

This discussion paper is/has been under review for the journal Biogeosciences (BG).
Please refer to the corresponding final paper in BG if available.

**The carbonate
system on the
Scotian Shelf**

E. H. Shadwick et al.

Spatio-temporal variability of the CO₂ system on the Scotian Shelf

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Received: 14 November 2011 – Accepted: 21 November 2011

– Published: 14 December 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Relative to their surface areas, coastal oceans and continental shelves host a disproportionately large fraction of ocean productivity. The Scotian Shelf is a biologically productive coastal region of the Northwestern Atlantic Ocean. This subpolar region is influenced by the outflow of the St. Lawrence Estuary system and acts as an annual source for atmospheric CO₂. As part of the Atlantic Zone Monitoring Program, dissolved inorganic carbon (DIC), total alkalinity, and surface CO₂ partial pressure measurements were made throughout the Scotian Shelf in 2007. A shelf-wide assessment of the spatio-temporal variability of the inorganic carbon system was made relying on observations in April and September. Between these periods, biological production results in a significant drawdown of inorganic nutrients and DIC in the surface mixed-layer, while hydrographic controls also influence seasonal changes in DIC. Net community production (NCP) over the spring and summer seasons was estimated on the basis of inorganic carbon data. We find significant spatial variability in NCP with the largest values in the Southwestern Browns Bank region and a general trend of increasing NCP with distance offshore. A bulk seasonal carbon budget suggests that along-shore and cross-shelf transport may result in the export of subsurface DIC from this region.

1 Introduction

Coastal oceans and continental shelves play an important role in the biogeochemical cycling of carbon. Coastal regions are supplied with carbon and nutrients from riverine and atmospheric input, and upwelling and entrainment; these regions sustain disproportionately high biological activity given their surface areas relative to the open ocean (e.g., Gattuso et al., 1998; Borges et al., 2005; Thomas et al., 2005; Shadwick and Thomas, 2011). The role of the global coastal ocean in the uptake of atmospheric CO₂ has long been under debate (Smith and Mackenzie, 1987; Smith and Hollibaugh, 1993;

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Cai et al., 2003; Borges et al., 2005; Cai et al., 2006). A recent synthesis of available observational data from numerous coastal regions suggests that, at the global scale, continental shelves are sinks for atmospheric CO₂ (Chen and Borges, 2009). Chen and Borges (2009) further suggest that, in general, temperate to subpolar continental shelf systems are undersaturated with respect to atmospheric CO₂ at the annual scale, and therefore act as CO₂ sinks. This has been confirmed in the (high latitude) Baltic (Thomas and Schneider, 1999) and North (Thomas et al., 2004) Seas. This situation has also been observed in the South (Jiang et al., 2008) and Middle Atlantic Bights (Boehme et al., 1998; DeGrandpre et al., 2002). In contrast to these systems, the nearby Gulf of Maine (Vandemark et al., 2010) and Scotian Shelf (Shadwick et al., 2010, 2011), two temperate continental shelf systems, have recently been characterised as sources of atmospheric CO₂ at the annual scale.

Uptake of atmospheric CO₂ on the Scotian Shelf occurs only briefly during and following the spring phytoplankton bloom. This bloom, which occurs at the annual minimum water temperature, is closely followed by a period of surface water warming. Although biological production continues through the summer months, this *p*CO₂ decrease is out-weighted by the thermodynamic increase in *p*CO₂ due to warming (Shadwick et al., 2011). In the autumn and winter seasons, a combination of wind-driven and convective mixing as well as episodic upwelling events, deepen the mixed-layer and facilitate the intrusion of carbon-rich subsurface waters to the surface layer. The region acts as a source of atmospheric CO₂ until the onset of the spring bloom in the following productive season as a result of this water column destratification (Shadwick et al., 2011).

The continental shelf pump mechanism (Tsunogai et al., 1999), which has the potential to transport dissolved carbon off the continental shelf into the adjacent deep ocean, is not thought to operate on the Scotian Shelf according to a recent modelling study (Fennel and Wilkin, 2009). Fennel and Wilkin (2009) suggest that vertical export of organic matter is insufficient for carbon export off the shelf since the respiratory products of this material are re-exposed to the surface under conditions of deep mixing that

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occur regularly in winter in the region. Accordingly, the majority of the outgassing on the Scotian Shelf occurs during the autumn and winter seasons when the combination of CO₂ supersaturation and wind forcing enhance air-sea fluxes (Shadwick et al., 2010, 2011).

5 Previous studies of the CO₂ system on the Scotian Shelf have focused largely on the surface mixed-layer (Shadwick et al., 2010, 2011). Here we present observations of the inorganic carbon system collected as part of the Atlantic Zone Monitoring Program (AZMP). In this study, the spatio-temporal variability of the inorganic carbon system parameters are evaluated based on full water-column sampling along four primary
10 transect lines throughout the Scotian Shelf region. Net community production (NCP) is estimated from changes in the dissolved inorganic carbon (DIC) inventory between the early-spring and autumn seasons and the spatial distribution of NCP is discussed. The seasonal changes in pH and aragonite saturation state as well as the spatial variability are presented. Seasonal observations of surface water pCO₂ throughout the Scotian
15 Shelf are also reported for the first time.

2 Methods

Discrete bottle samples were collected on spring and autumn cruises as part of the Atlantic Zone Monitoring Program (AZMP) at stations distributed along four transects throughout the Scotian Shelf (Fig. 1). Cruises took place in April and September 2007.
20 Approximately 350 samples were collected on each cruise from the entire water column with higher vertical resolution within the euphotic zone at all stations shown in Fig. 1. DIC and total alkalinity (TA) samples were tapped from 12-l Niskin bottles mounted on a General Oceanic 24-bottle rosette fitted with a SeaBird CTD such that all chemical data are associated with high precision in-situ temperature, and salinity data. Following
25 water collection, DIC and TA samples were poisoned with a solution of HgCl₂ to halt biological activity and stored in the dark at 4°C to await analysis. DIC and TA were analysed by coulometric and potentiometric titration, respectively, using a VINDTA 3C

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(Versatile Instrument for the Determination of Titration Alkalinity by Marianda) (see for example Johnson et al., 1993; Fransson et al., 2001; Bates et al., 2005 for a full description of the analytical methods for the determination of DIC and TA). Routine analysis of Certified Reference Materials (provided by A. G. Dickson, Scripps Institution of Oceanography) ensured that the uncertainty of the DIC and TA measurements was less than 2 and 3 $\mu\text{mol kg}^{-1}$, respectively. Following the determination of DIC and TA, discrete values of pH (on the total scale) and aragonite saturation state (Ω_{ar}) were computed using the standard set of carbonate system equations, excluding nutrients, with the CO₂Sys program of Lewis and Wallace (1998). We used the equilibrium constants of Mehrbach et al. (1973) refit by Dickson and Millero (1987). The calcium (Ca²⁺) concentration was assumed to be conservative and calculated from salinity

Underway *p*CO₂ measurements were made by a continuous flow equilibration system (see for example Kötzing et al. 1996 for a description of the method). The underway measurements were made by a non-dispersive, infrared spectrometer (LiCor, LI-7000). The system was located in the aft-laboratory of the ship and the intake depth was approximately 3 m below the water surface. Measurements were made every minute and used to compute hourly averages. The system was calibrated daily with both a CO₂-free reference gas (N₂) and a CO₂ calibration gas (328.99 ppm) provided by the US National Oceanic and Atmospheric Administration (NOAA). The data were corrected to in-situ water temperature and to 100 % humidity and have an associated uncertainty of less than 1 μatm . In addition to the April and September (2007) cruises, underway *p*CO₂ data in the Scotian Shelf region were collected in August 2007 and December 2010.

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3 Results

3.1 The carbonate system

The relationships between DIC and salinity and TA and salinity in the Scotian Shelf in both April and September are shown in Fig. 2. Surface salinity on the shelf extends from roughly 30 to 33 in the near surface waters with DIC concentrations between roughly $1900 \mu\text{mol kg}^{-1}$ and $2150 \mu\text{mol kg}^{-1}$ over this range of salinity. The maximum salinities (roughly 35.5) are found in the deeper waters of stations located offshore, particularly in the southwestern region of the Browns Bank Line (see Fig. 1). The maximum observed DIC concentrations are on the order of $2250 \mu\text{mol kg}^{-1}$.

Surface waters are more fresh in September due to the delivery of water from the Gulf of St. Lawrence in the late summer to the Scotian Shelf. The Gulf of St. Lawrence is sea-ice covered in winter, which limits the delivery of surface water to the Scotian Shelf for part of the year. The impact of this can also be seen in the relationship between salinity and TA (Fig. 2b). There is a nearly conservative relationship between TA and salinity on the Scotian Shelf in both April and September. However the slope of the relationship between salinity and TA changes with season; this is a reflection of the decreased delivery of water from the St. Lawrence estuary system in the winter (April) relative to the late summer (September) period (Shadwick and Thomas, 2011). TA on the Scotian Shelf ranges from a minimum concentration of roughly $2100 \mu\text{mol kg}^{-1}$ to a maximum of roughly $2350 \mu\text{mol kg}^{-1}$.

The relationship between salinity-normalised DIC (nDIC) and salinity is shown in Fig. 2c. The normalisation of DIC to a constant salinity, using the formulation of Friis et al. (2003), removes the effect of freshwater input (and removal) from the measured concentrations of DIC. Variability in the salinity-normalised concentrations are thus primarily controlled by water temperature (or the solubility of CO_2), air-sea exchange of CO_2 , the mixing of water masses, and biological processes. There is in general more variability in the relationship between nDIC and salinity (and DIC and salinity) in September than in April. The productive season on the Scotian Shelf begins in April

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with the onset of the spring phytoplankton bloom. The spring bloom occurs when the water temperature is still close to the annual minimum and the mixed-layer may be quite deep; in April the physical situation on the Scotian Shelf is representative of the winter season. In September, by contrast, the water is at the annual temperature maximum and salinity minimum and the physical system is representative of the summer season. The productive season on the Scotian Shelf extends from early April through October (Shadwick et al., 2011). The higher degree of variability in the relationship between nDIC and salinity in September relative to April is thus likely a reflection of the impact of biological process on the inorganic carbon concentration during the productive season. This will be discussed in more detail in Sect. 4.1.

The relationship between DIC and TA, again for April and September, is given in Fig. 2d. In April, the relationship between DIC and TA is nearly conservative. Similar to the relationships between DIC and salinity and nDIC and salinity discussed above, there is more variability in the relationship between DIC and TA in September relative to April. The DIC and TA minima in September are lower than the corresponding minima in April, largely due to the change in salinity associated with the delivery of water from the Gulf of St. Lawrence. It can also be seen that DIC is reduced relative to TA in September, compared to April. This is the result of biological production which reduces DIC and results in a modest increase in TA (due to the uptake of nitrate).

The property plots discussed above include all samples collected along the four primary transect lines (Fig. 1) in two seasons. The subsequent discussion will address the regional differences by examining the seasonal differences along individual transects.

3.2 Spatio-temporal variability in hydrographic and carbonate system parameters

3.2.1 The Halifax Line section

The water column on the Scotian Shelf can be simplistically characterised by a two-layer system in winter when relatively fresh shelf water overlies more saline

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slope-derived water (Loder et al., 1997). This situation can be seen in the profiles of
25 temperature and salinity along the Halifax Line (Fig. 3a,b). In summer and autumn, the
water column is characterised by a three-layer system with the development of a warm,
shallow surface-layer overlying the two-layer system (Loder et al., 1997). This can also
be seen in the profiles of temperature and salinity on the Halifax Line (Fig. 3e,f). In both
April and September, temperature and salinity increase with distance offshore along
the Halifax Line section. In particular, high salinity water was observed near the sur-
face at the offshore end of the Halifax Line section in September (Fig. 3f). The sections
5 of DIC and TA indicate similar on-off shore gradients, with the distribution of TA closely
resembling the distribution of salinity. The shoaling of the mixed-layer in September
can be seen in the profiles of all parameters along the Halifax section (Fig. 3).

The productive season on the Scotian Shelf begins in early April with the spring phy-
toplankton bloom. The observations presented here were collected between the 6th
10 and the 22nd of April. Hourly observations of surface water $p\text{CO}_2$ (made by a CARI-
OCA buoy) at station HL2 (Fig. 3) indicate that on the 2nd of April surface $p\text{CO}_2$ was
roughly $200 \mu\text{atm}$ (Shadwick et al., 2011). This is roughly $50 \mu\text{atm}$ lower than the mini-
mum $p\text{CO}_2$ observed at the height of the 2008 spring bloom, which was only 14 days
in duration (Shadwick et al., 2010, 2011). This indicates that the 2007 spring bloom
15 was well under way on the 2 April, several days before shipboard DIC and TA sampling
began throughout the region. The drawdown of DIC in the surface layer had therefore
already begun at the time of observation. Production in the region continues through
the summer and autumn (Shadwick et al., 2011); the surface DIC concentrations in
September are reduced relative to those observed in April (Fig. 3c,g) due to biological
20 production. This will be discussed in more detail in Sect. 4.1. In the subsurface layer,
there is a modest increase in DIC in September relative to April (Fig. 3c,g). This is due
to the remineralisation of organic matter produced in the surface layer throughout the
spring and summer, a part of which sinks and is respired at depth.

3.2.2 The Browns Bank Line section

25 The Browns Bank Line section extends from the southwestern corner of Nova Scotia offshore. This section represents an artificial boundary between the Scotian Shelf and the neighbouring Gulf of Maine (see Fig. 1). The temperature profiles in April on the Browns Bank Line section (Fig. 4a) reveal the same two-layer structure seen along the Halifax Line section: cold relatively fresh shelf water (see also Fig. 4b) overlies warmer, more saline slope water. In September, the waters warm at the surface, however, the warm surface layer is more shallow along the Browns Bank Line section than along the Halifax section, with the depth of warming increasing with distance offshore (Fig. 4e).

5 The cool intermediate layer seen along the Halifax Line section in September is less pronounced along the Browns Bank section and the intrusion of warm, saline water at the offshore end of the section can be seen (Fig. 4f). In April the surface waters indicate relatively low concentrations of DIC (Fig. 4c) likely due to the onset of biological activity before the observations were made (Sect. 3.2.1). In September (Fig. 4g) there is substantial (on the order of $100 \mu\text{mol kg}^{-1}$) increase in DIC in the upper water column relative to the April observations, particularly at the offshore end of the transect, despite the ongoing biological activity over this period. Part of the biological DIC drawdown is masked by the increase in DIC due to the increase in salinity occurring over the same period (see Fig. 4b,f). This will be discussed in more detail in Sect. 4.1. In the subsurface (at a depth of roughly 300 m), an increase in DIC in September relative to April was observed (Fig. 4c,g). As in the case of the Halifax Line section, this is the result of the remineralisation of organic matter delivered from the surface layer to the subsurface. The profiles of TA along the Browns Bank section closely follow the distribution of salinity in the water column in both seasons (Fig. 4d,h). Particularly low concentrations of TA are observed in the surface layer in April, and a significant increase can be seen in the surface waters in September. At intermediate depth at the offshore end of the section there is an increase in TA in September relative to April following the increase in salinity in this depth range.

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3.2.3 The Louisbourg Line section

25 The Louisbourg Line section lies to the north-east of the Halifax Line section and extends from the northeastern corner of Nova Scotia offshore (see Fig. 1). Of the sections extending offshore, it is most closely located to the outflow from the Gulf of St. Lawrence. The two-layer structure seen along the Halifax Line section is also seen along the Louisbourg section. In April, cold, relatively fresh, shelf water overlies warmer, more saline, slope water (Fig. 5a,b). In September, the development of a shallow, warm, surface layer pushes the shelf water down to form a cold intermediate layer which overlies the warmer slope water (Fig. 5e). The intrusion of warm water at the offshore end of the section at intermediate depth can be seen in September, as is the case at the offshore ends of the Halifax and Browns Bank sections. Between April (Fig. 5b) and September (Fig. 5f) surface salinity decreases, particularly at the onshore end of the section. Over the same period, subsurface salinity increases, particularly at the offshore end of the section. There is a significant decrease in surface DIC concentration between April (Fig. 5c) and September (Fig. 5), particularly at the nearshore stations, due to biological activity. Over the same period there is an increase in subsurface DIC concentration, in part due to the respiration of organic matter, and in part due to the parallel increase in subsurface salinity, particularly at the offshore end of the section. As in the case of the Halifax and Browns Bank sections, the profiles of TA in April (Fig. 5d) and September (Fig. 5h) closely resemble the profiles of salinity. There is a decrease in surface TA between April and September, particularly at the onshore stations, and an increase in subsurface TA over the same period, particularly at the offshore end of the section, which can be attributed to seasonal increases in salinity.

3.2.4 The Cabot Strait section

20 The Cabot Strait section extends across the Laurentian Channel from Northeastern Nova Scotia to Southwestern Newfoundland (see Fig. 1). The water column in the Cabot Strait exhibits a three-layer structure in winter; cold, fresh water from the St.

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Lawrence Estuary overlies warmer, more saline slope water which overlies a warm, saline bottom water mass called warm slope water (Khatiwala et al., 1999) (Fig. 6a). In summer and early autumn, a shallow warm surface layer develops in Cabot Strait as it does on the Scotian Shelf as discussed above (Fig. 6e). The profiles of temperature and salinity indicate a gradient between the Nova Scotia and Newfoundland sides of the Cabot Strait, with colder fresher water on the Nova Scotia side (Fig. 6a,b,e,f). The general circulation in the Cabot Strait is an inflow of water along the Newfoundland edge of the strait and an outflow at the Nova Scotia side. The gradient in temperature and salinity reflects the origin of the water at either side of the strait; the colder fresher water comes via the St. Lawrence Estuary. As in the case of the Halifax Line section, the distribution and seasonal change in TA closely resembles those of salinity (Fig. 6d,h). Surface DIC is reduced in September relative to April as a result of biological activity. This DIC drawdown is particularly evident in the Newfoundland edge of the Cabot Strait where in September very low DIC concentration is observed from the surface to the bottom of the water column (Fig. 6c,g). In the subsurface DIC is enhanced in September relative to April as a result of organic matter respiration (Fig. 6g).

3.2.5 The Shelf Edge section

The profiles along the Shelf Edge section were generated from only three stations: BBL6, HL6 and LL7 (see the red dashed line in Fig. 1). These profiles are therefore intended to give an idea of the structure of the water column along the shelf edge despite the coarser resolution relative to the sections discussed above. In April the upper water column is cold and relatively fresh with colder water at the Louisbourg side of the section and slightly warmer water at the more Southern Browns Bank section (Fig. 7a). The surface waters are relatively fresh and salinity increases with depth; there does not appear to be a gradient in salinity along the section at any depth in April (Fig. 7b). Higher near-surface DIC concentrations are observed at the Louisbourg side of the section in April (Fig. 7c) while the distribution of TA along the section resembles that of salinity (Fig. 7d). In September, the Browns Bank side of the section indicates

a warm, shallow surface layer, while the surface waters on the Louisbourg side of the section are cooler (Fig. 7e). The warmer, more southern waters at the Browns Bank section are also more saline than the waters of the same depth at the Louisbourg section (Fig. 7f). Surface DIC is reduced in September relative to April as the result of both freshening and biological production (Fig. 7g). In the subsurface there is no significant increase in DIC in September, relative to April, as seen along the Halifax and Cabot Strait sections as a result of organic matter respiration.

3.3 Surface water $p\text{CO}_2$

Seasonal maps of surface water $p\text{CO}_2$, from April, August, September, and December, are shown in Fig. 8. Please note that the December data were collected in 2010, while the other data were collected in 2007. The values presented support previous findings that the Scotian Shelf acts annually as a source for atmospheric CO_2 which were based on a highly temporally resolved (hourly) time-series from a single location (Shadwick et al., 2010, 2011). The surface $p\text{CO}_2$ data presented here, though collected in different years, have a much larger spatial range and allow the seasonal characteristics of surface $p\text{CO}_2$ to be illustrated. In April the surface waters are undersaturated with respect to the atmosphere and the annual minimum $p\text{CO}_2$ is observed. The lowest $p\text{CO}_2$ is observed in along the Browns Bank Line, at the end of the Halifax Line and in Cabot Strait (see Fig. 1). Higher $p\text{CO}_2$ was observed in April closer to shore between the Halifax and Louisbourg Lines and offshore near the Grand Banks. From mid-April to August, warming and the decay of the spring bloom contribute to surface supersaturation. The more spatially limited data from August indicate $p\text{CO}_2$ of greater than $400 \mu\text{atm}$ throughout the Central Scotian Shelf. In autumn there is a smaller phytoplankton bloom, and the waters start to cool; both biology and solubility therefore reduce surface $p\text{CO}_2$; in September, the $p\text{CO}_2$ was near atmospheric equilibrium throughout the region with lower values (on the order of $350 \mu\text{atm}$) observed in Cabot Strait and at the offshore end of the Louisbourg Line. In late autumn and winter the Scotian Shelf is subject to strong winds that deepen the mixed-layer considerably

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25 with respect to the shallow summer surface layer. This destratification of the water column facilitates the upward mixing of carbon-rich subsurface waters and despite the correspondingly lower water temperature, surface waters are supersaturated with respect to atmospheric CO₂. Observations along the Halifax Line in December were on the order of 415 μatm with highest observed values (~ 500 μatm) located at the offshore end of this line.

3.4 pH and aragonite saturation state

5 The surface water pH on the Scotian Shelf, computed from discrete values of DIC and TA is in the range of 8.05 to 8.25 (Fig. 9). Significant increases in surface pH are observed in April relative to September; this increase in pH is coincident with the DIC drawdown due to photosynthesis and also results in an increase in the aragonite saturation state (Ω_{ar} , Fig. 10). Along the Halifax Line section (Fig. 9a,b) the highest pH is observed in April at the surface and at the near-shore stations. By contrast, in September the highest values are observed in the surface waters further offshore (Fig. 9). This general pattern was also observed along the Browns Bank, and Louisbourg Line sections. Lower pH waters were observed at the near-shore stations in the subsurface (50–100 m) in both seasons. This low-pH, low Ω_{ar} , subsurface water will be discussed in more detail in Sect. 4.2. Along the Shelf Edge section a similar pattern of enhanced surface water pH and Ω_{ar} is observed in April and to a lesser extent in September (Fig. 9c,d). The highest surface values of pH were observed at the Louisbourg end of the section in April (Fig. 9c), with a broadening of this high-pH (low DIC) water towards the Browns Bank end of the section. In September a pronounced low-pH (high-DIC) subsurface layer is observed between roughly 50 and 100 m at the Louisbourg end of the Shelf Edge section (Fig. 9d). This feature will be discussed further in Sect. 4.2.

20 Seasonal profiles of the aragonite saturation state (Ω_{ar} , Fig. 10) do not indicate widespread conditions of undersaturation, however, the saturation state is overall relatively low in this region (Fig. 10). In April, the surface waters on the shelf exhibit values of Ω_{ar} between roughly 1.5 and 2.0 (Fig. 10a,b). In the Cabot Strait the surface

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25 values are significantly lower (Fig. 10c). In contrast, the surface waters on the shelf in September are much higher as a result of the biological CO₂ drawdown throughout the productive season; Ω_{ar} in September is > 2 along both the Halifax and Shelf Break Line transects (Fig. 10d,e). The impact of biology can also be seen in the Cabot Strait region; in September the surface waters have Ω_{ar} ranging from 1.8 to 2.4. Along the Newfoundland side of the Strait, the enhanced Ω_{ar} extends down to a depth of
5 250 m (Fig. 10f). At mid-depth in the Cabot Strait in September, the remineralisation of organic matter enhances the concentration of DIC and suppresses the aragonite saturation state; Ω_{ar} approaches a value of 1 in much of the cold, relatively DIC-rich, subsurface in Cabot Strait (see Figs. 6 and 10).

4 Discussion

10 4.1 Net community production

Changes in DIC and TA result from both physical and biological processes, the latter having a smaller influence on TA than on DIC. Photosynthesis, respiration (or remineralisation) and the formation of calcium carbonate are biologically mediated processes that influence DIC and TA concentrations in seawater. DIC and TA may also be influenced by physical processes such as lateral and vertical advection, and entrainment.
15 DIC is further influenced by the air-sea exchange of CO₂. On the Scotian Shelf the most important physical processes, with respect to the inorganic carbon system, are air-sea CO₂ exchange, vertical entrainment and lateral (or horizontal) advection (Shadwick et al., 2011). Biological processes also play an important role. Between the April and September occupations of stations throughout the Scotian Shelf (Fig. 1) large decreases (up to ~100 $\mu\text{mol kg}^{-1}$) were observed. Changes in salinity between spring and autumn contribute to changes in DIC. As mentioned above, air-sea exchange of CO₂ also contributes to changes in DIC. Between April and September, the Scotian Shelf acts as a net sink for atmospheric CO₂ due to the relatively large uptake in April
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25 and smaller outgassing in the summer months (Shadwick et al., 2011). Vertical entrainment supplies carbon-rich subsurface water to the surface layer increasing DIC.

We estimated the change in DIC in the surface layer due to biological processes, or net community production, (NCP), in the following way. DIC was normalised to a constant salinity to remove the effect of freshwater fluxes. The freshwater source to the Scotian Shelf comes from the Gulf of St. Lawrence via the Cabot Strait. Due to ice coverage in winter, the freshwater outflow is minor in the winter months and there is an pronounced maximum in late spring or early summer. The corresponding effect
5 of salinity on DIC is therefore restricted to the summer season (Shadwick et al., 2011). The DIC concentrations were normalised to a salinity of 35 using the formulation of Friis et al. (2003) to account for the non-zero DIC concentration of the freshwater end-member. A first estimate of NCP was computed at each station as the difference between the inventories of salinity-normalised DIC (nDIC) in April and September over
10 the depth range of 0 to 40 m (Table 1).

The relationships between nDIC and salinity in the surface (0 to 40 m) and subsurface (> 40 m) are given in Fig. 11. In the surface layer (Fig. 11a) changes in salinity between April and September, both positive and negative, can be seen. The black line in Fig. 11a is a linear best-fit to the April data; if nDIC in September falls below this line,
15 DIC has been reduced due to biological production and/or the outgassing of CO₂ to the atmosphere. If the September nDIC values are rather above this line the dominant process is respiration, and/or the uptake of atmospheric CO₂, and/or vertical entrainment. It can be seen from Fig. 11a that in general the September values are reduced relative to the April values and that biological production is the driver of these changes.
20 In the subsurface layer (Fig. 11b) the linear best-fit to the April data is also shown. As in the surface layer, nDIC falling above this line indicate respiration, while nDIC falling below this line represent production. In the subsurface layer, the September values fall largely above this line, indicating an increase in DIC in September relative to April. This increase in DIC is due to the subsurface remineralisation of organic matter produced
25 in the surface and exported below the mixed-layer.

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The relationship between nDIC and nitrate (not shown) gives further confirmation that biological production is driving the decrease in surface DIC in September (relative to April). Relative to April, both nDIC and NO_3 are reduced in September indicating the uptake of both inorganic carbon and nutrients in the surface layer. The estimates of NCP computed from differences in the inventories of nDIC are somewhat lower than the estimates of biological production on the Scotian Shelf over the same period made by Shadwick et al. (2011). Shadwick et al. (2011) estimated NCP by isolating changes in DIC due to biological processes using a box model for the mixed-layer at station Halifax Line 2 (HL2). Between April and September NCP at station HL2 was estimated to be 31.9 g C m^{-2} over the 5-month period, or roughly $6.4 \text{ g C m}^{-2} \text{ month}^{-1}$ (Shadwick et al., 2011). This is more than twice the estimate of NCP made for station HL2 with the present methods. One reason for this discrepancy is the fact that the field sampling took place after the onset of the spring bloom in the region and the pre-production DIC concentrations were not captured by the discrete sampling. Measurements of surface water $p\text{CO}_2$ from a CARIOCA buoy moored at station HL2 (Shadwick et al., 2011) indicate minimum $p\text{CO}_2$ on the 2nd of April, while the cruise took place from the 6th to the 22nd of April. There are no $p\text{CO}_2$ measurements of the initiation of the bloom in 2007, but measurements from 2008 indicate that the $p\text{CO}_2$ minimum in that year was reached 14 days after the onset of the spring bloom. Thus, while our shelf-wide measurements in April do represent the system before the majority of the productive season has taken place, many of the measurements were made after the onset of spring biological activity and the difference between the April and September DIC concentrations presented here may be an underestimate of the magnitude of the seasonal change on the Scotian Shelf. The estimate of NCP relies on the difference in the water column concentrations between April and September and an overestimate of the April minimum due to the mismatch between the onset of carbon uptake by photosynthesis and the field sampling, may explain part of the apparent underestimate in our values of NCP.

10 Another reason for the low values of NCP relative to the estimates of Shadwick et al. (2011) is the fact that air-sea CO₂ exchange and vertical entrainment, which, as discussed above, both make an important contribution to changes in DIC on the Scotian Shelf, have been excluded from this estimate of NCP. To account for the contribution from air-sea exchange the uptake of CO₂ computed by Shadwick et al. (2010) using an
15 algorithm to determine pCO₂ from temperature, chlorophyll-a concentration and wind speed, at all stations for the period from April to September 2007 were included in the computation of NCP (NCP_{as}). To account for the contribution from vertical entrainment the value of Shadwick et al. (2011) computed from profiles of DIC at station HL2 between April and September (1.4 g C m⁻² over the 5-month period) was also added to
20 the estimate of NCP (NCP_{as,ve}). Please note that the estimates of vertical entrainment were computed based on observations at a single, near-shore, station (44.3°, 63.3° W). In applying these values to all stations we have assumed that the net contribution vertical entrainment is constant throughout the region. All three estimates of NCP are summarised in Table 1. Accounting for contributions from air-sea CO₂ exchange and
25 vertical entrainment increases the estimated NCP at all stations. At station HL2 the value obtained here is still roughly half of the estimate of Shadwick et al. (2011) for the same five-month period. Part of this underestimate may be due to the timing of the April sampling as discussed above. The NCP estimate of Shadwick et al. (2011) was made using hourly data collected in 2008. Thus some of the discrepancy between their estimate and the one made here is likely due to interannual variability in the inorganic carbon system.

5 Our shelf-wide estimates of NCP indicate significant spatial variability. The estimates of NCP are shown spatially in Fig. 12. There is a general trend of increasing NCP with distance offshore along the Browns Bank, Halifax and Louisbourg sections. This is particularly apparent along the Browns Bank section where the NCP is roughly 6 times smaller than that estimated at the offshore end of the same section (Fig. 12 and Table 1). The largest values of NCP correspond to the offshore stations on the Browns Bank section. These waters are also warmer and more saline, under greater influence

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10 of the Gulf Stream. In the Cabot Strait section NCP was also fairly high with values in the center of the Strait roughly twice as large as those on either the Nova Scotia or Newfoundland side of the section.

Subsurface respiration throughout the Scotian Shelf was estimated similarly to the surface NCP (see Sect. 4.1 and Fig. 11b), but excludes the contribution from air-sea
15 CO₂ exchange. In this case the difference in subsurface nDIC inventory between April and September were positive, indicating a production of inorganic carbon. Assuming that this inorganic carbon is the respiratory product of organic matter produced at the surface and exported vertically beneath the mixed layer, a respiration inventory can be computed. The estimates of respiration are given in the last column of Table 1.

20 4.2 A bulk seasonal carbon budget for the Scotian Shelf

From the estimates of NCP and subsurface respiration, and using literature values for vertical export of particulate organic carbon (POC) and organic carbon burial in the sediments we construct a bulk carbon budget for the Scotian Shelf for the period from April to September. For this budget only the Browns Bank, Halifax and Louis-
25 bourg Line sections are considered (see Fig. 1). The surface NCP and subsurface respiration (R) are computed from the means of all values along these sections listed in Table 1. Estimates of primary production on the Scotian Shelf cover a fairly wide range from 8 g C m⁻² month⁻¹ using the annual estimate of Mills and Fournier (1979) to 27 g C m⁻² month⁻¹ using the daily estimate of Pommier et al. (2009) made for the decline of the 2003 spring bloom offshore of the region. Charette et al. (2001) estimated that 11 % to 25 % of primary production is exported from the surface in the Gulf of Maine based on three-dimensional steady state model of the natural tracer thori-
30 um 234. We have here assumed that vertical export of POC corresponds to 25% of primary production (NCP_{export} = 4.0 g C m⁻² month⁻¹). In the same study, the burial of organic carbon in the sediments in the Gulf of Maine was found to account for roughly 1 % of primary production (Charette et al., 2001); we have used the same fraction for POC burial (POC_{burial} = 0.2 g C m⁻² month⁻¹). The vertical entrainment term

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10 follows the estimate of Shadwick et al. (2011) for the period from April to September ($V_{\text{Ent}} = 1.5 \text{ g C m}^{-2} \text{ month}^{-1}$, see Sect. 4.1). The air-sea flux term is the mean value over the period from April to September for the Halifax, Louisbourg and Browns Bank sections ($F_{\text{CO}_2} = 0.5 \text{ g C m}^{-2} \text{ month}^{-1}$). The bulk budget based on the above quantities is shown schematically in Fig. 13.

15 The uncertainties of the estimates are large given that the NCP and respiration terms are based on the difference between April and September values for a given station. The seasonal budget is unbalanced, with an additional requirement of $2.2 \text{ g C m}^{-2} \text{ month}^{-1}$ required to fuel the production in the surface layer, and an excess of $2.3 \text{ g C m}^{-2} \text{ month}^{-1}$ that is not accounted for by respiration in the subsurface.

20 The seasonal budget has been balanced by attributing this to advection (Fig. 13). In the neighbouring Gulf of Maine it has been suggested that organic matter produced is consumed, or buried within the system (Charette et al., 2001). It has also been suggested, based on a modelling study, that the continental shelf pump mechanism, which has the potential to transport dissolved carbon off the continental shelf does not operate in the Scotian Shelf region (Fennel and Wilkin, 2009). Vertical export of organic matter is thought insufficient for carbon export from the shelf since the rem-
25 ineralised products of this material are brought to the surface by deep winter mixing and/or upwelling in the region (Fennel and Wilkin, 2009). The budget presented here indicates that vertical entrainment delivers roughly 40% of the amount of carbon that is exported as POC (Fig. 13) leaving a significant portion for along-shore or cross-shelf export. As the mixed-layer deepens in late autumn and winter, vertical entrainment delivers significantly more DIC to the surface layer than during the summer season (Shadwick et al., 2011), which may account for some or all of the DIC needed to fuel
5 the spring/summer production. However, at the annual scale, vertical entrainment of DIC is balanced by outgassing of CO_2 (Shadwick et al., 2011). Observations of subsurface DIC in September 2008 (not shown) along the same transects do not indicate an accumulation of DIC through the winter season, which may indicate a potential lateral transport of particulate or dissolved material.

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10 The seasonal carbon budget presented here suggests that a continental shelf pump mechanism (Tsunogai et al., 1999) may operate on the Scotian Shelf; carbon comes into the system in the upper water column and is exported by carbon-enriched sub-surface water linked by sinking POC indicated by the two advective closing terms in Fig. 13. Surface advective input comes from the Gulf of St. Lawrence (via Cabot Strait) due to the higher DIC end-member in the riverine freshwater (Shadwick et al., 2010, 2011). This surface input can be seen in both seasons at the Louisbourg end of the Shelf Edge section transect where the DIC concentrations are higher than those at the Browns Bank end of the section (see Figs. 4, 5, and 7). The higher DIC concentrations observed at the Louisbourg (relative to Browns Bank) may be influenced by biological production, and indeed the chlorophyll-a concentrations are higher at Browns Bank throughout the year (Shadwick et al., 2010). However, less biological production in the Louisbourg region of the shelf would allow more DIC to be advected southwestward towards Browns Bank via the Nova Scotia Current which flows roughly parallel to the coast and dominates the surface circulation in the region (Hannah et al., 2001).

20 The direction of the subsurface advection (along-shore, or cross-shelf) is more difficult to identify with the present approach. However, the possible contributions from both along-shore and cross-shelf advection may be seen from our observations. The shelf edge transect indicates higher subsurface (between roughly 50 and 150 m) DIC concentrations at the Louisbourg side, relative to the Browns Bank side in both seasons (see Fig. 7c,g). This is more visible in the section of pH (Fig. 9) particularly in September when the Louisbourg side exhibits much lower pH (higher DIC) water from roughly 50 to 100 m. The spreading of this low-pH (high-DIC) subsurface water from the Louisbourg section towards Browns Bank may indicate an along-shore transport of DIC-enriched water, likely due to the sinking and subsequent respiration of organic matter produced in the surface. An alternative (or additional) contribution to the subsurface advection may come from cross-shelf transport. Along the Halifax Line transect in September (Fig. 3e) an offshore spreading of cool subsurface water can be seen below the warm surface layer. This is perhaps more visible in the sections of pH and

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10 Ω_{ar} ; in both seasons the offshore spreading of low-pH, low- Ω_{ar} (and high-DIC) water can be seen from roughly 50 to 100 m (Figs. 9 and 10). The advective, or closing, terms have been estimated based on seasonal observations of DIC. The size of the imbalance in the budget presented here depends on the value of both primary and export production, which have in this approach been from the literature (see above). If for example a much smaller value of export production is used, there would be a smaller amount of “excess” subsurface DIC available for advection. However, observations of concentration gradients and dominant circulation patterns in the region support the potential contribution from along-shore and/or cross-shelf transport of inorganic carbon in the region.

20 5 Conclusions

The Scotian Shelf is a biologically productive region of the Northwestern Atlantic Ocean. This system is characterised by an autotrophic surface layer and acts as a source of atmospheric CO_2 on the annual scale. Seasonal production varies spatially throughout the region with the largest biological CO_2 drawdown found in the Southeastern Browns Bank region and a general trend of increasing production with distance offshore. Seasonal estimates of net community production and subsurface respiration based on shelf wide observations of the carbonate system were used to construct a bulk inorganic carbon budget for the region for the period from April to September.

5 Our results indicate the potential for a continental shelf pump mechanism in the region in which inorganic carbon is brought into the system from the Gulf of St. Lawrence at the surface and exported from the system at the subsurface by either along-shore or cross-shelf advection or some combination of the two. The explicit quantification of the advective terms in the seasonal budget goes beyond the limits of the methods presented here and should be the focus of future work in the region.

Acknowledgements. We are grateful to the captains, officers and crew of the *CCGS Hudson* for their co-operation in the collection of field data. This project was funded by the Canadian Natural Sciences and Engineering Research Council (NSERC), the Canadian Foundation for

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Climate and Atmospheric Sciences (CFCAS), and MetOcean Data Systems. This work contributes to IGBP/IHDP-LOICZ.

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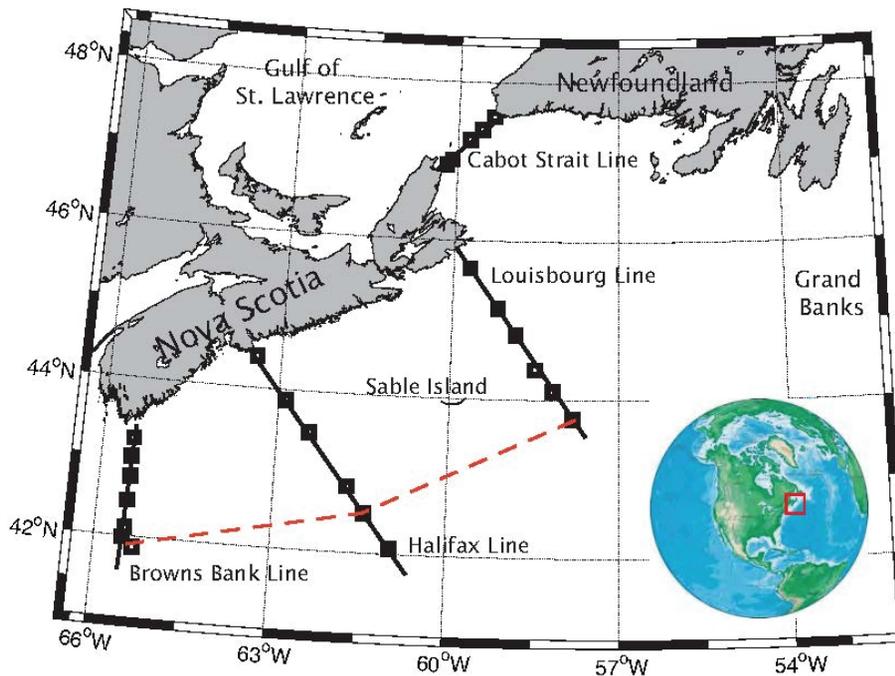


Fig. 1. Locations of stations samples along four primary transect lines in the Scotian Shelf region. The red dashed line indicates the shelf edge.

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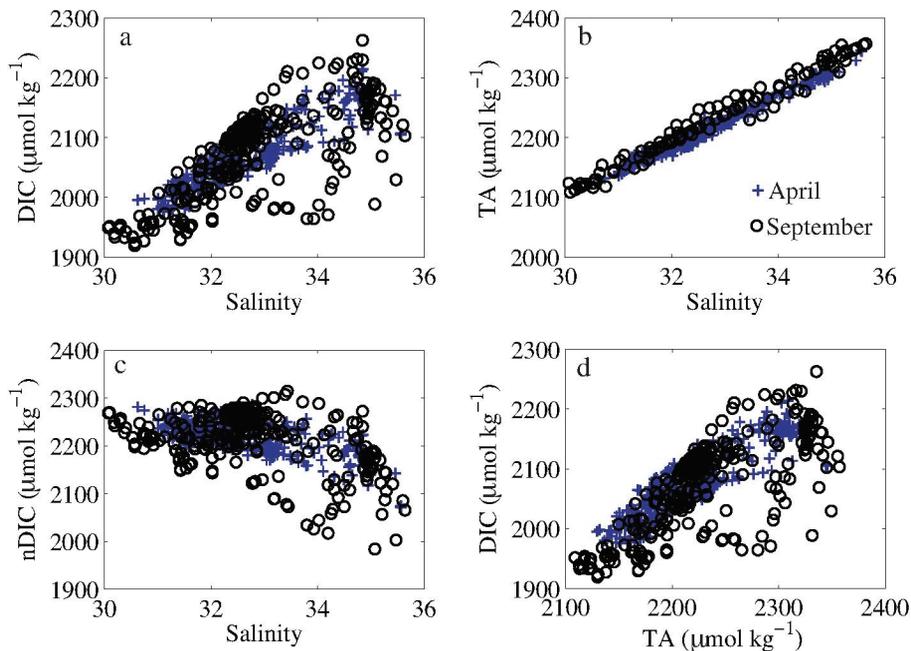


Fig. 2. Hydrographic and dissolved inorganic carbon properties observed in April and September on the Scotian Shelf. The relationships between: **(a)** DIC and salinity; **(b)** TA and salinity; **(c)** nDIC and salinity; and **(d)** DIC and TA.

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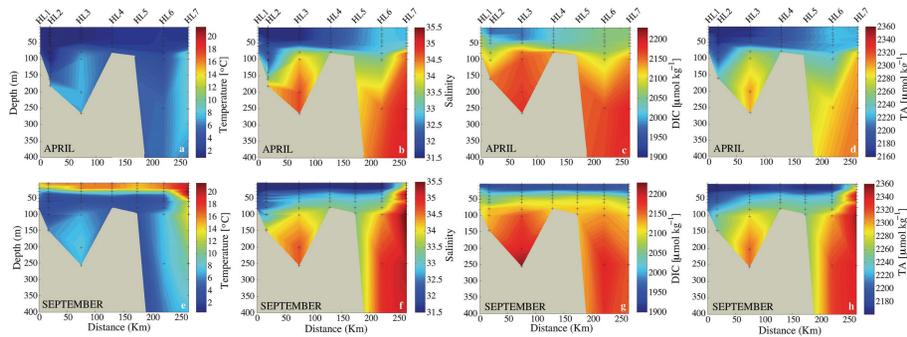


Fig. 3. Profiles of: (a and e) temperature; (b and f) salinity; (c and g) DIC; and (d and h) TA along the Halifax Line section (see Fig. 1) in April (top panels) and September (bottom panels).

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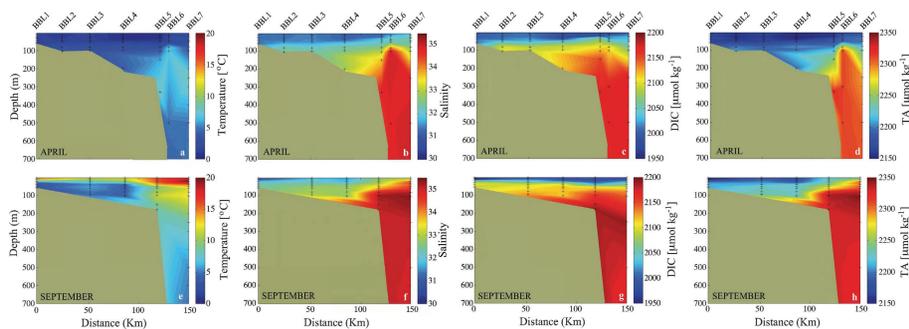


Fig. 4. Profiles of: (a and e) temperature; (b and f) salinity; (c and g) DIC; and (d and h) TA along the Browns Bank Line section (see Fig. 1) in April (top panels) and September (bottom panels).

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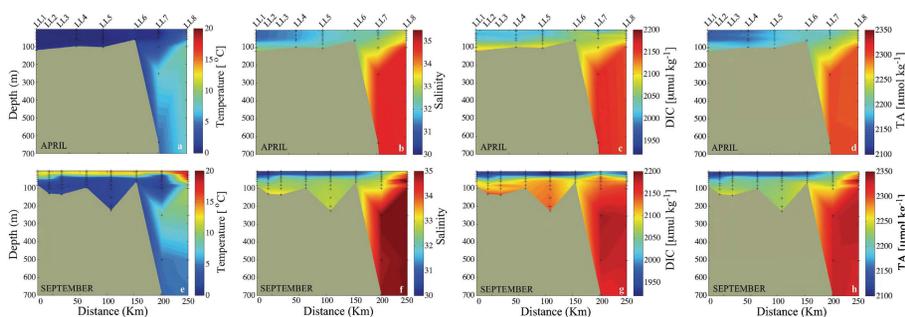


Fig. 5. Profiles of: (a and e) temperature; (b and f) salinity; (c and g) DIC; and (d and h) TA along the Louisbourg Line section (see Fig. 1) in April (top panels) and September (bottom panels).

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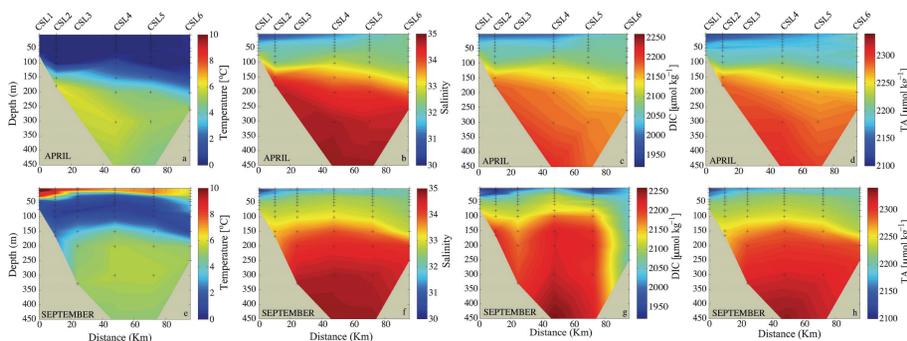


Fig. 6. Profiles of: **(a and e)** temperature; **(b and f)** salinity; **(c and g)** DIC; and **(d and h)** TA along the Cabot Strait Line section (see Fig. 1) in April (top panels) and September (bottom panels).

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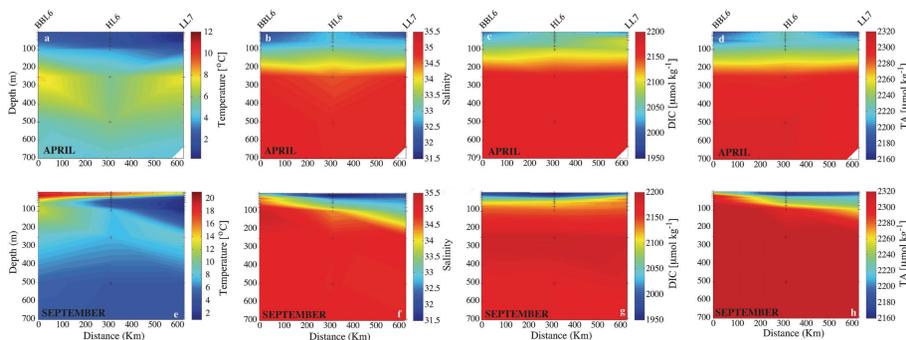


Fig. 7. Profiles of: (a and e) temperature; (b and f) salinity; (c and g) DIC; and (d and h) TA along the Shelf Edge Line section (the dashed line in Fig. 1) in April (top panels) and September (bottom panels).

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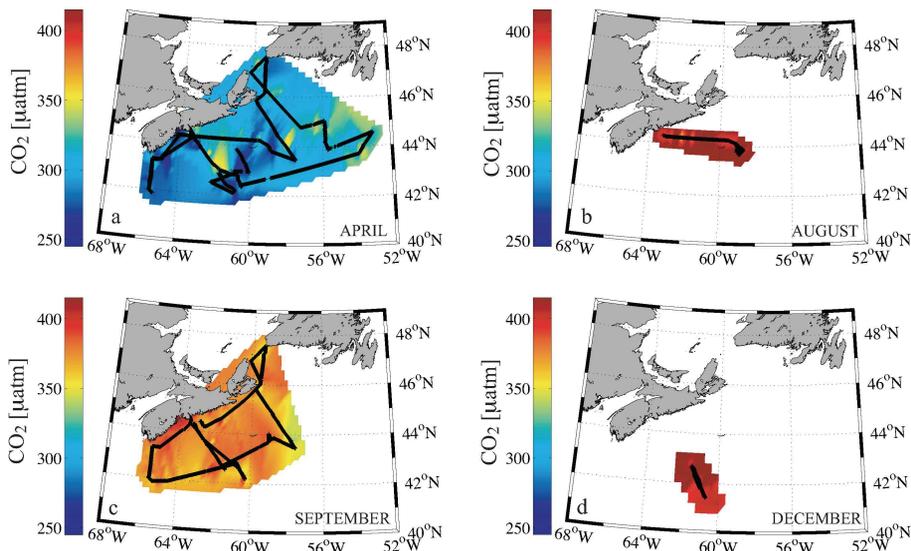


Fig. 8. Surface water $p\text{CO}_2$ on the Scotian Shelf in: **(a)** April; **(b)** August; **(c)** September; and **(d)** December. Atmospheric $p\text{CO}_2$ is roughly $390 \mu\text{atm}$ (Shadwick et al., 2010). Please note that the December data are from 2010 while all other data are from 2007.

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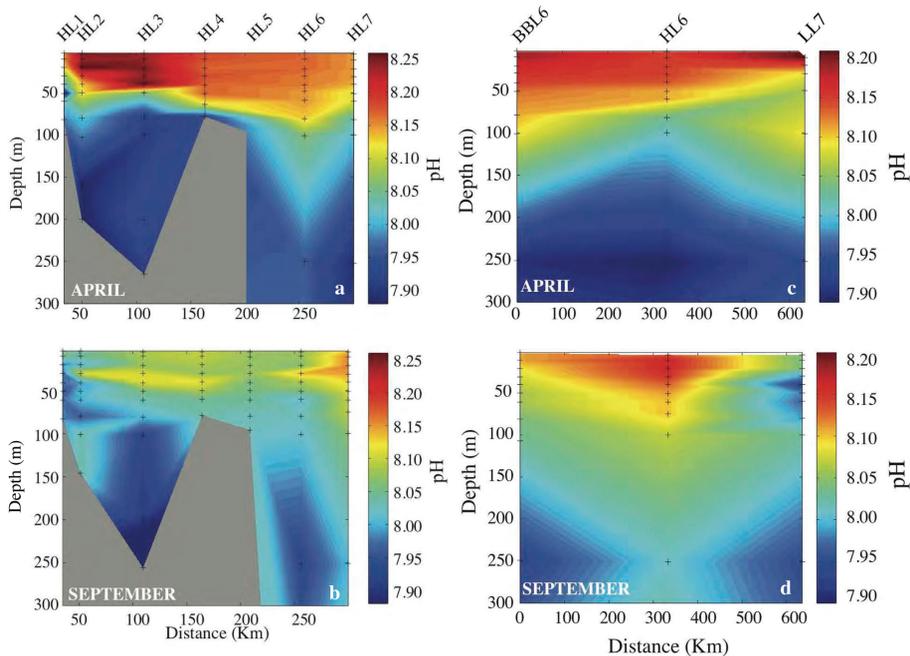


Fig. 9. Seasonal profiles of pH in the upper 300 m of the water column along the Halifax Line transect in **(a)** April, and **(b)** September and along the Shelf Break Line transect in **(c)** April, and **(d)** September.

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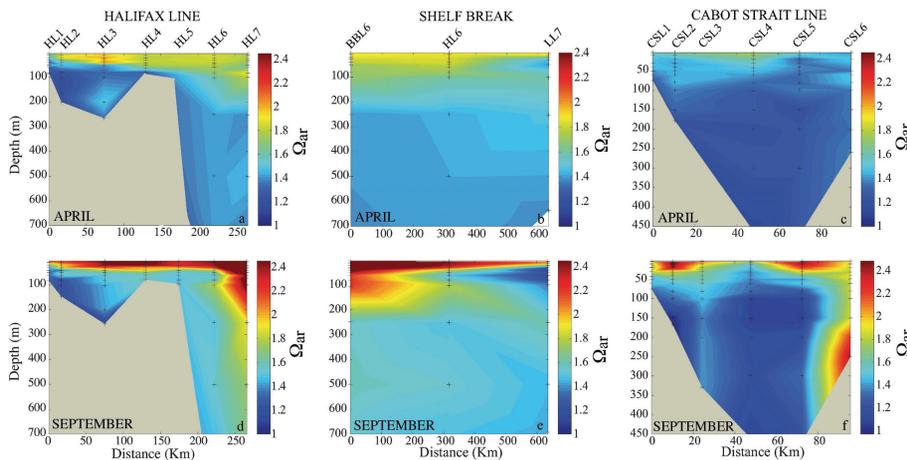


Fig. 10. Seasonal profiles of Ω_{ar} along (a) the Halifax, (b) the Shelf Break, and (c) the Cabot Strait Line transects (see Fig. 1).

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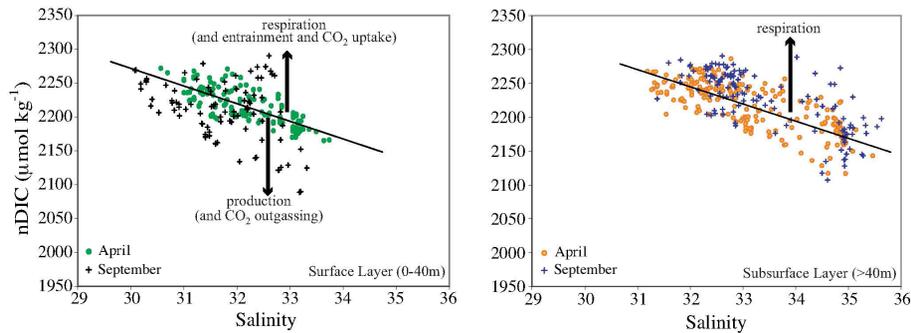
Shadwick et al., Scotian Shelf CO₂ System Figure 11

Fig. 11. The relationship between nDIC and salinity in (a) the surface and (b) the subsurface. The arrows indicate (schematically) the dominant processes controlling the changes in nDIC between April and September.

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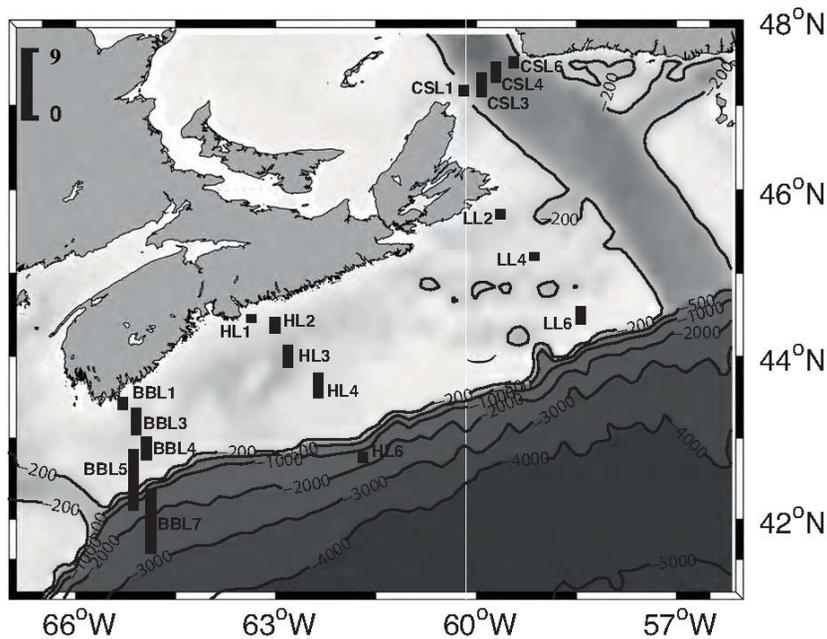
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Shadwick et al., Scotian Shelf CO₂ System Figure 12

Fig. 12. Spatial variability of the estimated NCP computed based on the difference in nDIC between April and September on the Scotian Shelf (see also Table 1).

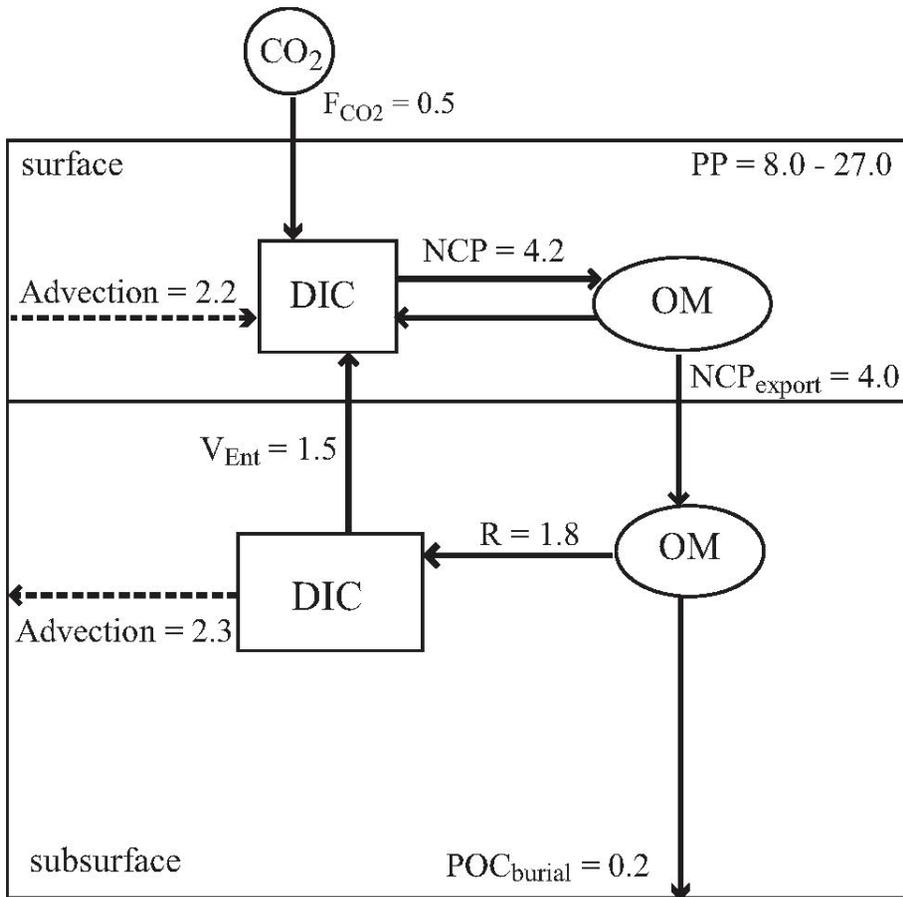


Fig. 13. A schematic representation of the seasonal carbon budget computed on the basis of DIC observations and literature values. All values are in units of $\text{g C m}^{-2} \text{ month}^{-1}$. The dashed arrows indicate the closing terms which have not been computed explicitly.

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