Biogeochemical study of aquatic ecosystems of India

A THESIS

Submitted for the award of Ph.D. degree of

MOHANLAL SUKHADIA UNIVERSITY

In the

Faculty of Science

By

Rupa Mukherjee



Under the supervision of

Dr. Sanjeev Kumar

Associate Professor Geosciences Division

Physical Research Laboratory, Ahmedabad, India

DEPARTMENT OF CHEMISTRY MOHANLAL SUKHADIA UNIVERSITY UDAIPUR, INDIA

2018

DECLARATION

I, Ms. Rupa Mukherjee, D/O Lt. Shanti Pada Mukherjee and Smt. Laxmi Mukherjee, permanent resident of Manbazar, Purulia, West Bengal-723131, hereby declare that the research work incorporated in the present thesis entitled "**Biogeochemical study of aquatic ecosystems of India**" is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from the secondary sources wherever required and I have run my entire thesis on the Anti-plagiarism software namely '**iThenticate**'. I solely own the responsibility for the originality of the entire content.

Date:

Rupa Mukherjee (Author)

Dedicated to my Parents and Brothers

Acknowledgements

The last five years of my journey venturing upon the audacious task of completing this thesis work would not have possible without the active support of many people, whose paths I have crossed for the first time and instantly became friends with and some were lifelong source of inspiration. Humbly, I acknowledge all these wonderful people whose contribution is not less than mine in bringing up this thesis to its present form.

First of all I would like to convey my gratitude to my thesis supervisor Dr. Sanjeev Kumar, for accepting me as his PhD student and being my persistent supporter and mentoring me during my PhD journey. He has provided me the appropriate guidance and has always been a motivation during the whole research period. It turns out that in all the matters related to my academics, be it working on a research problem or in making conclusion of a particular work, his kind remarks and suggestions were invaluable and have always brought much ease and fruitful results. I am highly thankful to him for tolerating my nuisance and will really miss our Tom & Jerry activities in the future.

I am thankful to my thesis Doctoral Student Committee (DSC) members, Prof. R. Ramesh (late), Prof. J. S. Ray and Dr. Arvind Singh for their valuable suggestions during my divisional seminars and reviews. As and when required, they have provided necessary remarks related to my thesis work. During the course of PhD, I was greatly benefited by presenting my progress in thesis work in front of academic committee from time to time. I am thankful to the Chairman and the members of the Academic Committee of PRL who took keen interest in my work progress. It's an honor to express my gratitude to Dr. Anil Bhardwaj, Director of PRL, who has kindly allowed me to present my thesis results in the workshops and conferences, held at national and international level. I have been highly benefited by attending these events.

I am grateful to Dr. Pradipta R. Muduli (Scientist at Wetland Research and Training Center (WRTC), Balugaon, Odisha) for his continuous support and help during my sampling in the Chilika lagoon and preparation of the manuscripts. Without him, it would have been very difficult for me to complete my thesis. I am also thankful to other members of WRTC for their support during my field work. I would like to express my sincere thanks to Dr. Sandeep Mukhopadhyay (Associate professor, Calcutta University), Dr. Manab Dutta and other group members for helping me during Hooghly-Sundarbans sampling.

I am greatly benefited from the innumerable academic interactions with faculty and research staff of Geosciences Division of PRL. I owe my thanks to Dr. R. D. Deshpande (Chairman, GSDN, PRL), Dr. Neeraj Rastogi, Prof. Sunil Singh, Dr. Vinay Rai, Dr. Ravi Bhushan and Dr. Anil Shukla. I would also like to thank Mr. R. A. Jani, Mrs. Sangeeta Verma, Vaghela Bhai, Lakhan Bhai, Bankim Bhai, Jaladhi Romi and Manoj Tank for their support whenever required during the course of my PhD. I owe my deep gratitude to Dr. Bhalamurugan Shivaraman, (Reader, AMOPH, PRL) for his guidance and valuable suggestions for my project during course work. I am very much thankful to him for his kind support during my stay at PRL. I am also thankful to all the people working at different sections of PRL such as administration, accounts, purchase, library, computer center, dispatch, dispensary, canteen, housekeeping and specially workshop people who helped me a lot during my thesis work at PRL.

Today, when I am finalizing my thesis, it gives me immense pleasure to thank my teachers who built the dream of being a researcher in my heart. I was very lucky to have so many helping and loving teachers like Bapi Da, Tulshi Kaku, Amrit Kaku, Sumanta Da, Prashanta Da, Mangal Sir, Partha Sir, Pawan Sir, Arindam Da, Laltu Sir, Dukhu Sir, Dayamoy Sir and N.D. Sir. I also thank all my respected teachers of Jagannath Kishore College and IIT Roorkee (Chemistry Department) for their valuable guidance and lessons. I express my gratitude to my M.Sc. project guide Dr. M. Shankar for his help, support and for giving me the flavor of research.

It would be nearly impossible for me to deny the unwavering support and love that I have received from my sweet batch-mates: Satish, Kuldeep, Navpreet, Rukmani, Prahlad, Kumar, Jabir, Ali, Chandan and Yasir who made my PRL days as "Happy Days" during the last five years. We have made it a point to celebrate each one's little success as an opportunity to celebrate and party every single time. I will cherish these moments for a long time in my life and wish I could be there with them in every ups and downs in their life.

I owe my love and thanks to my sweet lab junior Niharika, kiran, and Abdur for helping me to correct my thesis and for their joyful company. I would also like to thank my other lab juniors Atif, Deepika, Himanshu; and my loving seniors Bhavya Di, Manab Da for sharing their knowledge with me as well as for their great help during manuscript writing. I would also like to thank Lekhsmy Di, Midhun, and Shradhha for their help and support and I also owe thanks to Ikshu, Anirban Da, Damu, Trina Di, Shrema Di, Souvik Da and specially Biwin for their help and support.

There were funny instances where we would burst into laughter together. I would cherish these memories. I also thank my other senior colleagues at PRL with whom I have had the opportunity to discuss freely about my interests and seek support in times of need. It's a boon to have wonderful seniors like Tanmoy, Arko, Priyanka, Sushant, Sunil, Girish Chakrabarty, Amerandra, Monojit, Naveen Negi, Diptiranjan, Deepak, Lalit, Jinia and Chandana with whom I had thrilling discussions on many interesting topics during weekends. Their cordial support and friendly gesture during my initial years at PRL-Thaltej students' hostel has entrusted in me the confidence to carry out the thesis work.

It's always a pleasure to see one's predecessors venturing upon the similar paths one has came across and sharing their pleasant and triumphant occasions. It brings a jolly mood and has made my day several times, after friendly chat round the dinner tables at PRL-Thaltej canteen with fellow companions like Archita, Aarthy, Shivangi, Richa, Subir, Kaustav, Varun, Shefali, Nidhi, Rahul and Akanksha. I also thank some of my colleagues from PRL (Navrangpura Campus), Ashim, Venki (for helping me to arrange my thesis), Anil, Vishnu, Aman, Nijil. Thaltej Campus of PRL had been my second home cum place of research during the last five years. Here, I had the benefit of cherishing friendship with Chandan Gupta, Nisha, Priyank, Sandeep, Sushree, Ayan, Harish and enjoyed celebrating festivals like Holi, Garba and New Year (having horror themes) with great fervor and enthusiasm.

Words fail in expressing love, strength and encouragement of my family members towards me. If there are any two people to whom I would remain highly indebted beyond the realms of this material life, they are my parents, Shri Shanti Pada Mukherjee and Smt. Laxmi Mukherjee. I express my deep love and gratitude to my father who is no more with us now, but would have been the happiest person in the world to see me achieving my PhD degree. I owe my love and thank my mother for her never ending patience and struggle in providing me proper education. My thesis will be incomplete if I don't express my love and thanks to my two sweet brothers Sonu Dada and Falguni Dada who bestowed their best to get me success in my carrier and sacrificed so many desires for me. It is their continuous support and patience that I am able to complete my PhD. I am also thankful to my two boudi (Sushmita and Sonali) and my two cutie pie's Sanav and Saran for making our lives full of fun. I thank my all other family members from the bottom of my heart for all the encouragement. I would also like to thank Mrs. Sapna Ghosh and Dr. Sambhu nath Ghosh for their love and support. I am also thankful to my best friend Avijit for his unconditional help and support in every aspects and being with me in my good and bad days.

Finally, I am thankful to all the people that I have interacted so far, whose direct or indirect contribution has led me to the completion of this thesis.

Abstract

Coastal lagoons and estuarine ecosystems regularly undergo natural and anthropogenic forcings that make these ecosystems susceptible to eutrophication, particularly due to increased nutrient loading from anthropogenic activities. This causes these ecosystems to sustain high biological production leading to several cascading effects such as hypoxia and shift in community composition. At present, our knowledge of nitrogen and carbon cycling in such aquatic ecosystems of India, particularly with respect to rates of different biogeochemical processes, remains rudimentary. The present work aimed to study different aspects of nitrogen and carbon cycling in two such systems of India located at the interface of land and sea i.e., the Chilika lagoon and Hooghly-Sundarbans estuarine system. The study attempted to measure the rates of dissolved inorganic nitrogen and carbon uptake rates in the above-mentioned systems. Stable isotopic composition of nitrogen and carbon were also measured in organic and inorganic phases to understand the sources of organic matter and dissolved inorganic carbon dynamics, respectively. Based on the data gathered during the present study and that available in literature, a preliminary model for nitrogen budget was also constructed for the Chilika lagoon.

Overall, the results showed high dissolved inorganic nitrogen (nitrate and ammonium) uptake rates in the Chilika lagoon compared many other aquatic ecosystems with relatively higher preference for ammonium than nitrate. On an average, the turnover time for ammonium in the water column of the Chilika was shorter compared to nitrate suggesting faster cycling of ammonium in the lagoon. Interestingly, the nitrate and ammonium uptake rates in the bottom waters of the lagoon were comparable to the rates observed in the surface waters, pointing towards the importance of benthic biogeochemistry in shallow aquatic ecosystems like Chilika. The calculation of sector-wise uptake rates indicated the highest dissolved inorganic nitrogen fixation in the central sector of the lagoon. A preliminary investigation based on the present and literature data showed atmospheric deposition to be a major potential source of new nitrogen to the lagoon. Considerable N₂ fixation was observed in the

lagoon indicating diazotrophic activity in the lake despite high nitrate and ammonium concentration in the water column.

The northern sector of the lagoon showed the highest particulate organic carbon and nitrogen compared to other sectors with relatively lower carbon isotopic composition of particulate matter during postmonsoon suggesting dominance of terrestrial and freshwater inputs to the lagoon and/or production of freshwater phytoplankton during that season. Significant increase in carbon isotopic composition from particulate to sediment organic matter in the Chilika indicated biogeochemical transformation of organic matter in the water column and during burial.

The deviation of dissolved inorganic carbon and its carbon isotopic composition from the respective conservative mixing values suggested different processes to be active during different seasons in modulating the dissolved inorganic carbon dynamics in the lagoon with dominance of carbon dioxide outgassing and carbonate dissolution across seasons. The carbon uptake rates in the surface waters of the Chilika were higher during the monsoon and premonsoon compared to postmonsoon with comparable rates in the bottom waters.

In the Hooghly-Sundarbans system, the dissolved inorganic nitrogen (nitrate and ammonium) and carbon uptake rates in the anthropogenically influenced Hooghly estuary were significantly higher than the rates in the mangrove dominated Sundarbans. Similar to the Chilika, the preference for ammonium was higher compared to nitrate in the water column with faster turnover for ammonium within both Hooghly and Sundarbans.

The particulate organic carbon concentration in the Hooghly was marginally lower than the Sundarbans with relatively higher values in the freshwater zone of the Hooghly. On an average, carbon isotopic composition of particulate organic matter in the Hooghly was relatively lower compared to that of the Sundarbans suggesting relatively higher influence of terrestrial inputs in the Hooghly. Signals for marine influence or biogeochemical modification of particulate organic matter were found in the Sundarbans.

Abbreviations

‰	Per mil
$\delta^{13}C$	Isotopic composition of carbon with respect to V-PDB
$\delta^{15}N$	Isotopic composition of nitrogen with respect to Air-N2
С	Carbon
CIL	Cambridge Isotope Laboratories
Chla	Chlorophyll <i>a</i>
DIC	Dissolved Inorganic Carbon
DIN	Dissolved Inorganic Nitrogen
DIP	Dissolved Inorganic Phosphate
DON	Dissolved Organic Nitrogen
Ν	Nitrogen
HABs	Harmful Algal Blooms
IPCC	Intergovernmental Panel on Climate Change
IAEA	International Atomic Energy Agency
IRMS	Isotope Ratio Mass Spectrometer
O_2	Oxygen
Р	Phosphorous
POM	Particulate Organic Matter
POC	Particulate Organic Carbon
PON	Particulate Organic Nitrogen
SOM	Sediment Organic Matter
$\mathbf{C}_{\mathrm{org}}$	Organic Carbon
DO	Dissolved Oxygen
VPDB	Vienna-Pee-Dee-Belemnite

Contents

List o	figures	xi
List o	Tables	xiv
1	Introduction	1
	1.1 Nitrogen cycle in aquatic systems	2
	1.2 Carbon cycle in aquatic systems	4
	1.3 Excess reactive nitrogen: global perspective	5
	1.4 Excess reactive nitrogen: Indian perspective	7
	1.5 Anthropogenic carbon: global and Indian perspective	8
	1.6 Scope of the present work	9
	1.7 Outline of the thesis	. 11
2	Methodology	15
	2.1 Environmental parameters and nutrients	. 16
	2.2 Particulate organic carbon and nitrogen: concentration and isotopic	
	compositions	. 17
	2.3 Sediment organic carbon and nitrogen: concentrations and isotopic	
	compositions	. 18
	2.4 DIC and $\delta^{13}C_{DIC}$ analysis	. 19
	2.5 Dissolved inorganic nitrogen and carbon uptake rates	
	measurement	. 20
	2.6 Measurement of N ₂ fixation rates	. 22
3	Biogeochemistry of the Chilika lagoon	25
	3.1 Study area and sampling	27
	3.1.1 Chilika lagoon	. 27
	3.1.2 Bhitarkanika mangrove	30
	3.2 Environmental parameters and nutrients	32
	3.3 Particulate organic matter in the Chilika	34
	3.3.1 Isotopic composition and content of carbon and nitrogen	. 34

	3.3.2	Provenance and distribution of organic carbon and
		nitrogen in the Chilika lagoon 39
	3.3.3	δ^{13} C _{POM} and POC/Chla: distinguishing organic matter
		sources
3.4	N ₂ fixati	on in the Chilika lagoon
3.5	Dissolv	ed inorganic nitrogen (DIN) uptake in the Chilika
	3.5.1	Variations in NO ₃ ⁻ and NH ₄ ⁺ uptake rates in the surface waters
	3.5.2	Factors controlling DIN uptake in the Chilika lagoon
	3.5.3	Relative preference and turnover time of nutrients in the Chilika
	3.5.4	Surface and bottom DIN uptake during premonsoon
	3.5.5	Seasonal DIN uptake in the Chilika lagoon
	3.5.6	Sources and sinks of nitrogen in the Chilika lagoon
3.6	Carbon	uptake rates in the Chilika lagoon54
	3.6.1	Seasonal variation in carbon uptake rates in the Chilika lagoon
	3.6.2	Carbon uptake rates and environmental parameters
	3.6.3	Coupling of carbon and nitrogen uptake 59
3.7	Dissolv	ed inorganic carbon dynamics in the Chilika61
	3.7.1	Variation in DIC concentration, $\delta^{13}C_{DIC}$ and
		<i>p</i> CO ₂ in the Chilika
	3.7.2	Mixing curve approximation
	3.7.3	Biogeochemical processes modulating DIC in the Chilika 67
3.8]	Biogeoc Bhitarka	chemistry of sediments in the Chilika lagoon and anika mangrove
	3.8.1	Concentrations and isotopic compositions of carbon and nitrogen in sediment organic matter
	3.8.2	Sources of organic matter in the Unlika-Bhitarkanika
	2.9.2	sediments
	3.8.3	Deptn-wise transformation of sediment organic matter
	3.8.4	Proportion of terrestrial and marine sources to sediment

		organic matter	81
4	Biogeochem	istry of the Hooghly-Sundarbans estuarine system	85
	4.1 Study a	re and sampling	87
	4.1.1	The Hooghly estuary	87
	4.1.2	The Sundarbans	89
	4.1.3	Sampling and experiments	89
	4.2 Enviror	nmental parameters	90
	4.3 Nutrien	ts in the Hooghly-Sundarbans	91
	4.4 Sources Hooghl	s and transformation of particulate organic matter in the y-Sundarbans system	92
	4.5 Dissolv	ed inorganic nitrogen uptake in the Hooghly-Sundarbans.	94
	4.5.1	Variation in uptake rates	94
	4.5.2	Uptake rates and environmental parameters	97
	4.5.3	Nutrients preference and turnover times in the Hooghly-Sundarbans system	101
	4.6 Carbon	uptake rates in the Hooghly-Sundarbans	103
	4.7 Dissolv	ed inorganic carbon dynamics in the Hooghly-Sundarbans	
	system.		104
5	Summary a	nd scope for future work	113
	5.1 Particul system.	ate organic matter in the Chilika and Hooghly-Sundarbans	s 113
	5.2 Sedime	nt organic matter in the Chilika and Bhitarkanika mangrov	e114
	5.3 Dissolv	ed inorganic carbon dynamics in the Chilika and	
	Hooghl	y-Sundarbans system	115
	5.4 Carbon	uptake rates in the Chilika and Hooghly-Sundarbans	116
	5.5 Dissolv	ed inorganic nitrogen uptake and N ₂ fixation rates in the	
	Chilika		116
	5.6 Dissolv	ed inorganic nitrogen uptake rates in the Hooghly-	
	Sundarl	bans	118
	5.7 Scope f	for future work	118

List of Figures

Figure 1.1	Nitrogen cycle in aquatic ecosystem	.3
Figure 1.2	Simplified aquatic carbon cycle	.4
Figure 2.1	MAT 253 isotope ratio mass spectrometer at the Physical Research Laboratory, Ahmedabad used for sample analysis	18
Figure 2.2	Elemental analyzer (Flash 2000) attached to MAT 253 mass spectrometer	19
Figure 2.3	Filtration of samples after incubation	21
Figure 3.1	Different sectors of the Chilika lagoon showing locations for DIN uptake, C uptake, and N ₂ fixation rates along with samples collected for POM, DIC and $\delta^{13}C_{DIC}$	31
Figure 3.2	Sampling locations for SOM (C1 to C8) in different sectors of the Chilika lagoon	31
Figure 3.3	Core sampling locations for SOM in the Bhitarkanika mangroves	31
Figure 3.4	The variation in (a) POC/TSM, and (b) TSM with salinity in the Chilika during monsoon and postmonsoon	33
Figure 3.5	Variation in (a) $\delta^{13}C_{POM}$ with POC, and (b) $\delta^{15}N_{POM}$ with PON in the Chilika lagoon during different seasons	.39
Figure 3.6	Cross plot of POC/Chla ratio with $\delta^{13}C_{POM}$ in the Chilika lagoon	41
Figure 3.7	Spatial variation in N ₂ fixation rates in the Chilika lagoon during monsoon	42
Figure 3.8	Seasonal variation in NO ₃ ⁻ uptake rates in the surface waters of the Chilika lagoon	44
Figure 3.9	Seasonal variation in NH4 ⁺ uptake rates in the surface waters of the Chilika lagoon	45
Figure 3.10	Variations in total DIN uptake rates with (a) pH, (b) salinity, and (c) chla in the Chilika lagoon	46
Figure 3.11	Relationship of surface NO ₃ ⁻ and NH ₄ ⁺ uptake rates with respective concentrations during premonsoon in the Chilika lagoon	47
Figure 3.12	Variations in RPI of NO ₃ ⁻ and NH ₄ ⁺ during (a) monsoon, (b) premonsoon, and, (c) postmonsoon in the Chilika lagoon	48

Figure 3.13	Variations in <i>f</i> -ratio during (a) monsoon, (b) premonsoon, and (c) postmonsoon in the Chilika lagoon49
Figure 3.14	Turnover times of (a) NO ₃ ⁻ and (b) NH ₄ ⁺ during three seasons in the Chilika lagoon50
Figure 3.15	Spatial variations in surface and bottom uptake rates of (a) NO_3^- , and (b) NH_4^+ during premonsoon in the Chilika lagoon
Figure 3.16	Relationships between (a) NH4 ⁺ uptake rates with NH4 ⁺ concentrations, and (b) NO3 ⁻ uptake rates with NO3 ⁻ concentrations in the bottom waters of the Chilika during premonsoon51
Figure 3.17	Sector wise seasonal (a) NO ₃ ⁻ and (b) NH ₄ ⁺ fixation (uptake) in the Chilika lagoon
Figure 3.18	Major sources and sinks of DIN in the Chilika lagoon54
Figure 3.19	Seasonal variations in carbon uptake rates in the surface waters of the Chilika lagoon
Figure 3.20	Carbon uptake rates in surface and bottom waters during premonsoon in the Chilika57
Figure 3.21	Relationship between Chl <i>a</i> and carbon uptake rates in the Chilika lagoon59
Figure 3.22	Variation of <i>p</i> CO ₂ with AOU in the Chilika lagoon64
Figure 3.23	Observed and conservative mixing values of DIC and $\delta^{13}C_{DIC}$ in the Chilika for different seasons
Figure 3.24	Various processes controlling DIC and δ ¹³ C _{DIC} dynamics in the Chilika lagoon67
Figure 3.25	Relation between Δ DIC with Δ Ca in the Chilika lagoon70
Figure 3.26	Depth profiles of $\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$, $\&C_{org}$, $\&N$ and C_{org}/N ratio in SOM of the Chilika lagoon
Figure 3.27	Depth profiles of $\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$, % C_{org} , % N and C_{org}/N ratio in SOM of the Bhitarkanika mangrove
Figure 3.28	Relationships between (a) $\delta^{13}C_{SOM}$ and C_{org} : N ratio, and (b) $\delta^{15}N_{SOM}$ and C_{org} : N ratio of the Chilika lagoon and Bhitarkanika mangrove (all depths)80
Figure 3.29	δ^{13} C and δ^{15} N of SOM and POM in the Chilika lagoon80
Figure 3.30	Fraction of marine and terrestrial contributions to the organic matter pool of the Bhitarkanika mangrove sediments82

Figure 4.1	Sampling locations in the Hooghly estuary	88
Figure 4.2	Sampling locations at the estuaries of Sundarbans	90
Figure 4.3	Variability of $\delta^{13}C_{POM}$ and POC in the Hooghly-Sundarbans system.	94
Figure 4.4	Variations in NO ₃ ⁻ and NH ₄ ⁺ uptake rates in the Hooghly estuary	98
Figure 4.5	Variations in NO_3^- and NH_4^+ uptake rates in the Sundarbans	98
Figure 4.6	Relationship between (a) NO_3^- uptake rates with NO_3^- concentration, and (b) NH_4^+ uptake rates with NH_4^+ concentration in the Hooghly-Sundarbans system	99
Figure 4.7	Correlations between NO ₃ ⁻ and NH ₄ ⁺ uptake rates with TSM concentrations in the (a) Sundarbans, and (b) Hooghly estuary	100
Figure 4.8	Relationships between NO_3^- and NH_4^+ uptake rates with %DO for (a) Hooghly, and (b) Sundarbans	100
Figure 4.9	RPI of NO_3^- and NH_4^+ for (a) the Hooghly, and (b) the Sundarbans	102
Figure 4.10	<i>f</i> -ratio for (a) Hooghly, and (b) Sundarbans	102
Figure 4.11	Turnover times of NO_3^- and NH_4^+ for (a) the Hooghly, and (b) the Sundarbans	103
Figure 4.12	Variations in C uptake rates in (a) Hooghly (b) Sundarbans	104
Figure 4.13	DIC-salinity relationship for (a) the Hooghly estuary, and (b) the Sundarbans	106
Figure 4.14	$\delta^{13}C_{DIC}$ -salinity relationship for (a) the Hooghly, and (b) the Sundarbans	106
Figure 4.15	Deviation of DIC and $\delta^{13}C_{DIC}$ from the conservative mixing values for the Hooghly estuary	107

List of Tables

1	Nutrients and physico-chemical parameters in the Chilika lagoon during monsoon
2	Nutrients and physico-chemical parameters in the surface waters of the Chilika lagoon during premonsoon
3	Nutrients and physico-chemical parameters in the Chilika lagoon during postmonsoon
4	Nutrients concentration in the bottom waters of the Chilika during premonsoon
5	DIC concentrations and $\delta^{13}C_{DIC}$ values for the Chilika waters
6	$\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$, $\%C_{org}$, $\%N$ and C_{org}/N ratio of the SOM in the Indian estuaries, mangrove ecosystems and coastal ocean from the Published and present studies
7	The environmental parameters in the surface waters of the Hooghly estuary
8	The environmental parameters in the surface waters of the estuaries of Sundarbans
9	The DIC and $\delta^{13}C_{\text{DIC}}$ of groundwater (GW) and pore-water (PW) samples collected from the Hooghly-Sundarbans system

Chapter-1 Introduction

Biogeochemical cycle is defined as the pathways by which a chemical substance or an element moves through biotic and abiotic environments of the Earth, hence facilitates the transfer of matter from one form to another and also from one location to another (Schlesinger 1991). From the perspective of global change, biogeochemical cycling of elements such as nitrogen (N), carbon (C), phosphorous (P), oxygen (O), and sulphur (S) are important. Among these, N and C cycles are particularly captivating owing to their direct influence on climate and environmental change. Although N and C are indispensable to sustain life, excess of these elements in ecosystem leads to several ecological and environmental problems, such as increased algal productivity, shift in community structure, harmful algal bloom, hypoxia, greenhouse gas emission, acidification of soil and water bodies etc. According to some estimates, the amount of reactive N (biologically and chemically active form) such as nitrate (NO_3^-), ammonium (NH_4^+), nitrite (NO_2^-) etc. in the biosphere has doubled since pre-industrial era (Galloway et al., 2008), leading to biogeochemical imbalance in many natural ecosystems.

Despite being abundant in the Earth's atmosphere, gaseous form of N (unreactive N) is unavailable to most of the biology due to its strong triple bond ($N \equiv N$). Nitrogen is a limiting nutrient in major parts of the world oceans, which affects the primary production and hence the biological C pump, exerting significant role in global C sequestration (Falkowski et al., 1998; Gruber, 2004). Until pre-industrial era, other aquatic ecosystems viz. estuaries, coastal waters, and rivers were limited to reactive N; however, presently the scenario has reversed. Whereas reactive N in the open ocean is derived largely through microbial assimilation of gaseous N (N₂), aquatic systems such as estuaries and lagoons receive reactive N from many sources. These sources include agricultural and domestic wastes, industrial inputs, atmospheric deposition etc. Similarly, anthropogenic C is also being pumped in the system due to industrial and vehicular emissions ultimately affecting the ecosystem. Hence, aquatic ecosystems situated at the land-ocean interface, such as estuaries and lagoons (henceforth also referred as transitional ecosystems), receive extensive load of materials in the form of dissolved and particulate C, N, P and silica (Si) from rivers. This potentially leads to abundant biodiversity and biological productivity in transition zones, which complicates the N and C cycle in these zones compared to open ocean (Bianchi et al., 2007). Below is the brief overview of major processes related to N and C cycle in aquatic ecosystems.

1.1 Nitrogen cycle in aquatic systems

All the processes occurring in the aquatic N cycle are biologically mediated and many enzymes are involved in sustaining these processes (Figure 1.1). One of the major processes in the N cycle is N_2 fixation, which converts molecular N_2 to NH_4^+ . This N_2 fixation can only be performed by special types of organisms called N_2 fixers (e.g. *trichodesmium*). N_2 fixation is one of the important processes which supply new N to aquatic systems.



Figure 1.1: Nitrogen cycle in aquatic ecosystems.

The next process in the N cycle is nitrification, which is two step microbially mediated oxidation of NH_{4}^{+} to NO_{3}^{-} . The first step of nitrification is conversion of NH_{4}^{+} to NO_{2}^{-} by *nitrosomonas* bacteria and second is NO_{2}^{-} to NO_{3}^{-} by *nitrobactor*. Nitrification is the source of oxidized form of N in aquatic systems. Another process which is responsible for primary production (i.e., biomass formation) is assimilation. Assimilation is defined as the conversion of NH_{4}^{+} , NO_{3}^{-} and NO_{2}^{-} to organic matter. The most preferred form of N for assimilation is NH_{4}^{+} owing to its reduced form and easy transportation across the cell membrane (McCarthy et al., 1977; Raven et al., 1992; Glibert et al., 2016). The reverse of assimilation is re-mineralization, which is degradation of organic matter. The loss of N from an aquatic system occurs via two processes i.e., denitrification and anaerobic ammonium oxidation (anammox). These two processes ensues in oxygen minimum zones (OMZ). Denitrification involves series of reactions which produces molecular N₂ gas as end product from NO_{3}^{-} . Denitrification engender nitrous oxide (N₂O) as one of the intermediate products, which is a potent greenhouse gas affecting the Earth's radiation budget. In recent years,

anammox is luring considerable research interest. Anammox bacteria oxidizes NH_4^+ to N_2 using NO_2^- .

1.2 Carbon cycle in aquatic systems

Carbon is a fundamental element for all life forms on the Earth and contributes to ~ 50 % dry weight of the living matter. Thus health of the biosphere can be understood from the global production and decomposition of organic matter (Ussiri et al., 2017). The oxidation state of C varies from + 4 to – 6 but mostly it occurs in + 4 oxidation state as carbon dioxide (CO₂) and carbonate (CO₃²⁻). CO₂ is a trace constituent in the atmosphere comprising ~ 0.04 % of all the molecules present in the atmosphere and plays the most vital role in C cycle (Figure 1.2).



Figure 1.2: Simplified aquatic carbon cycle.

One of the most important processes in the C cycle is dissolution of atmospheric CO_2 at the air-water interface. Upon reacting with water after dissolution, CO_2 forms three different dissolved inorganic carbon (DIC) species. Abundance of these DIC species is highly dependent on pH of the system. For example, at pH 8.17, 90% of DIC exists in the form of bicarbonate (HCO₃⁻), 9% as CO_3^{2-} and the remaining 1% as aqueous CO₂ (Falkowski et al., 1998; Neven et al., 2011). The next step in C cycle is the primary productivity i.e., formation of organic matter via photosynthesis. During photosynthesis, HCO_3^- and aqueous CO_2 are taken up by phytoplankton which are the main sources of C for organic matter formation. The phytoplankton cells formed by photosynthesis are taken up by zooplankton present in the water column. Zooplanktons are the primary consumers in aquatic C cycle which are eaten by the higher trophic level consumers. The remaining phytoplankton biomass either living or dead sinks to the deeper ocean and gets exported to the sediment. Another process in the C cycle is called re-mineralization i.e., decomposition of organic matter. Decomposition is performed by bacteria present in the water and it reverts back DIC to the aquatic system. In addition, two more processes which contribute to the C cycle are carbonate precipitation and dissolution. The carbonate precipitation removes DIC from the system and eventually removes C; whereas carbonate dissolution adds DIC to the system. These two processes are highly dependent on the pH of the medium.

In recent years, the natural cycling of N and C have been significantly modified in transitional aquatic zones due to excess loading of these elements owing to anthropogenic activities. The consequences of excess loading of N and C in global and Indian waters have been briefly discussed below.

1.3 Excess reactive nitrogen: global perspective

Half of the human population on the Earth lives in coastal water and air sheds (Vitousek et al., 1997; Ache et al., 2015). Acceleration in urban, agricultural, and industrial revolution in the last few decades has led to unprecedented stress on the ecological health of the downstream riverine, coastal and estuarine bodies. From 2001 to 2010, use of urea as a fertilizer has increased at a rate of 3.8 % per year and in the past four

decades urea use has enhanced more than 100 fold (Glibert et al., 2006; Heffer and Prud'homme 2013). The incorporation of agricultural N into plant biomass is extremely inefficient owing to various N loss pathways such as leaching and run off from agriculture fields, ammonia (NH₃) volatilization, denitrification and other N transformation processes (Bouwman et al., 2009). This 'leaked N' ultimately leads to nutrient enrichment in lakes, rivers, wetlands and other aquatic systems. None of the transitional aquatic zones now a days are N deficient, and average NH4⁺ concentration greater than 5 μ mol L⁻¹ are very common in transitional aquatic ecosystems worldwide (Chen et al., 2010; Xu et al., 2012; Glibert et al., 2014a; Glibert et al., 2014b; Glibert et al., 2014c; Samanta et al., 2015; Barik et al., 2017). Nitrogen (in the form of urea) concentration up to 25 - 50 μ mol L⁻¹ have been reported in the Chesapeake Bay, heavily fertilized Yaqui Valley and other coastal areas (Lomas et al., 2002; Glibert et Apart from the above mentioned ecosystems, very high al., 2005, 2006). concentrations of urea (up to 150 μ mol L⁻¹) has been reported in the Lake Kinnet in Israel, some Polish lakes and many lakes in central Canada (Berman, 1974; Siuda & Chrost, 2006; Kudela et al., 2008; Switzer, 2008). Not only land derived, but airborne N deposition from fossil fuel burning and animal husbandry are also responsible for vegetation change in open habitats and species diversity all over Europe (Aerts, 1993; Bobbink et al., 2010). The atmospheric deposition of nutrients to ocean has been reported to be ~ 20 times that of Redfield ratio (Jickells, 2006; Peñuelas et al., 2012).

The increased nutrients load has degraded the water quality and also steered nutrient enrichment in most of the coastal ecosystems leading to eutrophication with increase in phytoplankton abundance, changes in elemental stoichiometry of biomass, shift in community composition (which further led to harmful algal blooms: HABs), reduction in dissolved O₂ in water column, fish kill etc. (Ryther & Dunstan, 1971; Paerl, 1988; Downing, 1997; Klausmeier et al., 2004; Beman et al., 2005; Heisler et al., 2008). The HABs can be harmful to food web and have the potential to impact human health as these cells produce toxic compounds. Upon decay, HABs may create hypoxia in the water column (Hallegraeff, 1993; Glibert et al., 2005; Backer & McGillicuddy Jr, 2006). In shallow water bodies, decrease in water clarity may further

promote ecosystem alterations and fetch in primary production from benthic to pelagic (Borum & Sand-Jensen, 1996; Krause-Jensen et al., 2012).

1.4 Excess reactive nitrogen: Indian perspective

Like many aquatic ecosystems in other parts of the world, Indian lakes, rivers, estuaries, and lagoons are also suffering from the excess N loading. Many studies have reported more than desirable N concentrations in numerous water bodies of India (Mukhopadhyay et al., 2002; Gupta et al., 2008; Bhavya et al., 2016; Barik et al., 2017). Biogeochemical modeling of C and N flux from the Hooghly estuary revealed annual DIC, dissolved inorganic nitrogen (DIN), dissolved reactive phosphate (DRP) and silicates (SiO₄⁴⁻) to be ~ 2.76×10^6 tones, 65.8×10^3 tones, 12.5×10^3 tones, and 42.8 \times 10³ tones, respectively (Mukhopadhyay et al., 2006). The longest estuary in the southern coast of India (Cochin estuary) also receives high dissolved inorganic phosphate (DIP: 1.37 kg d^{-1}) and NO₃⁻ (2.69 kg d⁻¹). The Cochin estuary exports ~ 0.91 kg d⁻¹ phosphate (PO₄³⁻) and ~ 1.71 kg d⁻¹ NO₃⁻ to the coastal ocean indicating recycling of nutrients in the estuary (Balachandran, 2001). Indian water bodies are not only affected by land derived reactive N but also suffers from atmospheric deposition. Significant impacts of dry and wet deposition have been reported from Indian Sundarbans (Biswas et al. 2005). The dry deposition rate of N in the mangroves of Sundarbans has been reported to be 2.26×10^3 kg N km⁻² yr⁻¹ with NH₄⁺ flux rate of 775.7 kg N km⁻² yr⁻¹ from air to water. Annual N flux from the proximate terrestrial sources was found to be 4.26×10^6 kg N yr⁻¹ of which 32.9 % was deposited on nearby coastal areas (Biswas et al., 2005).

Due to the anthropogenic loading, most of the Indian estuaries, such as the Hooghly estuary, are reported to be heterotrophic where respiration dominates over primary production (Mukhopadhyay et al., 2002, 2006). Not only estuaries, Asia's largest brackish water lagoon (Chilika) also showed signs of heterotrophy, particularly during monsoon season (Gupta et al., 2008; Muduli et al., 2012). Owing to the dominance of respiration over primary production, these estuaries also remains under saturated with respect to O_2 , which may eventually lead to hypoxia.

1.5 Anthropogenic carbon: global and Indian perspective

Atmospheric CO₂ concentration has increased from ~280 ppm (pre-industrial era) to ~ 402 ppm (<u>https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html</u>) in the present day. In other words, atmospheric CO₂ has increased ~ 40 % from 589 Pg C in 1750 to 849 \pm 5 Pg C in 2015 with an average atmospheric CO₂ increase of ~ 0.98 Pg C yr⁻¹ (Ciais et al., 2014; Le Quéré et al., 2015, 2016). Currently, ocean act as a sink for ~ 26% of all anthropogenic C emissions and also reduces C accumulation in the atmosphere which helps in slowing down the global climate change (Palevsky & Quay, 2017). Although the inland waters contribute ~ 1% of the Earth's surface, its collective contribution to the global C cycle is surprising. Roughly 2.7 Pg C is transported, mineralized and buried annually by inland waters, which is similar to the sink for anthropogenic CO₂ (~ 2.8 Pg C yr⁻¹; Battin et al., 2009; Tranvik et al., 2009).

There are three main driving factors for exchange of CO₂ between the ocean (or any aquatic body) and atmosphere. First is the chemical effect which regulates CO_2 solubility through temperature-salinity variations; second is the biological effect from the water surface owing to fixation, export of organic C and biogenic carbonate precipitation or dissolution; and third is the advection and mixing (Roy et al., 2011; Ciais et al., 2014; Hauck et al., 2015). The net decadal uptake of CO₂ by ocean and land for the year 2015 has been estimated to be 3.0 ± 0.5 and 1.9 ± 0.9 Pg C yr⁻¹, respectively (http://cdiac.ornl.gov/GCP/carbonbudget/2015/). After post-industrial era due to increase in CO_2 and methane (CH₄) concentrations, the land and ocean surface temperatures has been increased by ~ 0.85 ± 0.21 °C globally over the period of 1880 -2014 (IPCC 2014; Jones et al., 2013; Ruedy et al., 2015). It has also been reported that elevated CO_2 emission is also leading to CO_2 fertilization effect which is defined as increase in leaf photosynthesis with increasing atmospheric CO₂ (Zak et al., 2011; Kauwe et al., 2013). Another severe impact of rising levels of CO₂ is ocean acidification which is decline in pH and reduction in CO_3^{2-} mineral saturation state. In past 200 years, ocean consumed ~ 40% of atmospheric CO₂ emission leading to pH drop of ~ 0.1 of the world's ocean which is equivalent to 30% increase in ocean acidity (Caldeira & Wickett, 2003; Zeebe et al., 2008; Johnson & White, 2014). Ocean acidification has severe impact on ocean chemistry with major negative impact on marine life (Hoegh-Guldberg et al., 2007). Furthermore, global warming caused by anthropogenic CO_2 also led to increase in water column stratification as depicted by climate-ocean simulations. This will again reduce transport of C to the deeper ocean and hence affect sequestration of anthropogenic C (Manabe & Stouffer, 1993; Mitchell et al., 1995; Sarmiento et al., 1998; Joos et al., 1999). Studies on climate-ocean CO_2 perturbation are required to understand the change in climate and to control the permissible emission levels of C.

Some Indian estuaries and coastal ecosystems have been studied with respect to CO₂ and results indicate most of the ecosystems to be source of CO₂ i.e., flux of CO₂ is from water to atmosphere (Sarma et al., 2001; Bouillon et al., 2003; Biswas et al., 2004; Gupta et al., 2008; Muduli et al., 2012, 2013). Very high bacterial respiration $(20.7 \pm 0.7 \mu \text{molC L}^{-1} \text{ d}^{-1})$ has been observed in the Godavari estuary leading to very high partial pressure of CO₂ (*p*CO₂) of ~ 30000 µatm during peak discharge period (Sarma et al., 2011). Not only estuaries, coastal zones also showed *p*CO₂ more than atmospheric value suggesting heterotrophic activity, especially during peak discharge time (Prasad et al., 2013). The Arabian Sea, which is a part of the Indian Ocean, is also a perennial source of CO₂ as reported by many authors (Goyet et al., 1998; Sarma et al., 1998; Sarma, 2003).

1.6 Scope of the present work

India, being a highly populated country, is in urgent need to preserve its water resources from potential anthropogenic threats described earlier. However, in order to evolve a mitigation strategy to save these resources, first we need to thoroughly understand and quantify different biogeochemical processes occurring in Indian aquatic systems. Although significant studies vis-à-vis C and N cycling have been conducted in coastal and estuarine systems worldwide, limited studies exist in tropical settings like India (Sarma et al., 2014; Ye et al., 2015; Bardhan et al., 2015; Bhavya et al., 2016; Moynihan et al., 2016). These studies become particularly non-existent with respect to

lagoon systems (Muduli et al., 2012, 2013). Also, different sources of organic matter pool and its burial in transitional aquatic systems of India have rarely been investigated. Therefore, the main focus of the present thesis is to understand and quantify different aspects of N and C cycling in some major transitional aquatic ecosystems (defined here as aquatic systems situated at the interface of land and ocean such as lagoons and estuaries) of India. The ecosystems covered during the present study were the Chilika lagoon (Asia's largest brackish water lagoon), Hooghly estuary (anthropogenically impacted estuary) and the estuaries of Sundarbans (mangrove-dominated estuary).

Specifically, the present study focused around investigating following aspects:

- 1. Understanding the cycling and fate of N in transitional aquatic systems which receive high nutrient loads. Also, the aim was to investigate differences in N cycling of an anthropogenically dominated system from that of a mangrove-dominated one.
- 2. Understand the coupling of primary productivity (C uptake) and N uptake rates in CO₂ supersaturated systems.
- 3. Investigate if anthropogenically dominated systems have relatively higher primary productivity compared to mangrove-dominated ones.
- 4. Whether measurable N₂ fixation is possible in ecosystems receiving high nutrient loadings.
- 5. Investigate relative roles of riverine inputs, atmospheric deposition, and N₂ fixation as new N sources to a transitional aquatic system.
- 6. Understand the biogeochemical processes responsible for controlling DIC dynamics in transitional aquatic ecosystems.
- 7. Trace sources and transformations of organic matter in the water column and sediment.

To fulfill the above objectives, following studies were carried out:

- Dissolved inorganic N (DIN: NO₃⁻ + NH₄⁺) uptake rates were measured using ¹⁵N tracer technique in the Chilika lagoon during three seasons. DIN uptake rates were also measured in the Hooghly estuary and the estuaries of Sundarbans during postmonsoon.
- N₂ fixation rates were measured to identify diazotrophic activity in the Chilika lagoon following ¹⁵N₂ bubble method.
- 3. Primary productivity were measured using ¹³C tracer technique in the Chilika, the Hooghly estuary, and the estuaries of Sundarbans.
- 4. Dissolved inorganic carbon concentrations and its carbon isotopic compositions $(\delta^{13}C_{DIC})$ were measured during three seasons in the Chilika. This was also performed during postmonsoon in the Hooghly and the estuaries of Sundarbans to identify different processes governing DIC and $\delta^{13}C_{DIC}$ dynamics.
- 5. Particulate organic matter samples were collected to measure particulate organic nitrogen (PON) and particulate organic carbon (POC) concentrations along with δ^{13} C and δ^{15} N of organic matter in the above mentioned ecosystems.
- 6. For sediment organic matter (SOM) characterization, samples were analyzed for organic C (%C_{org}) and N (%N) content and their isotopic compositions ($\delta^{13}C_{SOM} \& \delta^{15}N_{SOM}$) in eight and three sediment cores collected from the Chilika lagoon and adjacent Bhitarkanika mangrove, respectively.

1.7 Outline of the thesis

The thesis contains five chapters. Details of the chapters are as follows:

Chapter-1

This chapter provides a brief overview of different processes related to N and C cycling in aquatic ecosystems. Also, apart from discussing past work vis-à-vis N and C cycling, global and Indian perspectives of consequences pertaining to anthropogenic effects on ecosystems have been discussed. The last part of the chapter discusses rationale and major scientific objectives of the present study.

Chapter-2

This chapter discusses methodologies followed during the present study, which include ¹³C and ¹⁵N tracer technique, N₂ fixation measurements, δ^{13} C and δ^{15} N measurements in organic matter along with PON and POC concentrations. Techniques for DIC and δ^{13} C_{DIC} measurements have also been described in this chapter.

Chapter-3

This chapter deals with biogeochemistry of the Chilika lagoon. The first part of the chapter discusses different sources of organic matter in the lagoon using δ^{13} C and δ^{15} N data. The second part describes about the findings of N₂ fixation experiment. The third part of the chapter provides detailed analysis of the results obtained from DIN uptake experiments and the fourth part deals with ¹³C primary productivity results. The fifth part explains DIC dynamics in the Chilika lagoon. The last part of the chapter deals with sediment biogeochemistry of the Chilika lagoon and the Bhitarkanika mangrove.

Chapter-4

In the first part of this chapter, sources of particulate organic matter (POM) in the Hooghly-Sundarbans system have been discussed. The second part includes results from the DIN uptake experiments. The third part deals with C uptake rates in the Hooghly estuary and the estuaries of Sundarbans. The DIC dynamics based on DIC concentrations and $\delta^{13}C_{\text{DIC}}$ have been discussed in the last.

Chapter-5

This chapter summarizes the results obtained from the present study and also suggests scope for future work.

Chapter 2 Methodology

The thesis covers studies related to different aspects of N and C cycling in three major ecosystems in India viz. the Chilika lagoon (Asia's largest brackish water lagoon), the Hooghly estuary (anthropogenically stressed estuary), and the Sundarbans (world's largest mangrove ecosystem). Sampling in the Chilika lagoon were conducted during three seasons i.e., monsoon (June 2015), premonsoon (April 2016), and postmonsoon (December 2016). The Hooghly estuary and the Sundarbans were sampled during postmonsoon (November 2016). Apart from the above-mentioned study areas, a small mangrove ecosystem (Bhitarkanika) near Chilika lagoon was also studied.

The results presented in the thesis include measurements of several basic environmental parameters along with N and C isotopic compositions in organic and inorganic phases. The thesis also incorporates results of isotopic tracer based experiments to assess the rates of DIN and C uptake by phytoplankton. Below is the brief overview of different methods used for data collection and experiments during this study.

2.1 Environmental parameters and nutrients

Data for water temperature, pH, salinity, and dissolved oxygen (DO) in the Chilika lagoon during the study period were collected in situ using multi-parameter water quality sonde (6 Series; DATA-BUOY; YSI, USA) along with Secchi disk depth. Samples collected for inorganic nutrients, viz. NO₃⁻, NH₄⁺, SiO₄⁴⁻ and DIP were passed through 0.45µ membrane filter paper (47mm) and measured by nutrient autoanalyzer (Skalar San⁺⁺) with an accuracy of ± 0.01 , ± 0.01 , ± 0.01 and ± 0.02 µmol L⁻¹, respectively (Grashoff et al., 1999). Chlorophyll a (Chla) was measured using 90% acetone extraction by UV - VIS spectrophotometer (Thermo Scientific, Evolution TM 201) as described in Strickland and Parsons (1984). Dissolved O_2 percentage (%DO) was calculated as: $\text{\%}DO = ([O_2]_{\text{Measured } x} 100 / [O_2]_{\text{Equilibrium}})$ where, $[O_2]_{\text{Equilibrium}}$ is the equilibrium DO concentration calculated at *in-situ* temperature and salinity (Weiss, 1970) and [O₂] Measured is the measured DO concentration of the lagoon water. Apparent oxygen utilization (AOU) was calculated as follows: $AOU = ([O_2]_{Equilibrium} - [O_2])$ Measured). Measurements of total alkalinity (TA) was carried out using titration method as described in APHA (2005). For measurement of total suspended matter (TSM) concentration, water samples were filtered in situ through pre-weighted Whatman GF/F filter paper and dried in hot air oven at 50 °C and final weights were noted. TSM concentrations were calculated based on deviation between final and initial weights of the filter paper and volume of the water filtered.

For the Hooghly estuary and the estuaries of Sundarban, water temperature and pH of the collected samples were measured *in situ* using thermometer and portable pH meter (Orion Star A211) fitted with a Ross type combination electrode calibrated (as described by Frankignoulle and Borges, 2001) on the NBS scale (reproducibility: ± 0.005 pH units). For TA estimation, 50 ml of filtered (0.7-µm filters) estuarine water was titrated onboard in a closed cell using 0.1 N HCl following potentiometric titration method (Bouillon et al., 2003). Salinity and DO concentrations were measured onboard, following the Mohr-Knudsen and Winkler titration methods, respectively (Grasshoff et al., 1983). Inorganic nutrients (i.e. NO₃⁻, NH₄⁺, SiO₄⁴⁻ and DIP) were

analyzed spectrophotometrically following Grasshoff et al. (1999). Procedure for calculating other parameters (e.g., %DO, AOU, TSM) were same as described for the Chilika lagoon.

2.2 Particulate organic carbon and nitrogen: concentrations and isotopic compositions

For measurements of PON and POC concentrations along with natural isotopic composition of N and C of POM ($\delta^{15}N_{POM}$ and $\delta^{13}C_{POM}$), approximately 0.3 - 0.5 L water samples from the above mentioned ecosystems were filtered using 0.7 µm pore sized 47 mm GF/F filters. After filtration, samples were dried overnight for mass spectrometric analysis, which was performed using isotope ratio mass spectrometer (Thermo scientific MAT 253; Figure 2.1) attached to an elemental analyzer (Flash 2000) via conflo (Figure 2.2). For measurements of POC and $\delta^{13}C_{POM}$, samples were decarbonated by exposing the filter papers containing POM to acid fumes (HCl). Samples for PON and $\delta^{15}N_{POM}$ were not treated with acid fumes. The POC and PON concentrations were calculated using calibration curves obtained by analysing compounds of known C (IAEA-CH-3 cellulose standard: 44.40 %) and N (protein: 13.32 % and IAEA-N-2 ammonium sulphate: 21.21 %) content against area (masses: 44, 45, 46 for C and 28, 29 and 30 for N) obtained using mass spectrometer (Figure 2.1). The variability in POC and PON for duplicate measurements were less than 10 %. The $\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$ in the present study have been reported as relative difference in isotopic ratios between sample and standard:

$$\delta^{15}N_{POM} \text{ or } \delta^{13}C_{POM} (\%) = \left(\frac{R \text{ sample} - R \text{ standard}}{R \text{ standard}}\right) \times 1000$$

where, R is the ratio of the abundance of heavy to light isotope. AIR (atmospheric N₂) and V-PDB are standards for N and C, respectively. The reproducibility for δ^{15} N was less than 0.3 permil (‰) (standard used: IAEA-N-2, (NH₄)₂SO₄, δ^{15} N = 20.3‰). The reproducibility for natural δ^{13} C_{POM} was less than 0.1 ‰ (standard used: IAEA-CH-3, cellulose, δ^{13} C = -24.7 ‰).



Figure 2.1: MAT 253 isotope ratio mass spectrometer at the Physical Research Laboratory, Ahmedabad used for sample analysis.

2.3 Sediment organic carbon and nitrogen: concentrations and isotopic compositions

For source characterization of SOM of the Chilika lagoon, eight sediment cores were collected using UWITEC corer operated from the boat, whereas three sediment cores for Bhitarkanika mangroves were collected using a gravity corer.

All SOM samples were dried at 60 °C for 24 - 48 h and grounded to a fine powder using a mortar and pestle. For $%C_{org}$ and $\delta^{13}C_{SOM}$ measurements in SOM, samples were acidified with HCl and heated overnight at 70 °C. Next day, the tubes containing decarbonated SOM were centrifuged and washed multiple times with ultrapure (Milli-Q) water to remove HCl completely as described by Nieuwenhuize et al. (1994). Analysis were performed on bulk samples for the measurement of %N and
$\delta^{15}N_{SOM}$. All isotopic analyses were performed using a MAT 253 isotope ratio mass spectrometer attached to an elemental analyzer (Flash 2000, Thermo). The $\delta^{13}C_{SOM}$ and $^{15}N_{SOM}$ were reported in ‰ deviations from the standards V-PDB and AIR, respectively. Analytical precision for $\delta^{13}C_{SOM}$ and $^{15}N_{SOM}$ were less than 0.1 and 0.3 ‰, respectively. Organic C and N concentrations in SOM samples were calculated using a calibration curve generated from a standard of known %C (IAEA-CH-3 cellulose standard: 44.40%) and %N (protein: 13.32 % and IAEA-N-2 ammonium sulphate: 21.21 %) against area (masses: 44, 45, 46 for C and 28, 29 and 30 for N) obtained using mass spectrometer.



Figure 2.2: Elemental analyzer (Flash 2000) attached to MAT 253 mass spectrometer.

2.4 DIC and $\delta^{13}C_{DIC}$ analysis

Samples for DIC concentrations and $\delta^{13}C_{DIC}$ from different ecosystems mentioned above were collected by gently overfilling teflon septa fitted glass vials followed by preservation with saturated HgCl₂ solution to cease microbial activity. The samples were kept at 4 °C during transportation to the laboratory. In the laboratory, DIC concentrations were measured using Coulometer (Model: UIC. Inc. CM - 5130) with < 5 % variability for duplicate measurements. For the measurements of $\delta^{13}C_{DIC}$, 12 ml septum vials containing 0.1 ml of 100 % orthophosphoric acid were flushed with He gas in a gas bench connected to MAT 253 mass spectrometer. After flushing with He, roughly 1 ml of samples were injected to these vials using a gas tight syringe to avoid contamination with atmospheric air. The vials containing acidified samples were kept at 28 °C for 18 hours to allow samples to react with the acid leading to release of CO₂. The released CO₂ was then analyzed for isotopic composition using MAT 253 mass spectrometer attached to a Gas Bench II unit. Sodium bicarbonate (NaHCO₃) of known isotopic composition ($\delta^{13}C_{DIC} = -11.4 \%$) was used as lab standard and final values of the samples were represented with respect to international standard (V-PDB). The reproducibility for $\delta^{13}C_{DIC}$ was less than 0.1 ‰. The CO₂ SYS.XLS (version14), developed by Pelletier et al. (2007), an updated version of the original (Lewis & Wallace, 1998), was used for computing *p*CO₂ and aqueous CO₂ using the dissociation constants of Cai and Wang (1998). CO₂ exchange fluxes across the water-atmosphere boundary of the estuary (FCO₂ in µmol m⁻² hr⁻¹) were calculated as follows (Raymond and Cole, 2001):

$$FCO_2 = k \times K_H^{CO2} \times [pCO_{2 \text{ (water)}} - pCO_{2 \text{ (atmosphere)}}]$$

Where, 'k' is the gas transfer velocity, calculated using the equations given by Liss and Merlivat (1986) and $K_{\rm H}^{\rm CO2}$ is the solubility of CO₂ calculated after Weiss (1974). The $p\rm CO_{2 (atmosphere)}$ was taken as global mean atmospheric CO₂ mixing ratio during 2015 and 2016 (Data source: <u>ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_annmean_gl.txt</u>).

2.5 Dissolved inorganic nitrogen and carbon uptake rates measurement

The uptake rates of DIN and C by phytoplankton in the studied aquatic systems were measured using isotope tracer techniques. Lower natural abundances of heavier isotopes (¹⁵N and ¹³C) compared to their lighter isotopes (¹⁴N and ¹²C) were used as a tool for isotope labelling experiments (Dugdale and Wilkerson, 1986). The main assumptions of this method were: (a) no discrimination between lighter and heavier

isotopes by phytoplankton during uptake, (b) no formation of nutrients during incubation period, and (c) no grazing by zooplankton.

The experiments to measure DIN uptake and C uptake rates in the Chilika were performed during three seasons i.e., monsoon (June 2015; 16 stations), premonsoon (April 2016; 15 stations) and postmonsoon (December 2016; 17 stations). Similar experiments were performed in the Hooghly-Sundarbans system during postmonsoon season (November 2016).

To perform these experiments, 0.5 L water samples were transferred in acidwashed polycarbonate Nalgene bottles in duplicate for DIN and C uptake rate measurements. These bottles were covered immediately with black cloth to avoid light shock to phytoplankton. Samples were spiked with 99 atom% enriched ¹⁵NH₄Cl, Na¹⁵NO₃, NaH¹³CO₃ to trace NH₄⁺, NO₃⁻ and C uptake rates, respectively. Tracer addition was around 10% of the ambient concentrations. Immediately after the tracer addition, sample bottles were deployed for incubation for 4 h, approximately symmetrical to the local noon. Post-incubated samples were filtered onto precombusted (4 h at 450 °C) 47 mm Whatman GF/F filters (Figure 2.3), and stored for the mass spectrometric analysis after drying at 50 °C overnight.



Figure 2.3: Filtration of samples after incubation.

Mass spectrometric analyses of post-incubation samples were performed using a continuous flow stable isotope ratio mass spectrometer (Delta V plus) connected to an elemental analyzer (Flash EA 2000), where ¹⁵N or ¹³C atom% and PON or POC content were measured. The uptake rates were calculated as follows (Dugdale & Wilkerson, 1986; Kanda et al., 2003):

Uptake rate (µmol N (or C) L⁻¹ h⁻¹) =
$$\frac{P \times \Delta I_p}{[T \times [(I_0 S_a + I_r S_t)/(S_a + S_t) - I_0]]}$$

where P is the amount of particulate N or C (μ mol L⁻¹) in post-incubation sample; ΔI_p is the increase in ¹⁵N atom% (or ¹³C atom% for C uptake) in particulate N (or C) during incubation; S_a and S_t are ambient and added concentrations (in μ mol L⁻¹), respectively; I_r and I_0 are ¹⁵N (or ¹³C) atom% of added tracer and natural ¹⁵N (or ¹³C) atom%, respectively; and T is the incubation time (hours). This equation assumes no formation of nutrients during the incubation, and therefore, rates presented here are representative of potential rates.

The relative uptakes of NO_3^- and NH_4^+ were also calculated using the relative preference index (McCarthy et al. 1977).

$$RPI_{x} = \frac{\begin{bmatrix} U_{x} \\ U_{x} + U_{y} \end{bmatrix}}{\begin{bmatrix} X \\ X + Y \end{bmatrix}}$$

Where, X and Y are concentrations of NO_3^- and NH_4^+ in µmol L^{-1} , respectively; Ux and Uy represents the corresponding uptake rates in µmol L^{-1} h⁻¹.

2.6 Measurement of N₂ fixation rates

Experiments to quantify N_2 fixation rates were performed during monsoon season at sixteen locations in the Chilika lagoon following ¹⁵N₂ bubble method using ¹⁵N₂ (98 + atom%) tracer gas purchased from the Cambridge Isotope Laboratory (CIL). Surface water samples were collected using a clean bucket and later on transferred to 300 ml borosilicate bottles (two light and one dark for each location). The dark bottles were covered with aluminum foil to ensure no light penetration into the bottles. These bottles

were filled to the brim and sealed tightly with septum caps to ensure no air bubble inside the bottles. 0.5 ml of ${}^{15}N_2$ was injected in each bottle using chromatographic syringe followed by gentle mixing. These bottles were incubated for three hours symmetrical to the local noon. Post-incubation samples were filtered using precombusted 47 mm GF/F filter papers and then dried in oven at 50 °C. Ambient N₂ concentrations for rate measurements were estimated following gas solubility table of Weiss (1970) using *in situ* temperature and salinity. The N₂ fixation rates were calculated using the formula given by Monotoya et al. (1996).

The main drawbacks of ¹⁵N₂ bubble methods are (a) incomplete dissolution of $^{15}N_2$ gas in the sample during incubation leading to underestimation of N₂ fixation rates (Mohr et al., 2010; Großkopf et al., 2012), (b) release of regenerated N during incubation (Bronk et al., 1994; Capone et al., 1994; Mulholland et al., 2004), and (c) presence of the impurities such as NO₃⁻, NH₄⁺, N₂O etc. in the N₂ tracer gas supplied by the distributors leading to underestimation of N₂ fixation rates (Dabundo et al., 2014). However, the N₂ gas used during this study (supplied by CIL) is known to have very low NH₄⁺ and non-detectable NO₃⁻ and N₂O concentrations as reported by Dabundo et al. (2014).

Details of the locations in the Chilika and Hooghly-Sundarbans system where the above mentioned measurements and experiments were performed are discussed in the respective chapters.

Chapter 3 Biogeochemistry of the Chilika lagoon

Coastal lagoons with shallow depths and large freshwater inflow are susceptible to nutrient enrichment from surface runoff, groundwater discharge, and atmospheric inputs (Del Amo et al., 1997; Aguilera et al., 2001; Paerl et al., 2002; Kennish and Paerl, 2010). Hence, the temporal and spatial variability in their water quality depend upon the relative strength of inputs from terrestrial and atmospheric sources along with tidal flows (Ganguly et al., 2015; Patra et al., 2016; Barik et al., 2017). Lagoons are also well documented as significant contributor of inorganic C to the atmosphere and retain high pCO_2 due to rapid increase in heterotrophic respiration of organic C (Frankignoulle et al., 1998; Cai et al., 1999; Hanson et al., 2003). Even though lagoons are smaller in size compared to other coastal bodies, they are important sites for terrigenous organic C mineralization (Jansson et al., 2000). Moreover, situated between land and sea, coastal lagoons act as filter retaining inorganic and organic nutrients (Newton et al., 2003; Kozlowsky-Suzuki and Bozelli, 2004). For the above reasons,

coastal lagoons have generated considerable research interest after 1970; though limited studies have been reported in peer reviewed literature (Panigrahi et al., 2009). One of the direct aftermaths of anthropogenic activities in recent years impacting estuarine and coastal ecosystems is the excess loading of nutrients along with terrestrial organic matter (Bhavya et al. 2016). These nutrients enter into the estuarine and coastal systems in the form of organic and inorganic N and P through rivers and atmosphere, causing biogeochemical imbalance, specifically with respect to N:P stoichiometry of the estuaries (Galloway et al., 2004). These increased nutrients promote primary productivity in receiving waters causing algal blooms, which may further make the system heterotrophic through the process of respiration by organic matter. In the present day, most of the world's estuarine zones are heterotrophic where pCO_2 exceeds ~ 2000 µatm (Borges, 2005; Green et al., 2006; Chen and Borges, 2009; Laruelle et al., 2010; Sarma et al., 2009, 2012a).

The understanding and quantification of different biogeochemical processes within the estuaries and lagoons are important to fully comprehend the cycling of climatologically and ecologically important elements like N and C within the system. The rates of N and C uptake along with their dependence on N and P distribution in tropical water bodies provide an insight into nutrient utilization within the system (Glibert et al., 2016). Stable isotopic composition of C and N in POM and SOM are important to understand the sources and transformation of organic matter within the aquatic system. The $\delta^{15}N_{POM}$ in shallow water bodies reflect the influence of N assimilation or organic matter mineralization in the water column as well as in sediments. The $\delta^{15}N_{POM}$ can also provide an insight into the availability and utilization of nutrients along with source identification of organic matter in benthic as well as pelagic environments. Nitrogen from residential wastewater and agricultural land-use is a major source of nutrient to the lagoons (Carpenter et al., 1998; Leavitt et al., 2006; Ying-Xin et al., 2007) and often have distinct isotopic compositions. The N isotopic composition of dissolved fraction in the water column is of particular importance as it may help to trace anthropogenically derived N sources due to distinct isotopic signature depending upon the origin and process involved (Mayer et al., 2002; Kendall et al., 2007; Peipoch et al., 2012). On the other hand, $\delta^{13}C_{POM}$ is important to distinguish between autochthonous and allochthonous sources of POM and SOM with distinct C isotopic signature. One of the major components of C cycle is DIC and identifying the controlling mechanisms of DIC variability in estuarine environments is important for understanding C biogeochemistry and to diagnose other important processes such as biological productivity, organic C degradation, carbonate dissolution or precipitation and CO₂ exchange.

The present study focusses on studying different aspects of N and C cycling in the Chilika lagoon. Literature suggests that research in Chilika has gained momentum with emphasis on environmental parameters monitoring, species identification and few aspects of C cycle (Gupta et al., 2008; Panigrahi et al., 2009; Muduli et al., 2012, 2013; Prasad et al., 2014; Srichandan et al., 2015a,b). Detailed studies with respect to quantification of rates of different biogeochemical processes related to N and C cycles are lacking in the lagoon. Hence, the specific goals of the present study were to (a) understand the origin and transformation of POM in the lagoon, (b) decipher the role of N₂ fixation as new N source to the lagoon, (c) measure the rates of DIN and C uptake in the lagoon, (d) generate a preliminary model for N budget of the Chilika, (e) identify the role of different biogeochemical processes influencing DIC and pCO_2 in the lagoon, and (f) trace the provenance and fate of SOM in the Chilika and nearby Bhitarkanika mangrove.

3.1 Study area and sampling

3.1.1 Chilika lagoon

Ecologically, the Chilika lagoon is a mixture of marine, brackish and freshwater with a mean depth of ~ 2 m (Gupta et al., 2008). For this study, based on topography, the lagoon was classified into four different sectors, viz. (1) the southern sector (surface area ~156 km²) connected with the sea through Palur canal, (2) the northern sector (surface area ~ 295 km²) which receives the maximum discharge through rivers, (3) the outer channel (surface area ~ 37 km²) that is connected with the sea, and (4) the central sector (surface area ~ 372 km²), which acts as a mixing zone of the northern sector and

the outer channel (Gupta et al., 2008; Muduli et al., 2012; Figure 3.1). The lagoon undergoes wide seasonal and annual changes in salinity, light availability, and nutrient inputs from 52 rivers and rivulets discharging into it (Barik et al., 2017). The lagoon is separated from the Bay of Bengal (BOB) by a 60 km long sand bar. Direct rainfall on the lagoon surface also makes a significant contribution towards freshwater input to the Chilika (Mohanty et al., 1996). Because of these external inputs, water depth of the lagoon increases by about 0.5 - 1 m during the southwest monsoon (Mohanty et al., 1996). The lagoon area encounters wind speed ranging from 4.45 - 7.02 m s⁻¹ during wet season and 0.97 - 3.89 m s⁻¹ during dry season (Gupta et al., 2008).

During winter (November - January), a large portion of this lagoon near Nalabana island in the central sector remains submerged and act as a wetland, which also serves as breeding and roosting grounds for thousands of migratory water fowl (Panigrahi et al., 2009; Fig. 3.1). The Chilika lagoon suffered excessive submerged and free floating (e.g. *Azolla, Eichhornia, Nymphea, Pistia, Ipomea*) weed growth in the past where weeded area escalated from 20 km² in 1972 to 685 km² in 2000 at a rate of 15 km² per year (Gupta et al., 2008; Panigrahi et al., 2009). Phytoplankton of the Chilika consists of a mixture of marine, brackish water and freshwater taxa, mainly represented by four groups of algae: diatoms (*Bacillariophyceae*), dinoflagellates (*Pyrrophyceae and Dinophyceae*), blue-green algae (*cyanobacteria*), and green algae (*Chlorophyceae*) (Srichandan et al., 2015a). Except for the northern sector, all other northern sector due to its freshwater regime supports a large population of euglenoids (Srichandan et al., 2015a).

Sampling and experiments

Experiments were performed to measure DIN uptake and C uptake rates along with rates of N₂ fixation in surface waters at sixteen locations during monsoon (all locations in Figure 3.1 except Stn. 17). Apart from measurements of several physico-chemical parameters, water samples were also collected for nutrients, TSM, PON, POC, $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$, DIC concentration, and $\delta^{13}C_{DIC}$ measurements at these locations.

Unfortunately, we lost eleven samples for $\delta^{13}C_{DIC}$ and six samples of DIC for monsoon during transportation. During postmonsoon, similar experiments (except N₂ fixation) and sample collection (except PON and $\delta^{15}N_{POM}$) along with measurements of physicochemical parameters were performed at seventeen locations throughout the lagoon (Figure 3.1). During premonsoon, experiments for DIN and C uptake rates along with samples collection for nutrients, PON, POC, $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$, DIC concentration, and $\delta^{13}C_{DIC}$ were performed in surface water at fifteen locations (all locations in Figure 3.1 except Stn. 13 & 17). Water samples were also collected from the bottom of the lagoon during premonsoon at eleven locations for DIN uptake rate measurements, PON, POC, and their isotopic compositions (all locations in Figure 3.1 except Stn. 4, 5, 9, 13, 15, 17). The C uptake rates, DIC concentrations, and $\delta^{13}C_{DIC}$ were also measured in the bottom waters during premonsoon at ten locations (all locations in figure 3.1 except Stn. 4, 5, 8, 9, 13, 15, 17) along with nutrients (NO₃⁻, NH₄⁺, PO₄³⁻, and SiO₄⁴⁻) at thirteen locations (except Stn. 5, 13, 15, and 17 in Figure 3.1). Samples for TSM were not collected during premonsoon. During postmonsoon, apart from measurements of physico-chemical parameters, water samples for POC, $\delta^{13}C_{POM}$, DIC concentration, and $\delta^{13}C_{DIC}$ from surrounding rivers draining into the Chilika and a canal (Palur) connected to nearby Rushikulya estuary were also collected (Figure 3.1). Two groundwater samples for DIC and $\delta^{13}C_{DIC}$ were also collected from two locations near the lagoon during postmonsoon. A brief description of the field sampling and experimental techniques has already been described in the methodology section (Chapter 2).

Apart from above samples, eight sediment cores (C-1 to C-8) were collected during Feb 2014 using UWITEC corer operated from the boat surface (Figure 3.2). The eight sediment cores were representatives of the different sectors of the lagoon. C-1 and C-2 represented the northern sector, whereas C-3 and C-4 were from the central sector. C-5 was collected from the mixing zone of the central and southern sector. C-6 and C-7 represented the southern sector and C-8 was from the outer channel area, where the marine influence was maximum. The maximum length of cores at each location was variable which were sampled at discrete depth intervals (C-1: surface, 10, 15 and 20 cm; C-2: surface, 10, 15, 20, 25 and 30 cm; C-3: surface, 10, 15 and 20 cm; C-4: surface, 10 and 15 cm; C-5: surface, 10 and 15 cm; C-6: surface, 10 and 15 cm; C-7: surface, 10 and 15 cm; and C-8: surface, 10, and 15 cm). The variation in length of sediment cores at each location was due to the difference in water column, difficulties in accessibility of sediment layer due to macrophytes and sea grasses, and the nature and depth of the sediment layer collected by the corer.

3.1.2 Bhitarkanika mangrove

Bhitarkanika is a mangrove wetland located in the northeastern corner of the Kendrapara district in the state of Odisha in India. Geographical coordinates of the Bhitarkanika is between 20°34' - 20°45' N latitudes and 86°49' - 87°03' E longitudes (Figure 3.3). Bhitarkanika is the second largest mangrove ecosystem in India, which has much significance in terms of ecological, geomorphological and biological perspectives. It is comprised of a variety of biomes including mangrove forests, rivers, creeks, estuaries, backwater, accreted land and mud flats. This mangrove flourishes in the deltaic region, formed by the rich alluvial deposits of Brahmani, Baitarani & the Dhamra rivers (Barik et al. 2016). It offers an example of a salt tolerant, complex and dynamic ecosystem that occurs in tropical and subtropical inter-tidal regions (Barik et al. 2016). Because of its rich biodiversity in flora and fauna, the mangrove has been declared as a Ramsar site, i.e., wetland of international importance (Reddy et al., 2007). Bhitarkanika is dominated by fine grain sized sediments, mostly sand, during premonsoon. Silt-clay fraction increases two fold from premonsoon to postmonsoon (Chauhan et al., 2014).

To study the sources of SOM in the Bhitarkanika and compare it with nearby Chilika lagoon, three sediment cores (A, B and C) from the Bhitarkanika mangroves were collected using a gravity corer during February 2015 (Figure 3.3). The sampling locations were chosen on the basis of river confluence with a creek along with the density of the mangrove vegetation. The sampling locations were restricted to three owing to the restrictions imposed by the Department of Wildlife Conservation as interior of the mangrove is habitat for crocodiles.



Figure 3.1: Different sectors of the Chilika lagoon showing locations for DIN uptake, C uptake, and N₂ fixation rates along with samples collected for POM, DIC and $\delta^{13}C_{DIC}$.



Figure 3.2: Sampling locations for SOM (C1 to C8) in different sectors of the Chilika lagoon.



Figure 3.3: Core sampling locations for SOM in the Bhitarkanika mangroves.

3.2 Environmental parameters and nutrients

The variations in surface water temperature in the Chilika were 26 - 30.10 °C, 25.50 - 27.96 °C, and 23.32 - 25.31 °C for monsoon, premonsoon, and postmonsoon, respectively (Tables 1, 2 & 3). The salinity of the lagoon varied from 0.10 to 18.23 during monsoon, 0.39 to 36.40 during premonsoon, and 1.59 to 10.82 during postmonsoon. Seasonal comparison suggested higher average salinity for premonsoon followed by monsoon and postmonsoon (Tables 1, 2 & 3). The higher average salinity in monsoon compared to postmonsoon was due to relatively lower rainfall during monsoon months. The northern sector locations showed lower salinity compared to other sectors during all the three seasons owing to active freshwater flow from the northeast rivers (Muduli et al., 2012) whereas, the southern sector showed stable salinity as this sector is connected to Rushikulya estuary through Palur canal (Figure 3.1). The outer channel showed higher salinity as these stations were located in the ocean influence zone. The central sector, which is the mixing zone, showed variable salinity. Some stations during premonsoon showed salinity very close to ocean salinity as residing water masses were of marine type. This is not surprising in the case of the

Chilika lagoon as the residence time of water is reported to be very high (premonsoon: 127 days; monsoon:12.3 days; Gupta et al., 2008). The pH of the lagoon during entire study period ranged from 7.08 to 8.69. TSM ranged from 45 - 261 mg L⁻¹ and 12.66 - 63.73 mg L⁻¹ for monsoon and postmonsoon, respectively (Figure 3.4b). The %DO in the Chilika during premonsoon varied from 59.93 - 83.43 %, whereas it was between 76.25 - 106.16 % for monsoon. For postmonsoon, %DO ranged from 89.29 - 142.52 %. Average %DO during the three seasons were 87.16 % (monsoon), 69.97 % (premonsoon), and 122.54 % (postmonsoon). Total alkalinity values in the lagoon ranged from 0.90 - 1.38 mmol L⁻¹, 1.23 - 1.87 mmol L⁻¹, and 1.28 - 1.79 mmol L⁻¹ during monsoon, premonsoon and postmonsoon, respectively. On an average, the northern sector of the lagoon showed lower TA compared to all other sectors. Chlorophyll *a* ranged from 1.10 - 30.10 µg L⁻¹ during premonsoon, whereas for monsoon it varied from 3.34 - 32.98 µg L⁻¹. During postmonsoon, Chl*a* ranged from 2.19 - 19.13 µg L⁻¹. Average Chl*a* values were 11.45, 7.25, and 7.40 µg L⁻¹ for monsoon, premonsoon and postmonsoon, respectively (Tables 1, 2 & 3).



Figure 3.4: The variation in (a) POC/TSM and (b) TSM with salinity in the Chilika during monsoon and postmonsoon.

The NO₃⁻ concentrations in the lagoon varied from 2.41 - 11.18 μ mol L⁻¹ (average ~ 5.77 ± 2.65 μ mol L⁻¹), 2.41 - 10.49 μ mol L⁻¹ (average ~ 4.52 ± 2.20 μ mol L⁻¹) and 1.02

- 5.62 µmol L⁻¹ (average ~ 3.01 ± 1.27 µmol L⁻¹) during monsoon, premonsoon, and postmonsoon, respectively. Similarly, NH₄⁺concentrations in the lagoon ranged from 5.13 - 8.95 µmol L⁻¹ (average ~ 6.31 ± 0.91µmol L⁻¹), 2.46 - 10.61 µmol L⁻¹ (average ~ 5.49 ± 2.36 µmol L⁻¹), and 1.16 - 6.79 µmol L⁻¹ (average ~ 4.65 ± 1.49 µmol L⁻¹) during monsoon, premonsoon, and postmonsoon, respectively. The average PO₄³⁻ concentration in the lagoon during three seasons were 0.90 ± 0.21 µmol L⁻¹ (monsoon), 0.48 ± 0.25 µmol L⁻¹ (premonsoon), and 0.19 ± 0.10 µmol L⁻¹ (postmonsoon). Similar to PO₄³⁻, average SiO₄⁴⁻ concentrations were 50.07 ± 16.31 µmol L⁻¹, 54.48 ± 14.17 µmol L⁻¹, and 50.59 ± 12.88 µmol L⁻¹ during monsoon, variations in NO₃⁻ and NH₄⁺ concentration of the bottom waters were 2.72 - 11.78 µmol L⁻¹ and 3.31 - 9.79 µmol L⁻¹, respectively. The range of PO₄³⁻ and SiO₄⁴⁻ concentrations in the bottom waters of the Chilika during premonsoon were 0.11 - 1.04 µmol L⁻¹ and 32.06 - 74.87 µmol L⁻¹, respectively (Table. 4).

3.3 Particulate organic matter in the Chilika

3.3.1 Isotopic compositions and contents of carbon and nitrogen

During premonsoon, $\delta^{13}C_{POM}$ in surface and bottom waters of the Chilika varied from -27.0 to -20.3 ‰ and -26.6 to -20.6 ‰, respectively. The $\delta^{13}C_{POM}$ in the surface waters during monsoon varied between -29.2 and -20.5 ‰, whereas for postmonsoon the same were between -29.5 to -22.9 ‰. The average $\delta^{13}C_{POM}$ in the surface water of the lagoon during premonsoon (-23.9 ± 2.2 ‰) and monsoon (-23.7 ± 2.0 ‰) was quite similar. Relatively lower $\delta^{13}C_{POM}$ ($\delta^{13}C_{POM}$: -26.2 ± 1.8 ‰) was found during postmonsoon. Particulate organic carbon concentrations showed large variation in the Chilika during premonsoon, where it ranged between 23.5 - 678 µmol L⁻¹ and 34.6 - 720 µmol L⁻¹ for surface and bottom waters, respectively. During monsoon and postmonsoon, POC ranged from 26.7 - 222.7 µmol L⁻¹ and 36.1 - 96.9 µmol L⁻¹, respectively (Figure 3.5a). The $\delta^{13}C_{POM}$ in river samples varied from -31.4 to -26.1 ‰ and in Palur canal, which is connected to Rushikulya estuary, it was -23.7 ‰. The POC

	Station	WT (°C)	Secchi Depth (m)	pН	Salinity	DO (%)	TA (mmol L ⁻¹)	NO3 ⁻ (μmol L ⁻¹)	NH4 ⁺ (μmol L ⁻¹)	SiO4 ⁴⁻ (µmol L ⁻¹)	PO4 ³⁻ (μmol L ⁻¹)	Chla (µg L ⁻¹)
Monsoon	1	29.50	0.27	8.36	5.62	106.16	0.90	6.05	7.59	90.00	1.41	25.00
	2	28.53	0.22	7.87	15.08	88.26	0.94	5.96	5.82	39.51	0.99	32.98
	3	29.00	0.28	8.05	0.1	83.54	1.24	6.17	6.38	37.51	1.15	3.96
	4	30.00	0.27	8.31	8.62	83.81	1.02	7.01	6.48	43.38	0.94	24.40
	5	28.90	0.52	8.16	0.26	76.25	1.34	7.96	5.5	37.95	0.86	8.21
	6	28.50	0.86	7.91	12.13	81.11	1.30	7.18	6.13	53.2	0.9	7.02
	7	28.00	0.85	8.4	4.52	88.31	1.19	2.99	8.95	60.69	0.79	3.34
	8	29.00	0.48	7.88	7.88	80.08	1.27	6.58	6.27	53.47	0.83	4.47
	9	28.31	1.07	8.5	16.16	78.99	1.17	2.41	5.89	45.92	0.83	4.87
	10	28.50	0.95	8.2	18.23	88.44	1.22	2.45	5.37	54.68	0.91	6.91
	11	30.10	1.08	8.3	7.57	88.79	1.38	4.67	6.31	66.03	1.15	5.94
	12	30.00	1.5	8.69	12.6	101.92	1.37	4.19	5.84	69.24	0.72	3.34
	13	28.20	1.02	8.3	12.03	90.84	1.38	3.37	6.56	66.89	0.66	19.25
	14	27.98	1.29	8.3	12.93	89.29	1.30	3.61	5.13	67.63	0.52	4.19
	15	26.00	0.32	8.12	14.34	80.68	1.33	10.55	6.38	32.6	0.79	24.24
	16	28.00	0.3	8.04	14.91	87.16	1.31	11.18	6.36	30.37	1.00	5.05

 Table. 1 Nutrients and physico-chemical parameters in the Chilika lagoon during monsoon (WT: water temperature).

		WT	Secchi Depth		<i>a</i> .	DO	TA	NO3 ⁻	NH4 ⁺	SiO ₄ ⁴⁻	PO4 ³⁻	Chla
	Station	(°C)	(m)	pН	Salinity	(%)	$(\mathbf{mmol} \mathbf{L}^{-1})$	(µmol L ⁻¹)	(µmol L ⁻¹)	(µmol L ⁻¹)	(µmol L ⁻¹)	(µg L ⁻¹)
Premonsoon	1	26.61	0.51	8.14	3.77	83.43	1.23	6.24	9.14	39.32	0.14	2.60
	2	26.72	0.27	7.08	5.28	78.67	1.27	3.61	3.76	53.62	0.12	13.20
	3	26.46	0.07	7.4	0.39	70.35	1.18	4.26	7.71	65.76	0.36	14.90
	4	26.19	0.82	7.14	30.14	74.13	1.56	2.41	3.44	26.74	0.7	2.60
	5	26.98	0.20	7.59	36.4	72.94	1.64	3.05	6.93	46.01	0.78	30.10
	6	25.58	0.33	7.38	21.44	63.01	1.59	4.09	5.75	56.21	0.5	5.20
	7	27.96	0.58	7.35	14.42	67.34	1.46	3.47	10.61	47.76	0.59	7.30
	8	26.53	0.70	7.35	16.33	70.42	1.59	5.95	6.48	46.07	0.35	2.40
	9	26.09	0.63	7.72	16.06	59.93	1.66	3.45	5.63	66.06	0.51	2.30
	10	26.77	0.80	7.12	16	69.44	1.55	7.54	3.23	76.28	0.3	1.40
	11	25.55	0.93	7.16	17.76	68.53	1.64	4.34	3.1	45	0.35	1.50
	12	25.96	0.90	7.14	15.89	68.53	1.47	10.49	4.71	52.06	0.2	1.10
	14	26.52	0.93	7.16	17.76	68.53	1.87	2.59	2.46	71.45	0.58	1.50
	15	25.90	0.25	7.43	17.63	68.95	1.39	2.54	3.91	48.76	0.91	18.60
	16	25.50	0.80	7.15	35.04	65.38	1.36	3.72	5.42	76.12	0.86	4.00

 Table. 2 Nutrients and physico-chemical parameters in the surface waters of the Chilika lagoon during premonsoon.

	Station	WT (°C)	Secchi Depth (m)	рН	Salinity	DO (%)	TA (mmol L ⁻¹)	NO3 ⁻ (µmol L ⁻¹)	NH4 ⁺ (μmol L ⁻¹)	SiO4 ⁴⁻ (µmol L ⁻¹)	PO4 ^{3.} (µmol L ⁻¹)	Chla (µg L ⁻¹)
Postmonsoon	1	25.04	0.66	7.64	1.59	117.85	1.28	3.36	5.26	56.76	0.1	11.27
	2	25.24	0.31	7.28	6.38	89.29	1.38	2.32	3.4	56.09	0.26	6.85
	3	24.41	0.56	7.55	1.77	122.62	1.37	4.02	5.42	86.99	0.12	8.24
	4	24.41	1.05	7.29	7.11	142.52	1.27	1.36	4.58	36.07	0.23	9.34
	5	23.32	1.07	7.93	2.59	140.19	1.78	3.76	4.07	53	0.15	19.13
	6	24.33	0.74	7.59	6.36	138.22	1.78	2.84	5.41	43.41	0.11	4.77
	7	24.49	0.88	8.21	7.23	126.76	1.61	3.04	1.16	44.75	0.12	16.39
	8	24.3	0.58	7.99	6.48	124.95	1.72	2.34	3.9	49.63	0.12	8.26
	9	25.31	0.89	8.15	7.72	125.69	1.54	2.45	5.94	52.58	0.17	5.51
	10	24.57	0.62	7.65	7.18	117.06	1.31	3.35	5.25	54.33	0.14	2.19
	11	24.36	0.86	7.62	9.83	118.28	1.62	5.32	6.45	44.69	0.18	4.55
	12	24.27	1.39	7.68	9.29	127.70	1.64	1.14	4.75	37.5	0.55	1.96
	13	25.26	1.98	7.65	10.82	128.60	1.57	2.63	6.62	33.91	0.2	3.12
	14	25.06	1.04	7.62	9.6	112.29	1.79	5.62	6.79	35.64	0.13	4.38
	15	23.49	0.81	7.11	2.21	126.14	1.19	3.25	3.56	63.77	0.21	0.69
	16	23.35	0.71	7.78	7.35	107.66	1.47	3.42	2.89	57.63	0.16	15.97
	17	23.6	0.94	7.79	9.2	117.33	139	1.02	3.55	53.27	0.21	3.19

 Table. 3 Nutrients and physico-chemical parameters in the Chilika lagoon during postmonsoon.

	Station	NO3 ⁻ (μmol L ⁻¹)	NH4 ⁺ (μmol L ⁻¹)	SiO4 ⁴⁻ (µmol L ⁻¹)	PO4 ³⁻ (μmol L ⁻¹)
Premonsoon	1	6.16	4.99	36.42	0.11
(Bottom)	2	5.31	3.57	50.24	0.14
	3	2.72	7.85	54.01	0.62
	4	3.36	6.68	32.06	0.84
	6	2.73	6.03	71.42	0.62
	7	3.49	9.79	43.07	0.64
	8	5.91	2.56	40.24	0.36
	9	2.76	5.17	35.46	0.47
	10	7.44	3.31	66.32	0.27
	11	4.35	5.39	45.39	0.32
	12	11.78	4.44	45.39	0.37
	14	6.93	3.76	73.22	0.47
	16	3.15	6.58	74.87	1.04

 Table. 4 Nutrients concentration in the bottom waters of the Chilika during premonsoon.

concentration in the riverine samples varied from 70.5 to 126.8 μ mol L⁻¹, whereas for Palur canal the same was 68.6 μ mol L⁻¹.

The $\delta^{15}N_{POM}$ in the Chilika during monsoon varied from 1.3 ‰ at Stn. 11 in the southern sector to a maximum of 8.3 ‰ at Stn. 16 near the outer channel with an average of ~ 4.0 ± 1.7 ‰. The PON concentration in the lagoon during the same season ranged from 4 µmol L⁻¹ (Stn. 12 - southern sector) to 32.3 µmol L⁻¹ (Stn. 2- northern sector) with an average of ~ 11.4 ± 7.3 µmol L⁻¹. During premonsoon, surface $\delta^{15}N_{POM}$ ranged between 4.8 (Stn. 9 - central sector) and 13.1 ‰ (Stn. 3- northern sector), whereas PON concentrations varied between 3.1 (Stn. 14 – southern sector) and 87.7 µmol L⁻¹ (Stn. 3 - northern sector; Fig 3.5b). For bottom samples, $\delta^{15}N_{POM}$ varied from 4 - 14.3 ‰ and PON concentration was between 4.6 and 94.8 µmol L⁻¹.



Figure 3.5: Variation in (a) $\delta^{13}C_{POM}$ with POC, and (b) $\delta^{15}N_{POM}$ with PON in the Chilika lagoon during different seasons.

3.3.2 Provenance and distribution of organic carbon and nitrogen in the Chilika lagoon

The Chilika is a large lagoon with inputs from more than 52 rivers and rivulets during different seasons (Gupta et al., 2008). The average POC concentration in the Chilika was the highest during premonsoon followed by monsoon and postmonsoon. Similar to POC, average PON was also the highest during premonsoon. The northern sector of the lagoon showed the highest POC and PON compared to other sectors during the whole study period. Seasonally, the highest average POC in the northern sector was during premonsoon (325.3 μ mol L⁻¹) followed by monsoon (128.5 μ mol L⁻¹) and postmonsoon (84.5 μ mol L⁻¹). Sources of high POC and PON (i.e., POM) to the northern sector could be of both allochthonous and autochthonous origin as this particular sector receives maximum discharge from surrounding river catchment (Figure 3.1 and 3.5). The highest POC during the study period was observed at the surface (678 μ mol L⁻¹) and bottom (720 μ mol L⁻¹) at Stn. 3 in the northern sector. Some studies have associated high POC due to mixing of zooplankton to the POM; however, this cannot be deciphered during the present study due to lack of suitable data in this

regard. No correlation was found between POC and salinity in any of the seasons. In the Chilika lagoon, POC makes larger contribution to the TSM pool during postmonsoon compared to monsoon (Figure 3.4), which has also been observed for another estuary in the southern India (Gautami Godavari; Bouillon et al., 2003).

The average $\delta^{13}C_{POM}$ were in the same range during monsoon and premonsoon, whereas it was relatively depleted in ¹³C for postmonsoon. This appears to be due to dominance of terrestrial and freshwater inputs to the lagoon and/or production of freshwater phytoplankton during postmonsoon as both are expected to have lower δ^{13} C_{POM} (Guo et al., 2015). This is also corroborated by the low δ^{13} C_{POM} observed in riverine samples during the study period (Fig. 3.5a). Among the different sectors, relatively lower $\delta^{13}C_{POM}$ were observed in the northern sector (Stn. 1, 2, 3) and the southern sector of the lagoon (Stn. 11, 12, 13, 14; Fig 3.5a) during postmonsoon compared to other stations and seasons. This was due to higher riverine discharge from the northeast rivers in the northern sector and mixing of water from the nearby Rushikulya estuary in the southern sector. Comparatively higher $\delta^{13}C_{POM}$ in the outer channel area during the entire study period was primarily due to higher marine influence in that sector. Similar to $\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$ during premonsoon (both surface and bottom) were also higher than monsoon due to dominance of marine water. Unfortunately, samples for $\delta^{15}N_{POM}$ could not be collected during postmonsoon in the lagoon. Irrespective of seasons, the northern sector of the lagoon showed terrestrial influence, whereas outer channel showed marine influence during this study.

3.3.3 $\delta^{13}C_{POM}$ and POC/Chla: distinguishing organic matter sources

Although $\delta^{13}C_{POM}$ is a powerful proxy to distinguish between organic matter sources, it discriminates "fresh" against detrital organic C if there is any effect of early diagenesis (Savoye et al., 2003). The POC/Chl*a* can act as an alternative source indicator for living phytoplankton. The POC/Chl*a* ratio lower than 200 is characteristic of newly produced phytoplankton in POM, whereas a value higher than 200 is characteristic of detrital or degraded matter (Cifuentes et al., 1988). The cross plot of POC/Chl*a* with $\delta^{13}C_{POM}$ during the present study forms a triangular structure with each

vortex pointing to a particular source (Figure 3.6). The uppermost point in the figure has the highest POC/Chl*a* ratio (~ 546) with $\delta^{13}C_{POM}$ value of -24 ‰ indicating influence of detrital organic matter. The data points belonging to low saline water during the study period occupy the lower left corner of the triangle showing $\delta^{13}C_{POM}$ and POC/Chl*a* ratio of -29.2 ‰ and 47.8, respectively, indicating contribution of freshwater phytoplankton in the lagoon. Data points in the lower right corner of the triangle with higher salinity belong to the living marine phytoplankton end member with a typical $\delta^{13}C_{POM} \sim -20.3$ ‰ and POC/Chl*a* ratio ~ 166.8. More than 50 % of the data points showed POC/Chl*a* ratio < 200 signifying the significance of autochthonous phytoplankton in the lagoon.



Figure 3.6: Cross plot of POC/Chl*a* ratio with δ^{13} C_{POM} in the Chilika lagoon.

3.4 N₂ fixation in the Chilika lagoon

Despite high DIN concentrations in the lagoon, considerable N₂ fixation rates were observed during monsoon season (0.02 - 1.99 nmolN $L^{-1} h^{-1}$; Figure 3.7). The highest rate was observed at Stn. 2 (northern sector) and the lowest at Stn. 6 (central sector). Among the different sectors of the lagoon, average N₂ fixation rates were the highest in the northern sector (0.89 nmolN $L^{-1} h^{-1}$) followed by outer channel (0.56 nmolN $L^{-1} h^{-1}$), central sector (0.34 nmolN $L^{-1} h^{-1}$), and southern sector (0.31 nmolN $L^{-1} h^{-1}$; Figure 3.7).



Figure 3.7: Spatial variation in N₂ fixation rates in the Chilika.

 N_2 fixation rates have been observed to be low in high DIN environment (>1 µmol L⁻¹), which suppresses the nitrogenase activity (Subramaniam and Carpenter, 1994; Capone et al., 1997; Mulholland and Capone, 2009). During the present study, despite high DIN concentrations, measurable N_2 fixation rates were observed with no

significant correlation with DIN concentrations or DIN uptake rates ($r^2 = 0.25$; p > 0.05; Fig not shown). The Stn. 2 in the northern sector showed particularly high N₂ fixation rate (~1.99 nmolN L⁻¹ h⁻¹) possibly due to presence of active N₂ fixing species at this location. In a recent study, the availability of N₂ fixing bacteria in sediments of the Chilika lagoon has been reported (Behera et al., 2017). This study also highlights the dominance of N₂ fixing bacteria in the rhizosphere sediment of the reed *Phragmities karke*, which is found in large parts of the northern sector. Since northern sector is the shallowest part of the lagoon, there could be possibility of such bacterial community in the water column due to sediment churning (Barik et al., 2017), enabling higher N₂ fixation. Similar to observations during the present study, considerable N₂ fixation rates have also been observed in the Cochin estuary (0.59–1.3 nmolN L⁻¹ h⁻¹) despite very high DIN concentrations (Bhavya et al., 2016).

3.5 Dissolved inorganic nitrogen (DIN) uptake in the Chilika 3.5.1 Variations in NO₃⁻ and NH₄⁺ uptake rates in the surface waters

During monsoon, NO_3^- uptake rates in the Chilika ranged from 0.004 to 1.42 µmolN $L^{-1}h^{-1}$, whereas NH_4^+ uptake rates varied from 0.19 to 1.76 µmolN $L^{-1}h^{-1}$. The highest NO_3^- and NH_4^+ uptake rates during monsoon were observed at Stn. 1 in the northern sector, whereas the lowest rates were observed at Stn. 8 in the central sector (Figure 3.8 and 3.9). During postmonsoon, NO_3^- uptake rates in the Chilika ranged from 0.003 (Stn. 7 - central sector) to 1.07 µmolN $L^{-1}h^{-1}$ (Stn. 14 - southern sector), whereas NH_4^+ uptake rates varied from 0.08 (Stn.7- central sector) to 1.42 µmolN $L^{-1}h^{-1}$ (Stn. 13 - southern sector; Figure 3.8 and 3.9). During premonsoon, NO_3^- and NH_4^+ uptake rates ranged from 0.01 (Stn. 7- central sector) to 1.74 µmolN $L^{-1}h^{-1}$ (Stn. 12 - southern sector) and 0.51 (Stn. 4 - central sector) to 1.92 µmolN $L^{-1}h^{-1}$ (Stn. 1 - northern sector), respectively.

The average NO₃⁻ uptake rates during three seasons were 0.51 ± 0.51 , 0.74 ± 0.46 , and $0.35 \pm 0.36 \mu$ molN L⁻¹ h⁻¹ during monsoon, premonsoon, and postmonsoon, respectively. Similarly, average NH₄⁺ uptake rates during three seasons were 1.11 ± 0.43 , 1.12 ± 0.43 , and $0.75 \pm 0.45 \mu$ molN L⁻¹ h⁻¹ for monsoon, premonsoon and

postmonsoon, respectively, suggesting similar NH_4^+ uptake during monsoon and premonsoon seasons compared to postmonsoon. On an average, NH_4^+ uptake was approximately twice compared to NO_3^- uptake in the lagoon during the three seasons. The NO_3^- and NH_4^+ uptake rates observed in the Chilika were higher than the other large aquatic ecosystems of the world (Gu et al., 1997; Gardner et al., 2004; Kumar et al., 2008) and a tropical estuary located in the southern coast of India (Cochin estuary; (Bhavya et al., 2016).



Figure 3.8: Seasonal variation in NO₃⁻ uptake rates in the surface waters of the Chilika lagoon.



Figure 3.9: Seasonal variation in NH_4^+ uptake rates in the surface waters of the Chilika lagoon.

3.5.2 Factors controlling DIN uptake in the Chilika lagoon

To understand the factors controlling DIN uptake rates in the Chilika lagoon, the relationships between DIN uptake rates and several factors such as pH, salinity, Chl*a*, and nutrients were investigated. No significant relationship was observed between DIN uptake rates and pH (Figure 3.10a). Similarly, DIN uptake rates did not show any significant relationship with salinity (Figure 3.10b). Individually, NO₃⁻ and NH₄⁺ uptake rates also did not show any significant relationship with these two parameters suggesting limited control of salinity and pH on DIN uptake rates in the Chilika. To investigate the influence of lagoon's biomass on NO₃⁻ and NH₄⁺ uptake rates, DIN uptake rates were plotted against Chl*a*. No significant correlation was observed between DIN uptake and Chl*a* (Figure 3.10c). When plotted individually, no relationship was found between NH₄⁺ uptake rates and Chl*a* for any season, whereas NO₃⁻ uptake rates showed a significant correlation during monsoon with Chl*a* (r² =

0.51; p = 0.002; Figure not shown) indicating the potential control of Chl*a* on NO₃⁻ uptake during that season. Despite having the highest Chl*a* concentration and sufficient nutrients at Stn. 5 (central sector) during postmonsoon, the observed low NO₃⁻ and NH₄⁺ uptake rates at that location is intriguing. A significant relationship was observed between surface NO₃⁻ and NH₄⁺ uptake rates with respective concentrations (Figure 3.11; NO₃⁻: $r^2 = 0.93$ and p < 0.05; NH₄⁺: $r^2 = 0.70$ and p < 0.05) in the lagoon during premonsoon suggesting significant control of substrate concentration on surface DIN uptake rates during that season. However, no such trend was observed during monsoon and postmonsoon. A significant correlation between DON and Chl*a* during premonsoon in the Chilika has also been reported suggesting DON uptake by phytoplankton (Ganguly et al., 2015). Overall, it appears that DIN uptake rates in the Chilika lagoon are not controlled by a single factor alone. Different factors appear to control DIN uptake during different seasons.



Figure 3.10: Variations in total DIN uptake rates with (a) pH, (b) salinity, and (c) chl*a* in the Chilika lagoon.



Figure 3.11: Relationship of surface NO_3^- and NH_4^+ uptake rates with respective concentrations during premonsoon in the Chilika lagoon.

3.5.3 Relative preference and turnover time of nutrients in the Chilika

Relative preference index (RPI) for both NO₃⁻ and NH₄⁺ were estimated to ascertain the relative preference for these two nutrients by phytoplankton in the Chilika lagoon. The RPI along with *f*-ratio (NO₃⁻ uptake divided by total DIN uptake) helps to understand the temporal fluctuation in preference for different nutrients by phytoplankton in aquatic systems. During the present study, RPI estimates indicate overall preference for NH₄⁺ compared to NO₃⁻ in the Chilika (Figure 3.12). The *f*-ratio also showed preference for NH₄⁺ in the lagoon as depicted by *f* -ratio < 0.5 at majority of the locations (Figure 3.13).

Preference for NH_4^+ with respect to NO_3^- owing to its lower energy requirement by phytoplankton cell has been reported in culture studies as well as field based experiments (McCarthy et al., 1977; Glibert et al., 2016; Jauzein et al., 2017). Inhibition of NO_3^- uptake in the presence of NH_4^+ could be one of the reasons for relatively lower NO_3^- uptake, a commonly observed feature in aquatic systems (e.g., Glibert et al., 1982; Harrison et al., 1987; McCarthy et al., 1999). Although the extent of inhibition is much more variable, the inhibition is potentially greater under nutrient replete conditions and the least when phytoplankton are N-starved (Conway, 1977; Dortch, 1990). During the present study, ambient conditions were nutrient replete and this might have contributed to relatively lower NO_3^- uptake. A recent study pointed out that preferential use of NH_4^+ is expected when NH_4^+ is available at a few µmol L^{-1} level (Glibert et al., 2016), as during the present study. However, highly elevated NH_4^+ (tens to hundreds of µmol L^{-1} level) can actually suppress rather than enhance the NH_4^+ based growth (Dagenais-Bellefeuille and Morse, 2013; Glibert et al., 2014).

Temporal variability in RPI and *f*-ratio suggested that the preference for NO_3^- during premonsoon was relatively higher compared to monsoon and postmonsoon. The resumption of NO_3^- uptake due to depletion of NH_4^+ concentration has been reported by many studies (Wilkerson et al., 2006; Parker et al., 2012). Such situation may influence diatom growth positively, which prefers NO_3^- (Glibert et al., 2016). However, there is no evidence of NH_4^+ depletion during the present study. Changes in species composition might have driven the higher NO_3^- preference during premonsoon.



Figure 3.12: Variations in RPI of NO_3^- and NH_4^+ during (a) monsoon, (b) premonsoon, and (c) postmonsoon in the Chilika lagoon.



Figure 3.13: Variations in f-ratio during (a) monsoon, (b) premonsoon, and (c) postmonsoon in the Chilika lagoon.

To trace the cycling of nutrients in the lagoon, turnover times of NO_3^- and NH_4^+ were calculated by dividing the nutrients concentration with respective uptake rates. On an average, turnover time for NH_4^+ was significantly shorter compared to NO_3^- underscoring faster cycling of NH_4^+ in the water column. During monsoon, Stn. 8 in the central sector showed the highest turnover time for NO_3^- (1700 hrs) and NH_4^+ (32 hrs) owing to high nutrient concentration and low uptake rates. This station is located nearby Nalabana bird sanctuary (Figure 3.1 and 3.14) which is breeding and roosting ground for thousands of migratory birds. On an average, the highest turnover time for NO_3^- and NH_4^+ were observed during monsoon, whereas the lowest was observed during premonsoon.

3.5.4 Surface and bottom DIN uptake during premonsoon

As described earlier, experiments to measure NO_3^- and NH_4^+ uptake rates in both surface and bottom waters were carried out in the Chilika during premonsoon to assess the DIN uptake near bottom of the lagoon. Average NO_3^- uptake in the surface and bottom waters were 0.74 ± 0.46 and $0.54 \pm 0.48 \mu molN L^{-1} h^{-1}$, whereas average NH_4^+ uptake rates were 1.12 ± 0.43 and $1.03 \pm 0.54 \mu molN L^{-1} h^{-1}$, respectively (Figure 3.15). Results indicated that the whole water column of the Chilika is almost equally productive with DIN uptake rates being approximately similar at both surface and the



Figure 3.14: Turnover times of (a) NO_3^- and (b) NH_4^+ during three seasons in the Chilika lagoon.

bottom of the lagoon. This is possibly due to light penetration to the bottom of the lagoon owing to its shallow depth. The DIN concentrations measured in the bottom waters were also approximately similar to surface suggesting possible efflux of nutrients from the sediment to the water column due to mineralization of SOM. Another evidence which supports the previous statement is benthic flux of DIC as measured by Muduli et al. (2013) in both weedy (694 Mg d^{-1}) and non-weedy (317 Mg d^{-1}) environments in the lagoon. Along with DIN, SiO₄⁴⁻ and PO₄³⁻ concentrations in the bottom waters were also similar to the surface which may further support higher DIN uptake in bottom waters (Table 2 and 4). From the present study it can be hypothesized that any shallow ecosystem where nutrients are present in optimum concentration, entire water column may be productive as observed in the Chilika. Observed bottom uptake of DIN also opens an eye towards lake-wide N and C budgeting of shallow aquatic systems as considering only surface productivity may underestimate the annual lake-wide budget. Similar to surface DIN uptake, a significant positive correlation was observed between NH₄⁺ uptake rates and NH₄⁺ concentrations (Figure 3.16a; $r^2 = 0.86$ and p < 0.05) for bottom waters. However, contrary to surface waters, NO₃⁻ uptake rates did not show significant relationship with NO_3^- concentrations (Figure 3.16b).



Figure 3.15: Spatial variations in surface and bottom uptake rates of (a) NO_3^- , and (b) NH_4^+ during premonsoon in the Chilika lagoon.



Figure 3.16: Relationships between (a) NH_4^+ uptake rates with NH_4^+ concentrations, and (b) NO_3^- uptake rates with NO_3^- concentrations in the bottom waters of the Chilika during premonsoon.

3.5.5 Seasonal DIN uptake in the Chilika lagoon

Based on the data of DIN uptake rates from three different seasons, an attempt was made to construct an annual DIN fixation budget for the Chilika. As the lagoon is equally productive on surface as well as bottom, uniform uptake rate as observed on

the surface has been assumed for the entire volume of the photic zone. For the calculation of photic zone, euphotic depths were multiplied by respective surface area of each sectors. Euphotic depths were obtained from measured Secchi disk depth (d) at each locations. Our data also showed variable Secchi disk depths during the three different season due to the variations in water level along with mixing with bottom waters. The extinction coefficient (k) at each station was 1.7/d (French et al., 1982), which was used further to calculate euphotic depth as 4.61/k (Keller, 1988). For some stations, the calculated euphotic depths were greater than the station depths. Therefore, at those locations where calculated euphotic depth was greater than the station depth, the station depth was considered as the euphotic depth. After calculating the euphotic depths, sectorial DIN fixation in the Chilika lagoon was calculated by multiplying average sector wise seasonal DIN uptake rates with average sectorial euphotic depth (seasonal) and surface area of the respective sectors. The total annual DIN fixation including all the sectors in the lagoon using this method was around 121.66 Gg, which included 31.68 Gg y⁻¹ of NO₃⁻ uptake and 89.98 Gg y⁻¹ of NH₄⁺ uptake. The sector wise annual DIN fixation was the highest in the central sector (47.75 Gg y^{-1}) followed by the southern sector (40.96 Gg y^{-1}), northern sector (30.15 Gg y^{-1}) and outer channel (2.80 Gg y⁻¹; Figure 3.17). The highest DIN fixation in the central sector was primarily due to relatively higher surface area compared to all other sectors.

3.5.6 Sources and sinks of nitrogen in the Chilika lagoon

Based on previous studies and the present measurements, quantification of sources and sinks of DIN in the Chilika lagoon have been attempted. Unfortunately there are many processes whose rates are still unknown in the lagoon, which are essential to construct the comprehensive lake-wide budget. Taking all seasons into account, annual NO_3^- and NH_4^+ uptake in the Chilika were estimated to be 31.68 and 89.98 Gg, respectively. Though the lagoon showed high rates of NO_3^- and NH_4^+ uptake, considerable N_2 fixation rates throughout the lagoon have also been observed during the present study. Considering the column integrated fixation, the annual new N introduced via N_2 fixation was estimated to be 0.06 Gg. Taking the lagoon's large surface area into

account, another source of new N to the lagoon is dry deposition of DIN. Since there is lack of dry DIN deposition data over the lagoon, the data reported for the coastal BOB (~ $27 \pm 20 \mu$ molN m⁻² d⁻¹; Srinivas et al., 2011) has been used to calculate the DIN deposition due to their close proximity. Assuming uniform deposition rate over the lagoon, DIN deposition of ~ 0.12 Gg Y^{-1} was estimated. As the lagoon is surrounded by many rivers and rivulets, rivers draining into the lagoon also contribute to the DIN pool of the lagoon. Considering the seasonal (premonsoon, monsoon and postmonsoon) DIN input as reported by Patra et al. (2016), the annual DIN flux to the lagoon via river drainage was 0.02 Gg. Figure 3.18 shows estimates of various sources and sinks of DIN to the Chilika as calculated during the present study. This also depicts processes whose values are still unknown. Overall, new N supplied to the lake via atmospheric deposition is significantly higher than the ones supplied through riverine input and N₂ fixation, which may be due to higher DIN deposition rate used during the calculation. Dry deposition data over the lagoon surface along with rates of other processes are required to build the comprehensive N budget of the lagoon.



Figure 3.17: Sector wise seasonal (a) NO_3^- and (b) NH_4^+ fixation (uptake) in the Chilika lagoon. NS: northern sector, CS: central sector, SS: southern sector, OC: outer channel.



Figure 3.18: Major sources and sinks of DIN in the Chilika lagoon. Question marks signifies unknown rates for those processes.

3.6 Carbon uptake rates in the Chilika lagoon

The movement of C in coastal ecosystems forms a major component of global C cycling (Bauer et al., 2013). The distinct and tightly coupled ecosystems connected to coastal ocean are rivers, lagoons, estuaries, wetlands and continental shelf (Cole et al., 2007; Regnier et al., 2013). The transformation of C occurs laterally through the aquatic continuum across the ecosystems as well as vertically by exchange with atmosphere through the formation of greenhouse gases. The anthropogenic perturbation which has increased flux of C to the inland waters since pre-industrial era has been estimated to be ~ 1.0 Pg C yr⁻¹ owing to export of C from soils (Regnier et al., 2013). Chilika is one of such ecosystem which bears the characteristics of coastal zones. As mentioned earlier, the lagoon suffers huge riverine flux during monsoon from many surrounding rivers and rivulets (Muduli et al., 2012). The previous as well as the present study show the lagoon to be rich in inorganic N containing nutrients (Patra et al., 2016; Barik et al., 2017). River borne nutrients are well known to enhance the phytoplankton growth
along with benthic invertebrates (Pennock and Sharp, 1986; Wilber, 1992; Dai et al., 2008). Measurement of primary productivity (C uptake rates) provides an idea about regional or global C fixation and the removal of N and P containing nutrients from the system. In this regard, C uptake rates were measured during three seasons in the Chilika lagoon using $H^{13}CO_3^{-}$ tracer technique.

3.6.1 Seasonal variation in carbon uptake rates in the Chilika lagoon

During monsoon, C uptake rates in the Chilika lagoon ranged from 1.21 (Stn. 16 - outer channel) to 11.23 μ molC L⁻¹h⁻¹ (Stn. 2 - northern sector) with an average of 3.63 ± 3.06 μ molC L⁻¹h⁻¹ (Figure 3.19). The C uptake rates during postmonsoon varied from 0.33 (Stn. 11 - southern sector) to 1.69 μ molC L⁻¹h⁻¹ (Stn. 3 - northern sector) with an average of ~ 0.86 ± 0.42 μ molC L⁻¹h⁻¹. In the surface waters during premonsoon, C uptake rates ranged from 0.32 (Stn. 4 - central sector) to 10.14 μ molC L⁻¹h⁻¹ (Stn. 5 - central sector). The average surface C uptake rate during premonsoon was ~ 2.38 ± 2.67 μ molC L⁻¹h⁻¹. The average C uptake rate in the surface waters was the highest during the monsoon followed by premonsoon and postmonsoon. During monsoon, the northern sector showed the highest C uptake followed by the outer channel, central sector and southern sector; whereas premonsoon showed a different trend with the highest C uptake in the outer channel followed by the northern, central and southern sector of the lagoon. Similar to DIN uptake, postmonsoon witnessed the lowest C uptake compared to other two seasons with the highest C uptake in the northern sector followed by central, outer and southern sectors (Figure 3.19).

The C uptake rates for bottom waters during premonsoon ranged from 0.02 (Stn. 10 - southern sector) to 5 μ molC L⁻¹ h⁻¹ (Stn. 2 - northern sector). The average C uptake rates for surface and bottom waters were 2.38 ± 2.67 and 1.82 ± 1.73 μ molC L⁻¹ h⁻¹ during premonsoon (Figure 3.20). Similar to DIN uptake, both surface and bottom waters showed comparable C uptake rates except for one location (Stn. 15 - outer channel), where bottom C uptake was significantly lower compared to surface uptake. The comparable N and C uptake rates in the surface and bottom waters of the Chilika lagoon confirms optimum availability of light and nutrients in the bottom waters of the

lagoon, emphasizing the role of benthic zone in the overall biogeochemistry of shallow aquatic systems.

3.6.2 Carbon uptake rates and environmental parameters

The C uptake rates (primary productivity) depend on various parameters such as nutrients, light intensity, temperature, salinity, pH, and Chla (Mulholland and Bernhardt, 2005; Thomas et al., 2012). Unavailability of N and P in optimum proportion is also known to affect the C uptake rates (Hodgkiss and Ho, 1997; Bhavya et al., 2017). Role of environmental parameters such as salinity, pH, %DO, and Chla on C uptake rates has been investigated in the Chilika lagoon. The Chla, an indicator for biomass, showed significant positive correlation with C uptake rates suggesting its role in biomass formation (Figure 3.21). The relationship between Chla and C uptake rates was highly significant for monsoon ($r^2 = 0.83$; p = 0.0003) and premonsoon ($r^2 = 0.83$; p = 0.0003) 0.87; p = 0.0001). It was relatively weak for postmonsoon due to relatively low C uptake rates despite high Chla concentrations (Figure 3.21) at three stations. The removal of these three stations results into strong relationship ($r^2 = 0.71$; p = 0.0001) between Chla and C uptake rates as observed for other seasons. These strong relationships clearly indicate the significant role of C uptake towards biomass formation in the Chilika during all seasons. The %DO, which is an indirect proxy for primary productivity, did not show any correlation with C uptake rates suggesting that the DO level in the Chilika lagoon may be primarily controlled by atmospheric dissolution of DO and not by primary productivity, a commonly observed phenomenon in most aquatic ecosystems (Odum, 1956; Morgan and Stumm, 1970). Similar to DIN uptake, salinity and pH did not show any significant relationship with C uptake rates.



Figure 3.19: Seasonal variations in carbon uptake rates in the surface waters of the Chilika lagoon.



Figure 3.20: Carbon uptake rates in surface and bottom waters during premonsoon in the Chilika.

Apart from the above mentioned environmental parameters, nutrient stoichiometry is an important parameter known to affect primary productivity. Nutrient stoichiometry has changed in the inland and coastal aquatic bodies as they receive anthropogenically derived nutrients from many sources. Chilika lagoon is also one of such examples which is suffering from the problem of nutrient enrichment as it receives nutrients by many sources such as riverine discharge, agricultural waste, nearby human settlements as well as from atmospheric deposition. The effect of nutrient stoichiometry on C uptake rates was investigated during the present study. A plot of C uptake rates with DIN: DIP ratio did not show any significant correlation for any of the studied seasons. This possibly indicated limited role of DIN: DIP stoichiometry on the C uptake rates in the Chilika under present scenario. Apart from DIN, DON has also been reported to be a dynamic component of reactive N and seasonally accumulates in coastal waters (Seitzinger et al., 2002; Berman and Bronk, 2003; Miyazaki et al., 2010; Violaki et al., 2010). A previous study has reported very high average DON concentration in the Chilika lagoon during May $(42.75 \pm 7.65 \mu mol L^{-1})$, August (35.51) $\pm 5.32 \,\mu$ mol L⁻¹), and December (39.93 $\pm 5.01 \,\mu$ mol L⁻¹) of 2011 (Ganguly et al., 2015). During the same study, a significant correlation between DON and Chla ($r^2 = 0.58$; p = 0.003) was observed during the month of May when freshwater flow was minimum. This suggest the preference of primary producers towards regenerated DON during non-monsoon months. Since DON uptake rates were not measured during the present study, a comprehensive study including DIN uptake, DON uptake, and C uptake rates along with nutrients concentration is warranted to understand the relative role of different species of reactive N on organic matter formation as well as the role of nutrient stoichiometry.



Figure 3.21: Relationship between Chla and carbon uptake rates in the Chilika.

3.6.3 Coupling of carbon and nitrogen uptake

Detailed analysis vis-à-vis coupling of C uptake and N uptake rates in the Chilika suggested that the uptake of these two elements by phytoplankton did not follow Redfield ratio (C:N ~106: 16) with the exception of two locations in the entire study period where it was close to Redfield ratio. The C uptake : DIN uptake ratio remained less than 6.6 at majority of stations during the present study. This indicates the possibility of C source other than HCO_3^- during primary productivity, possibly the aqueous CO_2 . The C uptake experiments during the present study used only HCO_3^- as tracer and effectively measured only HCO_3^- uptake rates. Although their uptake mechanism is different, both HCO_3^- and aqueous CO_2 are suitable substrates for phytoplankton and the response of phytoplankton with changing CO_2 concentration largely depends upon the C uptake mechanism (Colman and Rotatore, 1995; Korb et al., 1997; Elzenga et al., 2000; Tortell et al., 2002). There are different C concentration mechanism involved for CO_2 and HCO_3^- fixations. CO_2 being a neutral molecule enters into the cell membrane either by passive diffusion or by active transport; however,

similar mechanism is prohibited for HCO₃⁻ in algae owing to less solubility in lipid membrane and generation of negative electric potential difference across the plasmalemma (Miller et al., 1991; Rotatore and Colman, 1991; Rotatore and Colman, 1992; Rotatore et al., 1995; Raven, 1997; Li and Canvin, 1998; Neven et al., 2011). Thus, HCO₃⁻ incorporation occurs through direct active uptake as well as by conversion of HCO₃⁻ to CO₂ using carbonic anhydrase (Badger et al., 1998; Kaplan et al., 1998). There is some understanding regarding the ratio at which HCO₃⁻ and CO₂ are taken up by marine phytoplankton but it remains largely unknown for coastal species. A study by Burkhardt et al. (2001) showed that CO₂: HCO₃⁻ uptake ratio for two marine diatoms (*P. tricornutum* and *T. weissflogii*) decreased with decreasing CO₂ concentrations although there was uptake increment of substrate affinities for both CO₂ and HCO₃⁻ (Burkhardt et al., 2001). During the same study, half saturation concentrations of CO₂ and HCO₃⁻ were ≤ 5 and $< 700 \,\mu$ M for CO₂ and HCO₃⁻ uptake, respectively (Burkhardt et al., 2001).

During the present study, the deviation of C uptake: DIN uptake rates from the Redfield ratio could be due to uptake of aqueous CO_2 along with HCO_3^- . This is likely as the Chilika remains supersaturated with respect to CO₂ in all seasons (Gupta et., 2008). Except few locations, pCO_2 in surface waters of the Chilika was higher than atmospheric value during the present study as well (described in the following section). Aqueous CO₂ concentrations were also in the required range which varied from 3.94 to 206.33 µmol L⁻¹ during the present study. The deviation of C uptake : DIN uptake rates from the Redfield ratio has been observed in the Cochin estuary as well, which is also supersaturated with respect to CO₂ (Bhavya et al., 2017). A negative correlation between DIC concentrations and C uptake rates was observed during monsoon ($r^2 =$ 0.70; p = 0.002) and postmonsoon ($r^2 = 0.53$; p = 0.0009) which turned poor during premonsoon (figure not shown). Taken together, in order to understand the relative role of aqueous CO₂ and HCO₃⁻ during primary productivity in CO₂ supersaturated aquatic systems, simultaneous uptake rates measurement of both these species is warranted. This may also provide a clue whether using only HCO_3^{-1} tracer as a measure of primary productivity in such systems underestimates the primary productivity.

3.7 Dissolved inorganic carbon dynamics in the Chilika

Identifying the processes responsible for spatial and temporal variability of DIC in estuarine and lagoon systems is important to thoroughly understand its C biogeochemistry. The $\delta^{13}C_{DIC}$ is an important tool for distinguishing and tracing sources, sinks, and transformations of C in the water column (Quay and Stutsman, 2003). The measured DIC concentrations and $\delta^{13}C_{DIC}$ values in the transitional zones such as lagoons and estuaries depend upon various processes within such systems. The physical processes involved are sea-river water mixing, chemical weathering, supply of soil CO₂, CO₂ exchange with the atmosphere; whereas the biogeochemical processes involved are biological production, precipitation or dissolution of minerals such as carbonate, and respiration and degradation of organic matter (Alling et al., 2012; Samanta et al., 2015).

The factors controlling DIC concentration and $\delta^{13}C_{DIC}$ in the open ocean are well known, whereas spatial and temporal variation in $\delta^{13}C_{DIC}$ of estuaries and lagoons (coastal areas) are much more pronounced and influence of freshwater further complicates the signal (Gruber et al., 1999; Racapé et al., 2013). However, given the importance of estuaries and lagoons in overall C cycling, in particular CO₂ efflux to the atmosphere, it is important to study the DIC dynamics in these systems worldwide.

3.7.1 Variation in DIC concentration, $\delta^{13}C_{DIC}$ and pCO_2 in the Chilika

For monsoon, DIC concentrations ranged from 1193 - 2071 µmol L⁻¹ and during postmonsoon it varied from 1390 - 1907 µmol L⁻¹ (Table 5). Surface DIC concentrations during premonsoon ranged from 822 - 2250 µmol L⁻¹, whereas for bottom waters the same varied from 820 - 2227 µmol L⁻¹ (Table 5). For monsoon and postmonsoon, $\delta^{13}C_{\text{DIC}}$ ranged from - 4.5 to - 0.1 ‰ and - 7.1 to - 3.6 ‰, respectively (Table 5). Surface $\delta^{13}C_{\text{DIC}}$ in the lagoon during premonsoon ranged from - 8.2 to - 1.0 ‰ and for bottom waters the same varied from - 8.3 to - 2.7 ‰ (Table 5). In general, the northern sector showed lower DIC concentrations compared to other sectors with Stn. 1 having the lowest concentration during the study period. No spatial pattern in

 $\delta^{13}C_{DIC}$ was observed from the fresh to marine zone in the lagoon. Average $\delta^{13}C_{DIC}$ for the monsoon was relatively higher compared to other two seasons.

Variable pCO_2 was observed during three seasons. During monsoon, pCO_2 varied from 140 µatm to 1234 µatm with an average of 626 µatm, whereas during premonsoon the same ranged between 294 and 5862 µatm with the average of ~ 3411 µatm. The pCO_2 during postmonsoon ranged from 480 to 5902 µatm with an average of 1969 µatm (Figure 3.22).

3.7.2 Mixing curve approximation

The $\delta^{13}C_{DIC}$ in estuarine/lagoon water represents a bulk property whose values are influenced by different sources of C and processes that cause ¹³C versus ¹²C partitioning that affect the DIC pool (Atekwana et al., 2016). To understand the major processes affecting $\delta^{13}C_{DIC}$ and DIC concentrations in the lagoon, the concept of mixing curve approximation was employed through our data. Under conservative mixing, the value of DIC and $\delta^{13}C_{DIC}$ at a particular location in the lagoon would be dependent upon the fraction of each end members (sources) at that place. In an estuary/lagoon, likely dominant sources controlling DIC dynamics are the waters of two different salinities; i.e., freshwater and marine water. The DIC concentration and $\delta^{13}C_{DIC}$ due to such conservative mixing would be as follow:

 $DIC_{mix} = DIC_{f}F_{f} + DIC_{m}(1 - F_{f})$

Where, subscript f and m refer to freshwater and marine water end member, respectively. F_f is the fraction of freshwater that was calculated from salinity as:

$$F_{f} = 1 - \frac{[Sal]_{s}}{[Sal]_{m}}$$

Where 'sal' denotes salinity and s refers to sample. Similar to DIC_{mix} , $\delta^{13}C_{DIC(mix)}$ was calculated using equation adapted from Mook &Tan (1991) :

$$\delta^{13}C_{DIC(mix)} = \frac{Sal_s(DIC_f\delta^{13}C_f - DIC_m\delta^{13}C_m) + Sal_fDIC_m\delta^{13}C_m - Sal_mDIC_f\delta^{13}C_f}{Sal_s(DIC_f - DIC_m) + Sal_fDIC_m - Sal_mDIC_f}$$

Average DIC (1921 μ mol L⁻¹), $\delta^{13}C_{DIC}$ (-10.2 ‰) and salinity (0.35) values obtained for major rivers (Makara, Luna and, Bhargavi) draining into the Chilika were

considered as values for freshwater end member for these parameters during all seasons. During monsoon and postmonsoon, values for the marine end members (DIC: 1500 µmol L⁻¹; $\delta^{13}C_{DIC}$: – 1.2 ‰) have been taken from the reported data for the northern BOB (Dutta et al., 2010; Akhand et al., 2012). Marine end member values for DIC and $\delta^{13}C_{DIC}$ were taken as 1830 µmol L⁻¹ and – 0.4 ‰ for the calculation of DIC_{mix} during premonsoon (Sabine et al., 2002; Dutta et al., 2010). The salinity values mentioned in the above references were taken as marine end member value for salinity. Using the above-mentioned method, the calculated conservative mixing values for DIC and $\delta^{13}C_{DIC}$ along with observed values in the Chilika are shown in Figure 3.23. Majority of observed DIC and $\delta^{13}C_{DIC}$ values did not follow the conservative mixing line, which implies the presence of additional processes modifying DIC and $\delta^{13}C_{DIC}$ in the lagoon. Similar behavior of DIC and $\delta^{13}C_{DIC}$ has also been observed in other Indian estuaries (Bouillon et al., 2003; Samanta et al., 2015).

To decipher different processes responsible for controlling DIC dynamics in the Chilika, deviations of DIC and $\delta^{13}C_{\text{DIC}}$ from the conservative mixing values were calculated as follows (Alling et al., 2012):

$$\Delta \delta^{13} C_{DIC} = \delta^{13} C_{sample} - \delta^{13} C_{mix}$$
$$\Delta [DIC] = \frac{[DIC]_{sample} - [DIC]_{mix}}{[DIC]_{mix}}$$

Where, ΔDIC is deviation in DIC concentration relative to calculated conservative mixing concentration (DIC_{mix}). $\Delta \delta^{13}C_{DIC}$ is deviation from the conservative mixing calculated $\delta^{13}C_{DIC}$ and is simple difference in isotopic composition of sample to that of $\delta^{13}C_{DIC(mix)}$. Following Alling et al. (2012), a four-quadrant plot was obtained by plotting ΔDIC vs. $\Delta \delta^{13}C_{DIC}$. The sampling points around the centre of the plot represent locations where DIC and $\delta^{13}C_{DIC}$ values are solely influenced by conservative mixing (Figure 3.24). During the present study, however, only a few samples clustered around the centre and majority of samples were spread in different quadrants indicating influence of different biogeochemical and physical processes on DIC dynamics. The data in the Figure 3.24 can be explained by the combination of four processes: (i) decomposition or degradation of organic C (DC), (ii) carbonate dissolution (CD), (iii)

carbonate precipitation (CP), and (iv) outgassing of CO_2 (OG) or biological production (BP). The first two processes, i.e., DC and CD adds DIC to the system, whereas CP and OG/BP removes DIC from the system. Similarly, DC and CP depletes the DIC pool in ¹³C, whereas CD and OG/BP enriches the DIC pool in ¹³C.



Figure 3.22: Variation of *p*CO₂ with AOU in the Chilika lagoon.

	Monsoon		Premonsoon (surface)		Premonsoon (bottom)		Postmonsoon	
Station	DIC (umol L ⁻¹)	$\delta^{13}C_{DIC}$	DIC (umol L ⁻¹)	$\delta^{13}C_{DIC}$	DIC (umol L ⁻¹)	δ ¹³ C _{DIC} (‰)	DIC (umol L ⁻¹)	$\delta^{13}C_{DIC}$
1	1301	SL	822	-4.3	820	- 4.7	1390	- 5.0
2	1193	SL	1102	-4.0	1057	-4.1	1741	- 6.0
3	SL	SL	1215	- 7.7	1275	- 8.3	1508	-4.7
4	SL	SL	1853	- 3.8	2010	- 7.7	1746	- 5.7
5	2071	-4.4	1894	- 1.0	NA	NA	1688	-7.0
6	1896	- 3.6	2021	-4.2	2227	- 7.3	1733	- 5.5
7	1924	SL	2044	-8.2	NA	NA	1798	- 5.3
8	2028	-4.5	1745	- 3.1	1692	- 3.0	1751	- 5.6
9	SL	SL	1677	- 6.1	NA	NA	1820	- 5.1
10	SL	SL	2051	-4.0	1909	- 3.6	1853	- 5.0
11	1878	SL	1867	-4.7	1867	-4.7	1898	-4.8
12	1823	SL	1857	-4.1	1857	-4.1	1819	-4.7
13	SL	SL	NA	NA	NA	NA	1764	- 6.6
14	SL	SL	1967	-2.7	1967	-2.7	1834	- 4.6
15	1853	-2.8	1627	- 1.4	NA	NA	1675	-7.1
16	1909	-0.1	1642	- 1.1	NA	NA	1737	- 6.4
17	NA	NA	NA	NA	NA	NA	1907	- 3.6

Table 5. DIC concentrations and $\delta^{13}C_{DIC}$ values for the Chilika waters (SL: represents samples lost during transportation; NA: Sampling not performed at that location).



Figure 3.23: Observed and conservative mixing values of DIC and $\delta^{13}C_{DIC}$ in the Chilika for different seasons.



Figure 3.24: Various processes controlling DIC and $\delta^{13}C_{DIC}$ dynamics in the Chilika lagoon (BP: biological production; OG: outgassing of CO₂; CP: carbonate precipitation; CD: dissolution of carbonate; DC: degradation of organic carbon).

3.7.3 Biogeochemical processes modulating DIC in the Chilika

Degradation of organic carbon

Degradation of organic C or aerobic respiration can be an important process contributing to the DIC pool. Both dissolved organic C and POC degradation adds DIC to the system without substantial isotopic fractionation (Norrman et al., 1995; Hullar et al., 1996). In the Chilika, only five samples belonging to the central sector of the lagoon during premonsoon exhibited clear signature of degradation of organic matter on DIC (Figure 3.24). This may be due to macrophytic respiration in some part of the central sector. The net community respiration by the macrophytes in the Chilika is estimated to be around 3.67 gC m⁻³ d⁻¹ (by the *in situ* O₂ incubation experiment in dark) which can produce 153 µmol kg⁻¹ of DIC (Gupta et al., 2008). Furthermore, significant correlation between pCO_2 and AOU (r² = 0.61; p < 0.05) during monsoon also suggested influence of organic matter oxidation on the pCO_2 and hence on DIC (Figure 3.22). Oxidation of organic matter leading to high pCO_2 has also been observed in the Pearl River estuary in China (Zhai et al., 2005). Previous studies have found Chilika to be heterotrophic (specially the northern sector) with high partial pressure of CO_2 (Gupta et al., 2008). Carbon flux through net community respiration in the northern sector was 203 ± 70 mgC m⁻² h⁻¹ (Gupta et al., 2008). Bacterial respiration is also dominant in the northern sector of the lagoon contributing as high as 83% of the total CO_2 flux from the lagoon (Muduli et al., 2012). However, during the present study limited clear signature of organic matter degradation on DIC was observed.

Biological production and outgassing of CO2

Most of the samples belonging to postmonsoon and a few samples from premonsoon fell in the upper left quadrant indicating active biological production and/or outgassing of CO₂ during these periods (Figure 3.24). During postmonsoon, the lagoon was saturated with O₂ suggesting possibility of increased primary production as O₂ is a major by-product; however, as mentioned earlier, no relationship between %DO and C uptake rates was found during the present study. Our results also showed negative AOU during postmonsoon indicating active primary productivity (Figure 3.22). Although, lagoon was supersaturated with O₂ during postmonsoon, high *p*CO₂ was also observed during the same season. Except four locations, *p*CO₂ in the Chilika was higher than the atmospheric value suggesting the potential for CO₂ outgassing, which in turn modifies the DIC chemistry. Out of 42 sampling locations, only 4 showed negative FCO₂ indicating outgassing of CO₂ from the lagoon, making it largely a source of CO₂ to the regional atmosphere. Overall, it appears that there is significant spatial variability in processes modulating DIC dynamics in the lagoon during same season.

Carbonate dissolution

Carbonate dissolution adds DIC to the system and increases both DIC concentration and $\delta^{13}C_{\text{DIC}}$ in the water column. During the present study, 14 out of 42 samples belonging to all seasons showed the effect of carbonate dissolution (Figure 3.24). This signifies the importance of this process in controlling DIC and $\delta^{13}C_{\text{DIC}}$ in the Chilika on annual scale. To assess carbonate dissolution process, calcium carbonate saturation index (Ω) was calculated following Millero (2013).

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}^*}$$

Where $[Ca^{2+}] [CO_3^{2-}]$ is the ion product of the concentrations of Ca^{2+} and CO_3^{2-} and K_{sp}^* is the solubility product at *in situ* salinity and temperature. Ca^{2+} and CO_3^{2-} concentrations have been calculated based on thermodynamic formulas of Millero (2013) using *in situ* salinity, temperature and TA. Except one sample, $\Omega < 1$ was observed throughout indicating carbonate dissolution as an active process in the Chilika lagoon.

If dissolution of carbonate plays active role in the lagoon then it would supply excess calcium and hence will result in its non-conservative behavior in the lagoon. To calculate the deviation of dissolved Ca from the conservative mixing, mixing values were calculated using 12.12 mmol L⁻¹ as ocean end member (Sen Gupta et al., 1978) and 0.10 mmol L⁻¹ for freshwater end member (calculated following thermodynamic formula of Millero (2013) using average salinity of Makara, Luna, and Bhargavi Rivers). Mixing calculations of Ca showed excess Ca in the lagoon throughout. A plot of Δ Ca with Δ DIC showed significant correlation during premonsoon (Figure 3.25; r² = 0.67 and p < 0.0001) and postmonsoon (Figure 3.25; r² = 0.87 and p = 0.001) securing additional evidence for the occurrence of carbonate dissolution in the lagoon. Although all monsoon samples fell within carbonate dissolution quadrant (Figure 3.24), no correlation was observed between Δ Ca and Δ DIC for monsoon, which suggested simultaneous role of other process during that season.

Carbonate precipitation

Carbonate precipitation removes ¹³C from the system as during precipitation heavier isotope precipitates preferentially causing decrease in DIC as well as $\delta^{13}C_{DIC}$. During the present study, all samples showed $\Omega < 1$ except one sample during monsoon. This shows that carbonate precipitation does not play a significant role in controlling DIC dynamics in the lagoon. If the ionic product of Ca²⁺ and CO₃²⁻ exceeds the solubility product of these two components then carbonate would precipitate. In this study, although we have observed higher Ca²⁺ concentration, CO₃²⁻ concentration was lower and the product of these two never exceeded the solubility product. The station where we have observed $\Omega > 1$ (Stn. 12- southern sector) has the highest CO₃²⁻ concentration as well as relatively higher Ca²⁺ concentration.



Figure 3.25: Relation between Δ DIC with Δ Ca in the Chilika lagoon.

Overall, it appeared that DIC dynamics in the Chilika was shaped by the interplay of different processes during different seasons and locations. CO₂ outgassing and carbonate dissolution appeared to be modulating DIC across season and locations;

primary productivity appeared to be a dominant process in modifying DIC during postmonsoon. At few locations during premonsoon, degradation of organic matter appeared to play a dominant role.

Groundwater discharge

Although the processes mentioned above control the DIC dynamics in the Chilika lagoon, possibility of contribution from ground water needs to be explored. Groundwater is known to have high DIC and our two groundwater samples also showed very high DIC concentrations (Pantha Niwas: 9484 µmol L⁻¹ and Barkul: 10064 µmol L⁻¹). The TA/DIC ratio is considered to be a proxy for identification of ground water contribution to the aquatic system. During dry season, TA/DIC > 1 indicates ground water mediated DIC input to the estuarine system (Guo et al. 2008). During the present study, except for a few samples, TA/DIC ratio was < 1 implying that the Chilika is not significantly influenced by groundwater discharge and hence it may not have important role in controlling DIC chemistry.

3.8 Biogeochemistry of sediments in the Chilika lagoon and Bhitarkanika mangrove

The organic matter in the bottom sediments of transitional aquatic ecosystems (defined as SOM) is a complex mixture of components originating from marine as well as terrestrial sources (Tesi et al., 2007). The particulate detritus of plants in the water and on the land surrounding an aquatic system comprises the primary source of organic matter to the sediments (Meyers and Ishiwatari, 1993). The SOM participates in biogeochemical processes such as mineralization and supply nutrients to benthic animals and microbes (Meyers and Ishiwatari, 1993). Also, SOM are widely used as proxies for the reconstruction of paleo-climate and paleo-environment (Shen, 2013) along with acting as a global sink for CO₂ by locking it over a geological time scale (MacKenzie, 1981).

Similar to lagoons, intertidal mangrove ecosystems are also an important interface for the C and N cycle in tropical coastal environments. Mangrove sediments

are also known for long-term sequestration of organic C because of its high productivity and low sediment respiration to net primary production ratio and hence plays an important role in the global C cycle (Jennerjahn and Ittekkot, 2002; Alongi, 2014). The most extensive areas of mangrove forest occur on sedimentary shorelines, where large rivers discharge in low gradient coastlines (Bouillon et al., 2003).

The δ^{13} C and δ^{15} N are extensively used to trace the provenance of organic matter along with their transformations through processes such as mineralization or diagenetic alterations in marine and terrestrial environments (Davies et al., 2016; Koziorowska et al., 2016; Parker et al., 2016; Sun et al., 2016; Garzon-Garcia et al., 2017; Nitzsche et al., 2017). The δ^{13} C is particularly useful to distinguish between land and marine sources of organic matter (Sarma et al. 2012b; Krishna et al. 2013; Shynu et al. 2015; Lujanienė et al. 2016; Garzon-Garcia et al. 2017). In general, terrestrial organic matter has lower δ^{13} C and δ^{15} N compared to marine organic matter (Vizzini et al., 2005).

Along with δ^{13} C and δ^{15} N, C_{org}/N ratio also plays an important role in source identification of organic matter. Generally, marine algae have Corg/N ratios between 4 - 10, whereas vascular land plants have C_{org}/N ratios of ≥ 20 (Meyers, 1994). The mixing of organic matter from different sources cause a shift in δ^{13} C, δ^{15} N and C_{org}/N from their typical end member values, especially in the case of coastal settings (Lamb et al., 2006). To distinguish different sources of organic matter in mangrove and lagoon sediments and to estimate changes in source along with Corg burial over time, it is important to understand source indicators which clearly differentiate between different types of organic matter inputs (Lamb et al., 2006). Studies using Corg/N ratios as tracers of different organic matter end member showed that the ratio can be altered by many processes, including ammonification, nitrification and denitrification (Matson and Brinson, 1990; Thornton and McManus, 1994; Cifuentes et al., 1996; Andrews et al., 1998; Yamamuro, 2000; Graham et al., 2001). Decrease in Corg/N ratios with depth have also been observed due to absorption of organic or inorganic N onto silicate clay surfaces (Macko et al., 1993) or the incorporation of N by bacteria in decaying organic matter (Cifuentes et al., 1996). The magnitude of δ^{15} N changes will, however, depend on a range of factors such as availability of inorganic N substrate, N₂ fixation, δ^{15} N signature of the newly added N, and fractionation effect (Altabet et al., 1995; Meyers and Arnaboldi, 2008).

Limited Studies related to sources of organic matter and its burial in coastal and mangrove systems exists in tropical climate with a few reports from Indian estuaries (Prasad and Ramanathan, 2009; Ranjan et al. 2011; Sarma et al. 2012b; Krishna et al. 2013; Shynu et al. 2015; Sarkar et al. 2016). In particular, studies utilizing N isotopic composition of SOM are even more scarce compared to C owing to its complexity and narrow variability during an annual productivity cycle. Although $\delta^{15}N$ are increasingly used as tracers for the food chain and trophic interactions in lakes, more studies related to annual variations in $\delta^{15}N$ of sedimenting particles are needed for a better understanding of the factors controlling the cycling of N in aquatic systems (Bernasconi et al., 1997). Additionally, the coupling between suspended POM in the water column and SOM needs to be clearly understood. During the present study, an attempt was made to understand the dynamics and cycling of C and N at two Ramsar sites (Chilika lagoon and Bhitarkanika mangrove) in the east coast of India using stable isotopes measurements in sediments. The specific aims of this part of the thesis were: (1) characterization of different sources of organic matter at two contrasting ecosystems, (2) quantification of contributions from different sources to the organic matter pool using mixing model, (3) to investigate potential relationships between POM and SOM, and (4) to study transformation of organic matter during burial. The locations of the sediment cores in the Chilika lagoon and Bhitarkanika mangrove has been shown in Figures 3.2 and 3.3 and details of sampling depth and methodologies followed is described earlier.

3.8.1 Concentrations and isotopic compositions of carbon and nitrogen in sediment organic matter

The C_{org} , N and C_{org}/N ratio in cores C-1 to C-8 in the Chilika lagoon and Core A to Core C in the Bhitarkanika mangrove varied substantially. The depth profiles of

 $\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$, $%C_{org}$, %N and C_{org}/N ratio in the lagoon and mangrove sediments are shown in Figure 3.26 and 3.27.

Chilika lagoon

Organic C and N in the surface sediments of the Chilika lagoon varied from 0.20 to 1.86 % and 0.03 to 0.20 %, respectively. Average %C_{org} and %N were observed to be the highest at C-3 in the central sector of the lagoon compared to other sectors (Figure 3.26). At the majority of locations, C_{org}/N ratio showed a slight decrease with depth. Depth-wise changes in %C_{org} were more than %N. Increase in %C_{org} at 10 cm depth was observed for C-1, 2, 4, 6, and 7 whereas, decrease in %C_{org} was observed for C-3, 5, and 8 at the same depth (Figure 3.26). $\delta^{13}C_{SOM}$ in the Chilika lagoon's surface sediment varied from -21.9 ‰ (C-3) to -19.9 ‰ (C-8) and $\delta^{15}N_{SOM}$ ranged from 3.3 ‰ (C-5) to 4.6 ‰ (C-8). Except for C-1, no significant enrichment in $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ with depth where it increased from -21.6 to -18.9 ‰ and 3.7 to 6.2 ‰, respectively. Overall for all depths, mean $\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$, %C_{org} and %N were -21.1 ± 0.8 ‰, 4.2 ± 0.6 ‰, 0.84 ± 0.47 % and 0.11 ± 0.05 %, respectively (Figure 3.26).

Bhitarkanika mangrove

In the Bhitarkanika mangrove, the surface %C_{org} ranged between 1.10 % (Core C) to 1.34 % (Core B), whereas %N did not show any variability (0.07 - 0.08 %). Average %C_{org} was observed to be the highest at Core A compared to other two cores (Figure 3.27). %N showed a consistent decrease with depth in all three cores. %C_{org} showed a wider variation with depth in all cores with no particular trend (Figure 3.27). Large variation with no consistent depth-wise trend was observed for C_{org}/N ratio as well. At cores A, B and C, the C_{org}/N ratios varied from 13.20 to 18.83, 6.78 to 18.46 and 8.12 to 14.03, respectively. Surface $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ varied from -25.3 ‰ (Core A) to -24.3 ‰ (Core B) and 3.9 ‰ (Core C) to 4.7 ‰ (Core B), respectively. The three sediment cores showed different $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ profiles with depth. The overall increasing trend in $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ with depth was found for Core A. No such clear trend was observed at Core B. Core C showed slight depletion in $\delta^{15}N_{SOM}$ and an

overall increase in $\delta^{13}C_{SOM}$. Overall, for all depths, mean $\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$, %C_{org} and %N were -24.6 ± 0.8 ‰, 4.3 ± 0.5 ‰, 1.04 ± 0.26 %, 0.07 ± 0.01 %, respectively (Figure 3.27).

3.8.2 Sources of organic matter in the Chilika-Bhitarkanika sediments

The $\delta^{15}N_{SOM}$ in the Chilika and Bhitarkanika showed overlapping signatures (Chilika: 3.3 - 6.2 ‰; Bhitarkanika: 3.5 - 5.2 ‰), whereas $\delta^{13}C_{SOM}$ (Chilika: -22.3 to -18.9 ‰; Bhitarkanika: -25.8 to -22.6 ‰) and Corg/N ratio (Chilika: 1.43 to 12.36; Bhitarkanika: 6.78 to 18.83) were quite distinct (Figure 3.28). Based on $\delta^{13}C_{SOM}$ and C_{org}/N ratio, the source of organic matter in the Bhitarkanika mangrove sediments appears to be a mixture of terrigenous and marine origin. Carbon isotopic composition of POM in the water column of Chilika, a source of organic matter to the sediments, also indicated mixed, terrestrial and marine, signatures in different sectors of the lagoon (Figure 3.29). The $\delta^{13}C_{SOM}$ of the Chilika was on an average 2.6 % higher compared to $\delta^{13}C_{POM}$. Three hypotheses can be provided for this significant increase (p = 0.001) in δ^{13} C from POM to SOM in the lagoon. First, diagenetic alteration or decomposition of organic matter in the water column as well as in the sediment column evidenced by the benthic flux of DIC in both weedy (694 Mg d^{-1}) and non-weedy (317 Mg d^{-1}) environments of the lagoon (Muduli et al., 2013). This high flux of DIC suggests higher remineralization or decomposition rates in the lagoon. During decomposition of organic matter, the lighter isotopes (¹²C and ¹⁴N) gets preferentially mineralized leaving remaining organic pool enriched in the heavier (¹³C and ¹⁵N) isotopes. Secondly, domination of submersed aquatic vegetation in the lagoon (especially in the northern sector) can have important role in increasing the $\delta^{13}C_{SOM}$ as reported in Lake Panasoffkee (Brenner et al., 2006), where few aquatic submersed vegetation have high δ^{13} C values (e.g. Najas: -16 ‰; Vallisneria: : -16 ‰; Potamogeton: -13 ‰; Hydrilla: -13 ‰). This vegetation with high δ^{13} C may settle to the sediment after completing their life cycle leading to increase in $\delta^{13}C_{SOM}$ relative to $\delta^{13}C_{POM}$. Third, the high residence time of water in the lagoon (premonsoon: 127 days; monsoon:12.3 days;

(Gupta et al., 2008) may favour organic matter remineralization in the water column leading to increase in δ^{13} C.

Average $\delta^{13}C_{SOM}$ for mangrove sediments was ~ 3.5 ‰ lower compared to that of lagoon sediments indicating relatively higher terrestrial influence in the Bhitarkanika mangrove. Our data for $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ in the mangrove sediments fall in the range observed for Pichamvaram mangrove forest sediments ($\delta^{13}C_{SOM} = -$ 24.3 ± 1.8 ‰ and $\delta^{15}N_{SOM} = 4.2 \pm 0.86$ ‰; Ranjan et al., 2011) and $\delta^{13}C_{SOM}$ values of other mangrove/estuarine ecosystems in the world such as Vietnam ($\delta^{13}C_{SOM}$: –23.0 ± 0.4 ‰; Kennedy et al. 2004), Philippines ($\delta^{13}C_{SOM}$: –25.6 to –25.9 ‰; Kennedy et al. 2004), Tanzania ($\delta^{13}C_{SOM}$: –25.5 ‰; Muzuka and Shunula, 2006), and Florida ($\delta^{13}C_{SOM}$: –28.9 to –19.0‰; Hernandez et al., 2001). This indicates the uniformity in processes active in regulating the C dynamics in mangrove systems across the globe.

3.8.3 Depth-wise transformation of sediment organic matter

Based on a previous study, an attempt was made to determine the age of the collected cores in the Chilika lagoon. Sedimentation rates in different sectors of the lagoon are 0.76 cm/year, 0.80 cm/year and 0.28 cm/year for the northern, central and southern sectors, respectively (Unnikrishnan et al., 2009). Applying these sedimentation rates for the respective sectors, the approximate age of the sediment cores (from C-1 to C-8) were estimated to be 26, 39, 25, 18, 18, 53, 53, 18 years, respectively.

In the Chilika lagoon, the two sediment cores from the southern sector, which is connected to an estuary through Palur canal (Figure 3.2 and 3.26; C - 6 and C - 7) showed no significant depth-wise variability in $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$. The %C_{org} and C_{org}/N ratio in these cores, however, showed an increase at 10 cm depth indicating a possible change in organic matter source or preferential mobilization of N in the past.



Figure 3.26: Depth profiles of $\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$, $%C_{org}$, %N and C_{org}/N ratio in SOM of the Chilika lagoon.





Figure 3.27: Depth profiles of $\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$, $%C_{org}$, %N and C_{org}/N ratio in SOM of the Bhitarkanika mangrove.

 $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ of sediment cores in the central sector of the lagoon (Figure. 3.26; C-3, C-4 and C-5) did not demonstrate much change up to 10 cm, although there is an increment in $\delta^{15}N_{SOM}$ value in case of C-3 at 15 cm depth. C_{org}/N signal showed predominantly marine signature ($C_{org}/N < 10$) with small decrease with

depth. C-2 is located in the mixing zone of the northern and central sector which showed an increase in $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ along with C_{org}/N at 15 cm depth indicating active remineralization process with preferential N mobilization. C-1 in the northern sector of the lagoon showed a steady increase in $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ with depth, potentially suggesting increased marine influence or increased *in situ* phytoplankton production in the lagoon itself, which is counter intuitive as this sector suffers more fluvial input compared to other sectors. This increase can also be attributed to remineralization during burial process. The anomalous decrease in C_{org}/N with predominantly marine signature has been observed at 10 cm depth in C-1 probably indicating the formation of organic matter in N surplus environment (Fig 3.26). Core C-8, located in the outer channel clearly indicated the marine dominance with virtually no depth-wise variation.

Cross-plots of $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ vs. C_{org}/N (Figure 3.28) can be used to understand the dominance of different sources of organic matter in the study area. Although the $\delta^{13}C_{SOM}$ is a good indicator of organic matter source in mangrove and estuarine ecosystems, $\delta^{15}N_{SOM}$ and C_{org}/N ratios, sometimes, can be unreliable as they are influenced by diagenetic alterations (Prahl et al., 1997). The $\delta^{13}C_{SOM}$ vs. C_{org}/N and $\delta^{15}N_{SOM}$ vs. C_{org}/N (Figure 3.28) indicate that both lagoon and mangrove systems in the present study differ significantly in terms of organic matter characteristics. The $\delta^{15}N_{SOM}$ and $\delta^{13}C_{SOM}$ values of Chilika lagoon as well as Bhitarkanika mangrove are within the range reported in various aquatic systems within India (Table. 6).

The $\delta^{13}C_{SOM}$ of the Bhitarkanika mangrove lie between – 25.8 to –22.6 ‰ which point towards mixed marine and mangrove/terrestrial origin. Barring surface, Core A within the mangrove showed a general depth-wise increase in $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ (Figure 3.27; core A). C_{org}/N ratio, though fluctuating, showed predominantly terrestrial signature (C_{org}/N > 12). In core B, both $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ did not show significant variability with depth. C_{org}/N ratio, however, at this place showed the highest variability (6-18) with an anomalous decrease at 20 cm depth. The slight increase in $\delta^{13}C_{SOM}$ at same depth may be due to susceptibility for degradation of marine organic matter than terrestrial derived organic matter (Hedges et al., 1997). Variable $\delta^{13}C_{SOM}$ observed with depth may be because of diagenetic alteration in the past. All the three cores showed a consistent decrease in %N with depth but showed a significant variation in %C_{org} and hence the large variation in C_{org}/N ratios. The C_{org}/N ratios in all the cores fell within the range of terrestrial values possibly suggesting a mixture of vascular and non-vascular plants.



Figure 3.28: Relationships between (a) $\delta^{13}C_{SOM}$ and C_{org} : N ratio, and (b) $\delta^{15}N_{SOM}$ and C_{org} : N ratio of the Chilika lagoon and Bhitarkanika mangrove (all depths).



Figure 3.29: δ^{13} C and δ^{15} N of SOM and POM in the Chilika lagoon (only surface data).

3.8.4 Proportion of terrestrial and marine sources to sediment organic matter

Based on organic matter inputs from terrestrial and marine sources, two end-member mixing model was applied for the Bhitarkanika mangrove. The mixing ratio was calculated based on the formula given below (Calder and Parker, 1968; Koziorowska et al., 2016)

$$F_{terr} (\%) = \frac{\delta^{13} C_{mar} - \delta^{13} C_x}{\delta^{13} C_{mar} - \delta^{13} C_{terr}} \times 100$$

Where F_{terr} is the contribution from terrestrial and/mangrove fraction, $\delta^{13}C_{terr}$ is C isotopic composition of terrestrial end-member, $\delta^{13}C_{mar}$ is C isotopic composition of marine end-member, and $\delta^{13}C_x$ is measured $\delta^{13}C$ values of SOM. For the purpose of calculation, δ^{13} C of POM in the Chilika lagoon at the northernmost location during monsoon (- 29.2 ‰; Stn. 1) was considered as $\delta^{13}C_{terr}$. The $\delta^{13}C$ of POM observed at station 16 in the outer channel area (- 21.3 %; monsoon) was considered as $\delta^{13}C_{mar}$. Based on this, sediments from cores B and C showed that almost $\sim 60 - 70$ % of organic matter in these cores is composed of terrestrial/mangrove vegetation and rest is of marine origin (Figure 3.30). Core A indicated ~ 50 % terrestrial and ~ 50 % marine contribution as this particular station is located in the marine influence zone (Figure 3.30). An attempt was made to estimate the fraction of terrestrial contributions to the SOM of Chilika using the same end member values; the calculation showed overwhelmingly marine contribution as all data points of δ^{13} C for SOM fell within the marine range. However, this calculation did not take into account the increase in C isotopic composition of SOM in the Chilika due to biogeochemical transformations as evidenced by increase in δ^{13} C from POM to SOM.

The findings of the present study along with other similar studies (e.g., Meyers 1994; Gonneea et al. 2004) emphasize that the amount and type of organic matter in the sediments of aquatic and mangrove ecosystems vary over time and eventually contribute to their paleo-environmental and paleo-climatological records. Also, only a

small fraction of the suspended organic matter produced or brought in to the photic zone survives alterations during sinking and sedimentation in such systems. Despite being modified due to selective degradation, the small surviving fraction of organic matter gets incorporated in the bottom sediments preserving the source and environmental records in the elemental (C_{org}/N) and isotopic composition of organic matter ($\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$).



Figure 3.30: Fraction of marine and terrestrial contributions to the organic matter pool of the Bhitarkanika mangrove sediments.

Location	$\delta^{13}C_{SOM}$ (‰)	$\delta^{15}N_{SOM}$ (‰)	C _{org} (%)	N (%)	C _{org} : N	References	
Coringa estuary (mangrove creek)	-21.3 ± 1.0	4.4 ± 0.8	NA	NA	NA	(Bouillon et al., 2002)	
Coringa estuary (mangrove outlet)	-20.2 ± 1.1	4.4 ± 0.8	NA	NA	NA	(Bouillon et al., 2002)	
Chunnambar (riverine/mangrove)	-24.5 to -23.3	NA	0.4 - 0.6	NA	7.5 - 10.8	(Bouillon et al., 2004)	
Off Goa (Eastern Arabian sea)	-21.4 to -20.5	6 - 7.8	2.32 - 3.4	0.24 - 0.40	8.5 - 10.5	(Agnihotri et al., 2008)	
Pichavaram mangrove	-24.3 ± 1.8	4.2 ± 0.86	1.2 ± 0.52	0.08 ± 0.03	16.6 ± 4.1	(Ranjan et al., 2011)	
Pichavaram estuary	-23.2 ± 1.6	5.1 ± 1.3	0.37 ± 0.19	0.03 ± 0.01	12.3 ± 2.9	(Ranjan et al., 2011)	
Godavari estuary	-23.1 to -26.2	11.2 - 7.3	0.1 - 0.9	0.01 - 0.18	3.5 - 18.5	(Sarma et al., 2012b)	
Bay of Bengal (shelf region)	-23.3 to -16.7	3.7 - 13.5	0.63 - 1.64	0.02 - 0.13	9.2 - 46.6	(Krishna et al., 2013)	
Bay of Bengal (slope region)	-21.4 to -17.6	4.9 - 8.3	0.85 - 1.99	0.05 - 0.18	9.9 - 18.6	(Krishna et al., 2013)	
Mandovi estuary (wet season)	-27.2 to -21.6	4.0 -10.0	0 27 1 34	0.0 1- 0.07	11.9 - 24.3	(Shynu et al., 2015)	
Mandovi estuary (dry season)	-28.4 to -24.1	6.8 - 8.9	0.27 - 1.34				
Zuary estuary (wet season)	-26.5 to -25.2	0.01 - 6	0.24 0.52	0.02 0.06	8.57 - 12.5	(Shymu et al. 2015)	
Zuary estuary (dry season)	-26.3 to -24.5	-5.3 to + 5.3	0.24 - 0.32	0.02 - 0.00		(Silyilu et al., 2015)	
Vembanad lake (northern part)	-20.13 to -26.29	0.97 - 9.85	0.25 - 3.55	0.02 - 0.39	10.77 - 15.70	(Sarkar et al. 2016)	
Vembanad lake (southern part)	-24.96 to -27.19	1.07 - 7.24	0.37-4.49	0.03 - 0.34	12.44 - 17.12	(Sarkar et al. 2016)	
Chilika lagoon (estuary)	-21.10 ± 0.79	4.15 ± 0.63	0.84 ± 0.47	0.11 ± 0.05	14.47 ± 3.27	(present study)	
Bhitarkanika mangrove	-24.56 ± 0.80	4.28 ± 0.50	1.04 ± 0.26	0.07 ± 0.01	$7.30\pm\ 2.53$	(present study)	

Table 6. δ^{13} C_{SOM}, δ^{15} N_{SOM}, %C_{org}, %N and C_{org}/N ratio of the SOM in the Indian estuaries, mangrove ecosystems and coastal ocean from the published and present studies (NA: data not available)

Chapter 4 Biogeochemistry of the Hooghly-Sundarbans estuarine system

Estuaries connecting terrestrial and marine ecosystems record biogeochemical and hydrological processes operating between these two environments. Estuaries play an important role in modulating global C cycle and anthropogenic CO₂ budget (Bauer et al., 2013; Regnier et al., 2013; LeQuéré et al., 2016). Atmospheric CO₂ is sequestered into terrestrial systems through photosynthesis and weathering reactions and is transported to the ocean via rivers and estuaries. About 1×10^{15} g of C is discharged annually from the land to the ocean through rivers and estuaries (Degens et al., 1991). Approximately 40 % of this C is discharged as DIC and the rest as DOC and POC (Richey et al., 2002). Although estuaries forms only ~ 4% of the continental shelf regions, CO₂ efflux from the estuarine surface waters is comparable to CO₂ uptake in continental shelf regions of the world (Borges et al., 2005; Cai et al., 2006; Chen and Borges, 2009; Cai, 2011), suggesting estuaries to be not only active pathway for the

transport of C (Ittekkot and Laane, 1991) but also a hotspot for biogeochemical modification of organic matter (Frankignoulle et al., 1998).

Mangroves covering 137,760 km² along tropical and sub-tropical estuaries and coastlines (Giri et al. 2011) are among the most productive natural ecosystems in the world with net primary productivity of 218 ± 72 Tg C yr⁻¹ (Bouillon et al. 2008). The biogeochemical characteristics of a mangrove-dominated estuary is largely different from anthropogenically polluted estuary, where much of the organic matter is derived from domestic, agricultural and industrial wastes. In anthropogenically affected estuarine systems, heterotrophy generally dominates over autotrophy (Heip et al., 1995; Gattuso et al., 1998) and a substantial fraction of biologically reactive organic matter gets mineralized within the system (Servais et al., 1987; Ittekkot, 1988; Hopkinson et al., 1997; Moran et al., 1999). Our understanding about transformation of mangrove derived C and its subsequent export to the adjacent aquatic system appears to be limited, particularly when mangroves are disappearing at alarming rates worldwide (Dittmar and Lara, 2001a; 2001b). A significant fraction of mangrove sequestered C is supplied to intertidal mangrove sediment via litter fall, which undergoes biogeochemical transformations leading to emission of trace gases like CO2 and CH4 from the sediments. The rest is exported to adjacent coastal waters or gets buried in sediment layers as long-term sequestration (Jennerjhan and Ittekkot 2002; Barnes et al., 2006; Kristensen and Alongi, 2006; Donato et al., 2011; Linto et al., 2014). Lack of ample quantitative estimation of above-mentioned biogeochemical processes in many regions of the world restrains mangrove biogeochemists from an in-depth understanding of these processes, which again leads to uncertainty in the estimation of coastal C budget on global scale.

In India, research related to C biogeochemistry of estuarine ecosystems have been in focus since last two decades with emphasis on estuaries located in the southern India with a few reports on N biogeochemistry (e.g., Bouillon et al., 2003; Sarma et al., 2012a; Sarma et al., 2014; Bhavya et al., 2017; Bhavya et al. 2018). During the present study, the focus was on C and N biogeochemical differences of two adjacent estuarine systems, i.e., the Sundarbans and Hooghly estuary, which are part of Ganga-

Brahmaputra river system located in the northeastern India. Characteristically, these two estuaries are very different from each other with estuaries of Sundarbans being mangrove-dominated and Hooghly as anthropogenically influenced. Biogeochemical studies in these estuaries are limited to primary measurements with focus on trace gases (Mukhopadhyay et al., 2002; Biswas et al., 2004, 2007; Ganguly et al., 2008, 2009; Dutta et al., 2013, 2015a, 2015b, 2017), with exception of one comprehensive nutrient budget study at the Hooghly estuary (Mukhopadhyay et al., 2006). One of the major weaknesses of these studies are limited number of sampling locations, particularly in the Sundarbans. Given the vast expanse of these estuaries, extrapolation of data from these studies for the entire ecosystem may lead to overestimation/underestimation. Here, different aspects of N and C biogeochemistry in these two estuarine systems during postmonsoon with relatively better spatial coverage have been studied. The postmonsoon sampling was chosen as it identifies as season for peak mangrove leaf litter fall (Ray et al., 2011) that may have positive or negative feedback on estuarine C biogeochemistry as well as relatively stable estuarine condition for spatial sampling. Specifically, the objectives were to (i) trace the sources of POM in the Hooghly -Sundarbans system, (ii) quantify the rates of DIN and C uptake in these two contrasting ecosystems, and (iii) investigate factors controlling DIC dynamics in this region.

4.1 Study area and sampling

4.1.1 The Hooghly estuary

The Hooghly estuary lies approximately between $21^{\circ} 31' - 23^{\circ} 20'$ N and $87^{\circ} 45' - 88^{\circ} 45'$ E. It is the first deltaic offshoot of the river Ganges (AHEC, 2011). The depth of the estuary varies from ~ 21 m at the Diamond Harbour to ~ 8 m at the mouth of the estuary (CIFRI, 2012). The width of the river at the mouth of the estuary is ~ 25 km (Mukhopadhyay et al., 2006). Annual rainfall in the estuary varies from ~ 1310 mm to ~ 2300 mm (IMD, 2013) and it receives maximum rainfall during south-west monsoon (June - September). The freshwater discharge to the Hooghly River varies from 900 m³/s in the dry season to 4000 m³/s in the monsoon season (Mukhopadhyay et al., 2006).

The Hooghly estuary serves as the major navigable waterway for Kolkata and Haldia ports along with Sundarbans islands. As Hooghly river flows through the densely populated city of Kolkata, the estuary receives high amount of industrial effluents and urban waste waters (Sadhuram et al., 2005). The estuary remains wellmixed and vertically homogeneous throughout the year except for monsoon season (Gole and Vaidyaraman, 1967). Hooghly estuary ultimately mixes with the northern Bay of Bengal (BOB) near Sagar Island (Figure 4.1). Before mixing with the Bay the lower estuarine part divides into two channels near Kachuberia, one being main estuarine stream that directly mixes with the BOB and another smaller channel known as the Muriganga. The sampling locations in the Hooghly estuary during the present study is shown in Figure 4.1.



Figure 4.1: Sampling locations in the Hooghly estuary.

4.1.2 The Sundarbans

The main artery of the Sundarbans mangrove ecosystem is the tributaries of Hooghly River (Akhand et al., 2012). The Sundarbans (21° 32' - 22° 40' N; 88° 05' - 89° 00' E) is the largest mangrove forest in the world situated at the land-ocean boundary of the Ganges - Brahmaputra delta and the BOB. Since 1997, this natural mangrove forest is inscribed as a UNESCO world heritage site. The area of Sundarbans is $\sim 9360 \text{ km}^2$ as reserved forest of which 4200 km² is mangrove forest (Ray et al., 2011). This largest natural mangrove forest is crisscrossed with many distributaries of the Ganges, such as Hooghly, Mooriganga, Saptamukhi, Thakuran, Matla, Bidya, Gosaba, Haribhanga, which form archipelago of 102 islands. Out of these 102 islands, 54 are recouped for human settlement while the rest are in natural state (Ray et al., 2015). The dominant mangrove species in this intertidal ecosystem are Avicennia alba, Avicennia marina and Avicennia officinalis while Excoecaria agallocha and Ceriops decandra are found scattered (Ray et al., 2015). The present study was carried out at different locations spread around three major estuaries of the Indian Sundarbans (Saptamukhi (S1-S3), Thakuran (T1-T3) and Matla (M1-M4)). The sampling locations are shown in Figure 4.2. For the purpose of discussion, henceforth, both the estuarine systems will be discussed as 'Hooghly-Sundarbans system' and the estuaries of Sundarbans will be called 'Sundarbans' unless discussed individually.

4.1.3 Sampling and Experiments

Surface water samples were collected for experiments to measure DIN (NO₃⁻ + NH₄⁺) uptake, and C uptake rates measurement, POM characterization, DIC concentrations, and $\delta^{13}C_{\text{DIC}}$ at thirteen locations in the Hooghly estuary (Figure 4.1) and ten locations from three different estuaries of the Sundarbans (Figure 4.2) during postmonsoon. The physico-chemical parameters as mentioned earlier (Chapter 2) were also measured. Niskin bottle (Oceantest equipment; capacity: 5L) was used for sample collection. Apart from these samples, twelve groundwater samples (nine around Hooghly and three around Sundarbans) and a pore-water sample from Lothian Island (one of the virgin island of Sundarbans) were also collected for DIC and $\delta^{13}C_{\text{DIC}}$ measurements. A

brief description of the field sampling and experimental techniques used during the present study has been described in the methodology section (Chapter 2).



Figure 4.2: Sampling locations at the estuaries of Sundarbans (S1-S3: Saptamukhi; T1-T3: Thakuran; M1-M4: Matla).

4.2 Environmental parameters

During the study period, surface water temperature varied from 28 to 29 °C and 30.5 to 33 °C for the Sundarbans and Hooghly, respectively with no distinct spatial pattern (Table 7 and 8). Salinity of the estuaries of Sundarbans varied over a narrow range (12.74 - 16.69) with relatively lower values at the upper estuarine locations. Compared to Sundarbans, a slight salinity gradient was noticed at the Hooghly estuary (0.04 - 10.37). Based on the salinity observations during this study, Hooghly estuary can be classified as: [a] freshwater zone (H1-H6) and [b] mixing zone (H7 – H13). The %DO indicates the estuaries of Sundarbans (~ 91 – 104 %) to be relatively well oxygenated
compared to the Hooghly (70 – 104 %). Both pH and TA in the Hooghly estuary (pH: 7.31 to 8.29, TA: 1.80 to 2.86 meq L⁻¹) showed relatively wider variation compared to the estuaries of Sundarbans (pH: 8.01 to 8.13, TA: 2.01 to 2.29 meq L⁻¹; Table 7 and 8). No significant correlation was found between pH and salinity indicating that in Hooghly-Sundarbans system, variability of pH was not regulated by conservative mixing between marine and freshwaters.

4.3 Nutrients in the Hooghly-Sundarbans

In the Hooghly estuary, NO₃⁻ concentration varied from 26.17- 43.16 µmol L⁻¹ with an average of 35.64 \pm 5.86 µmol L⁻¹. Similarly, NH₄⁺ concentration ranged from 2.35 - 9.92 µmol L⁻¹ with an average of 3.51 \pm 1.96 µmol L⁻¹. The PO₄³⁻ and SiO₄⁴⁻ concentrations in the same ecosystem ranged from 0.46 - 2.48 and 81 - 183 µmol L⁻¹ with average values of 1.52 \pm 0.55 and 133 \pm 37 µmol L⁻¹, respectively. The highest values for NH₄⁺, PO₄³⁻ and SiO₄⁴⁻ were observed at Stn. H1, whereas NO₃⁻ concentration was the highest at Stn. H4.

The concentrations of NO₃⁻ in the Sundarbans varied from 17.45 to 27.71 µmol L⁻¹, whereas NH₄⁺ concentrations in the same ecosystem ranged between 1.58 and 3.74 µmol L⁻¹. The average values of NO₃⁻ and NH₄⁺ were 20.23 \pm 2.90 and 2.10 \pm 0.60 µmol L⁻¹, respectively. The PO₄³⁻ and SiO₄⁴⁻ concentrations in the same ecosystem ranged from 0.85 - 1.33 and 55 - 77 µmol L⁻¹. The highest values for NO₃⁻, PO₄³⁻, and SiO₄⁴⁻ were observed at Stn. S1; whereas the highest NH₄⁺ concentration was at Stn. M3. There were no specific spatial patterns for nutrients distribution in the Sundarbans.

In both the ecosystems, NO_3^- was several folds higher than NH_4^+ with higher average values in the Hooghly estuary compared to the Sundarbans. The higher concentration of NO_3^- in the Hooghly estuary is possibly due to urban and industrial waste along with agricultural effluents. There are many industries on both sides of the Hooghly River dumping their waste in the estuary. The source of NO_3^- in the Sundarbans is mainly riverine discharge with little influence from the agricultural effluents. Another possible reason for high NO_3^- in the Sundarbans could be connection of the Matla estuary to the Kolkata sewage system through the Ichhamoti River via Raymangal and Bidyadhari River systems. In the Kolkata sewage system, NO_3^- and NH_4^+ concentrations have been observed to the order of 100 µmol L⁻¹ (our own unpublished data) and may have influence on nutrient dynamics at these estuaries. Apart from these factors, nitrification could be another possible contributor to higher NO_3^- concentration in these two water bodies. Although NO_3^- was high in both the ecosystems, NH_4^+ concentration was comparatively very low. The exchange of NH_3 with the atmosphere could be one of the reasons for lower NH_4^+ concentrations in the estuaries of Sundarbans (Biswas et al., 2005). Another reason which may have influence in lowering the NH_4^+ in both the ecosystems is uptake by phytoplankton (Glibert et al., 2016).

4.4 Sources and transformation of particulate organic matter in the Hooghly-Sundarbans system

In the Sundarbans, POC concentration varied between 79.6 and 435.7 µmol L⁻¹ (mean: 181.4 ± 113.2 µmol L⁻¹) with no spatial pattern. Compared to that, marginally lower average POC value (167.1 ± 71.7 µmol L⁻¹) was estimated at the Hooghly (94.6 - 313.4 µmol L⁻¹) with relatively higher values in the freshwater zone (Figure 4.3). The $\delta^{13}C_{POM}$ values varied between -23.8 to -22.9 ‰ (mean: -23.3 ± 0.3 ‰) and -26.3 to - 23.5 ‰ (mean: -24.9 ± 0.9 ‰) for the Sundarbans and Hooghly estuary, respectively (Figure 4.3). Spatially, in the Hooghly, relatively lower $\delta^{13}C_{POM}$ values were observed in freshwater region compared to mixing zone while no such distinct trend was noticed at the Sundarbans. The observed $\delta^{13}C_{POM}$ of the Sundarbans were within the range of that reported for mangrove dominated Godavari estuary, South India ($\delta^{13}C_{POM}$: ~ -19 to - 29 ‰, Bouillon et al., 2003) and Khura and Trang rivers, Thailand ($\delta^{13}C_{POM} \sim -21$ to - 33 ‰; Miyajima et al., 2009). For the Hooghly, the observed $\delta^{13}C_{POM}$ were comparable with that previously reported by Samanta et al. (2015).

No significant correlation was found between TSM concentrations and salinity for both the estuaries (Sundarbans: p = 0.69, Hooghly: p = 0.40; Figure not shown). However, POC was negatively correlated with salinity in the Hooghly ($r^2 = 0.38$, p = 0.02; Figure not shown) but not at the Sundarbans, indicating freshwater run-off mediated addition of POC in the Hooghly estuary. Additionally, compared to other sampling locations relatively higher POC at 'H1', 'H3' and 'H4' at the Hooghly indicate contribution from nearby jute industry located on both sides of river bank at these locations. The POC formed relatively larger part of TSM in the Hooghly (0.96 - 4.22 %) compared to the Sundarbans (0.66 - 1.23 %). The lower contribution of POC to the TSM pool in the mangrove dominated Sundarbans may be due to low primary production owing to high TSM load (Ittekkot and Laane, 1991) as observed at mangrove region of the Godavari estuary as well (Bouillon et al., 2003).

Wide range for δ^{13} C_{POM} (rivers ~ -25 to -28 ‰; marine plankton ~ -18 to -22 ‰; C₃ plant ~ -23 to -34 ‰; C₄ plants ~ -9 to -17 ‰) have been reported by several researchers in different environments (Smith and Epstein, 1971; Hedges et al., 1997; Zhang et al., 1997; Dehairs et al., 2000; Bouillon et al., 2002). On an average, δ^{13} C_{POM} at the Hooghly was relatively lower compared to that of Sundarbans suggesting relatively higher influence of terrestrial inputs in the Hooghly. In the mixing zone of the Hooghly, significantly lower δ^{13} C_{POM} at 'H11' and 'H12' compared to other locations may be attributed to localized ¹³C depleted organic C influx to the estuary from adjacent mangroves and anthropogenic discharge, respectively. No significant correlation between δ^{13} C_{POM} and salinity was observed during the study period.

Despite being mangrove dominated region, relatively higher $\delta^{13}C_{POM}$ in the Sundarbans compared to mangroves ($\delta^{13}C \sim -27$ ‰; Miyajima et al., 2009) suggest marine influence or biogeochemical modification of POC within the estuarine system. Being well-oxygenated system, *in situ* aerobic biogeochemical transformation of POC is very likely to occur within the estuary; however, evidence for *in situ* aerobic POC mineralization was not obvious. Similar to open ocean environment, the possibility of organic carbon metabolism within isolated anoxic microhabitats of sinking POM exists in the mangrove dominated estuaries of the Indian Sundarbans (Reeburgh et al., 2007), which may favour production of trace gases, such as CH₄.



Figure 4.3: Variability of $\delta^{13}C_{POM}$ and POC in the Hooghly-Sundarbans system.

4.5 Dissolved inorganic nitrogen uptake in the Hooghly-Sundarbans

4.5.1 Variation in uptake rates

In the Hooghly estuary, NO₃⁻ uptake rates varied from 0.01 - 0.45 µmolN L⁻¹ h⁻¹, whereas for the Sundarbans it ranged between 0.01 - 0.09 µmolN L⁻¹ h⁻¹. The average NO₃⁻ uptake rates in the Hooghly estuary and the estuaries of Sundarbans were 0.16 ± 0.15 and 0.04 ± 0.03 µmolN L⁻¹ h⁻¹, respectively. Similarly, NH₄⁺ uptake rates in the Hooghly and Sundarbans varied from 0.07 - 1.10 and 0.22 - 0.67 µmolN L⁻¹ h⁻¹, respectively (Figures 4.4 and 4.5). The average value of NH₄⁺ uptake in the Hooghly estuary was 0.46 ± 0.26 µmolN L⁻¹ h⁻¹ and the same for the estuaries of Sundarbans was 0.37 ± 0.12 µmolN L⁻¹ h⁻¹. The highest NO₃⁻ and NH₄⁺ uptake rates in the Hooghly

	WT		DO		TA	TSM	NO ₃ -	NH4 ⁺	PO4 ³⁻	SiO4 ⁴⁻
Station	(°C)	Salinity	(%)	pН	(meq L ⁻¹)	$(mg L^{-1})$	(µmol L ⁻¹)			
H1	32.0	0.04	86.06	7.92	2.68	228.00	30.19	9.92	2.48	182.79
H2	33.0	0.07	85.02	7.71	1.92	72.67	33.67	2.35	1.46	161.00
H3	31.0	0.08	86.79	7.83	2.86	289.20	42.10	2.46	2.27	172.91
H4	31.0	0.13	70.53	7.73	2.57	175.33	43.16	2.77	2.10	172.05
H5	31.0	0.19	72.44	7.77	2.31	66.83	41.99	3.63	1.69	164.42
H6	30.5	0.32	75.61	7.31	1.88	106.50	42.14	2.80	1.67	160.15
H7	31.5	5.83	93.95	7.68	1.80	180.67	38.10	2.96	1.63	120.68
H8	31.0	5.19	98.79	7.31	1.95	112.79	36.83	3.10	1.35	121.60
H9	31.5	9.08	94.29	7.90	1.84	167.33	35.64	3.41	1.15	98.71
H10	31.5	9.72	88.19	8.08	2.02	107.00	31.85	3.16	1.25	91.46
H11	31.0	8.43	89.68	8.07	2.06	63.90	26.35	3.05	1.10	91.56
H12	31.5	5.83	103.62	8.29	1.95	37.80	35.12	3.30	1.10	110.47
H13	31.0	10.37	99.63	8.24	1.86	138.00	26.17	2.77	0.46	80.77

 Table 7. The environmental parameters in the surface waters of the Hooghly estuary (WT: water temperature)

Station	WT (°C)	Salinity	DO (%)	рН	TA (meq L ⁻¹)	TSM (mg L ⁻¹)	NO3 ⁻ (µmol L ⁻¹)	NH4 ⁺ (µmol L ⁻¹)	PO4 ³⁻ (µmol L ⁻¹)	SiO4 ⁴⁻ (µmol L ⁻¹)
S 1	28.5	12.74	91.86	8.02	2.11	280.00	27.71	1.86	1.33	77.32
S2	28.0	16.02	92.80	8.02	2.29	129.56	18.69	1.66	0.95	56.12
S 3	28.0	16.69	92.66	8.12	2.13	117.13	18.44	1.86	0.85	55.07
T1	29.0	14.30	92.24	8.05	2.15	79.63	19.49	1.74	0.87	59.23
T2	29.0	15.51	95.40	8.07	2.10	135.00	17.69	1.58	0.93	57.52
T3	28.5	16.55	91.27	8.11	2.13	213.14	17.45	1.80	1.31	55.68
M1	28.0	15.14	97.19	8.07	2.07	391.20	21.33	2.08	0.95	62.27
M2	28.0	15.14	95.92	8.12	2.01	740.80	19.57	2.35	1.27	63.36
M3	28.0	15.23	103.62	8.13	2.16	350.50	21.10	3.74	1.04	64.71
M4	28.5	14.78	95.67	8.04	2.15	122.60	22.10	2.24	1.25	61.04

 Table 8. The environmental parameters in the surface waters of the estuaries of Sundarbans.

estuary were at locations H13 and H5, respectively; whereas, for the estuaries of Sundarbans the highest values were at locations S1 and M2, respectively (Figure 4.4 and 4.5). Large spatial variations were observed for NO_3^- and NH_4^+ uptake rates in these two contrasting ecosystems with no particular trend.

Both NO_3^- and NH_4^+ uptake rates in the Hooghly estuary were higher than the estuaries of Sundarbans. The average NO_3^- uptake rate in the Hooghly was almost four times higher than that observed at the Sundarbans. The possible reason for relatively higher uptake rates in anthropogenically stressed Hooghly can be higher nutrient inputs in the Hooghly compared to that of Sundarbans. However, both these estuarine systems appear to be replete in nutrients (Tables 7 and 8). The POC concentrations in both these estuaries were also comparable. It is likely that given the relatively higher anthropogenic stress level in the Hooghly, the phytoplankton species composition could be different. The significantly higher NO_3^- uptake in the Hooghly suggested that there might be relatively higher abundance of species which preferred NO_3^- (such as diatoms). However, we do not have species data for the study period to corroborate this argument.

4.5.2 Uptake rates and environmental parameters

In the estuaries of Sundarbans, NO_3^- uptake rates showed significant positive correlation ($r^2 = 0.47$ and p < 0.05) with NO_3^- concentrations, whereas such correlation was missing for NH_4^+ uptake rates (Figure 4.6). For Hooghly estuary, no correlations were found between uptake rates and concentrations (Figure 4.6). This suggested limited role of nutrients concentration on the uptake rates in these nutrient replete estuaries. The TSM showed a significant positive correlation with NH_4^+ uptake rates ($r^2 = 0.84$ and p < 0.05) for Sundarbans which was not seen for NO_3^- uptake rates (Figure 4.7). No such relationship between TSM and uptake rates were found for Hooghly (Figure 4.7). The significant relationship between NH_4^+ uptake and TSM in the Sundarbans is intriguing as high TSM load is expected to lower the primary

production (i.e., lower the uptake of nutrients by phytoplankton; Ittekkot and Laane, 1991) as observed elsewhere (Bouillon et al., 2003).



Figure 4.4: Variations in NO₃⁻ and NH₄⁺ uptake rates in the Hooghly estuary.



Figure 4.5: Variations in NO₃⁻ and NH₄⁺ uptake rates in the Sundarbans.

Along with TSM, DO is another important parameter to understand the health of an ecosystem. The %DO showed a significant positive correlation with NO₃⁻ uptake rates ($r^2 = 0.49$ and p < 0.05) in the Hooghly estuary, which was missing for NH₄⁺ uptake rates (Figure 4.8a). Although %DO showed positive trend with uptake rates in the Sundarbans, the relationship was not significant (Figure 4.8b). As O₂ is produced during photosynthesis, the buildup of O₂ in the water column may be due to the observed higher uptake rates. Previous studies from the region have indicated higher productivity during postmonsoon compared to other seasons (Mukhopadhyay et al., 2002; Samanta et al., 2015). Although productivity is higher during postmonsoon, but the estuary remains undersaturated, as during the present study, with respect to DO owing to high turbidity and shallow euphotic depth (Mukhopadhyay et al., 2002). Overall, the lack of strong relationships between uptake rates and different factors suggested that DIN uptake rates in these estuaries are not controlled by a single dominant factor and needs to be thoroughly investigated in light of species composition.



Figure 4.6: Relationship between (a) NO_3^- uptake rates with NO_3^- concentration, and (b) NH_4^+ uptake rates with NH_4^+ concentration in the Hooghly-Sundarbans system.



Figure 4.7: Correlations between NO_3^- and NH_4^+ uptake rates with TSM concentrations in the (a) Sundarbans, and (b) Hooghly estuary.



Figure 4.8: Relationships between NO_3^- and NH_4^+ uptake rates with %DO for (a) Hooghly, and (b) Sundarbans.

4.5.3 Nutrients preference and turnover times in the Hooghly-Sundarbans system

In order to investigate the preference for nutrients in the Hooghly-Sundarbans system, RPI for both NO₃⁻ and NH₄⁺ was calculated. The RPI < 1 was observed for NO₃⁻ in both the ecosystems with relatively higher average value at the Hooghly compared to the Sundarbans (Figure 4.9). The RPI for NH₄⁺ was very high (> 4) in both Hooghly and Sundarbans. In the estuaries of Sundarbans, RPI for NH₄⁺ were almost similar except for M3, where it was relatively lower (Figure 4.9). Except for H1 in the Hooghly, RPI for NH₄⁺ was more than 6 throughout. The Saptamukhi estuary in the Sundarbans showed the highest RPI for NH₄⁺ in the Hooghly-Sundarbans were significantly higher than that for the Chilika; whereas RPI values for NO₃⁻ in the Hooghly-Sundarbans were lower than the Chilika.

The *f*-ratio (NO₃⁻ uptake to total DIN uptake) ranged between 0.08 to 0.47 for the Hooghly estuary and 0.03 and 0.21 in the estuaries of Sundarbans (Figure 4.10). The *f*-ratio was relatively higher at locations near estuarine mouth (H12-H13) compared to freshwater region in the Hooghly, whereas it was higher for Saptamukhi in the Sundarbans (Figure 4.10). The *f*-ratios for the Hooghly-Sundarbans, in general, were lower compared to that of the Chilika.

Overall, like many other aquatic ecosystems, NH_4^+ was the preferred substrate for phytoplankton in the Hooghly-Sundarbans system. However, given the high values of RPI for NH_4^+ and low *f*-ratio, this preference appears to be higher in the Hooghly-Sundarbans than many other aquatic systems, including the Chilika (Kumar et al., 2010; Mukherjee et al., 2018). The preference for reduced form of N, such as NH_4^+ , by phytoplankton is a well-known phenomenon and has been observed in many aquatic bodies around the globe (Dugdale and Goering, 1967; Glibert et al., 1982; Rees et al., 1995; Kumar et al., 2010; Bhavya et al., 2016). The possible reasons for lower $NO_3^$ uptake are higher energy requirement for the assimilation of NO_3^- and inhibition of NO_3^- uptake in the presence of NH_4^+ (McCarthy et al., 1983; Dortch, 1990; Glibert et al., 2016).



Figure 4.9: RPI of NO_3^- and NH_4^+ for (a) the Hooghly, and (b) the Sundarbans.



Figure 4.10: *f*-ratio for (a) Hooghly, and (b) Sundarbans.

The turnover times of NO_3^- and NH_4^+ were calculated in the Hooghly-Sundarbans to understand the cycling of these nitrogenous species within the system. The turnover times for NO_3^- in the Hooghly and the estuaries of Sundarbans ranged between 58 - 2377 h and 261 - 1662 h, respectively (Figure 4.11). The turnover time for NH_4^+ in the Hooghly varied from 3 - 75 h; whereas it was between 4 - 9 h in the Sundarbans (Figure 4.11). Barring two locations in the Hooghly (H1-H2), turnover times for NH_4^+ were almost similar for the entire Hooghly-Sundarban system. Overall, it appeared that NH_4^+ is cycled rapidly within both the ecosystems, whereas NO_3^- remained longer in the system. The faster turnover of NH_4^+ in the water column of the Hooghly-Sundarbans is similar to the Chilika.



Figure 4.11: Turnover times of NO_3^- and NH_4^+ for (a) the Hooghly, and (b) the Sundarbans.

4.6 Carbon uptake rates in the Hooghly-Sundarbans

In the Hooghly estuary, C uptake rates varied from 0.28 to 4.18 µmolC L⁻¹ h⁻¹ with an average of 1.53 ± 1.36 µmolC L⁻¹h⁻¹ (Figure 4.12a). Similarly, for the estuaries of sundarbans, the same ranged between 0.30 and 1.37 µmolC L⁻¹ h⁻¹ with an average of ~ 0.72 ± 0.32 µmolC L⁻¹ h⁻¹ (Figure 4.12b). There was no spatial pattern observed for C uptake rates in the system, except for Matla estuary in the Sundarbans where C uptake rates appeared to increase from the north to the south. The highest C uptake rate in the Hooghly was at Stn. H8, a location where there is influence of mangroves and human settlements. The Stn. S2 in the Saptamukhi estuary of the Sundarbans exhibited the highest C uptake in Sundarbans. Similar to DIN uptake rates, C uptake rates in the

Hooghly were also higher (twice) than the estuaries of Sundarbans. Overall, it appeared that the primary productivity in the anthropogenically stressed Hooghly was much more pronounced than the mangrove-dominated Sundarbans. One very clear difference between these two estuaries are the human interference, which led to relatively higher nutrient level in the Hooghly. However, as explored for DIN uptake rates, there was no significant effect of nutrients concentration on uptake rates in this nutrient replete estuary. Also, nutrient concentration in these estuaries were nowhere near limiting condition. The overall difference in light condition and species composition in these two estuarine systems may be responsible for the observed difference in the DIN and C uptake rates and needs to be thoroughly investigated. Similar to the Chilika, the uptake rates ratio for C and DIN did not follow the Redfield ratio and remained lower than 6.6. Similar to the Chilika, the Hooghly-Sundarbans system also witnessed pCO_2 higher than the atmospheric value, especially during postmonsoon (Samanta et al., 2015), and can be one of the reasons for the lower C:DIN uptake ratios (compared to Redfield ratio) suggesting alternate source of C other than HCO₃⁻.



Figure 4.12: Variations in C uptake rates in (a) Hooghly (b) Sundarbans.

4.7 Dissolved inorganic carbon dynamics in the Hooghly-Sundarbans system

In the Sundarbans, both DIC concentration and $\delta^{13}C_{DIC}$ varied over a relatively narrow range (DIC = 1683 to 1920 µmol L⁻¹, mean: 1745 ± 68 µmol L⁻¹; $\delta^{13}C_{DIC} = -5.9$ to – 4.3 ‰, mean: -5 ± 0.6 ‰) compared to the Hooghly estuary (DIC = 1678 to 2700 µmol L⁻¹, mean: 2083 ± 320 µmol L⁻¹; $\delta^{13}C_{DIC} = -8.6$ to -5.6 ‰, mean: -7 ± 0.9 ‰). The present DIC concentrations and $\delta^{13}C_{DIC}$ values for the mangrove dominated estuaries of the Sundarbans were in the range of that reported for the mangrove surrounding Khura and Trang rivers in peninsular Thailand (Miyajima et al., 2009). For the Hooghly estuary, the values were comparable with previously reported values by Samanta et al. (2015). Spatially, in the Hooghly, relatively higher DIC was noticed in the freshwater (H1 - H6) region. No consistent spatial trend in DIC and $\delta^{13}C_{DIC}$ was observed for the estuaries of Sundarbans.

In comparison to the estuarine surface waters, markedly higher DIC and depleted $\delta^{13}C_{DIC}$ were observed for the groundwater (Hooghly: DIC = 5655 to 11756 µmol L⁻¹, $\delta^{13}C_{DIC} = -12.7$ to -6.7 ‰; Sundarbans: DIC = 7524 to 13599 µmol L⁻¹, $\delta^{13}C_{DIC} = -10.6$ to -6.7 ‰) and pore water samples (Sundarbans: DIC = 13425 µmol L⁻¹; $\delta^{13}C_{DIC} = -18.1$ ‰) collected from the Hooghly-Sundarbans system (Table 9).

In the Hooghly, both DIC-salinity ($r^2 = 0.43$, p = 0.01; Figure 4.13a) and $\delta^{13}C_{DIC}$ - salinity ($r^2 = 0.58$, p = 0.003; Figure 4.14a) relationships were statistically significant, indicating conservative behavior of DIC in this estuary, making it an ideal site for application of two end member conservative mixing model (Ghosh et al., 2013, Samanta et al., 2015). Similar to the methodology followed for the Chilika lagoon, mixing curve approximation was also applied for the Hooghly estuary. For model calculation, average salinity, DIC and $\delta^{13}C_{DIC}$ of samples collected at ≤ 0.3 salinity during the present study were considered as values for freshwater end member, whereas respective values for marine end member were taken from Dutta et al. (2010) and Akhand et al. (2012). The DIC and $\delta^{13}C_{DIC}$ under conservative mixing condition and deviations (Δ DIC and $\Delta\delta^{13}C_{DIC}$) between observed and respective conservative mixing values were computed using Alling et al. (2012) to explore the role of *in situ* biogeochemical processes in modulating estuarine DIC dynamics.



Figure 4.13: DIC-salinity relationship for (a) the Hooghly estuary, and (b) the Sundarbans.



Figure 4.14: $\delta^{13}C_{DIC}$ -salinity relationship for (a) the Hooghly, and (b) the Sundarbans.



Figure 4.15: Deviation of DIC and $\delta^{13}C_{DIC}$ from the conservative mixing values for the Hooghly estuary.

Deviation plot (Δ DIC vs. $\Delta\delta^{13}C_{\text{DIC}}$; Figure 4.15) for samples of the Hooghly shows following patterns: (a) decrease in Δ DIC with increasing $\Delta\delta^{13}C_{\text{DIC}}$ (n = 5) indicating phytoplankton productivity and/or outgassing of CO₂ from wateratmosphere interface, (b) decrease in Δ DIC with decreasing $\Delta\delta^{13}C_{\text{DIC}}$ (n = 4) indicating carbonate precipitation, and (c) increase of Δ DIC with increasing $\Delta\delta^{13}C_{\text{DIC}}$ (n = 4) representing carbonate dissolution within the system. Based on these calculations, both organic and inorganic C metabolisms (productivity, carbonate precipitation and dissolution) along with physical processes (CO₂ outgassing across water-atmosphere interface) appear to regulate the DIC chemistry in the Hooghly estuary. Spatially, productivity/CO₂ outgassing appears to be dominant process in the mixing zone as most of the samples (5 out of 7) from this zone fall in this quadrant, whereas carbonate precipitation and/or dissolution are dominant in the freshwater zone. Further, ' Δ TA/ Δ DIC' can be used as a proxy to evaluate relative importance of biological productivity and CO₂ outgassing in the system. For primary productivity (106CO₂ + 122H₂O + 16HNO₃ + H₃PO₄ \rightarrow (CH₂O)₁₀₆(NH₃)₁₆H₃PO₄ + 138O₂), theoretical $\Delta TA/\Delta DIC$ is around – 0.16 (ΔTA = –17 and ΔDIC = 106, Cao et al., 2011), whereas the same is zero for CO₂ outgassing as it affects DIC without affecting TA (Guo et al., 2008). The $\Delta TA/\Delta DIC$ value for the sampling points located in the productivity/CO₂ outgassing quadrant is – 0.17, close to theoretically calculated value for the primary productivity. This suggest that primary productivity is the central process regulating DIC chemistry in the mixing zone of the Hooghly estuary.

In the Sundarbans, DIC - salinity relationship was not significant (p = 0.18; Figure 4.13b), however, $\delta^{13}C_{DIC}$ - salinity showed significant relationship (r² = 0.55, p = 0.009; Figure 4.14b), indicating mostly non-conservative behavior of DIC at the Sundarbans which is observed at other mangrove dominated systems as well (Miyajima et al., 2009). The non-conservative behavior of DIC limits the application of two end member mixing model for the Sundarbans. However, the role of mangrove derived organic C mineralization becomes important in regulating DIC chemistry in ecosystems like the Sundarbans. Two different mass balance equations as proposed by Miyajima et al. (2009) have been adopted to quantify mangrove derived DIC (Δ DIC_{Mangrove}) in the Sundarbans:

$$\Delta DIC_{Mangrove} (\Delta DIC_{M1}) = [DIC] - [DIC_{CM}]$$

Where, CM indicates conservative mixing. Since both Sundarbans and Hooghly estuarine system have same marine end member (BOB) and the Sundarbans are connected to the Hooghly estuary through different branches, similar end member values as Hooghly were used for this calculation as well. Theoretically, $\Delta DIC_{Mangrove}$ estimated based on DIC (ΔDIC_{M1}) and $\delta^{13}C_{DIC}$ (ΔDIC_{M2}) should be equal. The negative and unequal values of ΔDIC_{M2} (– 44 to 66 µmol L⁻¹) and ΔDIC_{M1} (–188 to 11 µmol L⁻¹) indicate large DIC out-flux over influx through mangrove derived organic C mineralization in this tropical mangrove system. The removal mechanisms include CO₂

outgassing across estuarine water-atmosphere boundary, phytoplankton uptake and export to adjacent continental shelf region (northern BOB, Ray et al., 2018).

Other than biogeochemical processes, factors such as groundwater and recirculated saline groundwater (synonymous to pore-water for mangroves; Tait et al., 2016) discharge to the estuary might also play significant role in estuarine DIC chemistry. High pCO₂, DIC, and low pH, TA/DIC are general characteristic of groundwater especially within carbonate aquifer region (Cai et al., 2003). Although all the parameters of ground water inorganic C system (like pH, TA and pCO_2) were not measured during the present study, groundwater DIC were ~ 5.57 and ~ 3.61 times higher compared to average surface water DIC in the Sundarbans and Hooghly, respectively. The markedly higher DIC in groundwater as well as similarity in its isotopic composition with estuarine DIC (Table 9) may stand as a signal for influence of groundwater on estuarine DIC biogeochemistry, with possibly higher influence at the Hooghly rather than Sundarbans as evident from TA/DIC values (Hooghly: 0.87 -1.14, Sundarbans: 1.12 - 1.34; Figure not shown). However, unavailability of any data on groundwater discharge rate from these systems limits us to quantitatively evaluate groundwater mediated DIC flux to the estuary. Pore-water DIC in the Sundarbans was \sim 7.63 times higher than the estuarine water indicating possibility of DIC input from the adjoining mangrove system to the estuary through pore-water exchange depending upon changes in hypsometric gradient during tidal fluctuation. Although pore water DIC was estimated at only one location, considering postmonsoon pore-water specific discharge and porosity as 0.008 cm min⁻¹ and 0.58 (Dutta et al., 2013, Dutta et al., 2015a), respectively, a first-time baseline value for advective DIC influx from mangrove sediment to the estuary can be estimated as ~ 774 mmol m⁻² d⁻¹ using Reav et al. (1995). However, significant impact of pore-water to estuarine DIC may be limited only in mangrove creek water (samples not collected) as evident from narrow variability of estuarine TA and DIC as well as no significant correlation between them (Figure not shown). A comprehensive investigation on ground and pore waters are needed to thoroughly understand their importance in controlling DIC chemistry of the Hooghly-Sundarbans system.

		DIC	δ ¹³ C _{DIC}
Ecosystem	Station	(µmol L ⁻¹)	(‰)
	H3GW	11765	- 12.7
	H4GW	6230	- 7.9
	H5GW	6327	- 9.0
	H6GW	7026	- 11.3
Hooghly	H7GW	5655	- 6.9
	H11GW	9115	-7.7
	H12GW	6858	-7.5
	H13GW	7258	-7.2
	Gangasagar GW	7246	- 6.7

13425

13599

8300

- 18.1

-6.7

- 10.6

Lothian PW

Kalash GW

Virat Bazar GW

Sundarbans

Table 9: The DIC and $\delta^{13}C_{DIC}$ of groundwater (GW) and pore-water (PW) samples collected from the Hooghly-Sundarbans system.

Chapter 5 Summary and scope for future work

This thesis attempted to provide insights into the cycling of N and C in some of the important aquatic ecosystems of India located at the interface of land and sea i.e., the Chilika lagoon, the Hooghly estuary, and the estuaries of Sundarbans. Through the extensive use of stable isotopic measurements in organic and inorganic phases, and experiments based on stable isotope based tracer techniques, the present work revealed different facets of biogeochemical cycling of bio-available elements in the above-mentioned ecosystems. The major findings of this thesis are summarized below.

5.1 Particulate organic matter in the Chilika and Hooghly-Sundarbans system

• The average POC and PON concentrations in the Chilika were the highest during premonsoon followed by monsoon and postmonsoon, possibly due to lower than average rainfall during monsoon sampling.

- Relatively lower $\delta^{13}C_{POM}$ during postmonsoon in the Chilika compared to monsoon and premonsoon suggested dominance of terrestrial and freshwater inputs to the lagoon and/or production of freshwater phytoplankton during postmonsoon as both are expected to have lower $\delta^{13}C_{POM}$.
- The northern sector of the lagoon showed the highest POC and PON compared to other sectors, which could be of both allochthonous and autochthonous origin as this particular sector receives maximum discharge from surrounding rivers.
- The average POC concentration in the Hooghly was marginally lower than the Sundarbans with relatively higher values in the freshwater zone of the Hooghly.
- On an average, $\delta^{13}C_{POM}$ of the Hooghly was relatively lower compared to that of the Sundarbans suggesting relatively higher influence of terrestrial inputs in the Hooghly.
- Despite being mangrove dominated region, relatively higher $\delta^{13}C_{POM}$ in the Sundarbans compared to mangroves suggested marine influence or biogeochemical modification of POC within the Sundarbans.

5.2 Sediment organic matter in the Chilika and Bhitarkanika mangrove

- The average isotopic composition of C and N in SOM and elemental ratios (C_{org}: N) indicated that the source of organic matter in the sediment of the Bhitarkanika mangrove was predominantly terrigenous with some contributions from marine sources.
- Calculations based on two-end member mixing model also indicated more than 50 % terrestrial contribution to SOM pool of the mangrove region.

- Significant increase in δ^{13} C of SOM compared to POM in the Chilika lagoon indicated biogeochemical transformation of organic matter in the water column and during burial.
- Increase in δ^{13} C of SOM in the lagoon can also be attributed to diagenetic alteration or contribution from the submersed aquatic vegetation.
- No relationship between δ¹³C of SOM and POM in the Chilika pointed towards lack of significant coupling between these two organic matter pools.

5.3 Dissolved inorganic carbon dynamics in the Chilika and Hooghly-Sundarbans system

- The DIC and $\delta^{13}C_{DIC}$ in the Chilika did not follow the conservative mixing line between riverine and marine waters.
- The northern sector of the lagoon showed relatively lower DIC concentrations compared to other sectors. No spatial pattern in $\delta^{13}C_{DIC}$ was observed from the fresh to marine zone in the lagoon.
- A model based on mixing curve approximation and deviation of DIC and $\delta^{13}C_{DIC}$ values from the conservative mixing values suggested significant spatial and temporal variability in processes modulating DIC dynamics in the lagoon.
- The CO₂ outgassing and carbonate dissolution appeared to be modulating DIC across seasons and locations, whereas primary productivity appeared to be a dominant process in modifying DIC during postmonsoon. At few locations during premonsoon, degradation of organic matter appeared to play a dominant role.
- No evidence of groundwater contribution on DIC was observed in the Chilika.

 Primary productivity appeared to be the central process in regulating DIC chemistry in mixing zone of the Hooghly estuary, whereas carbonate precipitation and/or dissolution were dominant in the freshwater zone. The evidence for large DIC out-flux was observed in the Sundarbans.

5.4 Carbon uptake rates in the Chilika and Hooghly-Sundarbans

- The average C uptake rates in the surface waters of the Chilika were higher during the monsoon and premonsoon compared to postmonsoon.
- As for DIN uptake, the C uptake in the surface waters was comparable to the bottom waters during premonsoon.
- The C uptake rates in the Hooghly were twice compared to the rates in the Sundarbans.
- The C uptake: DIN uptake in both Chilika and Hooghly-Sundarbans did not follow the Redfield ratio and largely remained < 6.6 suggesting C source other than HCO₃⁻ during primary productivity, possibly the aqueous CO₂.

5.5 Dissolved inorganic nitrogen uptake and N₂ fixation rates in the Chilika

- Overall, the DIN (NO₃⁻ and NH₄⁺) uptake rates in the Chilika were higher than other large aquatic ecosystems of the world, including some of the tropical estuaries.
- The average NH₄⁺ uptake rates in the Chilika were approximately twice compared to that of NO₃⁻ uptake rates.
- Like many other aquatic ecosystems, relative preference index and *f*-ratio in the Chilika suggested overall higher preference for NH₄⁺ than NO₃⁻, possibly due to lower energy requirements during NH₄⁺ assimilation.

- The DIN uptake rates in the Chilika were not controlled by a single factor alone. Different factors (such as nutrients, Chl*a* etc.) appeared to control DIN uptake during different seasons.
- On an average, turnover time for NH_4^+ was significantly shorter compared to NO_3^- underscoring faster cycling of NH_4^+ in the water column.
- The DIN uptake rates in the bottom waters of the Chilika were comparable to that of surface waters, possibly due to deeper light penetration, suggesting significant role of bottom waters in biogeochemistry of shallow aquatic ecosystems.
- The basin-wise sectoral DIN uptake estimates suggested the highest DIN fixation in the central sector of the lagoon followed by the southern, northern, and outer channel. The highest DIN fixation in the central sector was primarily due to relatively higher surface area compared to all other sectors.
- A preliminary investigation on sources of new N to the lagoon indicated atmospheric deposition to be a significant source compared to riverine inputs and N₂ fixation. However, this may be due to higher DIN deposition rate used during the calculation, which was taken from the published report for the coastal BOB. Dry deposition data over the lagoon surface along with rates of other processes are required to build the comprehensive N budget of the lagoon.
- Despite high NO₃⁻ and NH₄⁺concentrations, considerable N₂ fixation rates indicated diazotrophic activity within the lagoon.

5.6 Dissolved inorganic nitrogen uptake rates the Hooghly-Sundarbans

- Both NO₃⁻ and NH₄⁺ uptake rates in the Hooghly estuary were higher than the estuaries of Sundarbans. The average NO₃⁻ uptake rate in the Hooghly was almost four times higher than that of the Sundarbans.
- Despite very high concentrations of NO₃⁻, NH₄⁺ uptake rates were higher in the Hooghly-Sundarbans systems depicting its preference over NO₃⁻.
- Higher preference for NH₄⁺ compared to NO₃⁻ was also validated with high relative preference index and *f*-ratio in both Hooghly and Sundarbans.
- Higher DIN uptake rates in the Hooghly estuary compared to the Sundarbans point towards effect of anthropogenic inputs in the Hooghly compared to Sundarbans. However, both these estuarine systems are replete in nutrients. It is likely that higher anthropogenic stress in the Hooghly may trigger change in species composition leading to higher DIN uptake rates. This, however, remains to be tested.
- Turnover times of NO₃⁻ and NH₄⁺ indicated that NH₄⁺ is cycled rapidly within both Hooghly and Sundarbans, whereas NO₃⁻ remained in the system for a longer time.

5.7 Scope for future work

Despite recent focus on N and C cycling studies in different aquatic ecosystems of India, there remains the need to quantitatively study different biogeochemical processes. The quantification of these processes may help us to understand the effect of nutrient enrichment on ecosystems, which in turn will help to evolve the mitigation strategy to save these systems from further degradation. Below are the topics which need special attention in the ecosystems studied during the present study.

- The detailed quantification of N budget of the Chilika requires measurements of different processes (such as nitrification rates, denitrification rates, nutrient efflux from sediments, rates of mineralization etc.) on higher spatial and temporal scale.
- From the present study it appears that atmospheric deposition may form a prominent source of new N to the lagoon. However, this needs to be revisited in light of atmospheric deposition measurements over the Chilika lagoon. To the best our knowledge, there is no such data so far.
- The large part of the northern sector of the Chilika is invaded by *Phragmites karka*, which hampers the fisheries activities in the lagoon. However, the role of these invaded species in the overall biogeochemistry of the lagoon remains unknown, particularly their role in nutrient sequestration. An isotope tracer based experiment is needed to be designed to measure the uptake of nutrients by *Phragmites karka*.
- The Chilika lagoon is a breeding ground for thousands of migratory birds, which drops their fecal matter every year. A high resolution measurement of biogeochemical processes may help to understand the effect of avian migration on aquatic systems.
- Stable isotopic composition of different species of DIN (NO₃⁻ and NH₄⁺) in the lagoon, precipitation, and river waters is warranted to decipher the dominant source of nutrients to the lagoon.
- Similar to the Chilika, a number of biogeochemical processes related to N and C cycling remain unexplored in the Hooghly-Sundarbans system. The quantification of these processes is needed to fully understand the differences in biogeochemical behavior of contrasting ecosystems like Hooghly and Sundarbans.

- There appears to be contribution of groundwater on N and C biogeochemistry of both Hooghly and Sundarbans. This remains to be largely explored.
- The Sundarbans is large mangrove ecosystem which has not been covered spatially and temporally for most of the biogeochemical parameters. In the future, endeavor should be to cover large part of this system so that it can be represented fairly.
- The C uptake: N uptake ratio lower than the Redfield ratio in the studied ecosystems (which were largely CO₂ supersaturated) suggested that the methodology used during the present study to measure primary productivity (HCO₃⁻ as tracer) possibly needs a revisit as aqueous CO₂ may be acting as an alternative source in such systems. There is a need for ¹³CO₂ based experiments to be performed to decipher this puzzle.
- This thesis covered biogeochemical processes related to N and C cycling in aquatic systems at interface of land and ocean; however inland waters of India are still unexplored vis-à-vis N and C cycling processes. Considering the freshwater requirement to support huge population of India and threat to freshwater systems from eutrophication, there is a need to start studying inland water systems on urgent basis.

References

- Ache, B. W., Crossett, K. M., Pacheco, P. A., Adkins, J. E., & Wiley, P. C. (2015).
 "The coast" is complicated: a model to consistently describe the nation's coastal population. *Estuaries and Coasts*, 38(1), 151–155.
- Aerts, R. (1993). Competition between dominant plant species in heathlands. In *Heathlands* (pp. 125–151). Springer.
- Agnihotri, R., Kurian, S., Fernandes, M., Reshma, K., D'Souza, W., and Naqvi, S. W.
 a. (2008). Variability of subsurface denitrification and surface productivity in the coastal eastern Arabian Sea over the past seven centuries. *The Holocene*, 18, 755–764. Aguilera, P. A., Castro, H., Rescia, A., and Schmitz, M. F., 2001. Methodological development of an index of coastal water quality: application in a tourist area. *Environmental Management*, 27, 295–301.
- AHEC. (2011). Assessment of Cumulative impact on Hydropower project in Alakananda and Bhagirathi Basins. 7, 9.
- Akhand, A., Chanda, A., Dutta, S., and Hazra, S. (2012). Air–water carbon dioxide exchange dynamics along the outer estuarine transition zone of Sundarban, northern Bay of Bengal, India. *Marine Geology*, 139, 123–145.
- Alling, V., Porcelli, D., Mörth, C.-M., Anderson, L., Sanchez-Garcia, L., Gustafsson,
 Ö. (2012). Degradation of terrestrial organic carbon, primary production and out-gassing of CO 2 in the Laptev and East Siberian Seas as inferred from δ 13
 C values of DIC. *Geochimica Cosmochimica Acta*, 95, 143–159.
- Alongi, D. M. (2014). Carbon cycling and storage in mangrove forests. Annual Review Marine Science, 6, 195–219.
- Altabet, M. A., Francois, R., Murray, D. W., and Prell, W. L. (1995). Climate-related variations in denitrification in the Arabian Sea from sediment 15N/14N ratios. *Nature*, 373, 506–509.
- Andrews, J., Greenaway, A., and Dennis, P. (1998). Combined carbon isotope and C/N ratios as indicators of source and fate of organic matter in a poorly flushed,

tropical estuary: Hunts Bay, Kingston Harbour, Jamaica. *Estuarine Coastal Shelf Sciences*, 46, 743–756.

- APHA-AWWA-WEF, (2005). Standard Methods for the Examination of Water and Wastewater. 21st ed.
- Atekwana, E. A., Molwalefhe, L., Kgaodi, O., and Cruse, A. M. (2016). Effect of evapotranspiration on dissolved inorganic carbon and stable carbon isotopic evolution in rivers in semi-arid climates: The Okavango Delta in North West Botswana. *Journal of Hydrology: Regional Studies*, 7, 1–13.
- Backer, L. C., & McGillicuddy Jr, D. J. (2006). Harmful algal blooms: at the interface between coastal oceanography and human health. *Oceanography (Washington, DC)*, 19(2), 94.
- Badger, M. R., Andrews, T. J., Whitney, S., Ludwig, M., Yellowlees, D. C., Leggat, W. (1998). The diversity and coevolution of Rubisco, plastids, pyrenoids, and chloroplast-based CO₂-concentrating mechanisms in algae. *Canadian Journal of Botany*, 76, 1052–1071.
- Balachandran, K. (2001). Chemical oceanographic studies of the coastal waters of Cochin.
- Bardhan, P., Karapurkar, S., Shenoy, D., Kurian, S., Sarkar, A., Maya, M., et al. (2015).
 Carbon and nitrogen isotopic composition of suspended particulate organic matter in Zuari Estuary, west coast of India. *Journal of Marine System*, 141, 90–97.
- Barik, K. K., Mitra, D., Annadurai, R., Tripathy, J., and Nanda, S. (2016). Geospatial analysis of coastal environment: A case study on Bhitarkanika Mangroves, East coast of India. matter.
- Barik, S. K., Muduli, P. R., Mohanty, B., Behera, A. T., Mallick, S., Das, A., Pattnaik,
 A. K. (2017). Spatio-temporal variability and the impact of Phailin on water
 quality of Chilika lagoon. *Continental Shelf Research*, 136, 39–56.
- Barnes, J., Ramesh, R., Purvaja, R., Nirmal Rajkumar, A., Senthil Kumar, B., and Krithika, K. (2006). Tidal dynamics and rainfall control N₂O and CH₄

emissions from a pristine mangrove creek. Geophysical Research Letter, 33, L15405.

- Battin, T. J., Luyssaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., & Tranvik,L. J. (2009). The boundless carbon cycle. *Nature Geoscience*, 2(9), 598–600.
- Bauer, J. E., Cai, W.-J., Raymond, P. A., Bianchi, T. S., Hopkinson, C. S., and Regnier,P. A. (2013). The changing carbon cycle of the coastal ocean. *Nature*, 504, 61.
- Behera, P., Mahapatra, S., Mohapatra, M., Kimb, Y., Adhya, T.K., Raina, V., Suar, M., Pattnaik, A.K., Rastogi, G., 2017. Salinity and macrophyte drive the biogeography of the sedimentary bacterial communities in a brackish water tropical coastal lagoon. Science of the Total Environment, 595, 472–485.
- Beman, J. M., Arrigo, K. R., & Matson, P. A. (2005). Agricultural runoff fuels large phytoplankton blooms in vulnerable areas of the ocean. *Nature*, 434 (7030), 211–214.
- Berman, T., and Bronk, D. A. (2003). Dissolved organic nitrogen: a dynamic participant in aquatic ecosystems. *Aquatic Microbial Ecology*, 31, 279–305.
- Berman, T. (1974). Urea in the waters of Lake Kinneret (Sea of Galilee). *Limnology* and Oceanography, 19(6), 977–980.
- Bernasconi, S. M., Barbieri, A., and Simona, M. (1997). Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. *Limnology Oceanography*, 42, 1755–1765.
- Bhavya, P., Kumar, S., Gupta, G., Sudheesh, V., Sudharma, K., Varrier, D., ... Saravanane, N. (2016). Nitrogen uptake dynamics in a tropical eutrophic estuary (Cochin, India) and adjacent coastal waters. *Estuaries and Coasts*, 39(1), 54–67.
- Bhavya, P., Kumar, S., Gupta, G., Sudharma, K., Sudheesh, V., and Dhanya, K. (2017). Carbon isotopic composition of suspended particulate matter and dissolved inorganic carbon in the Cochin estuary during post-monsoon. *Current Science*, 00113891 110.

- Bhavya, P.S., Kumar, S., Gupta, G.V.M., Sudharma, K.V., and Sudheesh, V. (2018). Spatial-temporal variation in $\delta^{13}C_{DIC}$ of a tropical eutrophic estuary (Coachin estuary, India), *Continental Shelf Research*, 153, 75-85..
- Bianchi, T.S., 2007. Biogeochemistry of Estuaries. Oxford University Press, Oxford, 720 pp.
- Biswas, H., Mukhopadhyay, S., De, T., Sen, S., & Jana, T. (2004). Biogenic controls on the air—water carbon dioxide exchange in the Sundarban mangrove environment, northeast coast of Bay of Bengal, India. *Limnology and Oceanography*, 49(1), 95–101.
- Biswas, H., Chatterjee, A., Mukhopadhya, S., De, T., Sen, S., & Jana, T. (2005). Estimation of ammonia exchange at the land–ocean boundary condition of Sundarban mangrove, northeast coast of Bay of Bengal, India. *Atmospheric Environment*, 39(25), 4489–4499.
- Biswas, H., Mukhopadhyay, S.K., Sen, S., and Jana, T.K. (2007). Spatial and temporal patterns of methane dynamics in the tropical mangrove dominated estuary, NE Coast of Bay of Bengal, India. *Journal of Marine System*, 68, 55-64.
- Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Dentener, F. (2010). Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecological Applications*, 20(1), 30–59.
- Borges, A. V. (2005). Do we have enough pieces of the jigsaw to integrate CO₂ fluxes in the coastal ocean? *Estuaries*, 28, 3–27.
- Borges, A. V., Delille, B., and Frankignoulle, M. (2005). Budgeting sinks and sources of CO₂ in the coastal ocean: Diversity of ecosystems counts. *Geophysical Research Letter*, 32, L14601.
- Borum, J., & Sand-Jensen, K. (1996). Is total primary production in shallow coastal marine waters stimulated by nitrogen loading? *Oikos*, 406–410.
- Bouillon, S., Raman, A., Dauby, P., and Dehairs, F. (2002). Carbon and nitrogen stable isotope ratios of subtidal benthic invertebrates in an estuarine mangrove

ecosystem (Andhra Pradesh, India). *Estuarine Coastal Shelf Sciences*, 54, 901–913.

- Bouillon, S., Frankignoulle, M., Dehairs, F., Velimirov, B., Eiler, A., Abril, G., Borges,
 A. V. (2003). Inorganic and organic carbon biogeochemistry in the Gautami
 Godavari estuary (Andhra Pradesh, India) during pre- monsoon: The local
 impact of extensive mangrove forests. *Global Biogeochemical Cycles*, 17(4).
- Bouillon, S., Moens, T., Koedam, N., Dahdouh-Guebas, F., Baeyens, W., and Dehairs,
 F. (2004). Variability in the origin of carbon substrates for bacterial communities in mangrove sediments. *FEMS Microbiol. Ecology*, 49, 171–179.
- Bouillon, S., Borges, A. V., Castañeda-Moya, E., Diele, K., Dittmar, T., Duke, N. C., Kristensen, E., Lee, S. Y., Marchand, C., Middelburg, J. J., Rivera-Monroy, V. H., Smith, T. J., and Twilley, R. R. (2008). Mangrove production and carbon sinks: A revision of global budget estimates. *Global Biogeochemical Cycle*, 22, GB2013; 10.1029/2007GB003052.
- Bouwman, A., Beusen, A. H., & Billen, G. (2009). Human alteration of the global nitrogen and phosphorus soil balances for the period 1970–2050. *Global Biogeochemical Cycles*, 23(4).
- Brenner, M., Hodell, D. A., Leyden, B. W., Curtis, J. H., Kenney, W. F., Gu, B., et al. (2006). Mechanisms for organic matter and phosphorus burial in sedimentsof a shallow, subtropical, macrophyte-dominated lake. *Journal of Paleolimnology*, 35, 129–148.
- Bronk, D. A., Glibert, P. M., and Ward, B. B. (1994). Nitrogen uptake, dissolved organic nitrogen release, and new production. *Science*, 265, 1843–1846.
- Burkhardt, S., Amoroso, G., Riebesell, U., and Sültemeyer, D. (2001). CO₂ and HCO₃⁻ uptake in marine diatoms acclimated to different CO₂ concentrations. *Limnology Oceanography*, 46, 1378–1391.
- Caldeira, K., & Wickett, M. E. (2003). Oceanography: anthropogenic carbon and ocean pH. *Nature*, *425*(6956), 365–365.

- Calder, J. A., and Parker, P. L. (1968). Stable carbon isotope ratios as indexes of petrochemical pollution of aquatic systems. *Environmental Science & Technology*, 2, 535–539.
- Cai, W., and Wang, Y. (1998). The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnology Oceanography*, 43, 657–668.
- Cai, W., Pomeroy, L. R., Moran, M. A., and Wang, Y. (1999). Oxygen and carbon dioxide mass balance for the estuarine- intertidal marsh complex of five rivers in the southeastern US. *Limnology Oceanography*, 44, 639–649.
- Cai, W. J., Wang, Y., Krest, J., and Moore, W.S. (2003). The geochemistry of dissolved inorganic carbon in a surficial groundwater aquifer in North Inlet, South Carolina and the carbon fluxes to the coastal ocean. *Geochemica Cosmochemica Acta*, 67, 631–637.
- Cai, W.J., Dai, M., and Wang, Y. (2006). Air-sea exchange of carbon dioxide in ocean margins: A province-based synthesis. *Geophysical Research Letter*, 33, 2–5, 2006.
- Cai, W. J. (2011). Estuarine and coastal ocean carbon paradox: CO₂ sinks or sites of terrestrial carbon incineration. Annual Review of *Marine Science*, 3, 123–145, https://doi.org/10.1146/annurev-marine120709-142723.
- Cao, Z., Dai, M., Zheng, N., Wang, D., Li, Q., Zhai, W., Meng, F., and Gan, J. (2011).
 Dynamics of the carbonate system in a large continental shelf system under the influence of both a river plume and coastal upwelling. *Journal of Geophysical Research*, 116, G02010.
- Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., and Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological. Applications*, 8, 559–568.
- Capone, D. G., Ferrier, M. D., and Carpenter, E. J. (1994). Amino acid cycling in colonies of the planktonic marine cyanobacterium Trichodesmium thiebautii. *Applied and Environmental Microbiology*, 60, 3989–3995.
- Capone, D. G., Zehr, J. P., Paerl, H. W., Bergman, B., and Carpenter, E. J. (1997). Trichodesmium, a globally significant marine cyanobacterium. *Science*, 276, 1221–1229.
- Chauhan, R., Ramanathan, A., and Adhya, T. (2014). Patterns of seasonal variability in granulometric characteristics of Bhitarkanika Mangrove–estuarine complex, East coast of India.
- Chen, H., Yu, Z., Yao, Q., Mi, T., & Liu, P. (2010). Nutrient concentrations and fluxes in the Changjiang Estuary during summer. *Acta Oceanologica Sinica*, 29(2), 107–119.
- Chen, C.-T. A., and Borges, A. V. (2009). Reconciling opposing views on carbon cycling in the coastal ocean: continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO₂. *Deep Sea Research Part II Top. Stud. Oceanogr.* 56, 578–590.
- Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., Heimann, M. (2014).
 Carbon and other biogeochemical cycles. In *Climate change 2013: the physical* science basis. Contribution of Working Group I to the Fifth, Assessment Report of the Intergovernmental Panel on Climate Change (pp. 465–570). Cambridge University Press.
- CIFRI (2012) Present status of Hilsa in Hooghly Bhagirathi river. Central Inland Fisheries Research Institute. <www.cifri.ernet.in/179.pdf>.
- Cifuentes, L., Sharp, J., and Fogel, M. L. (1988). Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. *Limnology Oceanography*, 33, 1102– 1115.
- Cifuentes, L., Coffin, R., Solorzano, L., Cardenas, W., Espinoza, J., and Twilley, R. (1996). Isotopic and elemental variations of carbon and nitrogen in a mangrove estuary. *Estuarine Coastal and Shelf Science*, 43, 781–800.
- Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R.G., et al. (2007). Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10, 172–185.

- Colman, B., and Rotatore, C. (1995). Photosynthetic inorganic carbon uptake and accumulation in two marine diatoms. *Plant Cell Environment*, 18, 919–924.
- Conway H.L. (1977). Interaction of inorganic nitrogen in the uptake and assimilation by marine phytoplankton. Marine Biology, 39, 221-231.
- Dabundo, R., Lehmann, M. F., Treibergs, L., Tobias, C. R., Altabet, M. A., Moisander, P. H., et al. (2014). The contamination of commercial ¹⁵N₂ gas stocks with ¹⁵N– labeled nitrate and ammonium and consequences for nitrogen fixation measurements. *PloS One* 9, e110335.
- Dagenais-Bellefeuille, S., Morse, D., 2013. Putting the N in dinoflagellates. Frontiers in Microbiology, 4, 369.
- Dai, M., Zhai, W., Cai, W.-J., Callahan, J., Huang, B., Shang, S., et al. (2008). Effects of an estuarine plume-associated bloom on the carbonate system in the lower reaches of the Pearl River estuary and the coastal zone of the northern South China Sea. *Continental Shelf Research*, 28, 1416–1423.
- Davies, K. L., Pancost, R. D., Edwards, M. E., Anthony, K. M. W., and Langdon, P. G. (2016). Diploptene [delta] 13 C values from contemporary thermokarst lake sediments show complex spatial variation. *Biogeosciences*, 13, 2611.
- Degens, E.T., Kempe, S., and Richey, J.E. (1991). Summary: Biogeochemistry of major world rivers. In: Degens ET, Kempe S, and Richey JE (Eds.), Biogeochemistry of Major World Rivers, SCOPE 42. Chichester: John Wiley & Sons. pp 323 347, 1991.
- Dehairs, F., Rao, R.G., Chandra Mohan, P., Raman, A.V., Marguillier, S., and Hellings, L.(2000). Tracing mangrove carbon in suspended matter and aquatic fauna of the Gautami- Godavari Delta, Bay of Bengal (India). *Hydrobiologia*, 431, 225 241.
- Del Amo, Y., Le Pape, O., Tréguer, P., Quéguiner, B., Ménesguen, A., and Aminot, A. (1997). Impacts of high-nitrate freshwater inputs on macrotidal ecosystems. I.Seasonal evolution of nutrient limitation for the diatom-dominated

phytoplankton of the Bay of Brest (France). *Marine Ecology Progress Series*, 213–224.

- Dittmar, T., and Lara, R.J. (2001a). Do mangroves rather than rivers provide nutrients to coastal environments south of the Amazon River? Evidence from long-term flux measurements, *Marine Ecology Progress Series*, 213, 67 77.
- Dittmar, T., and Lara, R.J. (2001b). Driving forces behind nutrient and organic matter dynamics in a mangrove tidal creek in north Brazil, *Estuarine Coastal and Shelf Science*, 52, 249 – 259,
- Donato, D.C., Kauffman, J.B., Kurnianto, S., Stidham, M., and Murdiyarso, D. (2011). Mangroves among the most carbon-rich forests in the tropics. *Nature Geoscience*, 4, 293-297, doi: 10.1038/NGEO1123, 2011.
- Dortch, Q. (1990). The interaction between ammonium and nitrate uptake in phytoplankton. *Marine Ecology Progress Series Oldendorf*, 61, 183–201.
- Dugdale, R., and Goering, J. (1967). Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnology Oceanography*, 12, 196–206.
- Dugdale, R., and Wilkerson, F. (1986). The use of 15N to measure nitrogen uptake in eutrophic oceans; experimental considerations. *Limnology Oceanography*, 31, 673–689.
- Dutta, K., Prasad, G. R., Ray, D. K., and Raghav, S. (2010). Decadal changes of radiocarbon in the surface Bay of Bengal: Three decades after GEOSECS and one decade after WOCE. *Radiocarbon*, 52, 1191–1196.
- Dutta, M. K., Chowdhury, C., Jana, T. K., and Mukhopadhyay, S. K. (2013). Dynamics and exchange fluxes of methane in the estuarine mangrove environment of Sundarbans, NE coast of India. *Atmospheric Environment* 77, 631–639, doi: 10.1016/j.atmosenv.2013.05.050.
- Dutta, M. K., Mukherkjee, R., Jana, T. K., and Mukhopadhyay, S. K. (2015a). Biogeochemical dynamics of exogenous methane in an estuary associated to a mangrove biosphere; the Sundarbans, NE coast of India. *Marine Chemistry*, 170, 1–10,

- Dutta, M. K., Mukherkjee, R., Jana, T. K., and Mukhopadhyay, S. K. (2015b). Atmospheric fluxes and photo-oxidation of methane in the mangrove environment of the Sundarbans, NE coast of India; A case study from Lothian Island. *Agriculture and Forest Meteorology*, 213, 33–41.
- Dutta, M.K., Bianchi, T.S., and Mukhopadhyay, S.K. (2017). Mangrove methane biogeochemistry in the Indian Sundarbans: a proposed budget. *Frontiers in Marine Science*, 4, 187.
- Downing, J. A. (1997). Marine nitrogen: phosphorus stoichiometry and the global N: P cycle. *Biogeochemistry*, *37*(3), 237–252.
- Elzenga, J. T. M., Prins, H., and Stefels, J. (2000). The role of extracellular carbonic anhydrase activity in inorganic carbon utilization of Phaeocystis globosa (Prymnesiophyceae): a comparison with other marine algae using the isotopic disequilibrium technique. *Limnology Oceanography*, 45, 372–380.
- Falkowski, P. G., Barber, R. T., & Smetacek, V. (1998). Biogeochemical controls and feedbacks on ocean primary production. *Science*, 281(5374), 200–206.
- Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., et al. (1998). Carbon dioxide emission from European estuaries. *Science*, 282, 434– 436.
- Frankignoulle, M., and Borges, A. V. (2001). Direct and indirect pCO_2 measurements in a wide range of pCO_2 and salinity values (the Scheldt estuary). *Aquatic Geochemistry*, 7, 267 - 273.
- French, R. H., Cooper, J. J., and Vigg, S. (1982). Secchi disc relationships. JAWRA Journal of the American Water Resources Association, 18, 121–123.
- Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., et al. (2004). Nitrogen cycles: past, present, and future. *Biogeochemistry*, 70, 153–226.
- Galloway, J N., Townsend, A. R., Erisman, J. W. (2008). Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science, 320, 889–892.

- Ganguly, D., Dey, M., Mandal, S.K., De, T.K., and Jana, T.K. (2008). Energy dynamics and its implication to biosphere-atmosphere exchange of CO₂, H₂O and CH₄ in a tropical mangrove forest canopy. *Atmospheric Environment*, 42, 4172 – 4184, 2008.
- Ganguly, D., Dey, M., Sen, S., and Jana, T.K. (2009). Biosphere-atmosphere exchange of NOx in the tropical mangrove forest. *Journal of Geophysical Research*, 114, G04014.
- Ganguly, D., Patra, S., Muduli, P. R., Vardhan, K. V., Abhilash, K., Robin, R. (2015). Influence of nutrient input on the trophic state of a tropical brackish water lagoon. *Journal of Earth System Science*, 124, 1005–1017.
- Gardner, W. S., Lavrentyev, P. J., Cavaletto, J. F., McCarthy, M. J., Eadie, B. J., Johengen, T. H., et al. (2004). Distribution and dynamics of nitrogen and microbial plankton in southern Lake Michigan during spring transition 1999– 2000. *Journal of Geophysical Research Oceans*, 109.
- Garzon-Garcia, A., Laceby, J. P., Olley, J. M., and Bunn, S. E. (2017). Differentiating the sources of fine sediment, organic matter and nitrogen in a subtropical Australian catchment. *Science of the Total Environment*, 575, 1384–1394.
- Gattuso, J.-P., Frankignoulle, M., Bourge, I., Romaine, S., and Buddemeier, R. W. (1998). Effect of calcium carbonate saturation of seawater on coral calcification. *Global and Planetary Change*, 18,37-46.
- Ghosh, P., Chakrabarti, R., and Bhattacharya, S. K. (2013). Short and long-term temporal variations in salinity and the oxygen, carbon and hydrogen isotopic compositions of the Hooghly Estuary water, India, *Chemical Geology*, 335, 118–127.
- Giri, C., Ochieng, E., Tieszen, L., Zhu, Z., Singh, A., Loveland, T., Masek, J., and Duke, N. (2011). Status and distribution of mangrove forests of the world using earth observation satellite data. *Global Ecology and Biogeography*, 20(1), 154-159, 2011.

- Glibert, P. M., Biggs, D. C., and McCarthy, J. J. (1982). Utilization of ammonium and nitrate during austral summer in the Scotia Sea. *Deep Sea Res. Part Oceanogr. Res. Pap.* 29, 837–850.
- Glibert, P. M., Trice, T. M., Michael, B., & Lane, L. (2005). Urea in the tributaries of the Chesapeake and coastal bays of Maryland. Water, Air, & Soil Pollution, 160(1), 229–243.
- Glibert, P. M., Harrison, J., Heil, C., Seitzinger, S. (2006). Escalating worldwide use of urea–a global change contributing to coastal eutrophication. *Biogeochemistry*, 77(3), 441–463.
- Glibert, P. M., Hinkle, D. C., Sturgis, B., & Jesien, R. V. (2014a). Eutrophication of a Maryland/Virginia coastal lagoon: a tipping point, ecosystem changes, and potential causes. *Estuaries and Coasts*, 37(1), 128–146.
- Glibert, P. M., Maranger, R., Sobota, D. J., & Bouwman, L. (2014b). The Haber Bosch–harmful algal bloom (HB–HAB) link. *Environmental Research Letters*, 9(10), 105001.
- Glibert, P. M., Wilkerson, F. P., Dugdale, R. C., Parker, A. E., Alexander, J., Blaser, S., & Murasko, S. (2014c). Phytoplankton communities from San Francisco Bay Delta respond differently to oxidized and reduced nitrogen substrates—even under conditions that would otherwise suggest nitrogen sufficiency. *Frontiers in Marine Science*, 1, 17.
- Glibert, P. M., Wilkerson, F. P., Dugdale, R. C., Raven, J. A., Dupont, C. L., Leavitt, P. R., Kana, T. M. (2016). Pluses and minuses of ammonium and nitrate uptake and assimilation by phytoplankton and implications for productivity and community composition, with emphasis on nitrogen- enriched conditions. *Limnology and Oceanography*, 61(1), 165–197.
- Gole, C., and Vaidyaraman, P. (1967). "Salinity Distribution and Effect of Fresh Water Flows in the Hooghly River," *Coastal Engineering*, *1966*, 1412–1434.
- Gonneea, M. E., Paytan, A., and Herrera-Silveira, J. A. (2004). Tracing organic matter sources and carbon burial in mangrove sediments over the past 160 years. *Estuarine Coastal and Shelf Sciences*, 61, 211–227.

- Goyet, C., Millero, F., O'Sullivan, D., Eischeid, G., McCue, S., & Bellerby, R. (1998).
 Temporal variations of pCO2 in surface seawater of the Arabian Sea in 1995.
 Deep Sea Research Part I: Oceanographic Research Papers, 45(4–5), 609–623.
- Graham, M., Eaves, M., Farmer, J., Dobson, J., and Fallick, A. (2001). A study of carbon and nitrogen stable isotope and elemental ratios as potential indicators of source and fate of organic matter in sediments of the Forth Estuary, Scotland. *Estuarine Coastal and Shelf Sciences*, 52, 375–380.
- Grasshoff, K., Ehrharft, M., and Kremling, K. (1983). Methods of Seawater Analysis, 2nd Edn.Weinheim: Verlag Chemie.
- Grashoff, K., Kremling, K., and Ehrhard, M. (1999). Methods of Seawater Analysis. 3rd completely revised and extended edition
- Green, R. E., Bianchi, T. S., Dagg, M. J., Walker, N. D., and Breed, G. A. (2006). An organic carbon budget for the Mississippi River turbidity plume and plume contributions to air-sea CO 2 fluxes and bottom water hypoxia. *Estuaries Coasts*, 29, 579–597.
- Großkopf, T., Mohr, W., Baustian, T., Schunck, H., Gill, D., Kuypers, M. M., et al. (2012). Doubling of marine dinitrogen-fixation rates based on direct measurements. *Nature*, 488, 361.
- Gruber, N., Keeling, C. D., Bacastow, R. B., Guenther, P. R., Lueker, T. J., Wahlen, M., et al. (1999). Spatiotemporal patterns of carbon- 13 in the global surface oceans and the oceanic Suess effect. *Global Biogeochemical Cycles*, 13, 307– 335.
- Gruber, N. (2004). The dynamics of the marine nitrogen cycle and its influence on atmospheric CO₂ variations. In *The ocean carbon cycle and climate* (pp. 97– 148). Springer.
- Gu, B., Havens, K. E., Schelske, C. L., and Rosen, B. H. (1997). Uptake of dissolved nitrogen by phytoplankton in a eutrophic subtropical lake. *Journal of Plankton Research*, 19, 759–770.

- Guo, X., Cai, W.-J., Zhai, W., Dai, M., Wang, Y., and Chen, B. (2008). Seasonal variations in the inorganic carbon system in the Pearl River (Zhujiang) estuary. *Cont. Shelf Res.* 28, 1424–1434.
- Guo, W., Ye, F., Xu, S., and Jia, G. (2015). Seasonal variation in sources and processing of particulate organic carbon in the Pearl River estuary, South China. *Estuarine Coastal and Shelf Sciences*, 167, 540–548.
- Sen Gupta, R., Naik, S., and Singbal, S. (1978). A study of fluoride, calcium and magnesium in the Northern Indian Ocean. *Marine Chemistry*, 6, 125–141.
- Gupta, G., Sarma, V., Robin, R., Raman, A., Kumar, M. J., Rakesh, M., & Subramanian, B. (2008). Influence of net ecosystem metabolism in transferring riverine organic carbon to atmospheric CO₂ in a tropical coastal lagoon (Chilka Lake, India). *Biogeochemistry*, 87(3), 265–285.
- Hallegraeff, G. M. (1993). A review of harmful algal blooms and their apparent global increase. *Phycologia*, *32*(2), 79–99.
- Hanson, P. C., Bade, D. L., Carpenter, S. R., and Kratz, T. K. (2003). Lake metabolism: Relationships with dissolved organic carbon and phosphorus. *Limnology Oceanography* 48, 1112–1119.
- Harrison,W. G., Platt, T., and Lewis, M. R. (1987). "f-ratio and its relationship to ambient nitrate concentration in coastal waters". *Journal of Plankton Research*, 9, 235–248.
- Hauck, J., Völker, C., Wolf- Gladrow, D. A., Laufkötter, C., Vogt, M., Aumont, O., Dunne, J. (2015). On the Southern Ocean CO₂ uptake and the role of the biological carbon pump in the 21st century. *Global Biogeochemical Cycles*, 29(9), 1451–1470.
- Hedges, J., Keil, R., and Benner, R. (1997). What happens to terrestrial organic matter in the ocean? *Organic Geochemistry*, 27, 195–212.
- Heffer, P., and Prud'homme, M. (2013). Fertilizer outlook 2013–2017 81st IFA Annual Conf. (Chicago (USA), 20–22 May 2013) (www.fertilizer.org) Accessed June 22, 2014

- Heip, C. H. R., Goosen, N.K., Herman, P.M.J., Kromkamp, J., Middelburg, J.J., and Soetaert, K.: Production and consumption of biological particles in temperate tidal estuaries. *Oceanography Marine Biology Annual Review*, 33, 1–149, 1995.
- Heisler, J., Glibert, P. M., Burkholder, J. M., Anderson, D. M., Cochlan, W., Dennison,
 W. C., Humphries, E. (2008). Eutrophication and harmful algal blooms: a scientific consensus. *Harmful Algae*, 8(1), 3–13.
- Hernandez, M. E., Mead, R., Peralba, M. C., and Jaffé, R. (2001). Origin and transport of n-alkane-2-ones in a subtropical estuary: potential biomarkers for seagrassderived organic matter. *Organic Geochemistry*, 32, 21–32.
- Hodgkiss, I., and Ho, K. (1997). Are changes in N: P ratios in coastal waters the key to increased red tide blooms? *Hydrobiologia*, 352, 141–147.
- Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Caldeira, K. (2007). Coral reefs under rapid climate change and ocean acidification. *Science*, *318*(5857), 1737–1742.
- Hopkinson, C.S., Fry, B., Nolin, A. (1997). Stoichiometry of dissolved organic matter dynamics on the continental shelf of the Northeastern USA, *Continental Shelf Research*, 17, 473–489.
- Hullar, M., Fry, B., Peterson, B., and Wright, R. (1996). Microbial utilization of estuarine dissolved organic carbon: a stable isotope tracer approach tested by mass balance. *Applied Environmental Microbiology*, 62, 2489–2493.
- IMD (2013) District wise (South 24 Parganas) rainfall data for last five years. Indian Meteorological Department.

 $<\!\!www.imd.gov.\ in/section/hydro/distrainfall/webrain/wb/south24 parganas.txt\!>.$

- IPCC (2014) Climate change 2014: synthesis report. Contribution of working groups I, II and III to the fifth assessment report of the intergovernmental panel on climate change. Intergovernmental Panel on Climate Change, Geneva, Switzerland.
- Ittekkot V., Safiullah S., Mycke, B., and Seifert, R. (1988). Seasonal variability and geochemical significance of organic matter in the river Ganga, Bangladesh. *Nature*, 317, 800–802.

- Ittekkot, V., and Laane, R.W.P.M.: Fate of riverine particulate organic matter. In: Degens, E.T.; Kemp, S.; Richey, J.E., (1991). *Biogeochemistry of major world rivers. Chichester: Wiley*; 233-243.
- Jansson, M., Bergström, A.-K., Blomqvist, P., and Drakare, S. (2000). Allochthonous organic carbon and phytoplankton/bacterioplankton production relationships in lakes. *Ecology*, 81, 3250–3255.
- Jauzein, C., Couet, D., Blasco, T., and Lemée, R. (2017). Uptake of dissolved inorganic and organic nitrogen by the benthic toxic dinoflagellate Ostreopsis cf. ovata. *Harmful Algae*, 65, 9–18.
- Jennerjahn, T. C., and Ittekkot, V. (2002). Relevance of mangroves for the production and deposition of organic matter along tropical continental margins. *Naturwissenschaften*, 89, 23–30.
- Jickells, T. (2006). The role of air-sea exchange in the marine nitrogen cycle. Biogeosciences Discussions, 3(1), 183–210.
- Johnson, A., & White, N. D. (2014). Ocean acidification: The other climate change issue. *American Scientist*, *102*(1), 60.
- Jones, P.D., Parker, D.E., Osborn, T.J., Briffa, K.R. (2013). Global and hemispheric temperature anomalies —land and marine instrumental records. In: Trends: a compendium of data on global change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy. www.cdiac.ornl.gov/climate/temp/. Accessed 13 Mar 2015
- Joos, F., Plattner, G.-K., Stocker, T. F., Marchal, O., & Schmittner, A. (1999). Global warming and marine carbon cycle feedbacks on future atmospheric CO₂. *Science*, *284*(5413), 464–467.
- Kanda, J., Itoh, T., Ishikawa, D., and Watanabe, Y. (2003). Environmental control of nitrate uptake in the East China Sea. *Deep Sea Res. Part II Top. Stud. Oceanogr*, 50, 403–422.
- Kaplan, A., Ronen-Tarazi, M., Zer, H., Schwarz, R., Tchernov, D., Bonfil, D. J., et al.(1998). The inorganic carbon-concentrating mechanism in cyanobacteria:

induction and ecological significance. *Canadian Journal of Botany*, 76, 917–924.

- Kauwe, M. G., Medlyn, B. E., Zaehle, S., Walker, A. P., Dietze, M. C., Hickler, T., Prentice, I. C. (2013). Forest water use and water use efficiency at elevated CO₂: a model- data intercomparison at two contrasting temperate forest FACE sites. *Global Change Biology*, *19*(6), 1759–1779.
- Keller, A. A. (1988). Estimating phytoplankton productivity from light availability and biomass in the MERL mesocosms and Narragansett Bay. *Marine Ecology Progress Series Oldendorf*, 45, 159–168.
- Kendall, C., Elliott, E. M., and Wankel, S. D. (2007). Tracing anthropogenic inputs of nitrogen to ecosystems. *Stable Isotope in Ecology and Environmental Science*, 2, 375–449.
- Kennedy, H., Gacia, E., Kennedy, D., Papadimitriou, S., and Duarte, C. (2004). Organic carbon sources to SE Asian coastal sediments. *Estuarine Coastal and Shelf Sciences*, 60, 59–68.
- Kennish, M. J., and Paerl, H. W. (2010). Coastal lagoons: critical habitats of environmental change. CRC Press.
- Klausmeier, C. A., Litchman, E., Daufresne, T., & Levin, S. A. (2004). Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton. *Nature*, 429(6988), 171–174.
- Korb, R. E., Saville, P. J., Johnston, A. M., and Raven, J. A. (1997). Sources of inorganic carbon for photosynthesis by three species of marine diatom. *Journal* of Phycology, 33, 433–440.
- Koziorowska, K., Kuliński, K., and Pempkowiak, J. (2016). Sedimentary organic matter in two Spitsbergen fjords: Terrestrial and marine contributions based on carbon and nitrogen contents and stable isotopes composition. *Continental Shelf Research*, 113, 38–46.
- Kozlowsky-Suzuki, B., and Bozelli, R. L. (2004). Resilience of a zooplankton community subjected to marine intrusion in a tropical coastal lagoon. *Hydrobiologia*, 522, 165–177.

- Krause-Jensen, D., Markager, S., & Dalsgaard, T. (2012). Benthic and pelagic primary production in different nutrient regimes. *Estuaries and Coasts*, *35*(2), 527–545.
- Krishna, M., Naidu, S., Subbaiah, C. V, Sarma, V., and Reddy, N. (2013). Distribution and sources of organic matter in surface sediments of the eastern continental margin of India. *Journal of Geophysical Research: Biogeosciences*, 118, 1484– 1494.
- Kudela, R. M., Lane, J. Q., & Cochlan, W. P. (2008). The potential role of anthropogenically derived nitrogen in the growth of harmful algae in California, USA. *Harmful Algae*, 8(1), 103–110.
- Kumar, S., Sterner, R. W., and Finlay, J. C. (2008). Nitrogen and carbon uptake dynamics in Lake Superior. *Journal of Geophysical Research: Biogeosciences*, 113.
- Kumar, S., Ramesh, R., Dwivedi, R., Raman, M., Sheshshayee, M., and D'Souza, W. (2010). Nitrogen uptake in the northeastern Arabian Sea during winter cooling. *International Journal of Oceanography*, 2010.
- Lamb, A. L., Wilson, G. P., & Leng, M. J. (2006). A review of coastal palaeoclimate and relative sea-level reconstructions using δ 13 C and C/N ratios in organic material. *Earth-Science Reviews*, 75(1), 29–57.
- Laruelle, G. G., Dürr, H. H., Slomp, C. P., & Borges, A. V. (2010). Evaluation of sinks and sources of CO2 in the global coastal ocean using a spatially- explicit typology of estuaries and continental shelves. *Geophysical Research Letters*, 37(15).
- Leavitt, P. R., Brock, C. S., Ebel, C., and Patoine, A. (2006). Landscape- scale effects of urban nitrogen on a chain of freshwater lakes in central North America. *Limnology Oceanography*, 51, 2262–2277.
- Le Quéré, C., Moriarty, R., Andrew, R., Canadell, J., Sitch, S., Korsbakken, J., Boden, T. (2015). Global Carbon Budget 2015. *Earth System Science*, Data, 7, 349– 396.

- Le Quéré, C., Andrew, R., Canadell, J., Sitch, S., Korsbakken, J., Peters, G., ... Houghton, R. (2016). Global Carbon Budget 2016, *Earth System Science*, Data, 8, 605–649.
- Lewis, E., and Wallace, D. (1998). Program Developed for CO₂ System Calculations (Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Dept. of Energy, Oak Ridge, TN). ORNLCDIAC-105.
- Li, Q., and Canvin, D. T. (1998). Energy Sources for HCO₃⁻ and CO₂ Transport in Air-Grown Cells of Synechococcus UTEX 625. *Plant Physiology*, 116, 1125–1132.
- Linto N., Barnes, J., Ramachandran, R., Divia, J., Ramachandran, P., and Upstill-Goddard, R. C. (2014). Carbon dioxide and methane emissions from mangroveassociated waters of the Andaman Islands, Bay of Bengal, *Estuaries and Coasts*, 37, 381–398.
- Liss, P. S., and Merlivat, L. (1986). "Air sea gas exchange rates: introduction and synthesis," in The Role of Air Sea Exchange in Geochemical Cycling, ed P. Buat-Menard (Hingham, MA: D. Reidel) 113–129.
- Lomas, M. W., Trice, T. M., Glibert, P. M., Bronk, D. A., & McCarthy, J. J. (2002). Temporal and spatial dynamics of urea uptake and regeneration rates and concentrations in Chesapeake Bay. *Estuaries*, 25(3), 469–482.
- Lujanienė G, Mažeika J, Li H-C. (2016). Δ^{14} C and δ^{13} C as tracers of organic carbon in Baltic Sea sediments collected in coastal waters off Lithuania and in the Gotland Deep. *Journal of Radioanalytical and Nuclear Chemistry*, 307:2231– 2237.
- MacKenzie, F. (1981). Flux of organic carbon by rivers to the ocean. US Dep. Energy Wash. DC Ch Glob. Carbon Cycle Some Minor Sinks CO₂, 360–384.
- Macko, S. A., Engel, M. H., and Parker, P. L. (1993). "Early diagenesis of organic matter in sediments," in *Organic geochemistry*, (Springer), 211–224.
- Manabe, S., & Stouffer, R. J. (1993). Century-scale effects of increased atmospheric C02 on the ocean–atmosphere system. *Nature*, 364(6434), 215–218.

- Matson, E. a., and Brinson, M. M. (1990). Stable carbon isotopes and the C : N ratio In the estuaries of the Pamlico and Neuse Rivers. North Carolina. *Limnology Oceanography*, 35, 1290–1300.
- Mayer, B., Boyer, E. W., Goodale, C., Jaworski, N. A., Van Breemen, N., Howarth, R.
 W., Nadelhoffer, K. (2002). Sources of nitrate in rivers draining sixteen watersheds in the northeastern US: Isotopic constraints. In *The nitrogen cycle at regional to global scales* (pp. 171–197). Springer.
- McCarthy, J. J., Taylor, W. R., & Taft, J. L. (1977). Nitrogenous nutrition of the plankton in the Chesapeake Bay. 1. Nutrient availability and phytoplankton preferences. *Limnology Oceanography*, 22(6), 996–1011.
- McCarthy, J. J. (1983). Nitrogen cycling in nearsurface waters of the open ocean. *Nitrogen in Marine Environment*, 487–512.
- McCarthy, J. J., Garside, C., and Nevins, J. L. (1999). "Nitrogen dynamics during the Arabian Sea Northeast Monsoon," *Deep- Sea Research Part II*, vol. 46, no. 8-9, pp. 1623–1664.
- Meyers, P. A., and Ishiwatari, R. (1993). Lacustrine organic geochemistry-an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry*, 20, 867–900.
- Meyers, P. A. (1994). Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology*, *114*(3–4), 289–302.
- Meyers, P. A., and Arnaboldi, M. (2008). Paleoceanographic implications of nitrogen and organic carbon isotopic excursions in mid-Pleistocene sapropels from the Tyrrhenian and Levantine Basins, Mediterranean Sea. *Palaeogeography Palaeoclimatology Palaeoecology*, 266, 112–118.
- Miller, A. G., ESPIE, G. S., and Canvin, D. T. (1991). Active CO₂ transport in cyanobacteria. *Canadian Journal of Botany*, **69**: 925–935.
- Millero, F.J.: Chemical Oceanography, Fourth Edition, CRC press, Taylor and Francis Group, 2013.

- Mitchell, J. F., Johns, T., Gregory, J. M., & Tett, S. (1995). Climate response to increasing levels of greenhouse gases and sulphate aerosols. *Nature*, *376*(6540), 501–504.
- Miyazaki, Y., Kawamura, K., and Sawano, M. (2010). Size distributions of organic nitrogen and carbon in remote marine aerosols: Evidence of marine biological origin based on their isotopic ratios. *Geophysical Research Letter*, 37.
- Miyajima T., Tsuboi Y., Tanaka Y., and Koike, I.(2009). Export of inorganic carbon from two Southeast Asian mangrove forests to adjacent estuaries as estimated by the stable isotope composition of dissolved inorganic carbon, *Journal of Geophysical Research*, **114**, G01024.
- Mohanty, P., Dash, S., Mishra, P., and Murty, A. (1996). Heat and momentum fluxes over Chilka: A tropical lagoon. *Indian Journal of Marine Science*, 25, 184–188.
- Mohr, W., Grosskopf, T., Wallace, D. W., and LaRoche, J. (2010). Methodological underestimation of oceanic nitrogen fixation rates. *PLOS One* 5, e12583.
- Mook, W. G., and Tan, T. C. (1991). Stable carbon isotopes in rivers and estuaries. In Biogeochemistry of Major World Rivers (eds. E. T. Degens, S. Kempe and J. E. Richey). SCOPE, John Wiley and Sons Ltd, pp. 245–264

Morgan, J. J., and Stumm, W. (1970). Aquatic chemistry. Wiley.

- Moran, M.A., Sheldon Jr., W.M., and Sheldon, J.E. (1999). Biodegradation of riverine dissolved organic carbon in five estuaries of the south United States. *Estuaries*, 22, 55 64.
- Moynihan, M. A., Barbier, P., Olivier, F., Toupoint, N., and Meziane, T. (2016). Spatial and temporal dynamics of nano- and pico- size particulate organic matter (POM) in a coastal megatidal marine system. *Limnology. Oceanography*.
- Muduli, P. R., Kanuri, V. V., Robin, R., Kumar, B. C., Patra, S., Raman, A., Subramanian, B. (2012). Spatio-temporal variation of CO 2 emission from Chilika Lake, a tropical coastal lagoon, on the east coast of India. *Estuarine*, *Coastal and Shelf Science*, 113, 305–313.

- Muduli, P. R., Kanuri, V. V., Robin, R., Kumar, B. C., Patra, S., Raman, A., Subramanian, B. (2013). Distribution of dissolved inorganic carbon and net ecosystem production in a tropical brackish water lagoon, India. *Continental Shelf Research*, 64, 75–87.
- Mukherjee, R., Kumar, S., and Muduli, P. R. (2018). Spatial variation of nitrogen uptake rates in the largest brackish water lagoon of Asia (Chilika, India). *Estuarine Coastal and Shelf Sciences*.
- Mukhopadhyay, S., Biswas, H., De, T., Sen, S., & Jana, T. (2002). Seasonal effects on the air–water carbon dioxide exchange in the Hooghly estuary, NE coast of Bay of Bengal, India. *Journal of Environmental Monitoring*, *4*(4), 549–552.
- Mukhopadhyay, S., Biswas, H., De, T., & Jana, T. (2006). Fluxes of nutrients from the tropical River Hooghly at the land–ocean boundary of Sundarbans, NE Coast of Bay of Bengal, India. *Journal of Marine Systems*, 62(1), 9–21.
- Mulholland, M. R., Bronk, D. A., and Capone, D. G. (2004). Dinitrogen fixation and release of ammonium and dissolved organic nitrogen by Trichodesmium IMS101. Aquatic Microbial Ecology, 37, 85–94.
- Mulholland, M. R., and Bernhardt, P. W. (2005). The effect of growth rate, phosphorus concentration, and temperature on N2 fixation, carbon fixation, and nitrogen release in continuous cultures of Trichodesmium IMS101. *Limnology Oceanography*, 50, 839–849.
- Mulholland, M. R., and Capone, D. G. (2009). Dinitrogen fixation in the Indian Ocean. *Indian Ocean Biogeochemistry Process. Ecol. Var.*, 167–186.
- Muzuka, A. N., and Shunula, J. P. (2006). Stable isotope compositions of organic carbon and nitrogen of two mangrove stands along the Tanzanian coastal zone. *Estuarine Coastal and Shelf Sciences*, 66, 447–458.
- Neven, I. A., Stefels, J., van Heuven, S. M., de Baar, H. J., & Elzenga, J. T. M. (2011).
 High plasticity in inorganic carbon uptake by Southern Ocean phytoplankton in response to ambient CO₂. *Deep Sea Research Part II: Topical Studies in Oceanography*, 58(25), 2636–2646.

- Newton, A., Icely, J., Falcão, M., Nobre, A., Nunes, J., Ferreira, J., et al. (2003). Evaluation of eutrophication in the Ria Formosa coastal lagoon, Portugal. *Continental Shelf Research*, 23, 1945–1961.
- Nieuwenhuize, J., Maas, Y. E., and Middelburg, J. J. (1994). Rapid analysis of organic carbon and nitrogen in particulate materials. *Marine Chemistry*, 45, 217–224.
- Nitzsche, K. N., Kalettka, T., Premke, K., Lischeid, G., Gessler, A., and Kayler, Z. E. (2017). Land-use and hydroperiod affect kettle hole sediment carbon and nitrogen biogeochemistry. *Science of the Total Environment*, 574, 46–56.
- Norrman, B., Zwelfel, U. L., Hopkinson, C. S., and Brian, F. (1995). Production and utilization of dissolved organic carbon during an experimental diatom bloom. *Limnology Oceanography*, 40, 898–907.
- Odum, H. T. (1956). Primary production in flowing waters. *Limnology Oceanography*, 1, 102–117.
- Paerl, H. W. (1988). Nuisance phytoplankton blooms in coastal, estuarine, and inland waters. *Limnology and Oceanography*, 33(4part2), 823–843.
- Paerl, H. W., Dennis, R. L., and Whitall, D. R. (2002). Atmospheric deposition of nitrogen: Implications for nutrient over-enrichment of coastal waters. *Estuaries*, 25, 677–693.
- Palevsky, H. I., & Quay, P. D. (2017). Influence of biological carbon export on ocean carbon uptake over the annual cycle across the North Pacific Ocean. *Global Biogeochemical Cycles*, 31(1), 81–95.
- Panigrahi, S., Wikner, J., Panigrahy, R., Satapathy, K., and Acharya, B. (2009). Variability of nutrients and phytoplankton biomass in a shallow brackish water ecosystem (Chilika Lagoon, India). *Limnology*, 10, 73–85.
- Parker, A. E., Hogue, V. E., Wilkerson, F. P., and Dugdale, R. C. (2012). The effect of inorganic nitrogen speciation on primary production in the San Francisco Estuary. *Estuarine Coastal and Shelf Sciences* 104, 91–101.
- Parker, S. R., West, R. F., Boyd, E. S., Feyhl- Buska, J., Gammons, C. H., Johnston, T. B., et al. (2016). Biogeochemical and microbial seasonal dynamics between water column and sediment processes in a productive mountain lake:

Georgetown Lake, MT, USA. Journal of Geophysical Research Biogeosciences 121, 2064–2081.

- Patra, S., Raman, A., Ganguly, D., Robin, R., Muduli, P., Kanuri, V., et al. (2016). Influence of suspended particulate matter on nutrient biogeochemistry of a tropical shallow lagoon, Chilika, India. *Limnology*, 17, 223–238.
- Peipoch, M., Martí, E., & Gacia, E. (2012). Variability in δ15N natural abundance of basal resources in fluvial ecosystems: a meta-analysis. *Freshwater Science*, 31(3), 1003–1015.
- Pelletier, G., Lewis, E., and Wallace, D. (2007). CO2Sys. xls: A calculator for the CO2 system in seawater for microsoft excel/VBA. Wash. State Dep. Ecol. Natl. Lab. Olymp. WAUpton NY USA.
- Peñuelas, J., Sardans, J., Rivas-Ubach, A., and Janssens, I. A. (2012). The humaninduced imbalance between C, N and P in Earth's life system. *Global Change Biology*, 18 3–6
- Pennock, J. R., and Sharp, J. H. (1986). Phytoplankton production in the Delaware Estuary: temporal and spatial variability. *Marine Ecology Progress Series*, 143–155.
- Prahl, F. G., De Lange, G. J., Scholten, S., and Cowie, G. L. (1997). A case of postdepositional aerobic degradation of terrestrial organic matter in turbidite deposits from the Madeira Abyssal Plain. *Orgganic Geochemistry*, 27, 141– 152.
- Prasad, M. B. K., and Ramanathan, A. (2009). Organic matter characterization in a tropical estuarine-mangrove ecosystem of India: preliminary assessment by using stable isotopes and lignin phenols. *Estuarine Coastal and Shelf Sciences* 84, 617–624.
- Prasad, M., Sarma, V., Sarma, V., Krishna, M., & Reddy, N. (2013). Carbon dioxide emissions from the tropical Dowleiswaram Reservoir on the Godavari River, Southeast of India.

- Prasad, B., Srinivasu, P., Varma, P. S., Raman, A., and Ray, S. (2014). Dynamics of Dissolved Oxygen in relation to Saturation and Health of an Aquatic Body: A Case for Chilka Lagoon, India. *Journal of Ecosystem and Echography*.
- Quay, P., and Stutsman, J. (2003). Surface layer carbon budget for the subtropical N. Pacific: δ13C constraints at station ALOHA. *Deep Sea Research Part Oceanography Research Paper*, 50, 1045–1061.
- Racapé, V., Pierre, C., Metzl, N., Monaco, C. L., Reverdin, G., Olsen, A., et al. (2013). Anthropogenic carbon changes in the Irminger Basin (1981–2006): Coupling $\delta^{13}C_{DIC}$ and DIC observations. *Journal of Marine Systems*, 126, 24–32.
- Raven, J. (1997). Inorganic carbon acquisition by marine autotrophs. *Advances in Botanical Research*, 27, 85–209.
- Raven, J. A., Wollenweber, B., & Handley, L. L. (1992). A comparison of ammonium and nitrate as nitrogen sources for photolithotrophs. *New Phytologist*, *121*(1), 19–32.
- Ranjan, R. K., Routh, J., Ramanathan, A. L., and Klump, J. V. (2011). Elemental and stable isotope records of organic matter input and its fate in the Pichavaram mangrove-estuarine sediments (Tamil Nadu, India). *Marine Chemistry* 126, 163–172.
- Raymond, P. A. and Cole, J. J. (2001). Gas exchange in rivers and estuaries: Choosing a gas transfer velocity, Estuaries, 24, 312–317.
- Ray, R., Ganguly, D., Chowdhury, C., Dey, M., Das, S., Dutta, M.K., Mandal, S.K., Majumder, N., De, T.K., Mukhopadhyay, S.K., and Jana, T.K. (2011). Carbon sequestration and annual increase of carbon stock in a mangrove forest, *Atmospheric Environment*, 45, 5016-5024.
- Ray, R., Rixen, T., Baum, A., Malik, A., Gleixner, G., and Jana, T. (2015). Distribution, sources and biogeochemistry of organic matter in a mangrove dominated estuarine system (Indian Sundarbans) during the pre-monsoon. *Estuarine Coastal and Shelf Sciences*, 167, 404–413.
- Ray, R., Baum, A., Rixen, T., Gleixner, G., and Jana, T.K. (2018). Exportation of dissolved (inorganic and organic) and particulate carbon from mangroves and

its implication to the carbon budget in the Indian Sundarbans. *Science of the Total Environment*, 621, 535-547.

- Reay, W.G., Gallagher, D., and Simmons, G.M. (1995). Sediment water column nutrient exchanges in Southern Chesapeake Bay near shore environments, Virginia Water Resources Research Centre, Bulletin - 181b.
- Reeburgh, W. S. (2007). Oceanic methane biogeochemistry. *Chemical reviews*, 107(2), 486-513.
- Reddy, C. S., Pattanaik, C., and Murthy, M. (2007). Assessment and monitoring of mangroves of Bhitarkanika Wildlife Sanctuary, Orissa, India using remote sensing and GIS. *Current Science*, 1409–1415.
- Rees, A., Owens, N., Heath, M., Plummer, D., and Bellerby, R. (1995). Seasonal nitrogen assimilation and carbon fixation in a fjordic sea loch. *J. Plankton Res.* 17, 1307–1324.
- Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. A., et al. (2013). Anthropogenic perturbation of the carbon fluxes from land to ocean. *Nature Geoscience*, 6, 597.
- Richey, J.E., Melack, J.M., Aufdenkampe, A.K., Ballester, V.M., and Hess, L.L. (2002). Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO₂, Nature, 416, 617-620.
- Rotatore, C., and Colman, B. (1991). The localization of active inorganic carbon transport at the plasma membrane in *Chlorella ellipsoidea*. *Canadian Journal of Botany*, 69, 1025–1031.
- Rotatore, C., and Colman, B. (1992). Active uptake of CO₂ by the diatom *Navicula pelliculosa. Journal of Experimental Botany*, 43, 571–576.
- Rotator and M., Kuzuma. 1995. The active uptake of carbon dioxide by the marine diatoms *Phaeodactylum tricornutum* and *Cyclotella* sp. 1995. *Plant Cell Environment*, 18: 913–918.
- Roy, T., Bopp, L., Gehlen, M., Schneider, B., Cadule, P., Frölicher, T. L., Joos, F. (2011). Regional impacts of climate change and atmospheric CO₂ on future

ocean carbon uptake: A multimodel linear feedback analysis. *Journal of Climate*, 24(9), 2300–2318.

- Ruedy, R., Sato, M., & Lo, K. (2015). NASA GISS surface temperature (GISTEMP) analysis. Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy. Http:// Www. Cdiac. Ornl. Gov/ Trends/ Temp/ Hansen/ Hansen. Html. Accessed, 13.
- Ryther, J. H., & Dunstan, W. M. (1971). Nitrogen, phosphorus, and eutrophication in the coastal marine environment. *Science*, *171*(3975), 1008–1013.
- Sabine, C. L., Key, R. M., Feely, R. A., and Greeley, D. (2002). Inorganic carbon in the Indian Ocean: Distribution and dissolution processes. *Global Biogeochemical Cycles*, 16.
- Sadhuram, Y., Sarma, V., Murthy, T. R., and Rao, B. P. (2005). Seasonal variability of physico-chemical characteristics of the Haldia channel of Hooghly estuary, India. *Journal of Earth System Science*, 114, 37–49.
- Samanta, S., Dalai, T. K., Pattanaik, J. K., Rai, S. K., & Mazumdar, A. (2015). Dissolved inorganic carbon (DIC) and its δ^{13} C in the Ganga (Hooghly) River estuary, India: Evidence of DIC generation via organic carbon degradation and carbonate dissolution. *Geochimica Cosmochimica Acta*, 165, 226–248.
- Sarkar, A., Chakraborty, P., and Nagender Nath, B. (2016). Distribution and nature of sedimentary organic matter in a tropical estuary: An indicator of human intervention on environment. *Maine pollution Bulletin*, 102, 176–186.
- Sarma, V., Kumar, M. D., & George, M. (1998). The central and eastern Arabian Sea as a perennial source of atmospheric carbon dioxide. *Tellus B: Chemical and Physical Meteorology*, 50(2), 179–184.
- Sarma, V. V., Kumar, M. D., & Manerikar, M. (2001). Emission of carbon dioxide from a tropical estuarine system, Goa, India. *Geophysical Research Letters*, 28(7), 1239–1242.
- Sarma, V. (2003). Monthly variability in surface *p*CO₂ and net air- sea CO₂ flux in the Arabian Sea. *Journal of Geophysical Research: Oceans*, *108*(C8).

- Sarma, V., Gupta, S., Babu, P., Acharya, T., Harikrishnachari, N., Vishnuvardhan, K., et al. (2009). Influence of river discharge on plankton metabolic rates in the tropical monsoon driven Godavari estuary, India. *Estuarine Coastal and Shelf Sciences*, 85, 515–524.
- Sarma, V., Kumar, N., Prasad, V., Venkataramana, V., Appalanaidu, S., Sridevi, B., Acharyya, T. (2011). High CO₂ emissions from the tropical Godavari estuary (India) associated with monsoon river discharges. *Geophysical Research Letters*, 38(8).
- Sarma, V., Krishna, M., Rao, V., Viswanadham, R., Kumar, N., Kumari, T., et al. (2012a). Sources and sinks of CO₂ in the west coast of Bay of Bengal. *Tellus B: Chemical and Physical Meteoroogy*, 64, 10961.
- Sarma, V. V. S. S., Arya, J., Subbaiah, C. V., Naidu, S. A., Gawade, L., Kumar, P. P., et al. (2012b). Stable isotopes of carbon and nitrogen in suspended matter and sediments from the Godavari estuary. *Journal of Oceanography*, 68, 307–319.
- Sarma, V., Krishna, M., Prasad, V., Kumar, B., Naidu, S., Rao, G., et al. (2014). Distribution and sources of particulate organic matter in the Indian monsoonal estuaries during monsoon. *Journal of Geophysical Research Biogeosciences*, 119, 2095–2111.
- Sarmiento, J. L., Hughes, T. M., Stouffer, R. J., & Manabe, S. (1998). Simulated response of the ocean carbon cycle to anthropogenic climate warming. *Nature*, 393(6682), 245–249.
- Savoye, N., Aminot, A., Treguer, P., Fontugne, M., Naulet, N., and Kerouel, R. (2003).
 Dynamics of particulate organic matter δ15N and δ13C during spring phytoplankton blooms in a macrotidal ecosystem (Bay of Seine, France).
 Marine Ecology Progress Series, 255, 27–41.
- Schlesinger, W. H. (1991). Biogeochemistry: An analysis of global change. ACADEMIC PRESS (Second edition).
- Seitzinger, S., Kroeze, C., Bouwman, A., Caraco, N., Dentener, F., and Styles, R. (2002). Global patterns of dissolved inorganic and particulate nitrogen inputs

to coastal systems: Recent conditions and future projections. *Estuaries*, 25, 640–655.

- Servais, P., Billen, G., and Hascoet, M.C. (1987). Determination of the biodegradable fraction of dissolved organic matter in waters. *Water Research*, 21,445 50.
- Shen, J. (2013). Spatiotemporal variations of Chinese lakes and their driving mechanisms since the Last Glacial Maximum: A review and synthesis of lacustrine sediment archives. *Chinese Science Bulletin*, 1–15.
- Shynu, R., Purnachandra Rao, V., Sarma, V. V. S. S., Kessarkar, P. M., and Mani Murali, R. (2015). Sources and fate of organic matter in suspended and bottom sediments of the Mandovi and Zuari estuaries, western India. *Current Science*, 108, 226–238.
- Siuda, W., & Chrost, R. J. (2006). Urea and ureolytic activity in lakes of different trophic status. *Polish Journal of Microbiology*, *55*(3), 211–225.
- Smith, B.N., and Epstein, S. (1971). Two categories of ¹³C/¹²C ratios for higher plants. *Plant Physiology*, 47, 380 - 384.
- Srichandan, S., Kim, J. Y., Bhadury, P., Barik, S. K., Muduli, P. R., Samal, R. N., et al. (2015a). Spatiotemporal distribution and composition of phytoplankton assemblages in a coastal tropical lagoon: Chilika, India. *Environmental Monitoring Assessment*, 187, 47.
- Srichandan, S., Kim, J. Y., Kumar, A., Mishra, D. R., Bhadury, P., Muduli, P. R., et al. (2015b). Interannual and cyclone-driven variability in phytoplankton communities of a tropical coastal lagoon. *Marine Pollution Bulletin*, 101, 39– 52.
- Srinivas, B., Sarin, M., and Sarma, V. (2011). Atmospheric dry deposition of inorganic and organic nitrogen to the Bay of Bengal: impact of continental outflow. *Marine Chemistry*, 127, 170–179.
- Strickland, J.D.H., Parsons, T.R., 1984. A Practical Handbook of Seawater Analysis, third ed. Queen's Printer. Fisheries Research Board of Canada Bulletin, Ottawa, 167.

- Subramaniam, A., and Carpenter, E. (1994). An empirically derived protocol for the detection of blooms of the marine cyanobacterium Trichodesmium using CZCS imagery. *International Journal Remote Sensing*, 15, 1559–1569.
- Sun, W., Shen, J., Zhang, E., Hasebe, N., Kashiwaya, K., Chen, R., et al. (2016). Stable nitrogen isotope record of lacustrine sediments in Lake Onuma (Northern Japan) indicates regional hydrological variability during the past four centuries. *Quaternary International*, 397, 307–316.
- Switzer, T. (2008). Urea loading from a spring storm—Knysna estuary, South Africa. *Harmful Algae*, 8(1), 66–69.
- Tait, D. R., Maher, D. T., Macklin, P. A., and Santos, I. R. (2016). Mangrove pore water exchange across a latitudinal gradient, *Geophysical Research Letter*, 43, 3334–3341.
- Tesi, T., Miserocchi, S., Goni, M. e a1, Langone, L., Boldrin, A., and Turchetto, M. (2007). Organic matter origin and distribution in suspended particulate materials and surficial sediments from the western Adriatic Sea (Italy). *Estuarine Coastal and Shelf Sciences*, 73, 431–446.
- Thomas, M. K., Kremer, C. T., Klausmeier, C. A., and Litchman, E. (2012). A global pattern of thermal adaptation in marine phytoplankton. *Science*, 338, 1085–1088.
- Thornton, S., and McManus, J. (1994). Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary, Scotland. *Estuarine Coastal and Shelf Sciences*, 38, 219–233.
- Tortell, P. D., DiTullio, G. R., Sigman, D. M., and Morel, F. M. (2002). CO₂ effects on taxonomic composition and nutrient utilization in an equatorial Pacific phytoplankton assemblage. *Marine Ecology Progress Series*, 236, 37–43.
- Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Knoll, L. B. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, 54(6part2), 2298–2314.

- Unnikrishnan, W., Shahul, H., Velayudhan, K., Manjula, P., and Vasu, K. (2009). Estimation of sedimentation rate in Chilika lake, Orissa using environmental 210 Pb isotope systematics. *Journal of Applied. Geochemistry*, 11, 102–110.
- Ussiri, D. and Lal, R. Carbon Sequestration for Climate Change Mitigation and Adaptation, Springer International Publishing AG 2017.
- Violaki, K., Zarbas, P., and Mihalopoulos, N. (2010). Long-term measurements of dissolved organic nitrogen (DON) in atmospheric deposition in the Eastern Mediterranean: Fluxes, origin and biogeochemical implications. *Marine Chemistry*, 120, 179–186.
- Vitousek, P. M., Mooney, H. A., Lubchenco, J., & Melillo, J. M. (1997). Human domination of Earth's ecosystems. *Science*, 277(5325), 494–499.
- Vizzini, S., Savona, B., Caruso, M., Savona, A., & Mazzola, A. (2005). Analysis of stable carbon and nitrogen isotopes as a tool for assessing the environmental impact of aquaculture: a case study from the western Mediterranean. *Aquaculture International*, 13(1), 157–165.
- Weiss, R. (1970). The solubility of nitrogen, oxygen and argon in water and seawater. (Elsevier), 721–735.
- Weiss, R. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry*, 2(3), 203–215.
- Wilber, D. H. (1992). Associations between freshwater inflows and oyster productivity in Apalachicola Bay, Florida. *Estuarine Coastal and Shelf Sciences*, 35, 179– 190.
- Wilkerson, F. P., Dugdale, R. C., Hogue, V. E., and Marchi, A. (2006). Phytoplankton blooms and nitrogen productivity in San Francisco Bay. *Estuaries and Coasts*, 29, 401–416.
- Xu, J., Glibert, P. M., Liu, H., Yin, K., Yuan, X., Chen, M., & Harrison, P. J. (2012).
 Nitrogen sources and rates of phytoplankton uptake in different regions of Hong Kong waters in summer. *Estuaries and Coasts*, 35(2), 559–571.
- Yamamuro, M. (2000). Chemical tracers of sediment organic matter origins in two coastal lagoons. *Journal of Marine System*, 26, 127–134.

- Ye, F., Ni, Z., Xie, L., Wei, G., and Jia, G. (2015). Isotopic evidence for the turnover of biological reactive nitrogen in the Pearl River Estuary, south China. *Journal* of Geophysical Research, Biogeosciences 120, 661–672.
- Ying-Xin, X., Xiong, Z.-Q., Guang-Xi, X., Guo-Qing, S., and Zhao-Liang, Z. (2007). Assessment of Nitrogen Pollutant Sources in Surface Waters of Taihu Lake Region11Project supported by the State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences (No. 035109) and the National Natural Science Foundation of China (No. 30390080). *Pedosphere*, 17, 200–208.
- Zak, D. R., Pregitzer, K. S., Kubiske, M. E., & Burton, A. J. (2011). Forest productivity under elevated CO2 and O3: positive feedbacks to soil N cycling sustain decade- long net primary productivity enhancement by CO2. *Ecology Letters*, 14(12), 1220–1226.
- Zhai, W., Dai, M., Cai, W.-J., Wang, Y., and Wang, Z. (2005). High partial pressure of CO 2 and its maintaining mechanism in a subtropical estuary: the Pearl River estuary, China. *Marine Chemistry*, 93, 21–32
- Zhang J., Yu, Z.G., Liu, S.M., Xu, H., Wen, Q.B., and Shao B. (1997). Dominance of terrigenous particulate organic carbon in the high-turbidity Shuangtaizihe estuary, Chemical Geology, 138, 211 - 219.
- Zeebe, R. E., Zachos, J. C., Caldeira, K., & Tyrrell, T. (2008). Carbon emissions and acidification. *SCIENCE-NEW YORK THEN WASHINGTON-*, *321*(5885), 51.

Estuarine, Coastal and Shelf Science xxx (2018) 1-11

ELSEVIER

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science



journal homepage: www.elsevier.com/locate/ecss

Spatial variation of nitrogen uptake rates in the largest brackish water lagoon of Asia (Chilika, India)

Rupa Mukherjee^a, Sanjeev Kumar^{a,*}, Pradipta R. Muduli^b

^a Physical Research Laboratory, Navrangpura, Ahmedabad, 380009, India

^b Wetland Research and Training Centre, Chilika Development Authority, Odisha, 752030, India

ARTICLE INFO

Article history: Received 9 June 2017 Received in revised form 6 January 2018 Accepted 13 January 2018 Available online xxx

Keywords: Coastal lagoon Nitrogen uptake Organic matter origin Eutrophication

ABSTRACT

Inland and coastal water bodies around the world are susceptible to eutrophication due to inputs of anthropogenic nutrients, such as nitrogen (N) and phosphorus (P). Studies related to quantification of uptake rates of these nutrients and the factors governing these rates are limited in tropical aquatic systems, leading to inadequate understanding of N and carbon (C) cycling in these environments. Here, we report the rates of dissolved inorganic N (DIN) uptake and N₂ fixation along with N isotopic composition of particulate organic matter ($\delta^{15}N_{POM}$) in Asia's largest brackish water lagoon (Chilika, India). The experiments were carried out at sixteen different locations in the lagoon where NO₃ and NH⁴ uptake rates varied from 0.004 to 1.42 µmol N L⁻¹h⁻¹ (average ~ 0.51 ± 0.51 µmol N L⁻¹h⁻¹) and 0.19 -1.76 µmol N L⁻¹h⁻¹ (average ~ 1.11 ± 0.43 µmol N L⁻¹h⁻¹), respectively. In general, NH⁴ was preferred substrate in the lagoon showed diazotrophic activity as evidenced by considerable N₂ fixation rates at majority of stations. Preliminary calculations of the lagoon-wide N budgeting indicate N₂ fixation and atmospheric deposition to be significant sources of new N to the lagoon. $\delta^{15}N_{POM}$ in the lagoon ranged from 1.34 to 8.31‰ (average ~ 3.99 ± 1.68‰) indicating contributions from marine and terrestrial sources along with N₂ fixation to the organic matter pool.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Coastal lagoons with shallow depths and large freshwater inflow are susceptible to nutrient enrichment from surface runoff, groundwater discharge, and atmospheric inputs (Del Amo et al., 1997; Aguilera et al., 2001; Paerl et al., 2002; Kennish and Paerl, 2010). Hence, the temporal and spatial variability of their water quality depend upon the relative strength of inputs from terrestrial and atmospheric sources along with tidal flows (Ganguly et al., 2015; Patra et al., 2016; Barik et al., 2017). Over the last few decades, an enhancement in anthropogenic inputs of nitrogen (N) and phosphorus (P) has led to acceleration in eutrophication related problems in estuarine and lagoon environments (Fisher et al., 1995; Kinney and Roman, 1998; Cloern, 2001). Lagoons are well documented as significant contributor of inorganic carbon (C) to the atmosphere and retain high *p*CO₂ due to rapid increase in heterotrophic respiration of organic C (Frankignoulle et al., 1998; Cai et al.,

* Corresponding author. E-mail address: sanjeev@prl.res.in (S. Kumar).

https://doi.org/10.1016/j.ecss.2018.01.012 0272-7714/© 2018 Elsevier Ltd. All rights reserved. 1999; Hanson et al., 2003). Even though lagoons are smaller in size compared to other coastal bodies, they are important sites for terrigenous organic C mineralization (Jansson et al., 2000). Moreover, situated between land and sea, coastal lagoons act as filter retaining inorganic and organic nutrients (Newton et al., 2003; Kozlowsky-Suzuki and Bozelli, 2004). For the above reasons, coastal lagoons have generated considerable research interest after 1970 though limited studies have been reported in peer reviewed literature (Panigrahi et al., 2009).

One of the direct aftermaths of anthropogenic activities impacting estuarine and coastal ecosystems is the excess loading of nutrients along with terrestrial organic matter (Bhavya et al., 2016). These nutrients enter into the estuarine and coastal systems in form of organic and inorganic N and P through rivers and atmosphere, causing biogeochemical imbalance, specifically with respect to N:P stoichiometry, in the estuaries (Galloway et al., 2004). These increased nutrients promote primary productivity in receiving waters causing algal blooms. In shallow productive estuaries or lagoons, reduced water clarity can further cause significant changes in ecosystem structure and functioning such as shifts

from benthic dominated to pelagic dominated primary production (Borum and Sand-Jensen, 1996; Krause-Jensen et al., 2012) and a change towards dominance of planktivorous fish and filter feeders (Cloern, 2001).

Rates of N uptake and their dependence on N and P distribution in tropical water bodies provide an insight into nutrient utilization within the system (Bhavya et al., 2016; Glibert et al., 2016). Similarly, N isotopic composition of suspended particulate organic matter ($\delta^{15}N_{POM}$) in shallow water bodies reflects the influence of N assimilation or organic matter mineralization in the water column as well as sediments. $\delta^{15}N_{POM}$ can provide an insight into the availability and utilization of nutrients along with source identification of organic matter in benthic as well as pelagic environment. N from residential wastewater and agricultural land use is a major source of nutrients to the lagoons (Carpenter et al., 1998; Leavitt et al., 2006; Ying-Xin et al., 2007) and often have distinct isotopic compositions (Savage, 2005; Vander Zanden et al., 2005).

Although significant studies related to C and N cycling have been conducted in coastal systems worldwide, limited studies exist in tropical settings like India (Sarma et al., 2014; Ye et al., 2015; Bardhan et al., 2015; Bhavya et al., 2016; Moynihan et al., 2016). These studies become particularly non-existent with respect to lagoon systems (Muduli et al., 2012, 2013) with limited reports from temperate estuaries (e.g., Middelburg and Nieuwenhuize, 2000; Mulholland et al., 2003; Howarth et al., 2011). The present study focuses on Chilika, Asia's largest brackish water lagoon and a "Ramsar site", located on the east coast of India. Research in Chilika has gained momentum with emphasis on C cycling, environmental parameters monitoring and species identification (Gupta et al., 2008; Panigrahi et al., 2009; Muduli et al., 2012, 2013; Prasad et al., 2014; Srichandan et al., 2015) but no detailed study exists regarding N biogeochemistry of the lagoon. The present study focusses on measuring N uptake rates in the lagoon with the central hypotheses that N₂ fixation is not considerable in this lagoon due to high dissolved inorganic nitrogen (DIN) concentrations and N₂ fixation forms an insignificant portion of the total new N input to the lagoon compared to atmospheric and riverine inputs. The specific goals of the present study were to (a) measure the rates of N uptake in the lagoon, (b) understand the origin of particulate organic matter (POM) using spatial variation in $\delta^{15}N_{POM}$, (c) understand effect of riverine discharge on N uptake rates of the lagoon, (d) decipher role of N₂ fixation and atmospheric N deposition as N sources to the lagoon, and (e) generate a preliminary N assimilation budget for the Chilika.

2. Materials and methods

2.1. Study area

Ecologically, Chilika is a mixture of marine, brackish and freshwater ecosystems with a mean depth of ~2 m (Gupta et al., 2008). For this study, based on topography, the lagoon was classified into four different sectors, viz. southern sector (surface area ~156 km²) connected with the sea through Palur canal, northern sector (surface area ~295 km²) receives the maximum discharge through rivers, outer channel (surface area ~37 km²) connected with the sea, and central sector (surface area ~372 km²), the mixing zone of the northern sector and the outer channel (Gupta et al., 2008; Muduli et al., 2012, Fig. 1). The lagoon suffers wide seasonal and annual changes in salinity, light availability, and nutrient inputs from 52 rivers and rivulets discharging into the lagoon (Barik et al., 2017). The lagoon is separated from the Bay of Bengal (BOB) by a 60 km long sand bar. Direct rainfall on the lagoon surface also makes a significant contribution towards freshwater input into the Chilika (Mohanty et al., 1996). Because of these external inputs, water depth increases by about 0.5–1 m during the southwest monsoon (Mohanty et al., 1996). The lagoon area encounters wind speed ranging from 4.45 to 7.02 ms⁻¹ during wet season and 0.97–3.89 ms⁻¹ during dry season (Gupta et al., 2008).

During winter (November-January), a large portion of this lagoon near Nalabana island remains submerged and acts as a wetland, which also serves as breeding and roosting grounds for thousands of migratory water fowl (Panigrahi et al., 2009, Fig. 1). Chilika lagoon suffered excessive submerged and free floating (e.g. Azolla, Eichhornia, Nymphea, Pistia, Ipomea) weed growth in the past where weeded area escalated from 20 km^2 in 1972 to 685 km^2 in 2000 at a rate of 15 km² per year (Gupta et al., 2008; Panigrahi et al., 2009). Phytoplankton of Chilika consists of a mixture of marine, brackish water and freshwater taxa, mainly represented by four groups of algae: diatoms (Bacillariophyceae), dinoflagellates (Pyrrophyceae and Dinophyceae), blue-green algae (cyanobacteria) and green algae (Chlorophyceae; Srichandan et al., 2015). Except for the northern sector, different ecological sectors of the lagoon were dominated by diatoms, while the northern sector due to its freshwater regime supported the large population of euglenoids (Srichandan et al., 2015).

2.2. Methodology

For the present study, sampling was performed during 21–29th June, 2015 covering a spread of 16 different locations (Fig. 1) representing the south, the central and the northern sectors of the lagoon along with the outer channel. Surface water samples were collected at each location in a 20 L carboy and were brought back to the laboratory situated 🚍 coast of the lagoon (WRTC- Wetland Research and Training centre, Balugaon, Odisha, India). Sample was transferred in 0.5 L acid-washed polycarbonate Nalgene bottles in duplicate for NO_3^- and NH_4^+ uptake rates measurement. These bottles were covered immediately with black cloth to avoid light shock to phytoplankton. Samples were spiked with 99 atom% enriched ¹⁵NH₄Cl and Na¹⁵NO₃ to trace NH⁺₄ and NO⁻₃ uptake rates, respectively. Tracer addition was around 10% of the ambient concentrations. Immediately after the tracer addition, sample bottles were deployed for incubation for 4 h, approximately symmetrical to the local noon. Post-incubation samples were filtered onto precombusted (4 h at 450 °C) 47 mm Whatman GF/F filters and stored for mass spectrometric analysis after drying at 50 °C overnight.

Mass spectrometric analyses of post-incubated samples were performed using a continuous flow stable isotope ratio mass spectrometer (Delta V plus) connected to an elemental analyzer (Flash EA 2000), where ¹⁵N atom% and particulate organic N (PON) content were measured. The uptake rates were calculated as follows (Dugdale and Wilkerson, 1986; Kanda et al., 2003):

$$\text{Uptake rate} \left(\mu \text{mol N } L^{-1} h^{-1} \right) = P \times \mathcal{\Delta} I_p \Big/ \left[T \times \left[(I_0 S_a + I_r S_t) / (S_a + S_t) - I_0 \right] \right]$$

R. Mukherjee et al. / Estuarine, Coastal and Shelf Science xxx (2018) 1-11



Fig. 1. Average NO_3^- (first in the parentheses) and NH_4^+ (second in the parentheses) uptake rates (μ mol N L⁻¹h⁻¹) in the Chilika lagoon. The whole numbers above symbols indicate station numbers.

where P is the amount of particulate N (µmol L⁻¹) in postincubation sample, ΔI_p is the increase in ¹⁵N atom% in particulate N during incubation, S_a and S_t are ambient and added concentrations (in µmol L⁻¹), respectively, I_r and I_0 are ¹⁵N atom% of added tracer and natural ¹⁵N atom%, and T is the incubation time (hours). This equation assumes no formation of nutrient during the incubation, and therefore, rates presented here are representative of potential rates. During the present study, DIN uptake is considered as sum of NO₃ and NH[‡] uptake.

The relative uptakes of NO_3^- and NH_4^+ were also calculated using the relative preference index (McCarthy et al., 1977).

$$RPI_{x} = \left[U_{x}/U_{x} + U_{y}\right] / \left[X/X + Y\right]$$

Where, X and Y are concentrations of NO_3^- and NH_4^+ in µmol L^{-1} , respectively; Ux and Uy represent the corresponding uptake rates in µmol $L^{-1}h^{-1}$.

In order to determine the N₂ fixation rates, experiment was conducted using ${}^{15}N_2$ bubble method (Montoya et al., 1996) using ${}^{15}N_2$ (98 + atom%) tracer gas purchased from Cambridge Isotope Laboratories. For these experiments, water samples were transferred to three 250-ml borosilicate bottles (two lights and one dark). These bottles were filled to the brim and sealed tightly with septum caps to ensure the absence of air bubbles. 0.5 ml of ${}^{15}N_2$ enriched N₂ gas was injected into the sample bottles using a

chromatographic syringe followed by gentle mixing and 3 h of incubation. Post-incubated samples were filtered onto precombusted (at 450 °C) 47-mm Whatman GF/F filters and dried at 50 °C overnight. Ambient concentrations of dissolved N₂ gas were estimated using the gas solubility table of Weiss (1970) and N₂ fixation rates were calculated using the method proposed by Montoya et al. (1996).

For natural isotopic composition of PON, roughly 0.3-0.5 L water samples were filtered onto pre-combusted (4 h at 450 °C) 47 mm GF/F filters. After filtration, samples were dried and analyzed using isotope ratio mass spectrometer (MAT 253) connected to an elemental analyzer (Flash 2000). The variability in PON measurement for duplicate samples was less than 10%. The reproducibility for natural δ^{15} N was less than 0.3‰ (standard used IAEA-N-2, (NH₄)₂SO₄, δ^{15} N = 20.3‰).

Data for water temperature, pH, salinity, and dissolved oxygen during the study period were collected *in situ* using multiparameter water quality sonde (6 Series; DATA-BUOY; YSI, USA). Samples collected for inorganic nutrients, viz. NO₃⁻, NH₄⁺, SiO₄⁴⁻ and dissolved inorganic phosphate (DIP) were filtered through 0.45 µm membrane filter paper (47 mm) and measured by nutrient autoanalyzer (SKALAR SAN++) with an accuracy of ±0.01, ±0.01 and ± 0.02 µmol L⁻¹, respectively following Grashoff et al. (1999). Chlorophyll *a* (Chl *a*) was measured using 90% acetone extraction by UV–VIS spectrophotometer (Thermo Scientific Evolution TM 201) as described in Strickland and Parsons (1984).

4

R. Mukherjee et al. / Estuarine, Coastal and Shelf Science xxx (2018) 1-11

Table 1					
Nutrients and	physical	parameters	during	sampling	period.

Stations	WT (°C)	Secchi Depth (m)	Depth (m)	pН	Salinity	DO (%)	NO_3^- (µmol L ⁻¹)	SiO_4^{4-} (µmol L ⁻¹)	PO_4^{3-} (µmol L ⁻¹)	$\mathrm{NH_4^+}~(\mathrm{\mu mol}~\mathrm{L^{-1}})$	Chl a (µg L ⁻¹)
1	29.50	0.27	1.11	8.36	5.62	106.16	6.05	90.00	1.41	7.59	25.00
2	28.53	0.22	1.02	7.87	15.08	88.26	5.96	39.51	0.99	5.82	32.98
3	29.00	0.28	0.98	8.05	0.10	83.54	6.17	37.51	1.15	6.38	3.96
4	30.00	0.27	1.43	8.31	8.62	83.81	7.01	43.38	0.94	6.48	24.40
5	28.90	0.52	0.90	8.16	0.26	76.25	7.96	37.95	0.86	5.50	8.21
6	28.50	0.86	1.52	7.91	12.13	81.11	7.18	53.20	0.90	6.13	7.02
7	28.00	0.85	1.40	8.40	4.52	88.31	2.99	60.69	0.79	8.95	3.34
8	29.00	0.48	1.41	7.88	7.88	80.08	6.58	53.47	0.83	6.27	4.47
9	28.31	1.07	1.85	8.50	16.16	78.99	2.41	45.92	0.83	5.89	4.87
10	28.50	0.95	1.80	8.20	18.23	88.44	2.45	54.68	0.91	5.37	6.91
11	30.10	1.08	2.28	8.30	7.57	88.79	4.67	66.03	1.15	6.31	5.94
12	30.00	1.50	2.95	8.69	12.60	101.92	4.19	69.24	0.72	5.84	3.34
13	28.20	1.02	2.45	8.30	12.03	90.84	3.37	66.89	0.66	6.56	19.25
14	27.98	1.29	2.40	8.30	12.93	89.29	3.61	67.63	0.52	5.13	4.19
15	26.00	0.32	1.70	8.12	14.34	80.68	10.55	32.60	0.79	6.38	24.24
16	28.00	0.30	3.10	8.04	14.91	87.16	11.18	30.37	1.00	6.36	5.05

3. Results

3.1. Physical and chemical parameters

In general, the weather condition during sampling was partially cloudy and rainy due to pre-monsoon swells. The pH of the lagoon varied from 7.87 (Station 2 - northern sector) to 8.69 (Station 12 - southern sector; Table 1). Surface salinity of the lagoon ranged from 0.10 (Station 3 - northern sector) to 18.23 (station 10 - central sector; Table 1). Although relatively higher salinity was observed at locations in the outer channel, no coherent pattern was observed throughout the lagoon, possibly due to lack of mixing of newly rained freshwater with the saline water during sampling period. Water temperature of the lagoon varied from 26 °C to 30.1 °C during the time of sampling. Dissolved oxygen saturation (% DO) ranged between 76.25 and 106.16%. Chl *a* showed a large variation in the lagoon with a maximum at station 2 in the northern sector (32.98 μ g L⁻¹) and minimum at station 7 (3.34 μ g L⁻¹) in the central sector (Table 1).

3.2. Nutrients

 NO_3^- concentration in the lagoon varied from 2.41 to 11.18 $\mu mol \, L^{-1}$ (average ~ 5.77 \pm 2.65 $\mu mol \, L^{-1}$) with the maximum at station 16 in the outer channel (Table 1). Average NH_4^+ concentration in the lagoon was comparable to NO_3^- (average ~ 6.31 \pm 0.91 $\mu mol \, L^{-1}$) with the maximum concentration at station 7 of the central sector, possibly due to nearness to human settlement. Silicate varied from 30.37 to 90.00 $\mu mol \, L^{-1}$ with a maximum at station 1 in the northern sector. Phosphate concentrations ranged from 0.52 to 1.41 $\mu mol \, L^{-1}$ with the maximum at station 1 (Table 1).

3.3. NO_3^- and NH_4^+ uptake rates

 NO_3^- uptake rates in the Chilika ranged from 0.004 to $1.42~\mu mol~N~L^{-1}h^{-1}$ with an average of $0.51~\pm~0.51~\mu mol~N~L^{-1}~h^{-1}$, whereas NH_4^+ uptake rates varied from 0.19 to $1.76~\mu mol~N~L^{-1}~h^{-1}$ with an average of $1.11~\pm~0.43~\mu mol~N~L^{-1}~h^{-1}$ (Fig. 1). The highest NO_3^- and NH_4^+ uptake rates among the sixteen stations were observed at station 1 in the northern sector; whereas the lowest rates were observed at Station 8 in the central sector (Fig. 1). On an average, the NH_4^+ uptake rate in the lagoon was twice compared to that of NO_3^- uptake rate.

Both NO₃ (average ~ 1.24 \pm 0.30 µmol N L⁻¹h⁻¹) and NH₄⁺ (average ~ 1.59 \pm 0.19 µmol N L⁻¹h⁻¹) uptake rates were the highest

in the northern sector. In the central sector, the average NO_3^- and NH_4^+ uptake rates were $0.34 \pm 0.42 \,\mu mol \, N$ $L^{-1}h^{-1}$ and $0.97 \pm 0.47 \,\mu\text{mol}$ N L⁻¹h⁻¹, respectively; whereas for the southern sector values were $0.34\pm0.41\,\mu mol\,N~L^{-1}h^{-1}$ for NO_3^- and $1.01 \pm 0.38 \,\mu\text{mol}\,\text{N}\,\text{L}^{-1}\text{h}^{-1}$ for NH₄⁺. In the outer channel area, NO_3^- and NH_4^+ uptake rates were $0.33 \pm 0.39 \,\mu\text{mol}\,N \,L^{-1}h^{-1}$ and $1.09 \pm 0.35 \,\mu\text{mol N}$ L⁻¹h⁻¹, respectively. Average total DIN $(NO_3^- + NH_4^+)$ uptake rates in the northern sector of the lagoon was the highest $(2.83 \,\mu mol \, N \, L^{-1}h^{-1})$ followed by the outer channel (1.42 μmol N $L^{-1}h^{-1}$), the southern sector (1.35 μmol N $L^{-1}h^{-1}$) and the central sector (1.30 μ mol NL⁻¹h⁻¹). DIN uptake rates during the present study did not show significant correlation with salinity $(R^2 = 0.08; p = 0.28; Fig. 2a)$ and pH $(R^2 = 0.001; p = 0.90; Fig. 2b)$, whereas it was significant with Chl *a* $(R^2 = 0.39; p = 0.01; Fig. 2c)$. This significant relationship between DIN uptake and Chl a was primarily due to significant NO_3^- uptake - chl *a* relationship $(R^2 = 0.51; p = 0.002)$, which was insignificant for NH⁺₄ uptake - Chl $a (R^2 = 0.15; p = 0.14).$

3.4. N₂ fixation rates

Despite high DIN concentrations in the lagoon, considerable N₂ fixation rates were observed (0.02–1.99 nmol N L⁻¹h⁻¹; Fig. 3). The highest rate was observed at station 2 (northern sector) and the lowest at station 6 (central sector). Among the different sectors of the lagoon, average N₂ fixation rates were the highest in the northern sector (0.89 nmol N L⁻¹h⁻¹), followed by outer channel (0.56 nmol N L⁻¹h⁻¹), central sector (0.34 nmol N L⁻¹h⁻¹), and southern sector (0.31 nmol N L⁻¹h⁻¹).

3.5. Nitrogen isotopic composition of particulate organic matter ($\delta^{15} N_{POM}$)

 $\delta^{15} N_{POM}$ in the Chilika varied from 1.34‰ at station 11 in the southern sector to a maximum of 8.31‰ at station 16 near the outer channel with an average of ~3.99 \pm 1.68‰. The PON concentration in the lagoon ranged from 4.02 μ mol L⁻¹ (station 12 - southern sector) to 32.29 μ mol L⁻¹ (station 2- northern sector) with an average of ~11.36 \pm 7.28 μ mol L⁻¹ (Fig. 4).

Among the four sectors of the lagoon, average $\delta^{15}N_{POM}$ was the highest in the outer channel area (~6.91 \pm 1.98‰) and PON was the highest in the northern sector (~19.80 \pm 11.06 μ mol L^{-1}). In the rest of the sectors, $\delta^{15}N_{POM}$ were similar (northern ~3.54 \pm 0.74‰; southern ~ 3.01 \pm 1.76‰, and central ~ 3.91 \pm 1.04‰). Average PON concentration in the central sector was ~10.78 \pm 5.58 μ mol L^{-1} , whereas in the outer channel it was ~9.05 \pm 6.95 μ mol L^{-1} .

R. Mukherjee et al. / Estuarine, Coastal and Shelf Science xxx (2018) 1-11



Fig. 2. Relationships of DIN uptake rates with (a) salinity, (b) pH, and (c) Chl a in the lagoon.



Fig. 3. Average N_2 fixation rates (nmol N $L^{-1}h^{-1}$) at different locations within the lagoon. ND indicate absence of measurable N_2 fixation. The whole numbers above symbols indicate the station numbers.

southern sector had the lowest PON concentration (~7.21 \pm 2.58 $\mu mol \ L^{-1}$).

4. Discussion

Chilika lagoon is an example of N-replete environment with poorly understood N biogeochemistry (Ganguly et al., 2015). Carbon cycling has been studied in the lagoon with respect to dissolved inorganic and organic C, CO₂ flux in different seasons (Gupta et al., 2008; Muduli et al., 2012) along with net primary productivity (Ganguly et al., 2015). Apart from the above topics, there is a fair understanding of temporal variability in phytoplankton species composition, suspended particulate matter and nutrient concentrations in the lagoon (Srichandan et al., 2015; Ganguly et al., 2015; Patra et al., 2016; Barik et al., 2017). However, no such well documented studies exist for N cycling in the lagoon so far. Data are lacking on N transformation rates in this large lagoon leading to inadequate knowledge of the fate of nutrients and their effect on

Please cite this article in press as: Mukherjee, R., et al., Spatial variation of nitrogen uptake rates in the largest brackish water lagoon of Asia (Chilika, India), Estuarine, Coastal and Shelf Science (2018), https://doi.org/10.1016/j.ecss.2018.01.012

5

R. Mukherjee et al. / Estuarine, Coastal and Shelf Science xxx (2018) 1-11



Fig. 4. Spatial distribution of $\delta^{15}N_{POM}$ (%; first in the parentheses) and suspended particulate organic nitrogen concentrations (µmolN L⁻¹; second in the parentheses) within the lagoon. The whole numbers above symbols indicate the station numbers.

overall ecological health of the lagoon. Below we discuss different aspects of N assimilation and origin of POM based on results from the present study.

4.1. DIN uptake in the Chilika

Our results suggest that NO₃⁻ and NH⁴₄ uptake rates in the Chilika lagoon are relatively higher than the rates observed in many well studied large aquatic ecosystems of the world (e.g., Gu et al., 1997; Gardner et al., 2004; Kumar et al., 2008). The average rates observed in Chilika are approximately twice than that observed in the Cochin estuary (NO₃⁻: 0.20 μ mol L⁻¹h⁻¹; NH⁴₄: 0.59 μ mol L⁻¹h⁻¹), a tropical eutrophic estuary located in the same region (Bhavya et al., 2016).

f-ratios calculated by dividing NO₃⁻ uptake with the total DIN (NO₃⁻ + NH₄⁺) uptake rates suggest a general preference for NH₄⁺ at majority of locations in this nutrient enriched system (Fig. 5). Relative preference index (RPI), a useful parameter for measuring N sufficiency of the environment (McCarthy et al., 1977), was also calculated for this study. RPI> 1 was found for NH₄⁺ at majority of the stations which also reflects general preference for NH₄⁺ rather than NO₃⁻ in the lagoon (Fig. 5). During the present study, RPI > 1 for NO₃⁻ was found at a few stations (northern: 1 and southern: 14; Fig. 5). The *f*-ratio was also relatively higher at these locations. The higher preference for NO₃⁻ at these stations may be because of NO₃⁻ protists phytoplankton, however, we don't have species data for that particular period to strongly conclude the same.

case of various aquatic autotrophs (algae, bryophytes, and macrophytes) and heterotrophs (bacteria and fungi; Pastor et al., 2013). Relative preference for NH‡ has been observed in oligotrophic lagoons and streams (Dodds et al., 1991; Simon et al., 2005; Kumar et al., 2008; Martí et al., 2009; Gibson and O'Reilly, 2012; Gibson et al., 2015) as well as eutrophic estuaries (Bhavya et al., 2016). This pattern has also been reported from marine systems (e.g. Sambrotto, 2001; Kumar et al., 2010).

The preference for NH_4^+ is due to lower energy requirement by the cell as NH⁴ is more easily transported across the cell membrane compared to NO₃ (Glibert et al., 2016). Delayed uptake of NO₃ relative to that of NH⁺₄ occurred in some enclosure studies where 10 μ mol L⁻¹ NH₄⁺ resulted in termination of NO₃⁻ uptake by diatomdominated assemblages, whereas subsequent depletion of NH₄⁺ concentrations to $<4 \mu mol L^{-1}$ allowed acceleration of NO₃⁻ uptake and diatom growth (Wilkerson et al., 2006; Parker et al., 2012). Another reason of higher NH_4^+ over NO_3^- uptake could be species composition such as microalgae which prefers NH₄⁺ and have capacity for excess uptake over growth demand (Glibert et al., 1982; Rees et al., 1995). Although NH_4^+ is a preferred substrate for most of the phytoplankton, elevated NH⁺₄ (roughly several tens to hundreds of μ mol L⁻¹) can suppress the total N uptake and growth of some species (Dagenais-Bellefeuille and Morse, 2013; Glibert et al., 2014). Large diatoms prefer NO_3^- even though NH_4^+ is available at levels in excess of $10 \,\mu mol \, L^{-1}$ in cool nutrient-rich environments $(\text{Temp} < 20 \,^{\circ}\text{C} \text{ and } \text{NO}_{3}^{-} > 25 \,\mu\text{mol L}^{-1}; \text{ Maestrini et al., } 1982;$ Probyn, 1985; Lomas and Glibert, 1999a, 1999b).

Preferential assimilation of NH₄⁺ over NO₃⁻ has been reported in

Chilika being a brackish water system undergoes changes in

R. Mukherjee et al. / Estuarine, Coastal and Shelf Science xxx (2018) 1-11



Fig. 5. *f*-ratio (first in the parentheses), RPI_{N03-} (second in the parentheses), and RPI_{NH4+} (third in the parentheses) at different locations in the Chilika lagoon. The whole numbers above symbols indicate the station numbers.

salinity and pH, however these parameters were not significant in regulating DIN uptake rates of the system (Fig. 2). Chl *a* increased significantly with NO_3^- uptake but not with NH_4^+ uptake indicating influence of biomass on NO_3^- uptake.

The turnover times of NO_3^- and NH_4^+ pool in the lagoon, calculated by dividing the nutrient concentrations with the respective uptake rates, varied from 4.10 h (station 14- southern sector) to ~1700 h (station 8-central sector) for NO_{3}^{-} , whereas it varied from 3.90 h (station 3-northern sector) to 32.31 h (station 8- central sector) for NH_4^+ (Fig. 6). Lower turnover time of the DIN pool at majority of locations indicates that the available nutrient pool in the lagoon is assimilated and recycled fast, underscoring its dynamic nature. Similar trends in turnover time were observed in a tropical eutrophic estuary (Bhavya et al., 2016). Relatively higher turnover time at station 8 is due to relatively higher nutrient concentration and the lowest uptake rates (Table 1 and Fig. 1). The Chl a concentration at this location was also one of the lowest (4.47 μ g L⁻¹; Table 1). These observations are counterintuitive as N uptake rates at this location are expected to be higher because this particular station is located very close to the Nalabana bird sanctuary (Fig. 1), which is feeding and resting ground for thousands of migratory birds during winter. This makes the island highly productive as it experiences high nutrients (N, P and potassium) load due to guano deposition from birds enhancing the supply of nutrients to this particular site (Panigrahi et al., 2009).

Our results indicate significantly higher DIN uptake rate for the northern sector compared to other sectors (ANOVA, p = 0.03; Fig. 1). This may result from prominent mixing in the northern

sector due to high freshwater discharge from the surrounding rivers (Barik et al., 2017). Bacterial respiration was high in the northern sector as well (Muduli et al., 2012). High bacterial respiration along with high NO₃⁻ concentration, especially in the northern sector, leads to organic matter decomposition and hence lowering of the pH value. High N, low pH and low oxygen saturation are signatures of nitrification (Frankignoulle et al., 1996), however, nitrification in the lagoon was negligible (<0.4%) with 84.24 ± 62.97 nmol N L⁻¹h⁻¹ during the low flow period and four fold less during the high flow period (24.38 ± 34.92 nmol N L⁻¹h⁻¹; Muduli et al., 2012).

4.2. N₂ fixation in the Chilika

To account for the diazotrophic activity, N₂ fixation rates were measured in the lagoon. N₂ fixation rates have been observed to be low in high DIN environment (>1 µmol L⁻¹), which suppresses the nitrogenase activity (Subramaniam and Carpenter, 1994; Capone et al., 1997; Mulholland and Capone, 2009). During the present study, despite high DIN concentrations, measurable N₂ fixation rates were observed with no significant correlation with DIN concentrations (R² = 0.003; p = 0.85) or DIN uptake rates (R² = 0.25; p > 0.05; Fig. 7a and b). Station 2 in the northern sector showed particularly high N₂ fixation rate (~1.99 nmol N L⁻¹ h⁻¹) possibly due to active presence of N₂ fixing species at this location. In a recent study, the availability of N₂ fixing bacteria in sediments of Chilika lagoon has been reported (Behera et al., 2017). This study also highlights the dominance of N₂ fixing bacteria in the

R. Mukherjee et al. / Estuarine, Coastal and Shelf Science xxx (2018) 1-11



Fig. 6. Turnover time (hours) for NO₃⁻ (first in the parentheses) and NH₄⁺ (second in the parentheses) at different locations in the Chilika lagoon. The whole numbers above symbols indicate the station numbers.



Fig. 7. Relationships of N₂ fixation rates with (a) DIN concentrations, and (b) DIN uptake rates.

rhizosphere sediment of the reed *Phragmities karke*, which is found in large parts of the northern sector. Since northern sector is the shallowest part of the lagoon, there could be possibility of such bacterial community in the water column due to sediment churning (Barik et al., 2017), enabling higher N₂ fixation. Similar to observations during the present study, considerable N₂ fixation rates have also been observed in the Cochin estuary (0.59–1.3 nmol N $L^{-1}h^{-1}$) despite very high DIN concentrations (Bhavya et al., 2016).

4.3. Annual nitrogen fixation

Since data was insufficient to establish different pathways of the N cycling in this lagoon, we attempted to construct an annual N fixation budget using NO_3 and NH_4^+ uptake rates observed during the present study. The estimation was carried out sector-wise by assuming respective average surface uptake rates to be uniform for the entire volume of the photic zone. The photic zone was obtained

by multiplying the respective surface area with euphotic depth, which was calculated using measured secchi disk depth (d) at each station. The extinction coefficient (k) at each station was 1.7/ d (French et al., 1982), which was used to calculate euphotic depth as 4.61/k (Keller, 1988). At some areas of the Chilika, particularly in the southern sector, light is known to penetrate to the bottom. Therefore, at those locations where calculated euphotic depth was greater than the station depth, the station depth was considered as the euphotic depth. The total annual N fixation in the lagoon using this method was around 150 Gg which included NO_3^- uptake (34.83 Gg y⁻¹), NH^{\pm} uptake (114.52 Gg y⁻¹) and N₂ fixation (0.06 Gg y⁻¹). Annual nitrogen fixation was the highest in the central sector followed by the northern, southern and outer channel (Fig. 8). The highest N fixation in the central sector was primarily due to relatively higher surface area compared to all other sectors. Results also indicate that along with NO₃ and NH^{\pm} uptake, N₂ fixation contributed considerably towards the lagoon's N budget on an annual time scale.

4.4. Sources of nitrogen in the Chilika

Based on the present study and atmospheric N deposition data (Srinivas et al., 2011), external N sources to the lagoon were investigated. According to the methodology adopted for the annual budget estimation, new N introduced via N₂ fixation to the lagoon is $\sim 0.06 \text{ Gg y}^{-1}$. Nitrogen introduced to the lagoon through atmospheric deposition was also calculated based on the BOB DIN deposition data (Srinivas et al., 2011). For the calculation purpose, dry deposition flux of DIN over Chilika was assumed to be the same as BOB $(2-83 \,\mu mol \, m^{-2} d^{-1})$ with an average of $27 \pm 20 \,\mu\text{mol}\,\text{m}^{-2}\text{d}^{-1}$) due to their close proximity. Taking surface area of the Chilika into account and assuming uniform deposition rate of $27 \,\mu\text{mol}\,\text{m}^{-2}\,\text{d}^{-1}$ throughout the year, total DIN deposition over the lagoon is around 0.12 Gg y⁻¹. Similarly, N introduced to the lagoon through riverine discharge was calculated based on data from Patra et al. (2016). Using average influx of DIN (Patra et al., pre-monsoon $(43.77 \text{ mol d}^{-1})$, 2016) during monsoon $(2714.93 \text{ mol d}^{-1})$ and post-monsoon $(269.86 \text{ mol d}^{-1})$, annual input of DIN to the lagoon through rivers draining into the Chilika is around 0.005 Gg y⁻¹. Similarly, average dissolved organic nitrogen influx to the lagoon is around 0.004 Gg y^{-1} .

Based on above calculations, atmospheric deposition and N_2 fixation were major contributors as external N sources to the Chilika followed by riverine inputs. Better constraints on the budgets





of N sources to the lagoon, however, will require high resolution sampling. Overall, measurable N_2 fixation rates and its contribution as new N source to the lagoon disproves our central hypotheses, which assumed its smaller role in light of high DIN concentrations within the lagoon.

4.5. Origin of particulate organic matter

Movement of N from dissolved pool to the particulate phase is linked via formation and transformation (i.e., mineralization) of POM. Therefore, it is imperative to examine the origin and transformation of suspended POM using its N isotopic composition. $\delta^{15}N_{POM}$ in the Chilika showed a wide spatial variability (Fig. 4). Our data for all the surface samples during the study period showed average $\delta^{15}N_{POM}$ of 3.99 ± 1.68‰ (mean ± SD) and PON concentration of $11.36 \pm 7.78 \,\mu\text{mol}\,\text{L}^{-1}$ (mean \pm SD) which fall within the range of northern Indian estuaries reported earlier (Sarma et al., 2014). Station 16 in the outer channel area, which is very close to the ocean, showed $\delta^{15}N_{POM}$ of 8.31‰, which falls within the range of marine values (7–10%; Peters et al., 1978) showing dominance of marine phytoplankton at the lagoon-ocean interface. In the northern sector, which is largely influenced by terrestrial runoff, $\delta^{15}N_{POM}$ ranged between 2.80 and 4.28‰. Central sector $\delta^{15}N_{POM}$ varied from 2.04 to 5.47‰, whereas two southern sector stations (13 and 14) also exhibited similar $\delta^{15}N_{POM}$ (4.52 and 4.54‰, respectively). It appears that $\delta^{15}N_{\text{POM}}$ at these locations have been influenced by terrestrial inputs. Terrestrial particulate matter brought in by rivers to the lagoon may have lowered $\delta^{15}N_{POM}$ of the lagoon as naturally occurring land derived materials have low $\delta^{15}N_{POM}$ (mean of 2.5% for terrestrial organic matter (Sweeney et al., 1978); and 1.5‰ for terrestrial detrital component (Mariotti et al., 1984)) compared to marine POM (Kumar et al., 2004). Station 11 and 12 in the southern sector showed $\delta^{15}N_{POM}$ less than 2‰, which may have influence of N₂ fixation. The wide variation of $\delta^{15}N_{POM}$ in the Chilika lagoon (1.34‰–8.31‰) suggests variable sources of organic matter indicating mixture of marine and terrestrial pools along with N₂ fixation as possible contributors.

5. Conclusion

This study reports the rates of DIN (NO_3^- and NH_4^+) uptake and N_2 fixation along with $\delta^{15}N_{POM}$ in the Chilika lagoon. Our results indicate significantly higher DIN uptake rates along with high PON concentrations in the northern part of the lagoon compared to other parts possibly due to riverine inputs and mixing. Absence of correlations between N uptake rates with pH and salinity suggest limited role of these parameters in regulating N uptake rates in the lagoon. Like many other aquatic systems, NH⁺₄ was preferred substrate for the phytoplankton in the Chilika as well. Despite high NO_3^- and NH_4^+ concentrations, lagoon showed considerable N₂ fixation rates indicating diazotrophic activity. Although the lagoon is surrounded by many rivers and rivulets, atmospheric deposition and N₂ fixation are major contributors to the N pool followed by riverine inputs, which disproved central hypotheses of the study. However, for precise budgeting of N sources, high resolution sampling in the lagoon is needed. Wide variation of $\delta^{15}N_{POM}$ in the lagoon (1.34‰-8.31‰) suggests variable sources of organic matter indicating marine and terrestrial components along with N₂ fixation.

Acknowledgement

This research was funded through ISRO-Geosphere Biosphere Program (IGBP) of the Department of Space, Govt. of India. Part of the research work was carried out using WRTC laboratory facilities

10

ARTICLE IN PRESS

R. Mukherjee et al. / Estuarine, Coastal and Shelf Science xxx (2018) 1-11

developed through World Bank (ICZMP, Odisha) funding. Authors are thankful for the support provided by Dr. R.N. Samal and for the encouragement by Dr. A.K. Pattnaik (Ex-CE, CDA). We would also like to appreciate Mr. A. Das, Ms. N. Sharma, Mr. A. Chavda and Mrs. S. Mallick for the help in the field and laboratory during the study.

References

- Aguilera, P.A., Castro, H., Rescia, A., Schmitz, M.F., 2001. Methodological development of an index of coastal water quality: application in a tourist area. Environ. Manag. 27, 295–301.
- Bardhan, P., Karapurkar, S., Shenoy, D., Kurian, S., Sarkar, A., Maya, M., Naik, H., Varik, S., Naqvi, S., 2015. Carbon and nitrogen isotopic composition of suspended particulate organic matter in Zuari Estuary, west coast of India. J. Mar. Syst. 141, 90–97.
- Barik, S.K., Muduli, P.R., Mohanty, B., Behera, A.T., Mallick, S., Das, A., Samal, R., Rastogi, G., Pattnaik, A.K., 2017. Spatio-temporal variability and the impact of Phailin on water quality of Chilika lagoon. Continent. Shelf Res. 136, 39–56.
- Behera, P., Mahapatra, S., Mohapatra, M., Kimb, Y., Adhya, T.K., Raina, V., Suar, M., Pattnaik, A.K., Rastogi, G., 2017. Salinity and macrophyte drive the biogeography of the sedimentary bacterial communities in a brackish water tropical coastal lagoon. Sci. Total Environ. 595, 472–485.
- Bhavya, P., Kumar, S., Gupta, G., Sudheesh, V., Sudharma, K., Varrier, D., Dhanya, K., Saravanane, N., 2016. Nitrogen uptake dynamics in a tropical eutrophic estuary (Cochin, India) and adjacent coastal waters. Estuar. Coast 39, 54–67.
- Borum, J., Sand-Jensen, K., 1996. Is total primary production in shallow coastal marine waters stimulated by nitrogen loading? Oikos 406–410.
- Cai, W., Pomeroy, L.R., Moran, M.A., Wang, Y., 1999. Oxygen and carbon dioxide mass balance for the estuarine-intertidal marsh complex of five rivers in the southeastern US. Limnol. Oceanogr. 44, 639–649.
- Capone, D.G., Zehr, J.P., Paerl, H.W., Bergman, B., Carpenter, E.J., 1997. Trichodesmium, a globally significant marine cyanobacterium. Science 276, 1221–1229.
- Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. 8, 559–568.
- Cloern, J.E., 2001. Our evolving conceptual model of the coastal eutrophication problem. Mar. Ecol. Prog. Ser. 210, 223–253.
- Dagenais-Bellefeuille, S., Morse, D., 2013. Putting the N in dinoflagellates. Front. Microbiol. 4, 369.
- Del Amo, Y., Le Pape, O., Tréguer, P., Quéguiner, B., Ménesguen, A., Aminot, A., 1997. Impacts of high-nitrate freshwater inputs on macrotidal ecosystems. I. Seasonal evolution of nutrient limitation for the diatom-dominated phytoplankton of the Bay of Brest (France). Mar. Ecol. Prog. Ser. 213–224.
- Dodds, W.K., Priscu, J.C., Ellis, B.K., 1991. Seasonal uptake and regeneration of inorganic nitrogen and phosphorus in a large oligotrophic lake: sizefractionation and antibiotic treatment. J. Plankton Res. 13, 1339–1358.
- Dugdale, R., Wilkerson, F., 1986. The use of 15N to measure nitrogen uptake in eutrophic oceans; experimental considerations. Limnol. Oceanogr. 31, 673–689.
- Fisher, T., Melack, J., Grobbelaar, J., Howarth, R., 1995. Nutrient limitation of phytoplankton and eutrophication of inland, estuarine and marine waters. SCOPE-Sci. Comm. Probl. Environ. Int. Counc. Sci. UNIONS 54, 301–322.
- Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., Libert, E., Théate, J.-M., 1998. Carbon dioxide emission from European estuaries. Science 282, 434–436.
- Frankignoulle, M., Bourge, I., Wollast, R., 1996. Atmospheric CO2 fluxes in a highly polluted estuary (the Scheldt). Limnol. Oceanogr. 41 (2).
- French, R.H., Cooper, J.J., Vigg, S., 1982. Secchi disc relationships. JAWRA J. Am. Water Resour. Assoc. 18, 121–123.
- Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C., Green, P., Holland, E., 2004. Nitrogen cycles: past, present, and future. Biogeochemistry 70, 153–226.
 Ganguly, D., Patra, S., Muduli, P.R., Vardhan, K.V., Abhilash, K., Robin, R.,
- Ganguly, D., Patra, S., Muduli, P.R., Vardhan, K.V., Abhilash, K., Robin, R., Subramanian, B., 2015. Influence of nutrient input on the trophic state of a tropical brackish water lagoon. J. Earth Syst. Sci. 124, 1005–1017.
- Gardner, W.S., Lavrentyev, P.J., Cavaletto, J.F., McCarthy, M.J., Eadie, B.J., Johengen, T.H., Cotner, J.B., 2004. Distribution and dynamics of nitrogen and microbial plankton in southern Lake Michigan during spring transition 1999–2000. J. Geophys. Res. Oceans 109.
- Gibson, C.A., O'Reilly, C.M., 2012. Organic matter stoichiometry influences nitrogen and phosphorus uptake in a headwater stream. Freshw. Sci. 31, 395–407.
- Gibson, C.A., O'Reilly, C.M., Conine, A.L., Lipshutz, S.M., 2015. Nutrient uptake dynamics across a gradient of nutrient concentrations and ratios at the landscape scale. J. Geophys. Res. Biogeosci. 120, 326–340.
- Glibert, P.M., Biggs, D.C., McCarthy, J.J., 1982. Utilization of ammonium and nitrate during austral summer in the Scotia Sea. Deep-Sea Res. Part Oceanogr. Res. Pap. 29, 837–850.
- Glibert, P.M., Hinkle, D.C., Sturgis, B., Jesien, R.V., 2014. Eutrophication of a Maryland/Virginia coastal lagoon: a tipping point, ecosystem changes, and potential causes. Estuar. Coast 37, 128–146.
- Glibert, P.M., Wilkerson, F.P., Dugdale, R.C., Raven, J.A., Dupont, C.L., Leavitt, P.R., Parker, A.E., Burkholder, J.M., Kana, T.M., 2016. Pluses and minuses of ammonium and nitrate uptake and assimilation by phytoplankton and implications

for productivity and community composition, with emphasis on nitrogenenriched conditions. Limnol. Oceanogr. 61, 165–197.

- Grashoff, K., Kremling, K., Ehrhard, M., 1999. Methods of Seawater Analysis, 3rd completely revised and extended edition.
- Gu, B., Havens, K.E., Schelske, C.L., Rosen, B.H., 1997. Uptake of dissolved nitrogen by phytoplankton in a eutrophic subtropical lake. J. Plankton Res. 19, 759–770.
- Gupta, G., Sarma, V., Robin, R., Raman, A., Kumar, M.J., Rakesh, M., Subramanian, B., 2008. Influence of net ecosystem metabolism in transferring riverine organic carbon to atmospheric CO2 in a tropical coastal lagoon (Chilka Lake, India). Biogeochemistry 87, 265–285.
- Hanson, P.C., Bade, D.L., Carpenter, S.R., Kratz, T.K., 2003. Lake metabolism: relationships with dissolved organic carbon and phosphorus. Limnol. Oceanogr. 48, 1112–1119.
- Howarth, R., Chan, F., Conley, D.J., Garnier, J., Doney, S.C., Marino, R., Billen, G., 2011. Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. Front. Ecol. Environ. 9, 18–26.
- Jansson, M., Bergström, A.-K., Blomqvist, P., Drakare, S., 2000. Allochthonous organic carbon and phytoplankton/bacterioplankton production relationships in lakes. Ecology 81, 3250–3255.
- Kanda, J., Itoh, T., Ishikawa, D., Watanabe, Y., 2003. Environmental control of nitrate uptake in the East China Sea. Deep-Sea Res. Part II Top. Stud. Oceanogr. 50, 403–422.
- Keller, A.A., 1988. Estimating phytoplankton productivity from light availability and biomass in the MERL mesocosms and Narragansett Bay. Mar. Ecol. Prog. Ser. Oldendorf 45, 159–168.
- Kennish, M.J., Paerl, H.W., 2010. Coastal Lagoons: Critical Habitats of Environmental Change. CRC Press.
- Kinney, E.H., Roman, C.T., 1998. Response of primary producers to nutrient enrichment in a shallow estuary. Mar. Ecol. Prog. Ser. 163, 89–98.
- Kozlowsky-Suzuki, B., Bozelli, R.L., 2004. Resilience of a zooplankton community subjected to marine intrusion in a tropical coastal lagoon. Hydrobiologia 522, 165–177.
- Krause-Jensen, D., Markager, S., Dalsgaard, T., 2012. Benthic and pelagic primary production in different nutrient regimes. Estuar. Coast 35, 527–545.
- Kumar, S., Ramesh, R., Bhosle, N., Sardesai, S., Sheshshayee, M., 2004. Natural isotopic composition of nitrogen in suspended particulate matter in the Bay of Bengal. Biogeosciences 1, 63–70.
- Kumar, S., Ramesh, R., Dwivedi, R., Raman, M., Sheshshayee, M., D'Souza, W., 2010. Nitrogen uptake in the northeastern Arabian Sea during winter cooling. Int. J. Oceanogr. 2010.
- Kumar, S., Sterner, R.W., Finlay, J.C., 2008. Nitrogen and carbon uptake dynamics in Lake Superior. J. Geophys. Res. Biogeosci. 113.
- Leavitt, P.R., Brock, C.S., Ebel, C., Patoine, A., 2006. Landscape-scale effects of urban nitrogen on a chain of freshwater lakes in central North America. Limnol. Oceanogr. 51, 2262–2277.
- Lomas, M., Glibert, P., 1999a. Interactions between NH+ 4 and NO- 3 uptake and assimilation: comparison of diatoms and dinoflagellates at several growth temperatures. Mar. Biol. 133, 541–551.
- Lomas, M.W., Glibert, P.M., 1999b. Temperature regulation of nitrate uptake: a novel hypothesis about nitrate uptake and reduction in cool-water diatoms. Limnol. Oceanogr. 44, 556–572.
- Maestrini, S., Robert, J., Truquet, I., 1982. Simultaneous uptake of ammonium and nitrate by oyster-pond algae. Mar. Biol. Lett. (3)
- Mariotti, A., Lancelot, C., Billen, G., 1984. Natural isotopic composition of nitrogen as a tracer of origin for suspended organic matter in the Scheldt estuary. Geochim. Cosmochim. Acta 48, 549–555.
- Martí, E., Fonollà, P., von Schiller, D., Sabater, F., Argerich, A., Ribot, M., Riera, J.L., 2009. Variation in stream C, N and P uptake along an altitudinal gradient: a space-for-time analogue to assess potential impacts of climate change. Hydrol. Res. 40, 123–137.
- McCarthy, J.J., Taylor, W.R., Taft, J.L., 1977. Nitrogenous nutrition of the plankton in the Chesapeake Bay. 1. Nutrient availability and phytoplankton preferences. Limnol. Oceanogr. 22, 996–1011.
- Middelburg, J.J., Nieuwenhuize, J., 2000. Uptake of dissolved inorganic nitrogen in turbid, tidal estuaries. Mar. Ecol. Prog. Ser. 192, 79–88.
- Mohanty, P., Dash, S., Mishra, P., Murty, A., 1996. Heat and momentum fluxes over Chilka: a tropical lagoon. Indian J. Mar. Sci. 25, 184–188.
- Montoya, J.P., Voss, M., Kahler, P., Capone, D.G., 1996. A simple, high-precision, highsensitivity tracer assay for N₂ fixation. Appl. Environ. Microbiol. 62, 986–993.
- Moynihan, M.A., Barbier, P., Olivier, F., Toupoint, N., Meziane, T., 2016. Spatial and temporal dynamics of nano-and pico-size particulate organic matter (POM) in a coastal megatidal marine system. Limnol. Oceanogr. (61)
- Muduli, P.R., Kanuri, V.V., Robin, R., Kumar, B.C., Patra, S., Raman, A., Rao, G.N., Subramanian, B., 2013. Distribution of dissolved inorganic carbon and net ecosystem production in a tropical brackish water lagoon, India. Continent. Shelf Res. 64, 75–87.
- Muduli, P.R., Kanuri, V.V., Robin, R., Kumar, B.C., Patra, S., Raman, A., Rao, G.N., Subramanian, B., 2012. Spatio-temporal variation of CO 2 emission from Chilika Lake, a tropical coastal lagoon, on the east coast of India. Estuar. Coast. Shelf Sci. 113, 305–313.
- Mulholland, M.R., Capone, D.G., 2009. Dinitrogen fixation in the Indian Ocean. Indian Ocean Biogeochem. Process. Ecol. Var. 167–186.
- Mulholland, M.R., Lee, C., Glibert, P.M., 2003. Extracellular enzyme activity and uptake of carbon and nitrogen along an estuarine salinity and nutrient gradient. Mar. Ecol. Prog. Ser. 258, 3–17.
ARTICLE IN PRESS

R. Mukherjee et al. / Estuarine, Coastal and Shelf Science xxx (2018) 1-11

- Newton, A., Icely, J., Falcão, M., Nobre, A., Nunes, J., Ferreira, J., Vale, C., 2003. Evaluation of eutrophication in the Ria Formosa coastal lagoon, Portugal. Continent. Shelf Res. 23, 1945–1961.
- Paerl, H.W., Dennis, R.L., Whitall, D.R., 2002. Atmospheric deposition of nitrogen: implications for nutrient over-enrichment of coastal waters. Estuaries 25, 677–693.
- Panigrahi, S., Wikner, J., Panigrahy, R., Satapathy, K., Acharya, B., 2009. Variability of nutrients and phytoplankton biomass in a shallow brackish water ecosystem (Chilika Lagoon, India). Limnology 10, 73–85.
- Parker, A.E., Hogue, V.E., Wilkerson, F.P., Dugdale, R.C., 2012. The effect of inorganic nitrogen speciation on primary production in the San Francisco Estuary. Estuar. Coast. Shelf Sci. 104, 91–101.
- Pastor, A., Peipoch, M., Cañas, L., Chappuis, E., Ribot, M., Gacia, E., Riera, J.L., Martí, E., Sabater, F., 2013. Nitrogen stable isotopes in primary uptake compartments across streams differing in nutrient availability. Environ. Sci. Technol. 47, 10155–10162.
- Patra, S., Raman, A., Ganguly, D., Robin, R., Muduli, P., Kanuri, V., Abhilash, K., Kumar, B.C., Subramanian, B., 2016. Influence of suspended particulate matter on nutrient biogeochemistry of a tropical shallow lagoon, Chilika, India. Limnology 17, 223–238.
- Peters, K., Sweeney, R., Kaplan, I., 1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. Limnol. Oceanogr. 23, 598–604.
- Prasad, B., Srinivasu, P., Varma, P.S., Raman, A., Ray, S., 2014. Dynamics of dissolved oxygen in relation to saturation and health of an aquatic body: a case for Chilka lagoon, India. J. Ecosyst. 2014.
- Probyn, T., 1985. Nitrogen uptake by size-fractionated phytoplankton populations in the southern Benguela upwelling system. Mar. Ecol. Prog. Ser. Oldendorf 22, 249–258.
- Rees, A., Owens, N., Woodward, E., 1995. Phytoplankton nitrogen assimilation at low nutrient concentrations in the NW-Mediterranean Sea (July 1993). Water Pollut. Rep. 141–148.
- Sambrotto, R.N., 2001. Nitrogen production in the northern Arabian Sea during the spring intermonsoon and southwest monsoon seasons. Deep Sea Res. Part II Top. Stud. Oceanogr. 48, 1173–1198.
- Sarma, V., Krishna, M., Prasad, V., Kumar, B., Naidu, S., Rao, G., Viswanadham, R., Sridevi, T., Kumar, P., Reddy, N., 2014. Distribution and sources of particulate organic matter in the Indian monsoonal estuaries during monsoon. J. Geophys. Res. Biogeosci. 119, 2095–2111.

- Savage, C., 2005. Tracing the influence of sewage nitrogen in a coastal ecosystem using stable nitrogen isotopes. AMBIO J. Hum. Environ. 34, 145–150.
- Simon, K., Townsend, C., Biggs, B.J.F., Bowden, W., 2005. Temporal variation of N and P uptake in 2 New Zealand streams. J. North Am. Benthol. Soc. 24, 1–18.
- Srichandan, S., Kim, J.Y., Bhadury, P., Barik, S.K., Muduli, P.R., Samal, R.N., Pattnaik, A.K., Rastogi, G., 2015. Spatiotemporal distribution and composition of phytoplankton assemblages in a coastal tropical lagoon: Chilika, India. Environ. Monit. Assess. 187, 47.
- Srinivas, B., Sarin, M., Sarma, V., 2011. Atmospheric dry deposition of inorganic and organic nitrogen to the Bay of Bengal: impact of continental outflow. Mar. Chem. 127, 170–179.
- Strickland, J.D.H., Parsons, T.R., 1984. A Practical Handbook of Seawater Analysis, third ed. Queen's Printer. Fisheries Research Board of Canada Bulletin, Ottawa, p. 167.
- Subramaniam, A., Carpenter, E., 1994. An empirically derived protocol for the detection of blooms of the marine cyanobacterium Trichodesmium using CZCS imagery. Int. J. Rem. Sens. 15, 1559–1569.
- Sweeney, R., Liu, K.-K., Kaplan, I., 1978. Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In: Stable Isotopes in the Earth Sciences.
- Vander Zanden, M.J., Vadeboncoeur, Y., Diebel, M.W., Jeppesen, E., 2005. Primary consumer stable nitrogen isotopes as indicators of nutrient source. Environ. Sci. Technol. 39, 7509–7515.
- Weiss, R., 1970. The Solubility of Nitrogen, Oxygen and Argon in Water and Seawater. Presented at the Deep Sea Research and Oceanographic Abstracts. Elsevier, pp. 721–735.
- Wilkerson, F.P., Dugdale, R.C., Hogue, V.E., Marchi, A., 2006. Phytoplankton blooms and nitrogen productivity in San Francisco Bay. Estuar. Coast 29, 401–416.
- Ye, F., Ni, Z., Xie, L., Wei, G., Jia, G., 2015. Isotopic evidence for the turnover of biological reactive nitrogen in the Pearl River Estuary, south China. J. Geophys. Res. Biogeosciences 120, 661–672.
- Ying-Xin, X., Xiong, Z.-Q., Guang-Xi, X., Guo-Qing, S., Zhao-Liang, Z., 2007. Assessment of nitrogen pollutant sources in surface waters of Taihu lake Region11-Project supported by the state key laboratory of soil and sustainable agriculture, institute of soil science, Chinese academy of sciences (No. 035109) and the national natural science foundation of China (No. 30390080). Pedosphere 17, 200–208.