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Hurricane Arthur and its effect on the short-term variability of pCO_2 on the Scotian Shelf, NW Atlantic

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Abstract

The understanding of seasonal variability of carbon cycling on the Scotian Shelf, NW Atlantic Ocean, has improved in recent years, however, very little information is available regarding its short-term variability. In order to shed light on this aspect of carbon cycling on the Scotian Shelf we investigate the effects of Hurricane Arthur, which passed the region on July 5th 2014. The hurricane caused a substantial decline in the surface water partial pressure of CO_2 (pCO_2), even though the Scotian Shelf possesses CO_2 rich deep waters. High temporal resolution data of moored autonomous instruments demonstrate that there is a distinct layer of relatively cold water with low dissolved inorganic carbon (DIC) slightly above the thermocline, presumably due to a sustained population of phytoplankton. Strong storm-related wind mixing caused this cold intermediate layer with high phytoplankton biomass to be entrained into the surface mixed layer. At the surface, phytoplankton begin to grow more rapidly due to increased light. The combination of growth and mixing of low DIC water led to a short-term reduction in partial pressure of CO_2 until wind speeds relaxed and allowed for the restratification of the upper water column. These Hurricane-related processes caused a (net-) CO_2 uptake by the Scotian Shelf region that is comparable to the spring bloom, thus exerting a major impact on the annual CO_2 flux budget.

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1. Introduction

Coastal oceans constitute the interface of four compartments of the Earth system: land, ocean sediment and atmosphere. Relatively shallow waters in the coastal oceans facilitate the immediate interaction between the atmosphere and sediment (e.g. Thomas et al., 2009, Thomas and Borges, 2012). Coastal oceans receive runoff from land (Chen and Borges, 2009) and are impacted by the open oceans. They are a hot spot for biological production, accounting for a disproportionate amount of global ocean production relative to their surface area (Cai et al., 2003; Borges et al., 2005). Nutrients from rivers, the open ocean (e.g. Thomas et al., 2005), regenerated nutrients, and nutrients from shallow surface sediments fuel primary producers in coastal oceans. Consequently, coastal seas account for one-fifth to one-third of ocean primary production even though they only account for 8% of the ocean surface area (Walsh, 1991). Due to their dynamic nature, coastal oceans experience much higher spatial and temporal variability (diel, seasonal, and annual) than the open oceans.

The Scotian Shelf is a coastal ocean and these complex, multifactorial interactions result in challenges in determining the processes that control the high degree of variability reported in this region (Shadwick et al., 2010, 2011, Signorini et al., 2013, Shadwick and Thomas, 2014). Recent studies of the Scotian Shelf have focused primarily on monthly, seasonal, and inter-annual variability of carbon cycling (Shadwick et al., 2010, 2011, Shadwick and Thomas, 2014, Craig et al., 2015), but these longer-term trends are overlain by significant short-term variability (e.g. Vandemark et al., 2011, Thomas et al., 2012) that to date, have remained relatively unstudied. Storm activity on the Scotian Shelf has been shown to affect chlorophyll

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concentrations and timing of the phytoplankton bloom (e.g. Fuentes-Yaco et al., 2005, Greenan et al., 2004), but little is known regarding the role of short-term variability in governing carbon cycling on the Scotian Shelf. A deepened mechanistic understanding is required to reliably assess the role of short-term events on longer-term variability and to facilitate future predictions with respect to climate change and ocean acidification. In the present study, we utilize autonomous moored sensors, and in-situ sampling to investigate the short-term variability of the CO_2 on the Scotian Shelf, with a focus on the impact of Hurricane Arthur, which passed the Scotian Shelf region on July 5th, 2014.

2. Oceanographic Setting

The Scotian Shelf is located in the North West (NW) Atlantic Ocean at the boundary between the subtropical and subpolar gyres and extends from the Laurentian Channel to the Gulf of Maine (Figure 1). The primary feature on the Scotian Shelf is the Nova Scotia Current, which is mostly derived from the Gulf of St. Lawrence (Dever et al., 2016).

The Scotian Shelf can be described as a 2-layer system in the winter (Fig. 2, 3a,b), when convective activity and wind-driven mixing control the mixed layer depth (MLD) and prevent stratification of the surface layer. During this period, the MLD is at its deepest and temperature and salinity are homogeneously distributed within the mixed layer. Any deeper layers are beyond direct impact of seasonal processes. As the MLD shoals during spring and summer due to lower wind speeds, warmer surface temperature, and fresh water input (Urrego-Blanco and Sheng, 2012, Thomas et al., 2012), the Scotian Shelf transitions into a 3-layer system (Loder et al., 1997). The top layer of the 3-layer system in the summer is warm, shallow, and less saline; a result of the increased discharge from the St. Lawrence (Loder et al., 1997). Below the warm,

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shallow fresh layer is the cold intermediate layer (CIL); which consists of colder, saltier winter water. The third layer consists of the deeper waters below the winter MLD.

Sea surface temperature (SST) on the Scotian Shelf varies significantly over the course of the year, ranging from approximately 0°C during winter to as high as 20°C during the summer months (Figure 2i). Surface salinity (Fig. 2ii) in the shelf region is relatively fresh, ranging from around 30.5 during the winter to 29.5 during late summer when the peak discharge of the St. Lawrence River arrives (Loder et al., 1997, Shadwick et al., 2011, Dever et al., 2016). Salinity increases further off the shelf as a result of the warm salty water from the Gulf Stream, which transports water south of the Scotian Shelf towards Western Europe.

Nitrate on the shelf is heavily influenced by the growth and decay of phytoplankton (Figure 2). During the winter months when productivity is low and wind mixing is at its highest, nitrate levels at the surface are high. As vertical mixing decreases in the spring, phytoplankton begin to grow, quickly depleting the nitrate reservoir in the surface waters. This short but intense bloom heavily influences carbon cycling on the Scotian shelf. During this period the region shifts from being a source of CO_2 to the atmosphere to a sink because of the biological CO_2 drawdown (Shadwick et al., 2010, 2011). Chlorophyll a concentrations (Fig. 2d) demonstrate the intensity of the spring bloom during the months of March/April. The timing of the bloom varies between these two months depending on several factors including the onset of stratification (Shadwick et al., 2010, Greenan et al., 2004). Once the phytoplankton bloom consumes the available nitrate, the assemblage is taken over by smaller phytoplankton that prosper in the higher temperature, lower nutrient conditions (Craig et al., 2015; Li et al., 2006).

The subsurface chlorophyll maximum layer (SCML) is a feature almost ubiquitously found in stratified surface waters (Cullen, 2015). During the late spring and summer period, the surface layer on the Scotian Shelf, which is nutrient poor following the intense growth of the spring bloom, becomes strongly thermally stratified. The phytoplankton, therefore, accumulate in deeper waters where nutrient concentrations are sufficient to support growth, but where still enough light is present to drive photosynthesis (e.g. Cullen, 2015). This occurs at the nutricline, i.e. the transition from the warm, nutrient poor surface layer to the cooler, comparatively nutrient rich second layer. Additionally, in these lower light conditions, phytoplankton often employ the survival strategy of photoacclimation, whereby they increase their intracellular chlorophyll concentration to maximize light absorption. This can result in an increased ratio of chlorophyll to carbon (Chl:C ratio) at the SCML (Cullen, 2015). There is a suggestion of this summertime SCML in the climatological data from the region (Fig. 2iv) .

Observational studies reveal the Scotian Shelf to be a source of CO_2 to the atmosphere, except during the period of the spring bloom (Shadwick et al., 2010, 2011, see also Signorini et al., 2013 for discussion). Fluxes of CO_2 to the atmosphere are highly variable outside of the spring bloom period (Shadwick et al., 2010). Wind speeds impact the mixed layer depth, which in turn can impact CO_2 fluxes on the shelf (Shadwick et al., 2010, Greenan et al., 2008). As DIC increases with depth, mixing caused by strong wind events can entrain deeper, carbon-rich water. Shadwick et al. (2010, their Fig. 8) demonstrate how weather patterns can have a significant impact on monthly variation of CO_2 flux. The strength, timing and frequency of winter storms impact the timing of the spring bloom (Shadwick et al., 2010). Spectral analyses have shown that storm events occur at periods of 6 days and 3 weeks (Smith et al., 1978, Shadwick et al., 2010, Thomas et al., 2012).

A significant contributor to annual storm activity on the Scotian Shelf comes from hurricanes, with the 2003 hurricane season generating 14 named hurricanes in the Atlantic Ocean (Fuentes-Yaco et al., 2005). Hurricanes that affect the Western North Atlantic are formed mostly in the Eastern Atlantic Ocean near Africa (Fuentes-Yaco et al., 2005). After formation, the hurricanes move westward on the trade winds, veer northeast around 30° to 35°N as they meet the eastern prevailing winds from North America, and move towards, and often over, the Scotian Shelf and/or the Newfoundland Shelf (Fuentes-Yaco et al., 2005). Hurricanes passing through the northwest Atlantic can entrain cold nutrient rich water to the surface, which has been found to stimulate primary production (Fuentes-Yaco, 1997, Platt et al., 2005, Han et al., 2012). The timing of these storms has also been found to affect the timing and strength of the spring phytoplankton bloom (Greenan et al., 2004)

In this paper, we will focus on the effect of the passage of Hurricane Arthur on pCO_2 observed at our study site on the Scotian Shelf. We will consider pCO_2 conditions before, during, and after the storm's passage using highly temporally resolved measurements, and present mechanistic explanations for the observed phenomena.

3. Methods

3.1 Sampling Procedures

The CARIOCA buoy used in this study was equipped with sensors to acquire hourly measurements of temperature, conductivity, the partial pressure of CO_2 (pCO_2), salinity, sea surface temperature (SST), and chlorophyll-a fluorescence. An automated spectrophotometric technique was used to estimate pCO_2, and is fully described elsewhere (Bates et al., 2000;

Bakker et al., 2001; Bates et al., 2001; Hood and Merlivat, 2001). Conductivity and temperature were measured using a SeaBird conductivity sensor (SBE 41) and a Betatherm thermistor respectively. A WETstar fluorometer (WETLabs) measured chlorophyll-a (Chl-a) fluorescence. The buoy was deployed at the Halifax Line Station 2 (HL2; 44.3N, 63.3W, ~30km offshore from Halifax, Nova Scotia) from February 2014 to January 2015 in addition to other deployments that took place between 2007 and 2012 (e.g., Thomas et al., 2012)

From April 2007 to the end of July 2007, a SeaHorse moored vertical profiler was placed at the location of HL2, where it acquired profiles from the surface to a depth of approximately 100 m every 2 hours. It was equipped with temperature, salinity, and Chl-a fluorescence sensors. A complete description of the SeaHorse operation and sensor suite can be found in Greenan et al. (2008), or Craig et al. (2015).

Water column samples were collected through the semi-annual Atlantic Zone Monitoring Program (AZMP). The AZMP cruises occur during the Spring (April) and Fall (September – October) every year. Bi-weekly sampling of HL2 is also conducted whenever weather permits. Water samples are collected using 10 L Niskin bottles mounted on a 24-bottle rosette with a SeaBird CTD. Collected samples are then poisoned with mercury chloride ($HgCl_2$) to prevent biological activity before the pCO_2 concentration was measured using a VINDTA 3C system (Versatile Instrument for the Determination of Titration Alkalinity by Marianda). This was also used to determine alkalinity (TA) and DIC, and the measurement method is described in full detail by Johnson et al. (1993), Fransson et al. (2001), or Bates et al. (2005). Certified reference material was provided by G. Dickson (Scripps Institution of Oceanography) to determine the uncertainty of DIC and TA to ±2 and ±3 µmol kg^{-1}, respectively.

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Non-photochemical quenching (NPQ) in phytoplankton is a mechanism by which excess absorbed solar radiation can be dissipated in pathways other than Chl-a fluorescence (e.g., such as heat), and can reduce chl-a fluorescence by up to 80% (Kiefer, 1973). This was accounted for by using nighttime fluorescence from 0500UTC for analysis. 0500UTC was selected for all data analysis in order to minimize the impact of NPQ. Chl-a fluorescence was regressed against chl-a concentration determined with a fluorometer in the laboratory using *in situ* water samples; this enabled creation of a calibration curve for both the CARIOCA and SeaHorse data to allow comparison of measurements.

3.2 Computational Analysis

Temperature normalized pCO_2 was calculated using the equation from Takahashi et al. (2002) (Equation1).

$$pCO_2\left(T^{mean}\right) = pCO_2^{obs}\left[\exp\left(0.0423\left(T^{mean} - T^{obs}\right)\right)\right] \quad (1)$$

This normalization removes the thermodynamic effects of temperature on pCO_2 and reveals the non-temperature related, i.e., largely biological effects on pCO_2. The mean temperature used for this calculation is 10°C.

Using the method developed by Friis et al. (2003), DIC is normalized to salinity to remove the overlying salinity signal to better determine biological and anthropogenic impacts. DIC^S represents DIC normalized to salinity, S^{obs} represents the measured salinity value, DIC^{obs} represents the measured DIC value, S^{ref} represents the salinity standard used to calculate DIC_s, which in this case is 32, and $DIC^{S=0}$ represents the non-zero freshwater end member, which is 601 µmol DIC kg^{-1} taken from Shadwick et al. (2011).

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$$DIC^{S} = \frac{DIC^{obs} - DIC^{S=0}}{S^{obs}} * S^{ref} - DIC^{S=0} \quad (2)$$

Sea-air fluxes from the CARIOCA dataset were calculated using the flux calculation functions from Wanninkhof (2014) (Equation 3).

$$F = -0.251 * U^{2} * \left(\frac{Sc}{660}\right)^{-0.5} * K_{0} * \left(pCO_2^{Obs} - pCO_2^{Atm}\right) \quad (3)$$

Where F is in mol m^{-2} s^{-1}, U is wind speed (m s^{-1}), Sc is the Schmidt number, K_0 is gas solubility (mol L^{-1} atm^{-1}), pCO_2^{Obs} (µatm) is observed pCO_2, and pCO_2^{Atm} (µatm) is atmospheric pCO_2, for which 400 µatm is used. The widely used flux calculations from Wanninkhof (2014) were used, and have an estimated 20% level of uncertainty. Full details regarding the flux equation can be found in Wanninkhof (2014).

A spectral analysis was performed using the Fast Fourier Transform method on pCO_2. The frequency range encompassing a 6-day period is plotted to match storm frequencies found in previous work. The spectral analysis was performed to determine the frequency of storm events on the Scotian Shelf.

3.3 Comparison CARIOCA / SeaHorse

For mechanistic analysis, we use the SeaHorse vertical profiler from 2007 to help underpin the observations made from the 2014 CARIOCA dataset. Chl-a concentration determined in the laboratory using fluorometric analysis of *in situ* water samples were regressed against factory calibrated nighttime fluorescence from the CARIOCA and SeaHorse data sets. r^2 (RMSE) values were found to be 0.532 (0.2 mg m^{-3}) and 0.743 (0.4 mg m^{-3}) for the CARIOCA and SeaHorse, respectively. The poor agreement between the bottle and fluorescence Chl-a

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estimates is unsurprising since factory conversions of fluorescence to chlorophyll concentration rarely correspond well. This is due to several factors that include differences in fluorescence yield between the factory calibration standard and natural phytoplankton, differences in the water mass sampled (small volume illuminated by the fluorometers versus the larger water mass sampled by the Niskin bottle) and the fact that both estimates are subject to significant uncertainties. For these reasons, fluorescence estimates of Chl-a will be used in a qualitative manner to examine patterns and trends, rather than to determine exact concentrations.

A subset of the CARIOCA data collected from June 9th-17th (year days 160-168) 2007 are used to compare with the Seahorse data (Figure 4). The fluorescence for both data sets were converted to chlorophyll using the calibrations curves described above. Both sets show chlorophyll of similar magnitude, as well as a similar trend over the time series.

4. Results & Discussion

4.1 Observations of pCO_2, wind speed and fluorescence in 2014

Annual pCO_2 data from the 2014 CARIOCA dataset reveals that there is significant variability over the course of 2014 (Figure 5a). Although impacted by the variability, the key annual features are obvious and include: the phytoplankton bloom (year days 80-110), a summer baseline (year days 150-300), and a winter baseline (year days 50-75 and 300-365). The variability (or amplitude of variability) in pCO_2 is more pronounced during the summer months compared to the winter and spring bloom periods (see also Thomas et al., 2012). The low variability during the winter and the bloom is likely a result of the deeper, homogenous surface mixed layer, which in turn acts as a buffer for any short-term variability. A spectral analysis of pCO_2 reveals a 5.8 day period (= 1/f ⁄ 24; Fig. 6). This is in agreement with results from Smith et

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al. (1978), Shadwick et al. (2010), and Thomas et al. (2012) who found storm periods of around 6 days.

Wind speeds for 2014 (Figure 5b) show that during the winter, winds are stronger on the Scotian Shelf, with higher storm frequency, while wind speeds are generally lower during the spring and summer months. During the period of Hurricane Arthur wind speeds of up to 30 m s^{-1} were observed.

Fluorescence over the year (Figure 5c) clearly shows the spring bloom increase of up to a factor of 4 above the winter baseline. Similarly, during Hurricane Arthur, there is a doubling in fluorescence above the summer baseline values compared to the surrounding days. Later in the year, around year day 300, the fluorescence shows somewhat elevated values due to the minor fall bloom that occurs as increased wind speeds begin to deepen the mixed layer bringing nutrients to the surface (Greenan et al., 2004).

4.2 Hurricane Arthur

A prevalent feature of the time series is the sharp decrease in pCO_2 as wind speeds increase during the hurricane (Figure 5, days 180-200). Dissolved inorganic carbon increases with depth in this region (Shadwick et al. 2014), therefore it is expected that increased wind speed would increase pCO_2 as more carbon rich water is brought to the surface. However, wind and pCO_2 are negatively correlated (r =-0.77, not shown), with a significance level of 0.05, for the whole year. Decreases in pCO_2 with increases in wind are most evident from spring to early fall. This coincides with the period where the water column becomes a 3-layer system as a result of solar insolation and increased discharge from the Gulf of St Lawrence (Loder et al. 1997). For this study, we chose the most prominent decrease in pCO_2, which occurred during Hurricane

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Arthur on July 5th. The underlying assumption is that Hurricane Arthur can be compared to other periods where low pCO_2 is the result of high wind events within the spring to early fall period.

To identify the cause of the decrease in pCO_2 when wind speeds are high, surface water properties observed during the Hurricane Arthur period are examined in detail (Figure 7). SST drops by roughly 6 °C over a half day period. This indicates that water from the cold intermediate layer (CIL) was mixed into the surface by strong winds, causing rapid cooling. pCO_2 begins to decline before temperature, indicating that lower pCO_2 waters must lie above the thermocline, as water temperature changes after pCO_2 (Figure 7). Shadwick et al. (2014) have shown that DIC increases with depth, therefore for pCO_2 to decrease before temperature would indicate a mass of relatively low carbon containing water within the CIL, i.e., just underneath the upper part of the surface layer.

Normalizing the DIC observations from HL2 to a constant salinity (of 32) reveals the biological DIC fingerprint (Figure 8b). This approach yields a minimum in DIC in the subsurface layer at a depth of approximately 20-25 m, which indicates DIC uptake by phytoplankton. Further support for the existence of this enclosed layer is provided by a study by Shadwick et al. (2011), in which negative apparent oxygen utilization (AOU) values at this depth level were observed during the summer period. The enclosed layer is both sufficiently shallow for photosynthesis to occur and sufficiently deep to supply the required nutrients through vertical diffusion across the nutricline (Figure 2). When comparing the temperature minimum and salinity maximum from Figure 7 with the T/S profile of Figure 8, they reveal a deepening of the mixed layer to around 25 m, which matches well with the DIC profiles. Figure 8 also shows that the density steadily increases with depth, and that the DIC minimum lies below the upper part of the mixed layer in a stable layer between waters of lower (above) and higher (below) density.

To shed light on processes occurring within the CIL, we employ high-resolution water column data at HL2 collected from the 2007 SeaHorse vertical profiler. Although the Seahorse data was collected during a different year, we assume that the observed features are present every year as characteristics of the overall system. The data from the SeaHorse profiler reveal a variable but persistent chlorophyll-a maximum below the surface post-spring into summer (Figure 9). This persistent chlorophyll-a maximum occurs at roughly 25 m below the surface. This matches well with the profiles in Figure 8 that display normalized DIC minima at roughly the same depth.

When the temperature signal is removed by calculating $pCO_2(T_{mean})$, there is a drop in pCO_2 before temperature begins to decline, indicating a non-temperature related impact on pCO_2 (Figure 7). This line of argument is supported by the DIC minimum (Fig. 8) and the persistent chlorophyll-a layer below the surface (Fig. 9). As time progresses after the drop in $pCO_2(T_{mean})$, $pCO_2(T_{mean})$ begins to increase again while temperature remains constant. This is the result of continued mixing pushing further into deeper DIC-rich water. When this DIC-rich water is brought to the surface it results in an increased pCO_2. The disconnect between temperature and pCO_2 can be explained by considering the position of the subsurface chlorophyll maximum layer. This layer straddles the thermocline, where phytoplankton can utilize nutrients diffusing across the boundary, but still receive enough light for photosynthesis. As the upper layer is mixed by wind, these phytoplankton are mixed to the surface where they experience increased light exposure (compared with that at the SCML) that allows them to photosynthesize more efficiently and, therefore, draw down more CO_2. Following this initial mixing of the surface layer, mixing energy then becomes sufficient to entrain waters from the deeper CIL, resulting in a rise in pCO2 and a decrease in temperature (Fig. 7).

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A snapshot of SeaHorse profiles from June 9-17th 2007 were extracted and compared to data from the CARIOCA buoy during the same period (Figure 4, see methods). As with Hurricane Arthur, a passing storm (of weaker strength) during this period shows the same negative correlation between pCO_2 and wind speed. pCO_2 decreases for a period of time as wind speeds increase. There is also an increase in chlorophyll-a for both the CARIOCA and SeaHorse data (Figure 4).

The selected 3 days shown in Figure 10 reveal the evolution of the water column during the 2007 storm event. Before the storm there is a sub-surface chlorophyll maximum, which is below the maximum of the density gradient. The Brunt-Väisälä frequency (Fig. 10) also shows stable stratification at roughly 18 m depth on June 9th, followed by stable stratification at 38 m for June 15th, and on June 17th, stratification stabilizes further up the water column at 25m. Once the storm approaches the water column becomes mixed, increasing surface salinity and chlorophyll-a as well as homogenizing water density for the top 40 m. In this example however, temperature does not decrease at the surface as in Figure 7. However, Hurricane Arthur was a much stronger storm that resulted in deeper mixing of the water column and more cooling of the SST. When the storm subsides, the water column restores within 2 days to its original state. Surface chlorophyll and salinity return roughly to their pre-storm levels, and the SCML is again below the density gradient.

Fluorescence during the hurricane doubles, indicating that the mixed conditions of the water column favor phytoplankton growth (Figure 7). Nutrients at the surface are depleted during the summer months (Figure 2) and, therefore, the response of the phytoplankton implies that the hurricane mixed nutrients upward from deeper in the water column; similar to the storm observed in 2007 (Figures 4 and 10). This line of argument is also supported by the observed

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salinity increase. Mixing at the surface breaks through the fresh water layer at the surface, reaching into the deeper saline waters of the CIL; where nitrate is more abundant.

Also of note is the fast rate at which fluorescence increases. As discussed by Cullen (2015) the SCML contains a higher ratio of chlorophyll-a to carbon as a result of survival strategy in reduced light, therefore it can be speculated that the rapid increase of fluorescence could be the result of redistributed cells rather than new production. Integrating salinity over a depth of 50 m for June 9th and June 15th in Figure 10 yields a constant salinity inventory of 1474 m and 1482 m, respectively [unit {m}: salinity{unitless} * integration depth{m}]. On the assumption that mixing is conservative, integration of chlorophyll-a for June 9th and June 15th is also performed. The results were 105 mgChl m^{-2} and 158 mgChl m^{-2} respectively, indicating that the majority of chlorophyll a (approximately 2/3) observed at the surface is redistributed over the 5 day period the integration took place. The growth of the remaining 53 mgChl m^{-2} (approximately 1/3) can be attributed to rapid phytoplankton growth that would be expected to take place as a result of nutrients being mixed to the lit surface layer. This helps explain the rapid increase in fluorescence observed in Figure 6 as most of the increase is due to redistributed phytoplankton from the SCML.

Figure 7 also illustrates the breaking of the enclosed layer in the water column. Between year days 186 and 187 (Figure 7d, grey box), salinity increases in two separate steps. The first step coincides with the sharp decline in $pCO_2(T_{mean})$, indicating the mixing of the phytoplankton-rich enclosed layer to the surface. The second step aligns with the subsequent increase in $pCO_2(T_{mean})$ pointing to continued vertical mixing into deeper saline waters rich in DIC from the CIL. When compared to the wind speeds of Figure 7 in panel c, the second step also occurs during the wind speed maximum, when mixing would be at its strongest. When looking at the 3

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layers in Figure 2 during the summer (dark blue, blue and yellow layers), there is one salinity unit difference between them. The magnitude of salinity change during Hurricane Arthur is comparable.

4.3 Impact of Hurricane Arthur on Carbon Cycling

In order to quantitatively estimate the direct impact Hurricane Arthur had on carbon cycling, air-sea fluxes were calculated for 2014 (Table 1). The average daily flux for July was 0 mmolC m^{-2} day^{-1}, however when the impact of Hurricane Arthur is removed from the average the new flux value is -7 mmolC m^{-2} day^{-1}. If Hurricane Arthur was averaged alone, the flux would be 19 mmolC m^{-2} day^{-1}, nearly half the rate of the phytoplankton bloom (45 mmolC m^{-2} day^{-1}). The impact of the hurricane was substantial enough to cancel out the overall emission of CO_2 to the atmosphere for the month of July. This indicates that short-term storm events can have a significant impact on annual pCO_2 cycling for the Scotian Shelf in the regions affected by the storm.

5. Conclusions

From the analysis performed in this study a schematic of the water column structure has been developed (Fig. 11, see also Fig. 3). During the winter and early spring the top layer of the 2-layer system contains fresh cold water. During this period, the phytoplankton bloom occurs and the mixed layer depth (MLD) begins to shoal rapidly. Once summer is reached, and the outflow from the St. Lawrence is at its peak, the third surface layer forms, which consists of warm fresh water. Below that layer is the cold intermediate layer (CIL), which contains cooler and saltier water. In between the surface layer and the CIL is the temporary sub-surface

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chlorophyll maximum layer (SCML), a result of the strong density gradient between the layers (Fig. 10).

The data provides compelling evidence that there is an interaction between wind speed, pCO_2, and sub-surface phytoplankton. However, the timing of a storm event dictates the strength of its impact. Previous work has shown that deeper water is rich in DIC compared to the surface, and it was expected that mixing of deeper water should increase pCO_2 as a result. However, sub-surface phytoplankton has a relatively strong influence on carbon cycling during storm events. The effects of storms on pCO_2 vary based on whether the water column is a 2- or 3-layer system, and their timing during these 2- and 3-layer periods. Hurricane Arthur was a special case in that it impacted the shelf while it was in its a 3-layer phase. During this time, the entrained layer was stable as a result of the warm freshwater cap at the surface (Figure 11). This allowed phytoplankton to thrive at the boundary of the surface layer and the CIL, where there are more nutrients than in the upper mixed layer, but still enough light to drive photosynthesis. When the storm arrived and perturbed this enclosed layer, it caused a sharp decrease in pCO_2. It is anticipated that these findings will contribute to the general body of knowledge of how storms and their associated timing impact carbon cycling on the Scotian Shelf.

The study presented in this work largely rests on data from moored autonomous instruments such as the CARIOCA buoy, which supply observational data with high temporal coverage. The complementing use of SeaHorse data has expanded the observations into the vertical dimension, which facilitates the consideration of water column properties and their influence on the surface water CO_2 variability. In observational studies, a balance must always be found between temporal and spatial coverage, as for example discussed by Schiettecatte et al., (2007). It is clear that the use of data from moored instruments provides the high temporal resolution data needed to understand high-frequency variability. This strength of this study is at the expense of spatial coverage, and accordingly, we cannot fully exclude lateral processes, which might contribute to the variability of the CO_2 system as observed by our instruments.

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Figure Captions

Fig. 1: Regional view of the Scotian Shelf with primary currents shown. The red star depicts the location of the Seahorse and Carioca moorings. Reprinted with permission from Shadwick et al. (2010) ©Shadwick et al. 2010

Fig. 2: Climatologies for the Scotian Shelf. i) Temperature, ii) salinity, iii) nitrate, and iv) Chl-a. Reprinted with permission from Shadwick et al. (2011). © Elsevier

Fig. 3: Schematic demonstrating the evolution of the water column over the course of the year. The dashed line intersecting panels i), ii), and iii) represents the mixed layer. SCML in green represents the sub-surface chlorophyll maximum layer. Wind mixing is represented by the circular arrow in panels i), ii), and iii). Temperature and Salinity profiles provide an idealized view of the upper water column where panel a) corresponds to panel i), b) to ii), and c) to iii). The solid lines in panels a), b), and c) represent the location of the borders between the layers in their corresponding i), ii), and iii) panels.

Fig. 4: 2007 CARIOCA data set for June 9th-17th from the with the x-axis representing year days. The black line is pCO_2 (µatm), red line is wind (m s^{-1}), blue line solid is calibrated CARIOCA fluorescence (mg m^{-3}), and the blue dashed line is calibrated SeaHorse fluorescence (mg m^{-3}).

Fig. 5: 2014 time series data collected from the CARIOCA buoy with the x axis representing year day. Panel a shows pCO_2 in µatm, revealing a large amount of variation over the course of the year; with a minimum during the spring bloom and a high maximum over the course of the summer. Panel b shows wind speeds in m s^{-1}, with higher wind speeds during the winter period and lower speeds during the summer. Panel c shows fluorescence in arbitrary units with a spring broom clearly visible, and the rest of the year with generally low values. There is some evidence at a prolonged fall bloom after year day 300. The red bands represent the period where Hurricane Arthur (July 5th 2014) took place, and was selected as this feature stands out amongst the others.

Fig. 6: Spectral analysis of pCO2 from the CARIOCA buoy. Frequency is 1/h where h is hours, and power is in arbitrary units. The red bars represent the frequency range encompassing the 6-day period.

Fig. 7: Climatologies for Hurricane Arthur taken from the CARIOCA 2014 dataset, with the x axis representing year days. Each panel has pCO2 in black (µatm) and pCO2(Tmean) (µatm) in blue; with a different variable in each panel overlain: (a) temperature, (b) wind speed, (c) flourescence, and (d) salinity. The grey box in panel d is used to highlight the change in salinity.

Fig. 8: Vertical profiles taken from in-situ samples for HL2. a) salinity, and temperature (°C), and density (kg m^{-3}) were collected on June 28th, 7 days before Hurricane Arthur. b) DIC (µmol kg^{-1})

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depth (m) profile for July 22 and August 3, 2014 collected at HL2 along with their corresponding profiles normalized to a single salinity value of 32.

Fig. 9: SeaHorse vertical time series data collected at HL2. Fluorescence data is in mg m-3 and calibrated to in situ bottle data collected at HL2. White gap represents when the mooring was removed from the water for repairs. The black line represents the mixed layer depth in meters. The red line is a DIC profile from Figure 11, with its scale at the top right of the figure. Please note that the DIC profile is collected from the 2014 year, while the SeaHorse data is from 2007. This comparison is made to help underpin the mechanistic understanding of the water column structure.

Fig. 10: SeaHorse snapshots of a storm event between June 9th to June 17th 2007. X-axis contains chlorophyll (mg m^{-3}), salinity, temperature (°C) and density (kg m^{-3}); and y-axis is depth in metres. Wind speeds (m s^{-1}) for each day (5:00am to correspond with time of SeaHorse data) are included in each panel. Fluorescence values are calibrated to in-situ bottle data collected at HL2. The right hand side panels show the Brunt-Väisälä frequency for the respective days.

Fig. 11: Schematic demonstrating the process of how storms alter the water column structure. Phytoplankton near the interface between layer 1 and 2 are brought to the surface through wind induced mixing. Once near the surface the increased light allows them to grow rapidly, using the nutrients that are also brought to the surface. If the storm is strong enough or persists for a while the third layer is also breached. This bring up the higher DIC waters, raising pCO_2, as expected prior to this study.

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545 Table 1: Average daily sea-air fluxes (mmol $m^{-2}day^{-1}$) for each month available for the 2014 year using the Wanninkhof 2014 method. July is broken into 3 components: the month as a whole, the 8 days Hurricane Arthur impacted pCO_2, and the remaining 22 days averaged without hurricane Arthur. pCO2 (µatm), wind speed (m s^{-1}), temperature (°C), and salinity are averaged for each month (or segment in the case of Arthur and No Arthur).

Month	CO_2 Flux (mmol m^{-2} day^{-1})	pCO_2 (µatm)	Wind Speed (m s^{-1})	Temperature (°C)	Salinity
March	18	374	14.9	0.1	30.9
April	45	316	14.5	1.2	31.2
May	2	395	9.0	4.5	31.2
June	-3	430	9.1	9.9	30.9
July	0	423	12.2	12.6	31.1
Arthur	19	385	14.9	9.7	31.2
No Arthur	-7	436	11.2	13.6	31.0
August	-27	506	10.8	18.7	30.8
September	-30	481	13.4	17.8	30.8
October	-5	409	17.3	15.0	30.9
November	4	405	17.5	10.3	30.5
December	-8	413	16.3	5.5	30.5

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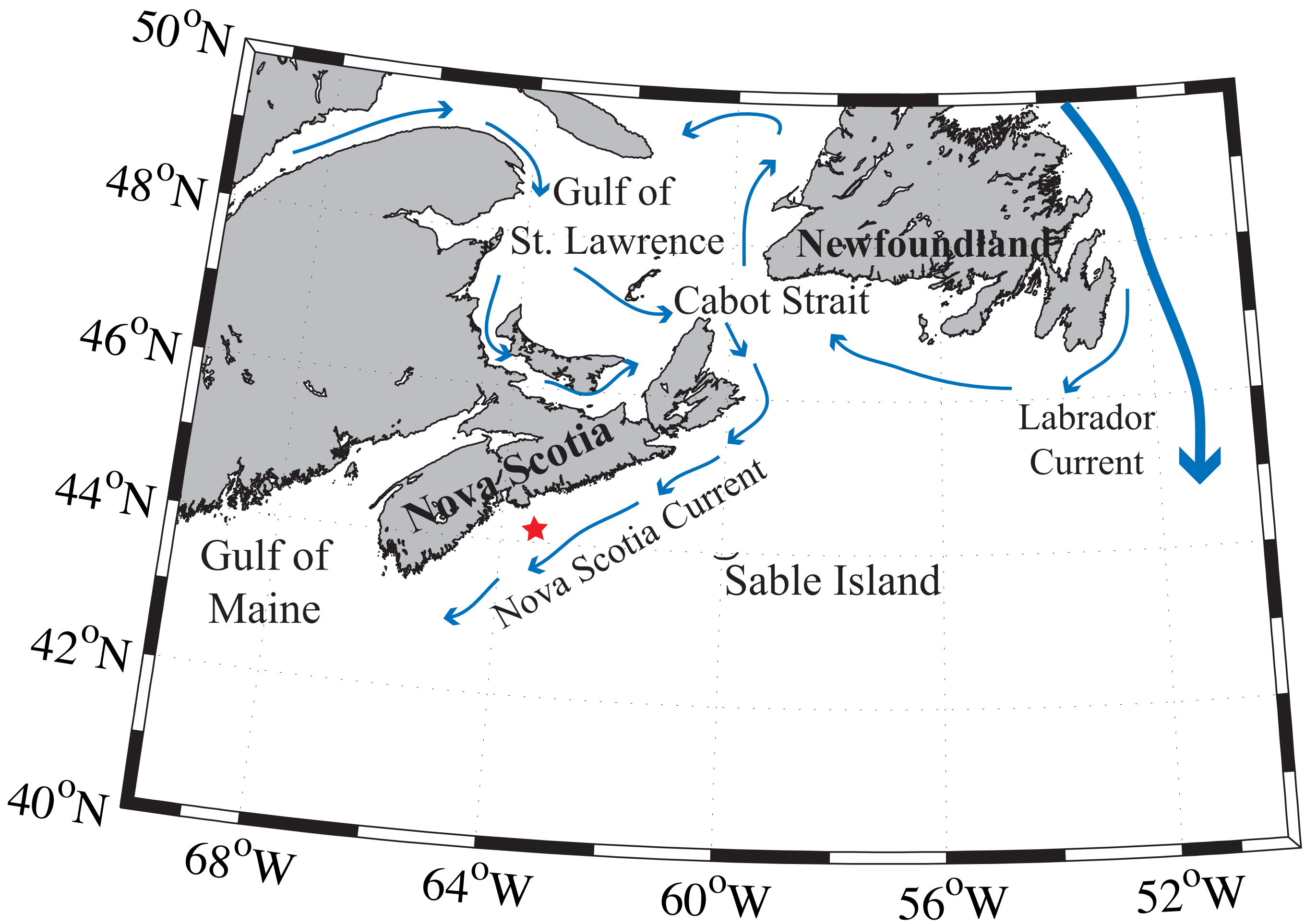

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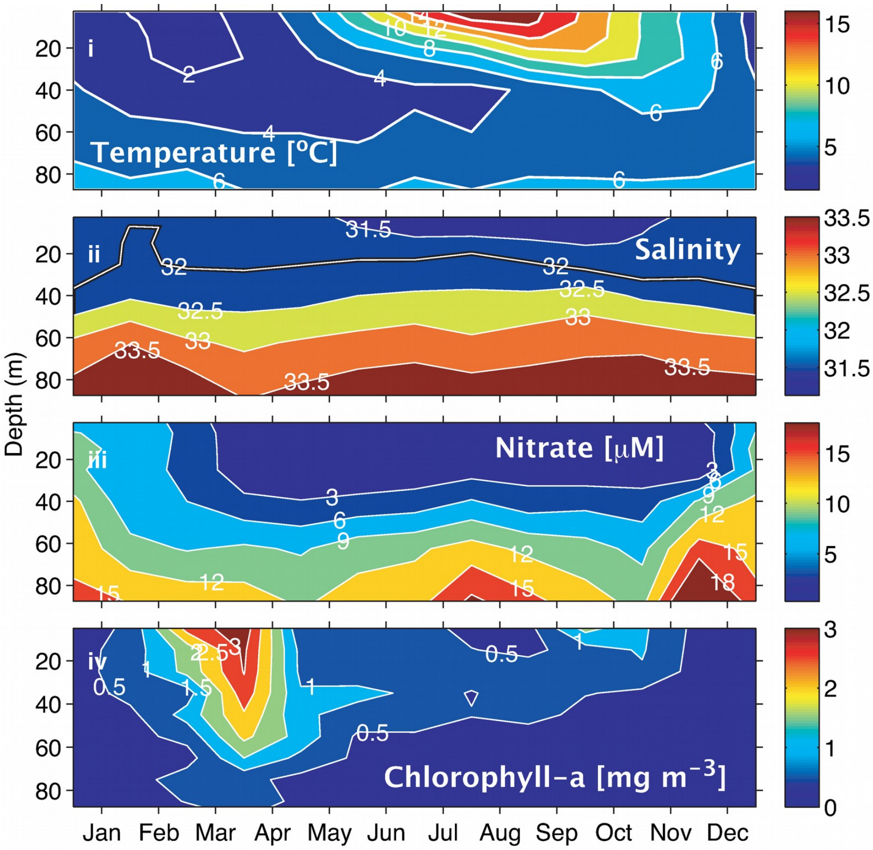

Lemay et al., Figure 2

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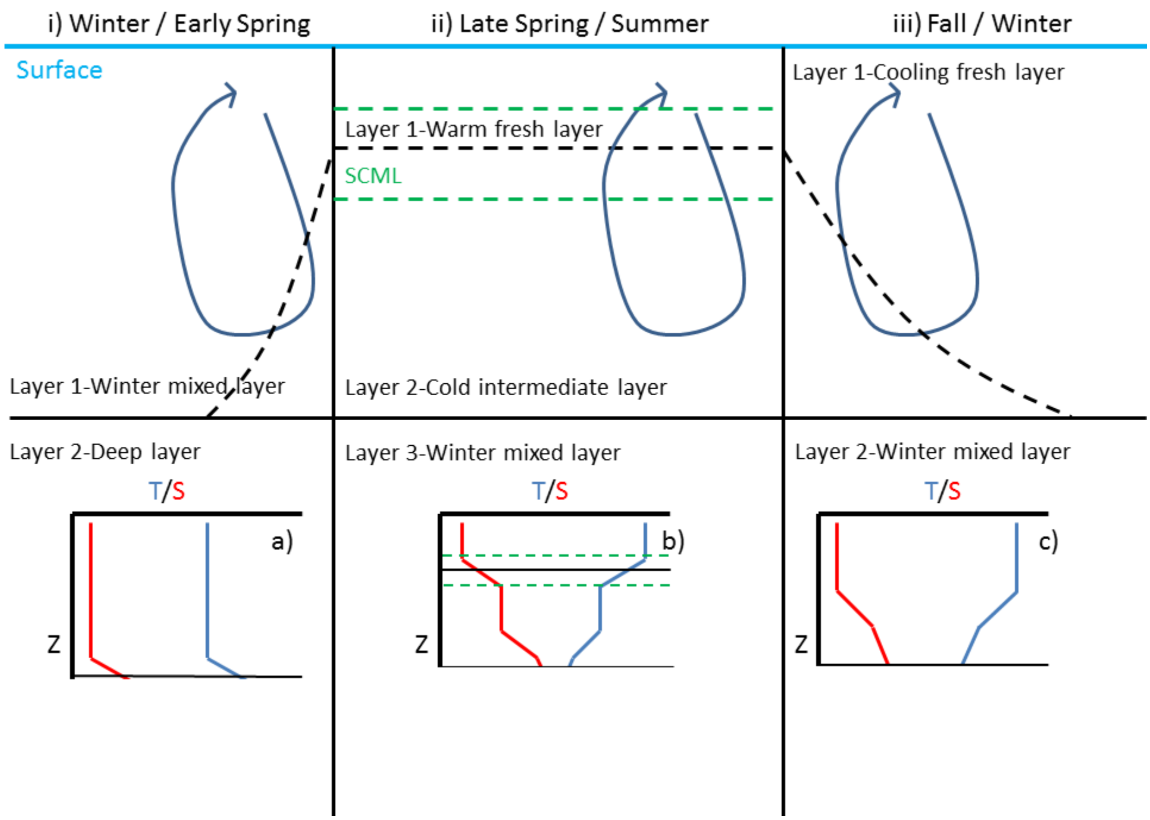

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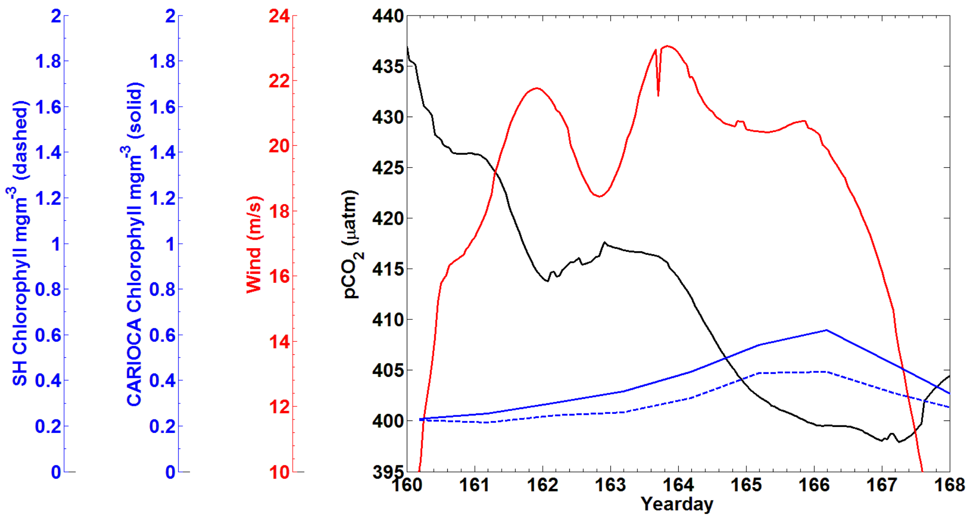

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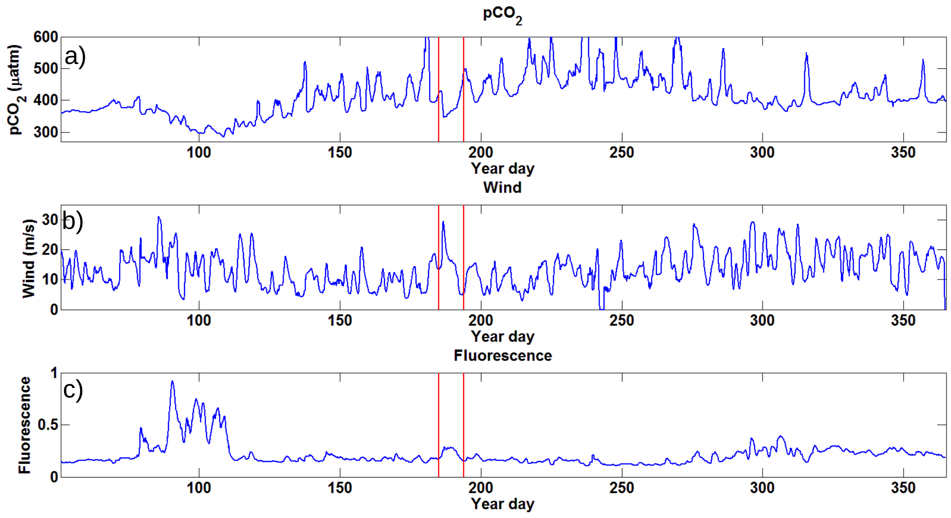

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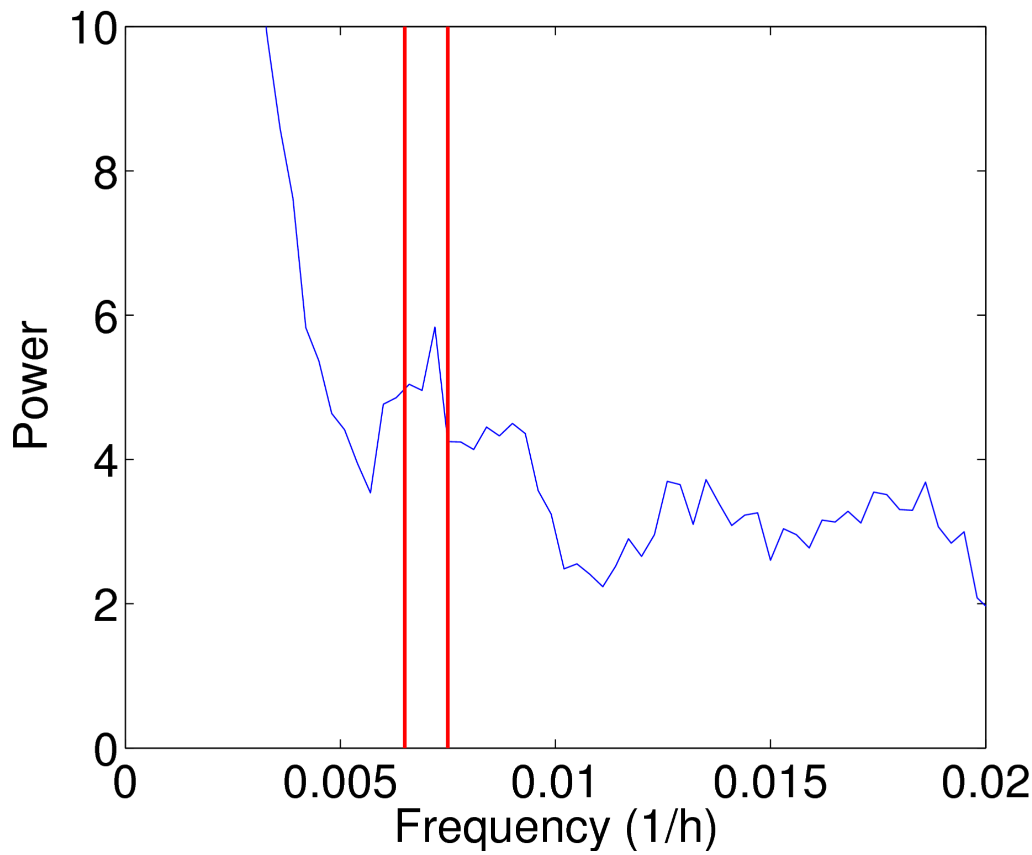

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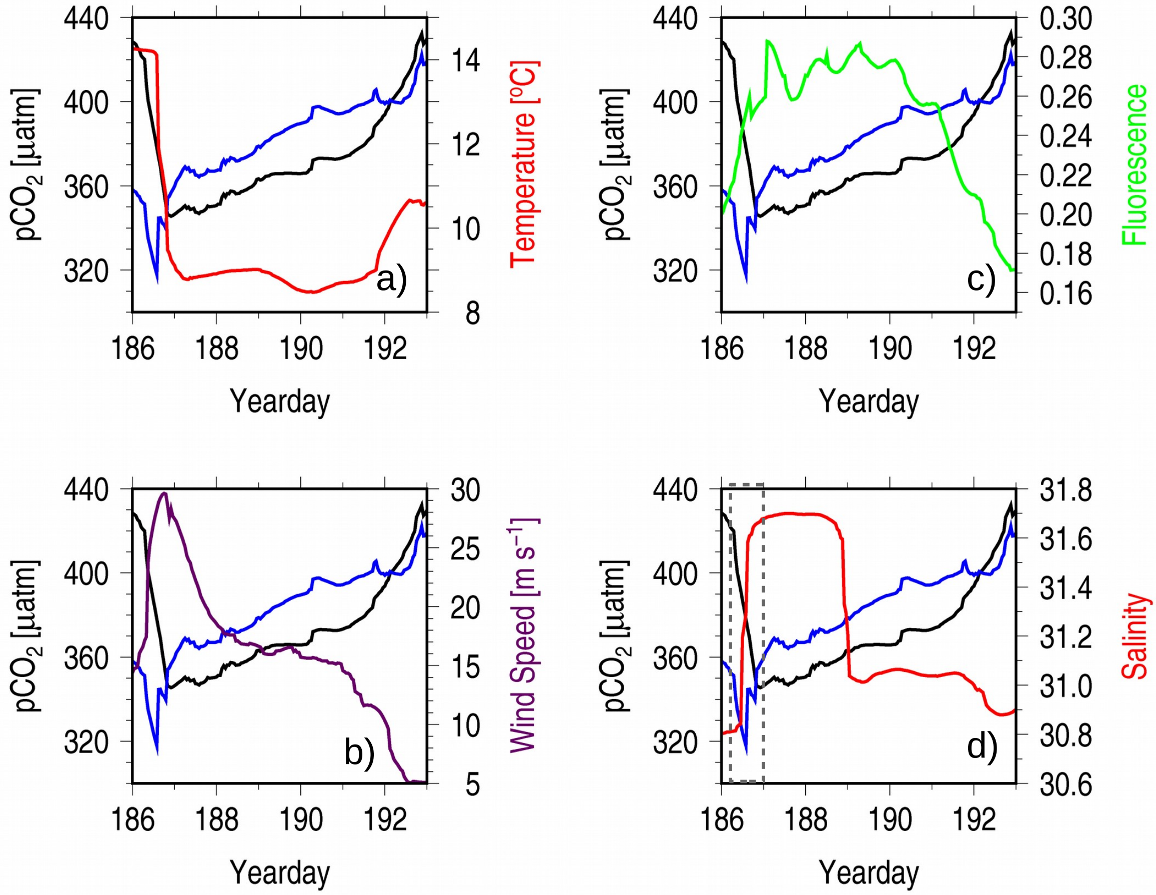

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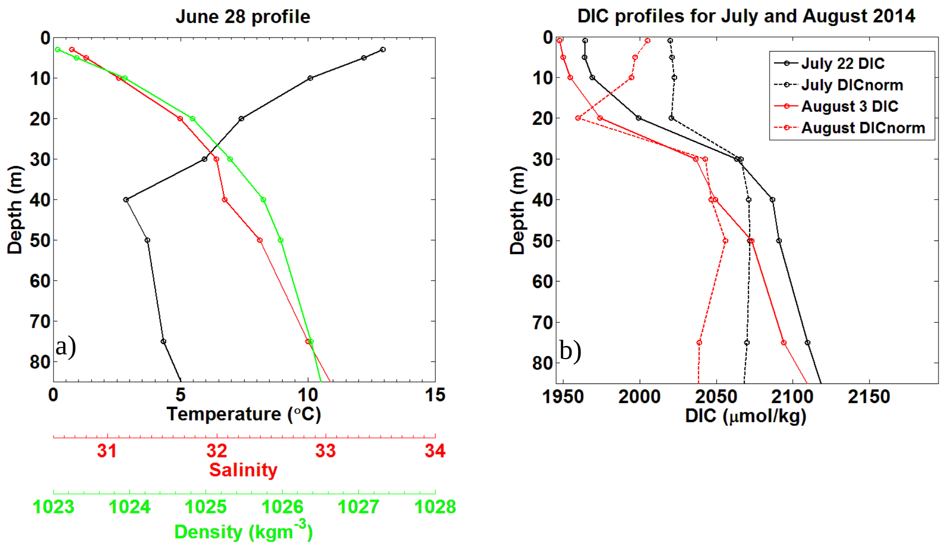

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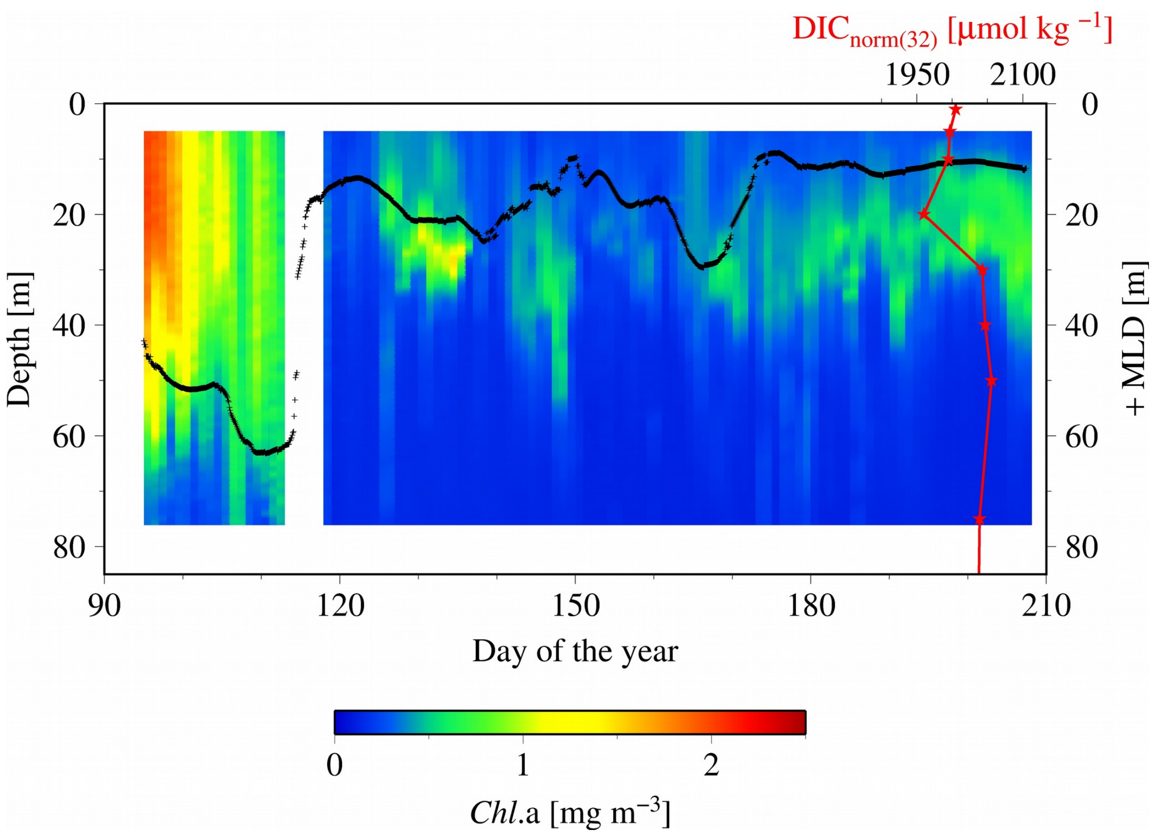

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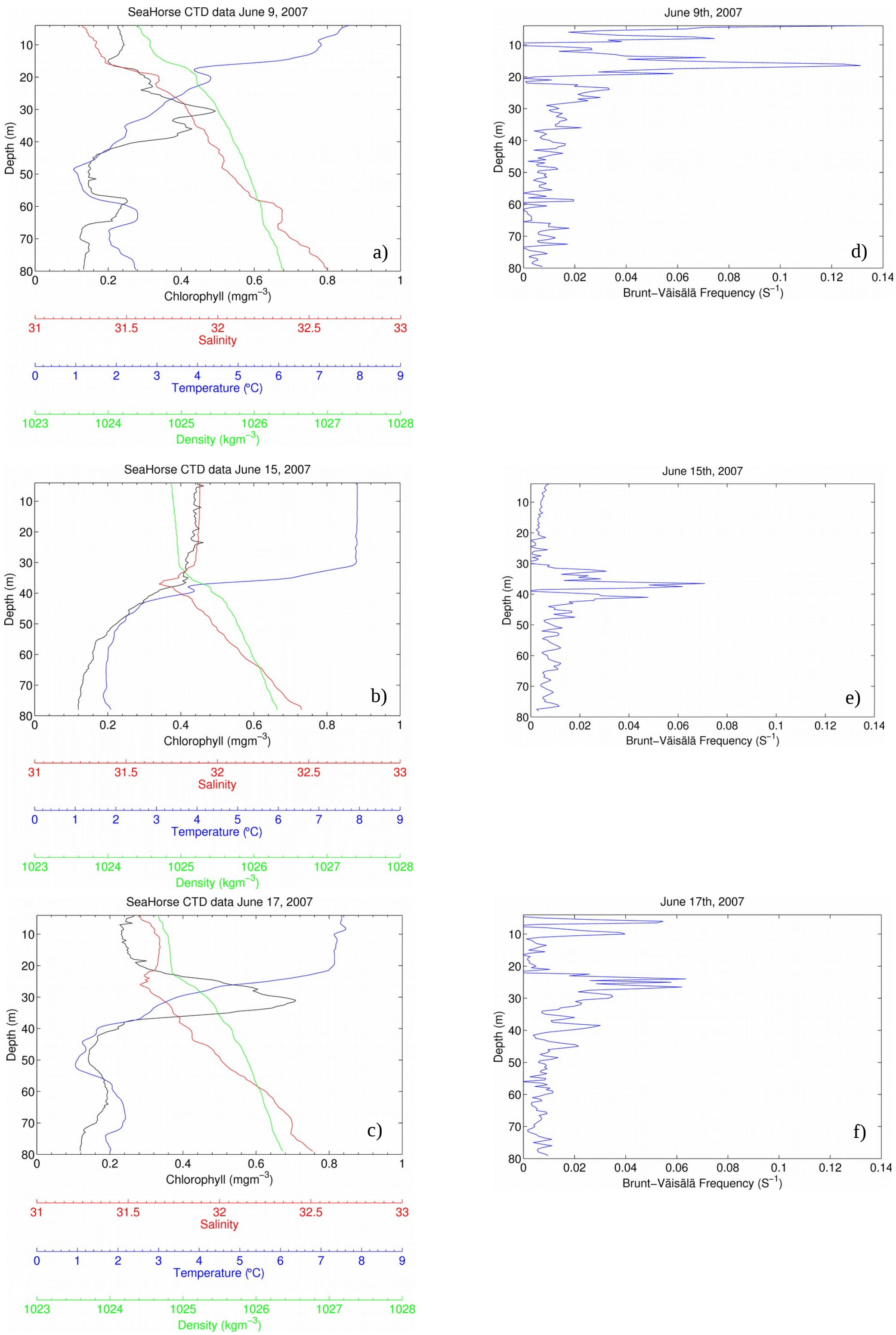

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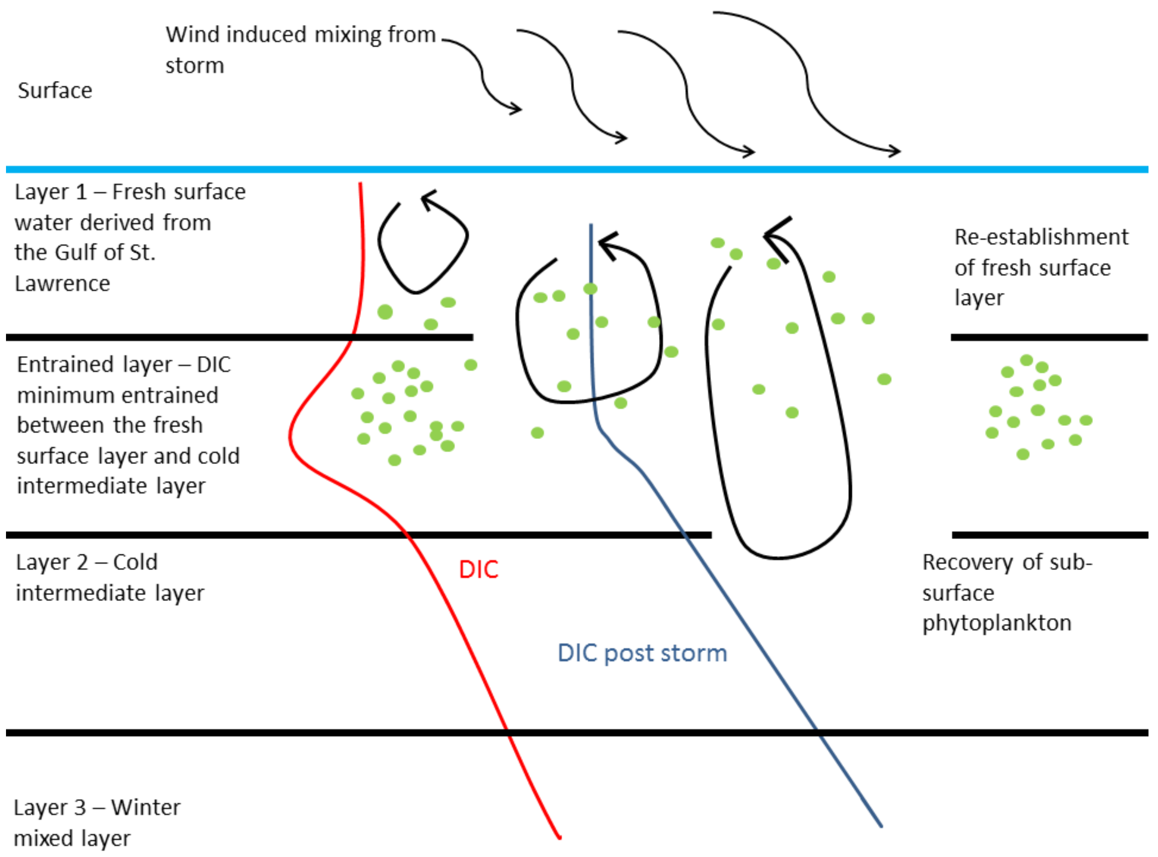

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