Indian subcontinent, covering an area of ∼120 km^2 (Fig. 4.8). It is an open macrophyte-dominated shallow basin (a relict sea) that consists of 300 islands, locally called ‘Bets’, and is formed by tectonic uplifting and sedimentation (Mokaria & Jethva, 2019). The surrounding areas of lakes are dominated by agriculture, fallow, and wastelands. Nalsarovar Lake basin has a gentle slope from northwest to south and receives water from the Brahmini and Bhogavo rivers (Vankar et al., 2018). The Nalsarovar Lake is surrounded by basaltic trap rocks of the Saurashtra in the west, Jurassic-Cretaceous sandstone in the northwest, Aravalli’s igneous and metamorphic rocks in the northeast, and quaternary alluvial plains in the east (Pandarinath et al., 1999), whereas the lake itself has quaternary alluvial plains and clay soils. The lake transitions from freshwater to saline depending on the precipitation patterns and subsequent evaporation presenting a dynamic habitat. Studies have revealed that the lake is home to a large number of migratory birds from winter to early summer and supports local communities, but it is also degrading due to anthropogenic activities (Kumar et al., 2007). The 'bets' in the lake that remain above water provide support to a variety of vegetation and act as nesting grounds for migratory birds.

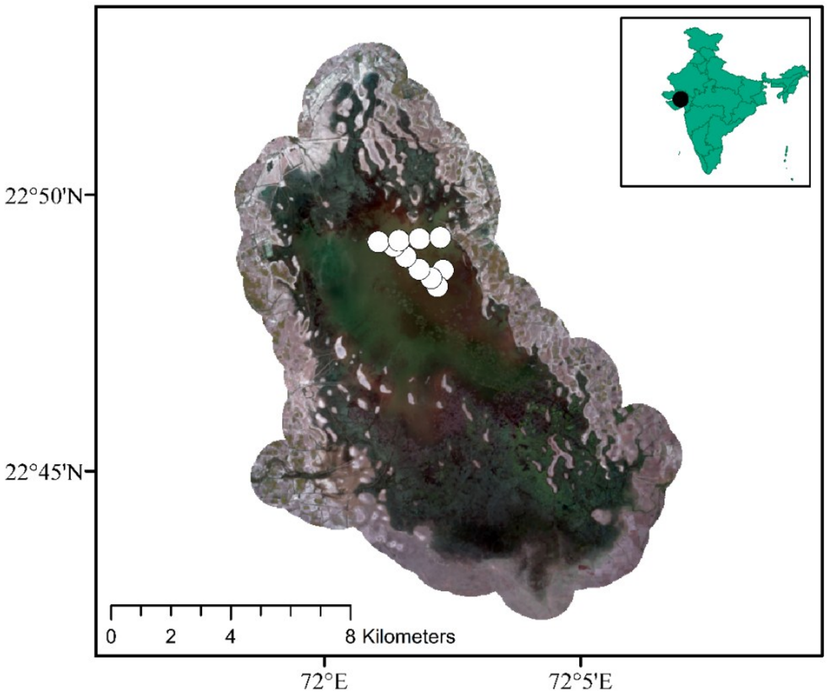


Fig. 4.8 Study area and sampling locations in the Nalsarovar Lake (white circles). The sampling was restricted to the region where water is normally available throughout the year. Also, the rest of the lake was inaccessible due to administrative and logistical reasons.

4.2.2 Sampling

To address the objectives of the study, sampling in the Nalsarovar Lake was conducted during three seasons: summer (May 2022, n = 9), monsoon (September 2022, n = 10), and winter (January 2023, n = 10) (Fig. 4.8). The lake water depth was minimum during summer (0.58 m) due to higher evaporation and increased during monsoon (1.34 m) with increased precipitation. Water level decreased again in winter (1.01 m) due to reduced precipitation and rising evaporation (Fig. 4.9). Also, the water was visibly clear during summer and winter (submerged macrophytes visible) and turbid during monsoon (Fig. 4.10). The protocols for lake water sampling for different parameters along with carbon and nitrogen assimilation rates experiments are discussed in Chapter 2.

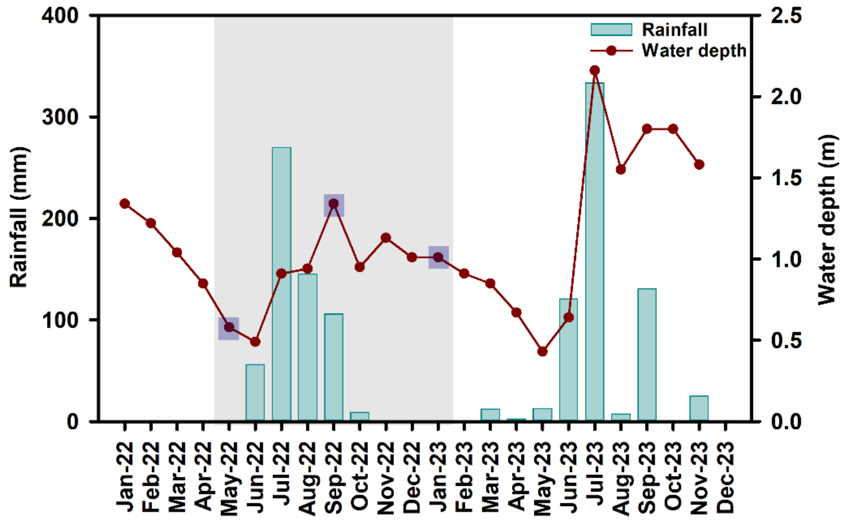


Fig. 4.9 Seasonal variability in rainfall (bar plots) and water depth (red scatter and line plots). Field campaigns are represented in light blue small squares (Water depth: monitoring station at the lake; Rainfall: IMD gridded data, https://indiawris.gov.in/wris).

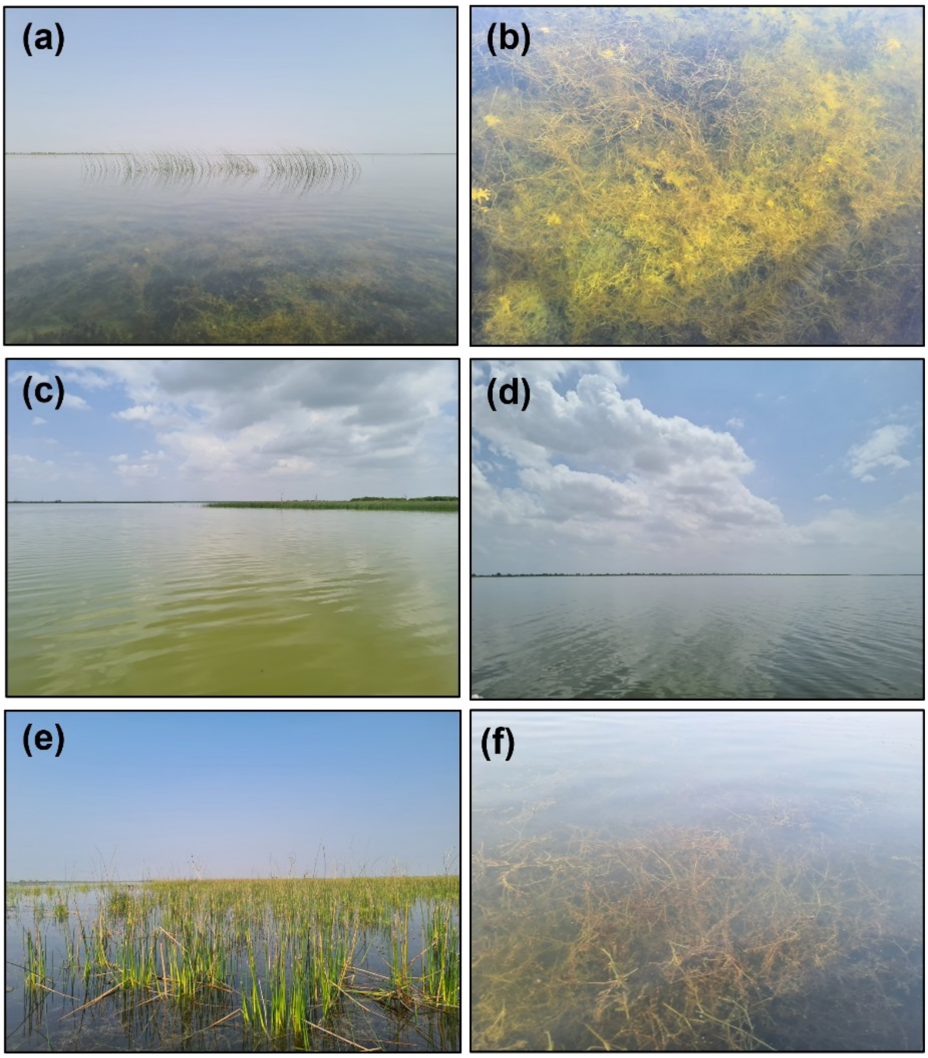


Fig. 4.10 Field photographs from the Nalsarovar Lake during summer (a and b), monsoon (c and d), and winter (e and f).

4.2.3 Results

4.2.3.1 Environmental parameters

The Nalsarovar Lake exhibited significant differences in the mean values of environmental parameters such as water temperature, pH, salinity, and DO among different seasons. Water temperature was significantly higher during summer (35.94 ± 1.10 °C) than during monsoon (30.79 ± 1.17 °C) and winter (23.52 ± 1.26 °C) (Fig. 4.11a). Surface water average pH during the three seasons was significantly different and decreased from summer (9.10 ± 0.35) to monsoon (8.73 ± 0.09) and increased again during winter (9.67 ± 0.19) (Fig. 4.11b). Although the lake was oxygenated throughout, DO varied significantly across seasons and was higher during summer (10.15 ± 3.20 mg L^{-1}) than monsoon (6.91 ± 0.53 mg L^{-1}) and winter (8.56 ± 0.97 mg L^{-1}) (Fig. 4.11c). The mean values of EC varied significantly and were the highest during summer (10.54 ± 0.47 mS cm^{-1}) and the lowest during monsoon (3.13 ± 0.50 mS cm^{-1}) to increase again during winter (4.17 ± 0.08 mS cm^{-1}) (Fig. 4.11d).

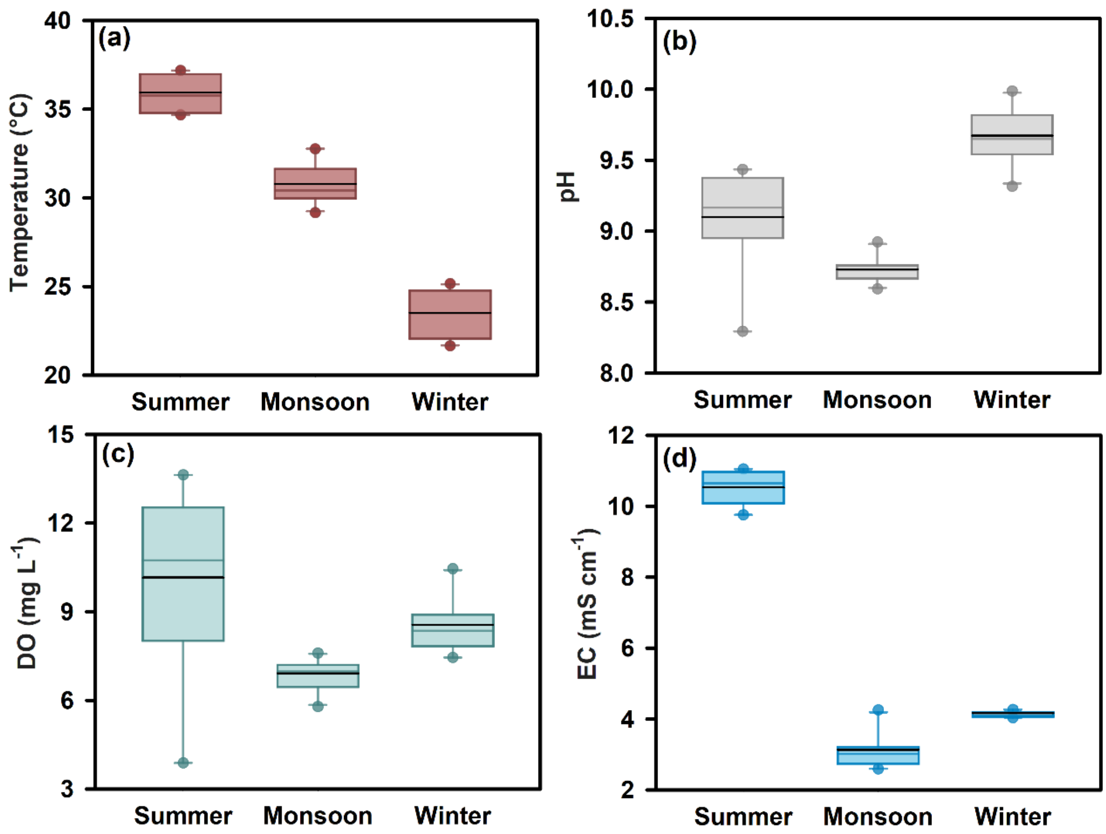


Fig. 4.11 Seasonal variation in environmental parameters, (a) temperature, (b) pH, (c) DO, and (d) EC of the surface water of the Nalsarovar Lake. The black lines represent the mean values.

4.2.3.2 Dissolved inorganic carbon, nutrients, and dissolved greenhouse gases

The lake water showed significant seasonal differences in the DIC concentration and $\delta^{13}C_{DIC}$. DIC concentration was higher during monsoon with relatively higher $\delta^{13}C_{DIC}$ (DIC = 2.84 ± 0.17 mM; $\delta^{13}C_{DIC}$ = −5.40 ± 0.53 ‰) compared to summer (DIC = 1.44 ± 0.55 mM; $\delta^{13}C_{DIC}$ = −12.46 ± 1.06 ‰) and winter (DIC = 1.35 ± 0.27 mM; $\delta^{13}C_{DIC}$ = −15.15 ± 2.67 ‰) (Fig. 4.12a).

Dissolved inorganic nitrogen concentrations varied slightly across three seasons (summer = 7.34 ± 3.34 µM, monsoon = 3.79 ± 1.48 µM, and winter = 4.73 ± 2.15 µM) (Fig. 4.12b). Within the DIN pool, NH_4^+ did not show significant difference across seasons, however, NOx exhibited a significant difference during summer (2.51 ± 1.88 µM) compared to monsoon (1.05 ± 1.14 µM) and winter (1.28 ± 0.90 µM) (Fig. 4.12b). No significant difference was observed in the mean dissolved PO_4^{3-} concentrations (summer = 0.22 ± 0.39 µM, monsoon = 0.12 ± 0.11 µM, and winter = 0.17 ± 0.15 µM) among different seasons (Fig. 4.12c). SiO_4^{4-} was significantly different during monsoon (299.02 ± 46.63 µM) than summer (91.16 ± 44.76 µM) and winter (91.07 ± 50.85 µM) (Fig. 4.12d). Inorganic N:P ratio was higher during summer (71.35 ± 39.25) than monsoon (38.36 ± 17.56) and winter (35.53 ± 16.27).

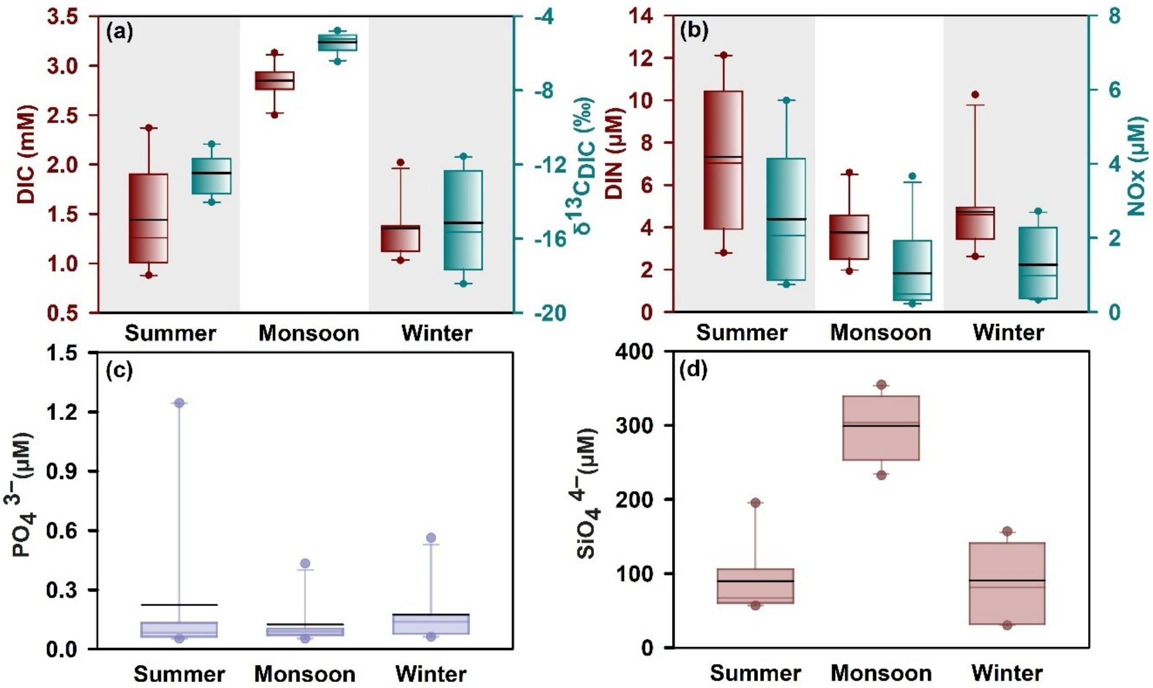


Fig. 4.12 Seasonal variation in (a) DIC (reddish) and $\delta^{13}C_{DIC}$ (greenish), (b) DIN (reddish) and NOx (greenish), (c) PO_4^{3-}, and (d) SiO_4^{4-} in the Nalsarovar Lake surface water. The black lines within the box represent the mean values.

Dissolved CO_2 concentration in the lake exhibited significant difference among seasons and increased from summer (8.47 ± 4.68 µM) to monsoon (320.53 ± 136.30 µM) and decreased again during winter (72.01 ± 14.76 µM) (Fig. 4.13). The concentrations of dissolved CH_4 also varied significantly and were higher during monsoon (740.47 ± 488.67 nM) than winter (226.52 ± 241.65 nM) and summer (265.99 ± 173.98 nM) (Fig. 4.13).

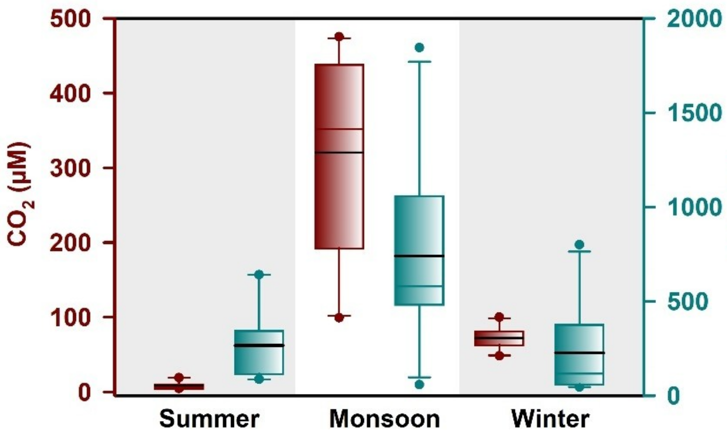


Fig. 4.13 Seasonal variation in dissolved CO_2 (reddish) and CH_4 (greenish) in the Nalsarovar Lake surface water. The black lines represent the mean values.

4.2.3.3 Primary production, nitrogen assimilation, and particulate organic matter

Carbon and nitrogen assimilation rates showed significant seasonal differences in the Nalsarovar Lake. PP increased from summer (0.59 ± 0.37 µM C h^{-1}) to monsoon (13.82 ± 2.57 µM C h^{-1}) and decreased again during winter (3.17 ± 1.18 µM C h^{-1}) (Fig. 4.14a). The N_2 fixation rates varied from below detection limit to 1.20 ± 0.76 nM N h^{-1} with an average of 0.28 ± 0.46 nM N h^{-1} during summer (Fig. 4.14b) and increased during monsoon (5.61 ± 1.89 nM N h^{-1}) to decrease again during winter (1.34 ± 1.57 nM N h^{-1}) (Fig. 4.14b). N_2 fixation rates were below detection limits at two sites in the lake during winter. NH_4^+ assimilation rates increased from summer (0.22 ± 0.07 µM N h^{-1}) to monsoon (0.90 ± 0.37 µM N h^{-1}) and decreased again during winter (0.48 ± 0.26 µM N h^{-1}) (Fig. 4.14c). NO_2^- assimilation rates were significantly higher during monsoon (11.01 ± 3.94 nM N h^{-1}) and winter (10.65 ± 2.61 nM N h^{-1}) than during summer (0.13 ± 0.14 nM N h^{-1}) (Fig. 4.14d).

The seasonal variation in PP coincided with POM concentrations in the lake [summer (POC = 66.54 ± 29.23 µM and PON = 7.75 ± 3.71 µM) < monsoon (POC = 633.29 ± 61.42 µM and PON = 75.24 ± 5.93 µM) > winter (POC = 262.06 ± 69.38 µM and PON = 28.42 ± 8.00 µM)) (Fig. 4.15a). POM concentrations were negatively correlated with $\delta^{13}C_{POM}$, which was the highest during summer (−22.09 ± 1.22 ‰) and the lowest during monsoon (−31.86 ± 1.01 ‰) to increase again during winter (−25.50 ± 1.03 ‰) (Fig. 4.15b). The $\delta^{15}N_{POM}$ decreased during winter (0.96 ± 0.53 ‰) compared to summer (3.07 ± 1.77 ‰) and monsoon (4.72 ± 1.10 ‰) (Fig. 4.15b). There was no significant difference in the C:N ratio during the three seasons (summer = 8.76 ± 1.17, monsoon = 8.43 ± 0.61, and winter = 9.32 ± 0.93).

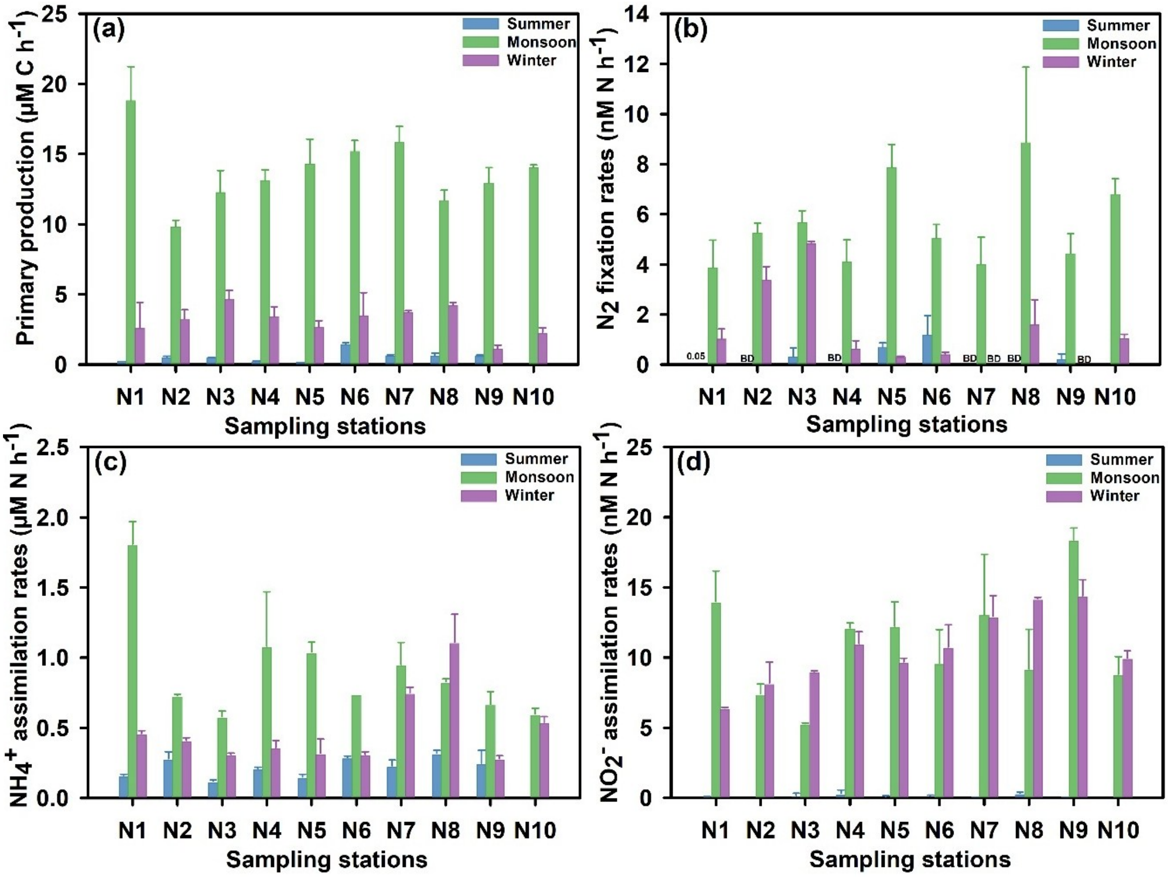


Fig. 4.14 Seasonal variation in the (a) primary production, (b) N_2 fixation rates, (c) NH_4^+ assimilation rates, and (d) NO_2^- assimilation rates in the Nalsarovar Lake. The error bar represents the standard deviation of duplicate samples.

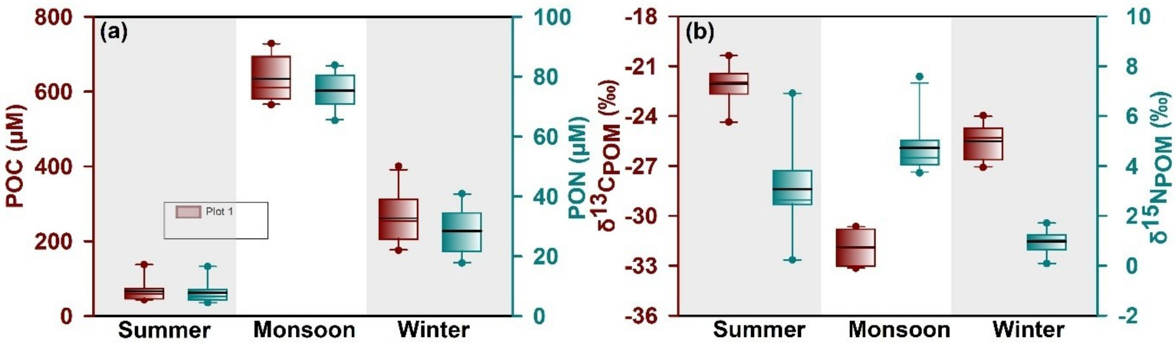


Fig. 4.15 Seasonal variation in (a) concentrations and (b) isotopic composition of particulate organic matter [POC (reddish) and PON (greenish)]. The black lines represent the mean values.

4.2.4 Discussion

4.2.4.1 Dissolved inorganic carbon, nutrients, and dissolved gases

Biological processes combined with geological processes may contribute to the seasonal variations in the DIC pool (Bade et al., 2004). During summer and winter, lower DIC with decreased $\delta^{13}C_{DIC}$ compared to monsoon might be attributed to the interplay of several processes such as photosynthesis by submerged macrophytes, plant respiration and decomposition of OM, CO_2 evasion at the air-water interface, and carbonate precipitation (Fig. 4.12a). A weak positive correlation was observed between DIC and $\delta^{13}C_{DIC}$ during summer and winter, suggesting the potential role of carbonate precipitation at higher pH (Fig. 4.16). The photosynthesis by submerged macrophytes is known to increase pH leading to the precipitation of calcium carbonate with soluble phosphorus resulting in decreased DIC and $\delta^{13}C_{DIC}$ (Murphy et al., 1983). An increase in DIC with higher $\delta^{13}C_{DIC}$ was observed from summer to monsoon (Fig. 4.12a). Usually, terrestrial runoff during monsoon brings ^{13}C depleted DIC into the lake, however, the contrasting signature was observed in the Nalsarovar Lake, implying that other processes are responsible for DIC dynamics. One of the reasons for the increased DIC concentrations with increased $\delta^{13}C_{DIC}$ might be calcium carbonate dissolution from sediment resuspension and weathering of basaltic (silicate) rocks found near the western part of the lake (Prasad et al., 1997; Havas et al., 2023). The second reason might be related to methanogenesis which affects $\delta^{13}C_{DIC}$ in the lake. CH_4 concentrations were high during monsoon mainly due to increased OM concentration which acts as a substrate for higher CH_4 production (Figs. 4.13 and 4.15a). This process provides ^{13}C depleted CH_4 and ^{13}C enriched CO_2 which contributes to the DIC pool in the lake, leading to the isotopically enriched signature of DIC. The higher $\delta^{13}C_{DIC}$ due to methanogenesis has also been observed previously in several studies (Gu & Schelske, 1996; Gu et al., 2004, 2006).

The Nalsarovar Lake potentially acted as a source of CO_2 during monsoon and winter but transformed into a sink during summer as the measured CO_2 concentration was lower than the equilibrium during summer (Fig. 4.13). The higher temperature during summer leads to significant water loss through evaporation, concentrating dissolved ions (major ions, unpublished) in the lake water, and increasing salinity. Due to low gas solubility at higher temperature and salinity along with photosynthesis by submerged macrophytes, aqueous CO_2 concentration during summer was lower in the lake (Engel et al., 2019; Wen et al., 2016). Higher dissolved CO_2 concentrations during monsoon resulted from the decomposition of OM, inputs from terrestrial ecosystems due to increased runoff, and diffusion from the atmosphere with rainwater (Cole & Caraco, 2001). Dissolved CO_2 concentration showed a negative relationship with pH, as the pH was lower when the proportion of CO_2 was higher in the total DIC pool (~ 11.44 % CO_2 during monsoon). pH increased from monsoon to winter as the dissolved CO_2 percentage decreased (~ 5.49 % during winter) in the DIC pool (Figs. 4.11b and 4.13). At lower temperature, increased gas solubility may elevate CO_2 and deplete the DIC pool in ^{13}C during winter compared to summer (Weiss, 1974; Gu et al., 2006).

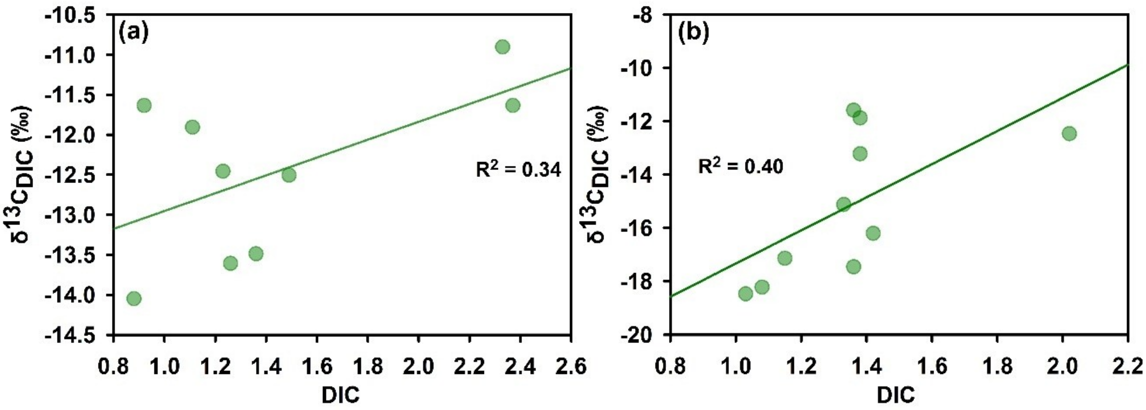


Fig. 4.16 Relationship between DIC and $\delta^{13}C_{DIC}$ in (a) summer and (b) winter in the Nalsarovar Lake.

Dissolved inorganic nitrogen concentration was higher during summer as the lake volume reduced and nutrients concentrated in the smaller area resulting from higher evaporation (Figs. 4.9 and 4.12b). Although increased rainfall replenishes nutrients through runoff from catchment and islets area (bets) during monsoon, a relative decrease in DIN concentration from summer to monsoon was due to the dilution effect and higher assimilation by phytoplankton (Gu et al., 1994, 2006). A small increase in DIN from monsoon to winter was due to the presence of migratory bird's guano, which contributed to the nutrient concentrations (Dessborn et al., 2016). Within the DIN pool, NO_3^- was lower than NH_4^+ in the lake (Fig. 4.12b). Cyanobacteria likely help maintain low NO_3^- levels in the lake water by consuming NO_3^- (Hu et al., 2000). After assimilation, NO_3^- is converted into NH_4^+ through the decomposition of OM, causing NH_4^+ accumulation in lakes (Heldt & Heldt, 2005). NH_4^+ is also released from sediments due to vertical mixing (Quirós, 2003). Lower NH_4^+ during monsoon was due to higher assimilation. The N:P ratio was high in the lake during all seasons referring to PO_4^{3-} limitation, but it was particularly higher during summer due to increased DIN (Spalinger and Bouwens, 2003). Decrease in the N:P ratio during monsoon might be related to external nutrient enrichment from runoff (Downing & McCauley, 1992). Lower PO_4^{3-} concentration in the lake was due to the requirement by diazotrophs, rapid consumption by organisms and submerged plants, and sediment retention in oxic environments (Horne & Goldman, 1994). Increased contribution from the catchment increased the SiO_4^{4-} concentration in the lake during monsoon (Fig. 4.12d).

4.2.4.2 Phytoplankton primary production and nitrogen assimilation

Phytoplankton primary production increased from summer to monsoon and decreased again during winter in the Nalsarovar Lake showing seasonal fluctuation and influence of biotic and abiotic factors (Fig. 4.14a). The PP values are within the range reported from previous studies from other lakes around the world (Table 4.1). Minimum PP was observed during summer as compared to monsoon and winter, which coincided with minimum POM due to a reduction in phytoplankton biomass (Figs. 4.14a and 4.15a). Phytoplankton productivity might be affected by other factors such as light, salinity, and CO_2 concentrations during summer despite having higher nutrient concentrations. The optimal temperature for phytoplankton growth is known to reduce when exposed to high radiation levels in clear water that could inhibit phytoplankton growth resulting in lower PP (Thorel et al., 2014; González-Olalla et al., 2022). Ryther (1956) reported that photosynthesis declines within the chlorophyte when the intensity is equivalent to full noon sunlight. Torremorell et al. (2009) observational study reported that photoinhibition along with water transparency impacts PP in reservoirs during the dry season. Other factors responsible for reduced PP during summer might be higher salinity as some freshwater species are not able to withstand osmotic stress (Li et al., 2021). It was assumed that the most critical change occurs at the lowest end of salinity, where a slight increase in salinity appears to decrease the biomass, PP, and consequently N_2 fixation rates in the lakes (Evans & Prepas, 1996). Lower PP during summer is correlated with lower dissolved CO_2 concentrations as well, which can limit PP and result in relatively higher $\delta^{13}C_{POM}$ under low CO_2 conditions (Mizutani & Wada, 1982). This isotopic enrichment is attributed either to the active uptake of carbon with minimal fractionation or the direct uptake of HCO_3^-, which is more enriched in ^{13}C than CO_2 (Mook et al., 1974; Tortell et al., 1997). Another reason for lower PP might be due to zooplankton, which consume phytoplankton and may be highly active during periods of clear water as they can take refuge in the submerged plants from the fishes in the lake environment and contribute to less phytoplankton biomass (Scheffer, 2001). The ε_{app} during summer was around 9 ‰ in response to decreasing CO_2 concentrations due to enhanced carbon demand and resulted in increased $\delta^{13}C_{POM}$ compared to monsoon (Lehmann et al., 2004). Lower DIC decreases the limiting effect of the carboxylation step during photosynthesis, and lower CO_2 concentrations led to transport-limited rather than carboxylation-limited assimilation, decreasing ε_{app} (O'Leary, 1988; Zohary et al., 1994).

Phytoplankton primary production increased several folds (~ 23-fold) from summer to monsoon along with increased water depth, which coincided with increased POM, DIC, and CO_2 concentrations (Fig. 4.14a). The increased influx of nutrients (e.g., DIN and PO_4^{3-}) with runoff from the surrounding catchment, and islets (agriculture-dominated lands) within lakes, contributed to the higher PP observed during monsoon (Peng et al., 2021b). The onset of frequent mixing by rainfall during monsoon led to high nutrient concentrations due to resuspended sediments in the water column. Usually, the macrophytes decline due to reduced sunlight by higher phytoplankton biomass and turbidity, leaving the sediments unprotected in the lake during monsoon (Spalinger & Bouwens, 2003). With less competition for nutrients and light, phytoplankton may experience a temporary surge in growth and change the lake into a temporarily phytoplankton-dominated state from a macrophytes-dominated state (Fig. 4.10). In this condition, the phosphorus released from sediments or coming through runoff is consumed rapidly (Horne & Goldman, 1994). Higher PP with decreased $\delta^{13}C_{POM}$ during monsoon than summer indicates increasing ε_{app} (~ 27 ‰), which is linked to the higher DIC concentration, especially enhanced dissolved CO_2 concentration in the DIC pool (~ 11.44 ± 4.31 %) (Figs. 4.14a, 4.15b, and 4.12a; Mizutani & Wada, 1982; Farquhar et al., 1989). The seasonal shift in isotopic fractionation between different carbon pools might also be attributed to changes in biological assemblages. During periods of higher PP, phytoplankton assimilate DIC rapidly, which can intensify the kinetic isotope effect, leading to depletion of ^{13}C in the POM relative to the DIC (Rau et al., 1989; Gu & Schelske, 1996). Previous studies have reported that water temperature affects phytoplankton $\delta^{13}C$ by changing enzymatic isotopic fractionation (~ 3 ‰), however, not as high as observed here (Fontugne & Duplessy, 1981). Decreased $\delta^{13}C_{POM}$ during monsoon may be due to terrestrial influence as well, however, the C:N ratio was within the range of freshwater phytoplankton and lower than the ratio of terrestrial plants, which does not indicate a significant effect of terrestrial input on the carbon cycle (Meyers & Ishiwatari, 1993). Zooplankton may be less active during periods of high turbidity or reduced macrophytes, which provide refuge from fishes in the lake, reducing the top-down control on phytoplankton. Also, DIN and PO_4^{3-} showed a negative correlation with the lake PP, which was due to higher consumption of nutrients by the phytoplankton during monsoon. Further, elevated CO_2 concentrations with reduced DO during monsoon were because of higher organic carbon availability, which enhances bacterial respiration and remineralization (Zeng & Masiello, 2010). Similar to the Nalsarovar, Lake Apopka (USA) was macrophyte-dominated and became phytoplankton-dominated due to nutrient inputs from farming and sewage discharge as a result of agricultural land (Schelske et al., 2000).

The nutrients and suspended load start to settle down due to enhanced sedimentation, as wetlands have the ability to trap sediments, and the resuspension of sediment stops when flow ceases after monsoon in the lake (Mereta et al., 2020). A significant reduction in external nutrient supply also destabilizes the turbid state, prompting it to switch back to the clear state. PP decreased from monsoon to winter with reduced water depth, temperature, sunlight, POM, DIC, and dissolved CO_2 concentration (Fig. 4.14a). Lower temperatures with reduced sunlight decreased the metabolic activity of phytoplankton resulting in lower PP and reduced POM (Gu & Alexander, 1993a; Gu et al., 1994). The nutrient concentration does not show a significant difference during winter than summer and monsoon, implying that other factors are influencing PP. The reduction in phytoplankton biomass led to decrease in PP with increased $\delta^{13}C_{POM}$ during winter than monsoon. However, PP was higher during winter than summer, which might be due to optimum temperature and radiation in clear water, and higher dissolved CO_2 concentration in the DIC pool. The ε_{app} decreased from monsoon to winter (~ 10.62 ‰) with decreasing CO_2 in the DIC pool, but it was similar to summer, leading to isotopically enriched (^{13}C) POM during winter and summer than monsoon.

A simultaneous increase in PP with N_2 fixation, NH_4^+, and NO_2^- assimilation rates suggests active nitrogen metabolism and no suppression of N_2 fixation process despite having higher DIN concentrations during monsoon and winter seasons (Fig. 4.14). The nitrogen assimilation rates are within the range reported from previous studies (Table 4.2). Lower N_2 fixation, NH_4^+, and NO_2^- assimilation rates were observed during summer, which coincided with lower PP and POM (Figs. 4.14 and 4.15a). Below detection limit or lower rates of N_2 fixation during summer might also be related to salinity and PO_4^{3-} concentrations, as salinity can reduce its activity, and PO_4^{3-} is required by the nitrogenase enzyme, which is responsible for this process (Howarth et al., 1988; Herbst, 1998).

Increase in N_2 fixation, NH_4^+, and NO_2^- assimilation rates from summer to monsoon coincided with increase in PP indicating enhanced nutrient assimilation by phytoplankton as the lake received nutrients from runoff and sediment resuspension (Fig. 4.14). This is corroborated by negative correlation between PP and DIN concentrations, suggesting the assimilation of DIN during higher growth periods (Alexander & Barsdate, 1971). During monsoon and winter, NH_4^+ and NO_2^- assimilation rates were not significantly different, but N_2 fixation was quite high during monsoon, signifying enhanced role of diazotrophic cyanobacteria in supporting phytoplankton biomass in the lake (Higgins et al., 2017). Cyanobacteria can fix atmospheric N_2, providing a source of new nutrients to the ecosystem, and potentially driving PP even when other nutrient concentrations are low. Higher N_2 fixation during monsoon might be due to PO_4^{3-} runoff from nearby agricultural fields providing favourable conditions for this process, and high demand for PO_4^{3-} leading to its depletion in the water column (Howarth et al., 2021).

The contribution of N_2 fixation to PP could also be seen in $\delta^{15}N_{POM}$, which remained below 5 ‰ throughout (Fig. 4.15b). Although the absolute N_2 fixation rate was high during monsoon, from this data, the proportional contribution of N_2 fixation appeared to be higher during winter, where $\delta^{15}N_{POM}$ was around 1 ‰. The decrease in $\delta^{15}N_{POM}$ during winter can also be due to the assimilation of isotopically light (^{14}N) DIN excreted by zooplankton and other microbes (Checkley & Miller, 1989). The nutrients from bird's guano also have low $\delta^{15}N$ because they feed on N_2-fixing plants. The Nalsarovar Lake has significant contribution from guano during winter as it hosts large number of migratory birds. Additionally, the assimilation of light NH_4^+ produced through microbial decomposition of OM leads to decreased $\delta^{15}N_{POM}$ (Miyake & Wada, 1971).

Previous studies have reported that the N:P supply ratio is a major factor determining the presence of N_2 fixers in lakes, with N_2 fixing cyanobacteria developing at N:P ratios less than 22:1 (Howarth et al., 1988; Smith et al., 1995). However, high N_2 fixation rates have been observed in this study with a higher N:P ratio.

4.2.5 Conclusion

The Nalsarovar Lake showed significant seasonal variations in environmental parameters and biogeochemical properties. The differences in PP, N_2 fixation, and nitrogen assimilation rates among seasons can be explained by variations in physio-chemical parameters with phytoplankton growth, nutrient concentrations, and community composition. This study suggests that changes in these rates were mediated by changes in the nutrient loading derived from precipitation (runoff) and changes in biogeochemical properties due to evaporation of the lake water. Higher salinity with higher radiation led to lower PP, N_2 fixation, and nitrogen assimilation rates during summer. Freshwater inflow during monsoon introduced new sources of nutrients to Nalsarovar. Even if these nutrients were in lower concentrations, it was sufficient enough to spur phytoplankton growth, especially when coupled with other favourable conditions. Higher nutrients and DIC from runoff with optimal light intensity and moderate temperature prevailing during monsoon enhanced PP. Relatively lower PP, N_2 fixation, and nitrogen assimilation rates during winter were due to lower metabolic activity at reduced temperature. Water level changes temporarily shift the lake regime from clear water to turbid state in this shallow lake, impacting the carbon and nitrogen assimilation processes.

4.3 Carbon and nitrogen assimilation rates in a (hyper)saline lake

Saline lakes are endorheic inland water bodies that serve as model systems for studying elemental cycles related to life thriving in extreme conditions and have cultural, archaeological, and economic values (Haynes & Hammer, 1978; Polykarpou et al., 2023). Such environments are found worldwide mostly in semi-arid/arid climatic settings and vary from saline to hypersaline, covering ~ 23 % of the overall lake area on land which includes the biggest lakes such as the Caspian Sea, Aral Sea, and Mono Lake (Jellison et al., 2008; Wurtsbaugh et al., 2017). These systems are critical for migratory birds, who use them as their nesting and breeding grounds (Polykarpou et al., 2023). Saline lakes are more productive than freshwater lakes due to their large DIC and organic carbon pool, as well as their ability to retain nutrients, salts, and OM within their hydrologically terminal basins (Hammer, 1981; Wetzel, 2001; Wurtsbaugh et al., 2017). These lakes are extensively studied by microbiologists to understand the species composition present in these extreme environments and are completely different from other aquatic ecosystems (Geddes et al., 1981; Herbst, 2001; Golubkov et al., 2007). The species present in these lakes require specific physiological adaptations to sustain osmotic pressure and survive in these ecosystems (Padisak & Naselli-Flores, 2021).

The carbon and nitrogen biogeochemical processes of saline lakes significantly differ in intensity from freshwaters, with more prevalent chemical processes such as carbonate precipitation/dissolution, chemical enhancement of CO_2 exchange rates, higher carbon burial rates, and stronger nitrogen retention capacity (Jellison et al., 1996; Wanninkhof & Knox, 1996; Jiang et al., 2023). Previous studies have reported the importance of these saline lakes in global carbon and nitrogen cycles suggesting their effect on greenhouse gas concentrations from OM decomposition (Duarte et al., 2008; Yılmaz et al., 2024). Saline lakes contribute around 0.11–0.15 Gt C yr^{-1} in total CO_2 emission, which is quite significant, given that emission from all lakes to the atmosphere is ~ 0.28–0.32 Gt CO_2 annually (Duarte et al., 2008). Climate change and anthropogenic activities are impacting these lakes and leading to reduction in water area and complete desiccation along with increased salinity, impacting carbon and nitrogen cycling processes (Williams, 1993a; Jellison et al., 2008; Wurtsbaugh et al., 2017). The role of saline lakes as carbon and nitrogen sinks or sources requires specific attention while estimating carbon emissions/burial in inland aquatic ecosystems. However, studies on carbon and nitrogen assimilation rates in saline lakes are sparse, resulting in an unclear picture of PP, N_2 fixation, and nutrient assimilation compared to freshwater systems (Hammer, 1981; Joint et al., 2002). Studies have reported evidence of declining species richness with increasing salinity; however, high salinity does not necessarily mean low productivity (Hammer, 1986; Horne & Goldman, 1994; Larson & Belovsky, 2013), which remains to be explored comprehensively. For example, cyanobacteria are commonly a member of the oxygenic phototrophic community, observed in freshwater lakes. As the rates of N_2 fixation by cyanobacteria have rarely been measured in saline lakes, particularly with very high PO_4^{3-} concentrations (~ 1 mM) (Sorokin et al., 2015), their exact mechanism of fixation in (hyper)saline lakes remains unexplored.

Despite the significant ecological role of inland saline ecosystems, they are often neglected in the global aquatic carbon and nitrogen budgets. Only a few studies on the saline systems have been carried out so far, that too in Africa and North America. Saline lakes located in regions like the Indian subcontinent, which experiences dynamic monsoon system, remain poorly explored (Sarkar et al., 2023). This research focuses on the effect of varied salinity along with anthropogenic disturbances on the PP, N_2 fixation, and nitrogen assimilation rates in a highly saline subtropical lake and associated water bodies located in arid climatic settings [Sambhar Salt Lake (SSL), India].

4.3.1 Study Area

Sambhar Salt Lake is one of the largest inland saline lakes (~225 km^2) located in the Indian state of Rajasthan and is flanked by the Thar Desert and Aravalli mountains. The lake is shallow and elliptical with a length of 22.5 km and width of 3.2–11.2 km and has a catchment area of around 7560 km^2 (Fig. 4.17; Sinha & Raymahashay, 2004). The formation of the lake resulted from neotectonics and aeolian activity of paleochannels and streams (Roy, 1999; Yadav et al., 2007). The basement of the lake primarily consists of metamorphic rocks from the Delhi and Aravalli Supergroups (Yadav, 1997).

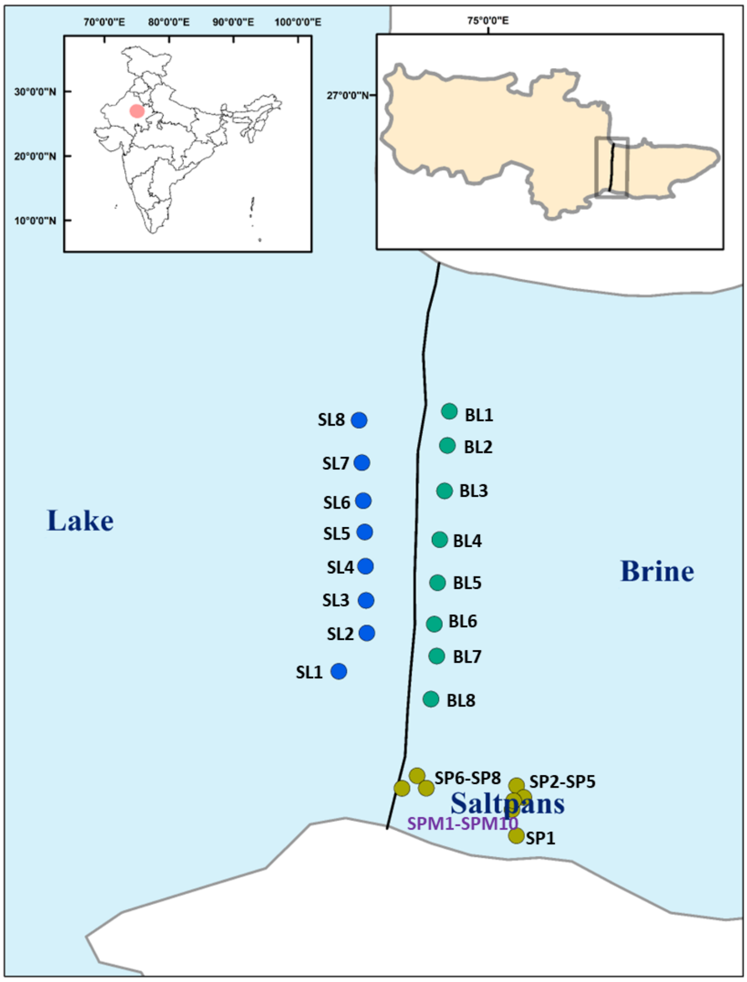


Fig. 4.17 Map of the Sambhar Salt Lake showing sampling locations in different classes (blue-lake, green-brine, and yellow-saltpans). The black line represents the location of the dam embankment separating the lake and the brine reservoir.

The main source of water is atmospheric precipitation and runoff from streams, where Mendha and Rupangarh are considered sources of salts to the lake (Yadav et al., 2007). The lake falls in a rain-shadow zone with mean annual precipitation varying from

100 to 500 mm (Sinha & Raymahashay, 2004; Yadav et al., 2007). After the monsoon, the lake undergoes evaporation and gets completely dried in summer. SSL has been facing issues of degradation due to anthropogenic activities in and around the lake, such as the construction of rail track, brine reservoir, trenches in the lake, and salt extraction (Vijay et al., 2016).

4.3.2 Sampling

To fulfil the objectives, the water sampling in the SSL was conducted during post-monsoon season (October 2022) in three different classes of water bodies representing different physio-chemical conditions: (i) Lake (n = 8); (ii) Brine reservoir (brine; n = 8) separated

Fig. 4.18 Field photographs of different water bodies of the Sambhar Salt Lake region. The top four photographs are from post-monsoon (October 2022) and the bottom two are from pre-monsoon (March 2023).

from the lake by a long dam; and (iii) Saltpans (SP; n = 8), which are small and shallow depressions on the ground found along the periphery of the lake (Figs. 4.17 and 4.18). The water from the lake is pumped into the brine reservoir through sluice gates to reach the degree of salinity required for salt extraction. Water sampling in the saltpans (SPM; n = 10) was also conducted during pre-monsoon (March 2023); however, due to logistic reasons and desiccation of the lake, water samples could not be collected from the lake and brine reservoir during this season (Fig. 4.18). The saltpans sampled during both seasons were not exactly the same, as they kept changing depending on the salt extraction. The protocols of water sampling and analyses for different parameters and experiments for rate measurements are described in Chapter 2.

4.3.3 Results

4.3.3.1 Environmental parameters

Significant differences were observed in environmental parameters such as water temperature, pH, salinity, and DO amongst the different water bodies (i.e., lake, brine reservoir, and saltpans) of SSL. Water temperature (36.46 ± 4.73 °C) of the saltpans was slightly higher than brine (29.58 ± 1.09 °C) and the lake (31.43 ± 1.14 °C) during post-monsoon. It was also higher than the saltpan water temperature during pre-monsoon (28.98 ± 3.29 °C) (Fig. 4.19a). Salinity varied among three classes of water bodies and higher salinity was observed in the brine (90.87 ± 5.98 g L^{-1}) than in the lake (31.83 ± 4.82 g L^{-1}) during post-monsoon. Saltpans had the highest salinity with huge variability and ranged from 138.52 g L^{-1} to 431.78 g L^{-1} during post-monsoon and 93.60 g L^{-1} to 356.04 g L^{-1} during pre-monsoon (Fig. 4.19b). Within saltpans, the water colour was pink and green during pre-monsoon, and it was observed that the green colour saltpans (110.48 ± 22.55 g L^{-1}, n = 4) were less saline than the pink colour ones (329.37 ± 16.47 g L^{-1}, n = 6) (Fig. 4.18). The pH was significantly higher in the lake (9.78 ± 0.21) and brine (9.56 ± 0.12) than in saltpans (9.28 ± 0.24) during post-monsoon. No significant difference was observed in the pH of saltpans during both post and pre-monsoon (9.26 ± 0.06) (Fig. 4.19c). The DO concentrations were significantly different in the lake (22.23 ± 2.37 mg L^{-1}) and brine (20.16 ± 1.64 mg L^{-1}) than in saltpans (16.63 ± 6.95 mg L^{-1}) during post-monsoon. DO significantly varied from post to pre-monsoon (10.21 ± 3.46 mg L^{-1}) in the saltpans (Fig. 4.19d).

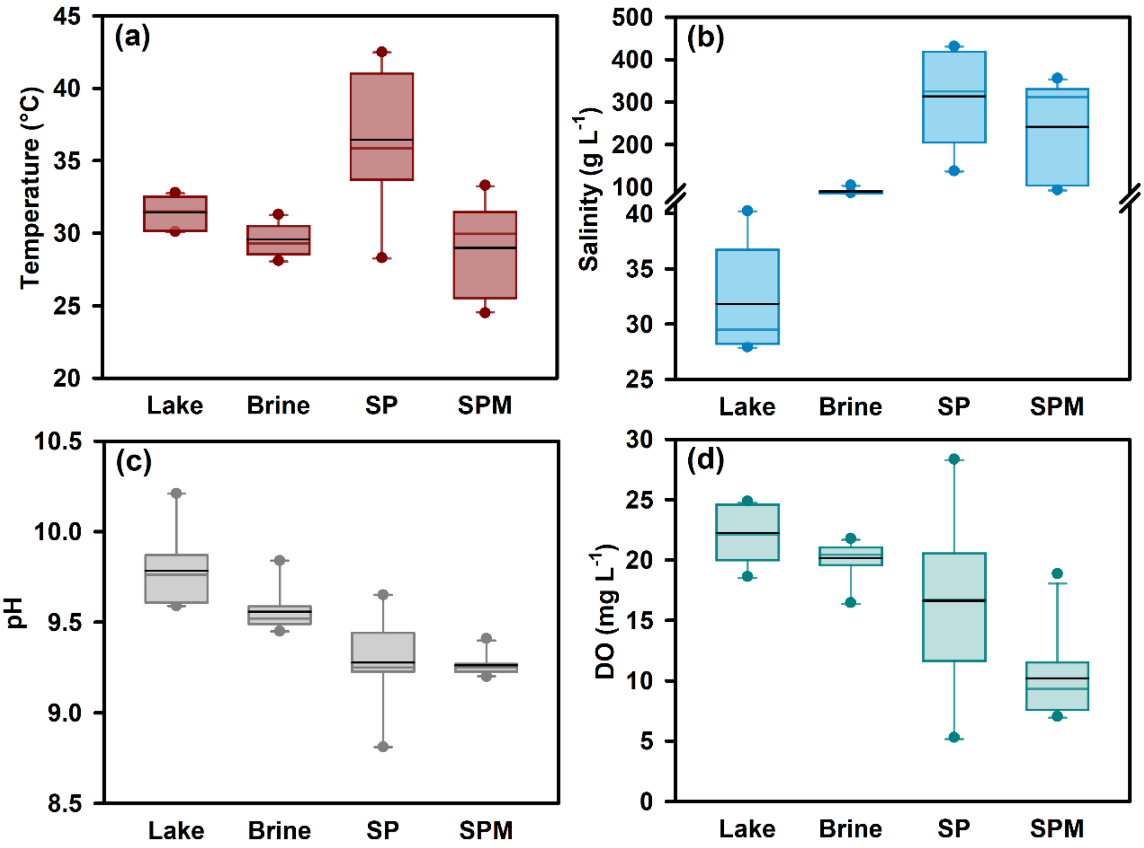


Fig. 4.19 Environmental parameters (a) temperature, (b) salinity, (c) pH, and (d) DO of different water bodies of the Sambhar Salt Lake. The black lines within the box represent the mean values. SP and SPM are for saltpans during post and pre-monsoon, respectively.

4.3.3.2 Dissolved inorganic carbon and nutrient concentrations

The SSL water exhibited significant differences in the DIC concentrations in the three classes. DIC concentration was the highest in the saltpans with large variability (224.96 ± 125.59 mM) than in the lake (45.25 ± 2.19 mM) and the brine (6.29 ± 0.82 mM) during post-monsoon (Fig. 4.20a). DIC isotopic composition ($\delta^{13}C_{DIC} = -8.83 \pm 0.97$ ‰) of the brine was significantly different than the lake ($\delta^{13}C_{DIC} = -3.99 \pm 0.14$ ‰) and saltpans ($\delta^{13}C_{DIC} = -3.41 \pm 0.44$ ‰) during this season. No significant difference was observed in DIC concentrations and $\delta^{13}C_{DIC}$ of the saltpans between post and pre-monsoon (DIC = 310.59 ± 224.51 mM; $\delta^{13}C_{DIC} = -3.65 \pm 0.44$ ‰) (Fig. 4.20a). However, the green colour saltpans (59.54 ± 21.80 mM) had lower DIC than the pink colour ones (477.96 ± 80.07 mM) during pre-monsoon. The concentrations of dissolved CO_2 in the lake (2.14 ± 1.57 µM) and the brine (2.67 ± 0.90 µM) were not significantly different. However, saltpans had the highest dissolved CO_2 with large variability during both post (134.45 ± 152.17 µM) and pre-monsoon (60.89 ± 33.20 µM). In saltpans, dissolved CO_2 was lower in the green ones (23.56 ± 9.78 µM) than the pink ones (85.77 ± 8.36 µM) during pre-monsoon (Fig. 4.20b).

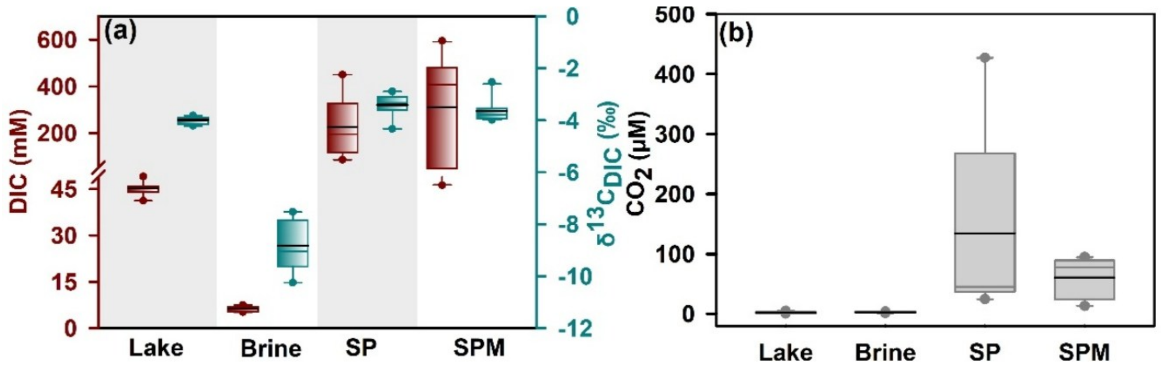


Fig. 4.20 Variation in (a) DIC concentrations (reddish) and $\delta^{13}C_{DIC}$ (greenish) and (b) dissolved CO_2 in different water bodies of the Sambhar Salt Lake. The black lines within the box represent the mean values. SP and SPM are for saltpans during post and pre-monsoon, respectively.

Dissolved inorganic nitrogen did not vary significantly amongst the three classes of water bodies (Fig. 4.21). NH_4^+ had the highest concentration with large variabilities across the study region during post-monsoon (lake = 77.60 ± 33.31 µM, brine = 43.12 ± 12.54 µM, and saltpans = 60.01 ± 24.96 µM). NOx did not show any significant difference across the three classes as well (lake = 2.60 ± 1.24 µM, brine = 2.59 ± 1.28 µM, and saltpans = 6.93 ± 3.52 µM) (Fig. 4.21). Except for two saltpans, NOx concentrations were below detection limit in all saltpans during pre-monsoon, whereas NH_4^+ varied from 0.82 to 29.33 µM with below detection limit in the three.

Significant differences in PO_4^{3-} and SiO_4^{4-} concentrations were observed in the study region. Average PO_4^{3-} concentrations were 10.35 ± 4.04 µM in the lake, 208.39 ± 11.10 µM in the brine, and 1122.78 ± 508.65 µM in the saltpans during post-monsoon (Fig. 4.22a). Average SiO_4^{4-} concentrations were 38.09 ± 7.94 µM in the lake, 336.97 ± 12.59 µM in the brine, and 183.33 ± 43.85 µM in the saltpans during the same season (Fig. 4.22b). No significant differences were observed in the PO_4^{3-} and SiO_4^{4-} concentrations in the saltpans between pre and post-monsoon. It was also observed that PO_4^{3-} and SiO_4^{4-} in the green colour saltpans (PO_4^{3-} = 55.20 ± 27.98 µM and SiO_4^{4-} = 100.06 ± 35.29 µM) were lower than the pink ones (PO_4^{3-} = 1131.16 ± 27.82 µM and SiO_4^{4-} = 385.46 ± 20.85 µM) during pre-monsoon. The inorganic N:P ratio was 8.91 ± 5.90 in the lake and less than 0.4 in the brine and saltpans.

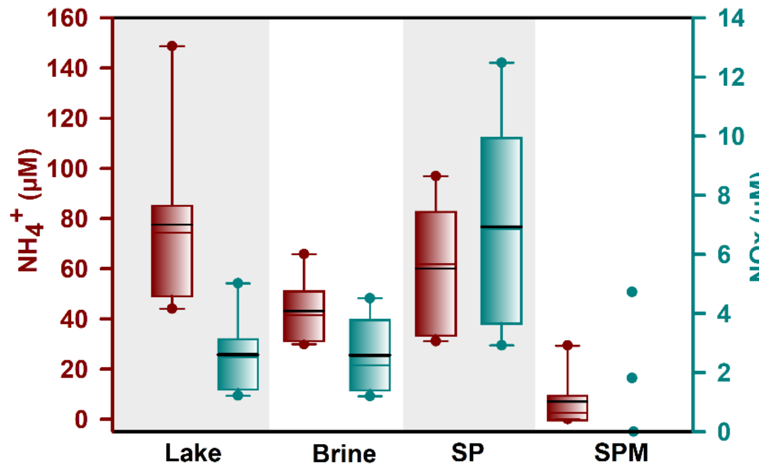


Fig. 4.21 Variation in dissolved inorganic nitrogen [NH_4^+ (reddish) and NOx (greenish)] concentrations in different water bodies of the Sambhar Salt Lake. SP and SPM are for saltpans during post and pre-monsoon, respectively. The black lines represent the mean values.

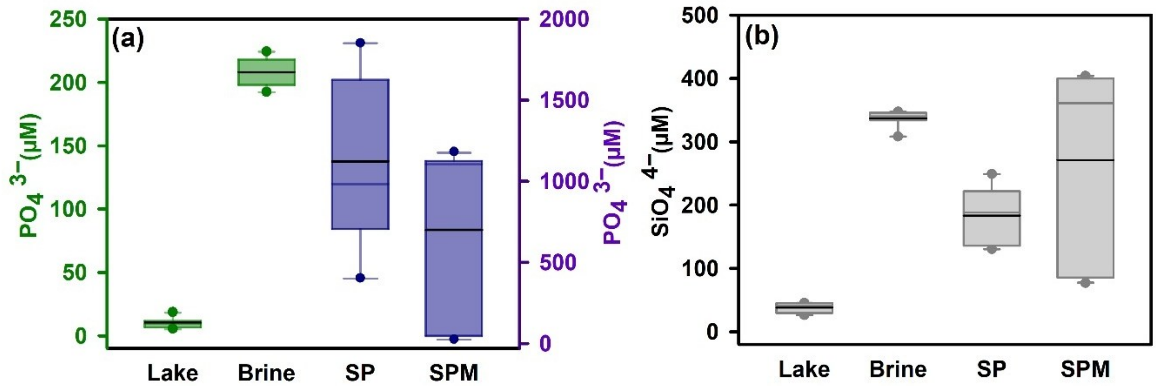


Fig. 4.22 Variation in (a) PO_4^{3-} and (b) SiO_4^{4-} concentrations in different water bodies of the Sambhar Salt Lake. The black lines represent the mean values. SP and SPM are for saltpans during post and pre-monsoon, respectively.

4.3.3.3. Particulate matter, primary production, and nitrogen assimilation

There was no significant difference in the POM concentrations between the lake (POC = 5.45 ± 2.27 mM and PON = 0.78 ± 0.33 mM) and brine (POC = 5.34 ± 0.54 mM and PON = 0.52 ± 0.06 mM) during post-monsoon (Fig. 4.23a). POM concentrations showed considerably large variation in the saltpans during both post (POC = 16.06 ± 19.13 mM and PON = 2.12 ± 2.07 mM) and pre-monsoon (POC = 14.01 ± 9.35 mM and PON = 2.37 ± 1.69 mM) (Fig. 4.23a). During pre-monsoon, the green colour saltpans showed lower POM (POC = 3.44 ± 2.50 mM and PON = 0.48 ± 0.32 mM) than the pink colour ones (POC = 21.05 ± 2.22 mM and PON = 3.63 ± 0.56 mM). The $\delta^{13}C_{POM}$ was significantly higher in the lake (−19.18 ± 0.56 ‰) than the brine (−23.28 ± 0.24 ‰) (Fig. 4.23b). $\delta^{13}C_{POM}$ in the saltpans did not exhibit any difference between seasons (post-monsoon = −24.08 ± 1.33 ‰

and pre-monsoon = −24.03 ± 2.19 ‰) and was similar to the brine (Fig. 4.23b). During pre-monsoon, saltpans with green colour water had lower $\delta^{13}C_{POM}$ (−26.40 ± 1.30 ‰) than the pink ones (−22.46 ± 0.41 ‰). The $\delta^{15}N_{POM}$ in the lake (−0.68 ± 0.39 ‰) and brine (0.39 ± 0.39 ‰) was not significantly different (Fig. 4.23b). However, significant difference in $\delta^{15}N_{POM}$ of the saltpans (4.59 ± 2.69 ‰) was observed compared to the lake and brine (Fig. 4.23b). The mean $\delta^{15}N_{POM}$ of the saltpans was 2.72 ± 1.99 ‰ during pre-monsoon, where the green colour saltpans showed lower $\delta^{15}N_{POM}$ (0.42 ± 0.31 ‰) than the pink colour saltpans (4.25 ± 0.21 ‰). There was a significant difference in the C:N ratio in the brine (10.46 ± 1.61) than the lake (7.08 ± 0.50) and saltpans (post-monsoon = 7.33 ± 1.29 and pre-monsoon = 6.36 ± 0.92).

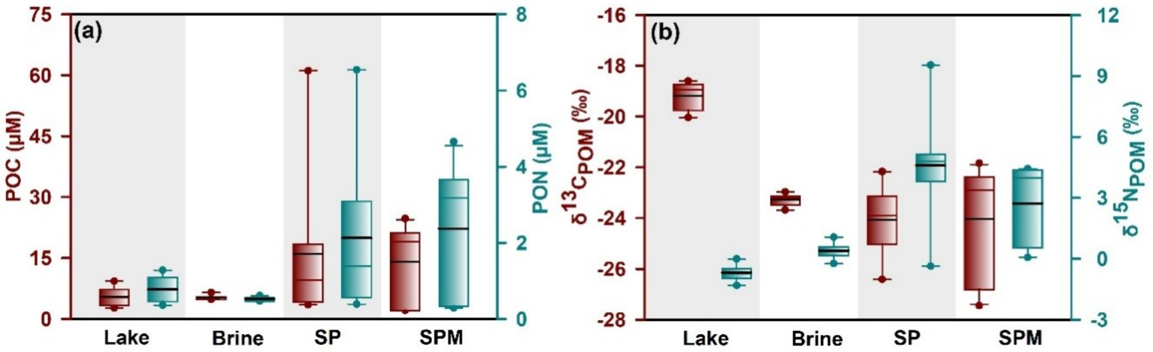


Fig. 4.23 Variation in (a) concentrations and (b) isotopic composition of particulate organic matter [POC (reddish) and PON (greenish)] in different water bodies of the Sambhar Salt Lake. SP and SPM are for saltpans during post and pre-monsoon, respectively. The black lines represent the mean values.

Phytoplankton primary production was significantly higher in the lake (273.16 ± 159.40 µM C h^{-1}) than the brine (66.79 ± 15.49 µM C h^{-1}) (Figs. 4.24a). PP in the saltpans was highly variable during post-monsoon (330.45 ± 423.97 µM C h^{-1}) than pre-monsoon (36.21 ± 23.03 µM C h^{-1}) (Fig. 4.24b). During post-monsoon, N_2 fixation rates were very high in the lake (575.70 ± 541.30 nM N h^{-1}) than the brine (2.32 ± 3.29 nM N h^{-1}) and saltpans (3.45 ± 7.07 nM N h^{-1}), where these rates were below detection limit at most locations (Fig 4.24 c and d). Within saltpans during pre-monsoon, N_2 fixation rates were quite high in the pink colour ones (207.89 ± 253.44 nM N h^{-1}) than the green ones (4.81 ± 4.97 nM N h^{-1}) with an average of 126.66 ± 218.21 nM N h^{-1}. It was below detection limit in two saltpans during pre-monsoon as well (Figs. 4.24 d). NH_4^+ assimilation rates in the lake (18.23 ± 7.58 µM N h^{-1}) and saltpans (15.44 ± 8.41 µM N h^{-1}) were significantly higher than the brine (9.14 ± 1.99 µM N h^{-1}) during post-monsoon (Figs. 4.24e and f). No significant difference was observed in NO_3^- assimilation rates in all three classes of water bodies during post-monsoon (brine = 0.52 ± 0.33 μM N h^{-1}, lake = 0.57 ± 0.17 μM N h^{-1}, saltpans = 1.18 ± 1.60 μM N h^{-1}; Figs. 4.24g and h). NH_4^+ assimilation (4.26 ± 1.85 μM N h^{-1}) and NO_3^- assimilation rates (0.28 ± 0.40 μM N h^{-1}) in the saltpans during pre-monsoon might have been overestimated due to higher addition of isotopic tracers. Despite this possibility, these rates were less than the rates in saltpans during post-monsoon (Figs. 4.24f and h).

4.3.4 Discussion

4.3.4.1 Dissolved inorganic carbon and nutrients cycling

All water bodies of SSL showed large variation in DIC concentrations due to their highly dynamic nature. The DIC concentrations were higher in the lake with increased $\delta^{13}C_{DIC}$ than the brine, which might be due to contributions from the catchment (Fig. 4.20a). Also, OM settled on the dried and desiccated lake surface during summer might get stirred up and remineralized in the lake during monsoon and post-monsoon, contributing to the DIC pool. The DIC released from pore water and sediment resuspension in shallow depth due to wind activity also contributes to the DIC pool. This DIC pool gets isotopically (^{13}C) enriched due to preferential uptake of ^{12}C during photosynthesis (as observed by high PP in the lake) and CO_2 outgassing at higher salinities, leading to higher $\delta^{13}C_{DIC}$ (Fig. 4.20a; Gu et al., 2004, 2006). With lower concentration and $\delta^{13}C_{DIC}$ than in lake and saltpans, a positive correlation between DIC concentration and $\delta^{13}C_{DIC}$ was observed in the brine (Figs. 4.20a and 4.25), which is due to carbonate precipitation (Alling et al., 2012). This decrease in $\delta^{13}C_{DIC}$ in the brine may also be due to terrestrial influence, as plants were observed along the periphery of the brine, which was absent near the lake. The highest DIC concentrations in the saltpans during both seasons might be due to evaporation along with groundwater DIC contributions. The $\delta^{13}C_{DIC}$ in the saltpans, which was similar to that of the lake, but higher than the brine, might be due to CO_2 outgassing at higher salinities. Kalff (2002) reported that saline lakes have significantly higher DIC concentrations compared to freshwater lakes, which was also observed here.

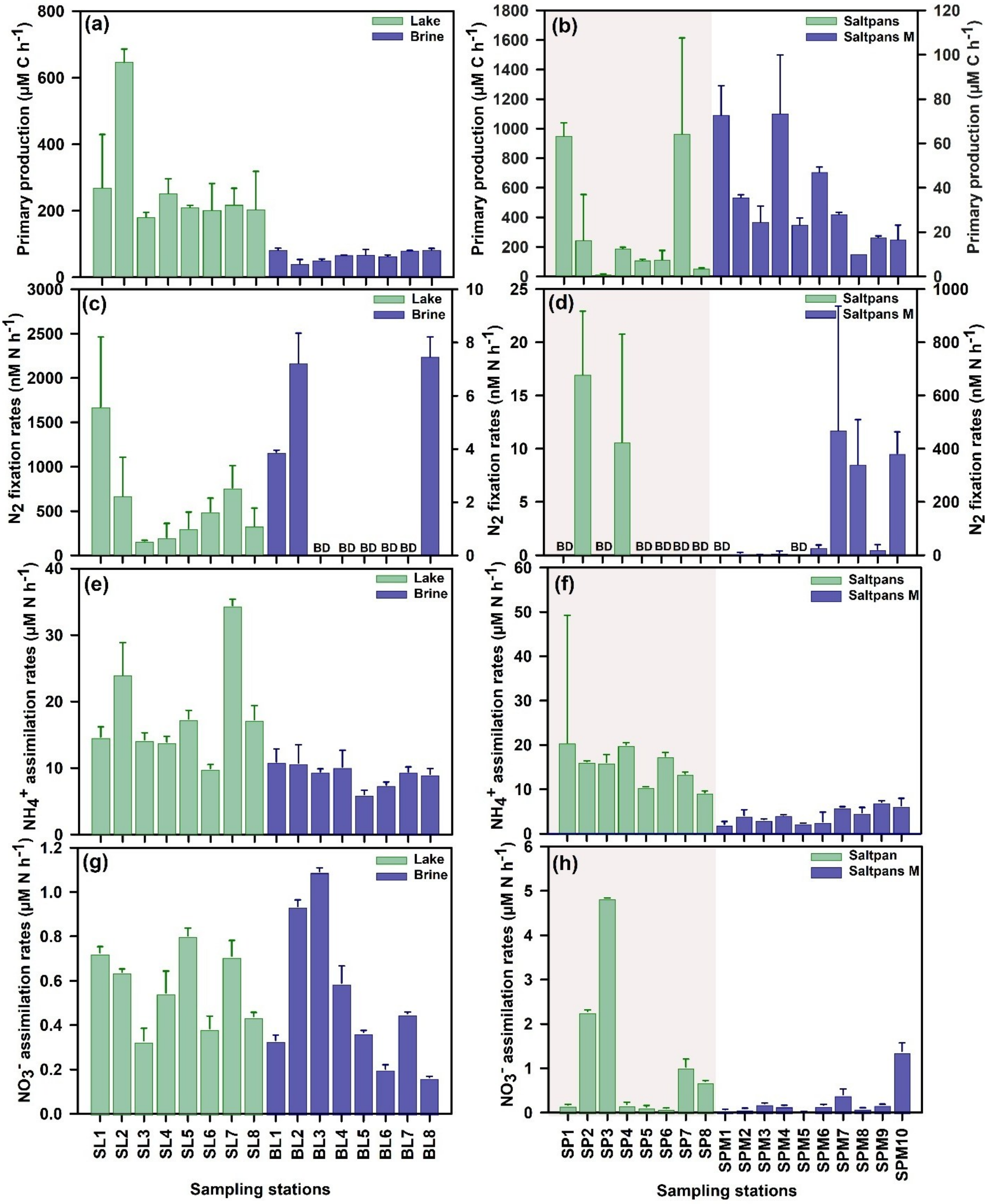


Fig. 4.24 Variation in the (a and b) primary production, (c and d) N_2 fixation rates, (e and f) NH_4^+ assimilation rates, and (g and h) NO_3^- assimilation rates in different water bodies of the Sambhar Salt Lake. Light pink and white shades in the right panel figures (b, d, f, and h) denote post and pre-monsoon, respectively, for the saltpans. The scale on the right y-axes (b, c, and d) is for the blue colour bar plots. Note the differences in the scales of the y-axes.

The dissolved CO_2 concentration in the lake and brine was less than the equilibrium concentration, which points towards their potential as CO_2 sink (Fig. 4.20b). Therefore, outgassing may have little role in modulating the DIC isotopic composition as postulated above. This aligns with other studies which advocate that saline lakes with pH > 9 act as CO_2 sink, while those with pH < 9 act as source to the atmosphere (Duarte et al., 2008). Dissolved CO_2 concentrations in the saltpans exceeded equilibrium levels, making them a potential source of CO_2 to the atmosphere. This is attributed to biological metabolism (lower PP), high DIC, and carbonate precipitation in salt-saturated conditions (McConnaughey et al., 1994; Barkan et al., 2001). Previously, one of the studies reported that increased aragonite precipitation and lower PP are responsible for CO_2 supersaturation in the Dead Sea (Barkan et al., 2001).

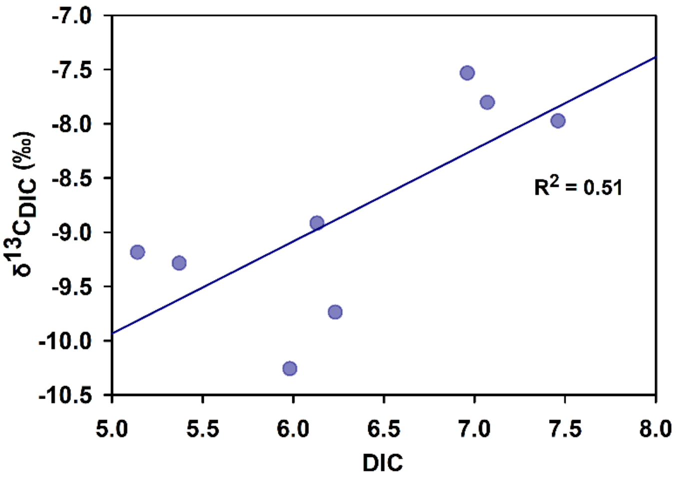


Fig. 4.25 Relationship between DIC and $\delta^{13}C_{DIC}$ in the brine reservoir.

Dissolved inorganic nitrogen concentration was high in all the water bodies during post-monsoon but was low during pre-monsoon in saltpans. NH_4^+ was the dominant species in the DIN pool, and NOx concentrations were very low in the studied region, as observed in other saline lakes (Fig. 4.21; Jellison et al., 1993; Sarkar et al., 2023). Lower NOx was due to the cessation of nitrification at higher salinities and pH (Kopprio et al., 2014; Sorokin et al., 2014). During monsoon, NO_3^- comes from watersheds due to fertilizers used in agriculture, and its rapid consumption along with excretion as NH_4^+ during the metabolism of organisms led to higher concentrations of NH_4^+. In saline lakes, PON recycling to NH_4^+, the DNRA process, and inhibition of nitrification/denitrification result in higher NH_4^+ accumulation (Priestley et al., 2022). The other causes for the suppression of nitrification might be photoinhibition, extreme energy cost, or the presence of bacteria that compete with nitrifiers for NH_4^+ in saline conditions (Guerrero & Jones, 1996; Oren, 1999). Higher

NH_4^+ in the lake than the brine might be due to the higher N_2 fixation rates contributing to this pool and efficient recycling of OM supported by higher biomass (Sorokin et al., 2014; Isaji et al., 2019). On the other hand, relatively less NH_4^+ concentrations in the brine and saltpans than the lake might be due to NH_4^+ assimilation by phytoplankton or consumption through another process (Fig. 4.21). The escape of ammonia (NH_3) at higher salinity and pH might also reduce NH_4^+ concentration in brine and saltpans (Doi et al., 2004; Isaji et al., 2019).

Phosphate concentrations were several folds higher in the brine and saltpans than in the lake due to enhanced PO_4^{3-} release from sediments at higher salinities (Fig. 4.22a). It might also result from water level reduction caused by evaporation and no outflow of water. PO_4^{3-} observed in the lake might be due to natural and anthropogenic inputs with runoff from the watershed during monsoon (Golubkov et al., 2007). Another reason for the extremely high PO_4^{3-} in the brine and saltpans might be related to a hypothesis that states that precipitation of calcium carbonate in hypersaline conditions causes low calcium concentrations, preventing apatite saturation. However, this hypothesis has not been proven by sedimentary calcium phases despite the positive correlation between DIC and PO_4^{3-} (Nathan & Sass, 1981). Relatively lower SiO_4^{4-} in the lake might be due to the presence of diatom species that consume SiO_4^{4-} and reduction in diatom diversity in saltpans and brine due to the nature of the system might have led to higher SiO_4^{4-} (Fig. 4.22b; Haynes & Hammer, 1978).

4.3.4.2 Phytoplankton primary production and nitrogen assimilation

Phytoplankton primary production in saline lakes is controlled by several factors such as temperature, salinity, nutrients, DIC, phytoplankton diversity, biomass, and zooplankton grazers (Hammer, 1981). PP was higher in the lake than the brine and saltpans, suggesting that higher salinity led to a reduction in PP (Figs. 4.24a and b). The PP estimates in this study are comparable to or higher than the rates previously reported from saline lakes around the world (Hammer, 1981 and references therein). PP was slightly higher in the saltpans than the brine, which can be attributed to relatively higher nutrient concentrations, especially nitrogen, to mitigate the negative effects of salinity on phytoplankton biomass and species to some extent (Watson et al., 1997; Larson & Belovsky, 2013). The reason for decreased PP at higher salinity might be due to reduction in species richness, as salinity is reported to be the main driver for taxonomic composition in saline lakes across the world (Horne & Goldman, 1994; Liu et al., 2016). There was no significant difference in the POM concentrations in the three water bodies indicating similar biomass, which suggests that difference in PP might be due to variation in species diversity (Fig. 4.23a; (Haynes & Hammer, 1978; Geddes et al., 1981; Golubkov et al., 2007). Low Chl a has been reported from saline lakes around the world, however, it might not be a good proxy for PP in saline environments (Campbell, 1978; Haynes & Hammer, 1978). The higher PP in the saltpans than the brine might be due to higher abundance of *Dunaliella salina* (Chlorophyte), which is the most found species in salt-saturated conditions (Oren, 2002, 2014). *Dunaliella salina* contains carotenoid pigments like β-carotene which gives green, pink, or orange colour to saltpans, as observed here (Fig. 4.18; Oren & Rodríguez-Valera, 2001; Oren, 2014). Pedrós-Alió et al. (2000) found that despite having *Dunaliella salina* in the crystallizer ponds (saltpans; >300 g/L), PP was below detection limit.

Enhanced PP with undersaturated CO_2 was observed in the lake and coincided with higher $\delta^{13}C_{POM}$ (Figs. 4.20b, 4.23b, and 4.24a). The CO_2 is utilized by the primary producer during photosynthesis, causing CO_2 reduction to the point where it could limit PP (Hein, 1997). This higher PP results in the supersaturation of DO in the lake (Sigee, 2004), which could be the case in the Sambhar Lake. Relatively higher $\delta^{13}C_{POM}$ in the lake than the brine and saltpans might be due to the active uptake of carbon with minor fractionation due to lower CO_2 or direct HCO_3^- uptake, which is heavier in ^{13}C than CO_2 (Fig. 4.23b; Zohary et al., 1994). Lower CO_2 concentration in the DIC pool due to enhanced uptake by phytoplankton led to increased pH in the lake as observed by a positive relation between PP and pH (Fig. 4.26; Hammer, 1981). The negative correlation of PP with DIC and a positive correlation between $\delta^{13}C_{POM}$ and $\delta^{13}C_{DIC}$ suggest that PP mainly controlled the DIC pool in the lake or vice-versa. Positive correlation of PO_4^{3-} with PP and POM suggests increase in PP due to PO_4^{3-} availability (Fig. 4.26).

The ε_{app} between the inorganic and organic carbon pool (~15 ‰) was same in the lake and brine, however, PP was lower in the brine. This lower PP might be due to less DIC and DIN in the brine. The ε_{app} was higher (~20 ‰) in the saltpans during both post and pre-monsoon periods, which showed the effect of higher DIC pool where phytoplankton could discriminate more against the heavier isotope resulting in lower $\delta^{13}C_{POM}$ compared to the lake (Fig. 4.23b; Rau et al., 1989). The C:N ratio (~7) in the lakes and saltpans suggests *in situ* OM production, whereas slightly higher C:N ratio in the brine (~10) may be due to some contribution from other sources of OM such as terrestrial-derived soil OM (Kendall et al., 2001). It was corroborated by relatively lower $\delta^{13}C_{DIC}$ with reduced PP in the brine, where uptake of DIC with lower $\delta^{13}C$ resulted in decreased $\delta^{13}C_{POM}$ (Figs. 4.20a and 4.23b). The PO_4^{3-} concentrations with POM and DIC were positively correlated in the saltpans, suggesting the effect of carbon cycling on PO_4^{3-}. Studies have reported that highly productive lakes are found mostly within the 3–50 mS cm^{-1} range of salinity (Haynes & Hammer, 1978; Hammer, 1981). The large variation observed in the POM concentrations in the saltpans coincided with salinities during both seasons (Fig. 4.23a). PP was less in the saltpans during pre-monsoon compared to post-monsoon (Fig. 4.24b), which might be due to several reasons: (i) the effect of dilution from groundwater as lake and brine were dried during pre-monsoon, (ii) nutrients were below detection limit and could not overcome salinity effect, (iii) POM concentrations were lower, and (iv) slow metabolic activity due to relatively lower temperature. During pre-monsoon, despite having significant differences in salinity, POM, $\delta^{13}C_{POM}$, DIC, CO_2, and SiO_4^{4-} between green colour and pink colour saltpans, no difference in PP was observed, which might be due to nitrogen limitation in both kinds of saltpans. More saline (pink) saltpans had higher concentrations of biogeochemical parameters than less saline ones (green) due to water evaporation and subsequent concentration.

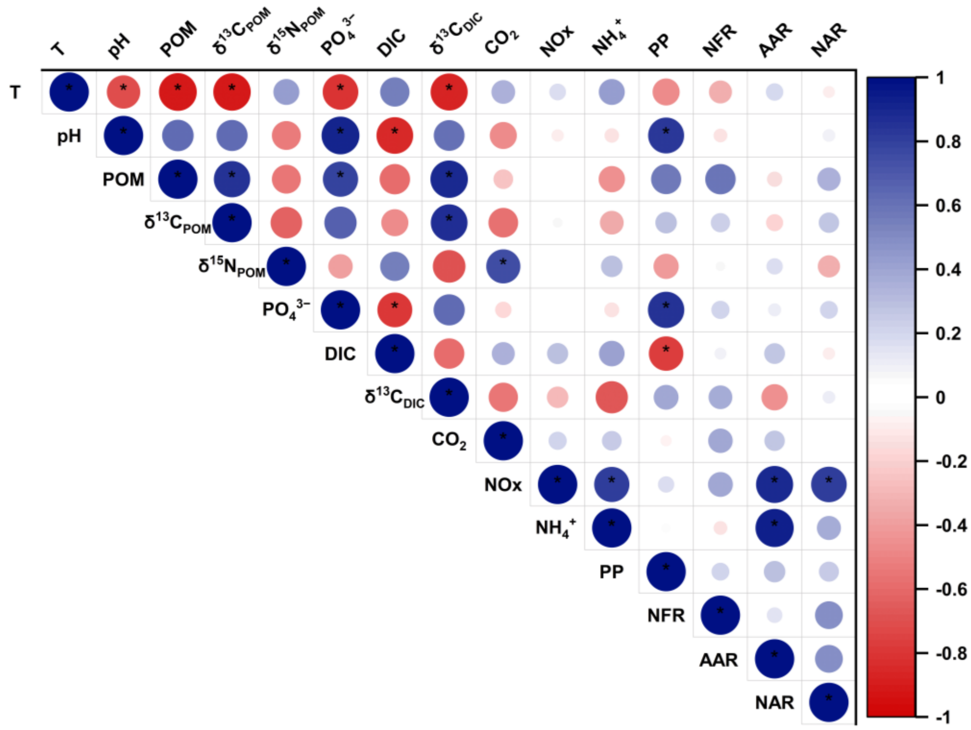


Fig. 4.26 Correlation plots (Pearson) between measured parameters in the lake. The star mark represents the significance level ($p < 0.05$). NFR = N_2 fixation rates, AAR = NH_4^+ assimilation rates, and NAR = NO_3^- assimilation rates.

The $\delta^{15}N_{POM}$ showed the signature of the presence of N_2 fixers (~ 0 ‰) in the lake and brine due to little or no fractionation during atmospheric N_2 (Air $\delta^{15}N$ = ~ 0 ‰) assimilation by biological communities (Fig. 4.23b). Here, several folds higher N_2 fixation rates with large variations were observed in the lake despite having higher DIN than the brine and saltpans (Figs. 4.24c and d). Lower PO_4^{3-} in the lake compared to saltpans and brine also points towards its consumption by N_2 fixers as the enzyme responsible for this process requires PO_4^{3-} (Fig. 4.22a). In saline lakes, abundant OM from PP is also known to support the extreme energy required by N_2 fixers (Isaji et al., 2019), which ultimately results in NH_4^+ accumulation after remineralization, as observed in the studied lake (Figs. 4.21 and 4.24).

N_2 fixation was reduced more than 50 times in the brine and saltpans than the lake, and it was below detection limit at most sites of the saltpans and brine (Figs. 4.24c and d). This large reduction in N_2 fixation rates in the brine and saltpans could be due to inhibition of nitrogenase enzyme biosynthesis due to high salinity in the presence of NH_4^+ (Herbst, 1998; Tripathi et al., 2002). Salinity is important for influencing phytoplankton biomass and distribution of taxonomic groups, most importantly N_2 fixing cyanobacteria (Williams, 1993b). Additionally, higher salinity can inhibit iron uptake by N_2 fixers and limit their ability (Evans & Prepas, 1996). The very low N:P ratio (< 0.4) in the brine and saltpan waters indicates nitrogen limitation for the phytoplankton in these environments despite having high DIN concentrations (Hayes et al., 2019; Haas et al., 2024). Blue-green algae, capable of N_2 fixation require relatively higher temperatures to thrive and are typically found in highly productive saline lakes with a salinity of less than 50 mS cm^{-1} (Hammer, 1981). The higher $\delta^{15}N_{POM}$ in the saltpans with higher NH_4^+ concentration in the DIN pool was due to evaporation and volatilization of NH_3 in high pH and salinity waters (Fig. 4.23b; Doi et al., 2004; Isaji et al., 2019). The PP in hypersaline conditions like brine and saltpans is supported by efficient recycling of NH_4^+ resulting from suppression of nitrification and nitrogen-loss processes. The NH_4^+ assimilation rates were significantly higher in the lake and saltpans than the brine, coinciding with NH_4^+ concentrations (Figs. 4.24e and f). Despite having lower PP in the brine and saltpans than the lake, no significant difference was observed in the NO_3^- assimilation rates in all classes suggesting it plays a vital role in brine and saltpans in supporting PP (Figs. 4.24g and h). Joint et al. (2002) reported that PP and nutrient assimilation rates decreased with high salinity despite having increased photosynthetic pigment concentrations. PP might be constrained by salinities, as high salinity and elevated ionic concentrations can inhibit nutrient uptake by algae (Caraco et al., 1993; Saros & Fritz, 2000). NH_4^+ was less in the brine than the lake and saltpans due to the suppression of N_2 fixation in that system and assimilation of NH_4^+ by primary producers. Similar NH_4^+ and NO_3^- assimilation rates in the lake and saltpans (but quite high N_2 fixation in the lake), indicate that PP in the saltpans largely depended on DIN uptake than N_2 fixation (Fig. 4.24). PP appeared to be dependent on NO_3^- in the brine, as a negative correlation was observed between these two. Lower PP in brine than the lake (~ 4-fold) with similar NO_3^- assimilation rates and lower NH_4^+ assimilation rates (~ 2-fold) also confirm the same (Fig. 4.24). The higher rates at lower salinities in the lake might be due to the influence of benthic activities, which might have been reduced at higher salinities in the brine and saltpans (Golubkov et al., 2007). A hard salt crust develops over sediments at higher salinities, reducing the effect of benthic activity in the water column (Joint et al., 2002). Ambient high concentrations of NH_4^+ and its higher assimilation rates compared to NO_3^-, suggested that apart from N_2 fixation, NH_4^+ was a major nutrient source to sustain PP in the lake.

The C:N assimilation ratio (PP or carbon uptake rates/NH_4^++NO_3^- assimilation rates) was different in the three classes of the SSL. There was a large variation in the C:N assimilation ratio in the lake and was higher than the brine and saltpans indicating relatively higher utilization of nitrogenous nutrients in supporting PP in the brine and saltpans. In general, C:N assimilation ratio was greater than the Redfield ratio in the study region (~ 6.6) indicating that, at instances, PP occurred when phytoplankton cells already had enough nitrogen for cell division (Joint et al., 2002). In saltpans during pre-monsoon, the C:N assimilation ratio was less than the Redfield ratio due to higher nutrient assimilation rates resulting in very low or below detection limit nutrient concentrations. In highly saline conditions, where osmotic stress is high, assimilation is favoured because it requires less energy (Joint et al., 2002).

4.3.5 Conclusion

Here, an attempt was made to understand the carbon (PP) and nitrogen assimilation (N_2 fixation, NH_4^+, and NO_3^- assimilation rates) in a saline lake and associated water bodies (saltpans and brine reservoir) ranging from saline to hypersaline conditions. The PP was the highest in the lake whose salinity was relatively lower than the brine and saltpans. Additionally, despite having high DIN concentrations, N_2 fixation rates in the lake were many folds higher than the brine and saltpans. NH_4^+ assimilation rates in the lake were significantly higher than the NO_3^- assimilation. Overall, the lake PP was largely sustained through the nitrogenous nutrient in the form of NH_4^+ and N_2 fixation. Lower PP and N_2 fixation in brine and saltpans than the lake clearly indicates the effect of salinity on microorganisms. N_2 fixation rates were inhibited by salinity and nutrients in the hypersaline conditions, whereas nutrient assimilation was relatively favoured due to less energy requirements.

4.4 Phytoplankton primary production in CO_2 supersaturated lacustrine ecosystems

Human activities in past decades have significantly increased the CO_2 concentrations in both the atmosphere and aquatic ecosystems around the world. This rise in CO_2 levels has resulted in the supersaturation of dissolved CO_2 in aquatic ecosystems such as lakes, rivers, estuaries, and coastal regions of the ocean, potentially altering the life of aquatic autotrophs (Cole et al., 1994; Raymond et al., 2013). This is one of the major issues faced by eutrophic systems where the partial pressure of CO_2 is higher than the atmosphere which might be due to external and internal sources. The main biogeochemical processes that can influence CO_2 in inland waters are microbial respiration, PP, and photochemical degradation of dissolved organic carbon (Tranvik, 1992; del Giorgio & Peters, 1994). The decomposition of OM received from terrestrial ecosystems and catchment soil weathering also leads to higher CO_2 in the inland waters (Hope et al., 1994). Studies have reported that an increase in dissolved CO_2 resulted in the enhancement of PP in aquatic ecosystems (Jansson et al., 2012; Liu et al., 2021). The changes in nutrient concentrations due to human influences also impacted these ecosystems, potentially changing the role of CO_2 (Bennett et al., 2001).

Phytoplankton primary production is calculated using the $H^{13}CO_3^-$ or $H^{14}CO_3^-$ isotope tracer technique in aquatic ecosystems worldwide (discussed in Chapter 2). In this method, it is assumed that phytoplankton utilize HCO_3^- for PP, which might not be the case all the time, particularly in CO_2 supersaturated ecosystems. The supersaturation of CO_2 in marine ecosystems may not affect PP as both species of DIC are equally preferred by marine organisms (Burkhardt et al., 2001). HCO_3^- assimilation might decrease when dissolved CO_2 is higher than the half-saturation constant for the Rubisco enzyme (70 µM) responsible for photosynthesis in autotrophs (Neven et al., 2011). In alkaline conditions, such as marine ecosystems, HCO_3^- ions typically dominate in the total DIC pool, where the dissolved CO_2 pool only contributes ~ 0.25–1.25 % (5–25 µM). Therefore, measurements for PP using HCO_3^- tracer may not lead to underestimation in marine ecosystems. However, this might not be the case for CO_2 supersaturated inland waters.

Dissolved CO_2 can vary from 1-80 % in the total DIC pool in the inland waters and estuaries, which might lead to increased CO_2 assimilation in these ecosystems (Bhavya et al., 2017). The influence of this supersaturated CO_2 on PP in inland waters is not properly understood. In inland waters, it has been reported that in HCO_3^- dominated ecosystems (pH = 6.35 to 10.33), some phytoplankton can utilize HCO_3^- for PP during higher growth rates, however, they may prefer dissolved CO_2 (Tortell et al., 1997; Alling et al., 2012). As marine autotrophs equally prefer HCO_3^- and CO_2, it is believed that phytoplankton might not be carbon-limited. However, studies have reported CO_2 limitation in some inland waters, where CO_2 was undersaturated, which might not be true for supersaturated systems (Zagarese et al., 2021). Autotrophs utilize a carbon concentration mechanism (CCM) for photosynthesis, where extracellular catalytic conversion of HCO_3^- to CO_2 takes place by carbonic anhydrase (CA) (Giordano et al., 2005). It is difficult to differentiate between HCO_3^- and CO_2 assimilation in the aquatic systems using the isotopic tracer technique as carbonate equilibria systems between different species of DIC are very dynamic, where the rate of conversion from one species to another species is very fast (Burkhardt et al., 2001). Thus, the assessment made here might only be taken as indicative. However, the use of tracers such as $H^{13}CO_3^-$ and $^{13}CO_2$ may provide some clues about the carbon assimilation in CO_2-supersaturated ecosystems. Most of the studies have focused on increasing CO_2 impact on PP, whereas the direct use of isotopic tracers of $^{13}CO_2$ and its comparison with $H^{13}CO_3^-$ assimilation has not been explored. To address this aspect, a series of experiments were conducted in inland waters (freshwater and saline lakes) using both $H^{13}CO_3^-$ (referred as $H^{13}CO_3^-$ assimilation rates, PP in the above sections) and $^{13}CO_2$ (referred as $^{13}CO_2$ assimilation rates).

4.4.1 Study area and sampling

Sampling for this experiment was conducted in the three lakes (Thol Lake, Nalsarovar Lake, and SSL) at similar locations and times mentioned in the above sections (Figs. 4.1, 4.8, and 4.17). For this experiment, in addition to the above experiments, two more bottles were spiked with $^{13}CO_2$ to observe its assimilation. The protocol for measurements of carbon assimilation rates is discussed in detail in Chapter 2. The below detection limit values were considered as zero.

4.4.2 Results

The $^{13}CO_2$ assimilation rates varied across all lacustrine ecosystems and seasons. In the Thol Lake, the $^{13}CO_2$ assimilation rates decreased from summer (168.07 ± 53.37 μM C h^{-1}) to monsoon (30.45 ± 15.55 μM C h^{-1}) (Fig. 4.27a). Whereas, in the Nalsarovar Lake, these rates increased from summer (0.55 ± 0.32 μM C h^{-1}) to monsoon (10.48 ± 2.64 μM C h^{-1}) and decreased again during winter (1.88 ± 1.08 μM C h^{-1}) (Fig. 4.27b). In SSL, $^{13}CO_2$ assimilation rates were higher in the lake (76.09 ± 43.43 μM C h^{-1}) and saltpans (42.84 ± 48.40 μM C h^{-1}) compared to the brine (9.40 ± 13.05 μM C h^{-1}) during post-monsoon. These rates were similar in the saltpans during post and pre-monsoon (72.41 ± 58.46 μM C h^{-1}) (Fig. 4.27c).

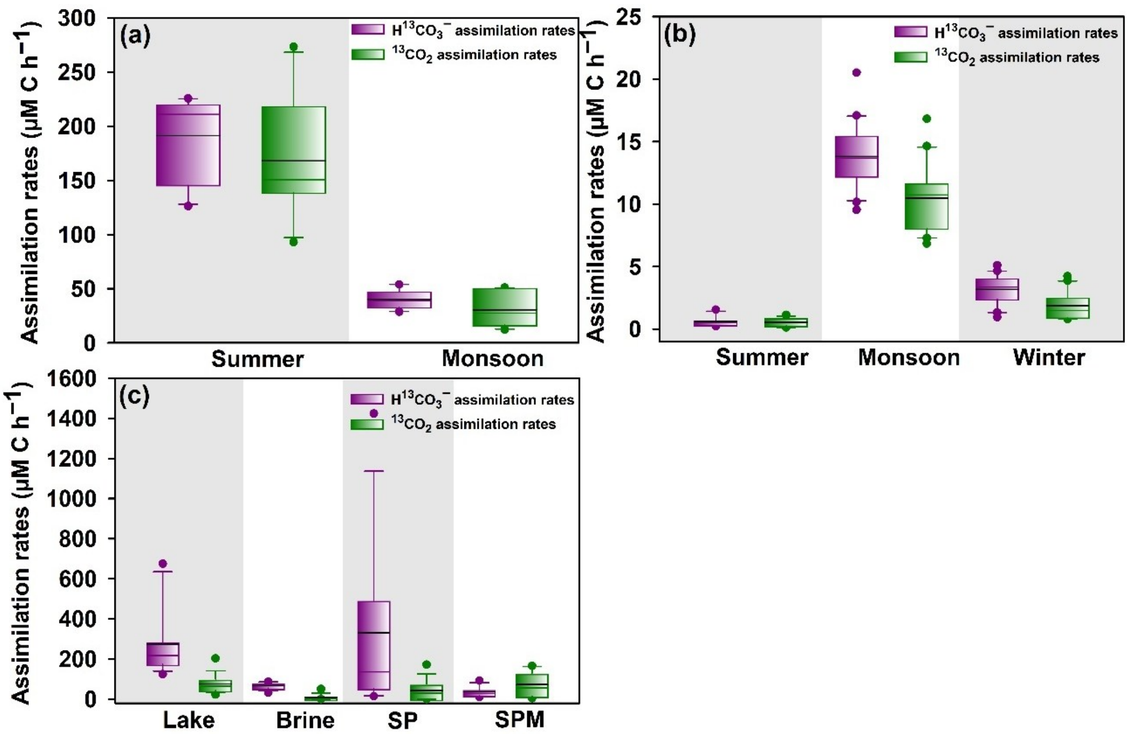


Fig. 4.27 Comparison of carbon assimilation using $H^{13}CO_3^-$ ($H^{13}CO_3^-$ assimilation rates; referred as PP in earlier sections) and $^{13}CO_2$ ($^{13}CO_2$ assimilation rates) in (a) Thol Lake, (b) Nalsarovar Lake, and (c) Sambhar Salt Lake. The black lines represent the mean values.

4.4.3 Discussion

Phytoplankton can disrupt the chemical equilibrium between DIC species either using CO_2 or HCO_3^- as carbon sources during photosynthesis. In this study, carbon assimilation was compared between rates measured using $H^{13}CO_3^-$ and $^{13}CO_2$ tracers. The results indicate no significant difference between $H^{13}CO_3^-$ and $^{13}CO_2$ assimilation rates in the Thol and Nalsarovar Lakes during different seasons (Figs. 4.27a and b). The dissolved CO_2 varied from 0.25–20.64 % in the total DIC pool of both lakes and was higher during monsoon than other seasons (Figs. 4.4b, 4.13, and 4.20b). In both lakes, CO_2 was supersaturated in all seasons except during summer in the Nalsarovar. Despite having CO_2 undersaturation during summer, rates using both tracers showed no significant difference, which might be due to the active uptake of both DIC species (HCO_3^- and CO_2). A significant difference was observed between $H^{13}CO_3^-$ and $^{13}CO_2$ assimilation rates in all water bodies of SSL during post-monsoon. The $H^{13}CO_3^-$ assimilation rates were higher than the $^{13}CO_2$ assimilation rates in the SSL. There was no significant seasonal difference between these rates in saltpans (Fig. 4.27c).

Sambhar Salt Lake is a (hyper)saline system that behaves differently from freshwater lakes (Thol and Nalsarovar) due to a very large pool of DIC. In SSL, DIC concentrations varied from ~ 5 to 590 mM, with the highest in the saltpans (Fig. 4.20a). Dissolved CO_2 concentrations were lower (< 0.1 %) in the total DIC pool in all water bodies of the SSL. The difference in rates might be related to the equilibration time between HCO_3^- and CO_2 in this large DIC pool of SSL. In eutrophic lakes, high CO_2 demand often leads to increased pH, shifting the major DIC pool from CO_2 dominance to isotopically heavier HCO_3^- (Lehmann et al., 2004). Another reason for the higher $H^{13}CO_3^-$ assimilation rates might be due to the undersaturation of CO_2 in the lake and the brine in the SSL, which acts as a potential sink of CO_2. It is believed that during periods of high productivity when CO_2 concentrations are lower, phytoplankton use HCO_3^- as an alternative carbon source (Tortell et al., 1997; Alling et al., 2012). Previous studies in semi-arid regions have highlighted cyanobacterial blooms resulting from drought-induced conditions for most of the year which are capable of utilizing HCO_3^- (Dantas et al., 2012). However, similar $H^{13}CO_3^-$ and $^{13}CO_2$ assimilation rates in saltpans during pre-monsoon, despite having < 0.1 % CO_2 in the DIC pool, suggested that different mechanisms/factors might be at play, such as phytoplankton community composition and environmental parameters. Despite having supersaturated CO_2, $^{13}CO_2$ assimilation rates were lower in the saltpans during post-monsoon, which could be due to phytoplankton species-specific preference for both inorganic carbon species.

Algae can preferentially uptake any species of inorganic carbon during photosynthesis, which depends on growth conditions; for example, *Dunaleilla tertiolecta* (saline environment species) prefers HCO_3^- regardless of CO_2 concentrations, whereas *Chlamydomonas reingardtii* (freshwater species) prefers CO_2 (Amoroso et al., 1998). In low-alkaline soft lakes, PP can be carbon-limited due to near-surface CO_2 depletion because of phytoplankton demand which reduces inward CO_2 fluxes (Kragh & Sand-Jensen, 2018; Zagarese et al., 2021). However, no carbon limitation for phytoplankton in high-alkaline hard water lakes with undersaturated CO_2 has been observed, which is due to a higher DIC pool (Kragh & Sand-Jensen, 2018). Generally, in alkaline lakes, such as SSL, the HCO_3^- dominates the DIC pool, which is difficult to utilize by phytoplankton (Stumm & Morgan, 1981). Chemical enhancement increases CO_2 in these systems and the carbonate buffering effect causes CO_2 to hydrate and deprotonate quickly into HCO_3^-. Thus, phytoplankton cannot directly receive CO_2 in these alkaline lakes through chemical enhancement (Bade & Cole, 2006). The phytoplankton inhabiting these lakes have evolved their strategies to utilize HCO_3^- in low CO_2 conditions for PP, which indicates a lack of CO_2 limitation (Price et al., 2008; Li et al., 2018). Calcium carbonate precipitation also releases CO_2 that happens near the algae membrane and can be another carbon source for PP (Kelts & Hsü, 1978). These mechanisms suggest that PP may not be carbon-limited in lacustrine ecosystems (Li et al., 2018).

Phytoplankton species can assimilate CO_2 through passive diffusion into the cell saving a significant amount of energy, however, it can efficiently seep out of the cells as well. An enzyme CA helps resolve this difficulty by fast conversion of transferred CO_2 to HCO_3^- (which is less diffusive than CO_2) and vice versa (Giordano et al., 2005). This process is known as the CCM, which improves Rubisco enzyme activity. Therefore, CO_2 may be the best form of DIC for cellular digestion, while HCO_3^- form aids in limiting outward leakage (Tortell et al., 1997). Few specific cyanobacteria and algae are capable of an active HCO_3^- uptake mechanism (Amoroso et al., 1998; Li et al., 2018). During low CO_2 concentrations, CA activity increases and results in active HCO_3^- uptake by phytoplankton for their carbon source. High affinity for inorganic carbon transport is found in cells in low CO_2 environments, whereas low affinity is present in cells cultured at higher CO_2 (Omata et al., 1999). Some algae preferentially utilize CO_2, however, they can assimilate HCO_3^- to meet their remaining requirement if CO_2 is insufficient (Giordano et al., 2005).

4.4.4 Conclusion

An exploratory study to understand the carbon assimilation in CO_2 supersaturated lacustrine ecosystems (freshwater and saline) was taken up using the isotopic tracers of different DIC species ($H^{13}CO_3^-$ and $^{13}CO_2$). Due to the fast equilibration between DIC species, it was not possible to differentiate between HCO_3^- and CO_2 assimilation clearly.

However, the results indicated that despite CO_2 supersaturation (dissolved CO_2 up to 20 % of total DIC pool), the carbon assimilation in freshwater systems (Thol and Nalsarovar) was similar for both $H^{13}CO_3^-$ and $^{13}CO_2$ additions. In the saline lake, carbon assimilation in experiments where HCO_3^- was added was significantly higher than the CO_2 added ones. It is important to note that dissolved CO_2 in the saline system was < 0.1 % of the total DIC pool. It is also possible that the added tracer was quickly converted into HCO_3^- via hydration and deprotonation.

Chapter 5

Riverine Ecosystem

Rivers were once considered merely conduits for transferring material with water, such as sediments, OM, nutrients, and organisms from land to the ocean. However, recent studies emphasize the importance of rivers for processing, storing, and moving carbon and nitrogen from terrestrial to marine ecosystems (Cole et al., 2007; Xia et al., 2018). These ecosystems have recently been included in the global budgets and Earth system models of carbon and nitrogen and are gaining increased attention (Nakayama, 2017). Riverine ecosystems across the world face various threats, including anthropogenic disturbances (such as changes in flow regimes and agricultural practices) and climate change (such as rising global temperatures, greenhouse gases, and changes in precipitation patterns). Even without climate change, human modifications to flow regimes, such as the construction of dams for water supply, hydropower, and flood control, are widespread and have fragmented major rivers globally (Nilsson et al., 2005; Vörösmarty et al., 2010). Nearly 63% of rivers longer than 1,000 km in length are no longer free-flowing, with only 23% maintaining a continuous flow to the ocean, highlighting significant global connectivity issues for rivers (Grill et al., 2019). These alterations significantly affect hydrological, biogeochemical, and ecological processes and functions, leading to a decline in biodiversity (Dudgeon et al., 2006; Vörösmarty et al., 2010). Additionally, tropical rivers are known to be source of CO_2 to the atmosphere.

In this chapter, the first section explores the effect of damming on PP and N_2 fixation rates in a tropical river continuum situated in a semi-arid climatic setting. The second section focuses on the influence of CO_2 supersaturation on carbon assimilation from the methodological perspective.

5.1 Effect of damming on PP and N_2 fixation in the riverine ecosystem

The riverine ecosystems worldwide face the major issue of discontinuation in the river flow continuum through damming, which impacts the biogeochemical cycle of carbon and nitrogen. Dammed reservoirs intensify nutrient transformation and removal by disrupting the movement of nutrients along river networks and affecting the terrestrial and coastal habitats downstream (Harrison et al., 2009; Maavara et al., 2020). It has long been hypothesized that increased water residence time and reduced turbulence in reservoirs might promote large standing stocks of primary producers, leading to increased PP (Baxter, 1977). PP plays an important role in transferring carbon from inorganic form to organic form using nutrients and sunlight, ultimately impacting the biological pump. A higher amount of fixed nitrogen is needed to support this higher PP in the reservoirs, which can be supplied through the N_2 fixation process (Akbarzadeh et al., 2019). The calm water and removal of nitrogen through denitrification and its burial in sediments within reservoirs facilitate the in-reservoir nitrogen cycle and create favourable conditions for N_2 fixation, which adds new nitrogen (Harrison et al., 2009; Cook et al., 2010). Although N_2 fixation is rarely considered in the budget of nitrogen cycle fluxes and has been neglected, it can be a dominant flux of new nitrogen, contributing up to 82 % to support the aquatic microorganisms (Howarth et al., 1988). However, neglecting N_2 fixation can undervalue the effectiveness of nitrogen removal, especially in limited reservoirs, as it provides fresh nitrogen to reservoirs. Global reservoir PP and N_2 fixation is expected to change with increased hydropower constructions in developing nations (Winemiller et al., 2016). PP and N_2 fixation in terrestrial and marine ecosystems are known to some extent, however, the underlying mechanism for these processes in riverine ecosystems is poorly understood, especially the effect of damming on these processes. The contribution of these processes to global riverine (and reservoir) carbon and nitrogen budgets is not well quantified due to the lack of data or estimates. With the existing level of information, it is challenging to evaluate the overall significance of PP and N_2 fixation in streams and reservoirs. Most of the work related to PP and N_2 fixation has been done in temperate regions, where low-order streams have the most concrete measures (Marcarelli et al., 2008; Welter et al., 2015), which reflects geographic and ecosystem bias in our understanding of processing. Therefore, more comprehensive measurements and analysis would be beneficial to our current understanding with a focus on tropical and subtropical regions, as large rivers dominate in these regions. This study explores the effect of changes in the flow regime of rivers or damming on the PP and N_2 fixation rates on a perennial river of western India (the Mahi River). The hypotheses of the study were (i) the change in flow regime from flowing streams to reservoirs (stagnant waters) would increase PP with higher biomass, and (ii) to support this enhanced PP in the reservoirs, N_2 fixation rates would be higher than the flowing stream waters.

5.1.1 Study Area

Mahi River is the third major river, with a length of 583 km and a drainage area of 34,843 km^2, draining into the Arabian Sea and flowing through the semi-arid regions of India (Fig. 5.1). Mahi River originates from Mahi Kanta hills of the Vindhyan mountain ranges present in the state of Madhya Pradesh. The river holds significant importance by supporting the irrigation and domestic needs of the regional population and transporting loads to the Arabian Sea. The Mahi River has two large dam reservoirs in its continuum [Mahisagar Bajaj Dam Reservoir (MBR) and Kadana Dam Reservoir (KR)], which support riverine discharge during summer. The watershed land use is mainly dominated by forest, agriculture, water bodies, wasteland, and grasslands. The geology in the catchment is mainly rocks of the Vindhyan groups, Deccan traps, Debari and Dilwara groups of the Aravalli supergroup, ultramafic, and quaternary alluvial plains (Sharma et al., 2013).

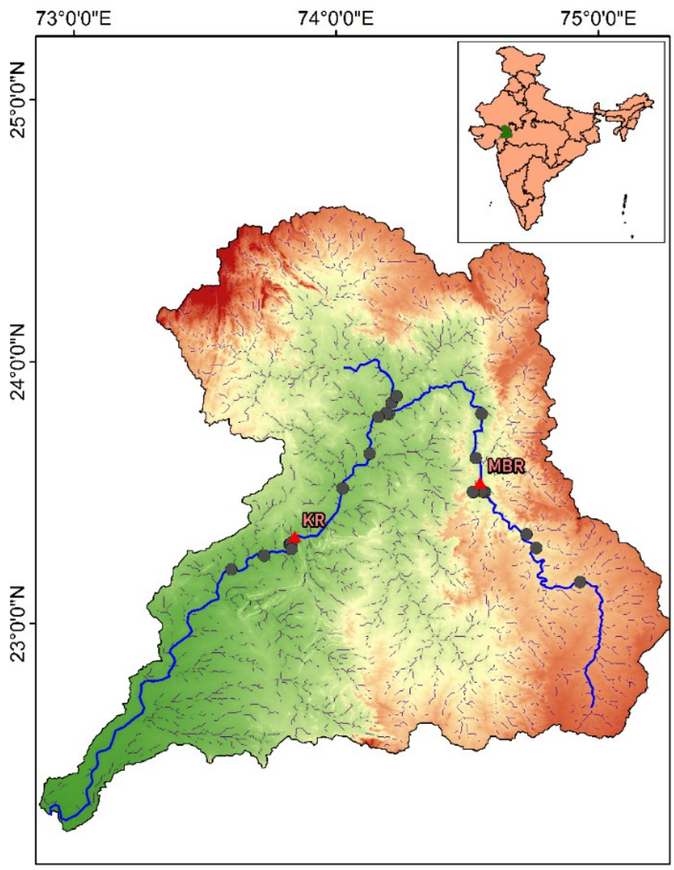


Fig. 5.1 Study area and sampling locations (grey circles) in the Mahi River basin. The blue line represents the mainstem, and the red triangles represent the location of the dammed reservoirs (Mahi Bajaj Sagar Dam and Kadana Dam) in the Mahi River.

5.1.2 Sampling

To address the above objective, the sampling was conducted in the Mahi River during high flow season (October 2023; Fig. 5.1). The samples were collected from 24 locations, with 3 from a tributary and 21 along the main river channel. The samples were taken from the middle of the stream accessed from a road bridge using a bucket. The samples were divided into the following classes: (i) upstream (US; n = 3), (ii) MBR (n = 5), (iii) midstream (MS; n = 6), (iv) KR (n = 4), (v) downstream (DS; n = 3), and (vi) Som tributary (T; n = 3) (Fig. 5.2). A detailed description of the sampling protocol for each parameter, experiments conducted for PP and N_2 fixation rate measurements, and analysis are discussed in Chapter 2.

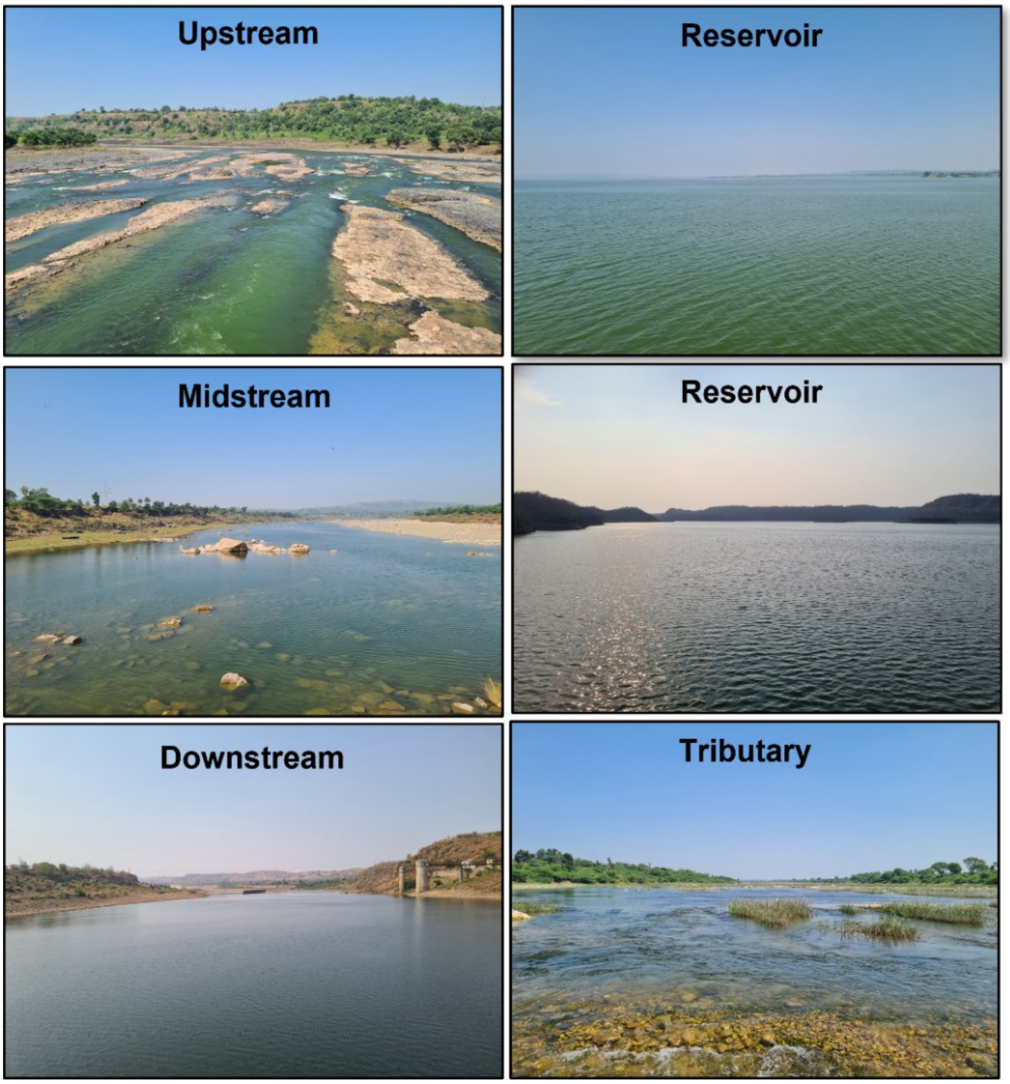


Fig. 5.2 Field photographs of different classes sampled in the Mahi River continuum.

5.1.3 Results

5.1.3.1 Environmental Parameters

The environmental parameters varied along the Mahi River continuum. The water temperature was the lowest in the downstream (28.23 ± 0.50 °C) and the highest in the Som tributary (31.1 ± 0.1 °C), which was similar to all other classes (30.03 ± 0.96 °C) (Fig. 5.3a). The EC was the lowest in the reservoirs (KR = 0.26 ± 0.01 mS cm^{-1} and KBR = 0.29 ± 0.01 mS cm^{-1}) and highest in the Som tributary (0.55 ± 0.01 mS cm^{-1}). The EC was also slightly higher in the mainstem water (upstream = 0.44 ± 0.04 mS cm^{-1}, midstream = 0.43 ± 0.07 mS cm^{-1}, and downstream = 0.32 ± 0.02 mS cm^{-1}) than the reservoirs (Fig. 5.3a).

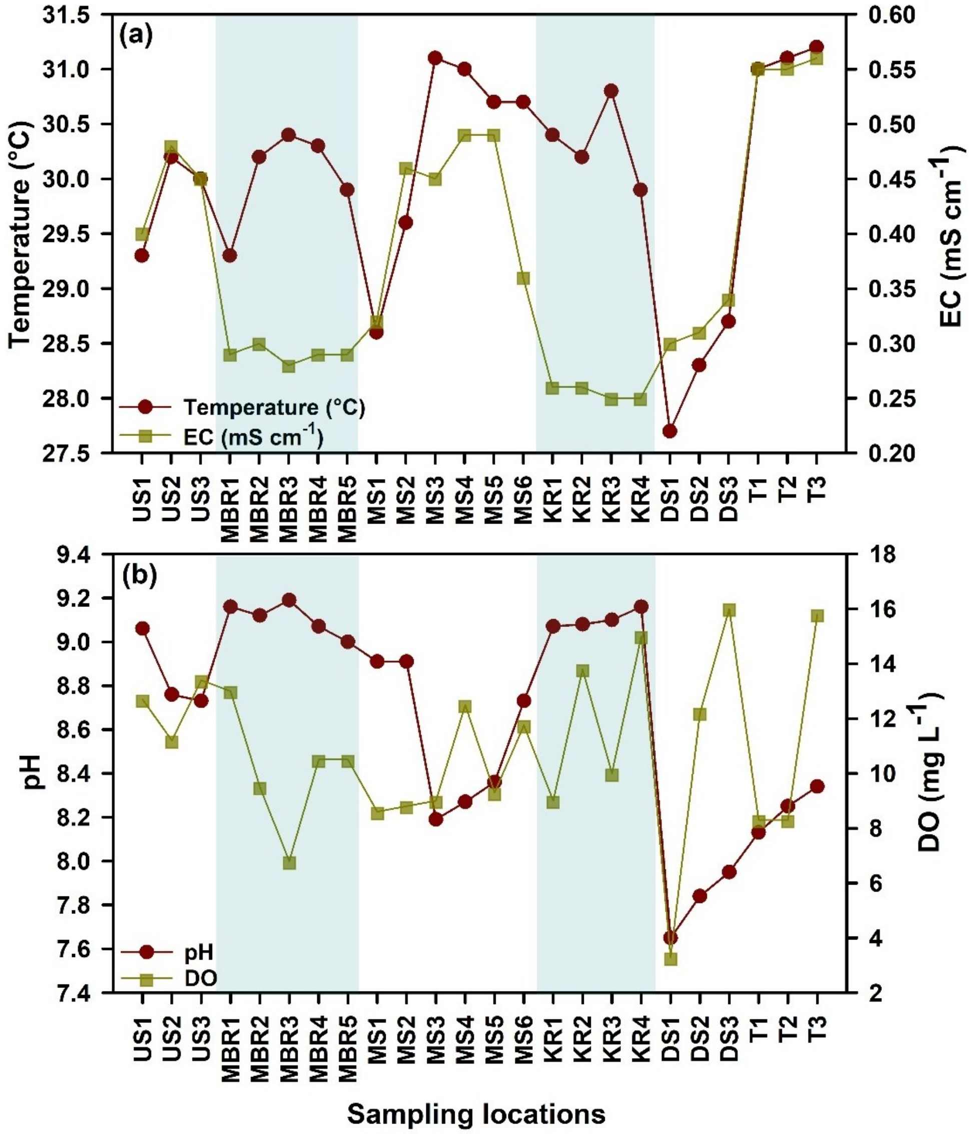


Fig. 5.3 (a) Temperature and EC and (b) pH and DO in different classes of the Mahi River continuum. The light greenish shaded areas represent the reservoirs.

The pH was similar in the upstream (8.85 ± 0.18), midstream (8.56 ± 0.33), and Som tributary (8.24 ± 0.11) and increased when flowing water entered reservoirs. The lowest pH was observed in downstream of the river (7.81 ± 0.15) and was the highest in reservoirs (MBR = 9.11 ± 0.08 and KR = 9.10 ± 0.04). The river water was alkaline throughout the continuum (Fig. 5.3b). The water in the river continuum was oxygenated throughout (10.80 ± 2.98 mg L^{-1}) with no significant difference in DO among different classes (Fig. 5.3b). The total suspended matter (TSM) concentrations were different in all the classes and decreased from reservoirs to flowing streams (upstream = 6.93 ± 1.29 mg L^{-1}, MBR = 7.02 ± 0.73 mg L^{-1}, midstream = 4.08 ± 1.75 mg L^{-1}, KR = 9.67 ± 2.21 mg L^{-1}, downstream = 2.57 ± 0.93 mg L^{-1}, and Som tributary = 1.87 ± 1.36 mg L^{-1}).

5.1.3.2 Dissolved inorganic carbon

Dissolved inorganic carbon showed variation in concentrations along the continuum with changes in $\delta^{13}C_{DIC}$ (Fig. 5.4). The DIC concentration varied from the lowest 1.60 ± 0.08 mM in the KR to the highest 4.01 ± 0.21 mM in the Som tributary. The $\delta^{13}C_{DIC}$ ranged from –5.61 ± 0.23 ‰ in the KR to –10.96 ± 0.42 ‰ in the downstream of the river course.

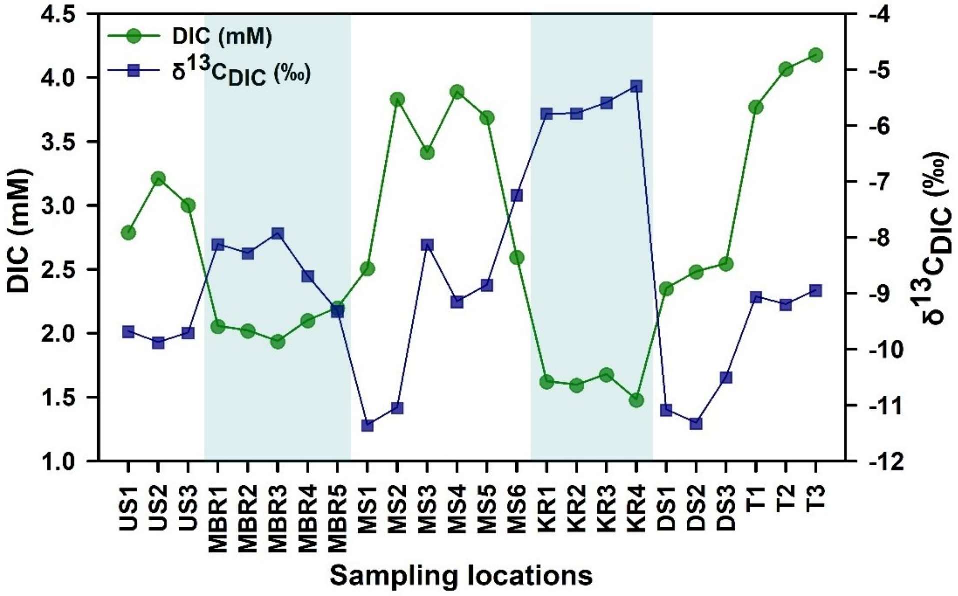


Fig. 5.4 Dissolved inorganic carbon concentration and its isotopic composition in different classes of the Mahi River continuum. The light greenish shaded areas represent the reservoirs.

The DIC concentration was higher in the upstream with low $\delta^{13}C_{DIC}$ (DIC = 3.00 ± 0.21 mM and $\delta^{13}C_{DIC}$ = –9.75 ± 0.11 ‰), which decreased with slight increment in $\delta^{13}C_{DIC}$ in the MBR (DIC = 2.06 ± 0.10 mM and $\delta^{13}C_{DIC}$ = –8.46 ± 0.55 ‰). There were no significant differences in DIC concentrations and $\delta^{13}C_{DIC}$ between midstream (DIC = 3.32 ± 0.62 mM and $\delta^{13}C_{DIC}$ = –9.29 ± 1.62 ‰) and Som tributary (DIC = 4.01 ± 0.21 mM and $\delta^{13}C_{DIC}$ = –9.06 ± 0.13 ‰). DIC concentrations increased again from KR to downstream (DIC = 2.46 ± 0.10 mM) (Fig. 5.4).

Dissolved CO_2 concentrations were high, and the river water was CO_2 supersaturated along the whole continuum. Dissolved CO_2 concentrations ranged from 495.57 ± 57.86 µM in the KR to 820.61 ± 143.75 µM in the Som tributary, with mean concentrations of 646.17 ± 159.83 µM among all classes. No significant difference was observed in the dissolved CO_2 concentrations among different classes (Fig. 5.5).

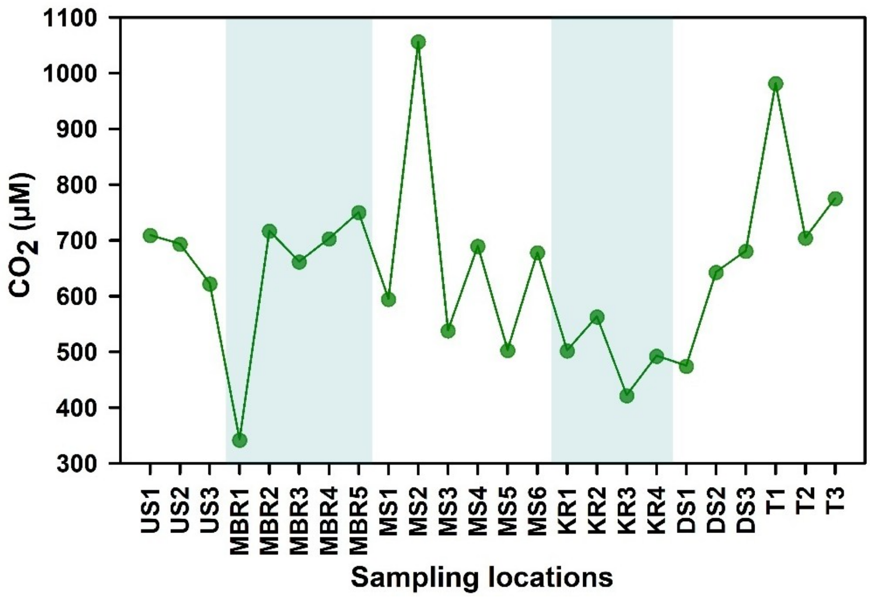


Fig. 5.5 Dissolved carbon dioxide concentrations in different classes of the Mahi River continuum. The light greenish shaded areas represent the reservoirs.

5.1.3.3 Phytoplankton primary production and N_2 fixation rates

Phytoplankton primary production was the lowest in the Som tributary (0.13 ± 0.02 µM C h^{-1}) to the highest in the MBR (5.14 ± 1.48 µM C h^{-1}). The average PP was comparable between the upstream (4.07 ± 1.56 µM C h^{-1}) and MBR. PP was higher in the KR (2.49 ± 0.57 µM C h^{-1}) compared to the midstream (0.71 ± 0.60 µM C h^{-1}) and downstream (1.03 ± 0.74 µM C h^{-1}) (Fig. 5.6a). N_2 fixation rates were below detection limit at most sites and varied from below detection limit to 3.63 ± 1.01 nM N h^{-1} along the river course. There was no significant difference in N_2 fixation rates between reservoirs and flowing streams (Fig. 5.6b).

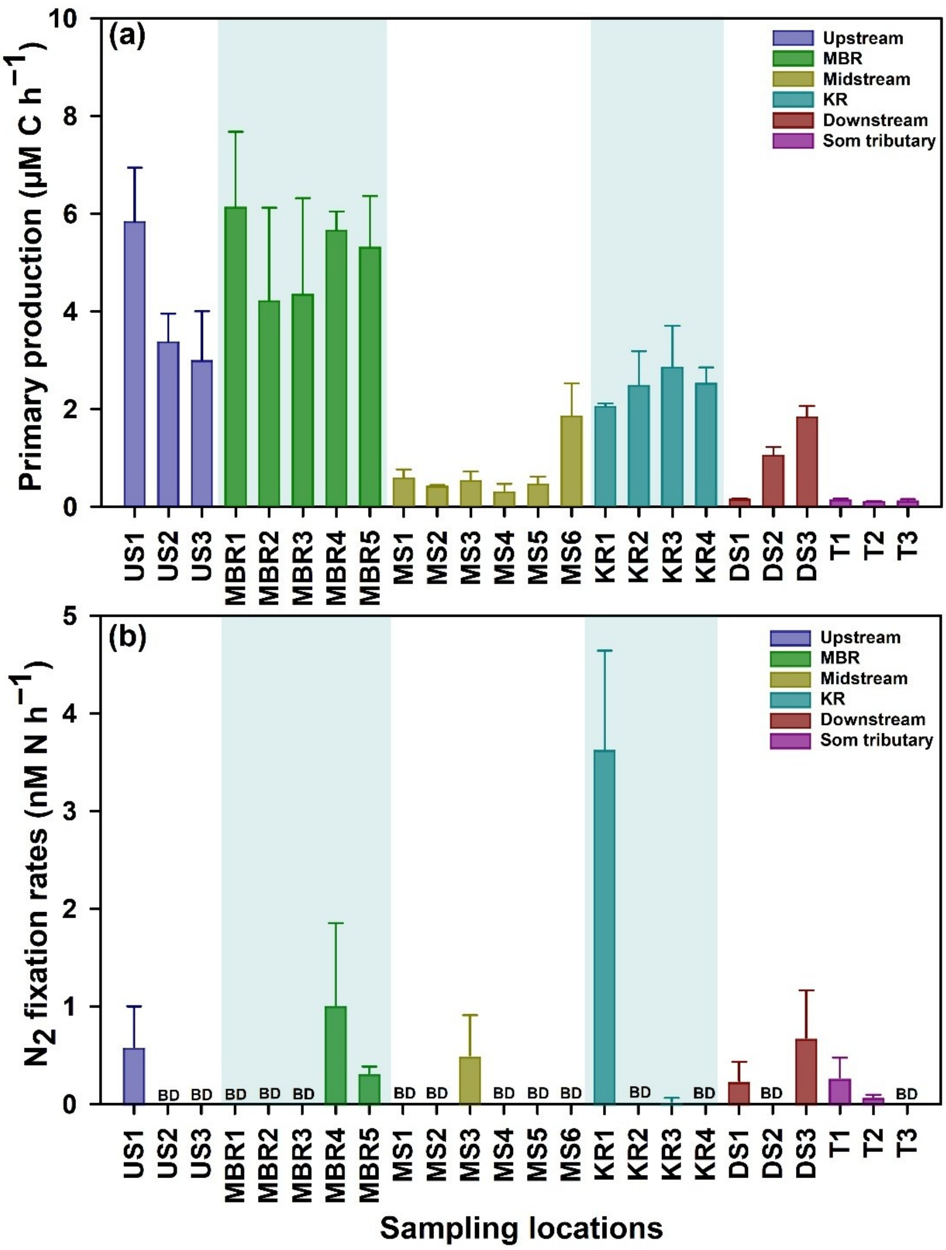


Fig. 5.6 (a) Primary production and (b) N_2 fixation rates in different classes of the Mahi River continuum. The light greenish shaded areas represent the reservoirs, and BD stands for below detection limit.

The concentrations of POM were higher in the reservoirs [MBR (POC = 213.56 ± 20.56 μM and PON = 32.01 ± 3.82 μM) and KR (POC = 299.65 ± 30.75 μM and PON = 46.22 ± 2.59 μM)] compared to the other stream classes [upstream (POC = 185.32 ± 35.07 μM and PON = 22.43 ± 1.58 μM), midstream (POC = 92.36 ± 49.99 μM and PON = 13.53 ± 8.10 μM), Som tributary (POC = 29.72 ± 3.99 μM and PON = 2.90 ± 0.41 μM), and downstream (POC = 44.50 ± 10.92 μM and PON = 7.22 ± 2.35 μM)] in the Mahi River (Fig. 5.7a). $\delta^{13}C_{POM}$ was the highest in the Som tributary (–27.09 ± 0.21 ‰) and KR (–27.67 ± 0.40 ‰) compared to other sample classes [upstream (–33.33 ± 0.71 ‰), MBR (–

31.62 ± 0.50 ‰), midstream (–32.71 ± 1.26 ‰), and downstream (–30.87 ± 2.66 ‰)]. The average $\delta^{15}N_{POM}$ in the Som tributary of the river was 6.06 ± 1.93 ‰. $\delta^{15}N_{POM}$ increased from upstream to downstream along the continuum (upstream = 3.53 ± 0.50 ‰, MBR = 3.84 ± 1.11 ‰, midstream = 5.28 ± 0.94 ‰, KR = 5.90 ± 0.49 ‰, and downstream = 6.75 ± 1.72 ‰) (Fig. 5.7b).

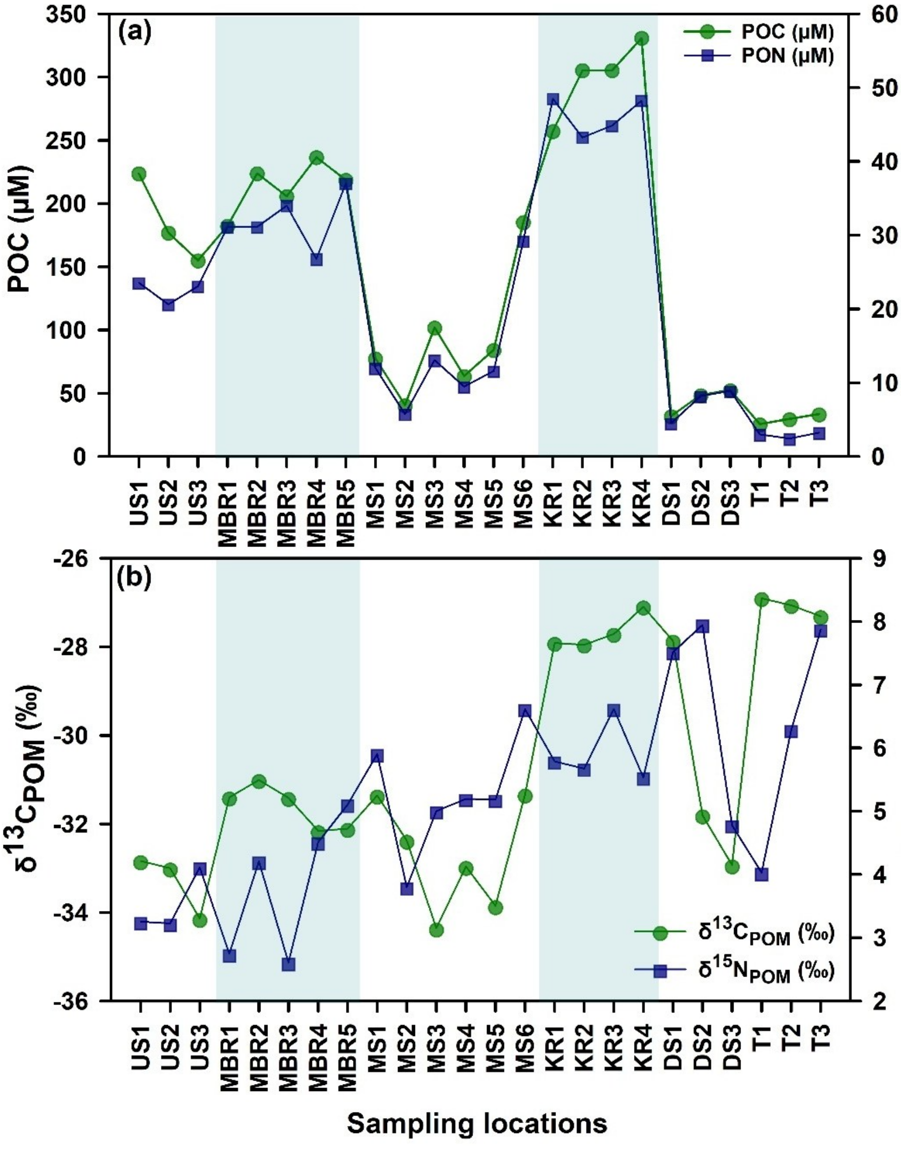


Fig. 5.7 Particulate organic matter (a) concentrations (POC and PON) and (b) isotopic compositions ($\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$) in different classes of the Mahi River continuum. The light greenish shaded areas represent the reservoirs.

The C:N ratio was slightly higher in the tributary (10.35 ± 1.81) than in other classes, which have similar C:N ratios (upstream = 8.27 ± 1.42, MBR = 6.77 ± 1.28, midstream = 6.95 ± 0.55, KR = 6.51 ± 0.81, and downstream = 6.31 ± 0.67) (Fig. 5.8).

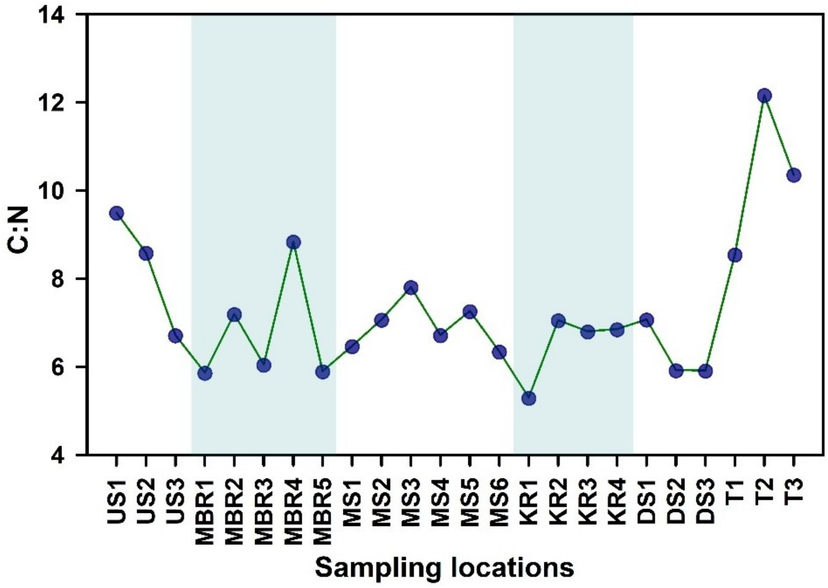


Fig. 5.8 Particulate organic matter C:N ratio in different classes of the Mahi River continuum. The light greenish shaded areas represent the reservoirs.

5.1.4. Discussion

5.1.4.1 Dissolved inorganic carbon dynamics

Dissolved inorganic carbon concentrations and $\delta^{13}C_{DIC}$ can be affected by several processes along the river continuum. The higher DIC concentrations in the Som tributary, upstream, and midstream flowing water might be due to higher rock weathering contribution from the drainage basin (Fig. 5.4; Meybeck, 1987). The silicate weathering is more likely to be the source of DIC due to the regional geology of the Mahi River basin (Sharma et al., 2012). The DIC values reported here are within the range reported from other rivers in several studies (Tamooh et al., 2013; Sarkar & Kumar, 2024). The range observed in $\delta^{13}C_{DIC}$ was due to the effect of several sources of DIC in the river and reservoirs (Fig. 5.4). A negative correlation between DIC concentrations and $\delta^{13}C_{DIC}$ in the river represents the addition of isotopically (^{13}C) depleted DIC by remineralization of OM (at places where DIC was higher) and assimilation of DIC (and/or outgassing of CO_2) at locations with lower DIC (Fig. 5.9). DIC concentration decreased with increasing $\delta^{13}C_{DIC}$ from flowing streams to reservoirs (MBR and KR), which was due to CO_2 outgassing and higher PP (Fig. 5.4; Alling et al., 2012). Another reason for declining DIC concentrations in reservoirs might be dilution caused by the addition of a large volume of water from different tributaries during the high flow period.

The whole continuum of the Mahi River was supersaturated with CO_2 indicating that it might be a potential source of CO_2 to the atmosphere, as reported for several other rivers as well (Cole & Caraco, 2001; Richey et al., 2002; Raymond et al., 2013). The supersaturation of CO_2 in the river water compared to the atmosphere might be attributed to *in situ* community respiration, lateral input of soil CO_2 through runoff, and decomposition of OM coming from terrestrial sources into the river during high flow regime (Fig. 5.5; Cole & Caraco, 2001; Richey et al., 2002). Generally, runoff brings DIC depleted in ^{13}C (and increased CO_2 concentrations) from the drainage basin dominated by terrestrial plants (Alling et al., 2012; Campeau et al., 2017). Dissolved CO_2 concentrations were negatively correlated with $\delta^{13}C_{DIC}$ and positively with DIC concentrations in the river channel, also suggesting OM fuelling the respiration in the Mahi River continuum (Fig. 5.9; Tamooh et al., 2013). The immediate downstream waters from the reservoirs showed increase in DIC with lower $\delta^{13}C_{DIC}$, which could be due to the release of subsurface water from reservoirs which might have undergone intense OM remineralization than the surface water (Fig. 5.4).

5.1.4.2 Phytoplankton primary production and N_2 fixation rates

According to the river continuum concept, canopy cover, turbidity, and water residence time affect PP in riverine ecosystems. However, the dominant factors vary depending on the stream order of the river (Vannote et al., 1980). Forested headwater streams (1st–3rd order) would be primarily heterotrophic due to metabolism driven by allochthonous material, while lack of extensive riparian canopy cover leads to autotrophic conditions in mid-order (4th–6th order) streams. However, most large rivers do not follow the original principles of the river continuum concept because of changed lateral exchange with floodplains and flow discontinuities.

In this study, PP showed a broad range along the Mahi River continuum with higher rates in the reservoirs than the Som tributary and mainstem of the river (Fig. 5.6a). These higher rates in reservoirs might be due to increased nutrients and sediment retention caused by higher water residence time and decreased turbulence (stagnant waters), which is favourable for phytoplankton growth (Maavara et al., 2020). In this study as well, increased PP in the reservoirs coincided with increased POM and decreased DIC (due to the higher utilization of DIC) (Figs. 5.6a and 5.7a). The same concept, to some extent, was also supported by a negative correlation of PP with DIC and a positive correlation with POM in the river channel (Fig. 5.9). The increased PP upstream of KBR might be due to higher light availability because of less turbidity and nutrients from runoff. A sharp decrease in POM concentrations was observed downstream of reservoirs, which might be due to increased settlement of POM into the reservoirs. The lower POM downstream of reservoirs coincided with declining PP and increased DIC concentrations due to relatively lower assimilation of DIC. Dilution from tributaries might also cause a decline in POM concentrations in the main channel. Relatively lower PP in the flowing streams than reservoirs was due to the effect of turbulence on phytoplankton communities, which could be more stable in stagnant waters such as lakes, ponds, and reservoirs (Mosisch & Bunn, 1997; Fraisse et al., 2015). Changes in flow regimes can affect the algal community biomass in tropical rivers (Davies et al., 2008). The increased PP in reservoirs than flowing waters also coincided with slightly higher $\delta^{13}C_{DIC}$, indicating the preferential assimilation of ^{12}C during photosynthesis by phytoplankton leaving the remaining DIC pool enriched in ^{13}C (Figs. 5.4 and 5.6a; Gu et al., 2006).

The $\delta^{13}C_{POM}$ is within the range of freshwater phytoplankton (–24 to –42 ‰ with an average of –30 ‰) (Kendall et al., 2001). The relative increase in $\delta^{13}C_{POM}$ in the reservoirs than their upstream waters resulted from the assimilation of relatively enriched DIC, confirmed by the positive correlation between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POM}$ (Fig. 5.9). Apart from processes discussed above, DIC fluctuations in this study also appear to be regulated by phytoplankton biomass, as evidenced by the positive correlation between $\delta^{13}C_{DIC}$ and POM. TSM was positively correlated with POC and PON and decreased from reservoirs to flowing stream waters, confirming the effect of damming and sediment retention through change in flow regime. TSM with slightly higher OM in reservoirs and upstream than other classes show signature of productive waters. The midstream, downstream, and Som tributary have TSM with low OM content compared to reservoirs indicating more weathering contribution in flowing waters or increased sedimentation in reservoirs.

Yu et al. (2008) reported that DIC concentrations and $\delta^{13}C_{DIC}$ can be affected by reservoir operating time (since construction) and found higher DIC with lower $\delta^{13}C_{DIC}$ with longer operating time. The MBR operating time is higher than the KR in the Mahi River basin which has higher DIC concentrations, lower $\delta^{13}C_{DIC,}$ and higher PP than the KR (Figs. 5.4 and 5.6a). In the reservoirs, nutrient retention increases in the bottom sediments due to the alteration of hydrodynamic conditions and decreased water flow velocity with time, leading to enhanced PP. Zhu et al. (2006) have reported higher PP in the Wujiangdu reservoir with a longer operating time than the Dongfeng reservoir. Miyajima et al. (1997) suggested that longer operating time for reservoirs led to higher nutrient concentrations and a larger contribution of biogenic DIC, leading to decreased $\delta^{13}C_{DIC}$. According to conventions, closing a dam results in longer water residence times, suspended particle settling, enhanced light intensity, and increased PP, which causes a decline in dissolved nutrient concentrations (Beusen et al., 2016). Low flow studies in inland waters showed higher PP due to decreased turbidity suggesting it to be a key component influencing PP in these ecosystems (Izagirre et al., 2008; Shen et al., 2015). It is widely believed that the net flows of nutrients along river systems decrease due to the presence of dams, leading to decreased PP.

N_2 fixation rates did not exhibit any significant difference among different classes of the Mahi River continuum and were below detection limit at more than half of the locations (Fig. 5.6b). Contrary to the hypothesis of the study, no specific trend in the N_2 fixation rates was observed. It was initially hypothesized that N_2 fixation rates would be higher in the reservoirs to support higher phytoplankton growth, as diazotrophs prefer calm water and stable conditions (Wu et al., 2018). Similar N_2 fixation in the main river channel and reservoirs might be attributed to several factors, such as nutrient input through runoff, flow regime, light intensity, DIN concentrations, and differences in diazotrophic communities. Cyanobacteria may be more prevalent in streams with consistent flow regimes (Marcarelli et al., 2008). Since N_2 fixation depends on both the succession of particular cyanobacteria and conditions that trigger the formation of heterocysts, forecasts of N_2 fixation in lakes and reservoirs are far more complex than those of PP (Howarth et al., 1988). Paerl (1985) founded that decrease in N_2 fixation caused by turbulence inhibits the formation of cyanobacteria-bacterial aggregates.

The PP and N_2 fixation rates reported here were within the range reported from other riverine ecosystems [0.057–2.20 μM C h^{-1}, (Wissmar et al., 1981); 0.57–57.33 μM C h^{-1}, (Forbes et al., 2008); and N_2 fixation rates = 0–6.9 nM N h^{-1}, (Geisler et al., 2020); 0–0.83 nM N h^{-1}, (Forbes et al., 2008); 0–3.43 nM N h^{-1}, (Horváth et al., 2013)] (Fig. 5.6). The PP was within the range reported from the Mahi River downstream (3.09 ± 4.12 μM C h^{-1}) during low flow conditions (Sarkar & Kumar, 2024). In some studies of stream-lake ecosystems, N_2 fixation increased when hydrologic nitrogen input was limited in these ecosystems (Scott et al., 2008; Marcarelli & Wurtsbaugh, 2009). N_2 fixation rates have been reported from desert streams due to a combination of high light, PO_4^{3-}, low flow conditions with nitrogen limitation, and flood-free growing seasons, which are favourable conditions for diazotrophs (Horne & Carmiggelt, 1975; Grimm & Petrone, 1997). Although calm waters are favourable for diazotrophs, the N_2 fixation rates in the mainstem Mahi water suggested that some diazotrophs might be able to sustain themselves in flowing waters as well (Fig. 5.6b).

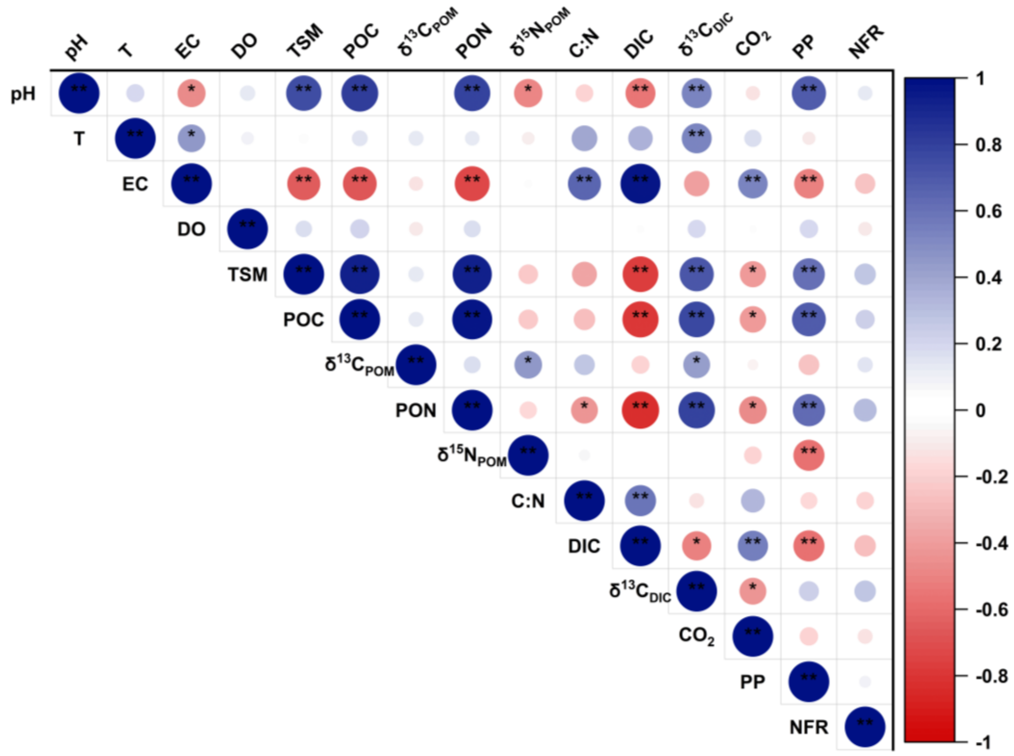


Fig. 5.9 Pearson's correlation plots among measured variables in the Mahi River continuum with significance levels of $p < 0.05$ (*) and $p < 0.01$ (**). NFR represents N_2 fixation rates.

In general, $\delta^{15}N_{POM}$ observed in the studied continuum might be attributed to OM from runoff or instream processes with changes in nutrient sources (Fig. 5.7b). The C:N ratio in the Som tributary was a little higher than other classes, probably due to the dominance of allochthonous OM having high C:N ratio, similar to soils (10–12) (Fig. 5.8; Meybeck, 1982). The low C:N ratio indicates the dominance of phytoplankton and algae in the reservoirs, midstream, and downstream rivers (Kendall et al., 2001). There was no significant relationship between $\delta^{15}N_{POM}$ and PON, indicating that different sources of nutrients might be responsible for the observed PP in the river water. The negative correlation between $\delta^{15}N_{POM}$ and PP might be linked to N_2 fixation, however, no correlation was observed here between PP and N_2 fixation (Fig. 5.9; Fry, 2006).

Maavara et al. (2015) reported that the reason for the higher N:P ratio in reservoirs is N_2 fixation in nitrogen-limited conditions combined with the comparatively more effective P removal through burial in reservoir sediments. Studies have reported that damming reduces nitrogen limitation in receiving water bodies by causing upward shifts in riverine N:P ratios, which is mostly caused by N_2 fixation in reservoirs (Cook et al., 2010; Akbarzadeh et al., 2019) that remains to be explored in the present system. Some studies indicated decreased N_2 fixation with increased fixed nitrogen in oligotrophic aquatic ecosystems (Marcarelli & Wurtsbaugh, 2007; Kunza & Hall, 2014). Anthropogenic activities such as the use of agricultural fertilizers, and the cultivation of legumes increased fixed nitrogen in the aquatic ecosystems and altered the nitrogen cycle which can also impact the PP and N_2 fixation in these ecosystems (Vitousek et al., 1997). Given all the observations discussed above, no significant N_2 fixation in the Mahi River continuum needs to be explored in conjunction with the N:P ratio in the system.

5.1.5 Conclusion

A tropical river continuum was studied to examine variations in different pools of carbon and nitrogen along with the PP and N_2 fixation rates, in response to changes in the flow regime. The results clearly suggest higher POM with enhanced PP in the reservoirs, indicating stagnant waters to be more favourable for phytoplankton growth than flowing waters. However, no significant difference in N_2 fixation rates was observed, suggesting factors other than the water stagnancy controlled diazotrophs. The DIC concentrations in the river continuum were mainly affected by the PP/outgassing and remineralization. The river water was consistently supersaturated with CO_2 and acted as a potential source to the atmosphere. The operating time of dams had a clear effect on the biogeochemical processes in the reservoirs. This study underscores the effect of increased water residence time on PP, N_2 fixation rates, and various in-stream processes.

5.2 Phytoplankton primary production in CO_2 supersaturated riverine ecosystem

Riverine ecosystems around the globe, especially in tropical regions, contain higher dissolved CO_2 concentrations and their CO_2 emissions are higher than the lakes. In rivers, respiration rates are higher as compared to PP, leading to supersaturation of CO_2. Additionally, reservoirs are known for their heterotrophic nature and supersaturation of CO_2 (Raymond et al., 2013). However, the effect of this supersaturated CO_2 on PP remains uncertain, particularly from the measurement perspective. The experiment discussed in Section 4.4 of Chapter 4 was also conducted in the Mahi River and its reservoirs, where dissolved CO_2 concentrations were higher (25.23 ± 6.78 % in the total DIC pool, n = 24) than in the lacustrine ecosystems presented there. In this study, the carbon assimilation rates using $^{13}CO_2$ were also measured and then compared with $H^{13}CO_3^-$ assimilation rates (already discussed in section 5.1) to trace the possible effect of CO_2 supersaturation in the Mahi River continuum. Experiments were conducted at the same locations as described in Section 5.1. Additionally, an extra (second) experiment was conducted in the reservoirs where both tracers ($H^{13}CO_3^-$ and $^{13}CO_2$) were added equally to confirm whether the results were consistent. This tracer addition scheme was different from other experiments discussed previously, where additions were < 10 % of ambient concentrations.

5.2.1 Results

The $^{13}CO_2$ assimilation rates were the lowest in the Som tributary (0.35 ± 0.16 µM C h^{-1}) and the highest in the upstream water (7.45 ± 3.35 µM C h^{-1}) and MBR (7.41 ± 2.51 µM C h^{-1}). In the KR, the $^{13}CO_2$ assimilation rates were 5.00 ± 1.96 µM C h^{-1}. The rates decreased significantly from MBR to midstream (0.86 ± 0.76 µM C h^{-1}) and KR to downstream (0.77 ± 0.48 µM C h^{-1}) (Fig. 5.10). In the second experiment, which was conducted in the reservoirs only (n = 8), the $^{13}CO_2$ assimilation rates were relatively lower in the MBR (7.49 ± 1.90 µM C h^{-1}) than KR (9.88 ± 2.75 µM C h^{-1}) (Fig. 5.11).

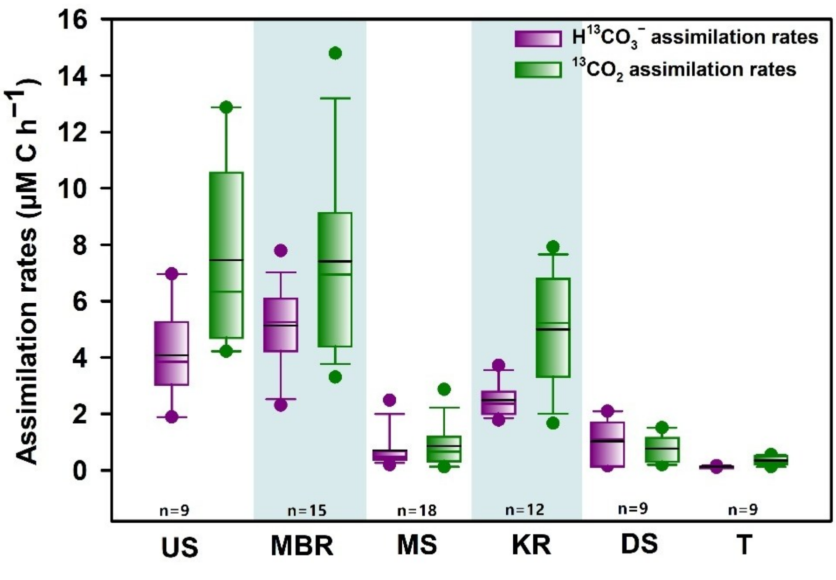


Fig. 5.10 Comparison between carbon assimilation using tracers of $H^{13}CO_3^-$ ($H^{13}CO_3^-$ assimilation rates) and $^{13}CO_2$ ($^{13}CO_2$ assimilation rates) in the continuum of the Mahi River. The black lines represent the mean values.

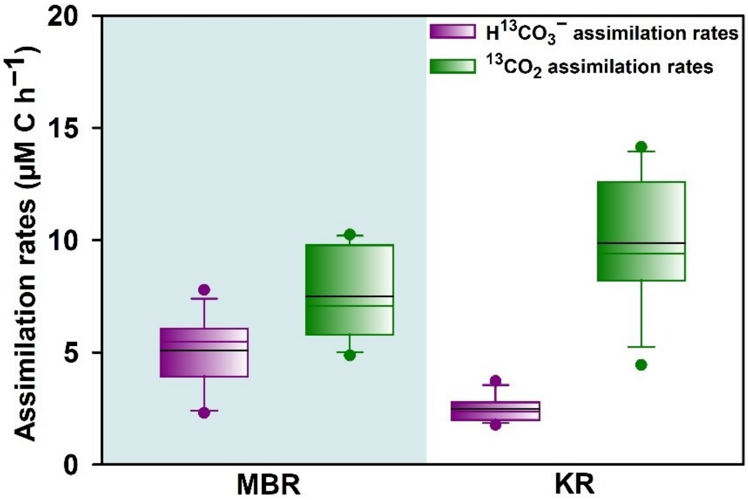


Fig. 5.11 Comparison between carbon assimilation using tracers of $H^{13}CO_3^-$ ($H^{13}CO_3^-$ assimilation rates) and $^{13}CO_2$ ($^{13}CO_2$ assimilation rates) in the reservoirs, when tracers were added equally (second experiment). The black lines represent the mean values.

5.2.2 Discussion

The objective of this study was to observe the influence of supersaturated CO_2 on carbon assimilation in the riverine ecosystem (Mahi River) and its reservoirs. It was observed that $^{13}CO_2$ assimilation rates were significantly higher than $H^{13}CO_3^-$ assimilation rates in reservoirs and upstream of the Mahi River (Fig. 5.10). In the MBR, the rates increased ~ 1.4-fold in $^{13}CO_2$ compared to $H^{13}CO_3^-$ and increased ~ 2-fold in KR. In the second experiment, a drastic increase in $^{13}CO_2$ assimilation rates (~ 4-fold) was observed as compared to $H^{13}CO_3^-$ assimilation rates in the KR, where dissolved CO_2 was > 30 % in the total DIC pool, which is completely different from the lacustrine ecosystems (Fig. 5.11). Also, $^{13}CO_2$ assimilation rates showed a similar pattern as observed for $H^{13}CO_3^-$ assimilation rates (PP in the above section) described in Section 5.1 (Fig 5.6a), where assimilation rates were significantly higher in the reservoirs compared to flowing water.

Results of the study indicate potential preference for CO_2 in these systems, however, given the fast equilibrium dynamics of carbonate system, it is difficult to assess the actual CO_2 rates. Therefore, the assessment made here may only be taken as an indicative. Studies have indicated that phytoplankton prefers CO_2 by diffusion or active transport due to its lower energy demand than $H^{13}CO_3^-$, which might have led to higher $^{13}CO_2$ assimilation rates in this study (Burkhardt et al., 2001). Another reason for the observed changes might be due to rapid assimilation of added tracer by phytoplankton (within 10 seconds at oceanic pH; Tortell et al., 1997). It has been suggested that the faster uptake might be due to the active transport of HCO_3^- or CO_2 (Rotatore et al., 1995). Studies have also reported increased algal growth rates with increased CO_2 concentrations indicating cellular uptake of CO_2 to be an important component during photosynthesis (Burkhardt et al., 1999). Nonetheless, there are substrate preferences for inorganic carbon assimilation that are organisms species-specific. For example, in the diatom *Phaeodactylum tricornutum,* the rate at which CO_2 is assimilated is twice that of HCO_3^-, indicating a preference for CO_2 by this species. However, *Thalassiosira weissflogii* acclimated to high CO_2, predominantly assimilate CO_2; while cells grown at low CO_2 mostly assimilate HCO_3^- (Burkhardt et al., 2001). Higher CO_2 can enhance its uptake, surpassing HCO_3^- uptake in supersaturated conditions (Zeebe & Wolf-Gladrow, 2001; Neven et al., 2011), leading to the kind of results observed in this study. HCO_3^- absorption can be significantly inhibited when CO_2 is greater than half of Rubisco's saturation constant (> 70 µM; Burkhardt et al., 2001). Additionally, the differences in rates might be due to the equilibration time between HCO_3^- and CO_2 in the DIC pool or due to differences in species compositions. Some algae use external CO_2 diffusion in freshwater and lack CCM such as red algae and chrysophytes, particularly in flowing water conditions that reduce the diffusion boundary layer (Giordano et al., 2005). CCM activity is controlled by several environmental parameters such as pH, salinity, temperature, CO_2, nutrient availability, and energy (Beardall et al., 1998; Beardall & Giordano, 2002). The rise in CO_2 concentrations in the external medium can downregulate CCM capacity and DIC transport such that the high affinity of DIC is decreased by rising CO_2 in *Chlamydomonas* (Sültemeyer et al., 1989; Amoroso et al., 1998). Due to the higher solubility of CO_2 at low temperatures and the resulting increased availability of CO_2, the requirement for a CCM is reduced (Raven, 1991; Raven et al., 2002).

5.2.3 Conclusion

This study was conducted to decipher carbon assimilation in a CO_2 supersaturated riverine ecosystem and its reservoirs using $H^{13}CO_3^-$ and $^{13}CO_2$ tracer technique. Although indicative, the results showed no significant difference in $H^{13}CO_3^-$ and $^{13}CO_2$ assimilation rates in midstream, downstream, and Som tributary. However, $^{13}CO_2$ assimilation rates were several times higher than $H^{13}CO_3^-$ assimilation rates in reservoirs and upstream regions, suggesting preference for CO_2 by phytoplankton present in these CO_2 supersaturated ecosystems, especially when CO_2 was > 20 % in the total DIC pool.

Chapter 6

Summary and future scope

6.1 Summary

The focus of this thesis was to understand the carbon and nitrogen assimilation rates and their controlling factors across various aquatic ecosystems. The studies were conducted in three different aquatic ecosystems — ocean, lake, and river — across different seasons. This study has advanced our current understanding of nutrient limitation and co-limitation on PP and N_2 fixation rates in the northern Indian Ocean. The data generated in the ocean also has the potential to aid the development of more accurate biogeochemical models to improve our understanding of the processes involved in the carbon and nitrogen cycles. Additionally, this study explored several aspects of the carbon and nitrogen biogeochemical cycling in lacustrine and riverine ecosystems using stable isotope-based tracer techniques and measurements in particulate, dissolved, organic, and inorganic phases. The results presented here are among the first results in inland waters of India.

Specifically, the major contributions of this thesis are as follows:

6.1.1 Marine ecosystems

The results obtained through the nutrient enrichment and stoichiometric experiments in the marine ecosystems point towards the following findings:

(i) The surface PP was lower in the Bay of Bengal than in the Arabian Sea during the fall inter-monsoon due to freshwater input and stratification hindering the vertical mixing of nutrients.

(ii) N_2 fixation rates were very low (< 1 nM N d^{-1}) and similar in both basins with the highest rates observed in the Andaman Sea.

(iii) The coastal Bay of Bengal and Andaman Sea showed co-limitation of nutrients for PP.

(iv) There was no limitation or co-limitation of nutrients for PP in the open Bay of Bengal, and phytoplankton were acclimated to existing oligotrophic conditions.

(v) N_2 fixation showed an increase when phosphate was added with molybdenum; aerosols addition also led to increase in N_2 fixation in the coastal Bay of Bengal. It increased after iron addition in the Andaman Sea.

(vi) The increase in N_2 fixation was observed after the addition of nitrogen alone or in combination with iron at some locations in the northern Indian Ocean.

(vii) PP in the Arabian Sea was primarily limited by nitrogen and co-limitation was observed in the coastal Arabian Sea and southern open Arabian Sea.

(viii) N_2 fixation did not show nutrient limitation in the southern Arabian Sea, whereas co-limitation was observed in the northern Arabian Sea.

(ix) Molybdenum limitation on PP was observed in the northern Indian Ocean despite its conservative behaviour.

(x) In general, increase in PP was observed in the northern Indian Ocean after addition of aerosols except in the open Bay of Bengal. However, aerosols addition did not fuel N_2 fixation.

(xi) No consistent increase or decrease in PP was observed due to stoichiometric manipulations at different concentration levels suggesting that changes in nutrient concentrations or proportions might not have a significant role in the northern Indian Ocean once the nutrient threshold is reached.

6.1.2 Lacustrine ecosystems

The following observations were made after experiments to measure carbon and nitrogen assimilation rates were conducted in lacustrine ecosystems:

(i) Shallow freshwater lakes in arid-semiarid regions showed seasonal variation in carbon and nitrogen assimilation rates with changes in lake water volume.

(ii) The closed basin (shallow lake) exhibits lower carbon and nitrogen assimilation rates with increased water volume, which coincides with decreased DIC, POM, nutrients, temperature, DO, $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POM}$, and increase in dissolved CO_2 concentrations, due to dilution of water during monsoon as compared to summer.

(iii) Contrary to the closed basin lake, the open basin lake showed a different pattern with higher carbon and nitrogen assimilation rates with increased water volume accompanied by rising POM, DIC, CO_2, and decreased salinity and temperature.

(iv) The higher carbon and nitrogen assimilation rates during monsoon in the open basin might be due to increased nutrients from runoff, which also led to a temporary regime shift in the lake, i.e., from clear water (macrophyte-dominated) during summer to turbid water (phytoplankton-dominated) during monsoon.

(v) The lower carbon and nitrogen assimilation rates during summer in the open lake coincided with increased salinity, temperature, and clear water with decreased water volume, indicating the effect of photoinhibition and osmotic stress on phytoplankton.

(vi) In the open basin lake, rates decreased from monsoon to winter with decreased temperature, which might be due to the decline in metabolic activity.

(vii) The rock weathering and methanogenesis appeared to be regulating the DIC dynamics in the open basin lake during monsoon as indicated by higher DIC concentrations with increased $\delta^{13}C_{DIC}$ compared to summer and winter.

(viii) In the saline lake system, PP and N_2 fixation rates decreased with increased salinity. However, DIN assimilation rates showed variable signatures with changes in salinity. Despite having low $\delta^{15}N_{POM}$ (N_2 fixation signature) at higher salinity, N_2 fixation rates were below detection limit.

(ix) Nutrient assimilation (NH_4^+ and NO_3^-) supported PP at higher salinities as N_2 fixation rates were very low and mostly below detection limit.

(x) Higher NH_4^+ assimilation rates than N_2 fixation in all the studied lakes (freshwater and saline) indicate relative preference for NH_4^+ due to lower energy requirements.

(xi) In the saline lake system, NH_4^+ was the dominant form of DIN, where NO_3^- was quite low. This was likely due to inhibition of nitrification at higher salinities and pH.

(xii) The saline lake was more productive than the freshwater lakes.

(xiii) Open freshwater lake showed potential as a CO_2 sink during summer and source during monsoon and winter. Closed basin lake was a potential source of CO_2 during both seasons. Saline lake and the brine reservoir acted as CO_2 sink, whereas saltpans were potential source.

(xiv) Despite having high DIN concentrations, measurable N_2 fixation rates suggest considerable diazotrophic activity in lacustrine ecosystems.

(xv) The carbon assimilation rates measured using two different tracers of carbon showed no significant difference in freshwater lakes. However, the saline lake showed decreased carbon assimilation using $^{13}CO_2$ tracer due to large DIC pool.

6.1.3 Riverine ecosystem

The following findings were made through carbon and nitrogen assimilation rate measurements in the riverine ecosystem:

(i) An increase in PP was observed from the flowing water of the river to the stagnant water of reservoirs during the high flow period in a riverine ecosystem situated in a semi-arid climatic setting, indicating that stagnant waters are more favourable for phytoplankton growth. The decreased PP in the flowing river water might be due to turbulence.

(ii) In the reservoirs, PP coincided with decreased DIC, increased $\delta^{13}C_{DIC}$ and POM, and enhanced dissolved CO_2 concentration in the DIC pool.

(iii) N_2 fixation rates did not show any difference between flowing river and reservoirs. In fact, it was below detection limit at half of the locations, suggesting that factors other than calm water regulate N_2 fixation in rivers.

(iv) The POM concentrations reduced drastically downstream of the reservoir, which might be due to the effect of sedimentation in reservoirs.

(v) The negative correlation between DIC and $\delta^{13}C_{DIC}$ indicated the effect of respiration/outgassing and PP on the DIC pool. Higher dissolved CO_2 than equilibrium suggested that the river might be a potential source of CO_2 to the atmosphere.

(vi) The carbon assimilation calculated using different tracers of ^{13}C showed no significant difference in flowing waters, however, it was significantly higher when $^{13}CO_2$ was used in the reservoirs.

6.2 Scope for future works

The findings of the present thesis have significantly added to our current understanding of the carbon and N_2 fixation in marine, lacustrine, and riverine ecosystems in (sub)tropical settings. But to comprehensively understand the complex nature of the cycling of carbon and nitrogen in our environment, a comprehensive work focussing on simultaneous quantitative estimation of different biogeochemical processes is desired. Some of the research aspects which need immediate attention are listed below:

(i) Further study and efforts are required to determine whether the limitation of macro- and micronutrients on PP and N_2 fixation are prevalent spatiotemporally throughout the northern Indian Ocean.

(ii) Studies focusing on molecular approaches involving the abundance and distribution of phytoplankton and diazotroph communities in all aquatic ecosystems are highly desirable.

(iii) In the Arabian Sea, studies have suggested that dust deposition affects the PP and N_2 fixation rates, therefore, dust addition experiments will help in understanding its impact on these processes.

(iv) Variation in nutrients (N:P) ratio in the changing climate affects phytoplankton community composition. Mesocosm experiments can explain this in a better way.

(v) Stable isotopic composition of NH_4^+ and NO_3^- will help understand the sources of nutrients to phytoplankton in aquatic ecosystems.

(vi) DIN uptake rates should be estimated in rivers along with PP and N_2 fixation rates to understand the effect of nutrient enrichment from watersheds.

(vii) To better understand the carbon and nitrogen budget in lacustrine ecosystems, quantification of other processes such as nitrification and denitrification on a spatiotemporal scale is needed.

(viii) As the effect of salinity and nutrients on carbon and nitrogen assimilation rates was observed in the lacustrine ecosystems, the experiments with varying salinity and nutrients with a focus on the phytoplankton community will provide better insights into these processes.

(ix) Studies are needed to enhance our comprehension and ability to model the combined impacts of temperature, water clarity, nutrients, and canopy cover on carbon and nitrogen assimilation rates in rivers.

(x) To investigate the effect of global climate change on river metabolism, research is required on a broader scale across watersheds with different hydrologic regimes, climatic settings, land use and land cover, and nutrient concentrations.

(xi) This thesis focused on carbon and nitrogen biogeochemical processes in inland waters in semiarid-arid climates; nevertheless, inland waters in other climatic conditions in India remained untouched. There is a need to investigate India's inland freshwaters because of their value to the society and degradation caused by human activity.

(xii) As regime shift was noticed in the open freshwater lake, a detailed monthly analysis of biogeochemical parameters will help in understanding this phenomenon.

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List of publications

Thesis related publications

1. **Ajayeta Rathi**, Himanshu Saxena, Deepika Sahoo, Sipai Nazirahmed, A. K. Sudheer, Arvind Singh, Sanjeev Kumar. Response of primary production to macro and micronutrient enrichments in the northern Indian Ocean. (Under preparation)
2. **Ajayeta Rathi**, Siddhartha Sarkar, Abdur Rahman, Mohammad Atif Khan, Sanjeev Kumar. High primary production and nitrogen fixation during summer in a shallow tropical lake. (Under preparation)

Other publications

1. Rahman, A., **Rathi, A**., Nambiar, R., Mishra, P. K., Anoop, A., Bhushan, R., & Kumar, S. (2021). Signatures of natural to anthropogenic transition in lake sediments from the Central Himalaya using stable isotopes. *Applied Geochemistry*, *134*, 105095. https://doi.org/10.1016/j.apgeochem.2021.105095
2. Sarkar, S., **Rathi, A**., Khan, M. A., & Kumar, S. (2024). Demystifying the particulate black carbon conundrum in aquatic systems. *Environmental Research Communications*, *6*(5), 051010. https://doi.org/10.1088/2515-7620/ad4e0f
3. Rahman, A., Shah, R. A., **Rathi, A.**, Yadava, M. G., & Kumar, S. (2024). Transport pathways of black carbon to a high mountain Himalayan lake during late Holocene: Inferences from nitrogen isotopes of black carbon. *Palaeogeography, Palaeoclimatology, Palaeoecology*, *633*, 111865. https://doi.org/10.1016/j.palaeo.2023.111865
4. Shaw, C., Rastogi, N., **Rathi, A.**, Kumar, S., & Meena, R. (2024). Sources and processes affecting the abundances of atmospheric NHx using $\delta^{15}N$ over northwestern Indo-Gangetic plain. *Chemosphere*, *359*, 142356. https://doi.org/10.1016/j.chemosphere.2024.142356
5. Agrawal, R. K., Mohanty, R. K., **Rathi, A.**, Mehta, S., Yadava, M. G., Kumar, S., & Laskar, A. H. (2024). Estimation of Groundwater Residence Time Using Radiocarbon and Stable Isotope Ratio in Dissolved Inorganic Carbon and Soil CO2. *Radiocarbon*, *66*(2), 249-266. https://doi.org/10.1017/RDC.2024.43

6. Sarkar, S., Rahman, A., Khan, M. A., **Rathi, A.**, Ragavan, P., Singh, A., & Kumar, S. (2024). Isotopic evidence for degradation of particulate black carbon in the ocean. *Geophysical Research Letters*, *51*(9), e2023GL106050. https://doi.org/10.1029/2023GL106050

Presentations at Conferences

1. **Rathi, A.**, Saxena, H., Nazirahmed, S., Sahoo, D., Sudheer, A. K., Singh, A., & Kumar, S. (2022, December). Role of Macro-and Micro-nutrients in Carbon and Nitrogen Fixation across the Northern Indian Ocean. In ***AGU Fall Meeting Abstracts*** (Vol. 2022, pp. B25A-04).
2. **Rathi, A.**, Sahoo, D., Saxena, H., Nazirahmed, S., Sudheer, A. K., Singh, A., & Kumar, S. (2023, May). Primary productivity in the northern Indian Ocean: role of nutrients stoichiometry. In ***EGU General Assembly Conference Abstracts*** (pp. EGU-11072).
3. **Rathi, A.**, Sarkar, S., Rahman, A., Khan, M. A., & Kumar, S. (2023, December). Effect of Lake Water Volume Reduction on Carbon and Nitrogen Assimilation in Semi-arid Freshwater Closed Basin. In ***AGU Fall Meeting Abstracts*** (Vol. 2023, No. 2162, pp. H43G-2162).
4. **Rathi, A.**, Sarkar, S., Rahman, A., & Kumar, S. (2024). Primary production and dinitrogen fixation in a subtropical inland saline environment. In ***EGU General Assembly Conference Abstracts*** (No. EGU24-14480). Copernicus Meetings.
5. **Rathi, A.**, Saxena. H., Sahoo, D., Nazirahmed, S., Singh, A., Sudheer, A.K., Kumar, S (2022). Effect of macro- and micro-nutrients on primary production and nitrogen fixation across the northern Indian Ocean. ***SOLAS Virtual Summer School 2022***.
6. **Rathi, A.**, Sarkar, S., Rahman, A., Khan, M. A., Kumar, S. Primary productivity in a lacustrine ecosystem of arid region. In ***Frontiers in Geosciences Research Conferences 2023***.