INFLUENCE OF UPWELLING ON SEASONAL HYPOXIA/ANOXIA AND GREENHOUSE GASES ALONG THE SOUTHWESTERN CONTINENTAL SHELF OF INDIA

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By

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I hereby declare that the thesis entitled, "**Influence of Upwelling on Seasonal Hypoxia/Anoxia and Greenhouse Gases along the Southwestern Continental Shelf of India**", is an authentic record of the research work conducted by me under the supervision and guidance of Dr. Jacob Chacko (Supervising Guide), Dr. S. Muraleedharan Nair (Co-Guide), Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi and Dr. G.V.M Gupta (Joint-Guide), Centre for Marine Living Resources and Ecology, Kochi and that no part of it has been presented for any other degree or diploma in any University.

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Preface

The south eastern Arabian Sea (‘*SEAS’*) is unique with distinct biogeochemical processes that transform it seasonally from oligotrophic to eutrophic conditions. This is brought about mainly by the semi-annual reversal of monsoon winds, which are of exceptional significance in relation to global productivity, nutrient inventories and climate changes. SEAS is bordered by highly populated coastal areas and hence the present study of biogeochemical processes has major socio-economic import. Being one of the largest seasonally occurring natural upwelling/hypoxic systems in the world, this region is also influenced by anthropogenic perturbations such as increased nutrient loading. The coastal hypoxic zones may also lead to significant increases in the production of greenhouse gases (N_2O, CH_4 and CO_2). The present study is an attempt at evaluating biogeochemical processes in the *SEAS* and their influence on elemental cycling and greenhouse gas emissions.

The Thesis is organised into **7 Chapters**.

Chapter 1 provides an overview of the role of coastal regions in biogeochemical cycles and the significance of upwelling in elemental cycling. The main objectives and scope of the study are also presented in this Chapter.

Chapter 2 describes the area of the study, protocols for sample collection and methods of analysis of various parameters.

Chapter 3 explains the evolution, propagation and decay of upwelling and associated biogeochemistry in the *SEAS*. It also dwells

upon the factors responsible for intensification of coastal oxygen deficiency in addition to providing a comparison of present observations with historical data set to asses long-term changes in oxygen saturation in the *SEAS*.

The dynamics of nitrous oxide is discussed in **Chapter 4**. It elaborates on the factors controlling the distribution of nitrous oxide (N_2O) concentration in the *SEAS* and also explains the variation in N_2O fluxes with time and space. A revised estimate of annual flux of N_2O from the south western Indian shelf is also provided.

Chapter 5 analyses the spatial distribution of methane, its sources and annual emission from the study region.

The dynamics of inorganic carbon components are dealt with in **Chapter 6**. The chapter discusses the change in carbon chemistry and its implications on biological properties, variations in pCO_2 fluxes and influencing factors.

Chapter 7 is an overall summary of the work, and highlights the salient conclusions emerging therefrom.

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Chapter 1

INTRODUCTION

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Coastal ecosystems play a very significant role in global biogeochemical cycles, even though they cover only 7% of the total oceanic area. Productivity and particulate matter loads are so high in coastal margins that almost half of the global integrated new production occurs over the continental shelves (Walsh, 1991; Doney and Hood, 2002). Therefore, biogeochemical responses of coastal ecosystems are important areas of research since they contribute to ~15% oceanic primary production, ~80% organic burial, ~50% carbonate deposition, ~90% remineralization and ~80% sink of suspended matter (Naqvi and Unnikrishan, 2009). They contribute to ~90% of the marine fish catch worth more than 40% of the world's ecosystem services (Gattuso *et al.*, 1998; Gattuso and Smith, 2007).

Coastal zones are of particular interest to mankind as they are characterised by high productivity which sustains major fishery resources,

as mentioned earlier. On-going developmental activities (urbanization, industrialization, reclamation of wetlands, etc.) impart immense stress on coastal water bodies. Today, nearly 60% of the human population is concentrated within ~50 km of the coast (Pernetta, 1994), exerting enormous pressure on the coastal environment and its natural resources (Flemming and Hansom, 2011). Thus, there is a growing need to understand the impact of natural and anthropogenic activities on the marine ecosystems in view of the projected climate change and global warming.

1.1 Upwelling ecosystems

Upwelling is the shoaling of sub-surface waters towards the surface layer of the coast and enhances the productivity. Upwelling areas are generally the most productive regions of the ocean. The intensity of coastal upwelling depends on winds, currents, orientation of continental margin and bathymetry (Lluch-Cota *et al.,* 2014). Upwelling areas, in general, are located along the eastern boundary currents (EBC) in the Pacific and Atlantic oceans. The EBCs at high latitudes flow poleward due to cyclonic circulation in the subpolar gyres. In contrast, monsoon upwelling in the northern Indian Ocean, particularly in Arabian Sea, is largely associated with winds and remote forcing (Shetye *et al*., 1990, 1991; Shankar *et al.,* 2002). The upward movement of bottom waters changes the properties of mixed layer considerably. This occurs by the replacement of oligotrophic, oxygenated warm water with cool, nutrient-replete and poorly-oxygenated bottom waters (Naqvi *et al.*, 2000). At the surface, these upwelled nutrients are quickly consumed by the primary

producers (phytoplankton) and are thus incorporated into biological cycling. Upwelling associated high primary production propagates through the food chain and increases fish production significantly. Though they occupy only <1% of the total oceanic area, coastal upwelling zones alone contribute to ~20% of the total fish catch (Pauly and Christensen, 1995). The upwelling regions are also known for the production and emission of climatically relevant greenhouse gases like nitrous oxide, methane, carbon dioxide. etc. (Naqvi and Jayakumar, 2000; Naqvi, 2002).

1.2 Upwelling in the Arabian Sea

The northern Indian Ocean is constituted by two basins *viz.* Arabian Sea (AS) and Bay of Bengal (BoB) separated by the Indian peninsula. Since BoB receives a large amount of freshwater (1.6×10^{12} m^3 y^{-1}; UNESCO, 1979), it sustains a thick layer of low saline waters in the surface limiting vertical mixing across the thermocline (Murty *et al*., 2000; Prasannakumar *et al.*, 2002). Thus, oceanic processes such as upwelling or convection are less prominent in BoB. Since AS has relatively lesser freshwater sources, the surface layer remains more saline. Hence, the mixed layer easily responds to changes in the air-sea interaction, as evident from the upwelling and down-welling processes in the region (Naqvi, 1991; Shankar *et al.*, 2002; Shetye, 2005). This leads to a series of upwelling events caused by winds during summer monsoon (SM) along the Somalia and Oman coasts and the southwest coast of India and to cooling-induced convective mixing during northeast monsoon in the northern Arabian Sea (Madhupratap *et al.*, 1996).

Because of these chain of upwelling events and enhanced levels of chlorophyll *a*, AS is considered as one of the most productive regions of the world oceans (Gardner *et al.*, 1999; Prasannakumar *et al.*, 2001; Wiggert *et al.*, 2005). The upwelling areas along the western Arabian Sea, such as the Somalia and Oman coastal systems, are less important compared to those along its eastern boundary due to the larger width of the western continental shelf of India. The wider shelf allows the upwelled waters to persist longer enough to make it oxygen depleted. Therefore, the upwelling systems along the west coast of India are more complicated and ecologically significant (Panikkar and Jayaraman, 1966).

In the past, several studies have been carried out on upwelling of the eastern Arabian Sea (Banse, 1959, 1968; Ramasastry and Myrland, 1959; Sharma, 1966, 1978; Shetye, 1984, Johannessen *et al.*, 1987; Shetye *et al.*, 1990; Shankar *et al.*, 2005). It is well known that upwelling along the western AS coast during SM, which is several folds stronger than on its east coast (Naqvi *et al.*, 2006), has a direct effect on the survival of fish eggs/larvae (Bakun and Parrish, 1982; Balan, 1984). Expansion of anoxia/hypoxia in the shelf waters associated with upwelling (Naqvi *et al.*, 1990, 1998; Naqvi and Noronha, 1991; Naqvi and Jayakumar, 2000; Rabalais *et al.*, 2001) has been a matter of concern as these are important sites for biogeochemical transformation of elements (Naqvi and Jayakumar 2000; Rejomon *et. al*., 2012).

1.3 Hypoxia and its influnce on elemental cycling

The west coast of India is environmentally more sensitive than the east coast primarily because it is bordering one of the most productive

ecosystems in the world, the Arabian Sea. Processes in the northern AS that leads to rich biological production throughout the year, known as the AS 'paradox' (Madhupratap *et al.*, 1996). Mid-depth oxygen deficiency in the AS is perhaps the most intensely observed phenomenon anywhere in the oceans. Oxygen concentration observed between 150 - 1000 m is <5µM in the central and northeastern Arabian Sea, rendering it as this an intense denitrification zone (Naqvi and Jayakumar, 2000). With such a delicate biogeochemical balance, the oceanic oxygen-deficient zones in the Arabian Sea will perhaps be among the first to react to potential anthropogenic perturbations such as increased nutrient loading (Naqvi *et al.*, 2000, 2009). A slight change in the mid-depth oxygen demand might bring about large changes in chemical fluxes. Most importantly, an expansion of the oxygen minimum zone towards coastal areas may have adverse impacts on biological resources (Naqvi *et al.*, 1998). It is still not clear as to how the ecosystem dwelling in suboxic conditions in the Arabian Sea respond to anthropogenic changes.

Oxygen deficiency over the continental shelf is modulated by a number of factors including coastal circulation/hydrography, oxygen content of upwelled water, shelf width and coastal productivity. Coastal hypoxia appears with intensification of upwelling when the enhanced production and subsequent increased particle flux increase the oxygen demand for oxidation of organic particles (Naqvi *et al.*, 2000). The upwelling in the AS is intense along the west coast because a wider shelf allows the upwelled waters to remain on the shelf for a longer time till the oxygen is completely utilized. It is also pointed that the eastern Arabian Sea is the only region where upwelling occurs in conjunction with high

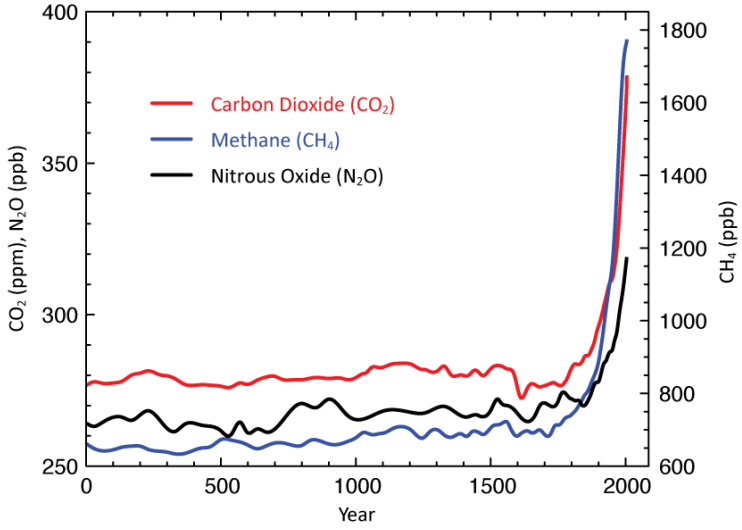
freshwater input leading to strong surface stratification. These effects have caused the western Indian shelf to be one of the largest coastal hypoxic zones in the world oceans (Naqvi *et al.*, 2000, 2009). The oxygen-deficient environment provides reducing conditions where NO_3 is reduced to N_2 and N_2O, Mn (IV) to Mn (II), Fe (III) to Fe (II), and iodate to iodide. Hypoxia has profound socio-economic impact too as it directly affects living resources and biodiversity (Naqvi *et al.*, 2006; Levin *et al.*, 2009). There is a dearth of studies focus on the biogeochemical and ecological impacts of hypoxic environments. Therefore, comprehensive studies are essential to predict the biogeochemical responses and climatic feedback from hypoxic systems.

1.4 Greenhouse Gases

Nitrous oxide (N_2O), methane (CH_4) and carbon dioxide (CO_2) are the three primary anthropogenic greenhouse gases (GHGs) in the atmosphere. Their tropospheric abundances is being monitored since the late 1950s in case of CO_2 and since the 1970s for N_2O and CH_4. The increasing concentration of these greenhouse gases (Fig.1.1, Table 1.1) in the atmosphere is widely recognized as the major causative factor of global warming and increased frequency of extreme weather events (Vitale *et al.*, 2011; Giorio and Nuzzo, 2012; IPCC, 2013).

Coastal ecosystems are diverse with region-specific characteristics, which, however, are not often reflected in the global greenhouse gas budgets. Estuaries and coastal areas are estimated to contribute up to 60% of total marine N_2O emissions (Bange *et al.*, 1996; Seitzinger *et al.*, 2000), and up to 75% of total marine CH_4 emissions (Bange *et al.*, 1994).

Shelf seas at lower latitudes are considered to be predominantly CO_2 sources while temperate and higher latitude shelf seas act as a CO_2 sink (Borges *et al.*, 2005; Laruelle *et al.*, 2010). Continental shelves cover less than 10% of the total ocean surface area and their air-sea CO_2 fluxes are about twice as large (Laruelle *et al.*, 2010) as the global average fluxes from the open oceans (Takahashi *et al.*, 2009). Although these shelves are major sources of CH_4 and N_2O to the atmosphere (Naqvi *et al.*, 2010), their fluxes remain poorly quantified. Spatial heterogeneity of coastal areas is a major challenge in estimating the fluxes of N_2O and CH_4. Quantification of the ocean-atmosphere exchange of greenhouse gases is, therefore, an essential prerequisite for understanding global biogeochemical cycles and their impacts on global climate change.



Source: https://www.ipcc.ch/publications_and_data/ar4/wg1/en/fig/faq-2-1-figure -1-errata.png

Figure 1.1. Atmospheric concentrations of CO_2, CH_4 and N_2O over the last 2,000 years

Table 1.1. Tropospheric concentration, radiative forcing (RF) and residence time of N_2O, CH_4 and CO_2

Gas	Pre-1750 tropospheric concentration	Atmospheric concentration in 2016	RF in 2016 (W m^{-2})	Atmospheric lifetime (years)
N_2O	270 ppb	328 ppb	0.2	121
CH_4	722 ppb	1834 ppb	0.5	12.4
CO_2	~280 ppm	399.5 ppm	1.94	~100-300*****

Source: http://cdiac.ess-dive.lbl.gov/pns/current_ghg.html

***** CO_2 removal determined by the rate of removal of carbon from the ocean surface (Annexe I in IPCC 2007) hence, no single adjustment time for CO_2 (Joos *et al.*, 2001).

1.4.1 Nitrous oxide

Nitrous oxide (N_2O), the third most important greenhouse gas in terms of anthropogenic contribution (Solomon *et al.*, 2007), has a very long residence time (~120 years) and has >300 fold higher global warming potential than CO_2. N_2O is an important precursor for nitric oxide (NO) radicals which are involved in the destruction of ozone in stratosphere (Crutzen, 1970; Nelvison and Hlland, 1997, Naqvi *et al.*, 2010). The N_2O concentration in the atmosphere is increasing steadily and the current levels (328 ppb) are higher by 21% since the pre-industrial period due to rapid growth of anthropogenic activities. The oceans account for about one-third of this emission (IPCC, 2007) of which, a major fraction is from hypoxic regions associated with upwelling (Nevison *et al.*, 2004; Farias *et al.*, 2007). Productive regions such as estuaries and coastal areas are also significant sources of greenhouse gases contributing to >60% of their global oceanic fluxes (Bouwman *et al.*, 1995; Nevison *et al.*, 1995; Bange *et al.*, 1996; Naqvi *et al.*, 2005; Zhang *et al.*, 2006).

Nitrification and denitrification are the major pathways of N_2O cycling in the ocean, although emission of N_2O depends on the dissolved oxygen levels (Goreau *et al.*, 1980; Codispoti *et al.*, 2005; Bange, 2006, 2010). The coupling of both of these processes leads to accumulation of N_2O in the water column while denitrification leads to its removal (Naqvi *et al.*, 2000; Codispoti *et al.*, 2001).

1.4.2 Carbon dioxide

Carbon dioxide (CO_2), the most significant greenhouse gas emitted through human activities, contributes ~64% to the global greenhouse emissions (Stocker *et al.*, 2013). Global CO_2 levels which have been on an exponential increase since the pre-industrial period, have currently peaked to 400 ppm in 2017. Such a trend would impact organic production and calcification rates drastically (Orr *et al.*, 2005; Borges and Gypens, 2010).

Coastal environments are normally more dynamic than oceanic regions and hence, are biogeochemically more reactive. The coastal waters are capable of sustaining 15-30% of oceanic primary production and burying ~80% of oceanic organic matter (Gattuso *et al.*, 1998). In addition, most of the benthic $CaCO_3$ precipitation (Balch *et al.*, 2005) and deposition (Gattuso *et al.*, 1998) occur in coastal environments. This disproportionate high carbon turnover rate (~7% of total oceanic surface area) is quite alarming as it could form a significant source of CO_2 at regional as well as global scales (Frankignoulle and Borges, 2001; Borges *et al.*, 2006). Assessment of sources and sink of coastal ocean carbon fluxes is essential to ascertain their impacts on global carbon budgets.

1.4.3 Methane

The global warming potential of Methane (CH_4) is ~25-40 times higher than that of CO_2 (IPCC, 2013). Elevated CH_4 levels can reduce the oxidizing capacity of the troposphere by depleting OH radicals (Hein *et al.*, 1997). Thus, atmospheric CH_4 plays an important role in regulating Earth's radiation balance and atmospheric chemistry (Cicerone and Oremland, 1988; Lashof and Ahuja, 1990). The high concentration of CH_4 (722 ppbv) in the atmosphere warrants its increased present day emissions compared to the pre-industrial era due to enhanced anthropogenic ativities (Blasing, 2016).

Tropical oceans are found to be a net source of CH_4 although their effective contribution to the global CH_4 budget is relatively small (Reeburgh, 2007; Kirschke *et al*., 2013). CH_4 emissions from coastal upwelling areas are indirectly linked to high biological production (Tilbrook and Karl, 1995). In the marine environment, CH_4 is produced strictly under anaerobic conditions such as those in sediments, interior of suspended particles, and in the guts of zooplankton (De Angelies and Lee 1994; Karl and Tilbook 1994; Holmes *et al.* 2000; Boetius *et al.* 2000). In some cases, a linear correlation is also found between CH_4 production and phytoplankton biomass (Oudot *et al.*, 2002; Damm *et al.*, 2008). This is probably because CH_4-rich subsurface waters are brought to the surface during the upwelling events (Kock *et al.*, 2008; Brown *et al.*, 2014). Karl *et al* (2008) argue that CH_4 may be produced by aerobic decomposition of methylphosphonate releasing phosphorus in phosphate poor environment. Inland waters and estuaries also contribute to high CH_4 production

(Upstill-Goggard *et al.*, 2000; Bakker *et al.*, 2014; Rao *et al.*, 2016, 2017). Coastal areas can also be good sources of methane through seepage from shallow gassy sediments (Borges *et al.*, 2016). While considerable progress has been made to understand the formation, distribution and emission of CH_4 in different coastal environments, lack of a comprehensive study from the southwest coast of India severely limits the biogeochemical responses of the *SEAS*.

1.5 Objectives of the present study

The southeastern Arabian Sea (*SEAS*) is very dynamic in terms of ecology and biogeochemistry. It is a unique system which combines a variety of biogeochemical features reflecting eutrophic or oligotrophic conditions as a consequence of upwelling, sinking and circulation. Wind driven upwelling during summer monsoon has a marked impact on the biogeochemistry resulting in high biological production. This is unique as compared to other coastal upwelling regions due to its spatial variation and intensity. The coastal upwelling that occurs between 9-13°N of *SEAS* is mainly caused by winds and remote forcing (Shetye *et al.*, 1990; Shah *et al.*, 2015), where three estuaries (Ashtamudi, Kochi and Netravati–Gurupura) bring fresh water into this area. Therefore, a combined effect of upwelling and coastal input is expected to influence this coastal environment during summer monsoon. Thus, understanding the export fluxes of nutrients is important to studying its impact on organic production, respiration, nitrification, denitrification and air-sea exchange.

The occurrence of seasonal oxygen deficiency associated with the summer monsoon has long been reported off the west coast of India (Banse,

1959, 1968; Naqvi et al., 2000, 2006, 2009). An intensification of this phenomenon was expected, with the increasing terrigenous nutrient load associated with the increasing population and industrialization along the west coast. Indeed, Naqvi et al. (2006, 2009) reported the occurrence of hydrogen sulphide in the bottom waters off Mangalore and Goa, which they attributed to intensification of hypoxia in the region. However, sustained observations at a site off Goa (the Candolim Time Series-CaTS) has confirmed the recurrence of sulfidic conditions during the late summer monsoon, while there was no evidence of progressive intensification of hypoxia/anoxia. The time series study rather pointed to a large inter-annual variability in extent and intensity of hypoxia.

Biogeochemical processes under hypoxia/anoxia can significantly influence the nutrient cycling and substantially increase the production of greenhouse gases (N_2O, CH_4 and CO_2). Although many studies have been undertaken in the recent past in the *SEAS*, yet none of them have systematically addressed the various stages of these processes and their effects on the coastal biogeochemistry. The present study therefore, evaluates the biogeochemical processes in the continental shelf of *SEAS* with the following objectives:

- ***Study of coastal upwelling, hypoxia and associated nutrient biogeochemistry***
- ***Identification of factors controlling the cycling and distribution of greenhouse gases viz. N_2O, CH_4 and CO_2***
- ***Estimation of seasonal fluxes of N_2O, CH_4 and CO_2***

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Chapter 2

MATERIALS AND METHODS

Contents

2.1 Study Region

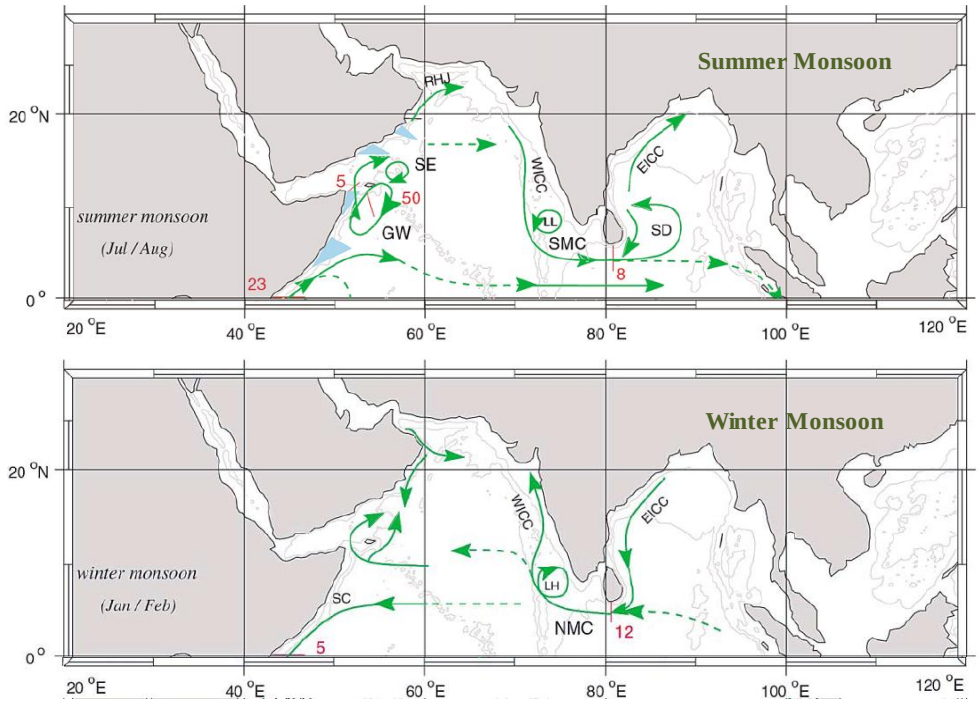
The northern Indian Ocean constitutes Arabian Sea (AS) and Bay of Bengal (BoB) separated by the Indian peninsula. Since the BoB receives huge amount of freshwater (1.6×10^{12} m^3 y^{-1}; UNESCO, 1979), strong stratification persists across the thermocline. Thus neither upwelling nor convection is prominent in BoB. But relatively low river-discharge to AS does not affect upwelling. The Arabian Sea, located in the north-western Indian Ocean, experiences regular occurrence of tropical monsoons. Biannually reversing winds and associated circulations during the summer and winter monsoons make the AS system highly productive.

The present study focuses on the southeastern Arabian Sea (*SEAS*) between ~ 8-13°N and 74-76°E. The biogeochemistry of this region is mainly controlled by the seasonally reversing winds and currents between the summer monsoon (SM) and the winter (WM) monsoon. *SEAS* experiences seasonally reversing West India Coastal currents (WICC) (Fig.2.1). It flows equatorward during SM (June-September), when there is

upwelling along the southwest coast of India coinciding with an anti-cyclonic eddy in the Lakshadweep Sea (Shetye, 1998; Schott and McCreary, 2001). During WM (November-February), the surface circulation reverses with the poleward flowing WICC and a cyclonic eddy in the Lakshadweep Sea. This reversal of surface circulation brings in high saline waters from the northern Arabian Sea (during SM) and low saline waters from the Bay of Bengal (during WM) into the *SEAS*. The transition periods of spring inter-monsoon and fall inter-monsoon are characterised by signals that are intermediate between SM and WM.

The *SEAS* is one of the most productive regions in the world (Sathyaprakash and Ramesh, 2007) mainly due to natural processes (Naqvi *et al*., 2000). The summer monsoon upwelling changes the biogeochemistry by transforming the *SEAS* in to a nutrient-replete system, which triggers enhanced primary production. The nutrient enrichment in the *SEAS* is also supported by their discharges through terrestrial input (Naqvi *et al*., 2006) from the Mandovi and Zuari rivers in Goa, the Kalinadi and Netravati rivers in Karnataka and other 41 rivers in Kerala including Cochin (Kochi) estuary (Bhavya *et al*., 2017). The Cochin estuary (CE), adjoining to the Kochi coastal waters, one of the largest estuarine systems along the south west coast of India, receives ~20×10^9 m^3 of freshwater annually from six rivers, with >90% of it during the monsoon months (June-September), and brings high nutrients to the estuary, making it highly productive. Increased anthropogenic activities of this region generate 1.04×10^5 m^3 of industrial and 0.26×10^3 m^3 of domestic wastes (untreated) per day (Balachandran *et al*., 2002; Martin *et al*., 2008), which

are being released directly into the estuary mostly without treatment. The discharge of these wastes through CE to adjacent coastal waters significantly influences its biogeochemistry.



(*Source: Schott and McCreary, 2001*)

Figure 2.1. Surface circulation in the north Indian Ocean

The *SEAS* is characterized by upwelling that makes the system a potential fishery zone in terms of fish egg laying, recruitment and succession (Madhupratap *et al*., 1994, 2001) making it an ecologically significant region (Panikkar and Jayaraman, 1966). West coast of India contributes ~70% fish yield of the total Arabian Sea production (Luis and Kawamura 2004) in which the southwest coast alone accounts for 53%

(Sanjeevan *et al*. 2009). One of the important aspects of the *SEAS* is the development of seasonal hypoxia/anoxia as a result of coastal upwelling and high surface production (Naqvi *et al*., 2009).

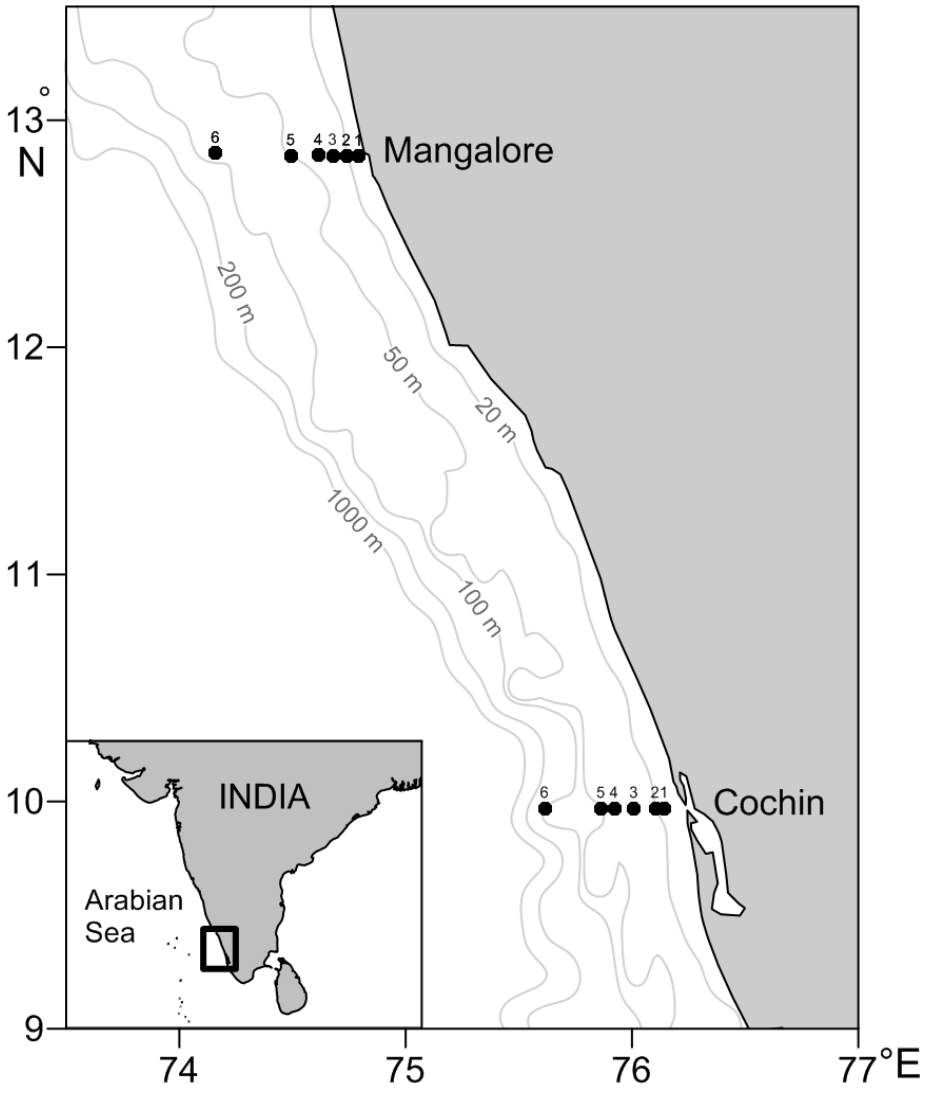


Figure 2.2. Study area and sampling locations.

The significant shelf width (~65-80 km) allows the upwelled waters to sustain long enough to make it oxygen depleted. This feature makes the western continental shelf of India a ''hot spot'' for N_2O production. Arabian Sea accounts for about one third of global mid-water column denitrification (Codispoti *et al*., 2001) which is estimated to be ~30 Tg N y^{-1} (Naqvi, 1987; Bange *et al*., 2000). Seasonal atmospheric driving forces make substantial variation in hydrography and trophic status transforming the Arabian Sea into a perennial source of CO_2 to the atmosphere (Sarma *et al*., 1998; Sarma, 2003).

2.2 Sampling and Analysis

Time series sampling was carried out 10 times from January to December 2012 along a transect in the shelf waters off Kochi (Fig. 2.2) as part of the project "*Time-Series studies on the biogeochemical aspects in the estuarine and coastal waters of Kochi, southwest coast of India (Kochi Time-Series, KoTS)"* using the FORV Sagar Sampada to chart the responses of the *SEAS* towards seasonal changes. The study period can be generally divided into four seasons viz., spring inter monsoon (SIM: March-May), summer monsoon (SM: June- September), fall inter monsoon (FIM: October-November) and winter monsoon (WM: December-February). In addition, the Mangalore shelf transect was also monitored three times in SIM (April), SM (September) and WM (December). There were six stations (bottom depth 13, 20, 30, 40, 50, and 100 m) in each transect and water samples were collected from standard depths (surface, 10, 20, 30, 40, 50, 75 and 100 m). Each transect sampling was generally carried out from morning (station 1) to evening (station 6).

Details of sampling dates and tidal activity are given in Table 2.1. Station 1 is located in the dredged navigation channel of the Cochin Port which connects the estuary and the sea. For convenience, both transects were classified into four zones *viz.* nearshore (station 1), inner shelf (stations 2 and 3), mid-shelf (stations 4 and 5) and outer shelf (station 6).

Table 2.1. Sampling inventory details with phase of the tide.

S.No.	Sampling period (2012)		Station 1	
	Month	**Dates**	**Starting time**	**Phase of the Tide**
		Off Kochi		
1	January	21-23	14 00 h	Low Tide
2	March	3-5	06 20 h	Intermediate
3	April	13-15	06 00 h	Intermediate
4	May	23-25	05 00 h	Low Tide
5	June	28-30	06 15 h	High Tide
6	July	27-29	06 00 h	High Tide
7	September	1-3	09 00 h	Intermediate
8	October	5-7	09 50 h	Low Tide
9	November	9-11	06 20 h	High Tide
10	December	8-10	05 10 h	High Tide
		Off Mangalore		
1	April	17-19	13 15 h	High Tide
2	September	6-9	06 00 h	Intermediate
3	December	13-15	06 40 h	Intermediate

Conductivity, Temperature and Depth (CTD) profiler (*SBE 11plus, Sea-Bird, Redmond, WA, USA*) attached to a rosette with Niskin samplers was employed for data collection and water sampling (Fig.2.3). First sub-samples were drawn for dissolved oxygen (DO) followed by samples for pH, total alkalinity (T_{Alk}), nitrous oxide (N_2O) and methane (CH_4) in glass

reagent bottles. Water samples for pH and T_{Alk} (125 ml each), CH_4 and N_2O (60 ml each) were collected carefully without introducing air-bubbles, poisoned with saturated mercuric chloride (0.3 ml/60 ml) to arrest microbial activity, and were then tightly stoppered and stored in dark until analysis. Water samples for nutrients, particulate organic carbon (POC) and chlorophyll were collected only after collecting samples for dissolved gases analyses.

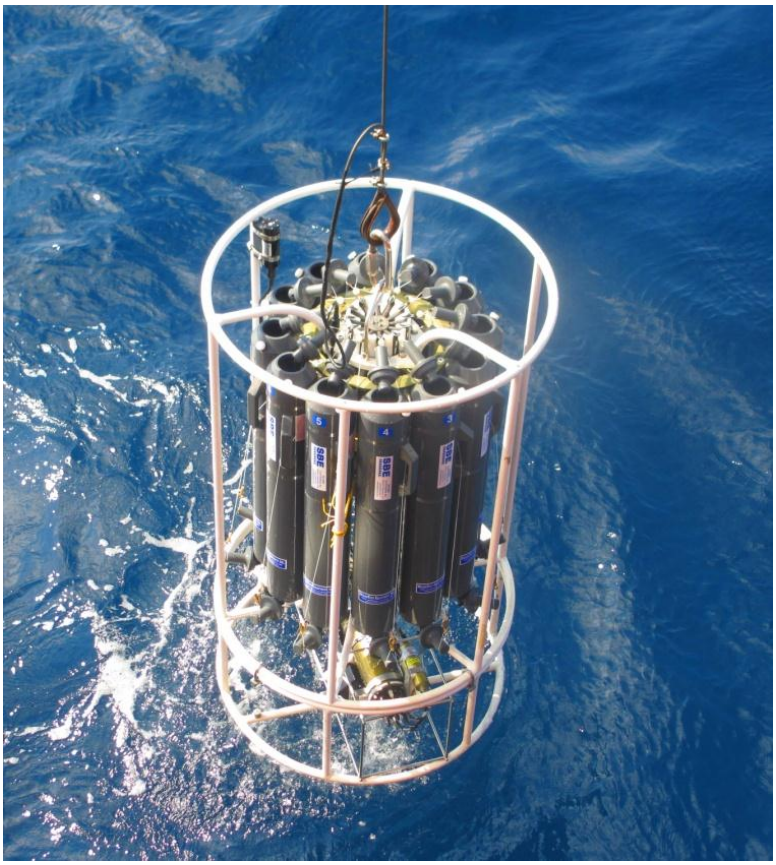


Figure 2.3. CTD Rosette attached with Niskin samplers

2.2.1 Temperature and salinity

Temperature and salinity were recorded using aforementioned CTD profiler with an accuracy of ±0.0003 S/m and ±0.001°C for conductivity and temperature respectively.

2.2.2 Dissolved Oxygen (DO)

The samples for dissolved oxygen (DO) were collected in 60 ml bottles, fixed with 0.5 ml each of Winkler reagents and titrated against 0.001N thiosulphate using starch as indicator (Grasshoff *et al.,* 1999). Since the NO_2 levels were generally low, sodium azide was not added for preventing interference with O_2 (Wong, 2011). The small amount of oxygen carried by the reagents was not considered. The detection limit was about 2 µM. Apparent Oxygen Utilization (AOU) was estimated as a difference between the theoretical O_2 solubility calculated according to Garcia and Gordon (1992) and the measured DO concentration.

2.2.3 Nutrients

Samples for nutrients (nitrate, nitrite, ammonium, phosphate and silicate) were analyzed using a Spectrophotometer (*Evolution 201, Thermo, USA*) onboard the vessel, following standard procedures (Grasshoff *et al.,* 1999). Analytical precision expressed as standard deviation for nitrate, nitrite, ammonium, phosphate and silicate were ±0.05, ±0.01, ±0.07, ±0.02 and ±0.03 µM respectively.

Nitrite and Nitrate: Nitrite determination based on reaction with an aromatic amine (Sulfanilamide) to form a diazonium compound, which gets coupled with N-(1-napthyl)-ethylenediamine, to form an azo dye. The absorbance of the dye was measured spectrophotometrically at 543 nm. The nitrate in the sample is reduced quantitatively to nitrite by passing through a column containing copperised cadmium granules. The conditions were so adjusted that the nitrate was quantitatively reduced to nitrite but not further. The nitrite thus produced was determined by diazotisation with sulfanilamide followed by coupling with N- (1-naphthyl) ethylene diamine dihydrochloride. Nitrite in the sample will pass through the reduction column without change. Hence the total nitrate plus nitrite will be determined by the method. The difference between samples analysed after reduction (nitrite+nitrate) and directly (nitrite) gives nitrate concentration in the sample.

Phosphate: Phosphate in seawater sample is allowed to react with acid – ammonium molybdate. The phosphomolybdate complex, is reduced by ascorbic acid in the presence of antimonyl ions (to accelerate the reaction) to a blue coloured complex containing 1:1 atomic ratio of phosphate and antimonyl ions. The extinction of the blue colour is measured at 880 nm using 5 cm cell. To avoid interference by silicate, the pH is kept below one.

Ammonium: Ammonium was determined by the indophenol blue method. Ammonium in the sample is allowed to react with hypochlorite in moderately alkaline solution to form monochloramine in presence of phenol, catalytic amounts of nitroprusside ion and excess of hypochlorite.

The absorbance of the Indophenol Blue complex is measured spectrophotometrically at 630nm. A citrate buffer is added to prevent the precipitation of Calcium and Magnesium Hydroxide and Carbonate present in sea water.

Silicate: The seawater sample is allowed to react with acid-molybdate reagent under conditions which result in the formation of silicomolybdate, phosphomolybdate and arsenomolybdate complexes. Oxalic acid is added to reduce the silicomolybdate complex to give a blue reduction compound and to simultaneously decompose any phosphomolybdate so that interference from phosphate and arsenate is eliminated. The absorbance of silicomolybdenum blue complex is measured spectrophotometerically at 810nm.

2.2.4 Chlorophyll *a*:

2 L of samples for chlorophyll (Chl *a*) estimation were filtered onboard through Whatman 47 mm GF/F filter (0.7 μm) under gentle vacuum (<50 mm Hg) and kept at -20°C till the analysis. Chl *a* pigments retained on the filters were later extracted with 90% acetone at 4°C in the dark for 12 h and measured fluorometrically (JGOFS, 1994).

2.2.5 Particulate organic carbon (POC)

The samples for POC were filtered through pre-combusted (4 hrs @ 450°C) 47 mm Whatman GF/F filters and stored at -20ºC until analysis. The samples were dried at 40ºC overnight, fumigated with HCl in a desiccators for 6 hrs to remove the inorganic carbon, again dried overnight and analysed using CHN analyser (*Flash EA 2000, Thermo, USA*).

IAEA-CH3-cellulose was used as a standard and the POC concentration in the filters was obtained from a linear fit equation (R^2 >0.99), where x axis is area and y axis is POC concentration of the standard.

2.2.7 Nitrous oxide and its fluxes

The dissolved nitrous oxide was analysed by multiple equilibration technique of McAullife (1971). 25 ml of the sample was equilibrated successively with an equal volume of ultrapure helium in a gas tight syringe by vigorously shaking the syringe at room temperature for 5 minutes using a wrist action shaker. After equilibration, the gas mixture from the headspace was injected through a 5 ml sampling loop into a gas chromatograph (*Shimadzu, 2010*) and separated over a Chromosorb column (80/100 mesh) at 40°C. N_2O was detected with a ^{63}Ni Electron Capture Detector (ECD). Precision of the analysis was ~ 4%. Calibration was achieved using a gas mixture of N_2O in nitrogen (*Alltech Associated Inc, IL. USA*). The percentage saturation of N_2O was calculated as,

$$N_2O \text{ saturation} = (C_w/C_a) \times 100,$$

where, C_w is the measured concentration of dissolved N_2O and C_a is the equilibrium concentration in seawater. C_a was calculated using

$$C_a = \beta\,(T, S)\, x' P$$

where, x' is the atmospheric dry mole fraction of N_2O, P is the atmospheric pressure and β is the Bunsen solubility as a function of *in situ* temperature and salinity (Weiss and Price, 1980). Surface saturation of N_2O was calculated relative to an average atmospheric concentration of

323 ppb as reported recently by Rao *et al*. (2013) for the east coast of India. ΔN_2O is derived as the difference between C_w and C_a.

The sea-air exchange flux density was computed from

$$F=k_w(u)\,(C_w-C_a)$$

where, k_w is the gas transfer velocity which depends on factors like wind speed, temperature, turbulence in both the atmosphere and the water (Liss and Merlivat, 1986; Upstill-Goddard, 2006). For N_2O, three different parameterizations were used (Liss and Merlivat, 1986 (LM86); Wanninkhof, 1992 (W92), Nightingale *et al*., 2000 (N00)) to calculate k_w.

k_w was adjusted by multiplying with $(Sc/600)^{-n}$ (n = 2/3 for wind speeds <3.6 m s^{-1} and n = 1/2 for wind speeds >3.6 m s^{-1}) for LM86, $(Sc/660)^{-0.5}$ for W92, and $(Sc/600)^{-0.5}$ for N00, where Sc is the Schmidt number for N_2O. Sc was calculated using empirical equations for the kinematic viscosity of seawater (Siedler and Peters, 1986) and the diffusion coefficient (in m^2 s^{-1}) of N_2O in water (Rhee, 2000). N_2O diffusion coefficients (DN_2O in m^2 s^{-1}) were calculated using Eq. (1) derived from the data given in Broecker and Peng (1974) and, alternatively, using the new Eq. (2) derived from a compilation of actual measurements (Rhee, 2000):

$$\log_{10} DN_2O = -1008.28/RT - 5.245 \quad (1)$$

$$DN_2O = 3.16 \times 10^{-6} \exp(-18370/RT), \quad (2)$$

where, T is the water temperature in K and R is the universal gas constant. Eq. (1) is based on 5 5 measurements of N_2O diffusion

coefficients in water in a temperature range from 14° to 25°C while Eq. (2) is based on 49 measurements in a water temperature ranges from 14° to 95º, thus providing a more reasonable fit for the N_2O diffusion with considerably reduced uncertainty of less than 10% (Rhee, 2000, Bange *et al*., 2001). Hourly wind speed measured onboard using Automated Weather Station (*Zenith*) installed 10 m above the sea surface was averaged to obtain daily mean and was used for calculation of transfer velocity.

2.2.8 Methane and its fluxes

Dissolved CH_4 in the seawater samples was also determined by multiple equilibration technique (McAullife, 1971) similar to that of N_2O. After equilibration with an equal volume of ultrapure helium, the headspace was injected through a 5 ml sampling loop into a gas chromatograph (*Shimadzu GC 2010 Series*) equipped with a Flame Ionization Detector. The separation was achieved over a 1.8m long stainless steel column (inner diameter 2mm) packed with molecular sieve (5A 80/100 mesh) maintained at a temperature of 60°C. The instrument was calibrated using several dilutions of a standard gas (*Scotty II Analysed Gases, Supelco, Inc., USA*). All carrier gases and combustion gases used were ultra-pure grade. The precision of measurement was 4%. Air samples were frequently run to monitor instrument response, which was linear within the range of concentrations encountered during the course of this study.

The sea–air flux of methane was calculated following Wanninkhof (1992). Equilibrium solubility of CH_4 was calculated according to

Wiesenburg and Guinasso (1979) using an average atmospheric CH_4 concentration of 1.90 ppm. The Schmidt number (Sc_{660}) for CH_4 was computed for a given salinity and temperature using the formulation given by Wanninkhof (1992). Hourly measured wind speed was averaged to obtain daily mean and was used for transfer velocity calculations.

2.2.9 CO_2 and its fluxes

CO_2 levels in aquatic systems are characterized by factors like pH, T_{Alk}, DIC, pCO_2 and fugacity of CO_2. T_{Alk} and DIC are temperature independent while the other variables are temperature-dependant. Knowledge of any two variables along with temperature, salinity and pressure allows the determination of the other variables. For the current study, pCO_2 was calculated indirectly using pH and T_{Alk}. Potentiometric Titrator (*907 Titrando; Metrohm, Switzerland*) was used for measuring pH and T_{Alk} (Frankignoulle *et al*., 2001). For the TA measurement, 50 ml of sample was titrated potentiometrically against 0.1 N HCl at 25°C to an end point of 4.5. The progress of the titration was monitored using a glass electrode/reference electrode pH cell. Total alkalinity was computed from the titrant volume. Sodium bicarbonate was used to standardise the HCl. The pH was calibrated on the NBS scale as described by Frankignoulle and Borges (2001) using NIST certified buffers (Merck) at 25°C. The pH values on NBS scale were first converted to the pH *in situ* and then to total scale. Analytical precision of pH was ±0.005. The accuracy of TA checked using the Certified Reference Material (provided by Dr. A. G. Dickson, Scripps Institute of Oceanography, USA, Batch No.111) was found to be within ±1%. Dissolved inorganic carbon (DIC) and partial

pressure of carbon dioxide (pCO_2) were computed from measured pH and T_{Alk} couple along with temperature, salinity, depth and nutrients (P and Si) using the carbonic acid dissociation constants over the salinity range derived by Waters *et al*., (2014) using the *CO_2SYS* programme (Lewis *et al*. 1998) with a precision of 9-13 µatm. The air-sea flux of CO_2 was estimated using atmospheric and water pCO_2 with daily averaged wind speed using the following empirical relation

$$F = kw\ \beta\ (pCO_{2water} - pCO_{2atm})$$

where, *kw* and β are the gas transfer velocity and solubility of CO_2 in sea water. The gas transfer velocity was calculated following Wanninkhof (1992). The solubility of CO_2 was calculated according to Wiess (1974) using an average atmospheric CO_2 concentration of 393 µatm for 2012 (ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_annmean_gl.txt). k_w was adjusted by multiplying with $(Sc/600)^{-0.5}$. A positive value indicates a gas efflux from the sea to the atmosphere and a negative value denotes the net flux from the atmosphere to the sea.

Chapter 3

INFLUENCE OF UPWELLING ON THE BIOGEOCHEMISTRY OF SOUTHEASTERN ARABIAN SEA SHELF

Contents

3.1 Introduction

The seasonally reversing winds and currents results in large changes in the mixed layer dynamics of the northern Indian Ocean, in particular, the Arabian Sea (AS), making it highly productive. During summer monsoon (SM), both the western and eastern AS experience upwelling which brings cold, low oxygen and nutrient-rich waters to the surface (Smitha, 2010; Shah *et al.,* 2015). During winter monsoon (WM), convective mixing enriches nutrient levels in the euphotic zone leading to enhanced biological production in the northern AS (Madhupratap *et al*., 1996, 2001; Prasanna Kumar *et al*., 2001; Wiggert *et al*., 2005). The enhanced organic production consequently increased the sinking particle flux and the increased demand

for their oxidation leads to severe oxygen depletion in the sub-surface depths (150 – 1000 m) to form oxygen minimum zone (OMZ). The OMZ (DO <20 µM) in the AS is believed to be the largest/thickest in the world and its horizontal propagation onto the continental shelf during upwelling results in severe coastal hypoxic/anoxic events (Naqvi and Jayakumar, 2000; Naqvi *et al*., 2000, 2006, 2009). In addition, upwelling and its intensity significantly influences the composition and abundance of biological production including fish eggs and larvae (Bakun and Parrish, 1982; Balan, 1984; Johannessen *et al*., 1987; Naqvi *et al*., 2006). Hence, the development of hypoxia/anoxia over the shelf associated with upwelling is considered as a major ecological event (Naqvi and Jayakumar, 2000; Rabalais *et al*., 2001).

Time-series measurements are necessary to understand the seasonal and interannual variability in oceanographic processes. Such measurements from the Indian Ocean are scanty compared to the Atlantic and Pacific. However, the first time-series observation from the Indian coast made by Banse (1968) off Kochi during 1958-1960 had reported the influence of summer monsoon on the hydrography and water quality of the southeastern Arabian Seas (*SEAS*). He opined that the upwelling is mainly caused by the currents and not the winds, as reported earlier by Ramasastry and Myrland (1959). Banse (1959) also observed significant variation in sea surface temperature (4–5°C) with annual maximum between April–May and minimum in July–August based on 16 years of surface data off Calicut (~11.3°N, *SEAS*). Subsequent measurements in the *SEAS* have tried to explain the physical dynamics of upwelling (Sharma, 1978; Johannessen *et al*., 1987; Schott and McCreary, 2001; Shankar *et al*., 2002; Shenoi *et*

al., 2005; Jayaram *et al*., 2010) but its effects on shelf system biogeochemistry were not studied in detail. Apart from the two years observations by Banse (1968) off Kochi, there are only two other sites in India, where continuous observations are being made in the coastal waters. They are in the coastal waters off Goa (Candolim time-series, CaTS since 1997) on the central west coast and off Visakhapatnam (since 2007) on the central east coast of India. This evidences the significance of time-series measurements, as they are indicators of long term changes in the seas in response to global climatic perturbations (Church *et al*., 2013).

In view of the above, the present time-series observations were conducted in the coastal waters off Kochi, *SEAS* at 30-45 days interval between January and December 2012 (total 10 observations) to address the biogeochemical responses to the seasonality/upwelling over the *SEAS* shelf.

3.2 Kochi shelf dynamics

3.2.1 Intra-annual variation in Hydrography

The sea surface temperature (SST) off Kochi during the study period (Fig. 3.1) exhibited a progressive warming between January (>28°C) and April (>30°C) coinciding with hot atmospheric conditions during premonsoon. Under the intense solar radiation SST showed maximum (30.08-30.7ºC) in April. By May, SST of inner shelf exhibited a temperature drop of 2.8 to 3.4ºC than that in April and the cooling continued till the peak of SM (August). The mixed layer depth (MLD, 0.2 density difference from surface) was thin (~20 m) during SM and thick

(~50m) in the outer shelf during winter monsoon (WM, November-December).

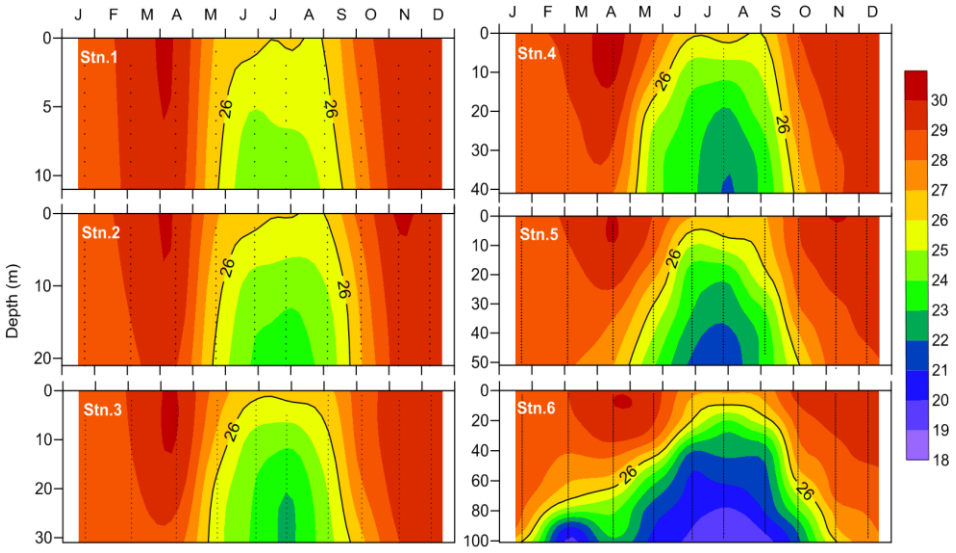


Figure 3.1. Monthly variation in temperature (°C) at different stations over the Cochin shelf. Refer Fig. 2.2 and/or Table 2.1 for station details.

The depth of 26°C isotherm (D_{26}) was generally seen to closely follow the MLD (Fig. 3.1) and stayed for maximum period during entire study, hence, D_{26} is considered here to track the upwelling. D_{26} was initially at 100 m in the outer shelf during January. It shoaled progressively to 80 m by March, remained consistent up to April, shoaled further to 10 m by July, thereafter dipped slightly to 20m in September and then sharply collapsed to ~70 m by October before its complete disappearance in November. This kind of oscillation discerns the following processes: (i) initiation of upwelling in the deeper layers during January-March and its progression to the upper layers during June-September, (ii) sharp

withdrawal of upwelling during September-October. It also further explained that the main progression of upwelling took about 4 months between April-July whereas its collapse happened within a month between September-October.

Satellite based studies often consider drop in SST as one of the criteria for upwelling (Shah *et al.,* 2015) but this study shows that there is a significant time lag between the appearance of upwelling at depth and its entry to the mixed layer. The D_{26} first appeared in the mid-shelf by the end of April and entered the inner shelf by mid-May, which shows that the time taken for advancement of upwelling between outer and mid-shelf is quite longer (100 days @ 0.22 km d^{-1}) than from mid-shelf to inner shelf (15 days @ 1.29 km d^{-1}). The rate of upwelling in terms of vertical upliftment of isotherms is on the order of 1.3-1.9 m d^{-1}. This is in agreement with ~1.5 m d^{-1} reported earlier for the *SEAS* by Johannessen *et al*. (1987). The upwelling is generally slow to begin with (March–April), but it gets momentum by May as D_{26} shoaled from about 45 m to 15 m and extended ~30 km toward the coast. By July, the D_{26} has reached near shore surface indicating the complete and peak spreading of upwelling over the entire shelf, which sustained up to August. MLD was at minimum (3-9 m) during the peak upwelling period. Similarly, the withdrawal of upwelling followed a sequence with the sharp withdrawal of D_{26} from the near shore to mid-shelf during August-September and finally from the outer shelf by October end. In response, SST increased by 2-3°C during November-December. Based on the time occupation of D_{26} in the shelf waters i.e. from the time of its onset to offset at the shelf entrance, the upwelling over the Kochi shelf has sustained for a total

period of 9 months from January - November. Therefore, the upwelling has a greater influence on the shelf biogeochemistry and biology.

The presence of warm (>28°C) and low saline (<34.5) waters during January in the upper 50 m of the outer, mid and inner shelves (Fig. 3.1, 3.2) could be identified as the intrusion of Bay of Bengal low saline waters (BBLSW) into this region. Prasannakumar *et al.* (2004) have shown that during winter, the East India Coastal Current (EICC) feeds the BBLSW to the West India Coastal Current (WICC) along the eastern Arabian Sea. Parallely, the outer shelf experienced the intrusion of Arabian Sea High-Salinity Water (ASHSW) at depth through upwelling resulting in stratification of the water column. Continuation of this hydrography for ~40 days (by March) has led to a warmer mixed layer (≥29°C) capped over a relatively cool and saline waters in the bottom. As the season changed to spring inter monsoon (April), the ASHSW advanced into the mid- shelf through upwelling as can been seen from the clear upliftment of the 35.5 isohaline from ~80 to 60 m between March - April and to ~15 m in May. At the same time, the BBLSW had completely withdrawn from the outer shelf and started withdrawing from the middle and inner shelves. This indicates that the displacement of BBLSW from the *SEAS* under the advent of upwelling progresses from the outer shelf to the inner shelf.

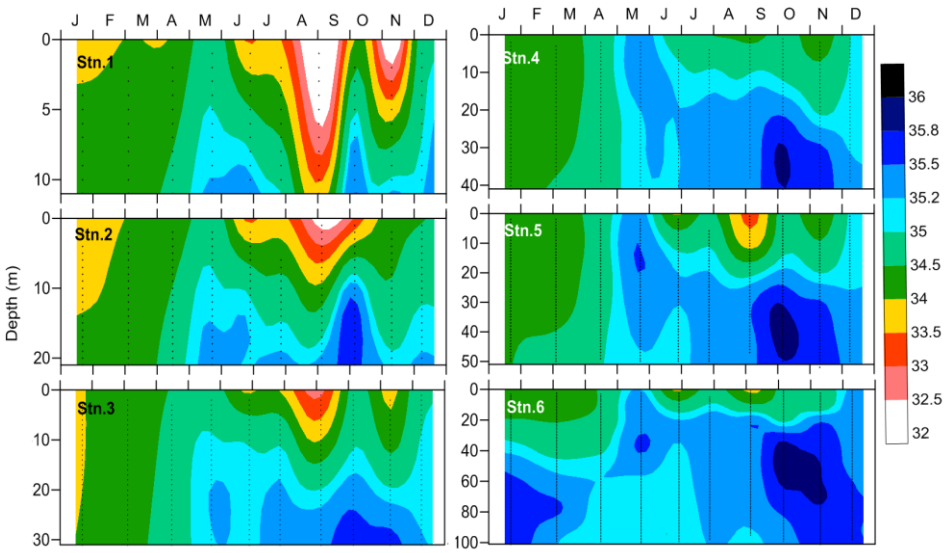
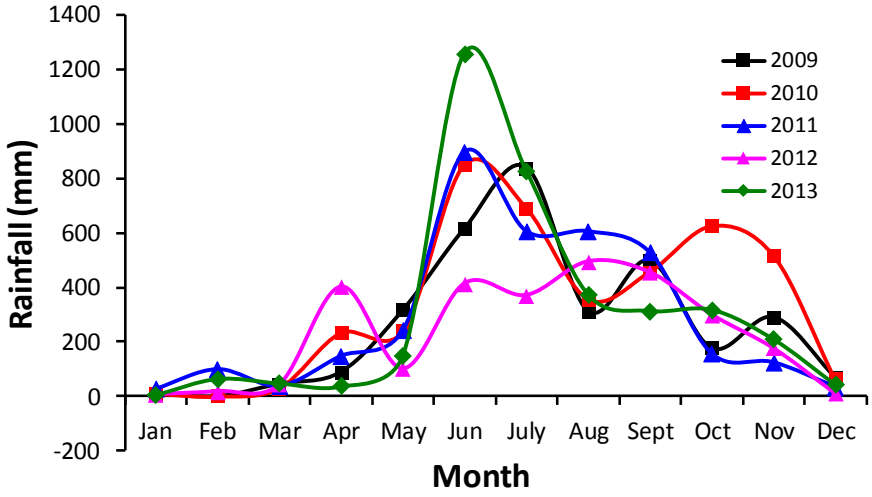


Figure 3.2. Monthly variation in Salinity along the Cochin transect

The year 2012 witnessed very poor monsoon rains over the study region (Fig.3.3). The freshwater input was considerably reduced due to sporadic and patchy monsoon. The influence of this patchy flow of fresh water can be noticed from the sea surface salinity (SSS) which dropped by about 1.5-2.0 between May-June (Fig. 3.2), was relatively high in July (33.8) and minimum in September (31.65). Overall, the monsoon precipitation considerably lowered the surface salinity to <34 (June–September) and established strong stratification. According to India Meteorological Department (2013), 2012 was an Indian Ocean Dipole (IOD) year with a relatively short duration during July–October; the IOD index was near neutral during June–July and positive from the beginning of August that resulted in deficient monsoon rainfall over the Indian subcontinent during the first half of the season followed by neutral and above normal rainfall during August and September, respectively.

Consistent to this, the study region did receive considerable rainfall just before our June and September observations, but the period preceding the July observations was largely dry when the upwelling was at peak. This pattern of rainfall is clearly reflected in the surface salinity distribution during SM (Figs. 3.2 and 3.3) with the lowest recorded in September.



(Source: http://hydro.imd.gov.in/hydrometweb/(S(1pvdct45dx3hde55iic13a45))/DistrictRaifall.aspx).

Figure 3.3. Monthly rainfall pattern over the Kochi region from 2009 to 2013

3.2.2 Response of Dissolved Oxygen and Nutrients to Upwelling

Monthly variations in DO (Fig. 3.4), nitrate (Fig. 3.5), nitrite (Fig. 3.6) ammonia (Fig. 3.7), phosphate (Fig. 3.8) and silicate (Fig. 3.9) have clearly showed the seasonality in the environmental conditions. The water column was well-mixed, oxygenated and nutrient-impoverished during January-April. During January, the upper 50 m remained saturated with oxygen (DO>200 µM) and depleted with nutrients (NO_3^-: <0.5 µM; PO_4^-:

0.2-0.3 µM) indicating oligotrophic conditions. Although euphotic column showed insignificant changes up to April, there was nutrient enrichment at depth over the outer shelf when DO reduced to 70-80 µM due to progression of upwelling. Subsequently, the DO depletion and nutrient enhancement continued to propagate towards the inner shelf by May and spread over the entire shelf region till September. The maximum effect of upwelling was seen between May and June which changed the subsurface waters (>30 m) to hypoxic (<50 µM) and nitrate rich (>10 µM) and entire water column between outer and mid-shelf occupied with very poor ammonia concentrations (<0.5 µM).

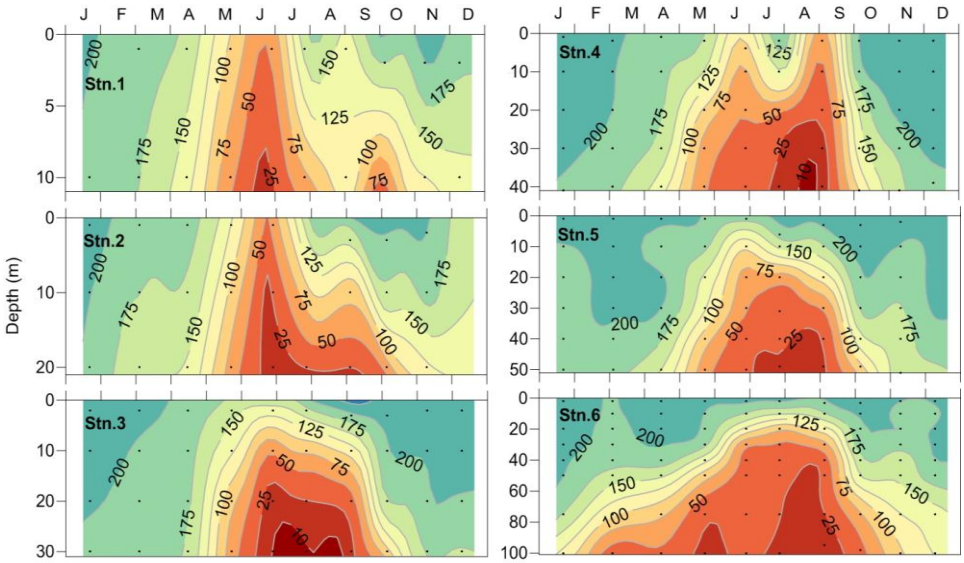


Figure 3.4. Distribution of dissolved oxygen (µM) in the coastal waters of Kochi

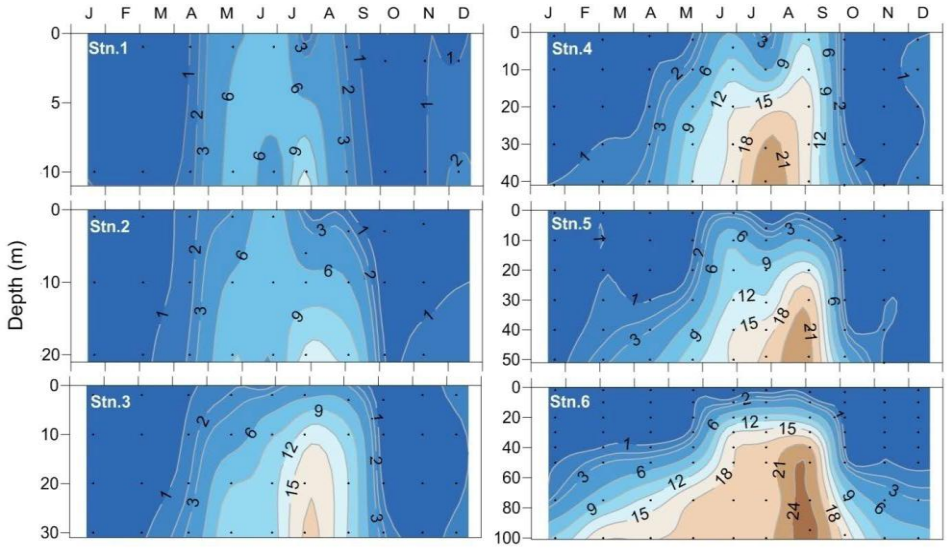


Figure 3.5. Variations in nitrate (μM) in the coastal waters of Kochi

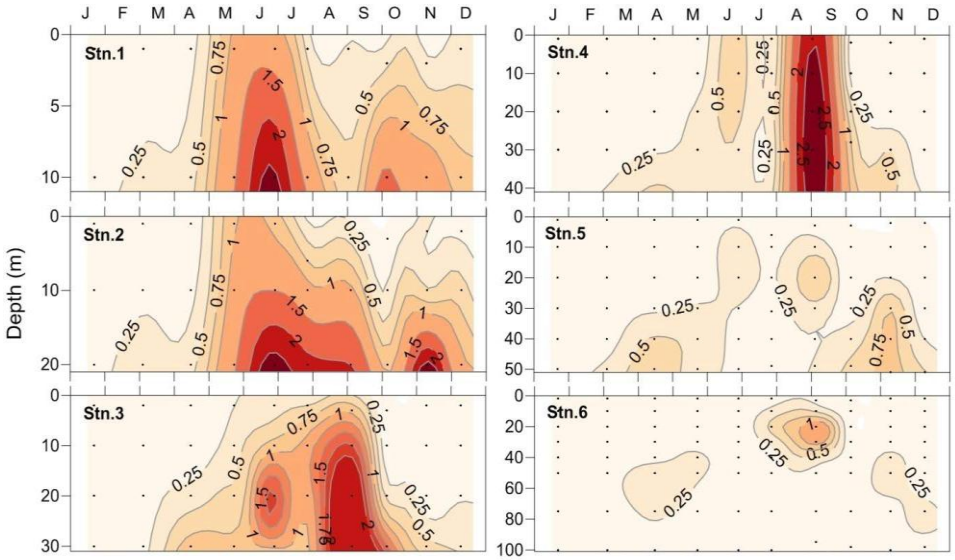


Figure 3.6. Monthly variation in nitrite (μM) along the off Kochi

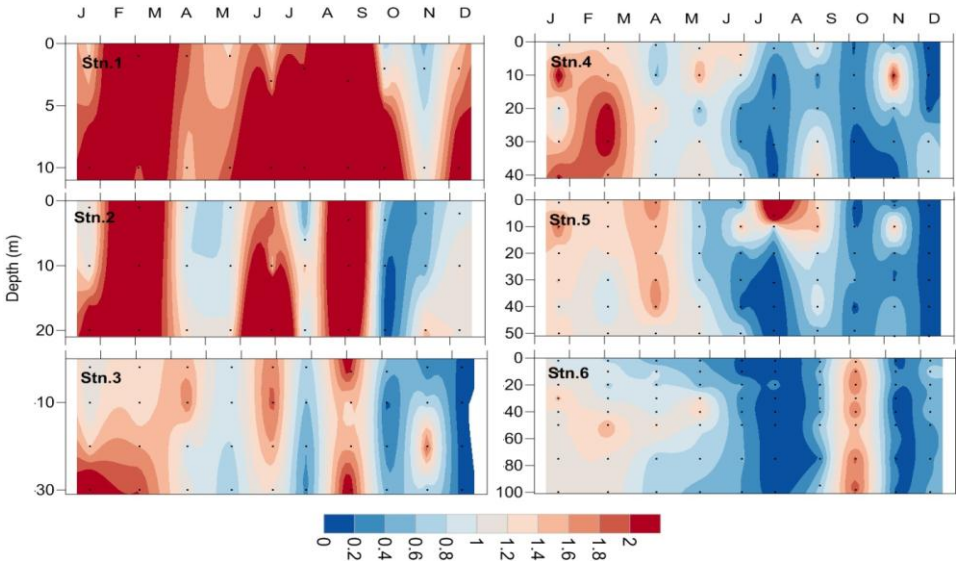


Figure 3.7. Monthly variation in Ammonia (μM) along the off Kochi

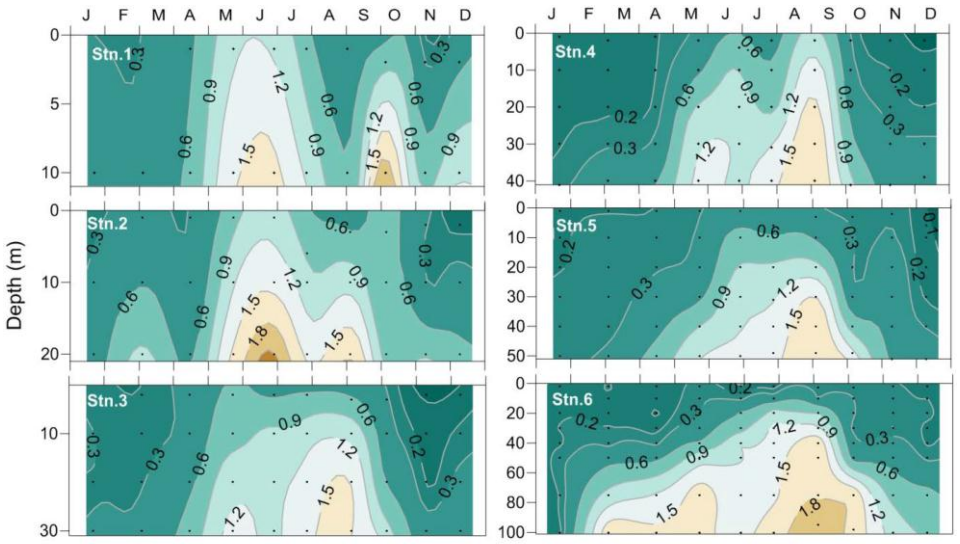


Figure 3.8. Variation in phosphate (μM) in the coastal waters of Kochi

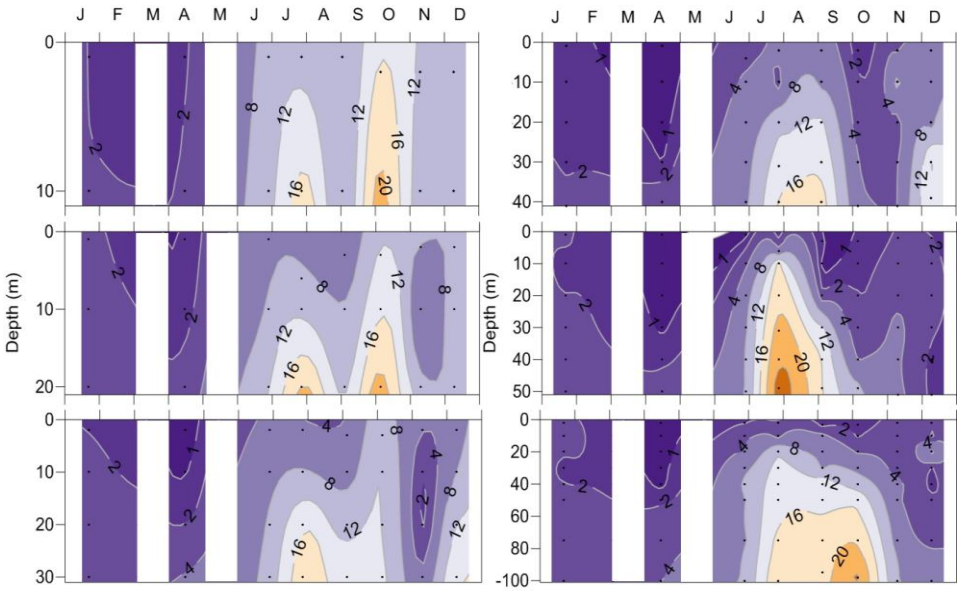


Figure 3.9. Monthly variation in Silicate (µM) along the off Kochi

Similar to N and P, silicate concentration also showed enrichment during SM upwelling (Fig. 3.9). These seasonal sequences of subsurface changes in hydrography, DO, and nutrients of 2012 are similar to the results by Banse (1968), Rao and Ramamirtham (1976), Sharma (1978), Menon and George (1977), and Johannessen *et al*. (1987).

The impact of upwelling was severe in surface waters of coastal stations (stations 1 and 2) in June, where the DO saturation was at its minimum (6.75% and 15.6%, respectively) and nutrient levels were at their maxima. These stations are affected by the monsoon discharges from the Cochin estuary, but as the sampling was conducted during the high tide in June (Table 2.1), the influence of runoff in the nearshore region is not expected to be very high. The atmospheric fallout of N

through rainfall (~4 μM of nitrate, Naqvi et al., 2000) also adds to the mixed layer concentrations, but this is much smaller relative to the supply through upwelling. High concentrations of nitrite in the nearshore and inner shelf regions in June (up to 3.2 μM, Fig. 3.6) associated with strongest hypoxia (7 μM) of the entire study is likely due to the denitrification in the anoxic seabed. Primary nitrite maximum was seen mostly at the bottom of euphotic zone, for example, at station 3 intermediate depths during SM and close to the bottom during non-upwelling periods (Fig. 3.6) due to oxidation of excretes of secondary producers and nitrification of ammonia. Similar maximum was also observed over the midshelf off Kochi during 1958–1960 (Karl Banse, personal communication).

The transition period (October) witnessed a sharp decline in nutrient concentrations (NO_3^-: 0.49±0.5, NO_2^-: 0.16±0.2 and PO_4^-: 0.29±0.1 μM) and rise in DO (>150 μM) following the abrupt withdrawal of upwelling and deepening of the mixed layer. Subsequently, the MLD deepened and the DO concentrations increased further to ~200 μM.

3.2.3 Changes in nutrient stoichiometry

A comparison of nutrient stoichiometry with Redfield ratio (N:Si:P= 16:15:1) reveals a clear seasonality (Fig. 3.10). The N/P ratio was low (<6) during FIM and WM but increased during SIM and SM periods (9-17). Between January and May, N/P increased from 5.5 to ~10 and further to 12.9 (June) coinciding with peak upwelling. It decreased

drastically to <6 in July, before reaching close to Redfield ratio (14) in September.

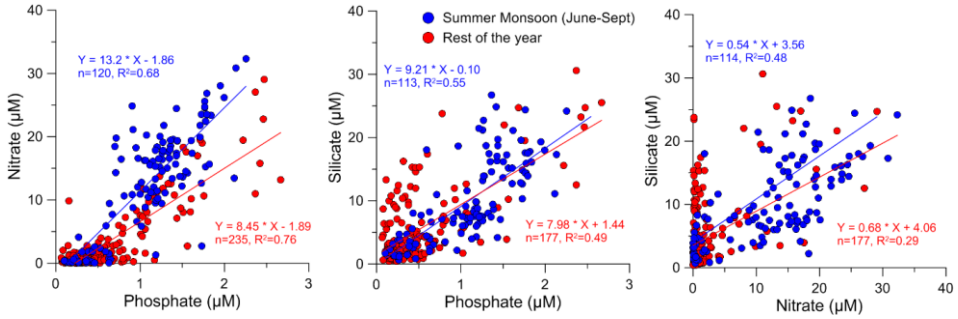


Figure 3.10. Variation in stoichiometric ratios of nutrients between summer monsoon and rest of the year.

Nutrient stoichiometry especially Si/P (9.2 and 8.0) and Si/N (0.55 and 0.7) ratios remained almost similar between summer upwelling (June-September) and rest of the year. N/P ratio was close to Redfield ratio during upwelling (13.6) compared to non-upwelling period (8.8) suggesting nitrogen deficiency during the latter period. Among the non-upwelling seasons, the N/P ratios of SIM (9.7) and WM (9.6) were comparable and higher than FIM (7.3).

3.2.4 Biological response to Upwelling and associated nutrients

The low Chl*a* levels (0.01 to 0.62 mg m^{-3}) during January-March (Fig. 3.11) indicates oligotrophic conditions. It increased in April due to the proliferation of *Trichodesmium erythreaum* (Jabir *et al*., 2013), the second dominant phytoplankton group after diatoms, under the prevailing calm, warm and bright sun light conditions. Sub-surface chlorophyll

maximum (SCM) was pertinently seen during this period supported by deeper photic depths and nutrients injection (at outer shelf) following upwelling.

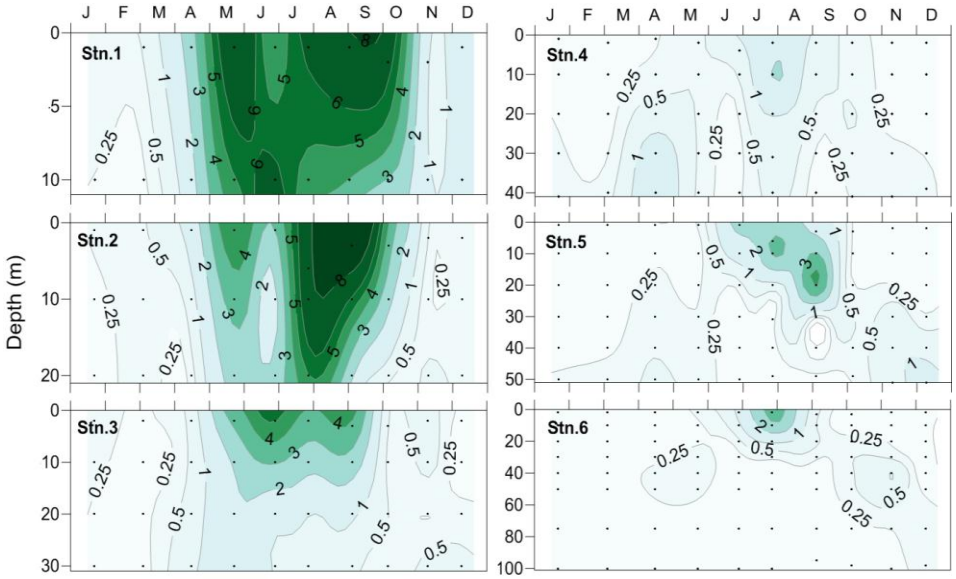


Figure 3.11. Monthly variation in Chlorophyll *a* (mg m^{-3}) along the off Kochi

With the onset of SM, since nutrients were adequately available, the SCM disappeared as the enhanced phytoplankton production is limited mostly within the shallow photic depth (~10 m) following the monsoon cloud cover. Although this is at maximum particularly up to inner shelf during June and September, high Chl*a* levels were seen extended up to upper 20 m beyond inner shelf during July when the region witnessed complete dry conditions (at least up to ten days) prior to the sampling period with no cloud cover resulting extension of euphotic depth to double to that during June.

Following the discrete patches of monsoon rains and cloud cover, the column stratification which was strong during June has substantially weakened and photic depth deepened during July, thereby the excess nutrients brought into the shelf coupled with good illumination conditions have promoted phytoplankton growth within the euphotic column. However, with the withdrawal of monsoon the Chl*a* in October quickly reduced to its pre-SM level culminating in oligotrophic conditions by December. The environmental conditions during WM were almost similar to those during SIM, but the Chl*a* concentrations during former were almost twice low to that during the latter period. The deeper photic depths during WM favored reappearance of SCM, albeit with low magnitude that the oligotrophic condition supported proliferation of relatively less intense *Trichodesmium* blooms in WM. This is supported by lower N/P ratios (3.0-4.5) in the SCM during WM compared to high ratios (7) during April indicating substantial N limitation for the primary production during the latter period.

3.3 Mangalore shelf dynamics in response to Upwelling and comparison with Kochi shelf

Like Kochi, coastal waters off Mangalore recorded clear seasonality in hydrographical and biogeochemical properties (Fig. 3.12). Maximum SST recorded in April (30.7±0.5°C) is influenced by hot atmospheric conditions. Significant drop in SST during September (27.1±0.21°C) indicates replacement of hot surface waters by cold bottom waters from off shore stations through upwelling. The D_{26} which was at ~70 m in the outer shelf by April has occupied mostly within upper 10 m over the entire shelf by September indicating peak upwelling. Although the D_{26}

remained at the similar depth off Kochi in April it shoaled only to ~20m between outer and midshelf by September (Fig. 3.1) indicating the variation in upwelling intensity between the shelves. By December, SST (29.4±0.23°C) raised again and absence of D_{26} indicates complete recession of upwelling from this shelf. The signature of BBLSW (<34.8) was seen mostly over the midshelf during April when ASHSW watermass in association with upwelling has occupied below 50 m in the outer shelf. Strong stratification has prevailed during September when salinity <33 has occupied within upper 5m of most of the shelf due to SM runoff/precipitation and ASHSW has located in the mid-depths. Nearshore recorded strongest stratification with surface salinity dropped to ~29. The stratification over the Mangalore shelf is much stronger than at Kochi as the former region is located adjacent to Western Ghats of India which results in higher monsoon precipitation/ runoff relative to Koch region. Thus the intense upwelling and runoff during SM has led to very strong thermohaline stratification in the coastal waters of Mangalore (Fig. 3.12).

Chl*a* was the lowest during April and December following similar patterns as Kochi. However, during September, a significant increase in Chl*a* was seen in the inner shelf waters off Mangalore (9.7±11 mg m^{-3}) when compared to Kochi (4.4±3.8 mg m^{-3}). Moreover, sinking dead plankton flux was enhanced at Mangalore (Phaeophytin; at Manglore- 3.2±3.5 mg m^{-3} and Kochi- 1.4±1.3 mg m^{-3}). The detailed comparison of biogeochemical responses between Mangalore and Kochi shelves to the upwelling is described in section 3.4 and Chapter 4.

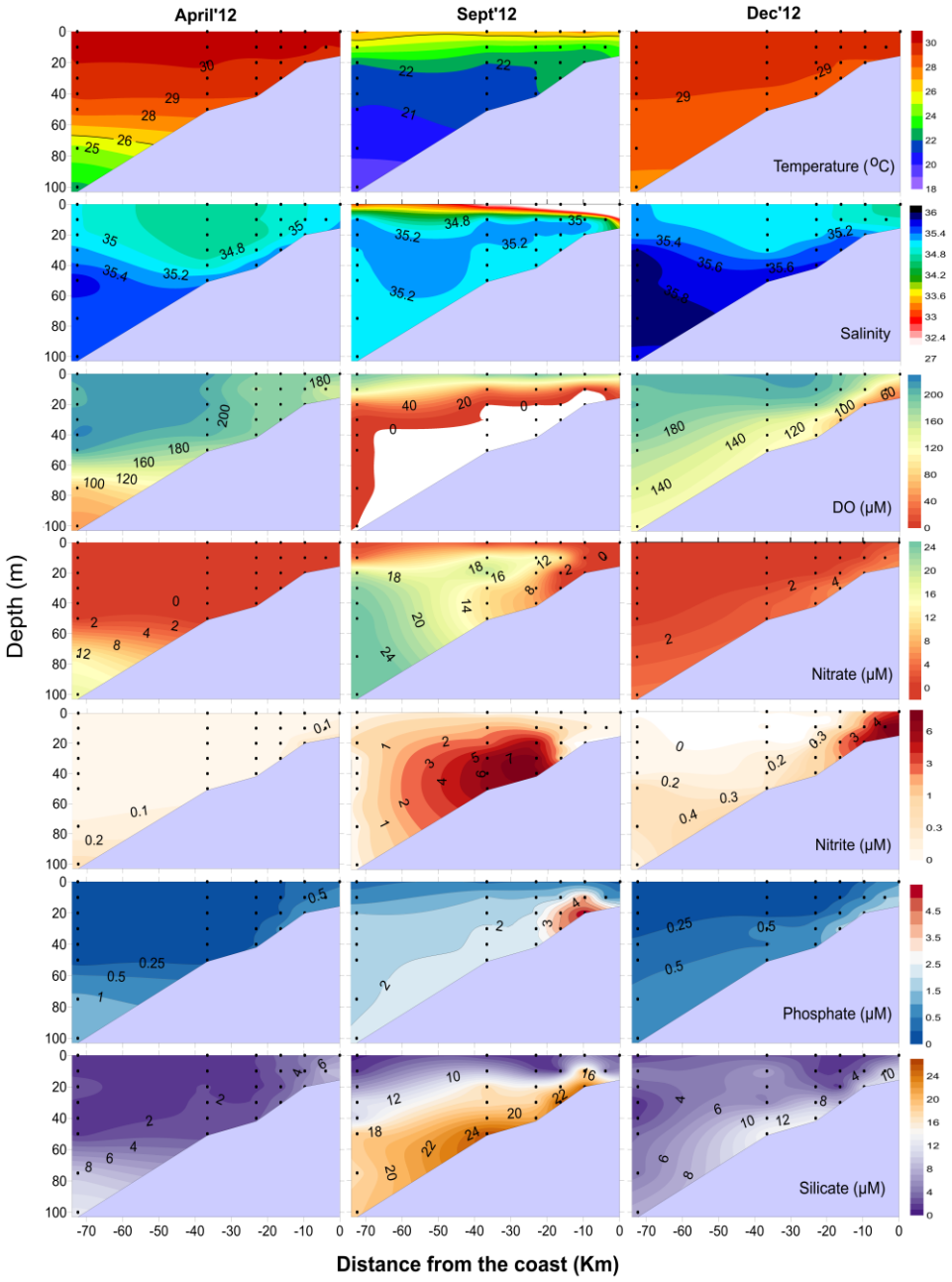


Figure 3.12. Seasonal distribution of temperature, salinity, dissolved oxygen (DO), nitrate, nitrite, phosphate and silicate along the Mangalore transect during 2012.

3.4 Comparison with historical Oxygen data (1958-60) from the Kochi shelf

Banse (1968) initiated the first time-series measurements of hydrographical parameters in the coastal waters of Kochi (at 50 m depth, ~45 km away from the coast) from July 1958 to January 1960. Here, an attempt is made to compare his historical results with the present time-series data of 2012 representing the same location (station 5; Fig. 3.13) in respect of any change in oxygen saturation. As stated earlier, 2012 was an Indian Ocean dipole (IOD) year and exhibited positive SST anomalies in the western Indian Ocean. The year 1958 was a negative IOD year whereas 1959 was a normal year (http://www.marine.csiro.au/~mcintosh/ Research_ENSO_ IOD_years.htm). 1958-59 data had shown strong inter-annual variability with a shift in the peak upwelling from August to October (in 1958 after ~1.5 months without data) in successive years, whereas 2012 showed peak upwelling in July. D_{26} was completely displaced from the water column by cold waters during peak upwelling in 1958 whereas it reached the surface during the corresponding period in 1959 and at about 10 m in 2012 (Fig. 3.13). Similarly, the bottom was penetrated by the 20°, 21°, and 22°C isotherms during peak upwelling in 1958, 1959 and 2012, respectively. This indicates relatively weaker upwelling in 2012 than in 1958 and 1959. Based on D_{26} distribution, the progression of upwelling has been found to be relatively faster in 2012 (2 months, May–July) compared to 1959 (5 months, June-October). However, the withdrawal of upwelling took about 2 months in 2012 which is comparable with that in 1958 but took less than a month in 1959. Salinity showed marked variations between the two sets of observations; especially at the surface, it was lower by more than one unit

during WM and SM of the former period. High salinity of 35.2–35.5, a signature of ASHSW, was mostly seen in the subsurface layers in 2012; such water mass was observed only during 1959 but not in 1958.

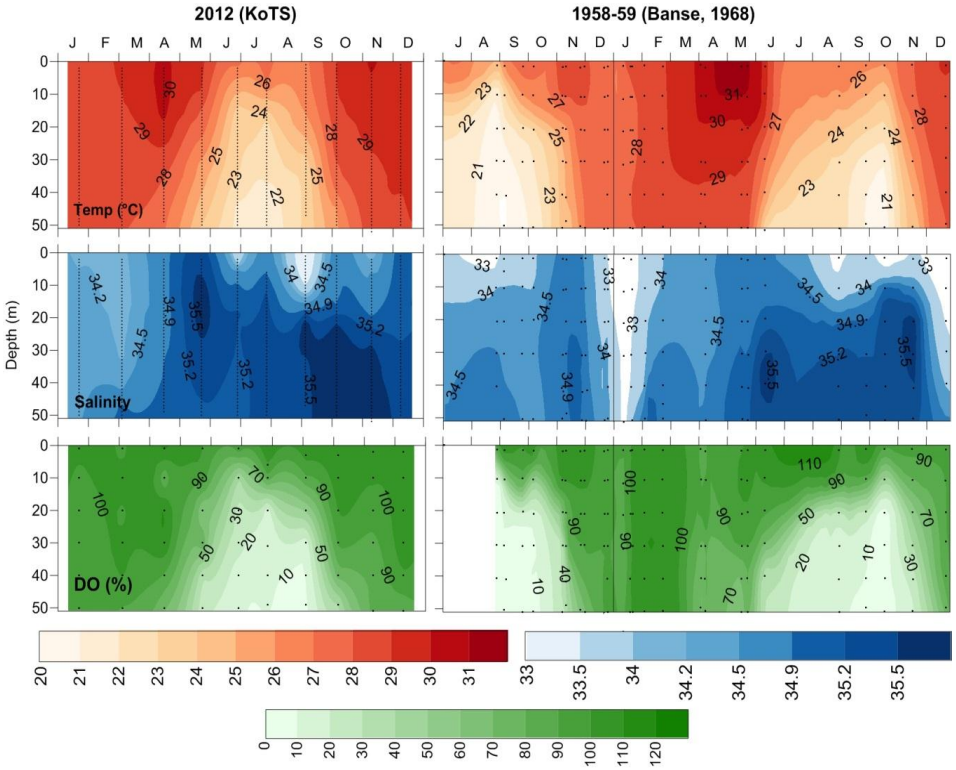


Figure 3.13. Comparison of KoTS 2012 results with that of 1958-59 (Banse, 1968) at station 5. (Reproduced with the permission of publisher)

The oxygen saturation generally showed consistency between the years (Fig. 3.13). However, a closer scrutiny during peak upwelling periods (Fig. 3.14) revealed that the oxygen saturation in the upper 10 m increased from 1958 (~18%) to 1959 (50%) and 2012 (86%), but below this depth the saturation was only 6-10% higher in 2012 compared to

earlier years. This could be due to (i) increased anthropogenic activities, (ii) variation in upwelling intensity and (iii) combination of both. The Cochin estuary (CE) has witnessed four to six fold increase in nitrate, phosphate and organic carbon levels over the years (1965-2005) following large-scale developmental activities (Martin *et al.*, 2010). Also, the turnover time of dissolved inorganic nitrogen in the Cochin estuary was found to be very fast (11±7.6 h for NH_4^+ and 118±115 h for NO_3^-) owing to high N uptake rates that are sustained by substrate replenishment rates, reflecting the estuarine response to eutrophication (Bhavya *et al.,* 2016). These N turnover rates are well within the flushing time of the estuary during monsoon (~5 days based on Gupta *et al*., 2009), hence supports the argument that much of the DIN is utilized or recycled within the estuary. This is in agreement with the studies from the Godavari estuary on the east coast of India (Sarma *et al.,* 2009, 2010) and other monsoonal estuaries of India (Krishna et al., 2016) which showed an efficient retention of nutrients (~91%) in the estuaries before reaching to the coastal ocean. Despite this, the estuarine export of DIN is significant during SM (5.5 μM NH_4^+ and 12.9 μM NO_3^- at the surface of CE mouth with salinity 5.36 during September 2012) causing oxygen depletion which can traced largely up to the nearshore region (~10 km into the sea; Figs 3.5 to 3.9). The estuarine discharge undergoes significant dilution once entered into the coastal sea thereby its impact is not significantly traceable beyond the nearshore region. This is supported by high carbon and nitrogen uptake rates in the nearshore region and their drastic decrease with increasing distance from the estuarine mouth (Bhavya *et al*., 2016, 2017). Therefore, the

observed variations in oxygen saturations at mid-shelf (station 5) could be largely attributed to the variation in upwelled water characteristics.

It is known that the coastal hypoxia during upwelling is dynamically linked to the offshore oxygen minimum zone (OMZ) in the Arabian Sea. The spreading of upwelling waters over the coastal zone allows an efficient consumption of nutrients to elevate the primary production which in turn causes further depletion of oxygen from an already oxygen deficient upwelling system. However, it should be noted here that the coastal waters of Kochi have never developed seasonal anoxia in the last four decades, whereas Mangalore and further north have always witnessed extreme (sulphidic) conditions due to recurrently occurring coastal anoxia (Naqvi *et al.*, 2009). Concomitantly, the present observations during September 2012 also showed two discernible water bodies: a subsurface anoxic system off Mangalore and sub-oxic waters (8-10 µM) off Kochi. This is because the upwelled waters at Mangalore are relatively more oxygen deficient compared to the upwelled waters entering the Kochi shelf. The oxygen content of the OMZ decreases northward, including in the West India Under Current that is a source of water upwelling over the shelf (Naqvi *et al.*, 2006). Moreover, the northern Arabian Sea processes (especially the winter convective mixing which has large interannual variability) largely influence the upwelling source waters north of Mangalore but not off Kochi.

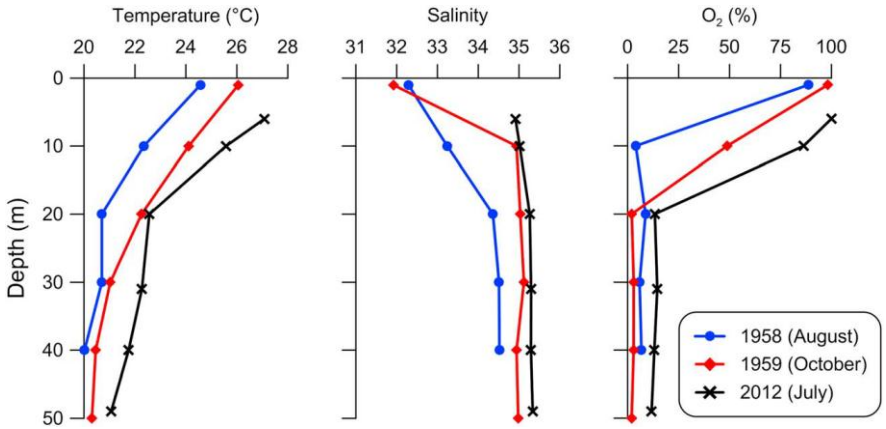


Figure 3.14. Comparison of historical profiles corresponding to peak upwelling months (refer Fig. 3.13).

As discussed earlier, stronger upwelling off Kochi brought up the poorly ventilated waters to shallower depth (10 m) in 1958-59 compared to 2012, where the upwelling was limited to 20 m. This has reduced the oxygen saturations of the surface layers considerably during 1958-59 (Fig. 3.14), though such a variation was not evident in the subsurface. The long residence time of upwelled waters over the shelf during 1958-59 would have increased the oxygen consumption as well. It is also possible that the upwelling intensity is linked to the depth of source water from offshore OMZ i.e. during 1958-59, the upwelling probably originated from deeper depth which is relatively cold and more oxygen deficient compared to that during 2012. This reveals that the variable upwelling intensity between the periods resulted in the observed differences in oxygen saturations.

The stronger upwelling in 1959 has also displayed enrichment of midshelf nutrients in 1959 especially nitrate (1–25 μM) relative to

2012 (0.03–18.5 μM). About 10-fold higher subsurface nitrite maximum (10–20 m) during peak upwelling period in the past (~2 μM) than the present period shows higher nitrification potential in the early days which was also responsible for highly depleted oxygen conditions. Nevertheless, the varied nutrients enrichment enhances phytoplankton (Chl*a*) production which also exhibits interannual variation due to varying upwelling intensity.

3.5 Summary

The study identified a clear intra-annual variability in biogeochemical properties in response to the combined effect of natural and anthropogenic activities. Upwelling was found to be a dominant process controlling the biogeochemistry of *SEAS* on an annual basis. The present study is the first to explain the evolution, propagation and withdrawal of upwelling and associated biogeochemical changes in the SEAS, though information on the remote forcing mechanisms requires further study. The upwelling was found to set in the deeper depths during January-March and progressed steadily to reach the mixed layer in May. It intensified over the entire shelf from June to September and withdrawn rapidly in October. The upwelling brings in drastic changes by transforming the *SEAS* to a nutrient-replete (eutrophic) system favouring enhanced primary production during summer monsoon. The subsequent increase in the sinking particle flux causes severe oxygen depletion resulting in a heterotrophic condition in the subsurface.

The studies earlier have shown increasing seasonal anoxia over the western continental shelf of India due to recurrence of sulphidic conditions (Naqvi et al., 2009), but the present study did not see the occurrence of such anoxia in the shelf waters of Kochi. But, it was not the

case in the north, as anoxia was noticed in the coastal waters of Mangalore due to upwelling of highly oxygen depleted waters relative to Kochi. The anoxia over the Mangalore resulted in sulphidic conditions in the nearshore region but this has never been noticed over the Kochi shelf. This shows that the intrusion of the offshore OMZ into the western continental shelf of India is critically poised and dynamically linked to the coastal upwelling. The upwelled waters from the central Arabian Sea are more oxygen depleted compared to a more oxygenated waters upwelled in southern Arabian Sea. An expansion of OMZ can increase the coastal hypoxic regions in the SEAS, while its intensification can induce significant changes in the biogeochemistry and bio-resources of the region. The prevalence of hypoxia (O_2 < 25 µM) could favour anaerobic respiration through denitrification leading to high efflux of greenhouse gases (details in Chapters 4 and 5).

Chapter 4

N_2O DYNAMICS IN RESPONSE TO UPWELLING INTENSITY AND DEGREE OF DEOXYGENATION

Contents

4.1 Introduction

Oceans are significant sources of N_2O to the troposphere (Nevison *et al*., 1995) contributing about 30% as natural and 17% as point sources (Albritton and Meira Filho, 2001). Marine N_2O is mainly an intermediate product during denitrification and as a side product during nitrification, and accumulates under anoxic and sub-oxic conditions (Codispoti *et al*., 2005). Its production under well-oxygenated conditions is common (Freing *et al*., 2012), but its concentrations are maximum in the oxygen minimum zone (OMZ) and in coastal areas experiencing upwelling and deoxygenation (Naqvi *et al*., 2000; Arévalo-Martínez *et al*., 2015). The oxygen deficiency over the continental shelf is regulated by factors such as regional circulation, shelf width, oxygen content of the upwelled waters, eutrophication and *in situ* primary production.

Globally, the major mid-water OMZs are present only in the eastern tropical Pacific and northern Indian Oceans. In the Pacific Ocean, the intense OMZ is associated with the productive eastern boundary upwelling systems (Capone and Hutchins, 2013) whereas in the Indian Ocean, it is located in the northern and central Arabian Sea (Naqvi, 2006; Banse *et al*., 2014). The restricted renewal of the mid-water depth waters experiencing increased O_2 demand for the oxidation of sinking particles from the productive surface layer leads to the development of one of the most thickest (between ~100 to 1200 m) OMZs anywhere in the world (Warren, 1994; Codispoti *et al*., 2001; Banse *et al*., 2014). Nevertheless, due to the semi-enclosed nature, the northern Indian Ocean contains about two-third of the global continental-margin area affected by natural oxygen deficiency (<0.2 mL L^{-1} or 9 µM; Helly and Levin, 2004). During the SW monsoon, the advection of low oxygen water through upwelling develops seasonal anoxia/hypoxia over the inner and mid-shelf regions of west coast of India which occupies two orders of less volume compared to its perennial open ocean counterpart, but it experiences extreme conditions (Naqvi *et al.*, 2000, 2006). This coastal O_2-deficient zone, the largest of its kind in the world (area ~200,000 km^2), is primarily of natural origin, but it appears to have intensified in recent years due to enhanced nutrient loading from land and resulted in high accumulation of N_2O over the shelf (Naqvi *et al*., 2006, 2010). The coastal upwelling systems such as found in the north-western Indian Ocean (Arabian Sea) and southeastern Pacific Ocean (off central Chile) have been identified as 'hot spots' for extremely high N_2O anomalies with N_2O saturations up to 8250% and 2426-12,244%, respectively (Naqvi *et al*., 2005; Cornejo *et al*., 2007; Arévalo-Martínez *et al*., 2015).

The N_2O emission from the Arabian Sea is three times larger than that from the Bay of Bengal (Naqvi and Noronha, 1991; Naqvi *et al*., 1994). When compared with the world oceans N_2O emission of ~ up to 9 Tg y^{-1} (Ciais, 2013), the contribution from the Arabian Sea (0.4–1.1 Tg y^{-1}) is 5–13%. The emission from the narrow western Indian continental shelf of India (4% of the total Arabian Sea area) alone contributed to approximately 15-35% of total emissions from the Arabian Sea (0.06-0.39 Tg N_2O y^{-1}) to the atmosphere (Naqvi *et al*., 2000). Therefore, the western Indian continental shelf of India is considered to be one of the most important oceanic sites of N_2O production (Naqvi *et al*., 2000, 2006a). However, previous studies were mainly in the shelf regions of central eastern Arabian Sea (CEAS) with very few data set from the south eastern Arabian Sea (*SEAS*). Therefore, the present study aims to fill this gap through a comparative study involving time series observations off Kochi (KoTS- Kochi Time Series) in the *SEAS* and seasonal sampling off Mangalore in the CEAS. This is the first time series study of N_2O from the shelf waters off Kochi (~10°N) and the only one other than that carried out off Goa (the Candolim Time Series, CaTS, ~15.5°N). The study also intends to find the role of upwelling intensity and oxygen concentration in its source water in ascertaining shelf biogeochemical response. The new data are used to revise estimate of annual flux of N_2O from the southwestern Indian shelf. This chapter highlights,

- Factors controlling the production of N_2O in the *SEAS* in relation to the OMZ
- The spatio-temporal variations in N_2O fluxes in the *SEAS*
- Revised N_2O budget from the *SEAS*

4.2 N_2O dynamics in the coastal waters of Kochi

The time-series N_2O concentrations over the Kochi shelf showed a clear seasonality (Fig. 4.1) with an increase from 9.2±5.2 nM (SIM) to 45±32 nM (SM) followed by a progressive decrease to 20±8 nM (FIM) and 8.8±2 nM (WM). The onset of SM (June) recorded the maximum N_2O concentration (61±47 nM), which coincided with coastal upwelling. High N_2O concentrations were observed up to inner shelf compared to mid-shelf and outer-shelf regions inferring that its production varied over the shelf. The N_2O concentrations in the inner shelf were low during April (8.0±1.2 nM), but increased substantially by June (119±50 nM) due to the combined effect of coastal upwelling and terrestrial input.

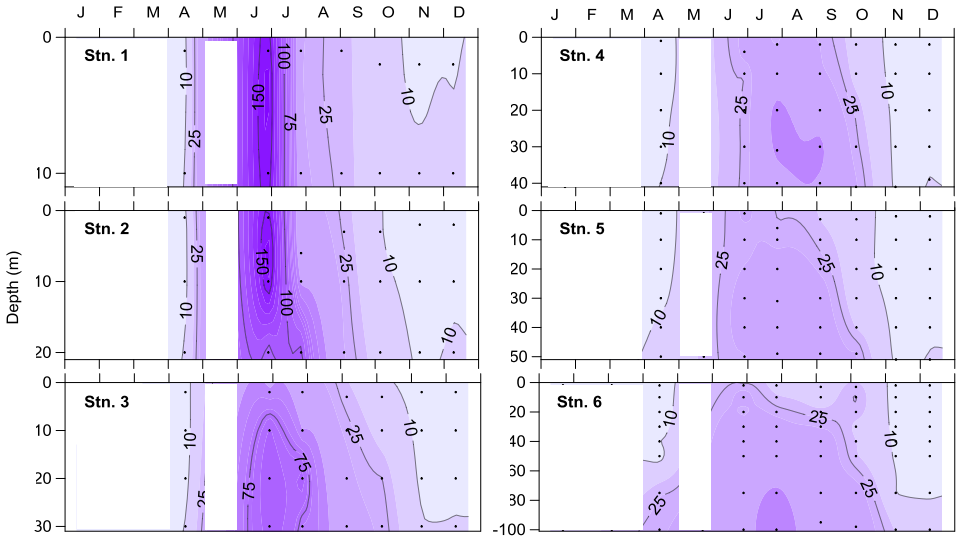


Figure 4.1. Time-series distribution of Nitrous oxide (nM) for stn.1 (13m), stn.2 (20m), stn.3 (30m), stn.4 (40m), stn.5 (50m) and stn.6 (100m) of Kochi.

The N_2O concentration in the inner shelf varied from 6.6 to 10.2 nM (average: 8±1.2 nM) in SIM, 22 to 164 nM (68±49 nM) in SM, 8.1 to 27 nM (12.4±5.6 nM) in FIM and 7.6 to 13.2 nM (9.3±1.8 nM) in WM. The biogeochemical properties of the inner shelf are largely influenced by the anthropogenic discharges from adjacent estuaries which are significant sources of N_2O (Barnes and Owens, 1999; Bange, 2006; Barnes and Upstill-Goddard, 2011). However, Indian estuaries are generally found to sustain low N_2O concentrations due to their efficient nitrogen assimilation capacity (Rao and Sarma, 2013). Kochi estuary also exhibited high nitrogen assimilative capacity (Bhavya *et al*., 2016), as evident from the consistently low N_2O concentrations during dry (12±5.6 nM) and wet (28±15 nM) seasons (Sudheesh *et al., in preparation*). Since most of the near shore observations were made during the flood tide, the export flux from the estuary is expected to be negligible and nitrification could be the major source of N_2O over the shelf during well oxygenated dry periods (Fig. 4.3). Contrastingly, elevated subsurface N_2O concentrations during SM were associated with hypoxic/sub-oxic waters indicating its possible production through denitrification. However, it should be noted that denitrification is triggered only when DO levels were <0.09 µM (Dalsgaard *et al*., 2012; Banse *et al*., 2014). This condition was never achieved in the coastal waters of Kochi even during the peak upwelling period (June), when the DO decrease was only up to 8.4 µM. However, there was a steep reduction in DO (<20 µM) and increase in NO_2 to ~3 µM (Fig. 4.4) in the inner shelf (>10 m), indicating to occasional, transient events of denitrification in the water column or close to sediment-water interface. But more so it is likely that the observed NO_2

and N_2O are predominantly mixed upward from denitrification in the underlying anoxic sediments. The stratification over the Kochi shelf is relatively weak during the SM (Fig. 3.2), thereby the nutrients injection through upwelling enhances the surface primary production. The subsequent organic sinking flux is expected to result in high DO demand in bottom waters, but the surplus ventilated upwelling waters together with weaker stratification seems to ensure enough oxygen supply to keep the sub-pycnocline waters just short of being denitrifying. Nitrification or/and assimilatory reduction of nitrate by phytoplankton (Vaccaro and Ryther, 1960) can be possible mechanisms in such conditions, but they cannot elevate nitrite and N_2O levels to the observed levels under hypoxic conditions. Therefore, denitrification in the underlying anoxic sediments appears to be quite significant, over weak nitrification and short-lived denitrification in the water column. As a result of the above processes, there was an 18 fold increase in the N_2O concentrations (119±43 nM) at stations 1 and 2 in June.

The N_2O concentrations in the outer and mid-shelf regions were always low ranging from 5.6-28 nM (avg.: 9.8±6.2) during the SIM, 14-58 nM (ave. 34±10) during the SM, 13-41 nM (avg.: 22±8) during the FIM and 6.5-19 nM (ave.8.7±2.3) during the WM. These concentrations were twice lower than the inner shelf as these regions are relatively unpolluted (Bhavya *et al*., 2016, 2018) evidenced by no marked change in DO concentrations when compared to five decades ago (Fig. 3.14). This indicates that the conditions encountered here, with modest build-up of N_2O under hypoxic/suboxic regimes, are mostly of natural origin associated with seasonal variation in upwelling.

4.3 N_2O variation in the coastal waters of Mangalore

Similar to Kochi, the shelf waters off Mangalore also showed seasonal variations (Fig. 4.2) associated with change in environmental condition. The N_2O concentrations off Mangalore ranged between 4.2-29 nM (7.6±5.7 nM), 9.5-202 nM (73±63 nM) and 6.6-13 nM (8.5±1.5 nM) during April (SIM), September (SM) and December (WM), respectively. The variation in N_2O concentrations over the shelf was minimum during SIM and WM while significant variation was observed during SM. N_2O concentrations were at its maximum in the midshelf waters (144±38 nM) compared to inner and outer shelf (31±14 and 49±6 nM) during this period. Significant accumulation of N_2O in the midshelf region coincides with anoxic and nitrite-rich water column during September (Fig. 4.2).

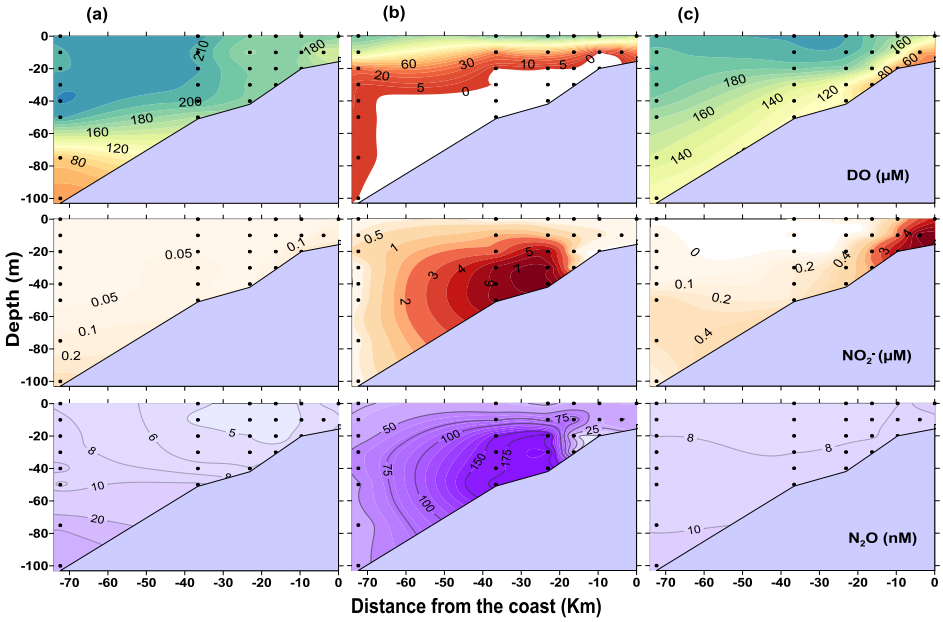


Figure 4.2. Distribution of dissolved oxygen (DO), nitrite (NO_2^-) and nitrous oxide along the off Mangalore during April (a), September (b) and December (c) of 2012

N_2O showed inverse relationship with DO (Fig. 4.4) during this period. The September N_2O concentrations off Mangalore (73±63 nM) were significantly higher than off Kochi (31±9.6 nM) but lower than those reported earlier (Naqvi *et al.*, 2009).

4.4 Factors controlling N_2O production

Nitrification (NH_4^+—›NO_2^-—› NO_3^-) and denitrification (NO_3^- —›NO_2^-—›N_2O—›N_2) are the major processes behind the production of N_2O in an oceanic environment (Bange *et al*., 2010). It is also known that during both the above processes, the yield of N_2O strongly depends on the concentration of dissolved oxygen (Goreau *et al*., 1980; Codispoti *et al*., 2005). Accordingly, the well oxygenated mixed layer of the entire study region during SIM and WM remained with very low N_2O concentrations (<10 nM) as was observed earlier (Naqvi *et al*., 2010). Nitrification is considered as the major mechanism responsible for N_2O production under such oxygenated conditions. This is evident from the significant correlations between N_2O and NO_3^-+NO_2^- (R^2=0.84, 0.79) and between ΔN_2O and AOU (R^2= 0.64, 0.55) for Kochi and Mangalore respectively (Fig. 4.3). In contrast, during the upwelling period, the increase in N_2O concentrations was mostly due to denitrification under oxygen depleted conditions. Bange and Andreae (1999) estimated that about 35% of the oceanic N_2O is produced during denitrification while the rest is produced by nitrification. It has been found that ~90% of N_2O production from the OMZs of Arabian Sea (Law and Ovens, 1990; Naqvi and Noronha, 1991) and eastern tropical Pacific Ocean (Kock *et al*., 2016) is through denitrification. The Arabian Sea is thus, recognized as a region of high

N_2O emission (Law and Owens, 1990; Naqvi and Noronha, 1991) as the upwelling and terrestrial discharge of nutrients fuel the biological production and the consequent severe demand for DO leads to denitrification (Gruber, 2004; Naqvi *et al*., 2000, 2006b). The exponential increase in N_2O concentration at DO <25 µM observed in the present study (Fig. 4.4) evidently infers an active denitrification. This critical DO concentration is well in agreement with an earlier reported value of 22 µM towards enhanced production of N_2O (Goreau *et al*., 1980; Codispoti *et al*., 2005).

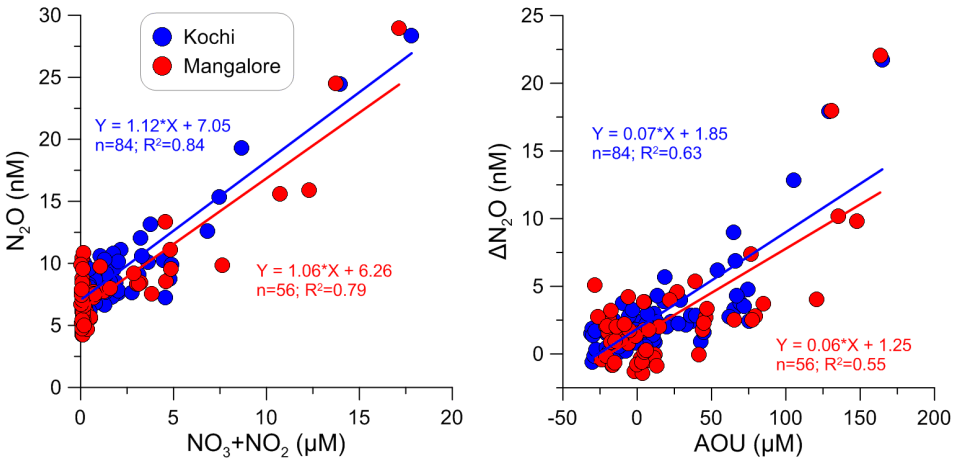


Figure 4.3. Relationship of N_2O vs $NO_3^-+NO_2^-$ and ΔN_2O vs AOU in the study area during dry (non-upwelling) periods.

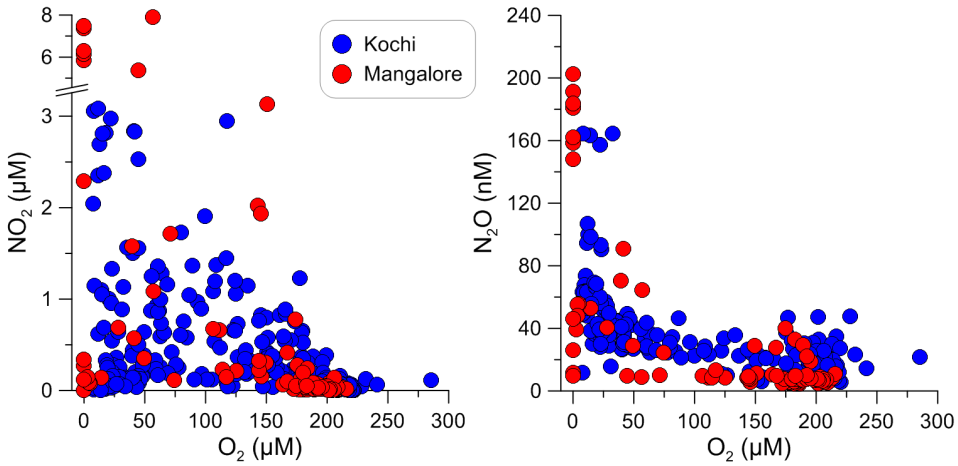


Figure 4.4. Relationship between DO (O_2), nitrite and N_2O in the study area during 2012.

4.5 Differences in biogeochemical responses of Kochi and Mangalore shelves to upwelling

The hypoxic zone in the western Indian shelf is believed to have intensified in recent years as a result of increased terrestrial nutrient loading and atmospheric deposition (Naqvi *et al*., 2000, 2006b, 2009). In contrast, results of the present study show that during September, propagation of anoxic upwelled waters over Mangalore shelf exerts a huge impact on the biogeochemical processes relative to off Kochi. This is evident from the enhanced concentration of N_2O in the Mangalore during September (maximum 202 nM; average 73±63 nM) than off Kochi (maximum 55 nM; average 23±9). The results of the present study are consistent with the earlier observations indicating that Kochi shelf has never gone below sub-oxic level (Banse, 1959, 1968), whereas Mangalore shelf recurrently turn to anoxic during SM (Naqvi *et al*., 2009). The extent of oxygen depletion over the shelf during SM depends on several

factors: (i) initial oxygen concentration in the upwelling water, (ii) upwelling intensity associated with horizontal circulation, (iii) stratification resulting from a combination of upwelling of cold saline water and runoff of warm freshwater plus local precipitation, which restricts aeration of subsurface waters, and (iv) subpycnocline oxygen demand that in turn depends on organic matter supply from the surface layer following fertilization by upwelling as well as anthropogenic supply.

The 21°C isotherm observed at shallow depths (~50 m) at the Mangalore shelf entrance (Fig. 3.12)was found to be much deeper (~80 m) off Kochi (Fig. 3.1). This shows that upwelling waters at Mangalore are cooler by ~1°C than at Kochi. Accordingly, at 100 m depth while the oxygen concentration was 14 μM off Kochi, it was below detection limit off Mangalore (Fig. 4.2). The permanent OMZ exists in the Arabian Sea has a southern boundary to the south of Mangalore up to 12°N (Naqvi, 1991). The upwelling waters at Mangalore are therefore sourced from the core of OMZ which are already denitrified. It is also likely that the upwelling off CEAS (Mangalore) is stronger, i.e., upwelling waters are originated from the deeper depths in the open ocean than in the *SEAS* (Kochi) (our unpublished data). This is consistent with the reported highly oxygen depleted to anoxic bottom waters at the shelf entrance of Mangalore all through SM months (0– <10 μM) (Naqvi *et al*., 2009) relative to those observed in the present study at Kochi (14–33 μM). Thus the difference in upwelling source water characteristics viz. relatively cooler and suboxic/anoxic waters advection at Mangalore compared to

Kochi is highly important leading to contrasting biogeochemical status of these shelves. The discernible very poor NO_3^- and NO_2^- concentrations at surface followed by steep rise at 10 m at least in the inner shelf clearly shows that nutrients input into upper stratified column from runoff, especially during September being late summer monsoon, is negligible compared to that supplied through upwelling. This is supported by recent findings that monsoonal estuaries of India including those on its western shelf assimilate anthropogenic nutrients as high as 91% thereby their discharge to coastal seas are very less (Bhavya *et al*., 2016; Krishna *et al*., 2016). Thus nutrients derived from relatively strong upwelling might have largely enhanced the biological production as evidenced by higher Chl *a* off Mangalore (9.7±11 mg m^{-3}) than off Kochi (4.4±3.8 mg m^{-3}). Consequently, a higher oxygen demand for sinking dead plankton flux at Mangalore (Phaeophytin: 3.2±3.5 mg m^{-3}) relative to Kochi (1.4±1.3 mg m^{-3}) in the already anoxic subpycnocline waters intensifies denitrification in the former region. The strong near-surface stratification off Mangalore act in unison to ensure a complete removal of DO beneath the thermocline not only over the inner shelf but also over the mid and outer shelf as well (Figs. 4.2, 4.5). This restriction in oxygen supply further adds stress on benthic mineralization to intensify the sedimentary anoxia leading to denitrification especially up to the midshelf. Complete deficiency of oxygen results in N loss mainly through denitrification (Naik, 2003; Naqvi *et al*., 2009), and when nitrate is fully exhausted sulfate reduction takes place in the sediments over the inner shelf of CEAS (Naqvi *et al*., 2009).

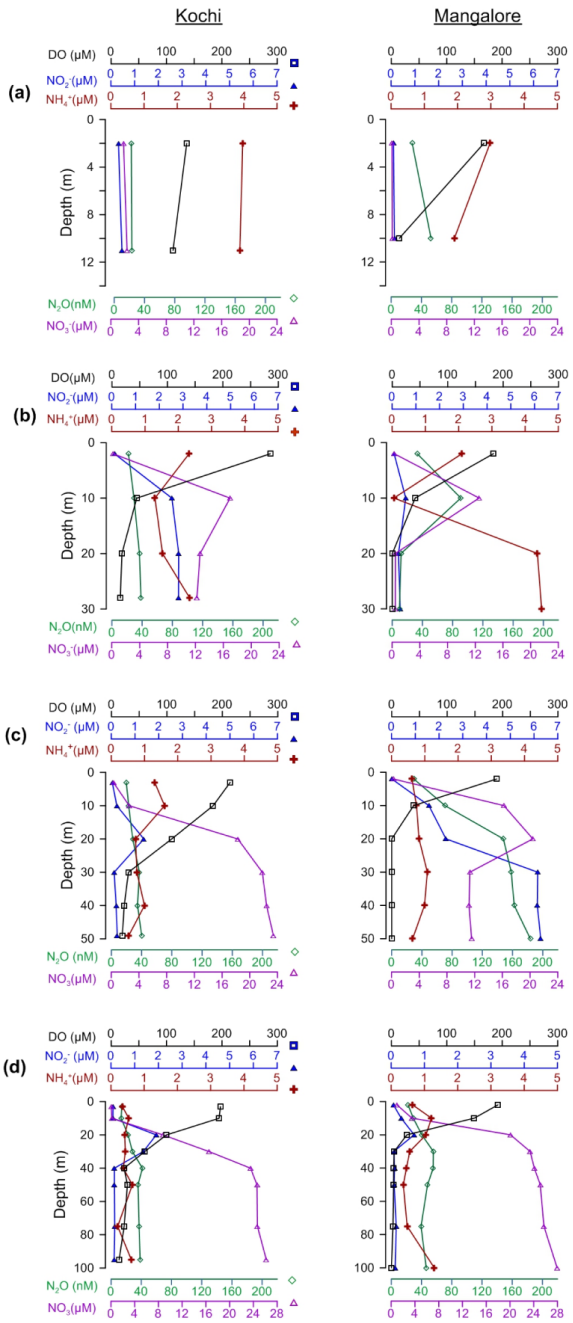


Figure 4.5. Comparison of vertical profiles for DO, nutrients and N_2O between Kochi and Mangalore for (a) nearshore, (b) inner shelf, (c) mid-shelf, and (d) outer shelf during September 2012.

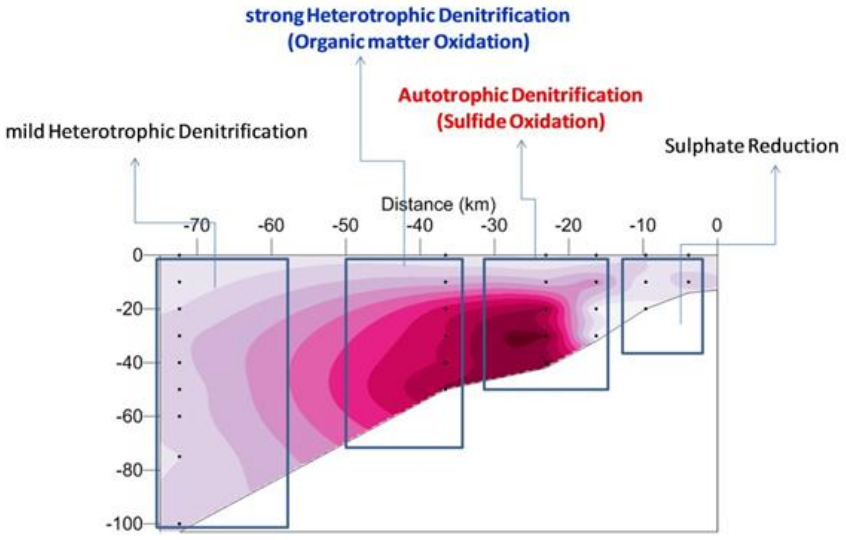


Figure 4.6. Zonal behavior of Mangalore shelf during late summer monsoon

High NH_4 (~5 µM) associated with highly depleted NO_3 (<0.5 µM) concentrations in the anoxic sub-pycnocline waters of Mangalore (Fig.4.5) indicate the anaerobic oxidation of sinking surface production while such signals are weak in the sub-oxic waters of Kochi. The central western shelf of India has been found to exhibit high benthic denitrification rate of 0.58-1.04 mmol N m^{-2} d^{-1} (Pratihary *et al*., 2014) which are consistent with those of 0.23-1.25 mmol m^{-2} d^{-1} reported earlier in this region (Naik and Naqvi, 2002; Naqvi *et al*., 2006a). The N_2O concentrations in the sub-pycnocline waters of Mangalore during September are distinctly low in the inner shelf (9.5-11.7 nM) than at mid-shelf (65-202 nM) despite NO_3 is highly depleted (<0.5 µM) under anoxic conditions in the former region (Figs.4.5b,c). H_2S smell was noticed from the bottom waters and surface sediments up to inner shelf during this

period, but its concentration was not measured. It is likely that chemolithoautotrophic bacteria often present in such sulfidic sediments (Lam and Kuypers, 2011) would have reduced NO_3 to N_2 through sulfide oxidation (Jorgensen and Nelson, 2004). The near absence of intermittent reduced forms like NO_2 and N_2O (Fig. 4.5a,b) up to inner shelf explains almost complete loss of N to molecular N_2. Such autotrophic denitrification has been found earlier in the sulfidic bottom waters off Goa also during late September (Naqvi *et al*., unpublished data) and benthic experiments estimated its potential rate as high as 3.21 mmol N m^{-2} d^{-1} (Pratihary *et al*., 2014). However, the sub-oxic to anoxic (non-sulfidic) sediments of mid-shelf with moderate sub pycnocline NO_3 concentrations (~12 µM) follows usual heterotrophic denitrification wherein the organic matter is oxidized by NO_3 or NO_2 resulting in N_2O production. It has been shown that non-sulfidic sediments overlayed by sub-oxic waters of central western shelf with moderate NO_3 concentrations could cause significant N loss through heterotrophic denitrification during July-August which switched to autotrophic denitrification by late September-October when sediments turned to sulfidic (Pratihary *et al*., 2014). It is pertinent to note that these periods coincided with a salient drop in oxygen content of the upwelling waters at the shelf entrance of Mangalore from being sub-oxic during July-August to anoxic by September (Naqvi *et al*., 2009), as was the case in our September observation also. This perhaps is a vital first-step (apart from primary productivity) in controlling the observed shift in sediment nature from non-sulfidic to sulfidic. This transition period was found to have highest build-up of N_2O (765 nM) over the central western shelf (Naqvi *et al*., 2000) and, in particular, at Mangalore (554 nM, Naqvi

et al., 2009). Though no such studies were ever made for the southwestern shelf of India, the non-sulfidic sub-oxic conditions prevailed over Kochi shelf all through SM upwelling would induce heterotrophic benthic denitrification and the N_2O thus produced is diffused into the water column above. The availability of moderate NO_3 concentrations in the sub-oxic bottom waters of Kochi inner shelf (~12 µM) when compared to its near absence from the similar region of Mangalore (<0.5 µM) indicate the highest degree of denitrification in the anoxic later region (Fig.4.5b). Overall, the shelf off Mangalore exhibited a clear gradient (Fig. 4.6) with autotrophic denitrifying environment up to inner shelf, strong heterotrophic denitrifying mid-shelf and mildly denitrifying outer-shelf, whereas the inner shelf of Kochi appears to have been influenced predominantly by heterotrophic sediment denitrification due to hypoxic/sub-oxic water column. These differences in biogeochemical responses over the western shelf of India are therefore predominantly governed by the varying upwelling intensities and associated DO concentrations

4.6 N_2O emission from the southwestern Indian shelf – a revised budget

The N_2O saturation levels off Kochi ranged from 101% to 2652% (Table 4.1) with high values occurring during the SM (574±720%) followed by the FIM (246±76%), the WM (140±12%), and the SIM (123±12%). Overall, oceanic surface waters are supersaturated with respect to atmospheric N_2O (3.5%) (Nevison *et al*., 1995). However, higher saturation levels are commonly seen in coastal upwelling zones (Bange *et al*., 1996, 2001). N_2O saturations observed in the surface waters

of the western Arabian Sea (300%) (Bange *et al*., 1996; de Wilde and Helder, 1997) and the north/central Arabian Sea (400%) (Jayakumar, 1999) appear modest when compared to those recorded over the shelf off Goa and Mangalore in the CEAS (up to 8250%) (Naqvi *et al*., 2006b, 2009) and off Kochi in the *SEAS* (2652%, present study). The coastal waters of Peru, experiencing similar upwelling conditions, accumulate even higher quantity of N_2O (up to 12,244%) (ArevaloMartınez *et al*., 2015).

Table 4.1. Monthly variation in concentration and air-sea fluxes of N_2O in the study region.

Month	Surface Conc. (nM)	Maximum subsurface (depth) conc. (nM)	Surface saturation (%)	Sea to air fluxes (µmol m^{-2} d^{-1})		
				LM86	W92	N00
Kochi						
April	5.6-7.6	28(100m)	100-135	0.15-5.9	0.29-11	0.2-7.6
June	25-164	164(10-20m)	418-2652	28-216	58-467	40-329
July	17-35	107(20m)	272-566	20-54	39-108	27-74
September	14-30	54(40m)	231-474	8-18	20-50	14-36
October	10-22	41(100m)	174-380	2.4-91	8.4-31	6.3-23
November	7.1-8.9	19(100m)	126-155	1.0-2.1	3.1-6.7	2.5-4.9
December	6.5-9	15(100m)	115-160	0.1-1.4	0.6-6.2	0.5-4.6
Mangalore						
April	4.4-7.6	29(100m)	82-137	-0.18-0.1	-1.3-2.7	-1.1-2.1
September	22.1-40.1	54(40m)	361-648	19-40	51-92	37-66
December	6.6-11.1	15 (100m)	116-194	0.06-0.5	0.22-2.02	0.2-2.03

The N_2O emissions estimated following Wanninkhof (1992) ranged from 0.29 to 467 µmol m^{-2} d^{-1} off Kochi, and from 21.3 to 92 µmol m^{-2} d^{-1} off Mangalore (Table 4.1). High efflux off Kochi in June and July is mainly due to relatively stronger winds; data are not available off Mangalore for this period. In September, when the SM winds are weak, nearly 2-fold higher effluxes are recorded off Mangalore than off Kochi. Both regions served as sources of N_2O to the atmosphere with one exception: off Mangalore (up to midshelf) weak N_2O flux was directed from the atmosphere to the sea in April. The sea-to-air fluxes obtained in the present study are significantly higher when compared to most other naturally occurring hypoxic systems (Table 4.2).

Table 4.2. Comparison of N_2O concentrations and fluxes from major naturally hypoxic shelf systems around the world.

Region	**Surface/mixed layer concentration (nM)**	**Max. subsurface (depth) concentration (nM)**	**Sea to air fluxes (µmol m^{-2} d^{-1})**	**Reference**
Off Peru. (ETSP)	7.6-986	-	27-1825	Arévalo-Martínez *et al*. (2015)
Off central Chile (ETSP)	6.7–59	245 (30 m)	−9.8–195	Cornejo *et al*. (2007)
	5.1–30.1	206 (40 m)	−7.7–42.9	Farias *et al*. (2009)
Oman shelf	9.7–24.7	48.8 (50 m)	N.G.	Naqvi et.al. (2010)
Eastern Indian shelf	4.9–12.0	42.0 (120 m)	−0.1–10.7	Naqvi *et al*. (1994)
	4.8-8.1	60(80m)	-54.8-45	Rao *et al*. (2013)
Western Indian shelf	5.3–436	765 (19 m)	−1.2–3243	Naqvi *et al*. (2006b)
	4.4-165	202(30m)	-1.1-467	Present study

Naqvi *et al*. (2000) quantified the N_2O emission from the entire western continental shelf of India as 0.06–0.39 Tg y^{-1} (1 Tg=10^{12}g) by extrapolating the sea-to air fluxes (derived by multiplying average N_2O concentration with LM86 and W92-based transfer velocities assuming wind speeds of 5–10 m s^{-1}) linearly to the entire western shelf area for a period of 6 months. This is significant when compared to the N_2O emission of 0.33–0.70 Tg N_2O y^{-1} from the open Arabian Sea (Bange *et al*., 2001b) considering that the western Indian shelf accounts for only 4% of the total area of the Arabian Sea. It must be noted that the high N_2O concentrations are confined mainly to the central shelf (11–17°N including Mangalore-Goa regions) as this region is only recurrently witnessing seasonal anoxia while the northern and southern shelves have always been reported with hypoxia and low N_2O concentrations, as was the case in the present study also. Thus linear extrapolation to entire western shelf without considering its significant DO and N_2O gradients would have resulted in overestimation of N_2O effluxes. We therefore attempt here to refine this estimate from the southwestern Indian shelf using present data and following a zonal and gridded extrapolation concept. For this, we divided the western shelf into three zones viz. 7–11°N, 11–14°N, and 14–21°N. The total N_2O emission estimated by Naqvi *et al*. (2000) was proportioned into these three zones as per the area of each zone (Table 4.3). N_2O fluxes from the zone 7°N to 11°N (SEAS) were estimated based on the year-long data off Kochi (10°N) generated in the present study. The annual emission for the zone 11–14°N was computed by combining present seasonal data (in April, September, and December) off Mangalore (12.8°N) with earlier data for peak upwelling

months (June to August which also include high buildup signals during transition period as explained above) from Naqvi *et al*. (2009). The Kochi and Mangalore segments of the shelf were subdivided into six grid boxes according to the water depth (viz. 0–15, 15–25, 25–35, 35–45, 45–75, 75–200 m) and the fluxes were computed for each grid box by multiplying the surface area of each grid box with the corresponding N_2O flux density. An extrapolation of these grid box fluxes to the 7–11°N area of the *SEAS* yielded a total N_2O flux of 0.007, 0.016, and 0.010 Tg y^{-1}, based on LM86, W92 and N00 transfer velocity parameterizations, respectively. Similarly, the N_2O emission from the zone 11 to 14°N was estimated at 0.012, 0.023, and 0.016 Tg y^{-1}, respectively, based on the above parameterizations. Combining these estimates, the revised estimate of N_2O efflux from the southwestern Indian shelf (7–14°N) comes to 0.019–0.039 Tg y^{-1} which is almost one-fourth of the earlier estimate (Table 3). It is likely that the emission from the northern zone (14–21°N) may also be lower than that reported previously, and so application of similar revised approach in conjunction with higher resolution sampling in space and time is needed for further refining the estimate of N_2O emission from the entire western Indian shelf. This is important in view of intensification of seasonal anoxia in recent times owing to the expansion of OMZ which may yield an upward-rise of N_2O concentrations. In such case, the elevated N_2O concentrations to some extent may compensate the lower effluxes due to revised approach

Table 4.3. Revised N_2O budget (Tg y^{-1}) along the western Indian shelf based on different parameterisations for gas transfer velocity.

Zone (°N)	Surface area (km^2)	Earlier Budget** (Naqvi *et al*., 2000)	Revised Budget (present study)			
			LM86	W92	N00	Updated range
7-11	30,871	0.010-0.067	0.007	0.016	0.011	0.007-0.016
11-14	39,368	0.013-0.085	0.012	0.023	0.016	0.012-0.023
14-17	39,369	0.013-0.085	--	--	--	--
17-21	70,392	0.023-0.156	--	--	--	--
Total	**1,80,000**	**0.060-0.390**	--	--	--	--

**Earlier budget was based on wind speeds of 5-10 m s^{-1} using LM86 and W92 wind parameterisations and fluxes extrapolated over six months period. Present high frequency data from Kochi (KoTS) and Mangalore (KoTS and Naqvi *et al*. (2009)) shelves are used for updating budget from the two southern zones (7-14°N).

4.7 Summary

The *SEAS* has been identified as a significant source of N_2O to the atmosphere, especially during the summer monsoon. The coastal upwelling results in seasonal buildup of N_2O in oxygen-depleted (<25 mM of DO) waters. N_2O accumulation is much higher off Mangalore than off Kochi. This difference is mainly attributed to the stronger upwelling and associated anoxic conditions coupled with higher productivity and stronger near-surface thermohaline stratification off Mangalore relative to Kochi. This leads to the development of intensely reducing conditions in bottom waters and underlying sediments off Mangalore that support enhanced production of N_2O. Off Kochi, by contrast, bottom waters remain just short of turning anoxic, thereby the modest buildup of N_2O may be largely limited to its production through sediment denitrification. Utilizing the high-resolution data of the present

study, our revised estimate of N_2O emission from the southwestern Indian shelf (south of 14°N) was only one-fourth (0.019–0.039 Tg y^{-1}) of the earlier estimate which is attributed to our new approach adopted in computing the annual fluxes. In view of the growing concerns about expanding OMZ and its influence on global climate change (via emissions of climate relevant trace gases such as N_2O), further studies are essential to refine the sea to air fluxes of greenhouse gases including N_2O and also to predict the responses of the biogeochemical processes over the entire shelf off west India to the ongoing regional (developmental activities) to global (e.g., warming) environmental changes. In addition to N_2O, the high rate of remineralisation process under intensively reducing environment might also have led to enhanced production and accumulation of CO_2 and CH_4. The dynamics of these GHGs under varying biogeochemical properties associated with change in environmental condition are discussed in the next chapter.

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Chapter 5

METHANE FLUXES FROM THE SOUTHWESTERN CONTINENTAL SHELF OF INDIA

Contents

5.1 Introduction

Coastal seas are found to be important sites of CH_4 (methane) production that contributes to ~20% emission of all greenhouse gases (IPCC 2007). Despite their relatively small spatial coverage from oceans (16%), the shelf region accounts to 75% of its CH_4 emission (Bange *et al*. 1994). Quantification of CH_4 emission from coastal zones becomes very difficult as these regions exhibit large variability in response to variations in the primary production, organic decomposition and upwelling intensity (Kock *et al*., 2008; Rehder *et al*., 2002; Sansone *et al*., 2001). A best example for this is the eastern Arabian Sea coastal upwelling system, one of the most biologically productive regions of world's ocean, where the magnitude of CH_4 emissions have not been well quantified.

The previous studies on CH_4 from the eastern Arabian Sea reported high supersaturation of CH_4 in the surface waters and several fold higher fluxes compared to oceanic averages (Owens *et al*. 1991; Patra *et al*. 1998;

Jayakumar *et al*. 2001). A significant part of its supersaturation has been proposed to be contributed by the release from sediments along the Indian continental shelf (Karisiddaiah and Veerayya, 1994, 1996). Bange *et al*. (1998) reported a mild supersaturation of CH_4 in the central Arabian Sea except in the upwelled waters. On the other hand, highly productive regions of west coast of India, with one of the largest naturally formed low-oxygen zone in the world (Naqvi *et al*., 2006, 2009), favour *in situ* production of CH_4 in the water column (Owens *et al*. 1991, Jayakumar *et al*., 2001).

Most of the CH_4 data from the Arabian Sea (AS) correspond to offshore regions and very few datasets are available from the coastal regions. The only available observations on CH_4 from the coastal regions of AS was by Jayakumar *et al*. (2001) which mainly focused on the northern Arabian Sea. Subsequent studies have reviewed the importance and cycling of CH_4 in the AS (Naqvi *et al*., 2005, 2010) with the help of data generated mostly during the Arabian Sea Process Study (1992–1997). They have reported that the coastal wetlands along the west coast of India potentially contribute CH_4 to the nearby coastal regions. However, comprehensive study on CH_4 distribution and, its emission from the coastal upwelling zones of southeastern Arabian Sea (*SEAS*) remain unknown. Therefore, the present study examined the CH_4 distribution and its emissions from the water column to delineate the influence of upwelling and estuarine contribution over the *SEAS* shelf. Accordingly, the present chapter focused on

- Factors influencing the distribution and variability of CH_4 in the study region
- Fluxes of CH_4 from the southwestern Indian shelf

5.2 CH_4 dynamics along the southwestern Indian shelf

The dissolved CH_4 in the Kochi (Figs. 5.1, 5.2) and Mangalore (Fig. 5.3) shelves were generally supersaturated with a gradual decrease towards outer shelf. The annual CH_4 concentrations in the Kochi shelf ranged from 10 to 152 nM (52±35 nM) in the near shore, 3 to 23 (7.6±5.03 nM) in the inner shelf, 2.1 to 13.4 nM (3.5±1.8 nM) in the mid-shelf and 2.1 to 5 nM (3±0.7 nM) in the outer-shelf. Similarly, CH_4 concentration off Mangalore varied from 9 to 133 (35.4±35 nM), 5 to 17 (10.4±3.4 nM), 1.8 to 6 (3±1.1 nM) and 1.8 to 4 nM (2.6±0.6 nM) respectively for nearshore, inner shelf, midshelf and outer shelf region. On an annual basis, relatively high CH_4 concentrations were recorded in the mid-shelf and outer-shelf regions during the peak SM upwelling (June/July), but the near-shore regions showed high concentrations during dry no-upwelling periods except during April at Mangalore. High tide conditions during the sampling in April (Table 2.1) could have resulted in lower contribution of CH_4 from the adjoining Nethravati estuary to the Mangalore nearshore region. Overall, the factors controlling the CH_4 saturation levels in the shelf waters could be its inputs through upwelling, estuarine export, sediment release and mixed layer production.

The significantly high levels of CH_4 during peak upwelling (216±54%) compared to post upwelling period (130±18%) suggest that upwelling has a greater influence on the dynamics of CH_4 in the *SEAS* shelf. Earlier studies (Owens *et al*. 1991; Bange *et al*. 1998; Upstill-Goddard *et al*. 1999) have also reported high supersaturation (124-286%) of CH_4 in the western Arabian Sea during SM that subsides following the retrieval of upwelling.

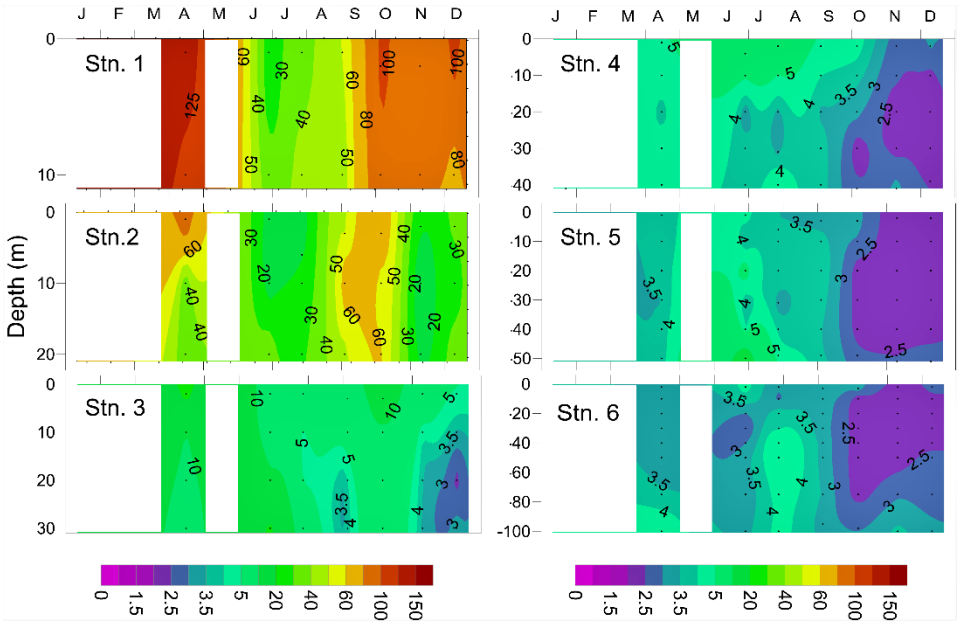

Figure 5.1. Monthly variation in CH_4 concentrations (nM) at different stations off Kochi

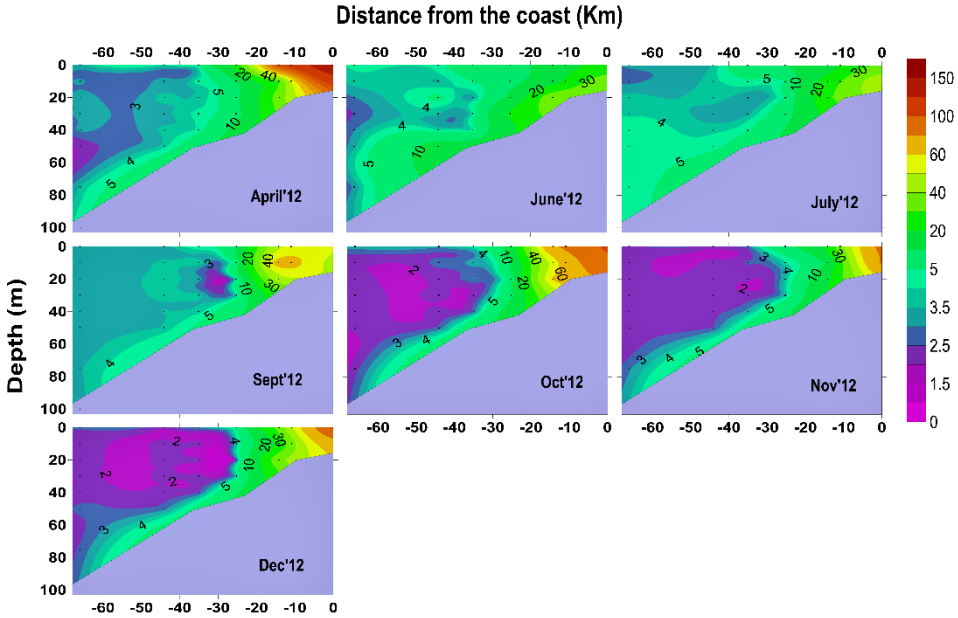

Figure 5.2. Monthly variation in CH_4 concentrations (nM) over the Kochi shelf

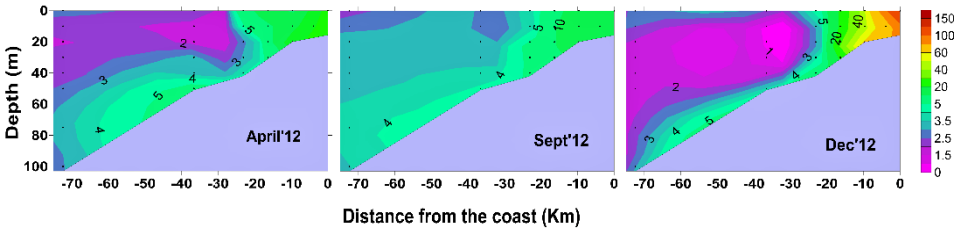

Figure 5.3. Seasonality in CH_4 concentrations (nM) over the Mangalore shelf

The CH_4 distribution generally showed a sharp decrease from the coast to offshore regions indicating its possible source from the adjacent estuary. The parallel studies from the Cochin estuary (CE), a wetland ecosystem influenced by large-scale industrialisation and urbanisation, showed that CH_4 levels (Fig. 5.4) are consistently high in April (SIM): 300 ± 246 nM, September (SM): 334 ± 277 nM and December (WM): 217±93 nM. Cochin estuary has been found to sustain high sediment organic carbon (3-5%) associated with high clay fraction (60-90%) in the downstream regions (Martin *et al*., 2010) and its high decomposition rate (Gupta *et al*., 2009, Rao and Sarma, 2016) has yielded substantially high benthic CH_4 fluxes to overlying water column as observed from the benthic chamber experiments (2.54 to 210 mg m^{-2} h^{-1}, Verma *et al*., 2002). Through tidal exchange its export flux contributes significantly to the CH_4 concentrations in the adjoining coastal regions during dry periods. However, the relatively low concentrations of CH_4 in the near shore waters (35±21 nM) when it was high at the lower estuary during SM (Fig. 5.4) is due to its dilution with upwelling waters which are about ten-fold low in CH_4 concentrations (3.5±0.5 nM). Rao and Sarma (2016) reported significantly high CH_4 flux to the atmosphere from Nethravathi estuary

(114 µmol m^{-2} d^{-1}) compared to the CE (5.32 µmol m^{-2} d^{-1}) during the wet period and comparable effluxes during the dry period (24.3 and 29.3 µmol $m^{-2}d^{-1}$ respectively). However, the parallel study from CE showed significantly high CH_4 concentrations (Fig. 5.4) and its effluxes (60 to 543 µmol m^{-2} d^{-1} with an annual average of 150±152 µmol m^{-2} d^{-1}) from CE compared to those by Rao and Sarma (2016). Notably, Nethravathi estuary, adjoining the Mangalore shelf, is a minor river system (surface area-18.5 km^2) compared to the CE (surface area-231 km^2) and is expected to contribute less export flux of CH_4 to the coastal waters. Nevertheless, the discharge of highly supersaturated waters to the nearby coastal region substantially contributed to nearshore CH_4 concentrations, more so at Cochin than Mangalore. Higher surface concentrations at the nearshore region compared to bottom during April and December (Fig. 5.4) supports the tidal export flux contribution of CH_4 from the CE.

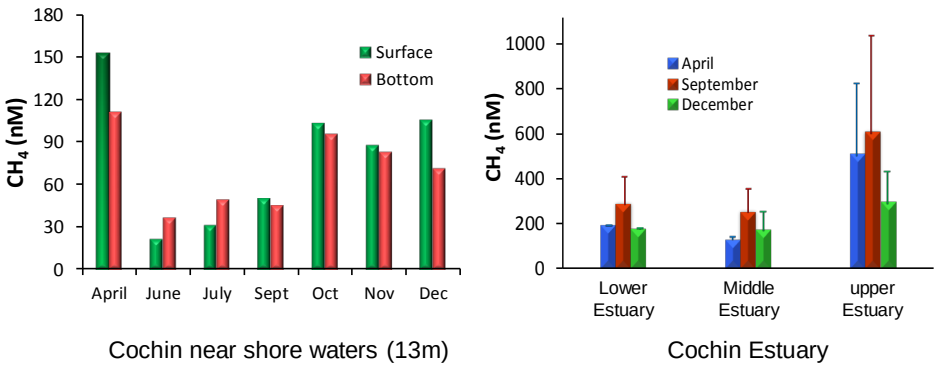

Figure 5.4. Comparison of CH_4 concentrations in the near shore and estuarine regions of Kochi

Consistently high bottom concentrations of CH_4 in both the shelves irrespective of season (Figs.5.1, 5.2 & 5.3) clearly show that it is more of

benthic origin. Sediment methanogenesis and its diffusion to the overlying waters would be the main source of CH_4 as reported elsewhere (Reeburgh, 2007; Naqvi *et al*., 2010; Borges *et al*., 2016). The inner continental shelf sediments of west coast of India were earlier reported as traps of CH_4 based on the discovery of gas-charged sediments (2.6 Tg CH_4) few meters beneath the surface (Karisiddaiah and Veerayya 1994, 1996). These authors also proposed the diffusion of CH_4 from the sediments to the overlying water column, estimated at 0.039 Tg y^{-1} which is nearly the same as the net atmospheric flux from the Arabian Sea reported by Owens *et al*. (1991). So, the seepage of CH_4 from the organic rich shallow sediments (Paropakari *et al*., 1987; Borges *et al*., 2016) and its accumulation in the overlying water column due to calm and less turbulent sea state conditions might be responsible for elevated CH_4 concentrations during dry periods. Significantly higher CH_4 concentrations up to the inner shelf of present study are supported by recent studies by Gireeshkumar *et al*. (2017) who reported up to 400 nM of CH_4 in the nearshore bottom waters of Alapuzha region (~9.2°N), south of present study area.

Distinctly high CH_4 concentrations were observed during oxic non-upwelling periods (dry period) compared to oxygen depleted upwelling period (wet period) (Figs. 5.1-5.3). Significant correlations of CH_4 with chlorophyll *a* and POC in the near-shore waters during non-upwelling periods (Fig. 5.5) indicate that apart from the estuarine inputs high phytoplankton production can also lead to water column methanogenesis (Owens *et al*., 1991; Karl *et al.,* 2008). Recent studies have found that CH_4 production is associated with nutrient depleted systems. For example, Karl *et*

al (2008) have argued that CH_4 is produced aerobically through decomposition of methylphosphonate that might serve as a source of phosphorus in phosphate poor environments. Whereas Damm *et al.* (2010) reported CH_4 production in nitrate-depleted systems that contained sufficient phosphate. The occurrence of such CH_4 production pathways during the oligotrophic non-upwelling periods could also enhance its concentrations in the *SEAS.*

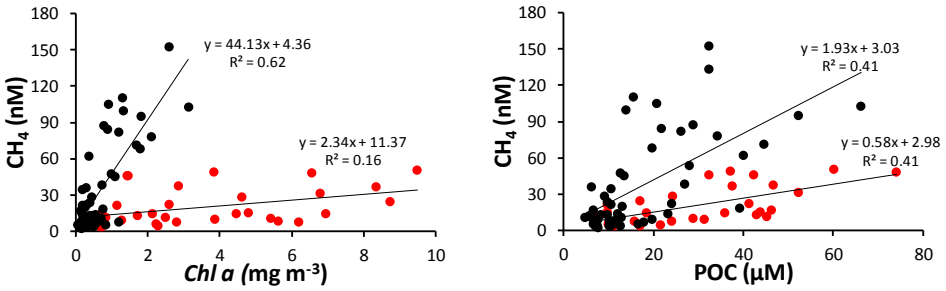

Figure 5.5. Correlations of CH_4 with *Chl a* and POC in the inner shelf during upwelling (red) and non-upwelling (black) periods

During September, the anoxic waters up to the inner shelf of Mangalore have been observed with lower CH_4 concentrations relative to similar regions of sub-oxic Kochi shelf (Figs.5.1 & 5.3). The sediment organic carbon at stations 1 and 2 of both the shelves (2.5-3.6%) were almost similar, so assuming the rate of methanogenesis in these two regions is comparable then the variation in water column CH_4 concentrations is possible only with its differential loss rate through oxidation. It is pertinent to note that despite intense denitrification the subpycnocline waters up to inner shelf of Mangalore during September are also distinctly low with N_2O concentrations (Fig. 4.5 a,b) as sulphide oxidation by chemolithoautotrophic bacteria has almost completely reduced NO_3 to molecular N_2 (refer section

4.5). It is also possible that this complete denitrification is supported by the anaerobic oxidation of CH_4 (Ettwig *et al*., 2010; Haroon *et al*., 2013) leading to latter's removal. Such a striking full cycle denitrification does not exist over the Kochi shallow waters, as observed by relatively higher N_2O concentrations here (Fig. 4.2 & 4.5) indicating that the loss rate of CH_4 through its oxidation in these sub-oxic waters are lower than at anoxic waters of Mangalore. This resulted in higher CH_4 accumulation over the Kochi shelf relative to Mangalore shelf. This is in agreement with the studies made elsewhere (Boetius *et al*., 2000; Beal *et al*., 2000) that an oxidative dissolution of Fe and Mn oxides or sulphate reduction favour high CH_4 oxidation in the inner-shelf regions.

5.3 Quantification of CH_4 emission

The CH_4 saturation levels off Kochi ranged from 109% to 8021% (Table 5.1) with maximum values in the nearshore region (3242±2168%) followed by inner shelf (567±302%), mid-shelf (174±49%), and outer shelf (167±29%). Lower saturation levels (102-7006%) were recorded off Mangalore which decreased drastically from nearshore (1920±2403%) to inner shelf (587±295%) and then to mid-shelf (172±41%) and outer shelf (121±18%). The significantly high nearshore saturation levels of CH_4 at Kochi compared to Mangalore is attributed its higher contribution from the adjoining highly eutrophic Cochin estuary relative to the Nethravathi estuary. The saturation levels observed in the mid and outer shelves were within the range reported earlier from the continental shelf of India by Jayakumar *et al*. (2001).

Table 5.1. Monthly variations in CH_4 saturation and fluxes from the study region.

Stn. No.	Month	Surface conc.(nM) (Average)	Maximum Subsurface (depth) conc. (nM)	Saturation (%)	Air-sea flux (μmol m^{-2} d^{-1})
Kochi					
1	April	3.3-152.4 (48±63.2)	110 (10m)	174-8021	4.9-227
2	June	4.2-22 (10±7)	37.5 (20m)	221-1153	19-51
3	July	3-31.5 (11.7±10.5)	49 (10m)	162-1656	7.6-93
4	Sept	3.2-50.4 (19.7±23)	49 (10m)	182-2651	3.9-85
5	Oct	3.2-103 (34±44.4)	47 (10m)	173-5423	3.3-46.4
6	Nov	2.1-87.33 (21±33)	82 (10m)	109-4596	2.1-150
7	Dec	2.1-105 (25±41)	70 (10m)	110-5527	1.1-154
Mangalore					
8	April	2.1-20.7 (9±8.1)	22 (10m)	123-1090	2.3-23
9	Sept	1.9-4.9 (3.3±1.2)	17 (10m)	102-258	3.7-10.5
10	Dec	2.2-133 (33.7±51.6)	84 (20)	114-7006	0.76-40

The air-sea CH_4 emissions from *SEAS* (7-14°N) ranged from 8.6 to 227 μmol m^{-2} d^{-1} in the nearshore, 3.9 to 35 μmol m^{-2} d^{-1} in the inner shelf, 0.76-10.7 μmol m^{-2} d^{-1} in the mid-shelf and 0.85 to 10 μmol m^{-2} d^{-1} in the offshore regions. The computed fluxes from the mid and outer shelves are comparable with earlier studies from the Arabian Sea (Owens *et al*., 1991; Patra *et al*., 1998; Jayakumar *et al*., 2001) and other coastal upwelling systems (Table 5.2). Also, these are similar to the range of global average CH_4 fluxes from the continental shelves (22 to 37 μmol m^{-2} d^{-1}; Bange *et al*., 1994). However, significantly higher fluxes from the nearshore region reveals the importance of these regions in contributing the global CH_4 flux as reported elsewhere (Borges *et al*., 2016). On an annual basis, the air-sea CH_4 emissions from the near-shore regions of *SEAS* (77±58 μmol m^{-2} d^{-1}) are 3-4 times higher than the global average from the continental

shelves (22–37 μmol m^{-2} d^{-1}; Bange *et al*., 1994) and ~200 times higher than the global average of open oceanic waters (0.2–0.5 μmol m^{-2} d^{-1}; Rhee *et al*., 2009).

Table 5.2. Comparison of CH_4 concentration from natural coastal hypoxic systems

Region	Surface/ mixed layer con. in nM	Maximum subsurface con. in nM (depth)	Sea to air flux (μmol m^{-2} d^{-1})	References
Eastern Tropical North Pacific Mexican Margin (open)	3.2-5.7	46 (340)	0.5-2.7	*Sansone et al.*, (2004)
Mexican Margin (Gulf of California Basins)	3-4.5	25-78 (400-530 m)	0.5-5.9	*Sansone et al.*, (2004)
Eastern Tropical South Pacific (Off central Chile)	3.1-29.2	79.9 (90m)	0.05-59.5	*Farías et al.*, (2009)
Eastern Tropical North Atlantic (Off Mauritinia)	2-5. 0	N.G	0.5-0.8	*Kock et al.*, (2008)
Eastern tropical South Atlantic (Off Namibia)	2.2-2870	5160 (18m)	3-752	Monteiro *et al*. (2006)
Bay of Bengal	3.2-38.3	12.9 (78m)	0.22-24.9	*Berner et al.*, (2003)
Eastern Arabian Sea (Indian Shelf)	2.6-47.6	44 (24m)	0.58-63.7	*Jayakumar*, (1999)
Southeastern Arabian Sea (Indian Shelf)	**2.1- 152**	**110 (10m)**	**1.1-227**	**Present study**

The annual sea-air flux of CH_4 from the *SEAS* shelf (7-14°N) is estimated with similar zonal approach adopted for N_2O (sec. 4.6, chapter 4). Annually, the estimated CH_4 fluxes ranged from 0.004 to 0.023 and from 0.0012 to 0.017 respectively for 7-11°N and 11-14°N. Combining these zones, CH_4 efflux from the southwestern Indian shelf (7–14°N) is estimated at 0.005-0.04 Tg yr^{-1}, which is accounted for 5-20% of its

emission from the Arabian Sea (0.1–0.2 Tg y^{-1}, Upstill-Goddard *et al*. 1999). Further, the CH_4 emissions from the offshore regions of Arabian Sea accounts only to <1% of its global oceanic emissions (Naqvi et al., 2005), however, the inclusion of emissions from the coastal Arabian Sea would elevate its global contribution. Therefore, it is suggested that zonal integration approach followed in this study need to be undertaken all along the western continental shelf of India to reduce uncertainties in Arabian Sea CH_4 emission estimations.

5.4 Summary

The present study observed that the *SEAS* is a major source of CH_4 to the atmosphere and exhibited large spatial and temporal variations. Significantly higher CH_4 in the nearshore waters is due to its combined inputs from sediments, water column production and estuarine export flux through tidal flushing. The present study did not record any increase in CH_4 concentrations during hypoxic/anoxic periods. In contrast, a decrease in CH_4 concentration in the nearshore waters of Mangalore during anoxic upwelling is attributed to its loss through anaerobic oxidation. The estimated CH_4 flux varied between 0.76 and 227 µmole m^{-2} d^{-1} with an annual emission of 0.005-0.04 Tg CH_4 from the *SEAS* (7-14^{o}N), which is approximately 5-20% of the total CH_4 emission from the Arabian Sea. However, further studies are essential to understand the changes in CH_4 emissions from the Indian continental shelves to the ongoing regional (e.g. eutrophication) and global (e.g. warming) environmental changes.

Chapter 6

INORGANIC CARBON DYNAMICS IN THE SOUTHEASTERN ARABIAN SEA

Contents

6.1 Introduction

The dissolved inorganic carbon (DIC) exists in different forms in the seawater: gaseous carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). Their distribution and conversions help in explaining the fate of CO_2 during air-sea interaction. The sea-air flux of CO_2 governed by its partial pressure (pCO_2) is generally controlled by the production-degradation-export of organic matter and by the shift in carbonate system, upwelling intensity and thermodynamical changes due to mixing of watermasses (Borges and Frankignoulle, 2003).

The carbon cycling in the coastal systems is highly dynamic due to rapid changes in nutrient and organic matter inputs (Borges et al., 2009). This is especially the case in coastal upwelling systems which are

generally supersaturated with CO_2 due to the deep upwelled waters (Feely *et al*., 2004; Evans *et al*., 2011). It has been observed that the enhanced primary production due to upwelling significantly lowers the pCO_2 (Walsh *et al*., 1988; Hales *et al*., 2005). There is large uncertainty in the contribution of these coastal environments to net global sea-air CO_2 exchange as the data is scarce and spatial and temporal variability is high (Borges *et al*., 2005; Cai *et al*., 2006). This is significant in the case of Arabian Sea which is known as perennial source of CO_2 to the atmosphere (Goyet *et al*., 1998; Sarma *et al*., 1998; Sarma 2003; Kanuri *et al*., 2017). Sarma *et al*. (2000) have observed that physical processes strongly controls the surface pCO_2 levels, which is very high along the southwest coast of India during summer monsoon upwelling.

Despite this, very few studies have been conducted to study the carbon dynamics in the coastal waters of Arabian Sea. In most of these studies, measurements were carried out with coarse resolutions along selected transects on a seasonal basis (Sarma *et al*., 1998; Millero *et al*., 1998). In several studies the pCO_2, DIC and total alkalinity (T_{Alk}) were derived using the regression equations based on *in situ* and remote sensing data for the SST, salinity and chlorophyll *a* (Goyet *et al*., 1998; Sabine *et al*., 1999; Sarma, 2003; Bates *et al*., 2006) on basin-scale. Kanuri *et al* (2017) reported a drastic seasonal variation in pCO_2 levels along the southeastern Arabian Sea. Therefore, the C cycling in the coastal waters of southwest coast of India seems to be strongly controlled by the seasonal upwelling and *in situ* biological processes (Sarma *et al*., 2000). The lack of systematic observations makes it highly uncertain to explain the carbon dynamics in the upwelling regions of eastern Arabian

Sea. More importantly, the paucity of observational data led to an error in the estimation of total Arabian Sea carbon fluxes. It is evident from the present study that upwelling is the major process that controls the biogeochemistry of *SEAS* with a residence time of about 9 months between its initiation and withdrawal. This is a significant factor in influencing the carbon chemistry, thereby this chapter explains the changes in carbon chemistry at various stage of upwelling in the *SEAS* under the following themes:

- Distribution of inorganic carbon components at various stages of upwelling
- Influence of upwelling on the saturation levels of calcite and aragonite
- Factors influencing the air-sea interaction of CO_2
- Quantification of CO_2 emission from the *SEAS*

6.2 Changes in the pH, DIC and T_{Alk} in the coastal waters (Kochi)

Monthly variations in pH (Fig. 6.1), DIC (Fig. 6.2) and T_{Alk} (Fig. 6.3) clearly indicated the seasonality in these parameters. During January, the entire shelf showed high pH (8.145±0.020) and low DIC (1930±25 μmol kg^{-1}) values. With the onset of upwelling (March), the OMZ waters started to rise up, as indicated by the drop in pH (7.880) and rise in DIC (2069 μmol kg^{-1}) at depths. In May-June, the waters just below 50 m became less alkaline (<7.900) and rich in DlC (>2000 μmol kg^{-1}) which continued up to September. The maximum effect of upwelling was seen between May and June as indicated by the lowest pH (7.753) and highest DIC (2100 μmol kg^{-1}) in the near shore region. Concurrent to the sharp

retrieval of upwelling in October, the reversal has turned the waters to alkaline with less DIC. Overall, following the phase of upwelling, the highly alkaline water column during SIM (8.117±0.054) has been acidified during SM (7.952±0.121) and again turned to alkaline during FIM (8.081±0.098) and WM (8.142±0.040). On an annual basis, the water column pH varied between 7.753 and 8.251 (8.061±0.116). These pH values are within the range reported recently by Kanuri *et al.* (2017) in the *SEAS*. Similarly, DIC also showed seasonality with lowest in SIM (1953±55 µmol kg^{-1}), FIM (2005±74 µmol kg^{-1}) and WM (1924±51 µmol kg^{-1}), and highest in (2078±77 µmol kg^{-1}). Annually, the DIC concentrations over the Kochi shelf varied from 1704 and 2222 µmol kg^{-1} (1995±93 µmol kg^{-1}). These results are in consistence with earlier reports from the same region (Sarma, 2003; Kanuri *et al.*, 2017).

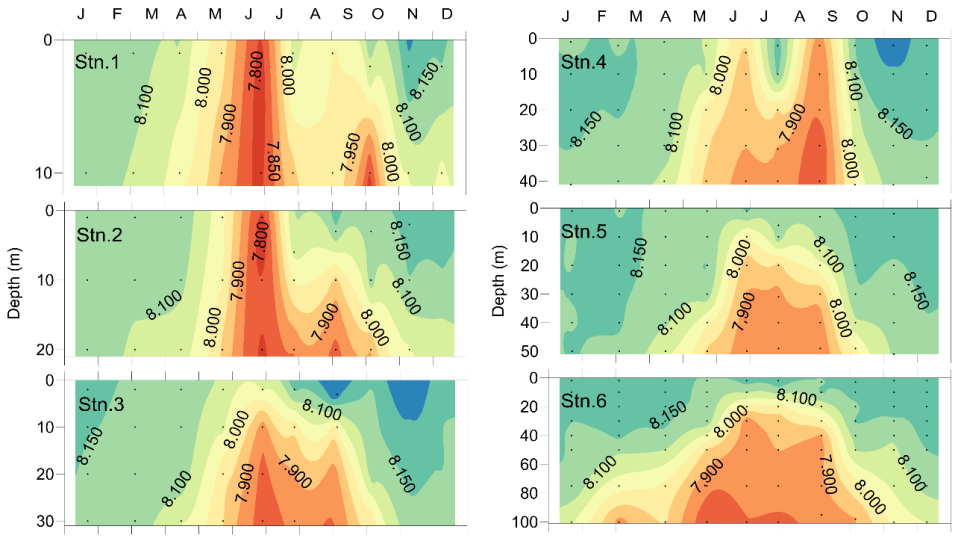

Figure 6.1. Monthly variation in pH at different stations over the Kochi shelf

The T_{Alk} in the study region ranged from 1992 to 2413 µmol kg^{-1} with an annual average of 2240±50 µmol kg^{-1}. Unlike pH and DIC, T_{Alk} did not show much seasonal variation though it correlated significantly with salinity (r^2=0.42; p<0.001). The average T_{Alk} was 2218±44 µmol kg^{-1} in WM, 2231±42 µmol kg^{-1} in SIM, 2251±61 µmol kg^{-1} in SM and 2267±33 µmol kg^{-1} in FIM. The T_{Alk}:DIC ratio is an indicator for relative abundance of carbonate species (eg: HCO_3^-, CO_3^{2-}) and buffering capacity of a system (minimum when T_{Alk}:DIC ~ 1). This ratio was consistent during non-upwelling periods (SIM: 1.14±0.02; FIM: 1.13±0.03; WM: 1.15±0.02) but decreased during upwelling (SM: 1.08±0.03) with an annual mean of 1.12±0.04.

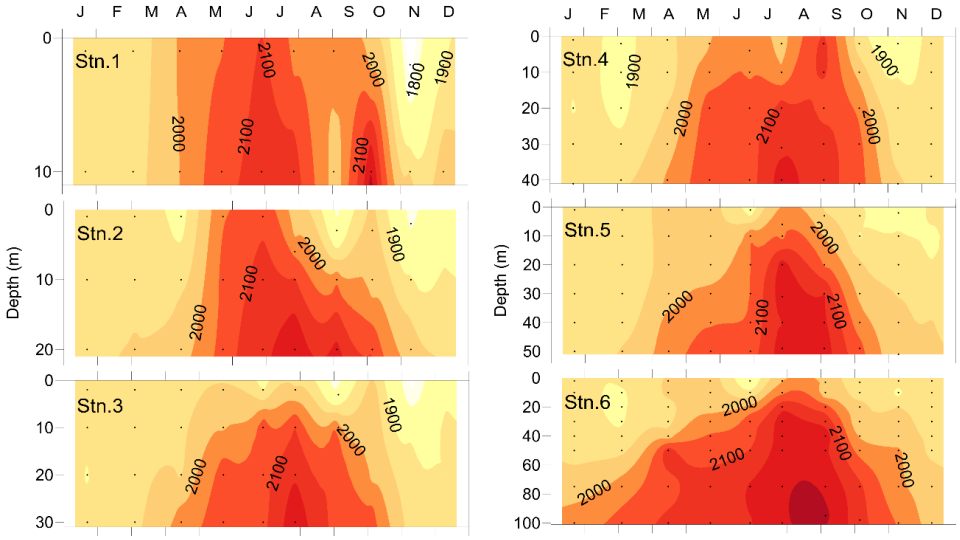

Figure 6.2. Monthly variation in DIC (µmol kg^{-1}) at different stations over the Kochi shelf

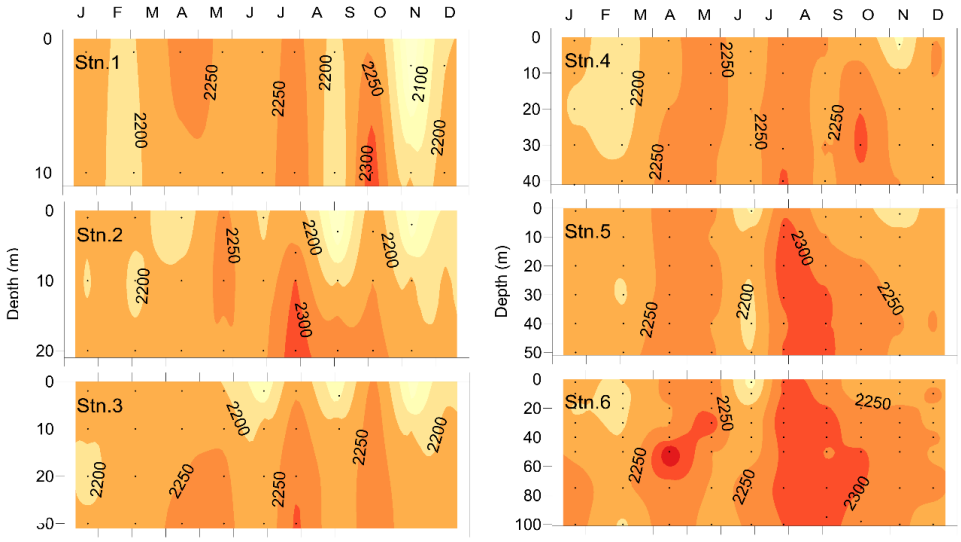

Figure 6.3. Monthly variation in T_{Alk} (µmol kg^{-1}) at different stations over the Kochi shelf

6.3 Variations in pH, DIC and T_{Alk} in the coastal waters (Mangalore)

The variation in the pH and DIC showed significant seasonality, whereas T_{Alk} showed minimum variations (Fig. 6.4) during the study period. Similar to Kochi, pH in this shelf also remained high in April (8.129±0.063) and decreased to the minimum in September (7.935±0.142) but rose marginally in December (8.094±0.077). The annual pH varied from 7.755 to 8.181 (8.053±0.131). The upwelling increased the DIC concentration from 1937±65 in April to 2078±124 µmol kg^{-1} in September and dropped again to 1926±31 µmol kg^{-1} in December. The annual DIC concentrations ranged from 1698 to 2200 µmol kg^{-1} with an average of 1987±109 µmol kg^{-1}. T_{Alk} ranged from 2020 to 2316 µmol kg^{-1} (2233±61 µmol kg^{-1}) and did not show any seasonal variation during the

study period. However, T_{Alk}:DIC varied significantly; 1.15±0.02 in April, 1.04±0.20 in September and 1.14±0.02 in December.

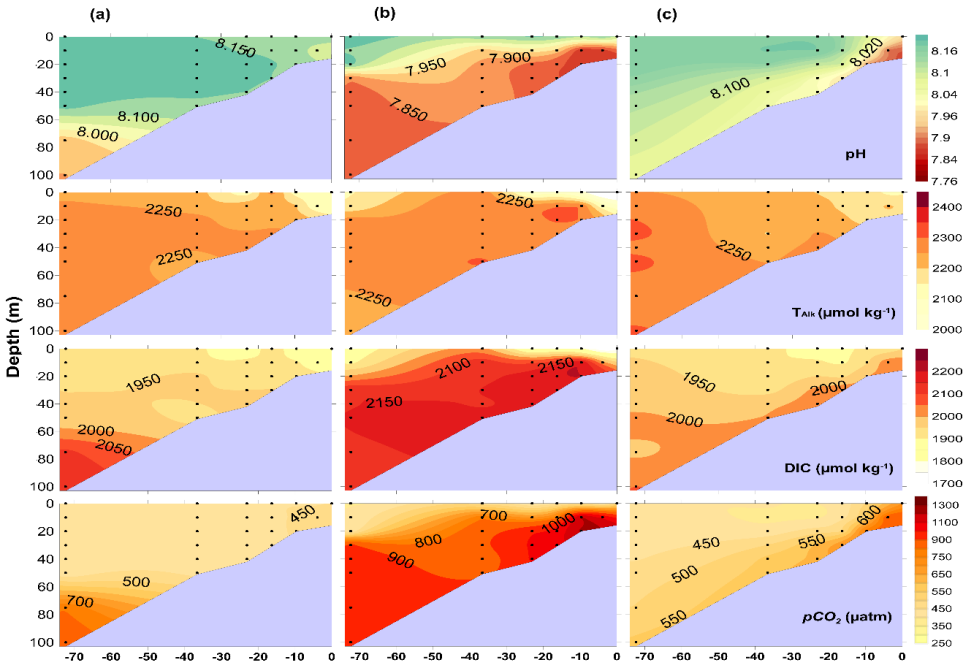

Figure 6.4. Variations in pCO_2 (µatm), pH, T_{Alk} (µmol kg^{-1}) and DIC (µmol kg^{-1}) along the coastal waters of Mangalore during (a) April, (b) September and (c) December

6.4 Variation in the *pCO₂*

The pCO_2 values along the Kochi shelf ranged from 254 to 1237 µatm with an annual average of 573±197 µatm. Except few values, the pCO_2 levels were higher than the atmospheric value (393 ppm during 2012; ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_annmean_gl.txt). With the advancement of upwelling the pCO_2 increased from SIM (478±79 µatm) to SM (760±211 µatm) and with the recession of upwelling it

decreased to FIM (545±180 µatm) and then to WM (441±53 µatm) (Fig. 6.5). Exceedingly high pCO_2 values (>1000 µatm) in the shallow stations (stns. 1 and 2) during June can be attributed to the combined effects of coastal upwelling and export from the Cochin estuary. It has been reported that the heterotrophic Cochin estuary is a perennial source of CO_2 to the adjoining coastal waters with its export flux ranged from 9.04 $\times 10^4$ gC d^{-1} in premonsoon to 36.3 $\times 10^4$ gC d^{-1} in summer monsoon (Gupta *et al*., 2009). Together with estuarine contribution, the upwelling induced hypoxia enriched with CO_2 favour its highest supersaturation especially in the shallow regions during peak SM. Although these shallow regions encountered with high phytoplankton production (Fig. 3.11) due to nutrient enrichment from SM upwelling their highest supersaturation with CO_2 shows that its combined supply through upwelling, terrestrial discharge and *in situ* production (community respiration) exceeded consumption. As a result *SEAS* has also been found to be net heterotrophic (Sarma, 2003). This is further supported by the parallel experimental studies made off Kochi that its inner shelf region was net heterotrophic during SM due to excess bacterial demand (respiration in excess of production). A marginal decrease in surface pCO_2 in the mid and outer shelf regions during SM was associated with high Chl*a* although the water column below 10 m was CO_2-rich due to upwelling. The high bacterial activity may be responsible for the CO_2 supersaturation in the sub surface, while high productivity prevailed in the euphotic layers.

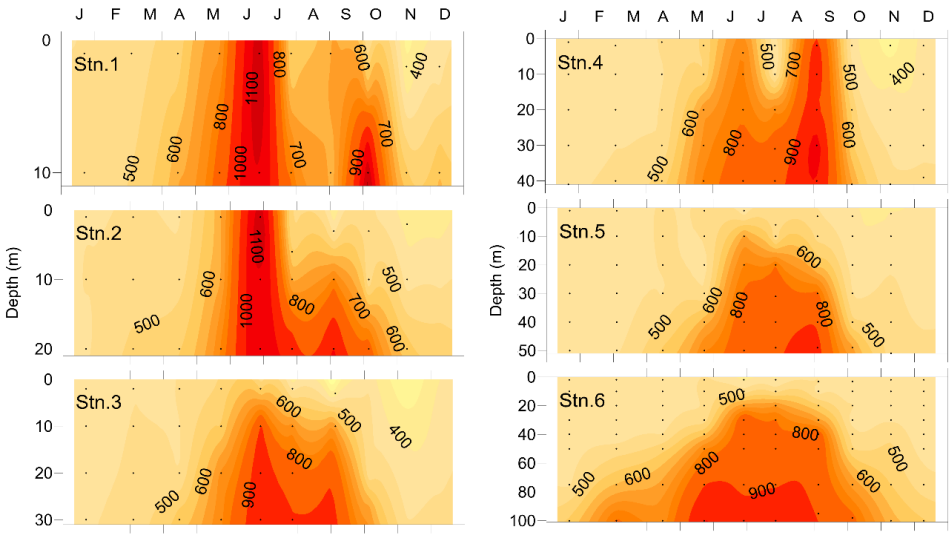

Figure 6.5. Monthly variation in pCO_2 (µatm) at different stations over the Kochi shelf

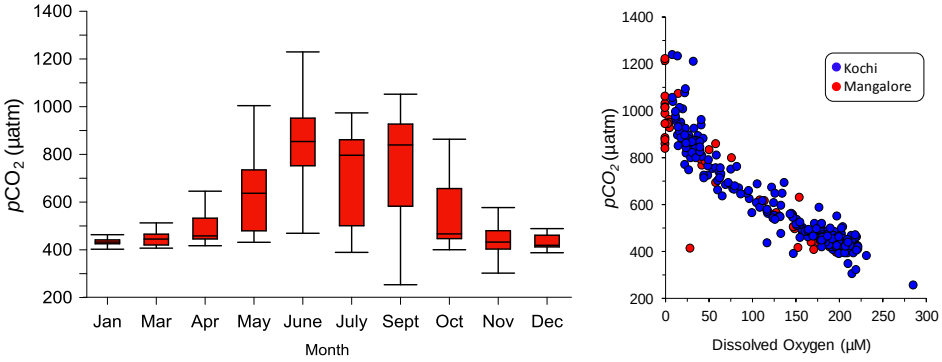

Figure 6.6. Monthly pCO_2 (µatm) variability and its relationship with DO in the *SEAS*

Similar to Kochi, coastal waters off Mangalore exhibited significant seasonal variation. The water column pCO_2 varied from 409 to 830 µatm (463±98 µatm), 393 to 1219 µatm (800±263 µatm) and 392 to 856 µatm (513±116 µatm) in April, September and December respectively. The

surface pCO_2 values were lowest during September, though it was about 4 times high in the subsurface. The exponential increase in the production of CO_2 when DO falls below 25 µM (Fig. 6.6) indicate the increased mineralization during upwelling leading to CO_2 enrichment (800±263 µatm) in the anoxic Mangalore shelf relative to the hypoxic Kochi shelf (755±197 µatm).

The annual mean surface pCO_2 of 374.4 µatm observed for the *SEAS* during 1996 (Sarma *et al*., 2000; atmospheric CO_2 361.7 ppm) was ~21% less than the mean value of 475 µatm observed in this study in 2012 (atmospheric CO_2 393 ppm). This shows that pCO_2 in the *SEAS* has increased at 6.3 µatm y^{-1} in the last 16 years when atmospheric CO_2 increased only at 1.96 µatm y^{-1}. However, the present value is comparable with the reported surface value of 476.5 µatm for 2015 from the same region (Kanuri *et al*., 2017). It should be noted that 2012 was an Indian Ocean dipole (IOD) year while 2015 was a strong El-Nino year (http://ggweather.com/enso/oni.htm); these warming years exhibit weak upwelling intensity (refer section 3.4 of Chapter 3), more so in 2015 El-Nino year (Gupta et al., unpublished), thereby the poor phytoplankton production can enhance the surface pCO_2. This is consistent with the earlier report (Sarma, 2006) that IOD events increase surface pCO_2 levels by 5 to 20 µatm and the weak winds of IODs reduce the CO_2 emission by 10%. Notwithstanding to these global events, the *SEAS* has still witnessed alarmingly high rate of pCO_2 increase in the last 16 years relative to the atmospheric increase. This might have a cascading adverse effects on the *SEAS* shelf ecosystem which augments detailed investigations to foresee future changes through long-term studies.

6.5 Changes in the saturation levels of calcite and aragonite

The degree of saturation of calcite (Ω_{Ca}) and aragonite (Ω_{Ar}) is defined as the ratio of ionic products of calcium and carbonate concentrations (at *in situ* temperature, salinity and pressure) to the solubility products of calcite (Kspc) and aragonite (Kspa)

$$\Omega_{Ca} = [Ca^{2+}] [CO_3^{2-}] / Kspc$$

$$\text{and } \Omega_{Ar} = [Ca^{2+}] [CO_3^{2-}] / Kspa$$

where, $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentration of calcium and carbonate ions in solution. A value of $\Omega > 1$ represents supersaturation and $\Omega < 1$ represents undersaturation. Seawater is considered saturated with calcite and aragonite when $\Omega = 1$. The degree of saturation state with respect to carbonate minerals control the formation and stability of biogenic and inorganic calcium carbonate (Kleypas *et al*. 1999; Broecker *et al*. 2001; Rushdi *et al*., 2015). The present study observed significant variation in the calcite and aragonite saturation levels in the shelf waters (Figs. 6.7 to 6.9). The entire shelf was supersaturated with respect to both calcite and aragonite during SIM (4.78±0.55 and 3.24±0.4) and WM (5±0.36 and 3.28±0.32). There was a substantial reduction in their saturation during SM upwelling (3.12±0.88 and 2.05±0.59 respectively for calcite and aragonite). The shelf waters of *SEAS* did not experience undersaturation ($\Omega < 1$) of calcite and aragonite despite the Mangalore shelf exhibited intense upwelling during peak SM.

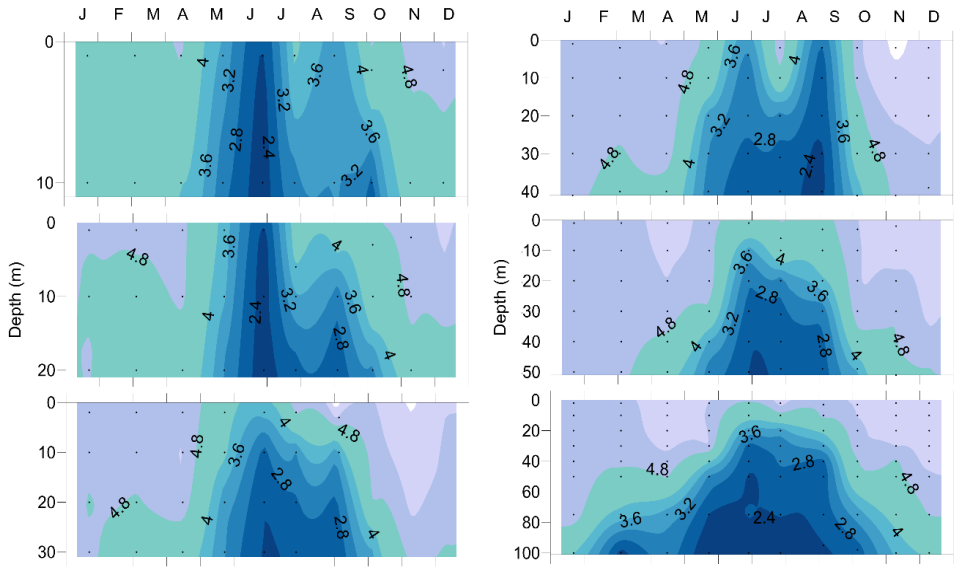

Figure 6.7. Monthly variation in calcite saturation state at different stations over the Kochi shelf

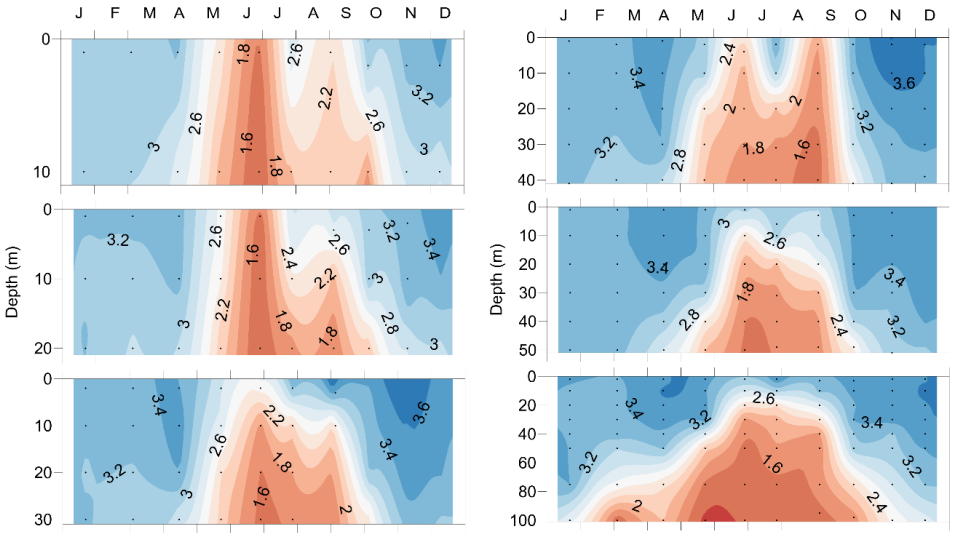

Figure 6.8. Monthly variation in aragonite saturation state at different stations over the Kochi shelf

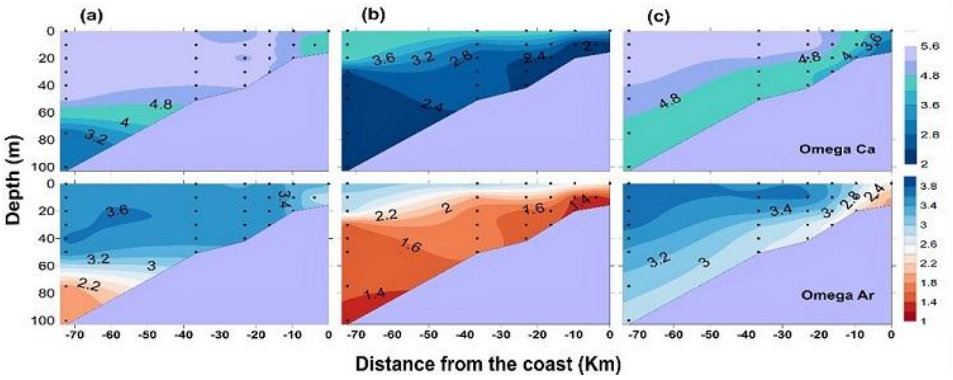

Figure 6.9. Variation in calcite (Ω_{Ca}) aragonite (Ω_{Ar}) saturation during April (a), September (b) and December (c) 2012 along the coastal waters off Mangalore

6.6 Carbonate chemistry and its implications on the biological properties

The decrease in calcite and aragonite saturation normally reduces the formation of calcifying organisms such as foraminifera, pteropods, and planktonic larvae of echinoderms (Gazeau *et al*. 2007; Jokiel *et al*. 2008; Comeau *et al*. 2009; Clark *et al*. 2009; Lombard *et al*. 2010). Benthic organisms are very sensitive to the changes in carbonate chemistry. Significant decrease in calcite and aragonite saturation levels in the study region during the peak upwelling period (Figs. 6.7 to 6.9) may alter benthic biodiversity and ecosystem functioning where the non-calcifying benthic organisms may dominate over benthic calcifiers or some of the calcifying benthos may disappear (Widdicombe and Spicer 2008; Kroeker *et al*. 2011). The geological records have also indicated that changes in calcium carbonate saturation have affected the evolution of calcifying organisms (Royer *et al*., 2001). A significant decline in echinoderm density with low diversity was noted in the northern part of

SEAS under the influence of seasonal hypoxia (Parameswaran *et al*., 2018). However, it is important to note that shell formation process in marine organisms is not tightly bound to the Ω=1 threshold, even though it is generally referenced as an abiotic threshold for calcium carbonate dissolution and precipitation. For example, depending on the life stage of an organism, shell dissolution in various marine calcifiers can start at Ω values ranging from 1.3 to 1.6 (Bednaršek *et al*., 2014; Waldbusser *et al*., 2015), while shell calcification can also occur at Ω values <1 (Comeau *et al*., 2010).

Recent observations reveal that aragonite undersaturated waters enter the ocean surface along eastern boundary of California during upwelling (Feely *et al*., 2008). In the present study, Ω_{Ar} values as low as 1.3 were recorded in the *SEAS* shelf during the peak upwelling period. Under the present scenario of climate change related ocean warming, increasing stratification, enhanced coastal upwelling, expanding oxygen minimum zones, and changes in freshwater delivery, the saturation levels are likely to decrease further.

While Ω mainly disturbs marine calcifiers, pCO_2 can disturb both calcifiers and non-calcifers to a state of hypercapnia (Feely *et al*., 2018). Hypercapnia is associated with the exposure of 1000 µatm pCO_2 condition for more than one month (McNeil and Sasse, 2016). High concentration of CO_2 (>900 µatm) is found to cause sensory impairment to many marine organisms including their larvae (Nilson *et al*., 2012). It is important here to note that the shallow waters of *SEAS* sustaining peak hypoxia and highest pCO_2 levels (>1000 µatm) during SM are characterised by lowest

macrobenthic diversity but with high abundance of polychaetes (Jaleel *et al.*, 2015; Sivadas *et al*. in preparation) which are physiologically adapted to hypoxic (Levin *et al*., 2009), and in turn, to acidified conditions. This change in hypoxia/acidification vis-à-vis benthic community will alter the feeding habits or may lead to the disappearance of demersal fishes (Banse, 1968).

6.7 Air-sea exchange and fluxes

The monthly estimates on the CO_2 fluxes are given in Table 6.1. It is evident that the *SEAS* was a net source of CO_2 to the atmosphere during the study period. The CO_2 saturation varied annually from 64 to 314% (145±50%) over the Kochi shelf, while it varied from 100 to 310% (150±58%) over the Mangalore shelf. Significant spatio-temporal variability in sea-air fluxes of CO_2 was noticed during the present study. Seasonally, the fluxes of CO_2 from the Kochi shelf ranged from -8.12 to 4.2 mmol m^{-2} d^{-1} (0.4±3.4 mmol m^{-2} d^{-1}) in WM, 2.07 to 11.42 mmol m^{-2} d^{-1} (5.32±2.44 mmol m^{-2} d^{-1}) in SIM, -0.9.05 to 76 mmol m^{-2} d^{-1} (16.18±23.7 mmol m^{-2} d^{-1}) in SM and 1.7 to 6.98 mmol m^{-2} d^{-1} (3.6±1.9 mmol m^{-2} d^{-1}) in FIM. The seasonal CO_2 fluxes from Mangalore coastal waters were 1.45 to 3.38 mmol m^{-2} d^{-1} (2.60±0.63 mmol m^{-2} d^{-1}), 0.06 to 6.63 mmol m^{-2} d^{-1} (2.94±2.63 mmol m^{-2} d^{-1}) and 0.15 to 3.53 mmol m^{-2} d^{-1} (1.05±1.22 mmol m^{-2} d^{-1}) respectively during SIM, SM and WM. The CO_2 fluxes from the present study (-0.98 to 76 mmol m^{-2} d^{-1}) during SM are comparable with recent report (-0.4 to 48.53 mmol m^{-2} d^{-1}; Kanuri et al., 2017) from the same region. Significantly high CO_2 fluxes from the nearshore of Kochi (13.7±21.64 mmol m^{-2} d^{-1}) compared to inner shelf (3.6±5.3 mmol m^{-2} d^{-1}),

mid (4.08±3.54 mmol m^{-2} d^{-1}) and outer shelf (2.50±1.81 mmol m^{-2} d^{-1}) regions follow their CO_2 enrichment.

Table 6.1. Monthly variation in concentration and air-sea fluxes of pCO_2 in the study region

Stn. No.	Month	Surface conc.(µatm) (Avg. ± SD)	Maximum Subsurface (depth) Conc. (µatm)	Surface saturation (%)	Air-sea flux (mmol m^{-2} d^{-1})
Kochi					
1	Jan	403-457 (433±18.7)	557 (100m)	102-116	0.68-4.2
2	March	420-466 (444±17.3)	815 (100m)	106-118	2.07-5.9
3	April	442-514 (463±24)	721 (100m)	112-130	4.1-11.4
4	May	461-685 (551±83)	1006 (100m)	117-174	5.9-17.2
5	June	390-1208 (746±356)	1090 (20m)	99-313	-0.25-76
6	July	405-548 (461±58)	975 (20m)	99-139	-0.36-17.5
7	Sept	460-937 (584±186)	1053 (30m)	64-238	-0.9.05-34.16
8	Oct	416-497 (446±30)	864 (20m)	105-126	1.7-6.98
9	Nov	388-423 (363±44)	622 (100m)	77-107	-8.12-2.8
10	Dec	412-419 (409±10)	604 (10m)	98-106	-0.35-2.1
Mangalore					
1	April	417-450 (437±11)	783 (100m)	106-114	1.4-3.4
2	Sept	394-462 (426±30)	1219 (20m)	100-120	0.06-6.6
3	Dec	408-627 (462±81)	856 (11)	102-159	0.15-3.5

Following the zonal approach, the CO_2 efflux was computed at 2.7 Tg y^{-1} for 7-11°N and 1.6 Tg y^{-1} for 11-14°N. Therefore, the annual CO_2 efflux from the *SEAS* (7-14°N) was estimated at 4.28 Tg y^{-1}. These estimates are prone to large uncertainty due to changes in the oceanic environment following global warming and associated air–sea CO_2 fluxes.

6.8 Summary

The chapter discusses the distribution of inorganic carbon components and its intra annual variability in the *SEAS* shelf based on time-series data. The carbon dynamics in the *SEAS* was found to be strongly controlled by coastal upwelling and *in situ* biological processes. On an annual basis, the CO_2 efflux from the *SEAS* (7-14°N) was estimated to be 4.28Tg y^{-1} indicating the study region as a significant source of CO_2. Significant increase in pCO_2 levels during the upwelling period induced drastic change in carbonate chemistry. The calcite and aragonite saturations decreased drastically during peak upwelling to influence the sensitive calcifying organisms. However, a significant increase in pCO_2 in the bottom layers seems to have negatively affected both calcifiers and non-calcifers, by subjecting them to the stress of hypercapnia. Future studies should therefore, focus more on the influence of pCO_2 on the biology of *SEAS* shelf.

Chapter 7

SUMMARY AND CONCLUSIONS

The south-eastern Arabian Sea (*SEAS*) is an eastern boundary upwelling system, characterised by seasonal upwelling and consequent high biological production during the summer monsoon and oligotrophic conditions during the winter monsoon. Apart from the upwelling during the summer monsoon, the southern part of the *SEAS* receives significant nutrient inputs from three estuaries (Ashtamudi ~9° N, Kochi ~10° N and Netravati-Gurupura, ~13°N) during this season. Biogeochemical and ecosystem processes in the *SEAS* reflect the influence of its dynamic circulation, and production regimes, particularly nutrient enrichment from both upwelling and terrestrial inputs. Oxygen depletion (hypoxia/anoxia) is recorded across almost the entire continental shelf of the *SEAS* during the summer monsoon owing to the combined influence of upwelling, nutrient enrichment, high biological production, stratification, and degradation of vast quantities of organic matter. Biogeochemical processes under hypoxia/anoxia have a significant influence on nutrient cycling and are known to substantially increase the production of greenhouse gases (N_2O, CH_4 and CO_2). The west coast of India is considered as a global hotspot for N_2O production as a result of seasonal upwelling and related anoxia. Although many studies have been

undertaken in the recent past in the *SEAS*, none of them have systematically addressed the influence of oceanic processes on coastal biogeochemistry and cycling of greenhouse gases. There are alarming reports on the expansion and intensification of oxygen deficient zones in the world ocean, as a result of climate change related ocean warming and stratification. Intensification of seasonal coastal hypoxia along the western margin of India was also reported earlier and was attributed at least in part to increased nitrogen load from terrestrial sources. This shows that the biogeochemical cycling and greenhouse gas emissions from the *SEAS* are likely to be very significantly impacted by the intensification of hypoxia/anoxia. The present study therefore, aims to evaluate the biogeochemical processes over the continental shelf of *SEAS* by studying the seasonal upwelling, hypoxia and associated nutrient biogeochemistry, and influence of these processes on cycling and fluxes of greenhouse gases (N_2O, CH_4 and CO_2). To address the same, ten repeated observations were made over the Kochi shelf, apart from three seasonal observations to its north over the Mangalore shelf, extending from nearshore (10m) to outer shelf (100m), during 2012. For the first time, this study has tracked the upwelling from its onset to offset over the *SEAS* shelf and the associated biogeochemical changes.

The study identified clear intra-annual variability in biogeochemical properties in response to the combined effect of natural and anthropogenic influences. By changing from an oligotrophic oxic system to nutrient-replete hypoxic/anoxic conditions, upwelling is the major process that regulates the biogeochemistry of this shelf. Upwelling sets at 100 m between January and March, reached surface of the inner-shelf in

May and peaked during June-July. It persisted over the entire shelf till September and withdrew completely and abruptly by October. Nutrient replenishment through upwelling enhanced the primary production during summer monsoon and the increased sinking organic flux caused severe oxygen depletion resulting in a heterotrophic system below euphotic depth. Contrary to the intensification theory of hypoxia over major coastal seas around the world, Kochi shelf has been found to maintain its oxygen concentrations compared to five decades ago as the adjoining Cochin estuary acts as a heavy sink zone for anthropogenic nutrients; the impact of estuarine discharges are, therefore, by large confined to nearshore regions. Further, the study pointed out that apart from inter-annual variability in extent and intensity of hypoxia, associated with naturally occurring upwelling, *SEAS* did not show any intensification of oxygen deficiency. This shows the steady healthy state of Kochi shelf.

The exponential increase in CO_2 and N_2O concentrations when dissolved oxygen (DO) falls <25 μM indicate that the intense summer upwelling is the active period for GHGs production. Unlike at Kochi, Mangalore shelf experiences advection of upwelling waters from the core of oxygen minimum zone. Upwelling of cold sub-oxic waters (0 to <10 μM DO) coupled with higher production and stronger thermohaline stratification led to development of intense reducing conditions in bottom waters and underlying sediments. This marked significant difference in upwelling intensity between Kochi and Mangalore induces contrasting biogeochemical behaviours.

Consistent with earlier reports, the present study recorded bottom sulphidic conditions over the anoxic nearshore regions off Mangalore during SM, while such conditions were not noted off Kochi. Complete removal of oxygen resulted in N-loss in the bottom waters off Mangalore, and the region experienced autotrophic denitrification up to the inner shelf, strong heterotrophic denitrification in the mid-shelf and mild denitrification in the outer-shelf. This classic biogeochemical pathway led to significant accumulation of N_2O in the mid and outer shelf waters off Mangalore. The shelf off Kochi, however, did not displayed such gradients in biogeochemical behaviour as its water column always sell short of becoming anoxic due to which its inner shelf was predominantly under the influence of heterotrophic sediment denitrification.

Variability in biogeochemical properties associated with upwelling significantly influenced carbon cycling in the *SEAS*. Intense respiratory demand associated with upwelling enhanced CO_2 production in the bottom waters. Subsequently, the acidic, CO_2-rich bottom waters induced a drastic change in carbonate chemistry. Significantly low calcite and aragonite saturations during upwelling influence the sensitive calcifying organisms. Moreover, a decrease in their saturation levels combined with hypoxia/anoxia and CO_2 rich conditions are expected to alter benthic biodiversity and ecosystem functioning.

Unlike N_2O and CO_2, lower CH_4 concentrations in the anoxic nearshore waters off Mangalore relative to hypoxic Kochi during summer monsoon suggests that CH_4 produced through sediment methanogenesis over the former region is substantially removed through its anaerobic

oxidation under the prevailing denitrifying conditions. The significantly higher CH_4 concentrations in the nearshore Kochi during non-upwelling periods were attributed to combined inputs from sediments, water column production and estuarine out flux through tidal flushing.

The significantly high concentration of greenhouse gases (N_2O, CH_4 and CO_2) in the nearshore waters was due at least in part to contributions from adjoining estuaries apart from upwelling. These combined effects transformed *SEAS* into a biogeochemically dynamic region of significant source for GHGs to the atmosphere. The computed GHGs fluxes from the *SEAS* (7-14°N) ranged from 42±85 µmol m^{-2} d^{-1} for N_2O, 30±47 µmole m^{-2} d^{-1} for CH_4 and 6.2±14 mmol m^{-2} d^{-1} for CO_2. Utilizing the high-resolution data of the present study, the annual fluxes from the *SEAS* shelf (7-14°N) were estimated at 0.019–0.039 Tg N_2O, 0.0053 Tg CH_4 and 4.28 Tg CO_2. The current estimated N_2O annual effluxes using gridded zonal approach were almost four-times lower than the earlier ones (average value applied to entire shelf area) which appear to be have been over estimations.

In view of the growing concerns on the expanding OMZ and its influence on global climate (via emissions of climate relevant trace gases like N_2O, CH_4 and CO_2), further studies are essential to provide a more refined understanding of the sea to air fluxes of these GHGs and also to predict the responses of the biogeochemical processes over the entire shelf off west India to the ongoing regional (developmental activities) and global (e.g., warming) environmental changes.

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ANNEXURES

Annexure 1

List of Abbreviations

AOU	Apparent Oxygen Utilization
AS	Arabian Sea
ASHSW	Arabian Sea High Saline Waters
BBLSW	Bay of Bengal Low Saline Waters
BoB	Bay of Bengal
CaTS	Candolim Time-Series,
CE	Cochin Estuary
CEAS	Central Eastern Arabian Sea
Chl	Chlorophyll
CTD	Conductivity, Temperature and Depth
DIC	Dissolved Inorganic Carbon
DIN	Dissolved Inorganic Nitrogen
DO	Dissolved Oxygen
EBC	Eastern Boundary Currents
ECD	Electron Capture Detector
EICC	East India Coastal Current
FIM	Fall Inter Monsoon
FORV	Fisheries Oceanographic Research Vessel
GHG	Greenhouse Gas
IOD	Indian Ocean Dipole
IPCC	Intergovernmental Panel on Climate Change
KoTS	Kochi Time Series
MLD	Mixed Layer Depth
NBS	National Bureau of Standards
NIST	National Institute of Standards and Technology
OMZ	Oxygen Minimum Zone

POC	Particulate Organic Carbon
SCM	Sub-Surface Chlorophyll Maximum
SEAS	Southeastern Arabian Sea
SIM	Spring Inter Monsoon
SM	Summer Monsoon
SSS	Sea Surface Salinity
SST	Sea Surface Temperature
WICC	West India Coastal Current
WICC	West India Coastal Currents
WM	Winter Monsoon
WM	Winter Monsoon

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Annexure 2

List of Publications

[1] Baliarsingh, S. K., Aneesh A. Lotliker, **V. Sudheesh**, Alakes Samanta, Sourav Das, and A. K. Vijayan (2018), Response of phytoplankton community and size classes to green Noctiluca bloom in the northern Arabian Sea, *Marine Poll. Bull.*, 129 (1), 222-230.

[2] Bhavya, P. S., Sanjeev Kumar, G. V. M. Gupta, K. V. Sudharma, and **V. Sudheesh** (2018), Spatio-temporal variation in δ13CDIC of a tropical eutrophic estuary (Cochin estuary, India) and adjacent Arabian Sea, *Cont. Shelf Res.*, 153, 75-85.

[3] **Sudheesh, V**., M. Movitha, A.A. Mohamed Hatha, K.R. Renjith, P. Resmi, Mujeeb Rahiman, and S.M. Nair (2017), Effects of seasonal anoxia on the distribution of phosphorus fractions in the surface sediments of southeastern Arabian Sea shelf. *Cont. Shelf Res.*,*150*, 57-64

[4] Bhavya, P.S., Sanjeev Kumar, G.V.M.Gupta, and **V.Sudheesh** (2017), Carbon Uptake Rates in the Cochin Estuary and Adjoining Coastal Arabian Sea, *Estuaries and Coasts*, *40*(2), 447-456.

[5] **Sudheesh, V**., G.V.M.Gupta, K.V.Sudharma, H.Naik, D.M.Shenoy, M. Sudhakar, and S.W.A.Naqvi (2016), Upwelling intensity modulates N_2O concentrations over the western Indian shelf, *J. Geophys. Res. Oceans*, 121(12), 8551-8565.