MEASUREMENT OF CARBON DIOXIDE FLUXES IN THE ARABIAN SEA USING REMOTE SENSING DATA

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Abstract

Spatial and seasonal distribution of carbon dioxide fluxes in the Arabian Sea was estimated for the period September 2002 to February 2012. The regulation of fluxes by ocean primary productivity and sea surface temperature was also studied. The CO\textsubscript{2} flux derivation involved a variety of satellite as well as climatology data such as sea surface temperature, chlorophyll, wind speed, sea level pressure, seawater salinity and CO\textsubscript{2} mole fraction. Using these data, the difference in CO\textsubscript{2} partial pressure in seawater and air (δpCO\textsubscript{2}), CO\textsubscript{2} solubility, gas transfer velocity and water density were calculated and from these parameters, the CO\textsubscript{2} flux over the Arabian Sea was derived. Spatially the study area was divided into north, west, east and south and seasonal changes were analysed for winter, pre-monsoon, monsoon and post-monsoon seasons. The fluxes showed both spatial and seasonal variations with highest values found in the western Arabian Sea (36-75 mmol m\textsuperscript{-2} day\textsuperscript{-1}) during monsoon followed by the northern region (5-20 mmol m\textsuperscript{-2} day\textsuperscript{-1}) in winter. The ocean primary productivity was derived using Vertically Generalised Production Model and satellite derived chlorophyll. The distribution of productivity showed high values in the north (1200-2300 mgC m\textsuperscript{-2} day\textsuperscript{-1}) during winter and west (850-1700 mgC m\textsuperscript{-2} day\textsuperscript{-1}) during monsoon. The productivity was observed to be low in the southern region (200-260 mgC m\textsuperscript{-2} day\textsuperscript{-1}) during pre-monsoon.

The comparison of fluxes with ocean productivity found a positive correlation in winter in all regions. Monsoonal correlation was found to be positive in the west, east and south while a negative correlation observed in the north. No considerable correlation was observed between the fluxes and productivity in west and east in the pre-monsoon season while in the north a positive correlation was observed. Fluxes were found to decrease with increase in productivity during post-monsoon in the south and west, and in the south during pre-monsoon. The correlation of CO\textsubscript{2} fluxes with SST was found to be negative in all seasons in the northern and eastern Arabian Sea. In the west, negative correlation was observed during monsoon, pre-monsoon and post-monsoon and in the southern region during winter, monsoon and pre-monsoon. An increase in fluxes with increased SST was found in the south during post-monsoon season.

Data collected during field study was used to develop an algorithm for deriving seawater pCO\textsubscript{2} for case 2 waters and the algorithm developed by Zhu et al (2009) was applied for case 1 waters. The results showed the values fall within range in the central and eastern regions in winter while above case 2 algorithms provided out of range values in northern case 2 waters. In the pre-monsoon, pCO\textsubscript{2} values were found to be within range in the east, south east and offshore waters in the north while the coastal waters in the north were not within limits. Monsoon pCO\textsubscript{2} values were within limits in the central, western and eastern Arabian Sea. It was found that the central and southern regions give values within range during pre-monsoon.
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# Abbreviations

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<tr>
<td>DIC</td>
<td>Dissolved Inorganic Carbon</td>
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<td>JGOFS</td>
<td>Joint Global Ocean Flux Study</td>
</tr>
<tr>
<td>mmol</td>
<td>milli mol</td>
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<tr>
<td>pCO₂</td>
<td>Partial pressure of carbon dioxide</td>
</tr>
<tr>
<td>pH₂O</td>
<td>saturation vapour pressure of seawater</td>
</tr>
<tr>
<td>Pₜ</td>
<td>Sea level pressure</td>
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<tr>
<td>SST</td>
<td>Sea Surface Temperature</td>
</tr>
<tr>
<td>TA</td>
<td>Total Alkalinity</td>
</tr>
<tr>
<td>Tg</td>
<td>Terra gram</td>
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Chapter 1
Introduction

Ocean and atmospheric circulations play key role in earth’s climate. Oceans have a large heat capacity of about 1000 times higher compared to that of atmosphere. This heat is mainly stored in the upper layers of ocean. The transport of this heat and water by ocean currents play crucial roles in regional climate while global climate is influenced by the large-scale thermohaline circulation (Solomon et al., 2007). Variations in atmospheric circulation considerably influence the circulation of oceans. Ocean circulations occur both at the surface and deeper layers.

1.1 Surface circulation

Atmospheric effects mainly act on surface ocean currents. They are driven by the frictional dragging action of wind on the surface. These circulations are mainly horizontal flows with high velocities. The wind systems responsible for these circulations are trade winds and westerlies. These wind movements result in the formation of large anticyclonic water circulation cells called gyres. Also, the mixing action of wind on the surface creates a uniform temperature layer called mixed layer. Below the mixed layer occurs a narrow zone of rapid temperature change termed thermocline.

1.2 Deep water circulation

The deep ocean that lies below the thermocline exhibits circulation patterns which are driven by the density of sea water. These circulations depend on the sea water salinity and temperature. Thus they are called thermohaline circulations which are comparatively slower than the surface circulations and move in both vertical and horizontal directions. The wind action also causes vertical movements in the ocean i.e., upwelling and downwelling. During the upwelling, nutrient rich deep waters move upward to reach the surface which enhances the primary productivity. This also brings the subsurface CO$_2$ rich water to the sea surface, resulting in the increased rate of CO$_2$ emissions to the atmosphere (Chester, 2000).

Oceans act as the source or sink of atmospheric gases. The biogeochemical cycles of the atmospheric gases play major roles in the global environment and the air-sea exchange of these gases are important in these cycles. Considering global scale processes within these gaseous cycles, carbon dioxide is one such important atmospheric gas which is exchanged through the air-sea interface and theses oceanic fluxes of carbon dioxide gas are significant in the global carbon cycle (Chester, 2000).

![Figure.1.1.Global flows of carbon in billion tons (Chester, 2000)](image-url)
Carbon dioxide is a meteorologically significant constituent of atmosphere which constitutes about 0.032% of air. Being an efficient absorber of earth emitted radiation, it has a considerable contribution to the heating of atmosphere (Lutgens and Tarbuck, 2004). The atmospheric concentration of carbon dioxide (CO\textsubscript{2}) gas is being regulated by continuous exchange of oceanic CO\textsubscript{2} at the sea surface through carbon cycle.

1.3 Carbon Cycle

The cycling of carbon between ocean and atmosphere involves a number of physical and biological processes. The flow of CO\textsubscript{2} from atmosphere to ocean and vice versa is a function of surface mixing, which is largely depended on wind speed, and the difference in the CO\textsubscript{2} concentration between air and sea water.

Atmospheric CO\textsubscript{2} enters the ocean waters by simple diffusion. It is taken up by the primary producers i.e., marine algae and photosynthetic bacteria and convert it into organic carbon. This is consumed by the zooplankton which are the secondary producers and thus it moves through the food chain. Finally it is released into the water through respiration and oxidative destruction and remineralisation of dead organisms (Chester, 2000; Botkin and Keller, 2000). Some marine organisms convert carbon in sea water into calcium carbonate for utilizing it as the building material for shells and skeletons. This carbon will sink to the deeper ocean and become a part of marine sediment after the organisms die thus locking the carbon for millions of years.

The changes in the uptake and release of CO\textsubscript{2} cause changes in ocean biogeochemistry thereby directly affecting climate system (Falkowski et al., 2000; Solomon et al., 2007). Oceans uptake CO\textsubscript{2} through the transfer process called solubility pump which is a function of gas solubility in sea water. This involves transfer of CO\textsubscript{2} across the air-sea interface into the mixed layer. CO\textsubscript{2} solubility is high in high latitude cold waters where it is transported into the deep waters. There are two other transfer processes called physical pump and biological pump through which the mixed layer carbon goes into the deeper ocean.

1.3 Physical pump

It involves downward mixing and down-welling which are associated with deep water mass formation and commencement of thermohaline circulation. The physical pump and the solubility pump are coupled.
1.4 Biological pump

It is the biogenic production of organic material and carbonate minerals in the ocean surface which are transported thereafter in to the deep ocean. The transport of carbon in to the deeper layers occurs through vertical gravitational settling of biogenic debris in the euphotic zone. This process generates a dissolved inorganic carbon gradient with low surface values which gradually increasing with depth. It reduces the sea surface CO$_2$ and enhances the uptake of CO$_2$ gas by oceans. The pathways involved in the biological pump are:

- **Biological organic carbon pump** is the sinking of CO$_2$ which is utilized in the photosynthetic carbon fixation:
  \[
  6\text{CO}_2 + 12\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 + 6\text{H}_2\text{O}
  \]

- **Biological carbonate pump** transports particulate inorganic carbon from surface to the deeper ocean:
  \[
  \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}
  \]

- **Sinking of faecal pellets**

- **Downward advection and diffusion of organic and inorganic carbon** (Chester, 2000; Zondervan et al., 2001).

![Figure 1.3. Biological pump (Buesseler et al., 2013)](image)

Anthropogenic activities such as fossil fuel combustion, industrial processes and forest burning for farming purposes have resulted in increase of atmospheric CO$_2$ levels in the past ten years as compared to the pre-industrial CO$_2$ concentration. A significant portion of this CO$_2$ is taken up by the oceans thus acting as largest reservoir of carbon in the biosphere. They store about 93% of the global carbon (Davila et al., 2007; Bernstein et al., 2007; Freely et al., 2001; Balino et al., 2000). This uptake is dependent on the circulation as well as carbonate chemistry of ocean. The increase in the CO$_2$ concentration acidifies the sea water and alters its chemical equilibrium. This reduces the ocean’s capacity to absorb the additional quantities of CO$_2$ added to the atmosphere due to the reduced buffering ability of ocean carbonate system (Prentice et al., 2001; Bindoff et al., 2007). On diffusing in to the ocean, CO$_2$ simply dissolves first to give free aqueous CO$_2$ i.e. CO$_2$(aq).

\[
\text{CO}_2(g) \rightarrow \text{CO}_2(\text{aq})
\]

Next, it reacts with water to form carbonic acid (H$_2$CO$_3$) until equilibrium is established:

\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})
\]

Carbonic acid is a weak acid and it immediately dissociates to bicarbonate and carbonate ions:

\[
\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-
\]
HCO$_3^-$ $\rightleftharpoons$ H$^+$+CO$_3^{2-}$  
(Dickson and Goet, 1994; Zeebe, 2012)

Thus CO$_2$ in sea water occurs mainly as three major inorganic forms: the undissociated form of free aqueous CO$_2$ and the dissociated forms of bicarbonate and carbonate ions. The free aqueous CO$_2$ concentration is proportional to the CO$_2$ partial pressure in sea water. The difference in the partial pressures of CO$_2$ in the sea water and the air above the sea surface determines the direction of the CO$_2$ gas flow between ocean and atmosphere. The CO$_2$ partial pressure (pCO$_2$) shows a greater variation in the sea surface compared to the atmosphere. Thus the CO$_2$ flux direction is controlled primarily by the changes in sea surface pCO$_2$ (Freely et al., 2001; Zeebe, 2012). The CO$_2$ partial pressure in sea water is mainly controlled by sea surface temperature and biological processes in the ocean such as photosynthesis and respiration. Although both these parameters show similar magnitude of effect on pCO$_2$, their effects are often found to be compensating, thus the net effect causes a balance between uptake and release of CO$_2$ by sea surface (Freely et al., 2001).

1.5 Effect of temperature

Warm ocean waters of low latitude cause a reducing effect on sea water pCO$_2$ due to the reduced CO$_2$ solubility with increase in temperatures while pCO$_2$ is found to be increasing in the cold high latitude waters because of high CO$_2$ solubility resulting in the increased dissolution of the gas in to the sea water.

1.6 Effect of biological processes

Phytoplankton affect the CO$_2$ absorption by sea water, especially during bloom conditions because increased rate of photosynthetic activity leading to increased uptake of CO$_2$ by the sea water (Chester, 2000).

Studies have been conducted worldwide to determine the effect of sea surface temperature (Andrie et al., 1986; Goet et al., 1991; Takahashi et al., 1993; Trela et al., 1995; Kumamoto et al., 1995; Goet and Peltzer, 1997; Sarma et al., 2000; Takahashi et al., 2002; Lefevre and Taylor, 2002; Zhai et al., 2005; Chen et al., 2007; Smalls Jr. and Read, 2008; Zhu et al., 2009) and biological processes (Trela et al., 1995; Kumamoto et al., 1995; Sarma et al., 2000; Takahashi et al., 2002; Smalls Jr. and Read, 2008; Zhu et al., 2009) on sea water CO$_2$ partial pressure and the distribution of ocean-atmosphere CO$_2$ fluxes (Andrie et al., 1986; Winn et al., 1994; Bakker et al., 1996; Takahashi et al., 1997; Sarma et al., 1998; Takahashi et al., 2002; Midorikawa et al., 2002; Sarma, 2003; Olsen et al., 2003; Zhai et al., 2005; Metzl et al., 2006; Bates, 2007; McNeil et al., 2007; Gonzalez-Davila et al., 2007; Arrigo and Van Dijken, 2007; Kondo and Tsukamoto, 2007; D’Ortenzio et al., 2008; Takahashi et al., 2009; Sardessai et al., 2010; Kivimae et al., 2010; Hilligsoe et al., 2011; Taillandier et al., 2012; Levy et al., 2012; Akhand et al., 2012; Otero et al., 2013).

The present study involved the estimation of CO$_2$ fluxes over Arabian Sea and deriving the relationships of sea surface temperature and ocean primary productivity on these CO$_2$ fluxes. Being a source of atmospheric CO$_2$ (Sarma et al., 1998; Sarma, 2003) and a region of high primary productivity (Ryther et al., 1996; Prasannakumar et al., 2009) Arabian sea, a part of the northern Indian Ocean, is a suitable oceanic region for studying ocean atmospheric interactions (Barber et al., 2001).
Chapter 2
Review of Literature

2.1 Studies conducted in Arabian Sea

The global climate system involves the tight linking of ocean and atmosphere and is affected by the regulation of global biogeochemical cycling of essential elements on earth by ocean atmospheric interactions. Human activities have been interrupting these natural cycles by the increased emission of CO\textsubscript{2} and other trace gases in to the atmosphere. About half of such anthropogenically emitted CO\textsubscript{2} is being taken up by the oceans, acting as a large CO\textsubscript{2} reservoir storing 50% more CO\textsubscript{2} than the atmosphere. A detailed study on the transformation, transport and recycling of carbon in the ocean is required for understanding the cycling of carbon between ocean and atmosphere and its effect on the climate system (Buesseler et al., 2013).

The CO\textsubscript{2} emissions from Arabian Sea during the SW monsoon was studied by Kortzinger et al. (1997) which showed a pCO\textsubscript{2} supersaturation condition during this season resulting in strong emissions to the atmosphere. Omani coast showed extreme supersaturation with surface pCO\textsubscript{2} values reaching up to 750 μatm. Elevated pCO\textsubscript{2} levels up to 525 μatm was found in region 300nm off the Omani coast in the SW monsoon with cold upwelled waters due to Ekman pumping. The flux densities varied from 2 mmol m\textsuperscript{-2} day\textsuperscript{-1} in the open ocean to 119 mmol m\textsuperscript{-2} day\textsuperscript{-1} in the coastal regions. The total emissions during this season was about 29.6-76 TgC which showed the significant role of this season for the annual emissions. The strong monsoonal wind forcing together with the intense coastal upwelling make Arabian Sea the source of CO\textsubscript{2} to the atmosphere.

Temporal variations of pCO\textsubscript{2} in the Arabian Sea was analysed by Goet et al. (1998) in the year 1995 which involved continuous measurements of sea surface pCO\textsubscript{2} and atmospheric pCO\textsubscript{2}. The coastal values in the western region showed 260 μatm. The temporal pCO\textsubscript{2} variations found to be very small in the offshore waters. The pCO\textsubscript{2} in the Arabian Sea was found to be regulated mainly by the strong physical circulation forcing caused by the seasonal monsoons. Sea surface temperature and wind speed data were used to find out the monthly and annual mean of CO\textsubscript{2} fluxes. The monthly mean values ranged 8.3- 44 mmol m\textsuperscript{-2} month\textsuperscript{-1} during most of the year, while in the SW monsoon, it reached up to 312.8 mmol m\textsuperscript{-2} month\textsuperscript{-1} in the Omani coast. This resulted from the intense upwelling. The annual mean CO\textsubscript{2} flux from sea to air was found to be around 7 TgC yr\textsuperscript{-1} thus acting as a CO\textsubscript{2} source.

Sarma et al. (1998) studied the seasonal and interannual variations in the total carbon dioxide (TCO\textsubscript{2}) and carbon dioxide partial pressure (pCO\textsubscript{2}) in the central and eastern Arabian Sea during the JGOFS programme. Coulometric methods were used to find out the TCO\textsubscript{2} and from TCO\textsubscript{2} and pH measurements, pCO\textsubscript{2} was computed. TCO\textsubscript{2} was found to be varying seasonally with change in the ocean circulation and biological production. It exhibited a high value in the winter season and was found low in SW monsoon. A higher value of pCO\textsubscript{2} than in the atmosphere was observed in all the seasons in the Arabian Sea, except the regions along Indian coast in the SW monsoon. The results of the study revealed the
Arabian Sea is acting as a perennial source of CO$_2$ in almost all seasons and it emits about 45 Tg C y$^{-1}$ to the atmosphere.

The work done by Sarma et al (2000) on the variability of pCO$_2$ with seasonal change and the effect of biological and physical processes in it in the mixed layer in the central and eastern Arabian sea analysed the pCO$_2$ changes for the inter-monsoon, northeast (NE) monsoon and southwest (SW) monsoon. The mixed layer depth was found to vary seasonally with values ranging from 80-120m in NE monsoon, 60-80m in SW monsoon and 20-30m in the inter-monsoon. This change was found to be occurring as a result of physical processes. The seasonal changes in pCO$_2$ resulted in the high range of 520-685 µatm and low values of around 266 µatm in the SW coast of India during the SW monsoon. This extreme values in the same region occurred due to the intense upwelling resulting in high values and influence of river influx causing the low range. During inter-monsoon, the highest value range observed in coastal waters was 416-527 µatm in the north and lowest was 375-446 µatm. The central Arabian Sea showed a pCO$_2$ range of 351-433 µatm in the NE monsoon, 379-475 µatm in the inter-monsoon and 385-432 µatm in the SW monsoon seasons. The analysis on the influence of temperature, oxygen and chlorophyll observed the regulation of pCO$_2$ in the SW and NE monsoons mainly by the physical processes whereas, during inter-monsoon, both physical and biological factors are significant.

The estimation and regulation of primary productivity in the Arabian Sea was carried out by Barber et al (2001) during the year 1995 as a part of JGOFS programme. The observations showed that the coastal areas contained the coolest waters with high nutrient content during SW monsoon season which extended up to 800km offshore. This was attributed by coastal upwelling, offshore upwelling, wind driven mixing, advection and eddy upwelling. During the NE monsoon, the convective mixing increased the nutrient contents up to 400-1000 km off shore region. SW monsoon was observed to be most productive with values 123 mmol C m$^{-2}$ day$^{-1}$ followed by the NE monsoon season with values 112 mmol C m$^{-2}$ day$^{-1}$. The onshore-offshore gradient of primary productivity was absent in 150-1000km off the Omani coast. The spring inter-monsoon productivity was found higher compared to that in tropical Pacific Ocean and North Pacific gyre region. The high Iron concentrations were found to act as a main factor in increased productivity. There was no light limitation observed for the productivity in any region in the Arabian Sea.

Sarma (2003) studied sea surface pCO$_2$ and air-sea CO$_2$ fluxes in the Arabian Sea using data from Indian and U.S JGOFS and Indian Land-Ocean interactions in the Coastal Zone process study programs. Multiple regression equations were developed from surface temperature, salinity and chlorophyll to derive dissolved inorganic carbon (DIC). Total alkalinity (TA) of sea water was computed from salinity and carbonate association constants were used to compute sea surface pCO$_2$. The study revealed large spatial as well as seasonal variability of pCO$_2$ and CO$_2$ fluxes in the Arabian Sea. The occurrence of low pCO$_2$ values was observed in the south west coast of India during NE monsoon due to the inflow of low saline waters during this season and high pCO$_2$ values during SW monsoon in the western coast. Open ocean exhibited high pCO$_2$ values in the northern region. Distribution of CO$_2$
fluxes showed a higher emission in the west coast of Arabian Sea. Results revealed that the Arabian Sea is acting as a CO$_2$ source which is about 90 TgC/yr.

Chlorophyll distributions in the northeastern Arabian Sea and southern Bay of Bengal were studied by Dey and Singh (2003) using Ocean Colour monitor data. The highest concentrations of chlorophyll were obtained in the Arabian Sea compared to Bay of Bengal especially in the northern region. The increased chlorophyll content was observed in the NE monsoon compared to pre-monsoon and post-monsoon seasons and coastal areas showed high chlorophyll than open ocean. High seasonal variations were observed in the chlorophyll concentrations in the Arabian Sea while those in the Bay of Bengal were found insignificant. The vertical mixing and upwelling in the Arabian Sea bringing up the nutrient rich water were found to be the major factors behind its high chlorophyll content while in Bay of Bengal, low nutrient waters limit the productivity.

A study on the primary productivity of Arabian Sea done by Marra and Barber (2005) showed temporal and spatial variations of phytoplankton biomass exist at different scales. These changes were found to be occurring due to the seasonal and diurnal variations in vertical mixing and thus not only controlled by the nutrient supply and irradiance. The spatial variations were attributed by the coastal upwelling and presence of mesoscale eddies. During the SW and NE monsoon seasons, an increase in the chlorophyll content was observed. The nutrient availability was found to act as a controlling factor on productivity only during the spring inter-monsoon. The mixed layer deepening was found to cause dilution which reduces the grazing rates and thus enhances the phytoplankton growth which results in the variability in the phytoplankton biomass.

2.2 Studies conducted in other regions

Takahashi et al (1993) studied the seasonal CO$_2$ and nutrient variations in the high-latitude oceanic regions. They analysed the pCO$_2$, CO$_2$ concentration and nutrient data to describe the seasonal relationships among these properties and to compare their inter-ocean variation. A reduction in the surface water pCO$_2$, CO$_2$ concentrations and nutrients was observed in the North Atlantic Ocean waters due to the spring phytoplankton blooms. This condition existed only until the exhaustion of the nutrients. Such seasonal behaviours were found to be limited to the high latitude waters north of 40°N. But the seasonal variations in the CO$_2$ concentrations and nutrients were found to be occurring more gradually in the North Pacific and a partial consumption of nutrients was observed in the subarctic North Pacific and Southern Ocean surface waters. During winter, the pCO$_2$, CO$_2$ concentrations and nutrients in the sub polar and polar waters of the North and South Atlantic and North Pacific Oceans were higher than in summer. In winter, the high latitude areas of north Atlantic, North Pacific and Weddel Sea were found as sources of CO$_2$ to atmosphere while in summer they were acting as sinks. The intense upwelling during winter and increased rates of photosynthesis during summer was considered to cause this seasonal change in emission. But the subtropical waters found to act as sources of CO$_2$ in summer and sinks during winter season. Here, the seasonal variation of pCO$_2$ was controlled mainly by temperature since the biological factors were found to be weak. The subtropical convergence region was acting
as an intense sink resulted from the combined effects of cooling in subtropical waters and high absorption of CO$_2$ by photosynthetic activity in sub polar waters.

The temporal variation of surface water pCO$_2$ was studied by Kumamoto et al (1995) in Iyo Nada in the Seto Inland Sea in Japan using infrared absorption method. The variation was found to be less during January to late May which was about 270-340 µatm while in September it was 200-450 µatm. The high values obtained in September in the north and south regions were found to be destruction of stratification by tidal currents leading to water mixing. The low values observed in the central region were attributed by the high chlorophyll content in tidal front, where a negative correlation found between the pCO$_2$ and chlorophyll. The highest temperature was in September which was 23-34°C and lowest was found in March with a range 11-13°C. A seasonal stratification was found in the month of August to October. The highest pCO$_2$ in the north was occurring in this season. Most of the region except the north in September showed low pCO$_2$ compared to the atmosphere which suggested that this region acts as a sink for atmospheric CO$_2$. The large variation in pCO$_2$ leads to vertical mixing of seawater in summer season. Detailed pCO$_2$ measurements were suggested for flux calculation in summer.

Takahashi et al (1997) estimated the global air-sea CO$_2$ flux from difference in CO$_2$ partial pressures. Around 250,000 observations on the pCO$_2$ difference between sea and air were taken from all over the globe. Lateral advection-diffusion transport equation was used to construct global monthly distributions of pCO$_2$ difference. This partial pressure measurements and CO$_2$ gas transfer coefficients were used to calculate the net CO$_2$ flux across the sea surface. The wind speed dependence on the gas transfer coefficients was formulated and the annual net flux uptake of oceans was estimated to be 0.6 - 1.34 GtC yr$^{-1}$. The analysis found out that the temperate and polar oceanic regions act as CO$_2$ sinks while the equatorial regions were sources. The most intense sink of CO$_2$ was found to be Atlantic Ocean which accounts for about 60% of the global uptake of CO$_2$ whereas, the Pacific equatorial belt was acting as the important source. In the case of Pacific Ocean, the equatorial sources of CO$_2$ were balanced by the temperate sinks, thus acting as a neutral one. The uptake of both Indian and Southern Oceans were about 20%.

The global sea –air CO$_2$ flux calculation was carried out by Takahashi et al (2002) using climatological monthly pCO$_2$ data and seasonal effects of biological factors and temperature. Mean monthly wind speed data was used to estimate the monthly as well as annual flux. The annual flux uptake was estimated to be 2.2 Pg C yr$^{-1}$. The major CO$_2$ sinks were found to be the regions between 40° and 60° latitudes in both the hemispheres. This was found to be attributed to the mixing of pole-ward flowing warm waters and the nutrient rich cold sub polar waters. This cooling effect on the warm waters as well as the biological CO$_2$ uptake decreased the pCO$_2$ in the sub polar waters. Also, the oceanic uptake of CO$_2$ in the low pCO$_2$ waters was enhanced by the high wind speed over these waters. The seasonal changes in pCO$_2$ in a particular area were controlled by the biological and temperature effects while the seasonal maximum of pCO$_2$ was regulated by the upwelling and temperature. The effect of biological component was strong in equatorial and sub-polar regions, the north western Arabian Sea, the eastern equatorial Pacific, the subarctic North
Atlantic and Antarctic coastal waters. The sub tropical gyre areas were influenced mainly by the temperature.

Bates (2007) studied the interannual variability of the oceanic CO$_2$ sink over a period of 2 decades in the North Atlantic subtropical gyre. Continuous monitoring of oceanic CO$_2$ from 1983-2005 showed an increasing trend in the annual rates of dissolved inorganic carbon (DIC) and pCO$_2$ with increase in atmospheric CO$_2$. A decrease in seawater pH, CO$_3^{2-}$ concentration and CaCO$_3$ saturation states was also observed. The rates of CO$_2$ sinks and sources were not found to be seasonally balanced since the winter flux uptake was greater than the summer out-flux. Thus the region was found to act as annual CO$_2$ sink. The net air-sea CO$_2$ flux rate was estimated to be an interannual range of $-850$ to $-1200$ mmol CO$_2$ m$^{-2}$ yr$^{-1}$. The summer fluxes were enhanced by the occurrence of hurricanes. During the study period, an increase of about 5-17% was observed in the annual rate of net CO$_2$ flux. The summer and fall season fluxes were found to be correlated with the North Atlantic Oscillation (NAO) variability. But winter fluxes showed poor correlation with NAO or Arctic Oscillation (AO) while they were high during the El-Nino years than La Nina years. This less correlation could be attributed by the anticorrelation of windspeed and CO$_2$ partial pressure differences in winter.

Zhu et al (2009) estimated the sea surface CO$_2$ partial pressure and CO$_2$ fluxes in the northern South China Sea using satellite data on SST, chlorophyll and wind. Two algorithms were developed using regression analysis for deriving sea surface pCO$_2$, the first one with insitu SST data and the other with insitu SST and chlorophyll measurements. The satellite derived pCO$_2$ was compared with the insitu values which showed a root-mean-square error of 4.6 µatm. The results showed an agreement with the past measurements, suggesting that the satellite data can be applied to the CO$_2$ measurements in the South China Sea. Monthly mean wind data was used to estimate the sea-air CO$_2$ flux. The algorithm was found to give good results in the summer season in the region. They suggested more insitu measurements for effective temporal and spatial coverage.
Chapter 3
Study Area

3.1 Study area

Arabian Sea is selected as the study area for this project (0-31°N, 30-77.5°E). Since the study involves deriving relationship between the CO$_2$ fluxes over the sea and its primary productivity, the area is divided based on the productivity into north, south, east and west regions to analyse the spatial variation. Also, seasonal changes are analysed for winter, pre-monsoon, monsoon and post monsoon seasons.

3.1.1 Physiography

Arabian Sea is a tropical basin situated in the north western part of Indian Ocean. Except for the southern part which is the rest of Indian ocean, it is land locked from the west by the Africa and Arabian Peninsula, north by Iran and Pakistan and east by India. It has a surface area about 3,862,000 sq km. Its maximum width measures around 2400km and width reaches up to 5803 meters occurs in Wheatley Deep. Indus, Netravathi, Sharavathi, Narmada, Tapti and Mahi are some of the major rivers flowing to Arabian Sea. It has four important branches; the Gulf of Aden in the southwest, Gulf of Oman to the northwest and Gulf of Cambay and Kutch on the Indian coast. Its islands include Socotra, Lakshadweep, Minicoy and Amindivi. The major ports are Karachi and Mumbai (Goetz, 1987).

3.1.2 Oceanography

It is among the most biologically productive oceanic regions due to the blooms caused by the wind driven upwelling in the summer along Somalian and Arabian coasts and southern part of the west coast of India and cooling and convective mixing in the northern Arabian Sea during winter. This oceanic region is dominated by semi-annually reversing monsoon wind system. During winter season, it receives cool, dry continental air from northeast trade winds and during summer it experiences moisture laden maritime air brought by the southwest winds (Prasannakumar et al., 2009, Tang et al., 2002). High salinity values of 36.6psu were found during December in the region north of 15° while equatorial region showed lower values of 35psu (Prasannakumar and Narvekar, 2005). Low values of sea surface temperatures of about 20°C were recorded during December in the region north to the Gulf of Kutch while the temperatures attained a peak value of 30°C in May (Prasannakumar and Narvekar, 2005, Tang et al., 2005). The surface temperatures generally increase towards east and a homogeneous surface layer of warm water with a temperature about 28°C occurs to the east of 65°E. In the southern region, this warm layer extend gradually towards west. A well developed mixed layer is present in the eastern part and its thickness increases towards east and south which is caused by strong surface heating and wind mixing. The thermocline depth increases towards east of 64°E and goes beyond 40m. A well developed thermocline with greater temperature gradients can be seen along the southern boundary of Arabian Sea.

The major water movements include:

- Eastward flow of Persian Gulf waters up to 63°E and sinking there to subsurface layers.
- A strong southward flow along southeast of Socotra island in the upper 300m layer.
• Moderately strong subsurface flow below 20m at 20°N between 66° 55'E and 65° 00'E.
• Moderate intensity subsurface water movements at 15° 30'N between 63° 00'E and 66° 00'E
• Subsurface water movements at 12°N between 59°-62°E at greater than 50m depth.

(Panikkar, 1967)

3.2 Data used

3.2.1 Satellite/Climatology data

A number of parameters were taken from satellite data for the period 2002 September to 2012 February for the study. The details of satellite data used are summarised in table.3.1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
<th>Spatial resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>SST</td>
<td>MODIS-AQUA</td>
<td>4km</td>
</tr>
<tr>
<td>Chl-a</td>
<td>MODIS-AQUA</td>
<td>4km</td>
</tr>
<tr>
<td>CO₂ molefraction</td>
<td>AQUA-AIRS</td>
<td>2.5°×2°</td>
</tr>
<tr>
<td>Wind speed</td>
<td>AMSRE</td>
<td>0.25°×0.25°</td>
</tr>
<tr>
<td>Sea level pressure</td>
<td>MERRA</td>
<td>2/3°×1/2°</td>
</tr>
<tr>
<td>Salinity</td>
<td>World Ocean Atlas</td>
<td>1°×1°</td>
</tr>
</tbody>
</table>

3.2.2 Field data

Field study has been carried out in the coastal waters off Cochin for parameters sea surface temperature, chlorophyll-a and sea water CO₂ concentration.
Chapter 4  
Methodology

Satellite data analysis as well as field measurements are carried out in this study. Satellite data are used to derive carbon dioxide flux and ocean primary productivity while field data is used to develop algorithm for deriving carbon dioxide partial pressure of sea water.

4.1 Satellite data analysis

4.1.1 Estimation of carbon dioxide flux

Carbon dioxide flux estimation between ocean and atmosphere involves a number of parameters which are derived from satellite data.

\[
F = K_{wa} \cdot K_0 \cdot (p_{CO2SW} - p_{CO2Air}) \cdot 24 \cdot (1 + \frac{\sigma}{1000}) \cdot 0.01
\]  
(Robbins et al., 2010)

\[F\] is the net ocean-atmosphere carbon dioxide flux in mmol/m²/day

\[K_{wa}\] is the CO₂ gas transfer velocity in m/s; it is derived from sea surface temperature and wind speed (Wanninkhof, 1992)

\[
K_{wa} = 0.31 \cdot U^2 \cdot \left(\frac{660}{5c}\right)^{1/2}
\]  
(2)
$K_{wa}$ normalised to a Schmidt number of 660 for sea water at 20°C

$U$ is wind speed in m/s at 10m above surface

$Sc$ is the Schmidt number derived from sea surface temperature

\[
Sc = A - Bt + Ct^2 - Dt^3
\]  

(3)

$A = 2073.1 \quad B = 125.62 \quad C = 3.6276 \quad D = 0.043219$

t is temperature in degree celsius

$Ko$ is $CO_2$ solubility in mol/l/atm in sea water derived as a function of sea surface temperature and salinity (Weiss, 1974)

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

(4)

$T$ is temperature in Kelvin

$S$ is salinity in practical salinity units (psu)

$A_1 = -58.0931 \quad A_2 = 90.5069 \quad A_3 = 22.2940 \quad B_1 = 0.027766 \quad B_2 = -0.025888 \quad B_3 = 0.0050578$

The partial pressure of sea water ($CO_2^{SW}$) is derived as a function of satellite obtained sea surface temperature and chlorophyll-a (Zhu et al., 2009); it is given by

\[
pCO_{2SW} = 6.31T^2 + 61.9\text{Chl-a}^2 - 365.85T - 94.41\text{Chl-a} + 5715.94
\]

(5)

Chl-a is sea water chlorophyll concentration in mg/m$^3$

$T$ is sea surface temperature in degree celsius.

$pCO_{2Air}$ is the partial pressure of $CO_2$ in the air derived from the formula

\[
pCO_{2Air} = xCO_2^{Air} \cdot (P_T - PH_{2O})
\]

(Dickson and Goet, 1994, Dickson et al., 2007)

$xCO_2$ is $CO_2$ mole fraction in ppm

$P_T$ is sea level pressure in atmosphere

$PH_{2O}$ is saturation vapour pressure of sea water in atmosphere (Weiss and Price, 1980)

\[
PH_{2O} = \exp \left( 24.4543 - 67.4509 \left(\frac{T}{100}\right) - 4.8489 \times \ln \left(\frac{T}{100}\right) - 0.000544 \times S \right)
\]

(7)

$T$ is sea surface temperature in Kelvin

$S$ is salinity in psu

$\sigma$ is the density anomaly of sea water
\[ \sigma = \rho - 1000 \] (8)


\[ \rho \] is the density of sea water in kg/m\(^3\) derived as a function of salinity and temperature

\[ \rho(S,t,0) = p_w + (b_0 + b_1 t + b_2 t^2 + b_3 t^3 + b_4 t^4) S + (c_0 + c_1 t + c_2 t^2) S^{3/2} + d_0 S^2 \] (9)

\[ b_0 = 8.24493 \times 10^{-1} \quad c_0 = -5.72466 \times 10^{-3} \]
\[ b_1 = -4.0899 \times 10^{-3} \quad c_1 = 1.0227 \times 10^{-4} \]
\[ b_2 = 7.6438 \times 10^{-5} \quad c_2 = -1.6546 \times 10^{-6} \]
\[ b_3 = -8.2467 \times 10^{-7} \quad d_0 = 4.8314 \times 10^{-4} \]
\[ b_4 = 5.3875 \times 10^{-9} \]

\[ p_w \] is the density of pure water

\[ p_w = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5 \] (10)

\[ a_0 = 999.842594 \quad a_1 = 6.793952 \times 10^{-2} \quad a_2 = -9.095290 \times 10^{-3} \]
\[ a_3 = 1.001685 \times 10^{-4} \quad a_4 = -1.120083 \times 10^{-6} \quad a_5 = 6.536332 \times 10^{-9} \]

**4.1.2 Determination of column primary productivity**

Vertically Generalized Production Model (VGPM) is used to calculate column primary productivity from satellite derived Chlorophyll-a, sea surface temperature and sea surface daily photosynthetically active radiation (PAR).

The VGPM formula can be given as

\[ PP_{eu} = 0.66125 * P_{opt}^B * E_0^{E0+4.1} * C_{SAT} * Z_{eu} * D_{IRR} \] (11)

(Behrenfeld and Falkowski, 1997)
PP\textsubscript{eu} is the daily carbon fixation in mgCm\textsuperscript{-2}d\textsuperscript{-1} integrated to euphotic depth Z\textsubscript{eu} in meter.

Euphotic depth is derived as a function of chlorophyll

\[
Z_{eu} = \begin{cases} 
568.2(C_{TOT})^{0.746}, & \text{if } C_{TOT} < 102 \\
200.0(C_{TOT})^{0.293}, & \text{if } C_{TOT} > 102
\end{cases} \tag{12}
\]

\[
C_{TOT} = \begin{cases} 
38.0(C_{SAT})^{0.425}, & \text{if } C_{SAT} < 1.0 \\
40.2(C_{SAT})^{0.507}, & \text{if } C_{SAT} \geq 1.0
\end{cases} \tag{13}
\]

C\textsubscript{SAT} = satellite derived surface chlorophyll concentration (mg chl m\textsuperscript{-3})

P\textsubscript{opt} \textsuperscript{B} is optimal daily carbon fixation rate within a water column [mgC(mg Chl)\textsuperscript{-1}h\textsuperscript{-1}] derived as a function of sea surface temperature

\[
P_{opt}^{B} = \begin{cases} 
1.13 & \text{if } T < -1.0 \\
4.00 & \text{if } T > 28.5 \\
1.2956 + 2.749 \times 10^{-1} \times T + 6.17 \times 10^{-2} \times T^2 - 2.05 \times 10^{-3} \times T^3 + 2.462 \times 10^{-4} \times T^4 - 1.348 \times 10^{-5} \times T^5 + 3.413 \times 10^{-6} \times T^6 - 3.27 \times 10^{-7} \times T^7 & \text{if } T \geq 28.5
\end{cases} \tag{14}
\]

T is sea surface temperature in degree Celsius

E\textsubscript{0} is sea surface daily PAR (mol quanta m\textsuperscript{-2} d\textsuperscript{-1})

D\textsubscript{IRR} is daily photoperiod calculated in decimal hours for the middle of the month.

### 4.2 Field data collection and analysis

Field data collection was carried out in the coastal waters off Cochin (Figure 4.3) for satellite data validation and developing regional algorithm for sea water carbon dioxide partial pressure in the coastal waters. 20 samples each were collected for analysis of chlorophyll and carbon dioxide concentration. Laboratory analysis was carried out at National Institute of Oceanography, Regional Centre, Cochin.
4.2.1 Sampling and analysis

a. Sea surface temperature

- Sea surface temperature was measured at the time of sampling using mercury-in-glass thermometer

![Figure. 4.4 Measuring Secchi disc depth](image1)

![Figure. 4.5 Measuring SST](image2)

b. Chlorophyll-a

- Water samples were collected in clean polythene bottles
- Filtered through 47mm Whatman GF/F filters
- Filters were folded half twice, added 10ml 90% acetone and incubated overnight in dark at 4°C
- Chlorophyll-a concentration was measured using fluorometer at 440nm wavelength

![Figure. 4.6 Filtering Chlorophyll samples](image3)

![Figure. 4.7 Chlorophyll measurement](image4)
c. Sea water pCO$_2$

- Water samples were collected in 125ml stoppered borosilicate glass bottles and kept in dark at 0°C
- Analysis of samples were carried out within 12 hours to prevent CO$_2$ gas depletion and titrimetric method was used (Clesceri et al., 1998)
- 50ml water sample was taken, 4 drops of phenolphthalein indicator were added and titrated against 0.0227N standard NaOH solution until the development of a pink colour.

Partial pressure of CO$_2$ was calculated from the CO$_2$ concentration using the formula

$$f_{CO2} = \frac{[CO2]}{Ko}$$  \hspace{1cm} (16)

(Dickson & Goyet, 1994)

$[CO2]$ is the sea water CO$_2$ concentration

Ko is the CO$_2$ solubility in sea water

$$pCO_2(\mu atm) = f_{CO2}(\mu atm)*[1.00436-4.669*10^{-5}*SST({}^\circ C)]$$  \hspace{1cm} (17)

(Kozyr, 2012)

4.3 Developing algorithm for pCO$_{2\text{SW}}$ in Arabian Sea

Sea water CO$_2$ partial pressure (pCO$_{2\text{SW}}$) is influenced largely by two key parameters i.e. sea surface temperature and ocean primary productivity. Algorithms for different areas have been already developed for deriving sea water partial pressure of CO$_2$. (Zhu et al., 2009)
4.3.1 Regional algorithm for sea water CO$_2$ in case 2 waters using field data

An attempt has been made in this study to develop a regional algorithm for coastal waters off Cochin using the sea surface temperature, chlorophyll and CO$_2$ concentration from field data. Regression analysis is performed to correlate SST and Chlorophyll concentration with pCO$_{2SW}$ and an algorithm has been developed to derive pCO$_{2SW}$ from SST and Chlorophyll.

The study area was classified in to case 1 and 2 waters based on the criteria described by Matsushita et al (2012) which is given as: Rrs (412) ≥ Rrs (443) belongs to case-1 water; otherwise case-2 water. Rrs (412) and Rrs (443) are the remote sensing reflectance at 412 and 443nm respectively provided by SeaWIFS.

Algorithm developed from the field data was used for case 2 waters and the algorithm derived for northern South China Sea has been used for case 1 waters. The JGOFS data was used to estimate the RMS error for this algorithm.
Chapter 5
Results

Carbon dioxide (CO$_2$) fluxes and ocean primary productivity analysis were carried out for the period September 2002 –February 2012 using remote sensing data and compared to find out how the fluxes vary with variation in ocean productivity. In addition to the above, comparison was done between the CO$_2$ fluxes and sea surface temperature to understand the effect of sea surface temperature on the fluxes. An algorithm was developed for case 2 waters using regression analysis of field data off Cochin. For case 1 waters the algorithm developed for the North China Sea was used to derive sea surface pCO$_2$ for the winter, pre-monsoon, monsoon and post-monsoon seasons.

5.1 Deriving Carbon dioxide fluxes

Study area was divided into north, west, east and south. The analysis was carried out to study the variation in CO$_2$ fluxes for winter, pre-monsoon, monsoon and post-monsoon seasons to understand the spatial as well as seasonal distribution of fluxes.

5.1.1 CO$_2$ fluxes in the north

- In winter, fluxes were in the range 5-20 mmol m$^{-2}$ day$^{-1}$
- In pre-monsoon, fluxes were 1.3-12.5 mmol m$^{-2}$ day$^{-1}$
- Monsoon fluxes range from 5-25 mmol m$^{-2}$ day$^{-1}$
- Fluxes ranged between 0.8-3 mmol m$^{-2}$ day$^{-1}$ in the post-monsoon season

![CO$_2$ Fluxes-North](image)

**Figure. 5.1 CO$_2$ Fluxes-North**

5.1.2 CO$_2$ fluxes in the west

- Winter values range from 7.5-15 mmol m$^{-2}$ day$^{-1}$
- Fluxes were 1.3-4.5 mmol m$^{-2}$ day$^{-1}$ during pre-monsoon
- In monsoon, fluxes ranged 36-75 mmol m$^{-2}$ day$^{-1}$
• Post-monsoon has showed a flux range of 2-6.5 mmol m\(^{-2}\) day\(^{-1}\)

![Figure. 5.2 CO\(_2\) Fluxes-West](image)

5.1.3 CO\(_2\) fluxes in the east

• In winter, fluxes ranged 1.6-9.5 mmol m\(^{-2}\) day\(^{-1}\)
• In pre-monsoon fluxes were 1.5-2.5 mmol m\(^{-2}\) day\(^{-1}\)
• Monsoon has a flux range of 7.9-16.5 mmol m\(^{-2}\) day\(^{-1}\)
• Fluxes were in the range 1.4-3.4 mmol m\(^{-2}\) day\(^{-1}\) during post-monsoon

![Figure. 5.3 CO\(_2\) Fluxes-East](image)

5.1.4 CO\(_2\) fluxes in the south

• A flux range of 1.8-5.8 mmol m\(^{-2}\) day\(^{-1}\) was observed in winter
• Pre-monsoon showed the range 1.8-3.1 mmol m\(^{-2}\) day\(^{-1}\)
- In monsoon flux values were found to be 2.5-7.2 mmol m\(^{-2}\) day\(^{-1}\)
- In post-monsoon fluxes ranged between 1.3-3 mmol m\(^{-2}\) day\(^{-1}\)

![CO\(_2\) Fluxes South](image)

**Figure. 5.4 CO\(_2\) Fluxes-South**

![CO\(_2\) Fluxes Seasonal Variation](image)

**Figure. 5.5 CO\(_2\) Fluxes-Seasonal Variation**
Table. 5.1 Spatial & Seasonal Distribution of CO$_2$ Fluxes

<table>
<thead>
<tr>
<th>Seasons</th>
<th>CO$_2$ Fluxes (mmol m$^{-2}$ day$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>North</td>
</tr>
<tr>
<td>Winter</td>
<td>5-20</td>
</tr>
<tr>
<td>Pre-monsoon</td>
<td>1.3-12.5</td>
</tr>
<tr>
<td>Monsoon</td>
<td>5-25</td>
</tr>
<tr>
<td>Post-monsoon</td>
<td>0.8-3</td>
</tr>
</tbody>
</table>

5.2 Estimation of ocean primary productivity
Primary productivity in the Arabian Sea was estimated and seasonal as well as spatial distribution was analysed.

5.2.1 Primary productivity in the north

- Winter values ranged from 1200-2300 mgC m$^{-2}$day$^{-1}$
- In pre-monsoon productivity ranged between 340-1300 mgC m$^{-2}$day$^{-1}$
- Monsoon productivity was found to be in the range 1000-1350 mgC m$^{-2}$day$^{-1}$
- Productivity was in the range 520-1050 mgC m$^{-2}$day$^{-1}$ during post-monsoon

![Primary Productivity - North](image-url)
5.2.2 Primary productivity in the west

- In winter, productivity range was 620-1100 mgC m\(^{-2}\)day\(^{-1}\)
- Pre-monsoon showed a range of 280-465 mgC m\(^{-2}\)day\(^{-1}\)
- Monsoon values were in the range 850-1700 mgC m\(^{-2}\)day\(^{-1}\)
- 550-815 mgC m\(^{-2}\)day\(^{-1}\) range was found in post-monsoon

5.2.3 Primary productivity in the east

- Eastern region showed a productivity range of 275-700 mgC m\(^{-2}\)day\(^{-1}\) in winter season
- Pre-monsoon season has a value range 225-400 mgC m\(^{-2}\)day\(^{-1}\)
- Productivity was in the range 435-845 mgC m\(^{-2}\)day\(^{-1}\) for monsoon season
- A range of 285-385 mgC m\(^{-2}\)day\(^{-1}\) was observed during post-monsoon

![Primary Productivity-West](image.png)

**Figure 5.7 Primary Productivity- West**
5.2.4 Primary productivity in the south

- In the south, winter has a value range of 245-410 mgC m$^{-2}$day$^{-1}$.
- During pre-monsoon productivity was found to be in the range 200-260 mgC m$^{-2}$day$^{-1}$.
- In the monsoon season, a range of 230-340 mgC m$^{-2}$day$^{-1}$ was obtained.
- Post-monsoon season has a range between 250-440 mgC m$^{-2}$day$^{-1}$.

Figure. 5.8 Primary Productivity- East

Figure. 5.9 Primary Productivity- South
5.3 Comparison of CO$_2$ fluxes with ocean primary productivity

5.3.1 CO$_2$ fluxes Vs. Productivity- North

- Fluxes showed an increasing trend with increase in productivity in winter
- Fluxes increased with increase in productivity in pre-monsoon
- Slight decrease in fluxes was observed during monsoon season with increase in productivity
- Post-monsoon showed a decreasing flux trend with increase in productivity
5.3.2 CO₂ fluxes Vs. Productivity- West

- Fluxes increased with increase in productivity in winter
- No considerable variation in flux with increase in productivity during pre-monsoon
- Increase in flux values with increase in productivity in monsoon
- A decreasing trend in fluxes with increase in productivity in post-monsoon
5.3.3 CO₂ fluxes Vs. Productivity- East

- Winter fluxes increased with increase in productivity
- In pre-monsoon, productivity was found to be not much effect on CO₂ fluxes
- An increasing trend was observed in the flux values with increased productivity during monsoon
- Not much effect of productivity on fluxes in post monsoon

5.3.4 CO₂ fluxes Vs. Productivity- South

- Increasing fluxes in winter with increased productivity
- Flux values were showing a decrease with increase in productivity in pre-monsoon
• In monsoon, fluxes increased with increase in productivity
• Slight decrease in flux values with increase in productivity in post-monsoon

**Figure. 5.14 CO₂ Flux Vs. Primary Productivity - South**

5.4 Comparison of CO₂ fluxes with sea surface temperature

5.4.1 CO₂ fluxes Vs. SST - North

• A slight decreasing trend in flux values in winter with increase in SST
• Pre-monsoon fluxes showed an inverse relation with SST
• Decreasing fluxes with increased SST in monsoon season
• Fluxes decreased with increase in SST in post-monsoon
5.4.2 CO₂ fluxes Vs. SST- West

- West region did not show any influence of SST on fluxes during winter
- Fluxes showed slight decrease with increase in SST in pre-monsoon
- Fluxes were decreasing in monsoon with increased SST
- Slight decreasing trend was observed in flux values in post-monsoon with increasing SST
5.4.3 \( CO_2 \) fluxes Vs. SST - East

- Flux values showed inverse relation with SST in winter
- Decreasing fluxes in pre-monsoon with increase in SST
- Monsoon fluxes decreased with increase in SST
- In post-monsoon, fluxes were decreasing with increase in SST
5.4.4 CO₂ fluxes Vs. SST - South

- A strong inverse relation observed between flux values and SST in winter
- Decreasing fluxes in pre-monsoon with increasing SST
- Fluxes were showing a steep decrease with increasing SST in monsoon
- Decreasing trend in fluxes with increased SST during post-monsoon

Figure 5.18 CO₂ Flux Vs. SST - South

5.3 Analysis of sea surface pCO₂ derived for case 1 and case 2 waters of Arabian Sea

An algorithm was developed from field data off Cochin coast (summarised in table 5.3) for case 2 waters.
Table 5.3 Data collected during field study off Cochin coast.

<table>
<thead>
<tr>
<th>SST</th>
<th>Chl-a</th>
<th>pCO$_{2SW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>2.62</td>
<td>228.1441</td>
</tr>
<tr>
<td>29</td>
<td>2.06</td>
<td>233.6827</td>
</tr>
<tr>
<td>28.5</td>
<td>1.39</td>
<td>76.96991</td>
</tr>
<tr>
<td>28.5</td>
<td>0.96</td>
<td>153.9398</td>
</tr>
<tr>
<td>28.5</td>
<td>0.46</td>
<td>153.9398</td>
</tr>
<tr>
<td>28.5</td>
<td>0.41</td>
<td>153.9398</td>
</tr>
<tr>
<td>28.5</td>
<td>0.37</td>
<td>230.9097</td>
</tr>
<tr>
<td>28.5</td>
<td>0.39</td>
<td>76.96991</td>
</tr>
<tr>
<td>28.5</td>
<td>0.39</td>
<td>153.9398</td>
</tr>
<tr>
<td>28.5</td>
<td>0.23</td>
<td>153.9398</td>
</tr>
<tr>
<td>28</td>
<td>0.22</td>
<td>228.1441</td>
</tr>
<tr>
<td>28.5</td>
<td>0.21</td>
<td>307.8797</td>
</tr>
<tr>
<td>28</td>
<td>0.34</td>
<td>233.6827</td>
</tr>
<tr>
<td>28.5</td>
<td>0.46</td>
<td>230.9097</td>
</tr>
<tr>
<td>28.5</td>
<td>0.9</td>
<td>76.96991</td>
</tr>
<tr>
<td>28.5</td>
<td>1.2</td>
<td>230.9097</td>
</tr>
<tr>
<td>29</td>
<td>1.53</td>
<td>233.6827</td>
</tr>
<tr>
<td>29.5</td>
<td>3.18</td>
<td>236.4625</td>
</tr>
<tr>
<td>29.5</td>
<td>1.65</td>
<td>236.4625</td>
</tr>
<tr>
<td>30</td>
<td>3.54</td>
<td>239.2489</td>
</tr>
</tbody>
</table>

The algorithm can be given as:

\[
pCO_2(\mu\text{atm}) = b_0 + b_1 \cdot \text{SST} + b_2 \cdot \text{Chl-a} + b_3 \cdot \text{SST}^2 + b_4 \cdot \text{Chl-a}^2 + b_5 \cdot \text{SST} \cdot \text{Chl-a} + b_6 \cdot \text{SST}^3 + b_7 \cdot \text{Chl-a}^3 + b_8 \cdot \text{SST}^2 \cdot \text{Chl-a} + b_9 \cdot \text{SST} \cdot \text{Chl-a}^2
\]

Table 5.4 Algorithm Coefficients

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>b0</td>
<td>9363160.099</td>
</tr>
<tr>
<td>b1</td>
<td>-960905.9</td>
</tr>
<tr>
<td>b2</td>
<td>-88662.499</td>
</tr>
<tr>
<td>b3</td>
<td>32820.09</td>
</tr>
<tr>
<td>b4</td>
<td>-11673.899</td>
</tr>
<tr>
<td>b5</td>
<td>7618.302</td>
</tr>
<tr>
<td>b6</td>
<td>-373.022</td>
</tr>
<tr>
<td>b7</td>
<td>-144.2</td>
</tr>
<tr>
<td>b8</td>
<td>-158.852</td>
</tr>
<tr>
<td>b9</td>
<td>429.21</td>
</tr>
</tbody>
</table>

5.5.1 Distribution of sea surface pCO$_2$ in winter

Winter pCO$_2$ values ranged from about 140-200 $\mu$atm in the east and south-east region to >750 $\mu$atm in the east and central Arabian Sea.
5.5.2 Distribution of sea surface pCO$_2$ in pre-monsoon

Pre-monsoon pCO$_2$ was in the range 140-250 µatm in the east, west and central regions of Arabian Sea to values >750 µatm in the east and south-east regions.

5.5.3 Distribution of sea surface pCO$_2$ in monsoon

pCO$_2$ range was about 400-700 µatm in the west and north regions to values >750 µatm in the southern part.
5.5.3 Distribution of sea surface pCO$_2$ in post-monsoon

Surface pCO$_2$ was observed to be >750 µatm in the southern and central Arabian Sea.

<table>
<thead>
<tr>
<th>Seasons</th>
<th>pCO$_2$(µatm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td>140- &gt;750</td>
</tr>
<tr>
<td>Pre-monsoon</td>
<td>140- &gt;750</td>
</tr>
<tr>
<td>Monsoon</td>
<td>400- &gt;750</td>
</tr>
<tr>
<td>Post-monsoon</td>
<td>&gt;750</td>
</tr>
</tbody>
</table>
Chapter 6  
Discussions

6.1 Distribution of CO$_2$ fluxes

CO$_2$ fluxes were calculated and analysed for understanding the seasonal as well as spatial distribution over Arabian Sea. Seasonally, the fluxes were analysed for winter, pre-monsoon, monsoon and post-monsoon seasons. Spatial variation was studied for northern, western, eastern and southern regions of Arabian Sea.

In all the four regions, highest flux values were obtained in the monsoon season which ranged from 2.5-7.2 mmol m$^{-2}$ day$^{-1}$ in the south (Figure. 5.4) to 36-75 mmol m$^{-2}$ day$^{-1}$ in the west (Figure.5.2), followed by winter with a range of 1.8-5.8 mmol m$^{-2}$ day$^{-1}$ (Figure.5.4) observed in the south to 5-20 mmol m$^{-2}$ day$^{-1}$ in the north (Figure. 5.1). The increased emission of CO$_2$ in the monsoon season can be due to the upwelling of subsurface waters rich in CO$_2$ resulting in the CO$_2$ oversaturation in the sea surface. The Findlater jet is one among the factors for upwelling in the monsoon enhancing the surface pCO$_2$ values especially in the west were highest flux values were observed during monsoon (Madhupratap et al. 1996; Takahashi et al., 1997; Sarma et al., 1998; Sarma et al, 2000; Barber et al., 2001; Takahashi et al., 2002; Marra and Barber, 2005, Takahashi et al., 2009).

In the winter season, the convective mixing brings subsurface waters enriched with CO$_2$ thus increasing the fluxes (Madhupratap et al, 1996; Sarma, 2003). The pre-monsoon and post monsoon flux values in the west, east and south were considerably lower than that in the monsoon and winter which showed a minimum value range of 1.5-2.5 mmol m$^{-2}$ day$^{-1}$ in the east (Figure. 5.3) to a maximum of 1.3-4.5 mmol m$^{-2}$ day$^{-1}$ found in west (Figure. 5.2) during pre-monsoon, while that in the post-monsoon ranged a minimum of 1.3-3 mmol m$^{-2}$ day$^{-1}$ in south (Figure. 5.4) to about 2-6.5 mmol m$^{-2}$ day$^{-1}$ in west (Figure. 5.2). This can be due to the absence of the upwelling and convective mixing because of stratification of surface layers hindering the vertical transport. Also the CO$_2$ fixation during photosynthesis can result in the reduction of surface CO$_2$ (Madhupratap et al, 1996; Sarma et al., 2000; Takahashi et al., 2002).

In the northern Arabian Sea, the pre-monsoon flux values were found to be considerably higher (Figure. 5.1) which was found to be 1.3-12.5 mmol m$^{-2}$ day$^{-1}$ than that in the post monsoon which ranged 0.8-3 mmol m$^{-2}$ day$^{-1}$. This might be due to the higher bacterial respiration during pre-monsoon season leading to increased CO$_2$ levels in the ocean waters (Sarma et al., 1998; Sarma et al, 2000; Sarma, 2003). Pre-monsoon fluxes were high in the north (Figure. 5.1) which reached up to a value of 12.5 mmol m$^{-2}$ day$^{-1}$ compared to other parts which may be because of the increased CO$_2$ levels in the waters caused by the high winter production (Sarma, 2003). All over the Arabian Sea, the highest fluxes were contributed by the north and west region (Takahashi et al., 2002, Takahashi et al., 2009). The spatial and seasonal distribution of fluxes are summarised in table 5.1.

6.2 Primary productivity in the Arabian Sea

Winter and monsoon seasons showed high productivity in the north, west and east regions. Among these, the highest range in winter was observed in the north (Figure.5.6) with a range of 1200-2300 mgC m$^{-2}$ day$^{-1}$ and lowest in east (Figure. 5.8) ranged 275-700 mgC m$^{-2}$ day$^{-1}$. In the monsoon season, high value range was in the west (Figure. 5.7) which showed 850-1700 mgC m$^{-2}$ day$^{-1}$ and lowest in the east (Figure. 5.8) which was 435-835 mgC
This high productivity can be the result of the monsoonal upwelling and winter convective mixing that bring nutrients from the subsurface hence triggering the ocean primary productivity, the absence of which caused a reduction in the productivity in pre-monsoon and post monsoon seasons (Sarma et al., 2000; Barber et al., 2001; Tang et al., 2002; Marra and Barber, 2005). The pre-monsoon productivity range was found to be 225-400 mgC m$^{-2}$ day$^{-1}$ in the east (Figure. 5.8) to about 340-1300 mgC m$^{-2}$ day$^{-1}$ in the north (Figure. 5.6). The increased rates of bacterial respiration and the time lag between the production and respiration might be the cause of reduced productivity (Sarma, 2003).

North and south areas showed a high productivity observed during winter than in the monsoon as observed by Madhupratap et al (1996) in the north-eastern Arabian Sea. The winter cooling experienced by the northern Arabian Sea is characterised by sea surface temperature reduction and densification leading to the formation of high salinity waters. This is followed by sinking and convective mixing which brings nutrients to the surface waters from the thermocline thus enhancing the productivity (Chauhan et al., 2001). During winter, onshore and offshore chlorophyll blooms characterise the northern Arabian Sea which also can result in the high winter productivity (Dey and Singh, 2003). Highest productivity during monsoon was observed in the western region caused by the upwelling in the Oman coast (Barber et al., 2001).

In all seasons, productivity was found to be low in the southern (Figure. 5.9) Arabian Sea which did not show any considerable seasonal variation in the productivity values. The minimum range showed 200-260 mgC m$^{-2}$ day$^{-1}$ in the pre-monsoon and maximum was found in the post-monsoon with a range 250-440 mgC m$^{-2}$ day$^{-1}$. This low productivity trend can be due to the effect of increase in SST while going to the offshore regions and the resulting stratification in the surface layers and reduction in the upward transport of nutrients (Sarma, 2003). Increase in temperature also causes increase in respiration rates and heterotrophic activities in the surface waters. Also, the nutrient concentration in the surface waters decreases offshore and the mixed layer depth increases which can result in reduced productivity (Sarma et al., 2000; takahashi et al., 2002; Marra and Barber, 2005). The western and northern regions were found to be the highest productive regions in the Arabian Sea (Tang et al., 2002; Prasannakumar et al., 2009). The spatial and seasonal distribution of primary productivity is summarised in table. 5.2.

6.3 Comparison of CO$_2$ fluxes with ocean primary productivity

Spatial as well as seasonal comparison was carried out to find the influence of primary productivity on CO$_2$ fluxes. Winter season showed a positive correlation between the fluxes and productivity in all the four regions (Figure 5.11A, 5.12A, 5.13A, 5.14A). This might be attributed to the winter convective mixing which brings the CO$_2$ enriched subsurface waters and nutrients thus enhancing the fluxes and productivity respectively (Sarma et al., 2000; Takahashi et al., 2002; Sarma, 2003; Marra and Barber, 2005). High production leads to high respiration rates and enhanced CO$_2$ levels in the surface waters (Sarma et al., 1998; Sarma et al., 2000).

During Monsoon, fluxes were found to be increasing with increase in the productivity in east (Figure.5.13C), west (Figure.5.12C) and south (Figure.5.14.C) which can be the result of monsoonal upwelling bringing CO$_2$ and nutrients to the surface (Sarma et al., 2000; Takahashi et al., 2002; Marra and Barber, 2005). North fluxes appeared to be slightly decreasing with the biological production during monsoon (Figure.5.11C) since it can be due to the river runoff bringing low saline high nutrient waters from Oman and Pakistan which reduces the CO$_2$ while increases the productivity (Sarma et al., 1998) and intense
rainfall leading to low saturation levels of CO$_2$ (Watts et al., 2002). It can also be due to a reduction in alkalinity as observed by Sarma et al. (1998).

Pre-monsoon productivity did not show much correlation with fluxes in the west (Figure 5.12.B) and east (Figure 5.13.B) regions since both were low and not having much variation in values during pre-monsoon due to absence of the upwelling (Sarma et al., 2000; Marra and Barber, 2005). North (Figure 5.11.B) region showed a considerable correlation with productivity in the pre-monsoon season which might have resulted from the higher CO$_2$ levels contributed by the high bacterial respiration rates in the surface layers during this season with increased productivity (Sarma et al., 1998; Sarma et al., 2000; Sarma, 2003).

In the south, slight decrease in fluxes was observed with increase in productivity during pre-monsoon (Figure 5.14.B) and post-monsoon (Figure 5.14.D) seasons. The western (Figure 5.12.D) region also showed a reduced trend in fluxes with increase in primary production in post-monsoon. This may be due to the biological uptake of surface CO$_2$ during primary production, together with the absence of CO$_2$ replenishment in these seasons (Sarma et al., 2000; Takahashi, 2002).

### 6.4 Comparison of CO$_2$ fluxes with Sea surface temperature

Comparison of CO$_2$ fluxes with sea surface temperature in the Arabian Sea was carried out to find out the temperature effects on the fluxes. Fluxes showed a negative correlation with SST in all the seasons in the northern (Figure 5.15.A, B, C, D) and eastern (Figure 5.17.A, B, C, D) Arabian Sea. In the west, the negative correlation was observed in the monsoon (Figure 5.16.C), pre-monsoon (Figure 5.16.B) and post-monsoon (Figure 5.16.D) seasons while that in south was found to be during winter (Figure 5.18.A), pre-monsoon (Figure 5.18.B) and monsoon (Figure 5.18.C) seasons.

The decreasing effect of SST on the CO$_2$ fluxes in the winter and monsoon seasons can be attributed to the surface cooling of the waters in these seasons due to the upwelling and convective mixing bringing cold CO$_2$ rich waters to the surface (Madhupratap et al., 1996; Sarma et al., 2000; Sarma, 2003). In the western region, the SST did not show much effect on the fluxes.

During pre-monsoon and post-monsoon, increase in the sea surface temperatures results in the stratification of upper ocean layers which hinder the upward transport of CO$_2$ rich waters thus reducing the fluxes (Sarma et al., 2000; Takahashi, 2002). In the south, an increase in fluxes was found with increase in SST during post monsoon (Figure 5.18.D). This positive correlation can be due to the increase in sea surface temperature in the offshore regions (Marra and Barber, 2005) causing decreased CO$_2$ solubility in this season (Sarma, 2003; Sarma et al., 2000).

### 6.5 Analysis of sea surface pCO$_2$ derived for case 1 and case 2 waters

Sea surface pCO$_2$ was derived for case 2 waters of Arabian Sea using algorithm developed from the field data collected from coastal waters off Cochin and for case 1 waters using algorithm developed for the Northern South China Sea (Zhu et al., 2009). Analysis was carried out in the four seasons i.e. winter, pre-monsoon, monsoon and post-monsoon.

The algorithm was found to be giving pCO$_2$ values within range in winter (Figure 5.19) in the east and central Arabian Sea. In winter, the central Arabian Sea was having pCO$_2$ values in the range 390-440 µatm which is similar to the observations of Sarma (2003). From west
to east, a decrease in pCO₂ values was found ranging from 140-380 µatm in the eastern part which may be attributed to the low saline water mass from Bay of Bengal in this season (Sarma, 2003). Towards north and some parts near to the eastern coast, pCO₂ values showed an increasing trend which ranged from 450 to >750 µatm in the eastern region and >750 in the upper region of central Arabian Sea. This might have resulted from the convective mixing in the coastal areas (Sarma et al., 2000). The pCO₂ range given by northern and western coastal waters was not within limits since the temperature conditions and Chlorophyll concentrations in these regions differ from that of the field data collected in this season due to the intensive winter convection compared to the other regions (Sarma, 2003).

In the pre-monsoon season (Figure 5.20), the pCO₂ values were increased in the eastern Arabian Sea which can be due to the reduction in the influence of low salinity waters (Sarma, 2003). The range observed was about 380 to >750 µatm in the south-east Arabian Sea. In the north region of central Arabian Sea and its adjacent regions of western and eastern parts, a reduction in the pCO₂ was observed which ranged from 140-260 µatm. The change in the surface circulation pattern from equator to pole-ward in the pre-monsoon, which brings low pCO₂ waters towards north can be the reason behind this surface pCO₂ reduction (Sarma, 2003). The northern open ocean waters showed high pCO₂ range of about 450 to >750 µatm which might be caused by the thermodynamic response of sea waters resulting from the increased sea surface temperature and consequent decrease in CO₂ solubility (Sarma, 2003). The high bacterial respiration rates also increase the pCO₂ levels in surface waters in this season (Sarma et al., 1998; Sarma et al., 2000; Sarma, 2003). The northern coastal waters were not found to be giving pCO₂ values within range.

In the monsoon season (Figure 5.21), pCO₂ values exhibited an increase in all the regions of Arabian Sea. The central Arabian Sea showed pCO₂ values ranging from 450 to >750 µatm caused by the open ocean upwelling driven by the Findlater jet (Madhupratap et al., 1996; Sarma, 2003). In the western region, pCO₂ values increase up to >700 µatm as observed by Sarma (2003) which could have resulted from the strong coastal upwelling. Eastern coastal regions showed pCO₂ values reaching up to >750 µatm which might be caused by the intense coastal upwelling along the SW coast of India (Sarma, 2000; Sarma, 2003).

In the post-monsoon season (Figure 5.22), the algorithm has given higher values in the central and southern Arabian Sea which showed values >750 µatm in the south and central region. Increased sea surface temperatures leading to decreased CO₂ solubility in waters as well as higher rates of decomposition of organic matter generated during the preceding monsoon might have caused such increase in the pCO₂ values in this season (Sarma et al., 1998; Sarma et al., 2000; Sarma, 2003). The results are summarised in table 5.4.
Chapter 7
Conclusions

Distribution of CO$_2$ fluxes in the Arabian Sea was estimated and compared with the ocean primary productivity and sea surface temperature to understand how they regulate seasonally and spatially the sea-air CO$_2$ flow. The fluxes were found to vary seasonally as well as spatially with high values obtained in the north-western Arabian Sea during monsoon season followed by the winter. The monsoon fluxes were found to reach a value range of 36-75 mmol m$^{-2}$ day$^{-1}$ in the west and in winter it was 5-20 mmol m$^{-2}$ day$^{-1}$ in the north region. Such high flux range could be attributed by the monsoonal upwelling and winter convective mixing. The lowest values were observed in the southern region especially in the post-monsoon season which ranged 1.3-3 mmol m$^{-2}$ day$^{-1}$. These reduced rates might have caused by the offshore increase in temperatures leading to stratification of the upper layers and the absence of upwelling and convective mixing in this season.

In all seasons, the primary productivity in the Arabian Sea was observed to be high in the north-western region, with highest values in monsoon and winter. In winter, the high value ranged 1200-2300 mgC m$^{-2}$ day$^{-1}$ in the north and in monsoon, it showed the range 850-1700 mgC m$^{-2}$ day$^{-1}$ in the west. Monsoonal upwelling and winter convective mixing bringing nutrients to the surface layers could have resulted in the enhanced productivity. Southern region showed less productivity in all seasons with minimum values going up to 200-260 mgC m$^{-2}$ day$^{-1}$ in the pre-monsoon season. This could be attributed to the stratification of surface layers which hinder the upward movement of nutrients.

The comparison between the CO$_2$ fluxes and the productivity showed a positive correlation between them in all the regions in winter which could be due to the convective mixing which enhances the fluxes and productivity simultaneously. Monsoonal upwelling also showed an increasing effect on both the parameters in the west, east and south while a slight decrease in the northern fluxes observed which might be caused by the river influx. West and east regions did not exhibit much correlation in the pre-monsoon season since both were not varying much due to the absence of upwelling. High correlation between fluxes and productivity observed in the north which could be resulted from the high bacterial respiration leading to increased surface CO$_2$ levels and enhanced productivity. The biological uptake of CO$_2$ together with the absence of CO$_2$ replenishment might have resulted in the decreased fluxes with increase in productivity in southern region in pre-monsoon and post-monsoon as well as in west during post-monsoon season.

The comparison of CO$_2$ fluxes with SST showed a negative correlation in all the seasons in the northern and eastern Arabian Sea. Western region showed the negative correlation during monsoon, pre-monsoon and post-monsoon while the in the south it was observed during winter, monsoon and pre-monsoon seasons. This negative trend is attributed to the surface cooling during the upwelling and convective mixing during the monsoon and winter seasons respectively. The decreasing trend in fluxes with increased SST during pre-monsoon and post-monsoon might be caused by the absence of the upwelling and vertical
mixing together with increase in SST leading to the surface stratification. Decreased solubility of CO$_2$ could have caused the increase in fluxes with SST in the south.

The algorithm developed using the insitu data from field was used to derive sea surface pCO$_2$ in the case 2 waters and the algorithm developed for South China Sea by Zhu et al (2009) used for the case1 waters. The algorithm was found to give pCO$_2$ values within range in the winter in east and central Arabian Sea. In the north-western coast it was not giving pCO$_2$ value within range. In the pre-monsoon season, the results obtained were found to be within range in the east and south-east regions and northern offshore areas. The northern coastal values were not found to be within range. Monsoon values were found to be within range in the central, western and eastern regions. Post-monsoon values were found to be within range only in the central and southern Arabian Sea. The out of range values observed in the present study cannot be attributed to any single factor in the present analysis. However, the relationships can be improved further by increasing number of temporal and spatial insitu observation in future.
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