Variations in the inorganic carbon components in the thermal fronts during winter in the northeastern Arabian Sea

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Abstract

In order to examine the variations in inorganic carbon components in the thermal fronts, seven fronts have been sampled in the northeastern Arabian Sea during winter. The sea surface temperature (SST) was cooler by 0.2 to 1.03°C within the fronts sampled and three out of seven fronts have relatively saltier (by 0.04 to 0.10) and others were fresher (by 0.03 to 0.13) compared to outside the front. Increase in chlorophyll-a (Chl-a) was observed by 0.05 to 0.6 mg m⁻³ in the four fronts and marginal decrease was noticed in other fronts (0.02-0.23 mg m⁻³). The increase in Chl-a within the front from that of outside showed linear relation with magnitude of difference in temperature and salinity suggesting that enhanced vertical mixing brought nutrients to surface to support phytoplankton biomass in the fronts. Dissolved Oxygen was relatively under-saturated by ~1.6% in the frontal zone compared to outside suggesting that dominant heterotrophy in the former region due to availability of high phytoplankton biomass. Dissolved inorganic carbon (DIC) was higher in the frontal zone by 3 to 41.5 μM than outside. The salinity normalized DIC displayed linear relation with Chl-a and inverse correlation with dissolved oxygen saturation suggesting that both auto and heterotrophic activities may be responsible for changes in DIC in the frontal zone. The higher levels (by 3 to 50 μatm) were noticed in the frontal zone compared to outside, however, the magnitude of difference was linearly correlated with difference in SST and Chl-a between within and outside front. Based on the simple model, it was noticed that biological and mixing effects were dominant controlling factors for pCO₂ followed by thermal and flux effect. The biological effect was dominant at front 1 and 3 while mixing effect controls at fronts 2, 4 and 6. This study suggests that fronts act as a source or sink depends on the strength of the mixing process associating with biological response and also age of the front.
1. Introduction

Ocean fronts are generally defined as an interface among two or more water masses with different characteristics. Frontal zones are known to hinder the exchange of material between inshore and offshore (Brink et al., 1987) and therefore they are important zones to arrest spreading of pollutants. Frontal regions are rich in nutrients and highly productive (Franks, 1992; Fiala et al., 1994; Pitcher et al., 1998; Basterretxea and Aristegui, 2000; Jacquet et al., 2002; Brown et al., 2008; Munk et al., 2003; Nammalwar et al., 2013). Thus, fronts represent enriched habitats that contribute disproportionately to regional productivity, nutrient cycling, trophic ecology, carbon fluxes and sequestration. Hence these regions are attracted by several marine researchers to study mechanisms associated with frontal formation and material cycling (Chen et al., 1983; Liu et al., 2003; Zhao et al., 1985; Lu et al., 2010; Li et al., 2000).

Several studies have been conducted to examine the physical and biogeochemical characteristics of the frontal zones in the temperate region. For instance, Borges and Frankignoulle (2003) observed thermal front (Ushant front) in the Western English Channel. This front is formed between the warm stratified northern waters and the colder permanently well-mixed southern waters of the Eastern Channel (Pingree et al., 1979). The thermal fronts were also noticed between destratified and stratified waters along the Armorican Shelf and Western English Channel. Very low pCO₂, high dissolved oxygen and Chlorophyll-a was found in the warmer waters and vice versa on the colder waters suggesting that high DIC fixation by phytoplankton in the warmer waters of the frontal structure in the western English Channel (Jordan and Joint, 1984; Borges and Frankignoulle, 2003; Harlay et al., 2010) and shelf break of Bay of Biscay (Suykens et al., 2010). Loggerwell et al. (2001) suggested that recruitment success of Pacific sardine may be related to climate-related variability in mesoscale eddies. Subduction at fronts are possible explanation for the massive imbalance of new versus export production that arises when only contemporaneous processes in homogeneous water parcels are considered (e.g. Stukel et al., 2011). Recently, it was noticed that high CO₂ fluxes were associated with Subtropical frontal zone in the Southern Ocean using drifters and it has an important implications on sequestration of atmospheric CO₂ (Boutin et al., 2008; Resplandy et al., 2014). The studies on fronts in the tropical region, such as Indian Ocean, were mainly concentrated on identifying potential fishing zone (PFZ). Since more than a decade, satellite based sea surface temperature (SST) and chlorophyll features have been used to differentiate water masses in the northeastern Indian Ocean in context of understanding PFZs (Solanki et al., 1998,
Intensive ground truth data have been collected and found that 70-80% of success was achieved on identifying PFZ using remote sensing data (Solanki et al., 1998; 2000; Nammalwar et al., 2013). However, no efforts have been made so far to quantify biogeochemical processes in the frontal zone in the Indian Ocean.

The northern Arabian Sea (northwestern Indian Ocean) is highly productive zone during winter (November to March) due to injection of nutrients to surface through convective mixing (Madhupratap et al., 1996). Despite high nutrients (nitrate >2 μM), primary production is significantly lower during winter than summer (Bhattathiri et al., 1996; Barber et al., 2001) and was attributed to deeper mixed layer than euphotic depth during former season. As a result, phytoplankton experiences both dark and light cycles lead to decrease in phytoplankton growth. On the other hand, several fronts form in the northeastern Arabian Sea due to advection of low saline waters from the near-shore by offshore winds along the Indian peninsula. Recently first ever observations were carried out on frontal zone to characterize the chemical and biological features. They noticed that fronts are associated with high nutrients and phytoplankton biomass compared to outside and was attributed to enhanced vertical mixing in the frontal zone (Vipin et al., 2014; Rajdeep et al., 2014). Such increased mixing and nutrient input not only enhances biological production but also impacts air-sea exchange of CO₂ at the interface. However, no efforts have been carried out so far to understand influence of fronts on pCO₂ levels in the Indian Ocean.

The Arabian Sea is known for perennial source of CO₂ to the atmosphere (Goyet et al., 1997; Sarma et al., 1998; Sarma 2003). Most of these measurements were carried out at seasonal time-scale with coarse resolution (1° interval) along the selected transects (Sarma et al., 1998; Millero et al., 1998) or extrapolation to entire basin using remote sensing SST and chlorophyll –a (Chl-a) based on regression equation developed for pCO₂ with SST (Goyet et al., 1997), SST and Chl-a (Sabine et al., 2000) or dissolved inorganic carbon (DIC) and total alkalinity (TA) with SST, salinity and Chl-a (Sarma, 2003; Bates et al., 2006). Recently Sarma et al. (2013) estimated fluxes of CO₂ from the Indian Ocean between 1990 and 2009 using interpolated data, biogeochemical models, ocean and atmospheric inversions and noticed that the seasonal variations in the CO₂ fluxes were ill simulated by all these models in the northern Indian Ocean compared to observations. This was attributed to problems associated with simulations of monsoon circulation in this zone. It was noticed that the measured pCO₂ were significantly lower than simulated during winter and vice versa during summer in the Arabian Sea. It is
also possible that observations might have missed meso-scale features that might lead to underestimation of CO₂ flux. In order to examine the same, an experiment was conducted to understand how pCO₂ levels varied in the frontal zone in the northeastern Arabian Sea and how important these meso-scale features on exchange at the air-water interface during northeast monsoon. In this experiment we would like to test the hypothesis that all fronts will have high Chlorophyll-a (Chl-a) and efflux CO₂ to atmosphere due to intensive vertical mixing.

**Material and methods**

In order to identify the fronts, near real time, Sea Surface Temperature (SST) data from various sensors (AVHRR) were used to identify possible locations of fronts. The fronts have been identified as gradient in temperature by 0.25°C. This information was immediately transmitted to the onboard research vessel to gear the ship towards the identified location. The details of the identification of fronts were given elsewhere (Vipin et al., 2014).

Surface water samples were collected onboard research vessel R/V Sindhu Sankalp (#SSK 60) from 22nd January to 3rd February 2014 in the northeastern Arabian Sea (Fig. 1). During the cruise, samples were collected on seven selected fronts representing open ocean region, which is influenced by winter convective mixing with relatively higher Chl-a (Front 1, 2 and 5), coastal region (Front 3 and 4) and oligotrophic region (front 6 and 7) where relatively low Chl-a was noticed (Fig. 1). The interest of selecting fronts from different region is to examine how different physico-chemical characteristics of the water in the frontal zone from that of outside with different back ground values. Fifty nine samples were collected in 7 transects covering both frontal and non-frontal regions in each transect.

Water sampling was carried out using a Seabird Conductivity-Temperature-Depth-rosette system fitted with 10 L Niskin bottles. Chl-a was measured using fluorescence sensor (Wet Labs, USA) fitted to the CTD rosette. The fluorescence sensor was calibrated using measured Chl-a following acetone extraction method given in the JGOFS protocols (JGOFS, 1996). Dissolved oxygen (DO) was estimated using Winkler’s method following automated potentiometric end point detection (Carritt and Carpenter, 1966). The pH and total alkalinity (TA) were measured by potentiometric (Metrohm, Zofingen, Switzerland) Gran titration method following standard operating procedures suggested by the Department of Energy (DOE) (1998). Dissolved inorganic carbon (DIC) was measured using a Coulometer (UIC Inc., Joliet, Illinois, USA) attached to an automated subsampling system (Sarma, 1998). The precisions for pH, TA
and DIC were ±0.002, ±2.0 and ±1.8 μmol l⁻¹, respectively. The accuracy of the measurements of pH, TA and DIC were ±0.005, ±4.5 and 3.8 μmol l⁻¹ respectively. The pCO₂ was computed using measured salinity, temperature, nutrients (phosphate and silicate), pH and DIC using CO2 SYS program (Lewis and Wallace, 1998). The CO₂ dissociation constants given by Millero et al. (2006) for 0 to 40 salinity range were used. The computed pCO₂ is an estimated accuracy of ±10 μatm. Air-water flux of CO₂ was estimated using formulations given by Wanninkhof (2014) using surface pCO₂ levels and measured wind speed at 10 m above the sea levels.

3. Results and Discussion

The northeastern Arabian Sea, off the Gujarat Coast, is highly productive region during northeast (NE) monsoon (December to February) due to availability of nutrients through winter convective mixing (Banse and McClain, 1986; Prasanna Kumar et al., 1996; Madhupratap et al., 1996) that comprises extensive fishing grounds (Solanki et al., 2003; 2005). During this period, offshore winds along the Indian peninsula induce fronts that enhance the primary production and high fish production (Solanki et al., 2005).

3.1. Variations in hydrographic properties within and outside the fronts

The width of the fronts typically varies between 10 and 20 kms with variable lengths in the study region (Vipin et al., 2014). The currents during this period were northwest direction with the speed of ~1 m/s hence fronts also move rapidly in the same direction. The surface temperature in the frontal zone were 0.56 to 1.02° C cooler than the surrounding waters, except in the front 7 where the difference was quite low (0.2° C) (Fig. 2; Table 1). Borges and Frankignoule (2003) noticed thermal fronts in the English Channel and adjacent areas during warm period of the year (September 1999) and also over the Armorican Shelf. The temperature change observed in the frontal zones of the Arabian Sea is an order of magnitude less than that observed in the English Channel (Borges and Frankignoule, 2003) and northwest European continental margin (northern Bay of Biscay; Suykens et al., 2010) and Southern Ocean (Boutin et al., 2008; Resplandy et al., 2014). The salinity difference within and outside front was ranged from 0.03 to 0.13 in the fronts sampled. The salinity in the fronts were lower than outside at fronts 1, 3, 5 and 6 (0.04 - 0.1) whereas it was increased at other fronts (0.03 to 0.13). Significant increase in Chl-a was noticed within the front by 0.05 to 0.61 mg m⁻³ compared to the outside, except at fronts 2, 4, and 5. The increase in Chl-a was ~21 to 122% compared to outside the front. The increase in
Chl-a within the front from that of outside showed significant linear relation with difference in temperature ($r^2=0.58$; $p<0.001$) and inversely with salinity ($r^2=0.69$; $p<0.001$) suggesting that increased vertical mixing lead to enhanced nutrients that supported phytoplankton biomass in the frontal region (Fig. 3a,b). The increase in Chl-a in the frontal zone was as high as 8 mg m$^{-3}$ in the fronts observed along the European continental margin and northeast Atlantic Ocean (Borges and Frankignoulle, 2003; Harlay et al., 2010; Suykens et al., 2010) suggesting that more intense mixing is possible. Recently Rajdeep et al. (2014) noticed increase in nutrients concentrations in the frontal zone compared to outside in the northern Arabian Sea suggesting that enhanced vertical mixing supported high biological production. In the present study dissolved oxygen concentrations were ranged from 212 to 226 μM within the front and it was lower than that of outside front (211 to 228 μM). The dissolved oxygen in the surface waters was close to saturation (102.6±2%) in the entire study region, however, slight undersaturation was noticed in the front 2 and 3 (~99.4%). Overall oxygen saturation was lower in the frontal zone than outside by ~1.6% suggesting that dominant heterotrophy in the front than outside due to availability of high phytoplankton biomass. Borges and Frankignoulle (2003) noticed that higher Chl-a is associated with high oxygen saturation suggesting that active biological production on the warmer side of the frontal zone in the English Channel.

3.2. Variations in dissolved inorganic components within and outside fronts

Dissolved inorganic carbon (DIC) varied from 2040 to 2193 μM in the study region and relatively higher concentrations were observed in the north of study region (north of 19.5° N) than south by about 50 μM (Figure 2; Table 1). Such differences were consistent with the temperature, which was cooler in the north than south suggesting that intense convective mixing in the north lead to injection of DIC rich waters from the subsurface (Sarma et al., 1996). The DIC concentrations were significantly higher in the frontal zone (by 3 to 41.5 μM) than outside that could possibly due to either vertical mixing or intense heterotrophic activity (Table 1). DIC showed strong inverse relation with temperature ($r^2=0.66$; $p<0.001$), salinity ($r^2=0.31$; $p<0.05$), except in coastal front, and depth of mixed layer ($r^2=0.42$; $p<0.001$) suggesting that vertical mixing could be potential reason for increased DIC in the study region (Fig. 4a,b). In order to differentiate physical versus biological processes, DIC was normalized to constant salinity following Friis et al (2003) and correlated with Chl-a ($r^2=0.41$; $p<0.001$) and dissolved oxygen saturation ($r^2=0.43$; $p<0.001$), which are measure of biological processes (Fig. 4c,d). These relationships suggest that both biological and physical processes are important in controlling DIC concentrations in
the surface waters. Significant correlation with Chl-a cannot be expected as DIC is also modified by heterotrophic activity and also Chl-a is not a measure of primary production as several other factors such as light, mixing, grazing etc also determines primary production. On the other hand strong relation of DIC with dissolve oxygen saturation suggests that dominant heterotrophic activity may be responsible for increased DIC in the study region. Dissolved oxygen was relatively undersaturated by 1.5% in the frontal zone compared to outside associated with high DIC suggesting that dominant heterotrophy in the frontal zone.

Total alkalinity ranged between 2376 and 2483 μM in the study region and displayed significant correlation with salinity ($r^2=0.35; p<0.001$) and followed the similar trend of DIC. The TA:DIC ratio is an indicator of the relative abundance of carbonate species (e.g., HCO$_3^-$ and CO$_3^{2-}$) and also for buffering capacity (intensity) as it attains a minimum when TA:DIC $\sim$ 1. The TA/DIC ratio was varied from 1.127 to 1.183 and these ratios were significantly lower in the fronts 1-5 with mean of 1.143±0.007 than fronts 6 and 7 (1.168±0.011) in the oligotrophic zone. Lower TA:DIC ratios in the northern fronts (1-5) were due to predominant vertical mixing, as indicated by temperature. The TA:DIC ratio was lower on the front (1.147) than outside (1.157) suggesting that decreased buffering capacity in the former than latter due to dominant vertical mixing.

The surface water pH varied between 8.121 and 8.252 in the study region and relatively higher pH was observed in the north of 19.5° N than south. pH showed significant inverse correlation with salinity ($r^2=0.42; p<0.001$) suggesting that advection of low saline coastal waters contained relatively acidic pH, which were influenced by river discharge from Narmada and Tapti. Both Narmada and Tapti contains relatively higher pCO$_2$ (>1000 μatm) due to intense modification of organic matter (Sarma et al., 2012). pH also displayed significant relation with temperature ($r^2=0.72; p<0.001$) suggesting that mixing with deeper waters decreased pH in the northern part of our study region. pH in the frontal region was relatively lower (0.019) than outside front suggesting that vertical mixing or dominant heterotrophy decreased pH in the frontal zone.

*Variations pCO$_2$ levels and fluxes of CO$_2$ to atmosphere*

pCO$_2$ in the study region ranged from 350 to 495 μatm during study period. pCO$_2$ levels were relatively higher in the vicinity of fronts 1-5 (453±23 μatm) whereas lower at fronts 6-7 (387±29 μatm) (Figure 2). Such distribution pattern is consistent with SST and Chl-a. pCO$_2$ showed significant inversion
correlation with SST ($r^2=0.76; p<0.001$) and dissolve oxygen ($r^2=0.42; p<0.001$) and weak relation with Chl-a ($r^2=0.16; p<0.01$) suggesting that both physical and biological processes are responsible for variations in pCO$_2$. Sukyens et al. (2010) noticed inverse relation between degree of stratification and pCO$_2$ (also DIC) in the northeast European continental margin. Though increased stratification decreases the nutrients inputs however it increases light availability that lead to enhanced phytoplankton activity and decrease in inorganic carbon components (Margalef, 1997). On the average pCO$_2$ in the frontal zone were relatively higher by 3 to 50 $\mu$atm compared to outside, however, the magnitude of difference seems to be depending on the variations in SST and Chl-a between within and outside front.

Borges and Frankignoule (2003) noticed low pCO$_2$ and high oxygen saturation associated with high Chl-a in the warmer waters of the front in the western channel and the Armorican Shelf suggesting active biological utilization of CO$_2$ within the front. The magnitude of changes in SST and Chl-a, within the front from that of outside, showed significant negative relation with change in pCO$_2$ suggesting that both physical and biological processes were responsible for variations in pCO$_2$ in the fronts (Fig. 3c,d). However, pCO$_2$ at fronts 4 and 6 were deviated from the relation with SST compared to other fronts suggesting that different processes may be controlling their changes. For instance, the temperature drop in front 1 was ~1.1$^\circ$C compared to outside whereas Chl-a increased by 0.6 mg m$^{-3}$ associating with decrease in pCO$_2$ by ~27 $\mu$atm. On the other hand, the decrease in SST was low at Front 5 (~0.6$^\circ$C) associating with slight increase in Chl-a by 0.09 mg m$^{-3}$, where pCO$_2$ difference between within and outside front was minimal (~3 $\mu$atm) suggesting that vertical mixing and biological response controls the pCO$_2$ levels in the front (Table 1). Hence, both difference in SST, Chl-a between within front and outside inversely correlated with difference in pCO$_2$ suggesting both physical and biological processes are responsible for their variations.

In order to examine the role of physical and biological processes on variations in pCO$_2$ in the frontal and non-frontal zone, the contribution of different effects on pCO$_2$ was estimated following Louanchi et al. (1996) model. Based on the difference in characteristics of inorganic carbon within the front and outside, the contribution of changes in pCO$_2$ due to biological process (primary production and respiration; Biological effect), mixing with subsurface waters (Mixing effect), variations in temperature resulted from changes in solubility (Thermal effect) and variations in fluxes at sea-air interface (Flux effect) were evaluated (Fig. 5). This analysis suggested that biological and mixing effects were dominant controlling factors followed by thermal and fluxes. Both biological and thermal effects decreased pCO$_2$
by 8 to 54 and 6 to 24 μatm respectively whereas mixing increased pCO₂ by 15 to 78 μatm at different fronts sampled. On the other hand, the contribution of flux effect in variations in pCO₂ were relatively low due to weak winds, however, it decreased pCO₂ by 3-8 μatm at front 1-5 and increased by 8-10 at front 6 and 7. The dominance of each of these effects was different at various fronts sampled. For instance, biological effect was dominant at front 1 (54 μatm) and front 3 (44 μatm) whereas mixing effect contributed significantly at front 2 (78 μatm) and front 4 (65 μatm). In order to understand the net effect of these processes on pCO₂, the processes decreasing the pCO₂ (biological, thermal and flux effects) were summed and compared with the mixing effect that increased the levels. It suggested that biological effect was dominant at front 1 and 3 where nearly 1 mg m⁻³ of Chl-a was observed resulting in low pCO₂ levels even compared to the outside of the front by 10-27 μatm (Table 1). In contrast, mixing effect was dominant at fronts 2, 4 and 6 where low Chl-a (0.6-0.7 mg m⁻³) was observed with relatively higher pCO₂ levels in the front (~25-50 μatm) than outside. On the other hand, the variations in pCO₂ within and outside front were almost equal (<8 μatm) where both biological + thermal effects were almost equivalent to mixing and flux effect. Sarma et al. (2000) noticed that mixing effect is the dominant among others during northeast monsoon in the Arabian Sea due to convective mixing. It is known that frontal zone contains relatively higher concentrations of nutrients; however, it would take some time for biology to respond to increased nutrient levels. Therefore, mixing effect dominates the enhanced pCO₂ levels in the initial phase of the front formation while biological processes may dominate at the latter stage. However, this study cannot conclude that whether fronts are net source or sink for atmospheric CO₂ and can be confirmed only through time-series observations on the front to examine the net fluxes. This study suggested that all fronts need not have high chlorophyll-a and flux of CO₂ to atmosphere however the age of the front and biological response to physical mixing determine the conditions in the frontal zones in the northern Arabian Sea.

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References


Table 1: Physical and biogeochemical properties within and outside various fronts sampled in the northeastern Arabian Sea

<table>
<thead>
<tr>
<th>Front</th>
<th>Temperature (°C)</th>
<th>Salinity</th>
<th>DO (μM)</th>
<th>Chl-a (mg m⁻³)</th>
<th>DIC (μM)</th>
<th>pH</th>
<th>pCO₂ (μatm)</th>
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<td>Front</td>
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<tr>
<td>F 1</td>
<td>24.63±0.24</td>
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<td>36.44±0.02</td>
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<td>188±5</td>
<td>183±3</td>
<td>1.1±0.5</td>
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<tr>
<td>F 2</td>
<td>24.80±0.14</td>
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<td>36.30±0.05</td>
<td>36.34±0.03</td>
<td>189±5</td>
<td>196±4</td>
<td>0.8±0.3</td>
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<tr>
<td>F 3</td>
<td>24.59±0.02</td>
<td>25.39±0.11</td>
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<td>36.31±0.02</td>
<td>184±7</td>
<td>188±6</td>
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<tr>
<td>F 4</td>
<td>24.47±0.11</td>
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<td>36.05±0.01</td>
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<td>F 5</td>
<td>24.83±0.10</td>
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<td>F 7</td>
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Figure 1: Thermal fronts during the sampling period and cruise track

Figure 2: Distribution of sea surface a) temperature (°C), b) salinity, c) Chlorophyll-a (mg m\(^{-3}\)), d) dissolved oxygen (\(\mu\)M), e) pH, f) total alkalinity (\(\mu\)M), g) dissolved inorganic carbon (\(\mu\)M) and h) pCO\(_2\) (\(\mu\)atm).

Figure 3: Relationship of a) variations in SST and Chl-a, b) variations in salinity and Chl-a, c) changes in SST and pCO\(_2\) and d) changes in Chl-a and pCO\(_2\) between within and outside front.

Figure 4: Relationship of dissolved inorganic carbon with a) SST, b) SSS and normalized DIC with c) Chl-a and d) dissolved oxygen saturation.

Figure 5: Effects of biological, mixing, thermal and flux on pCO\(_2\) distribution at various fronts
Figure 2:
Figure 3:

(a) Change in Chl-a in the front (mg m\(^{-3}\)) against Decrease in SST in the front (°C).
(b) Change in salinity in the front against Change in SST in the front (°C).
(c) Change in pCO\(_2\) (μatm) against Change in SST in the front (°C).
(d) Change in Chl-a in the front (mg m\(^{-3}\)) against Change in SST in the front (°C).
Figure 4:
Figure 5:

![Graph showing pCO$_2$ (μatm) for different fronts. The graph includes bars labeled Biological Mixing, Thermal, and Flux.](image-url)