

Carbon Dioxide in the Coastal Ocean: A Case Study in the Scotian Shelf Region

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INTRODUCTION

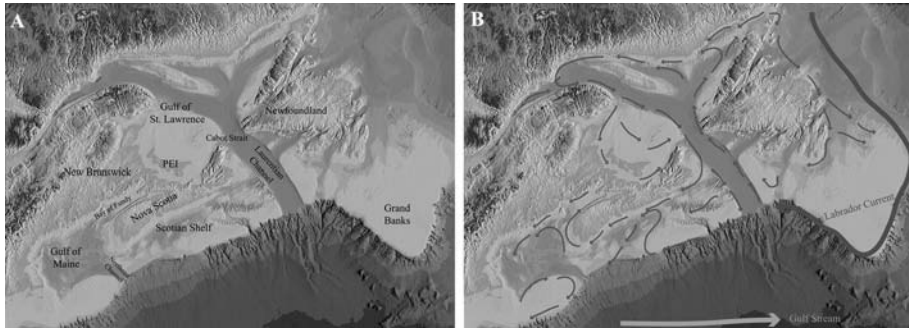
The Atlantic Coast of Canada hosts rugged beaches, picturesque fishing villages, and rich maritime history. This region is also home to an area called the Scotian Shelf, a 700-km long section of the continental shelf off Nova Scotia. Bounded by the Laurentian Channel to the northeast and by the Northeast Channel and the Gulf of Maine to the southwest, it varies in width from 120 to 240 km covering roughly 120,000 km² with an average depth of 90 m (Fig. 1). The Scotian Shelf, along with the Grand Banks, is one of the most heavily utilized fishing areas in the Canadian Atlantic region. The region also hosts the Gully Marine Protected Area and is home to several species of marine mammals and deep-sea corals that are threatened by the commercial fishing industry.¹ The major commercial fish species are demersal groundfish, including cod, haddock, pollock, halibut, and various species of flatfish; the principal pelagic fish species (by biomass) on the continental shelf are herring, mackerel, bluefin tuna, and capelin.² The Scotian Shelf contains critical habitat for the endangered North Atlantic right whale, with some 30 percent of the remaining population occupying a feeding area in Roseway Basin and the adjacent Bay of Fundy.³ The northern bottlenose whale is found offshore in the deep waters along the shelf edge, particularly in the Gully region east of Sable Island, where a unique,

1. S.E. Gass and J.H.M. Willison, "An assessment of the distribution of deep-sea corals in Atlantic Canada by using both scientific and local forms of knowledge," in *Cold water corals and ecosystems*, ed. A. Freiwald and J.M. Roberts (Berlin: Springer, 2005), 223–245; A.S.M. Vanderlaan and C.T. Taggart, "Vessel collisions with whales: the probability of lethal injury based on vessel speed," *Marine Mammal Science* 23 (2007): 144–156.

2. K.C.T. Zwanenburg, D. Bowen, A. Bundy, K. Frank, K. Drinkwater, R. O'Boyle, D. Sameoto and M. Sinclair, "Decadal changes in the Scotian Shelf Large Marine Ecosystem," in *Large Marine Ecosystems of the North Atlantic*, ed. K. Sherman and H. R. Skjoldal (Amsterdam: Elsevier, 2001): 105–150.

3. Vanderlaan and Taggart, n. 1 above.

FIG. 1.—The Scotian Shelf and the larger geographic setting (A) and a schematic representation of the dominant, long-term mean circulation in the region (B). The thick purple arrow represents schematically the Labrador Current, and orange arrow represents schematically the Gulf Stream, the influence of which is primarily offshore.



non-migratory population of individuals feeds on abundant squid.⁴ In the Northwest Atlantic, the major breeding colonies of gray seals are located on the sea ice in the Gulf of St. Lawrence and on Sable Island, with smaller colonies along the Eastern Shore of Nova Scotia and Cape Breton.⁵ The Nova Scotian coast is an important migratory staging area for waterfowl and shorebirds, while offshore waters host wintering dovebies, murres, shearwaters, and common eiders.⁶ Furthermore, a wide range of economically important shellfish species are found here, many with important spawning and nursery grounds in the region. The source of food to these marine mammals, fish and sea birds comes from the lower trophic levels, comprised of phytoplankton and zooplankton. Photosynthesis by phytoplankton fixes inorganic carbon, or carbon dioxide (CO_2), using energy from sunlight. These plants are grazed by zooplankton, which are in turn eaten by fish and whales, and thus the carbon fixed by phytoplankton makes its way into the food web. Despite their moderate surface areas, coastal seas and continental margins such as the Scotian Shelf play a crucial role in the global ocean carbon cycle due to their high ecosystem activity⁷ as detailed in the following sections.

4. S.K. Hooker, H. Whitehead, S. Gowans and R.W. Baird, "Fluctuations in distribution and patterns of individual range use of northern bottlenose whales," *Marine Ecology Progress Series* 225 (2002): 287–297.

5. W.D. Bowen, J. McMillan and R. Mohn, "Sustained exponential population growth of grey seals at Sable Island, Nova Scotia," *ICES Journal of Marine Science* 60 (2003): 1265–1274.

6. R.G.B. Brown, "Oceanographic factors as determinants of the winter range of the dovekie (*alle alle*) off Atlantic Canada," *Colonial Waterbirds* 11 (1988): 176–180.

7. A.V. Borges, B. Delille and M. Frankignoulle, "Budgeting sources and sinks of CO_2 in the coastal ocean: diversity of ecosystems counts," *Geophysical Research Letters*

Acidification of the oceans through uptake of anthropogenic CO₂ has become an active area of research over the last few years.⁸ International activities are being initiated in response to the unprecedented threat of ocean acidification to marine ecosystems at the global scale. Continuing acidification of the oceans has irreversibly been triggered by the increasing concentration of atmospheric CO₂, and mitigation measures are presently lacking. It has been shown that the vulnerability of North Atlantic Ocean waters to acidification increases in shallow and high latitude regions, primarily as a function of decreasing temperature and chemical composition.⁹ The Canadian Atlantic coast is thus particularly vulnerable to the effects of acidification as a high-latitude, shallow-shelf sea, influenced by Arctic and sub-Arctic waters. Eutrophication is defined as an increase of primary production in an ecosystem, as a result of an increased availability of nutrients. Eutrophication is often the result of pollution from sewage or agricultural fertilizers, which increase the concentrations of nitrate and phosphate, and may negatively impact the marine ecosystem by depleting oxygen and lowering water quality.¹⁰ Increased nutrient input from land via rivers, groundwater or the atmosphere, plays a further role in affecting coastal waters both by potentially altering ecosystem structure and by influencing the pH.¹¹ Ocean acidification most directly impacts organisms that form

32 (2005): L14601; W.-J. Cai, M. Dai and Y. Wang, "Air-sea exchange of carbon dioxide in ocean margins: A province-based synthesis," *Geophysical Research Letters* 56 (2006): 578–590.

8. J.C. Orr et al., "Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms," *Nature* 437 (2005): 681–696; S.C. Doney, "Dangers of ocean acidification," *Scientific American* 294 (2006): 58–65; J.A. Kleypas, R.A. Feely, V.J. Fabry, C. Langdon, C. L. Sabine and L.L. Robbins, "Impacts of Ocean Acidification on Coral Reefs and other Marine Calcifiers: A Guide for Future Research," *Report on a workshop held 18–20 April, 2005, St. Petersburg, FL, USA*, (2006), available online: <<http://isse.ucar.edu/florida>>.

9. H. Thomas, A.E.F. Prowe, S. van Heuven, Y. Bozec, H.J.W. de Baar, L.-S. Schiettecatte, K. Suykens, M. Kone, A.V. Borges, I.D. Lima and S.C. Doney, "Rapid decline of the CO₂ buffering capacity in the North Sea and implications for the North Atlantic Ocean," *Global Biogeochemical Cycles* 21 (2007): GB4001.

10. For example, J.H. Ryther and W.M. Dunstan, "Nitrogen, phosphorus, and eutrophication in the coastal marine environment," *Science* 171 (1971): 1008–1013.

11. J.N. Galloway, F.J. Dentener, D.G. Capone, E.W. Boyer, R.W. Howarth, S.P. Seitzinger, G.P. Asner, C.C. Cleveland, P.A. Green and E.A. Holland et al., "Nitrogen cycles: past, present and future," *Biogeochemistry* 70 (2004): 153–226; S.C. Doney, N. Mahowald, I. Lima, R.A. Feely, F.T. Mackenzie, J.-F. Lamarque and P.J. Rasch, "Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system," *PNAS* 104 (2007): 14,580–14,585; H. Thomas, D. Unger, J. Zhang, K.-K. Liu and E.H. Shadwick, "Biogeochemical cycling in semi-enclosed marine system and continental margins," in *Watersheds, Bays, and Bounded Seas*, eds. E.R. Urban Jr., B. Sundby, P. Malanotte-Rizzoli and J.M. Melillo (Washington: Island Press, 2009), 169–190; A.V. Borges and N. Gypens, "Carbonate chemistry in the coastal zone responds more strongly to eutrophication than to ocean acidification," *Limnology and Oceanography* 55 (2010): 346–353.

calcium carbonate (CaCO_3) shells and skeletons, because acidity increases the solubility of CaCO_3 .¹² These organisms include phytoplankton such as coccolithophores, zooplankton such as pteropods and foraminifera, sea urchins, mollusks and corals. Since CaCO_3 shells and skeletons are naturally more soluble at lower temperature and higher pressure, high latitude and deep-water ecosystems are more vulnerable to the added stress of ocean acidification. Furthermore, early life stages often carry thinner, more fragile shells, potentially making them more vulnerable to changing environmental conditions. Many calcifying organisms play a crucial role in the marine food web and are thus directly relevant to the human food supply. These organisms may themselves be commercially exploitable, as in the case of oysters, mussels and scallops, or support other commercially exploitable species by serving as prey or habitat. Shellfish aquaculture continues to grow in Nova Scotia.¹³

Here we report findings from the very first detailed study of the inorganic carbon cycle on the Scotian Shelf. Our study adds to the understanding of the carbon system in Canadian coastal waters. An understanding of the coastal ocean response to both natural and human-induced forcing is essential to the assessment of prospects and risks to fisheries and aquaculture in our maritime regions. There is a general global consensus that the “business as usual” treatment of anthropogenic CO_2 emissions through the burning of fossil fuels should be exchanged for strategies that reduce societal dependence on CO_2 to mitigate and manage future environmental impacts. However, in order to assess the effectiveness of any current or future mitigation strategy, accurate quantification of CO_2 emissions and their environmental impacts must be made to ensure that the reductions of CO_2 emissions are actually met. Assessing the impact of anthropogenic change is complicated by the lack of baseline studies in many regions. Coastal ocean regions are particularly poorly studied compared to their open ocean counterparts, despite their importance to society through fisheries and aquaculture. Pristine ocean conditions no longer exist; coastal environments have long been subjected to human activities through sewage treatment and the use of fertilizer and other pollutants. It is therefore difficult to assess relatively short-term impacts on systems that have been under the influence of

12. For example, U. Riebesell, I. Zondervan, B. Rost, P.D. Tortell, R.E. Zeebe and F.M.M. More, “Reduced calcification of marine plankton in response to increased atmospheric CO_2 ,” *Nature* 407 (2000): 364–367; B. Delille, J. Harlay, I. Zondervan, S. Jacquet, L. Chou, R. Wollast, R.G.J. Bellerby, M. Frankignoulle, A.V. Borges, U. Riebesell and J.-P. Gattuso, “Response of primary production and calcification to changes of pCO_2 during experimental blooms of coccolithophorid *Emiliania Huxley*,” *Global Biogeochemical Cycles* 19 (2005); F. Gazeau, C. Quiblier, J.M. Jansen, J.-P. Gattuso, J.J. Middelburg, and C.H.R. Heip, “Impact of elevated CO_2 on shellfish calcification,” *Geophysical Research Letters* 34, 7 (2007), L07603.

13. Nova Scotia Fisheries and Aquaculture, “Growing our Future: Long-term Planning for Aquatic Farming in Nova Scotia,” 2009, available online: <<http://www.gov.ns.ca/fish/aquaculture>>.

anthropogenic forcing for centuries. However, over the last decade, it has become clear that sustained time-series observations are essential to understanding natural and anthropogenic changes in the global carbon cycle on land, in the ocean, and in the atmosphere. Model simulations validated with high quality observational data can improve our understanding of complex systems and their response to environmental change. Canada's oceans are a valuable living and non-living resource providing food, power, transport, and security as well as recreation to our society. Measures to monitor the ocean's response to change will help to inform policy aimed at mitigating the effects of climate change and developing strategies to sustainably manage Canada's marine resources.

THE CARBON CYCLE AND THE COASTAL OCEAN

The carbon cycle is governed by many different biological, chemical and physical processes, which transfer carbon between the major storage pools called reservoirs. The global carbon cycle comprises four major carbon reservoirs: the atmosphere, the terrestrial biosphere (including plants, trees, soils and frozen soils or permafrost), the oceans, and the underlying sediments (including fossil fuel deposits and carbonate rocks). The global carbon budget is a balance of the exchanges of carbon that take place between these reservoirs over various time scales. In pre-industrial times, the global carbon cycle was in roughly steady state with fluxes into and out of the carbon reservoirs in balance. The release of CO₂ into the atmosphere by the combustion of fossil fuels has increased pre-industrial concentrations from roughly 280 ppm to present-day levels of nearly 390 ppm.¹⁴ Over only decades, the combustion of fossil fuels released quantities of carbon to the atmosphere that accumulated in the sedimentary reservoirs over millions of years. The conversion of tropical forest to agricultural land and cement production release additional CO₂ to the atmosphere. The anthropogenic release of CO₂ is currently larger than can be balanced by natural biological and geological removal processes which act over much longer timescales.

The oceans act as a significant reservoir for inorganic carbon, containing 50 times more CO₂ than the atmosphere.¹⁵ Roughly half of the anthropogenic CO₂

14. A.W. King, L. Dilling, G.P. Zimmerman, D.M. Fairman, R.A. Houghton, G. Marland, A.Z. Rose and T.J. Wilbanks, "What is the carbon cycle and why care?," in *The First State of the Carbon Cycle Report (SOCCR): The North American Carbon Budget and Implications for the Global Carbon Cycle*, U.S. Climate Change Science Program (Washington D.C., 2007): 15–20; C.D. Keeling and T.P. Whorf, "Atmospheric CO₂ records from sites in the SIO sampling network," in *Trends: A compendium of data on global change*, Carbon Dioxide Information Analysis Center (Oak Ridge, Tenn.: Oak Ridge National Laboratory, 2009).

15. N. Gruber, P. Friedlingstein, C. B. Field, R. Valentini, M. Heimann, J. D. Richey, P. Romero Lankao, E.-D. Schulze and C.-T. A. Chen, "The vulnerability of the carbon cycle in the 21st century: An assessment of carbon-climate-human interactions,"

emitted to the atmosphere is taken up by the ocean.¹⁶ Phytoplankton convert CO₂ to particulate organic carbon (POC), a portion of which settles out of the surface layer, and is therefore removed from the atmosphere by a combination of biological and physical processes.¹⁷ Coastal seas and continental margins play an important role in the global carbon cycle by linking the terrestrial, oceanic, and atmospheric reservoirs.¹⁸ Compared to the open ocean, the proximity of the surface sediments to the air-sea interface, in both space and time, is enhanced in the coastal ocean.¹⁹ Although the coastal ocean represents only 8 percent of the total ocean surface area, roughly one-fifth to one-third of the global marine primary production takes place in these seas.²⁰ Furthermore, the coastal ocean plays a prominent role in the absorption of atmospheric CO₂, potentially transferring it to the deep ocean via the continental shelf pump—a mechanism that feeds cold, dense, carbon-rich waters from the shelf region to the sub-surface waters of the adjacent deep ocean where they are sequestered from the atmosphere.²¹ However, a recent modeling study suggests that the continental shelf pump mechanism, which has the potential to transport dissolved carbon off the continental shelf, does not operate on the Scotian Shelf.²² Vertical sinking of organic material is insufficient for carbon export since the respiratory products

in *The global carbon cycle: integrating humans, climate, and the natural world*, ed. C.B. Field and M.R. Raupach (Washington: SCOPE, 2004), 45–77; King et al., n. 14 above.

16. C.L. Sabine, R.A. Feely, N. Gruber, R.M. Key, K. Lee, J.L. Bullister, R. Wanninkhof, C.S. Wong, D.W.R. Wallace, B. Tilbrook, F.J. Millero, T.-H. Peng, A. Kozyr, T. Ono and A.F. Rios, “The oceanic sink for anthropogenic CO₂,” *Science* 305 (2004): 367–371; Gruber, n. 15 above.

17. N. Gruber and J.L. Sarmiento, “Large-scale biogeochemical-physical interactions in elemental cycles,” in *The Sea*, ed. A.R. Robinson, J.J. McCarthy and B.J. Rothschild (New York: John Wiley & Sons Inc., 2002), 337–400.

18. J.J. Walsh, “Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen,” *Nature* 350 (1991): 753–755; A.J. Andersson and F.T. Mackenzie, “Shallow-water oceans: a source or a sink of atmospheric CO₂,” *Frontiers in Ecology and the Environment* 2 (2004): 348–353.

19. H. Thomas, L.-S. Schiettecatte, K. Suykens, Y.J.M. Koné, E.H. Shadwick, A.E.F. Prowe, Y. Bozec, H.J.W. de Baar and A.V. Borges, “Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments,” *Biogeosciences* 6 (2009): 267–274.

20. Walsh, n. 18 above; J.P. Gattuso, M. Frankignoulle and R. Wollast, “Carbon and carbonate metabolism in coastal aquatic ecosystems,” *Annual Reviews of Ecological Systems* 29 (1998): 405–434.

21. S. Tsunogai, S. Watanabe and T. Sato, “Is there a ‘continental shelf pump’ for the absorption of atmospheric CO₂,” *Tellus* 51 (1999): 701–712; H. Thomas, Y. Bozec, K. Elkalay and H.J.W. de Baar, “Enhanced Open Ocean Storage of CO₂ from Shelf Sea Pumping,” *Science* 304 (2004): 1005–1008; Y. Bozec, H. Thomas, K. Elkalay and H.J.W. de Baar, “The continental shelf pump for CO₂ in the North Sea – evidence from summer observation,” *Marine Chemistry* 93 (2005): 131–147.

22. K. Fennel and J. Wilkin, “Quantifying biological carbon export for the north-west North Atlantic continental shelves,” *Geophysical Research Letters* 36 (2009): L18605.

of this material are re-exposed to the surface under conditions of deep winter mixing, which will be discussed in more detail.²³

Roughly 50 percent of the global population lives within 100 km of the shore; the North American Atlantic coast is heavily populated and thus directly impacted by anthropogenic activity.²⁴ Before reliable assessment of the vulnerability of coastal systems to climate change can be made, present-day carbon stocks must be quantified, and natural variability understood. Carbon fluxes have been investigated in several coastal ocean and continental shelf regions in the last few years.²⁵ However, these environments exhibit strong spatial and temporal heterogeneity, and integrative global assessments²⁶ have not yet achieved high fidelity. The research presented here reflects the state of knowledge of the CO₂ system in the Scotian Shelf region.

DATA AND METHODS

The discrete chemical and hydrographic data presented in the following sections were collected during April and September 2008 cruises of the Canadian Coast Guard Ship *Hudson* as part of the Atlantic Zone Monitoring Program (AZMP),²⁷ implemented in 1998 by the Canadian Department of Fisheries and

23. See section “Seasonal variations in DIC and pCO₂.”

24. R. Najjar, D.E. Butman, W.-J. Cai, M.A.M. Friedrichs, K.D. Kroeger, A. Mannino, P.A. Raymond, J. Salisbury, D.C. Vandemark and P. Vlahos, “Carbon budget for the continental shelf of the eastern United States: A preliminary synthesis,” *Ocean Carbon and Biogeochemistry News* 3 (2010): 1–4.

25. For example, T.-H. Peng, J.-J. Hung, R. Wanninkhof and F.J. Millero, “Carbon budget in the East China Sea in spring,” *Tellus* 51 (1999): 531–540; H. Thomas and B. Schneider, “The seasonal cycle of carbon dioxide in Baltic Sea surface waters,” *Journal of Marine Systems* 22 (1999): 53–67; M. Frankignoulle and A.V. Borges, “European continental shelf as a significant sink for atmospheric carbon dioxide,” *Global Biogeochemical Cycles* 15 (2001): 569–576; W.-J. Cai, Z.A. Wang and Y. Wang, “The role of marsh-dominated heterotrophic continental margins in transport of CO₂ between the atmosphere, the land-sea interface and the ocean,” *Geophysical Research Letters* 30, 16 (2003): 1849; H. Thomas, Y. Bozec, K. Elkalay, H.J.W. de Baar, A.V. Borges and L.-S. Schiettecatte, “Controls of the surface water partial pressure of CO₂ in the North Sea,” *Biogeosciences* 2 (2005): 323–334; Y. Bozec, H. Thomas, L.-S. Schiettecatte, A.V. Borges, K. Elkalay, H.J.W. de Baar, “Assessment of the processes controlling seasonal variations of dissolved inorganic carbon in the North Sea,” *Limnology and Oceanography* 51 (2006): 2746–2762.

26. Borges et al., n. 7 above; Cai et al., n. 7 above; C.-T.A. Chen and A. Borges, “Reconciling opposing views on carbon cycling in the coastal ocean: Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO₂,” *Deep-Sea Research II* 56 (8–10), (2009): 578–590.

27. For details of the AZMP, see: <<http://www.bio.gc.ca/monitoring-monitorage/azmp-pmza/index-eng.htm>>.

Oceans (DFO). The primary goal of the AZMP is the maintenance of a long-term, relatively high temporal resolution, observational program in the Canadian Northwestern Atlantic Ocean. Approximately 350 seawater samples were collected on each cruise along four primary transect lines covering the Scotian Shelf regions. Samples were taken from the entire water column with higher vertical resolution within the euphotic zone. Seawater samples were tapped from 20-litre Niskin bottles mounted on a General Oceanic 24-bottle rosette fitted with a conductivity, temperature and depth sensor (CTD, SeaBird) such that all chemical data are associated with high precision in-situ temperature, salinity and oxygen data.

With respect to the CO₂ system in seawater, there are four measureable parameters: the partial pressure of CO₂ (pCO₂), dissolved inorganic carbon (DIC), total alkalinity (TA), and pH. With measurements of any two of these parameters, the other two measureable parameters can be computed. Following seawater collection, measurements of DIC and TA were made by coulometric and potentiometric titration, respectively, using a Versatile Instrument for the Determination of Total Alkalinity (VINDTA 3C, Marianda).²⁸ 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 μmol/kg, respectively. Following the determination of DIC and TA, a computation of pH and aragonite saturation state (Ω_{ar}) was computed using the standard set of carbonate system equations.²⁹

In addition to discrete samples of DIC and TA, continuous measurements of pCO₂ from an autonomous moored CARIOCA buoy are presented. The CARIOCA buoy was moored at station ‘Halifax Line 2’, hereafter HL2, (44.3° N and 63.3° W) from April to December, 2007; January to July, 2008; and October, 2009 to February 2010. The CARIOCA buoy makes hourly measurements of sea-surface temperature (SST), sea-surface salinity, chlorophyll-*a* (chl-*a*) concentration, and pCO₂. The pCO₂ measurements were made by an

28. For a detailed description of the analytical methods for the determination of DIC and TA, see K.M. Johnson, K.D. Wills, D.B. Butler, W.K. Johnson and C.S. Wong, “Coulometric total carbon dioxide analysis for marine studies: Maximizing the performance of an automated gas extraction system and coulometric detector,” *Marine Chemistry* 44 (1993): 167–188.

29. We used the dissociation constants of Mehrbach et al., refit by Dickson and Millero. See C. Mehrbach, C.H. Culbertson, J.E. Hawley and R.M. Pytkowicz, “Measurement of the apparent dissociation constant of carbonic acid in seawater at atmospheric pressure,” *Limnology and Oceanography* 18 (1973): 897–907; A.G. Dickson and F.J. Millero, “A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media,” *Deep-Sea Research I* 34 (1987): 1733–1743. For the pCO₂, pH and Ω_{ar} computations the CO2SYS program was used, see E. Lewis and D.W.R. Wallace, “Program developed for CO₂ systems calculations,” Carbon Dioxide Information Analysis Center (CDIAC) Report 105, 1998.

automated spectrophotometer technique.³⁰ Atmospheric CO₂ and wind speed data presented were measured at the Sable Island Meteorological Station (43.9° N and 60.3° W) and were provided by Environment Canada.

PHYSICAL AND BIOLOGICAL CONDITIONS ON THE SCOTIAN SHELF

The Scotian Shelf is uniquely located at the junction of the North Atlantic sub-polar and sub-tropical gyres, downstream of the St. Lawrence River system.³¹ The Scotian Shelf is considered an open continental shelf, or regional sea, system, as opposed to closed system as in the case of the Arctic Archipelago.³² The shelf-scale circulation is dominated by the Nova Scotia Current, which flows to the southwest roughly parallel to the coast, and an extension of the Labrador Current, flowing in the same direction, along the shelf edge (Fig. 1). Water transport by the Nova Scotian Current varies seasonally in strength reaching peak values of roughly 2 Sverdrups (Sv) in winter and spring, with a summer minimum of 0.4 Sv.³³ Smaller scale circulation features are generated by topographic steering around submarine banks, (i.e., Browns Bank, Sable Island Bank, and Georges Bank), and cross-shelf channels.³⁴ Tidal forcing and episodic wind-driven upwelling also influence the region;³⁵ the former will be discussed in more detail in the next section.

30. See N.R. Bates, L. Samuels and L. Merlivat, "Biogeochemical and physical factors influencing seawater fCO₂ and air-sea CO₂ exchange on the Bermuda coral reef," *Limnology and Oceanography* 46 (2001): 833–846 for a description of the method used to measure pCO₂.

31. J.W. Loder, G. Han, C.G. Hannah, D.A. Greenberg and P.C. Smith, "Hydrography and baroclinic circulation in the Scotian Shelf region: Winter versus summer," *Canadian Journal of Fisheries and Aquatic Sciences* 54 (1997): 40–56.

32. M. Meybeck, H.H. Dürr, S. Roussennac and W. Ludwig, "Regional seas and their interception of riverine fluxes to oceans," *Marine Chemistry* 10 (2007): 301–325.

33. A Sverdrup (Sv) is a unit of measure of volume transport equivalent to 10⁶ cubic meters per second. The global input of rivers to the ocean is roughly equal to 1 Sv; J.W. Loder, C.G. Hannah, B.D. Petrie and E.A. Gonzalez, "Hydrographic transport variability on the Halifax section," *Journal of Geophysical Research* 108 (2003): 8003, doi:10.1029/2001JC001267.

34. J.W. Loder, C.K. Ross and P.C. Smith, "A space and time-scale characterization of circulation and mixing over a submarine bank with application to the Northwestern Atlantic continental shelf," *Canadian Journal of Fisheries and Aquatic Sciences* 45 (1988): 1860–1885; C.G. Hannah, J.A. Shore, J.W. Loder and C.E. Naimie, "Seasonal circulation on the western and central Scotian Shelf," *Journal of Physical Oceanography* 31 (2001): 591–615.

35. B. Petrie, B.J. Topliss and D.G. Wright, "Coastal upwelling and eddy development off Nova Scotia," *Journal of Geophysical Research* 29 (1987): 12,979–12,991; Loder et al., n. 31 above; B.J.W. Greenan, B.D. Petrie, W.G. Harrison and N.S. Oakey, "Are the spring and fall blooms on the Scotian Shelf related to short-term physical events?," *Continental Shelf Research* 24 (2004): 603–625.

Coastal and Shelf-Edge Upwelling

A persistent alongshore wind with the coast on the left (looking downwind) in the northern hemisphere will result in an offshore flow in the surface waters, which is compensated by a shoreward flow of deeper waters, which are upwelled to the surface. Coastal upwelling and the associated favorable wind conditions on the Scotian Shelf have long been recognized.³⁶ Strong winds of speeds greater than 10 m/s, blowing to the northeast, and persisting for several days force relatively cold, saline water toward the surface, displacing the warmer, fresher water offshore.³⁷ Upwelling events have frequently been observed in the region in winter,³⁸ and modeling studies have reproduced these observed events.³⁹ Furthermore, these events may play a role in initiating and sustaining the spring phytoplankton bloom by displacing nutrient-depleted surface water and bring nutrient-rich waters up to the surface.⁴⁰

Temperature and Salinity

The seasonal cycle in surface water temperature on the Scotian Shelf has an annual range of nearly 20 °C, (from an annual minimum of 0 °C to a maximum of 18 °C to 20 °C), which is among the largest in the world.⁴¹ The seasonal variation in surface temperature is primarily due to surface heat fluxes.⁴² The mean temperature in the upper 10 m of the water column in early April, reflecting winter and spring conditions, and in September, reflecting summer and autumn conditions, are shown in Fig. 2. In the spring, the advection of sub-zero waters from Cabot Strait (to the north) influences surface water temperature, which is nearly homogeneous on the shelf. The southwestern outflow from Cabot Strait can also be identified as the major source of fresh water to the region. The salinity increases further offshore due to the northward transport of warm, saline, Gulf Stream waters (Fig. 1). In autumn, the surface temperature is warmest in the central Scotian Shelf and increases with distance from shore. The waters in

36. *Id.*; H.B. Hachey, "The effect of a storm on an inshore area with markedly stratified waters," *Journal of the Biological Board of Canada* 1 (1935): 227–237.

37. B.D. Petrie, "Current Response at the Shelf Break to Transient Wind Forcing," *Journal of Geophysical Research* 88 (1983): 9567–9578.

38. *Id.*

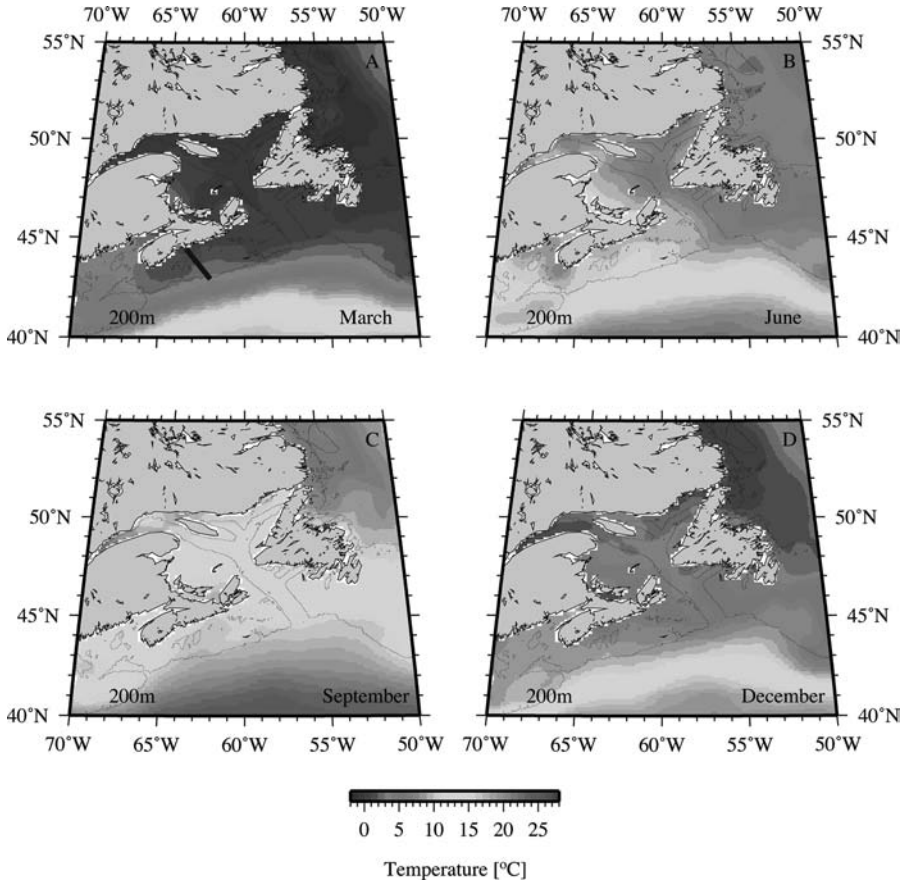
39. S. Donohue, "A numerical model of an upwelling event off the coast of Nova Scotia," (M.Sc. Thesis, Royal Military College of Canada, 2000).

40. Petrie et al., n. 35 above; Greenan et al., n. 35 above.

41. J.U. Umoh and K.R. Thompson, "Surface heat flux, horizontal advection, and the seasonal evolution of water temperature on the Scotian Shelf," *Journal of Geophysical Research* 99 (1994): 20,403–20,416; Loder et al., n. 31 above.

42. Umoh and Thompson, n. 41 above.

FIG. 2.—Mean temperature in the upper 10 meters of the water column on the Scotian Shelf in: (A) March, (B) June, (C) September, and (D) December. The solid line in (A) indicates the transect referred to as the ‘Halifax Line’. The section plots shown subsequent figures were generated from samples collected along this transect. Y. Geshelin, J. Sheng and R.J. Greatbatch, “Monthly mean climatologies of temperature and salinity in the western North Atlantic,” *Can. Tech. Rep. Hydrogr. Ocean. Sci.* 153 (1999).



Cabot Strait remain relatively cool. The peak in river discharge from the St. Lawrence is delivered to the Scotian Shelf between June and October; surface salinity is typically decreased by 1 part, from roughly 30.5 to 29.5 parts per thousand, as a result of this input.⁴³

43. Loder et al., n. 31 above.

Winter Convection

The minimum sea-surface temperature on the Scotian Shelf ranges between 1 °C and 2 °C (Fig. 2). The minimum winter air temperature over the Scotian Shelf is much colder,⁴⁴ with temperatures ranging from -20 °C to -5 °C. The surface of the ocean therefore loses heat to the atmosphere when the air temperature is less than the sea-surface temperature. The loss of heat causes the surface waters to become colder, and denser. These dense waters will sink and be replaced by warmer waters from below. The process, called convective mixing, can also occur due to surface evaporation that leaves behind salty, dense waters that will sink below the underlying fresher water. Convection occurs in the winter season on the Scotian Shelf. In this region, wind speed exerts some control over the depth of convective mixing; an increase in wind strength removes more heat from the surface waters and deepens the extent of the convection. The impact of winter convection can be seen in the increase in the depth of penetration of relatively warm waters (down to 50 meters) in the autumn and winter (Fig. 3 and 4). The impact of winter convection on the seasonal cycle of CO₂ on the Scotian Shelf will be discussed in more detail.

Water Mass Composition

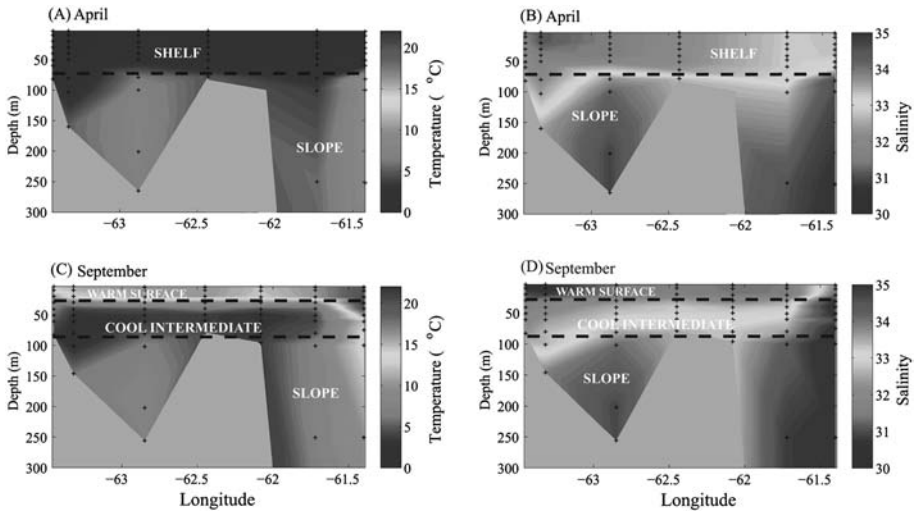
The origin and composition of water masses along the northeastern North American coast are well known.⁴⁵ As many as eight distinct water masses have been identified on the Scotian Shelf on the basis of oxygen isotope and salinity data.⁴⁶ For simplicity, the water column in the region can be characterized by a two-layer system in winter when relatively fresh shelf water overlies more saline slope-derived water, and a three-layer system in summer with the development

44. Air temperature data is from the Sable Island Meteorological Station for the period from 1971 to 2000, available online: <<http://www.climate.weatheroffice.gc.ca>>.

45. For example, H.B. Bigelow, "Physical oceanography of the Gulf of Maine," *Bulletin of U.S. Bureau of Fisheries* 640 (1927): 511–1027; H.B. Hachey, "The waters of the Scotian Shelf," *Journal of the Fisheries Research Board of Canada* 5 (1942): 377–397; D.C. Chapman and R.C. Beardsley, "On the origin of the shelf water in the middle Atlantic bight," *Journal of Physical Oceanography* 19 (1989): 384–391; J.W. Loder, B. Petrie and G. Gawarkiewicz, "The coastal ocean off northeastern North America: A large-scale view," in *The Sea, The Global Coastal Ocean: Regional Studies and Syntheses*, ed. A.R. Robinson and K.H. Brink (New York: John Wiley & Sons Inc., 1998), 105–133.

46. R.W. Houghton and R.G. Fairbanks, "Water sources for Georges Bank," *Deep-Sea Res. II* 48 (2001): 95–114; S. Khatiwala, R.G. Fairbanks, and R. Houghton, "Freshwater sources to the coastal ocean off northeastern North America: evidence from H₂¹⁸O/H₂¹⁶O," *Journal of Geophysical Research* 104 (1999): 18,241–18,255.

FIG. 3.—Sections of temperature and salinity based on discrete data collected in April and September 2008, along the Halifax Line transect (shown in Fig. 2A). In winter the water column can be described by a simple two-layer system (A and B), while in summer surface warming causes a three-layer system to develop (C and D). The boundaries between water masses are shown schematically by the black dashed lines, however in the real ocean setting these boundaries need not lie along a constant depth.



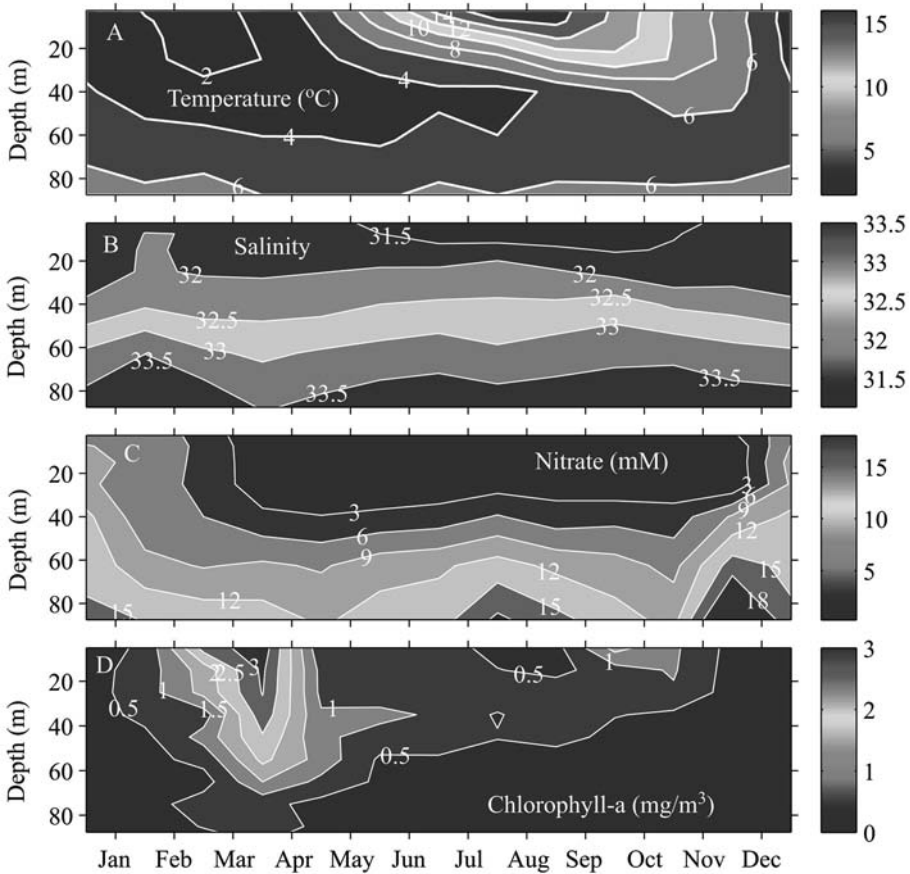
of a warm, shallow surface layer overlying the two-layer system.⁴⁷ Sections of temperature and salinity in early spring (April) and late summer (September) are shown in Fig. 3. In early spring (and winter), the upper 60 meters of the water column are well mixed and dominated by cold, relatively fresh water originating in the Gulf of St. Lawrence; underlying this is warmer, more saline, slope water (Fig. 3 and 4). In summer and autumn the water column is strongly stratified. The near-surface waters warm to greater than 16 °C forming a shallow surface layer, with the shelf water comprising a cold intermediate layer. The warmer, more saline slope water is present beneath the intermediate layer (Fig. 3 C, D and 4). In all seasons, the freshest waters are found near the surface and the coast, and the more saline slope waters found at depth and further offshore.

Most of the total alkalinity (TA) in seawater originates from the river input due to the weathering of (predominately carbonate) rocks on land.⁴⁸

47. Loder et al., n. 31 above.

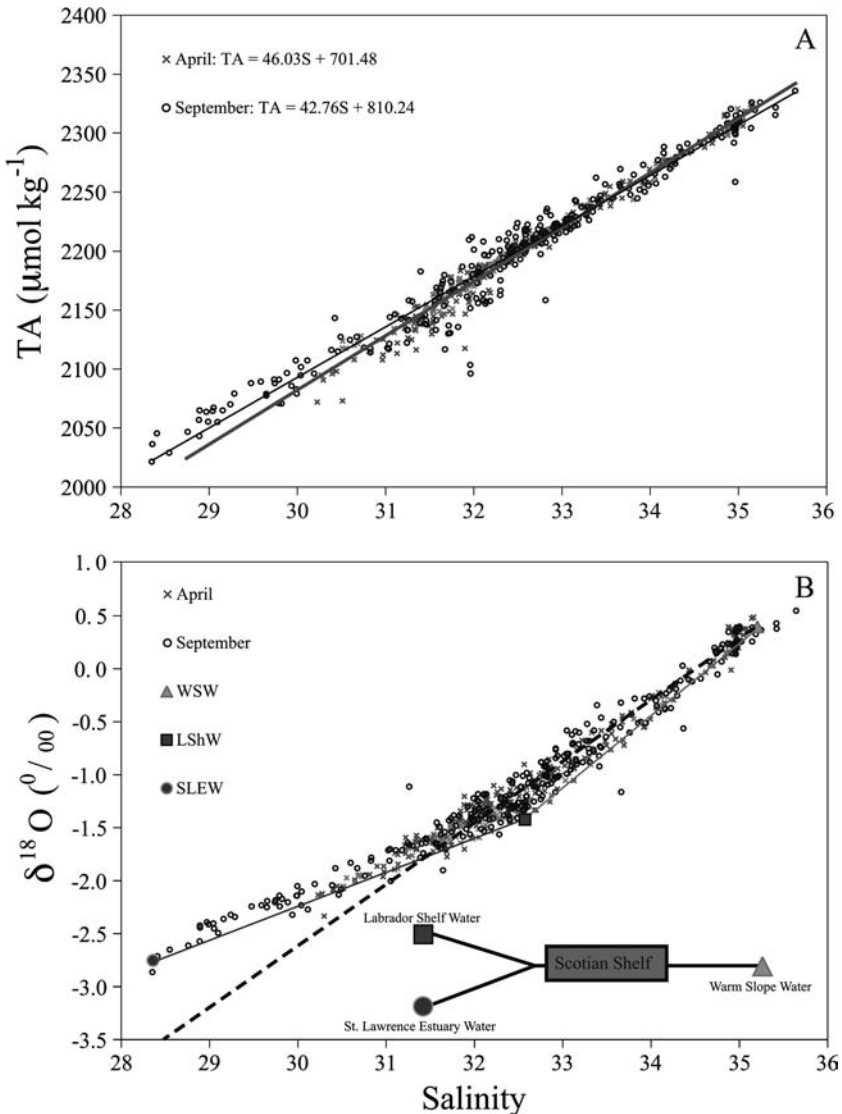
48. F.M.M. Morel and J.G. Hering, *Principles and Applications of Aquatic Chemistry* (New York: John Wiley & Sons Inc., 1993).

FIG. 4.—A climatology of (A) temperature, (B) salinity, (C) nitrate, and (D) chlorophyll-*a* concentration on the Scotian Shelf, based on historical archives from the Bedford Institute of Oceanography. This climatology demonstrates the coincidence of spring bloom and the nutrient depletion of the upper part of the water column in this area of the continental shelf. Figure redrawn from Shadwick et al., (2010) with permission from Elsevier.



The absolute value of TA in a given volume of seawater in the ocean therefore largely corresponds to the salinity of that water. There is a strong linear relationship between TA and salinity (Fig. 5A) on the Scotian Shelf. This would suggest a two end-member system in the region, with a less saline water mass from the Gulf of St. Lawrence mixing with a more saline, Gulf Stream influenced, water mass from the open ocean further offshore. There is a seasonal signal in this two end-member mixing relationship evident in the change in the slope and intercept of the linear fit to the TA and salinity data. This seasonality is investigated further by the application of oxygen isotope ($\delta^{18}\text{O}$) data.

FIG. 5.—(A) The relationship between total alkalinity (TA) and salinity on the Scotian Shelf based on discrete data collected in April (blue x) and September (open circles) 2008. The linear best-fit lines for spring ($n=419$, $r^2=0.97$, $p<0.001$) and autumn ($n=384$, $r^2=0.91$, $p<0.001$) are also given. (B) The relationship between $\delta^{18}\text{O}$ and salinity on the Scotian Shelf in spring (blue x) and autumn (open circles). A schematic representation of water mass composition on the Scotian Shelf is shown in the bottom right corner. At surface and intermediate depths SLEW and LShW mix, largely in the Gulf of St. Lawrence. Labrador Slope water is modified by mixing with warm, saline Gulf Stream influenced water to form WSW, which occupies the lower water column in the region. Seasonality in the contribution of SLEW reflects formation of sea ice in the St. Lawrence estuary.



There are few conservative water mass tracers that can be used in the ocean, and the oxygen isotope $\delta^{18}\text{O}$ of seawater is among them. Furthermore, this parameter allows fresh water from different sources (rivers, sea ice, and precipitation) to be distinguished. The relationship between $\delta^{18}\text{O}$ and salinity in the Scotian Shelf region is given in Fig. 5B. We identify three source waters on the Scotian Shelf: (1) Warm Slope Water (WSW) is Labrador Slope water modified by mixing with warm saline waters of Gulf Stream origin; (2) Labrador Shelf water (LShW) enters the Gulf of St. Lawrence, via the inner branch of the Labrador Current, at intermediate depth through the Strait of Belle Isle;⁴⁹ and (3) St. Lawrence Estuary Water (SLEW) which is strongly influenced by fresh water flowing out of the St. Lawrence River. The composition of the water in the Scotian Shelf region is a mixture of these three source waters (SLEW, LShW and WSW) with the magnitude of the contribution from SLEW varying seasonally (Fig. 5B), changing the slope of the relationship between TA and salinity in the region (Fig. 5A). In September, the Scotian Shelf receives the maximum discharge from the Gulf of St. Lawrence and the contribution from SLEW is also at a maximum. In contrast, in April the Scotian Shelf receives a much smaller contribution from SLEW due to the formation of sea ice in the Gulf of St. Lawrence in winter, and is more strongly influenced by LShW at this time (Fig. 5B). A typical value of glacial melt-water and Arctic river water in the Labrador Sea is $\delta^{18}\text{O} = -21\%$.⁵⁰ The black dashed line in Fig. 5B represents the mixing between WSW and Arctic river waters. The LShW falls to the right of this mixing line due to the influence of brine rejection during sea-ice formation, which increases salinity without changing the $\delta^{18}\text{O}$. Thus, while there is information to be gained from the relationship between TA and salinity on the Scotian Shelf, a more sensitive parameter is needed for a full description of the water masses in this region.

Biological Production

The North Atlantic spring phytoplankton bloom is an annually occurring, widespread biological event. As the days lengthen in the northern hemisphere spring, the increased availability of light and nutrients, which have accumulated over the winter, fuel the growth of phytoplankton in the surface ocean. This bloom begins north of the Sargasso Sea and moves northward through the Atlantic into the North Sea constituting a significant sink for atmospheric CO_2 .⁵¹ The magnitude, timing, and extent of this bloom vary from year

49. Khatiwala et al., n. 46 above.

50. *Id.*

51. D.A. Siegel, S.C. Doney and J.A. Yoder, "The North Atlantic spring phytoplankton bloom and Sverdrup's critical depth hypothesis," *Science* 296 (2002): 730–733.

to year.⁵² Chlorophyll-*a* fluorescence is often used as a proxy for phytoplankton biomass (Fig. 4).⁵³ During the spring bloom on the Scotian Shelf, which occurs with remarkable annual consistency near the first week of April, chlorophyll-*a* concentration increases nearly tenfold in a matter of days. This rapid increase in phytoplankton biomass utilizes the nutrients, which have accumulated in the subsurface as result of organic matter remineralization, or respiration, and are brought up to the surface. The spring bloom is dominated by large phytoplankton size-classes and is terminated by the exhaustion of nitrate and silicate.⁵⁴ The phytoplankton community on the Scotian Shelf is mainly comprised of diatom species, providing the main food source to bottom-dwelling filter feeders. On the Scotian Shelf the spring bloom is the dominant control on phytoplankton biomass, though the more moderate summer production also plays a role.⁵⁵ The spring bloom accounts for roughly one-third of the total annual primary production on the Scotian Shelf,⁵⁶ estimates of which range from 60 to 130 g C/m²/yr.⁽⁵⁷⁾ It represents the dominant source of primary productivity, setting the upper limit on organic matter export, production of higher trophic levels, and supply to benthic communities.⁵⁸ During the remainder of the year surface nitrate concentrations remain fairly low (Fig. 4) and smaller-sized phytoplankton dominate. Local vertical mixing, or upwelling, may re-supply nutrients to the surface layer in summer, and production continues through October.⁵⁹

52. For example, B.J.W. Greenan, B.D. Petrie, W.G. Harrison and P.M. Strain, "The onset and evolution of a spring bloom on the Scotian Shelf," *Limnology and Oceanography* 53 (2008): 1759–1775.

53. D.A. Kiefer, "Fluorescence properties of natural phytoplankton populations," *Marine Biology* 22 (1973): 263–269; P. Falkowski and D.A. Kiefer, "Chlorophyll *a* fluorescence in phytoplankton: relationship to photosynthesis and biomass," *Journal of Plankton Research* 7 (1985): 715–731.

54. L. Mousseau, L. Legendre and L. Fortier, "Dynamics of size-fractionated phytoplankton and trophic pathways on the Scotian Shelf and at the shelf break," *Aquatic Microbial Ecology* 10 (1996): 149–163.

55. E.H. Shadwick, H. Thomas, K. Azetsu-Scott, B.J.W. Greenan, E. Head and E. Horne, "Seasonal variability of dissolved inorganic carbon and surface water pCO₂ in the Scotian Shelf region of the Northwestern Atlantic," *Marine Chemistry* (2010) doi: 10.1016/j.marchem.2010.11.004

56. R.O. Fournier, J. Marra, R. Bohrer and M. Van Det, "Plankton dynamics and nutrient enrichment of the Scotian Shelf," *Journal of the Fisheries Research Board of Canada* 34 (1977): 1004–1018.

57. E.L. Mills and R.O. Fournier, "Fish production and the marine ecosystem on the Scotian Shelf, eastern Canada," *Marine Biology* 54 (1979): 101–108, Mousseau et al., n. 54 above.

58. R.W. Eppley, "Autotrophic production of particulate matter," in *Analysis of Marine Ecosystems*, ed. A.R. Longhurst, (New York: Academic Press, 1981), 343–361.

59. Shadwick et al., n. 55 above.

The North Atlantic Oscillation

The North Atlantic Oscillation (NAO) is a northern hemisphere atmospheric climate mode related to the difference in sea-level pressure (SLP) between the Icelandic Low and the Azores High.⁶⁰ The relative strengths and positions of these two systems vary from year to year, controlling the strength and position of the prevailing westerly winds. A large SLP difference between the two locations corresponds to a positive NAO index, a small SLP difference to a negative NAO index. The NAO is an index of the dominant atmospheric forcing over the North Atlantic Ocean influencing air temperature, wind, and precipitation. During positive phases of the NAO, the prevailing westerly winds become more intense and the North Atlantic storm track shifts to the north. This northward shift results in warmer, milder conditions over the western North Atlantic Ocean and along the east coast of North America and in northern Europe, and colder, stormier conditions over Greenland.⁶¹ During negative phases of the NAO the situation is reversed; the westerly winds diminish in intensity and the storm track is shifted to the south. This results in colder, stormier conditions in the western North Atlantic and over the eastern North American coast, warmer milder conditions over Greenland, and colder, drier conditions in northern Europe.⁶²

The NAO also impacts the circulation patterns of the North Atlantic Ocean. In negative phases of the NAO convection in the Labrador Sea becomes shallower, and volume transport by the Labrador Current increases. In contrast, during positive phases of the NAO, convection in the Labrador Sea is deeper and more intense, and transport by the shallow Labrador Current is decreased.⁶³ It has been shown that the NAO can influence hydrographic properties on the northeastern Atlantic continental shelf.⁶⁴ During periods of negative NAO index, relatively cold, fresh conditions are seen on the eastern Scotian Shelf and in the Gulf of St. Lawrence due to the increased transport of Labrador slope water to the region.⁶⁵ Over the last decade, the NAO index has generally been

60. D.W.J. Thompson and J.M. Wallace, "The Arctic Oscillation signature in the wintertime geopotential height and temperature fields," *Geophysical Research Letters* 25 (1998): 1297–1300; D.W.J. Thompson and J.M. Wallace, "Regional climate impacts of the northern hemisphere annular mode," *Science* 293 (2001): 85–89.

61. J.W. Hurrell, "Decadal trends in the North Atlantic Oscillation: Regional temperatures and precipitation," *Science* 269 (1995): 676–679; R. Dickson, J. Lazier, J. Meincke, P. Rhines and J. Swift, "Long-term coordinated changes in the convective activity of the North Atlantic," *Progress in Oceanography* 38 (1996): 241–295.

62. *Id.*

63. B. Dickson, "From the Labrador Sea to global change," *Nature* 386 (1997): 649–650; R.G. Curry, M.S. McCartney and T.M. Joyce, "Oceanic transport of sub-polar climate signals to mid-depth subtropical waters," *Nature* 388 (1998): 575–577.

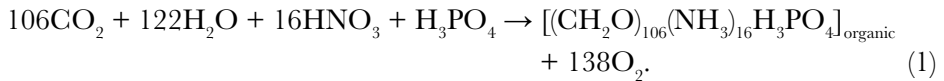
64. B. Petrie, "Does the North Atlantic Oscillation affect hydrographic properties on the Canadian Atlantic continental shelf?," *Atmosphere-Ocean* 45 (2007): 141–151.

65. E.H. Shadwick, H. Thomas, A. Comeau, S.E. Craig, C.W. Hunt and J.E. Salisbury, "Air-Sea CO₂ fluxes on the Scotian Shelf: seasonal to multi-annual variability," *Biogeosciences* 7 (2010): 3851–3867.

negative or near-neutral; the impact on the carbon system on the Scotian Shelf as a potential consequence of the NAO will be discussed in more detail.⁶⁶

THE CO₂ SYSTEM ON THE SCOTIAN SHELF

It is useful to describe processes affecting the carbonate system in seawater with respect to the associated changes in dissolved inorganic carbon (DIC) and TA, which are shown schematically in Fig. 6. With respect to the inorganic carbon system, photosynthesis and aerobic respiration are the dominant biological processes. Photosynthesis by algae can be described by the following equation:



Photosynthesis produces, on average, organic matter with carbon and nutrients in Redfield ratio,⁶⁷ i.e., C:N:P = 106:16:1. Photosynthesis therefore reduces DIC, as 106 moles of CO₂ per mole of phosphate (H₃PO₄) are consumed in the production of organic matter. There is a modest increase in TA (16 moles) by photosynthesis due to the consumption of nitrate (NO₃⁻).⁶⁸ Respiration converts organic matter to inorganic carbon (and nutrients), and DIC is increased, with a corresponding modest decrease in TA. The formation of calcium carbonate (CaCO₃) reduces both DIC and TA in the ratio of 1:2, while dissolution has the inverse effect. The uptake of atmospheric CO₂ increases DIC, but TA remains unchanged since the charge balance in the system has not been affected. Similarly, the out-gassing of CO₂ from the ocean decreases DIC without changing TA.⁶⁹

As discussed above, the formation and dissolution of calcium carbonate (CaCO₃) play an important role in the inorganic carbon system in seawater. A determining factor with respect to the formation and dissolution of CaCO₃ is the calcium carbonate saturation state of seawater. The CaCO₃ saturation state, Ω, is expressed as:

$$\Omega = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K_{\text{sp}}^* \quad (2)$$

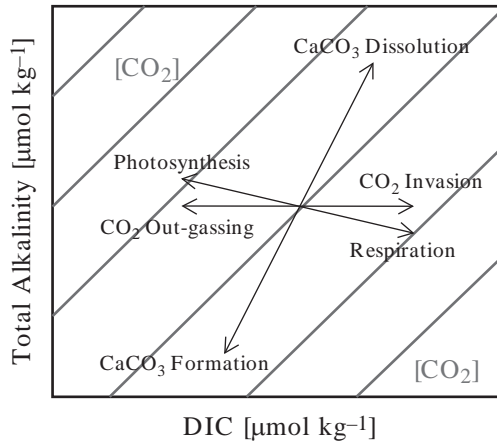
66. See subsection below "Interannual variability."

67. A.C. Redfield, B.H. Ketchum and F.A. Richards, "The influence of organisms on the composition of sea-water," in *The Composition of Seawater. Comparative and Descriptive Oceanography. The Sea: Ideas and Observations on Progress in the Study of the Seas*, ed. M.N. Hill (New York: Interscience Publishers, 1963), 26–77.

68. For example, J.C. Goldman and P.G. Brewer, "Effect of nitrogen source and growth rate on phytoplankton-mediated changes in alkalinity," *Limnology and Oceanography* 25 (1980): 352–357.

69. R.E. Zeebe and D. Wolf-Gladrow, *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes* (Amsterdam: Elsevier, 2001).

FIG. 6.—The effect of various processes on DIC and TA. The solid diagonal lines indicate levels of constant dissolved CO₂, increasing from the top left to the bottom right. The invasion/release of CO₂ increases/decreases the concentration of DIC, while TA remains unchanged. Photosynthesis/respiration and the formation/dissolution of CaCO₃ will alter the concentrations of CO₂, DIC, and TA.



where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentrations of Ca^{2+} and CO_3^{2-} in seawater, respectively, and K_{sp}^* is the stoichiometric solubility product at in-situ temperature, salinity, and pressure.⁷⁰ Due to the quasi-conservative behavior of calcium in the ocean, variations in $[Ca^{2+}]$ are relatively small and closely related to changes in salinity;⁷¹ the $CaCO_3$ saturation state is therefore more strongly influenced by the carbonate ion concentration, which will be discussed in more detail.⁷² Values of $\Omega > 1$ correspond to supersaturation, permitting formation of $CaCO_3$ and values of $\Omega < 1$ correspond to undersaturation, permitting dissolution of $CaCO_3$.

The concentration of CO_2 is related to the partial pressure (pCO_2) by Henry's Law:

$$[CO_2] = \alpha pCO_2, \tag{3}$$

where α is the Henry constant, or coefficient of solubility,⁷³ which depends mainly on temperature, and to a lesser degree on salinity. Water temperature exerts a strong control on pCO_2 (Fig. 7), and the relationship between

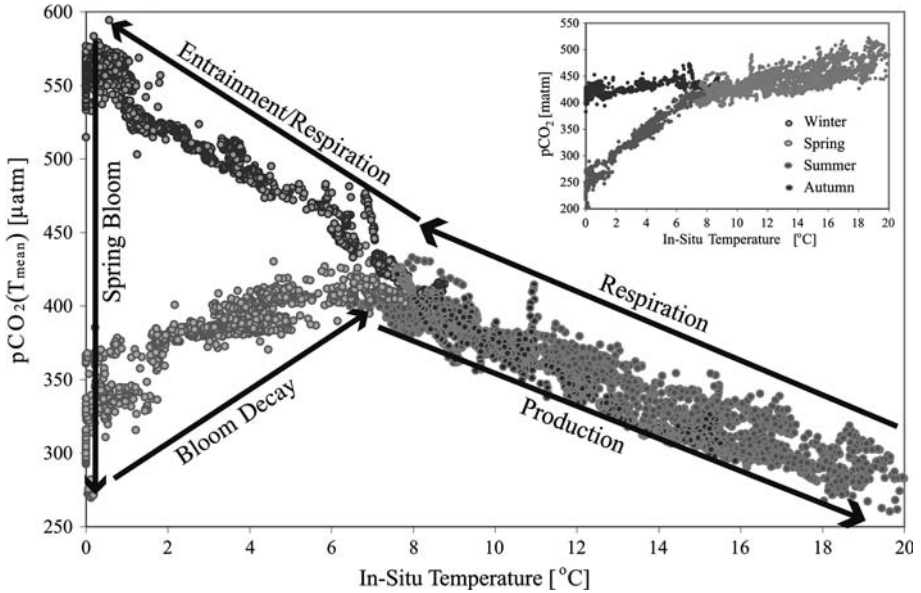
70. *Id.*

71. *Id.*

72. See section below on "Ocean Acidification."

73. R.F. Weiss, "Carbon dioxide in water and seawater: The solubility of a non-ideal gas," *Marine Chemistry* 2 (1974): 203–215.

FIG. 7.—Values of surface water $p\text{CO}_2$, from CARIOCA measurements at station HL2, are normalized to a constant, annual mean surface temperature ($T_{\text{mean}} = 7.0^\circ\text{C}$), and plotted versus their observed temperature. Seasons are distinguished by color. The dominant mechanisms acting in each of the seasons are shown schematically by the black arrow. Inset: surface $p\text{CO}_2$ is plotted against in-situ temperature, with seasons distinguished by color. Figure follows Shadwick et al., (2010).



the two variables is well understood. For a 1°C change in temperature we expect a 4 percent change in $p\text{CO}_2$.⁷⁴ In other words, for 1°C of warming, at a mean $p\text{CO}_2$ of $400\ \mu\text{atm}$, we expect an increase in of $16\ \mu\text{atm}$. An exchange of CO_2 between the atmosphere and the ocean occurs when there is a gradient in CO_2 across the air-sea interface. The mass transfer of CO_2 is largely driven by the concentration difference between the atmosphere and the sea surface, and the turbulence at the air-sea interface. The air-sea exchange of CO_2 is computed using the following equation:

$$F_{\text{CO}_2} = k \alpha \Delta p\text{CO}_2 \quad (4)$$

where F_{CO_2} ($\text{mol}/\text{m}^2/\text{s}$) is the air-sea CO_2 flux, k (m/s) is the gas transfer velocity parameterized as a function of wind speed, α ($\text{mol}/\text{atm}/\text{m}^3$) is the coefficient of

74. T. Takahashi, S.C. Sutherland, C. Sweeney, A. Poisson, N. Metzl, B. Tillbrook, N. Bates, R. Wanninkhof, R.A. Feely, C. Sabine, J. Olafsson and Y. Nojiri, "Global air-sea CO_2 flux based on climatological surface ocean $p\text{CO}_2$, and seasonal biological and temperature effects," *Deep-Sea Res. II* 49 (2002): 1601–1622.

solubility, and $\Delta p\text{CO}_2$ is the gradient of $p\text{CO}_2$ between the sea surface and the atmosphere (i.e., $\Delta p\text{CO}_2 = p\text{CO}_2^{\text{sea}} - p\text{CO}_2^{\text{air}}$). The gas transfer velocity was computed with the formulation of Wanninkhof for short-term winds and hourly wind speeds measured at the Sable Island Meteorological Station.⁷⁵

Seasonal Variations in DIC and $p\text{CO}_2$

During the winter, the surface waters of the Scotian Shelf are quite cold (near 0°C), and the partial pressure of CO_2 ($p\text{CO}_2$) is relatively constant and supersaturated with respect to atmospheric CO_2 with values of roughly $420\ \mu\text{atm}$ (Fig. 7). The surface DIC concentration is at its maximum in winter due in part to respiration of organic matter, but mainly due to the delivery of carbon-rich water from below (Fig. 8). In winter, the mixed-layer deepens due to wind forcing, and waters with higher concentrations of inorganic carbon and nutrients are delivered to the surface layer. With the onset of the spring bloom, the surface waters of the Scotian Shelf rapidly become undersaturated with respect to atmospheric CO_2 . In 2008, the surface $p\text{CO}_2$ decreased from $430\ \mu\text{atm}$ to $250\ \mu\text{atm}$ over a period of nine days (Fig. 9). There is a corresponding decrease in DIC in the surface layer between winter and spring due to the uptake of inorganic carbon to fuel the phytoplankton bloom. Heterotrophic organisms graze much of the algae produced by the bloom. However, some of the organic matter produced at the surface will accumulate, become heavy, and sink out of the surface layer. The remineralization (or respiration) of the organic matter exported to the subsurface layer increases the concentration of DIC in this layer. The strength of the bloom is largely determined by the winter pre-conditioning of the system. Strong winter winds and a deep mixed-layer supply more inorganic nutrients to fuel the spring bloom than a shallower, more poorly mixed water column. The spring bloom occurs when the water is still near the minimum winter temperature (Fig. 7) allowing the competing effects of thermodynamics (warming increases $p\text{CO}_2$) and biology (photosynthesis decreases $p\text{CO}_2$) to be distinguished. The effect of temperature on $p\text{CO}_2$ is well understood, and an empirical correction to remove the effect of temperature has been defined:⁷⁶

$$p\text{CO}_2(T_{\text{mean}}) = p\text{CO}_2(\text{obs})[\exp(0.0423(T_{\text{mean}} - T_{\text{obs}}))] \quad (4)$$

where T_{mean} is the annual mean sea-surface temperature, and ‘obs’ refers to the observed, or in-situ temperature and $p\text{CO}_2(\text{obs})$ the in-situ $p\text{CO}_2$. The correction of $p\text{CO}_2$ to the annual mean temperature allows the effects of

75. R. Wanninkhof, “Relationships between wind speed and gas exchange over the ocean,” *Journal of Geophysical Research* 97 (1992): 7373–7382; see also “Data and Methods.”

76. Takahashi et al., n. 74 above.

FIG. 8.—Sections of dissolved inorganic carbon (DIC) and total alkalinity (TA) concentration along the Halifax Line transect (shown in Fig. 2A) based on discrete data collected in (A and C) April and (B and D) September 2008.

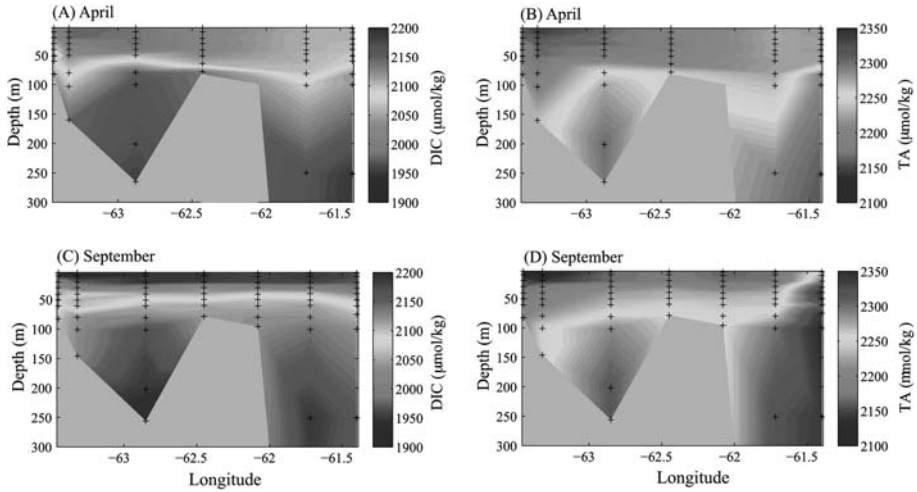
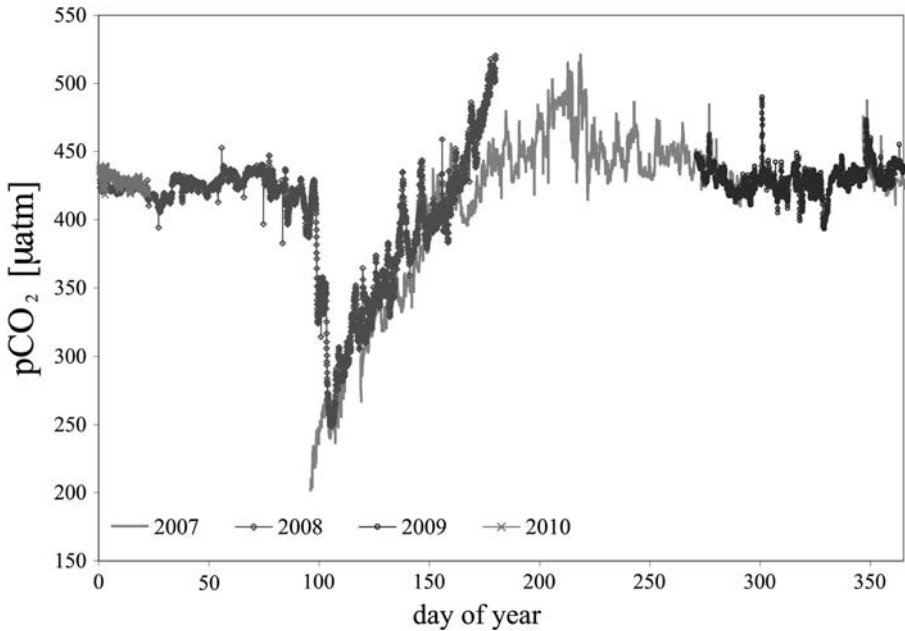
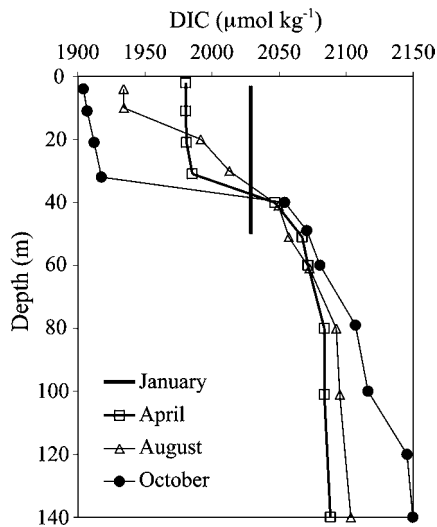


FIG. 9.—Hourly surface water $p\text{CO}_2$ measured by the CARIOCA at station HL2 from 2007 to 2010. The annual cycle is driven by the spring phytoplankton bloom, the summer warming of the surface waters, and the late summer biological production, and shows very little interannual variability over the measurement period.



non-temperature dependent processes to be clearly seen. In other words, by removing the effect of temperature from $p\text{CO}_2$, the dominant mechanisms such as photosynthesis or entrainment, acting, for example, over a particular season, may emerge. The temperature corrected $p\text{CO}_2$ is plotted against in-situ temperature, with the seasons distinguished by color, in Fig. 7. It can clearly be seen that the spring bloom occurs at the annual temperature minimum and results in a large reduction of $p\text{CO}_2$. The decay of this bloom is coincident with the warming of the surface waters in late spring, and the $p\text{CO}_2(T_{\text{mean}})$ increases as photosynthesis ceases and respiration dominates in the surface waters. Over the summer, while the waters warm, $p\text{CO}_2(T_{\text{mean}})$ continues to decrease indicating the uptake of CO_2 by biological processes outside of the dominant spring bloom period. Vertical export of this material fuels the respiration in the subsurface and increases the subsurface DIC concentration between spring and summer (Fig. 10). This late summer production reduces the temperature-corrected $p\text{CO}_2$ by almost $100 \mu\text{atm}$, making a significant contribution to the annual biological production in the region.⁷⁷ In autumn, the surface waters cool and there is an increase in $p\text{CO}_2(T_{\text{mean}})$ when the surface waters are dominated by respiration of the organic matter supplied by the late summer production. In autumn, surface DIC concentrations are at the annual minimum due partly to the uptake of CO_2 by biological processes through the spring and summer, but also as a result of

FIG. 10.—Seasonal profiles of DIC at station HL2 in 2008.



77. Shadwick et al., n. 55 above.

dilution of DIC due to the delivery of fresher water from the Gulf St. Lawrence. The autumn subsurface DIC concentration corresponds to the annual maximum due to the remineralization of the accumulated organic matter produced in the surface layer over the spring and summer. Most of this respired material remains in the subsurface through the summer and early autumn because of the relatively strong stratification over this period, which inhibits vertical mixing (Fig. 4). Later in autumn, the frequency and magnitude of storms in the region is increased, breaking down the surface stratification and allowing the carbon-rich subsurface waters to be entrained into the surface layer. In winter, convection also forces DIC-rich water from the subsurface into the surface layer. The autumn and winter values of $p\text{CO}_2(T_{\text{mean}})$ are enhanced by roughly 100 μatm , due to the combined effects of respiration and mixing, while over the same period the water temperature decreases to the annual minimum.

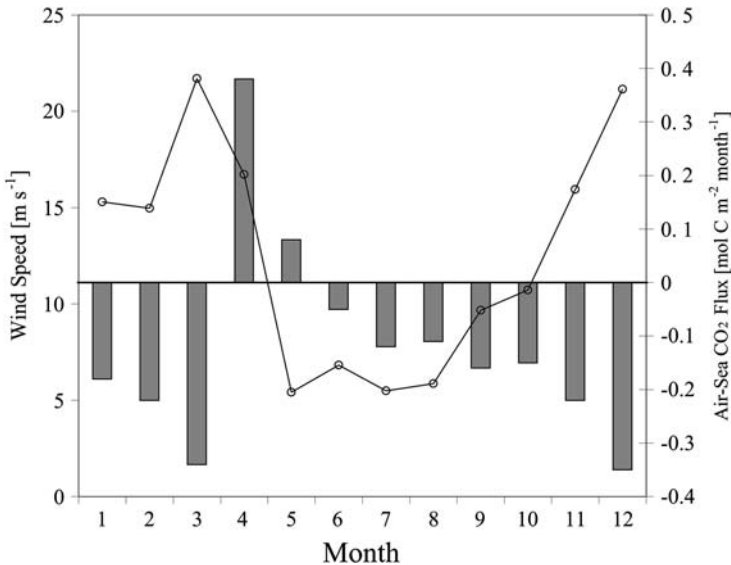
Air-Sea CO_2 Fluxes

As discussed in the preceding section, the transfer of CO_2 from the atmosphere to the ocean is largely controlled by the gradient in CO_2 concentration between the two reservoirs ($\Delta p\text{CO}_2$) and the turbulence at the air-sea interface.⁷⁸ The turbulence reflects the sea-state, and wind speed, both in-situ, and in the preceding days and hours, and swell, and breaking waves may also contribute. In general, however, wind speed exerts the primary control on sea-state and turbulence. The annual cycle of integrated monthly wind speed measured at the Sable Island Meteorological Station⁷⁹ and the annual cycle of monthly air-sea CO_2 fluxes measured at station HL2, roughly 30 km offshore from Halifax, are given in Fig. 11. There is a correlation between wind speed and (the magnitude of the) air-sea CO_2 flux. In winter, the waters are supersaturated with respect to atmospheric CO_2 , thus the $\Delta p\text{CO}_2$ is positive, and there is an outgassing of CO_2 to the atmosphere. Over the same period the region experiences high winds which enhance the outgassing of CO_2 . In contrast, in April the spring bloom draws down DIC, and the surface waters are undersaturated with respect to the atmosphere (i.e., $\Delta p\text{CO}_2 < 0$). The wind speed is still relatively high in early spring, and there is a strong uptake of CO_2 by the ocean. The much smaller uptake observed in May is primarily due to the decrease in $\Delta p\text{CO}_2$ by the decay of the spring bloom and to a reduction in wind speed (Fig. 11). Over the summer, the winds are much weaker, and although the surface waters are supersaturated with respect to atmospheric CO_2 from June onward, the outgassing is modest compared to the winter season. The magnitude of the flux increases from October due to both the increase in wind speed and the positive evolution of $\Delta p\text{CO}_2$

78. See Equation 4.

79. Environment Canada, available online: <<http://climate.weatheroffice.gc.ca>>.

FIG. 11.—The annual cycle of monthly wind speed (m/s) (line) measured at the Sable Island Meteorological Station, and the air-sea CO₂ flux (mol C/m²/month) (bars) for the year 2008 at station HL2.



from the intrusion of CO₂-rich waters from the subsurface and the cessation of biological production in the surface layer.

DISCUSSION

Trophic Status and Atmospheric CO₂

Oceanic metabolism is an important concept in defining particular regions of the ocean as potential sinks for atmospheric CO₂.⁸⁰ The metabolism, or trophic status, of a marine system, or region, is often described with respect to the production or consumption of organic matter.⁸¹ Systems are defined as autotrophic if there is a net production of organic matter and a net depletion of inorganic carbon and nutrients, or, in other words, if gross primary production exceeds respiration. These systems may potentially export this excess organic carbon.

80. S.V. Smith and J.T. Hollibaugh, "Coastal metabolism and the ocean organic carbon balance," *Reviews of Geophysics* 31 (1993): 75–89.

81. *Id.*; Gattuso, n. 20; H. Thomas, Y. Bozec, H.J.W. de Baar, K. Elkalay, M. Frankignoulle, L.-S. Schiettecatte, G. Kattner and A.V. Borges, "The Carbon Budget of the North Sea," *Biogeosciences* 2 (2005): 87–96.

The reverse situation defines heterotrophic systems; in this case there is a net consumption of organic matter and a net production, or release, of inorganic carbon and nutrients with respiration dominating gross primary production. Ideally, the atmosphere fuels the CO₂ demand of autotrophic systems with rivers also potentially acting as sources of inorganic carbon.⁸² Depending on the initial $\Delta p\text{CO}_2$ state of these systems, they may exhibit enhanced CO₂ uptake ($p\text{CO}_2^{\text{ocean}} < p\text{CO}_2^{\text{atm}}$), or diminished outgassing of CO₂ to the atmosphere ($p\text{CO}_2^{\text{ocean}} > p\text{CO}_2^{\text{atm}}$). Heterotrophic systems require a source of organic carbon to fuel respiration, and in supersaturated conditions will exhibit enhanced outgassing of CO₂ to the atmosphere, while in undersaturated waters CO₂ uptake will be reduced.⁸³ Therefore, autotrophic systems, though production exceeds respiration, do not necessarily act as sinks for atmospheric CO₂, and respiration-dominated heterotrophic systems do not necessarily release CO₂ to the atmosphere. The initial conditions of the system, with respect to surface pCO₂, condition this uptake/release. The North Sea, for example, is an overall heterotrophic system that acts as a sink for atmospheric CO₂ over the annual scale.⁸⁴ A more general classification would be seasonally stratified systems such as the Bay of Biscay,⁸⁵ or permanently stratified systems such as the Baltic Sea.⁸⁶ The opposite situation, autotrophic systems acting as sources for atmospheric CO₂, is often found in upwelling systems where the intrusion of DIC-rich subsurface water into the surface layer maintains CO₂ supersaturation despite the large production (and export) of organic matter in these systems. The Scotian Shelf acts as an upwelling system in this respect. There is a significant production of organic matter during the spring bloom and also throughout the summer, and the surface waters are found to be autotrophic.⁸⁷ However, the combined effect of summer warming and the injection of high-carbon subsurface water through wind-driven vertical mixing or upwelling in autumn and winter, maintains high surface pCO₂, and the region therefore acts as a net source of CO₂ to the atmosphere.⁸⁸

Interannual Variability

Spatial and temporal variability in the coastal ocean is generally much higher than in the open ocean. Interannual variability in the timing, duration, and

82. Thomas et al., n. 81 above.

83. *Id.*

84. H.J. Lenhart, J. Pätsch, W. Kühn, A. Moll and T. Pohlmann, "Investigation on the trophic state of the North Sea for three years (1994–1996) simulated with the ecosystem model ERSEM – the role of a sharp NAOI decline," *Biogeosciences Discuss.* 1 (2004): 725–753; Thomas et al., n. 81 above.

85. Frankignoulle and Borges, n. 25 above.

86. Thomas and Schneider, n. 25 above.

87. Shadwick, n. 55 above.

88. *Id.*

spatial extent of the spring bloom on the Scotian Shelf has been recorded.⁸⁹ The effects of this variability extend beyond the bloom period and will certainly influence the CO₂ system in this region.⁹⁰ Highly temporally resolved measurements from a single location, roughly 30 km offshore from Halifax (Fig. 1 and 9) indicate that the annual cycle of pCO₂ follows the same general trend over the observation period with the spring bloom (Fig. 9), the summer warming, and the autumn and winter mixing dominating. However, observations from 2010 indicate that the spring bloom occurred nearly 3 weeks earlier than in 2007 and 2008. Furthermore, the sea-surface temperature was nearly 3 °C warmer at the beginning of April in 2010 compared to both 2007 and 2008. The full water column sampling of DIC and TA collected on consecutive April and September cruises show the same general patterns. The impact of photosynthesis, the delivery of the fresh water from the Gulf of St. Lawrence, and seasonal warming/cooling, can be seen in the surface waters, while the build up of DIC reflects the corresponding biological activity in the subsurface (Fig. 8). However, both the pCO₂ and the DIC and TA measurements are based on the years 2006 through 2008, and the time-series is likely not long enough for a significant trend to emerge. Interannual variability on the Scotian Shelf is therefore investigated using ten years of sea-surface temperature data obtained by remote sensing.⁹¹

Monthly sea-surface temperature (SST) anomaly for the central Scotian Shelf from 1999 to 2008 is plotted in Fig. 12. The mean seasonal cycle of SST was computed using the mean value for each month over the ten-year period (i.e., mean of all January values, mean of all February values, etc.). The SST anomaly is defined as the deviation from the mean seasonal cycle. The SST anomaly indicates a cooling of 0.13 °C per year, or 1.3 °C over the decade.⁹² As discussed in a previous section, this cooling may be associated with the enhanced delivery of cold water from the Labrador Sea to the Scotian Shelf and may reflect the local expression of the NAO.⁹³ Since temperature exerts a strong control on surface water pCO₂, and consequently ΔpCO_2 , this decadal trend towards colder water will have consequences for the inorganic carbon system and air-sea CO₂ fluxes on the Scotian Shelf. A cooling of 1.3 °C over ten years would result in a decrease in ΔpCO_2 of roughly 22 μatm over the same period, using the 4 percent change in pCO₂ for a 1 °C change in temperature, and a mean value of pCO₂ = 420 μatm . This decrease in ΔpCO_2 , on the order of 20 μatm over the decade, has a non-negligible (weakening) effect on the outgassing of CO₂ to the atmosphere, driving the system towards uptake. It has been

89. Greenan et al., n. 52 above.

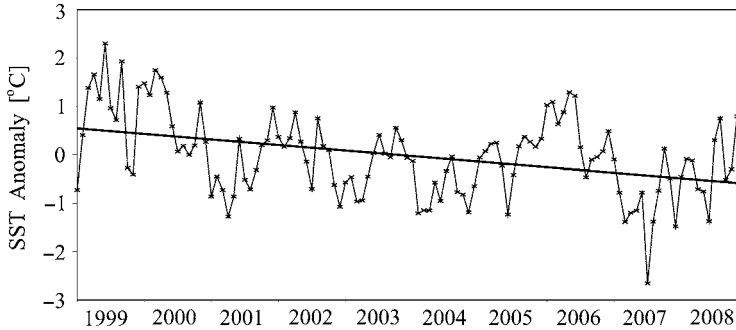
90. Shadwick et al., n. 65 above.

91. The SST data was acquired from the Pathfinder AVHRR equal-area 9-km best-SST data product or a 2° by 2° box in the central Scotian Shelf.

92. Shadwick et al., n. 65 above.

93. Petrie, n. 64 above.

FIG. 12.—Monthly sea-surface temperature anomaly for the central Scotian Shelf from 1999 to 2008.



suggested, based on the results of a modeling study in the region,⁹⁴ that interannual variability in air-sea CO₂ flux on the eastern North American continental shelf is due in part to NAO forcing. Warming between (low NAO) 1985 and (high NAO) 1990 has been proposed as the cause of weaker CO₂ uptake in the Gulf of Maine; this interpretation is in agreement with our finding that the decadal cooling on the Scotian Shelf has driven the system towards stronger uptake.⁹⁵

Ocean Acidification

As described briefly above, the rise in atmospheric CO₂ due to fossil fuel emissions is partially offset by the oceans' uptake of CO₂.⁹⁶ As CO₂ dissolves in seawater, the pH is reduced, making the water more acidic; this process has recently been coined 'ocean acidification'.⁹⁷ During the 20th century increasing concentrations of atmospheric CO₂ have decreased the surface ocean pH by 0.1 units.⁹⁸ To the best of our knowledge, the ocean has never experienced such a rapid acidification.⁹⁹ Should CO₂ concentration continue to rise, by the end of this

94. M. Previdi, K. Fennel, J. Wilkin and D. Haidvogel, "Interannual variability in atmospheric CO₂ uptake on the northeast U.S. continental shelf," *Journal of Geophysical Research* 114 (2009): G04003.

95. Shadwick et al., n. 65 above.

96. Sabine et al., n. 16 above.

97. K. Caldeira and M.E. Wickett, "Oceanography: Anthropogenic carbon and ocean pH," *Nature* 425 (2003): 365, Orr et al., n. 8 above.

98. O. Hoegh-Guldberg et al., "Coral Reefs under Rapid Climate Change and Ocean Acidification," *Science* 318 (2007): 1737–1742.

99. Caldeira and Wickett, n. 97 above.

century, changes in surface ocean pH that are greater in magnitude and also faster than those experienced during the transitions from glacial to interglacial periods may occur.¹⁰⁰ The reaction between CO₂ and DIC in seawater reduces the availability of carbonate ions; coincident with the 0.1 unit decrease in pH is a depletion of seawater carbonate (CO₃²⁻) concentrations by roughly 30 μmol/kg.¹⁰¹ Acidification will directly impact a wide range of marine organisms that build shells from calcium carbonate, from planktonic coccolithophores, to mollusks, to shallow-water and deep-sea corals. Aragonite is the dominant crystalline form of calcium carbonate deposited in the skeletons of deep-sea corals. Experimental studies have shown that increasing seawater CO₂ decreases coral calcification and growth by the inhibition of aragonite formation as carbonate ion concentrations decrease.¹⁰² A change in carbonate ion concentration results in a proportional change in the aragonite saturation state (Ω_{ar}) such that as ocean acidification continues, surface ocean Ω_{ar} values will decline. In regions where $\Omega_{\text{ar}} > 1.0$, the formation of skeletons and shells is possible. Conversely, if $\Omega_{\text{ar}} < 1.0$, the water is corrosive and the dissolution of aragonite shells can occur.

The average surface ocean pH is roughly 8.1; on the Scotian Shelf the surface values are slightly above this global mean. The seasonal profiles of Ω_{ar} do not indicate widespread conditions of undersaturation, however, the saturation state is relatively low in this region (Fig. 13). As in the case of pCO₂ and DIC, the limited time-series of data presented here does not allow a longer-term trend to be distinguished. The decadal decrease in SST and corresponding decrease in ΔpCO₂ drives the system on the Scotian Shelf towards greater uptake of CO₂ and consequently lower pH, adding complexity to any observed trend in acidification in this region. In April, the surface water pH and Ω_{ar} are relatively high due to the uptake of CO₂ by photosynthesis. However, at a depth of 150 to 200 m in April, Ω_{ar} approaches undersaturation in the relatively high pCO₂ near-shore waters (Fig. 13). Although much of the acidic character of these subsurface waters is the natural result of seasonal respiration at intermediate depth, the ocean, and the North Atlantic in particular, continues to accumulate anthropogenic CO₂.¹⁰³ Upwelling is a common physical feature on the Scotian Shelf.¹⁰⁴ This process brings high-carbon, low Ω_{ar} waters to the surface and exposes coastal organisms living on or near the seafloor to less saturated waters. Using the annual average sea-surface temperature ($\text{SST}_{\text{avg}} = 7^\circ\text{C}$), sea-surface salinity

100. P.N. Pearson and M.R. Palmer, "Atmospheric carbon dioxide concentrations over the past 60 million years," *Nature* 406 (2000): 695–699.

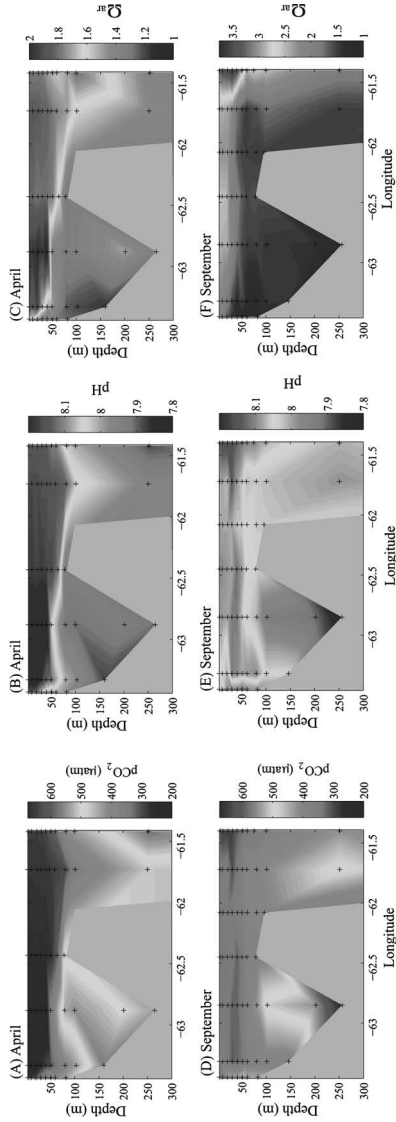
101. Hoegh-Guldberg, see n. 98 above.

102. J.A. Kleypas and C. Langdon, "Coral reefs and changing seawater chemistry," in *Coral Reefs and Climate Change: Science and Management*, ed. J.T. Phinney, O. Hoegh-Guldberg, J. Kleypas, W. Skirving and A. Strong, AGU Monograph Series, Coastal and Estuarine Studies 61 (2006): 73–110.

103. Sabine et al., n. 16 above.

104. Petrie et al., n. 35 above.

FIG. 13.—Sections of $p\text{CO}_2$, pH, and Ω_{ar} along the Halifax Line transect in April (top panels) and September (bottom panels) 2008. These values are computed from discrete measurements of DIC and TA.



($SSS_{avg} = 30.9$), surface TA ($TA_{avg} = 2150 \mu\text{mol/kg}$), surface DIC ($DIC_{avg} = 1950 \mu\text{mol/kg}$), and surface $p\text{CO}_2$ ($p\text{CO}_2(\text{avg}) = 420 \mu\text{atm}$), the average annual surface aragonite saturation state is $\Omega_{ar} = 1.48$. If we assume that the surface waters of the Scotian Shelf equilibrate with the atmosphere with respect to the concentration of CO_2 , the aragonite saturation state in the surface waters will reach aragonite undersaturation when the atmospheric concentration of CO_2 rises above $675 \mu\text{atm}$, or 1.7 times the current level of $390 \mu\text{atm}$. According to the model estimates of the Intergovernmental Panel on Climate Change (IPCC), under a variety of emission strategies, atmospheric emissions will reach $675 \mu\text{atm}$ between 2080 and 2100.¹⁰⁵

It has been suggested that upwelling could potentially magnify the effects of acidification.¹⁰⁶ However, we might consider this point from the opposite side: waters from the deep ocean are presently (naturally) acidified due to the remineralization of organic matter, which produces CO_2 and lowers pH. These waters could be considered the least vulnerable to the effects of acidification since their natural range of pH is low. On the other hand, coastal ecosystems in areas which do not experience episodic upwelling, and areas influenced by rivers could be considered most vulnerable due to the direct influence of atmospheric CO_2 , potentially shifting these systems toward undersaturation with respect to carbonate minerals. This is in contrast to upwelling waters, which already reveal undersaturation (i.e., $\Omega_{ar} < 1$). Further complicating the understanding of the role of ocean acidification is the role of natural variability occurring over multi-annual time scales. For example, the North Atlantic Ocean sink for CO_2 has weakened over the last decade; this change in CO_2 uptake, and consequently in surface ocean pH, has been linked to the large scale atmospheric and ocean forcing related to the NAO.¹⁰⁷ Similarly, the wind-driven upwelling in the Southern Ocean, which brings CO_2 -rich waters to the surface and results in a flux of CO_2 to the atmosphere, is influenced by multi-annual variability related to the Southern Annular Mode, and some regions are found to act as CO_2 sinks, decreasing the surface pH, during weak wind regimes.¹⁰⁸ Thus, the vulnerability

105. IPCC Synthesis Report, "Climate Change 2001: A contribution of working groups I, II and III to the 3rd Assessment Report of the Intergovernmental Panel on Climate Change," ed. R.T. Watson and the Core Writing Team (Cambridge: Cambridge University Press, 2001).

106. R.A. Feely, C.L. Sabine, J.M. Hernandez-Ayon, D. Ianson, B. Hales, "Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf," *Science* 320 (2008): 1490–1492.

107. H. Thomas, A.E.F. Prowe, I.D. Lima, S.C. Doney, R. Wanninkhof, R.J. Greatbatch, U. Schuster and A. Corbiere, "Changes in the North Atlantic Oscillation influence CO_2 uptake in the North Atlantic Ocean over the past 2 decades," *Global Biogeochemical Cycles* 22 (2008): GB4027, doi:10.1029/2007GB003167.

108. A.V. Borges, B. Tilbrook, N. Metzl, A. Lenton, and B. Delille, "Inter-annual variability of the carbon dioxide ocean sink south of Tasmania," *Biogeosciences* 5 (2008): 141–155.

of a particular ocean system to increased absorption of CO_2 , and consequently lower pH, will strongly depend not only on the present-day CO_2 uptake (or release) and the anthropogenic increases in atmospheric CO_2 , but also on the processes controlling natural variability, which can be significant. These processes may be particularly important in the coastal zone since it is influenced not only by the atmosphere, but also by rivers, sediments, and the adjacent open ocean depending on the timescale of interest.¹⁰⁹ In some coastal systems the effects of eutrophication may be more significant than those related to ocean acidification.¹¹⁰ The need to identify small changes in a spatially and temporally variable system highlights the importance of understanding the baseline conditions in coastal systems such that trends due to anthropogenic forcing may be understood over all relevant timescales.

CONCLUSION

The coastal ocean is vulnerable to anthropogenic activities occurring on land and in the atmosphere since it receives fresh water, nutrient and sedimentary inputs from the coast. These coastal regions play an important role in the absorption of atmospheric CO_2 , as well as supplying essential food for human consumption. The work presented here provides a baseline assessment of the CO_2 system in the Scotian Shelf region and a quantification of the drivers of seasonal and interannual variability. This region is strongly influenced by atmospheric forcing through the North Atlantic Oscillation and exhibits significant interannual variability as a result. This natural variability has the potential to mask anthropogenic effects such as the longer-term trend of declining pH as a result of increased uptake of atmospheric CO_2 . This research highlights the necessity of long-term monitoring programs to assess the current state of our oceans and predict their response to change.

The global realization that societal dependence on fossil fuels has a profound influence on the health of our planet is leading to advancements in our understanding of natural systems and their vulnerability to change. The ocean is warming and becoming more acidic as a direct consequence of increasing concentrations of atmospheric CO_2 . The ramifications of ocean acidification are of clear relevance to the commercial fishing industry in Atlantic Canada, which has experienced major declines in the recent decades. Shellfish aquaculture and fisheries are important commercial industries in Nova Scotia; commercial aquaculture supplies nearly half of all the fish and shellfish consumed globally by humans, and increases in this proportion are projected.¹¹¹ Mitigation

109. Meybeck et al., n. 32 above.

110. Borges and Gypens, n. 11 above.

111. "Half of fish consumed globally is now raised on farms, study finds," *Science Daily* Sept. 8, 2009 <<http://www.sciencedaily.com>>.

measures to lessen the impact of the irreversible acidification of the global ocean are presently lacking. Canada has one of the largest coastlines in the world. There is an opportunity for Canada to lead global efforts to adapt to climate change by implementing policies that promote the sustainable use of our ocean resources. The collapse of the Atlantic cod fishery through mismanagement of this living resource need not be a precedent for Canadian fisheries and oceans policy. The challenge presented by climate change and ocean acidification can be met with innovation, adaptation, and policies aimed at a future in which human impact on the environment is reduced.

Fig. 1

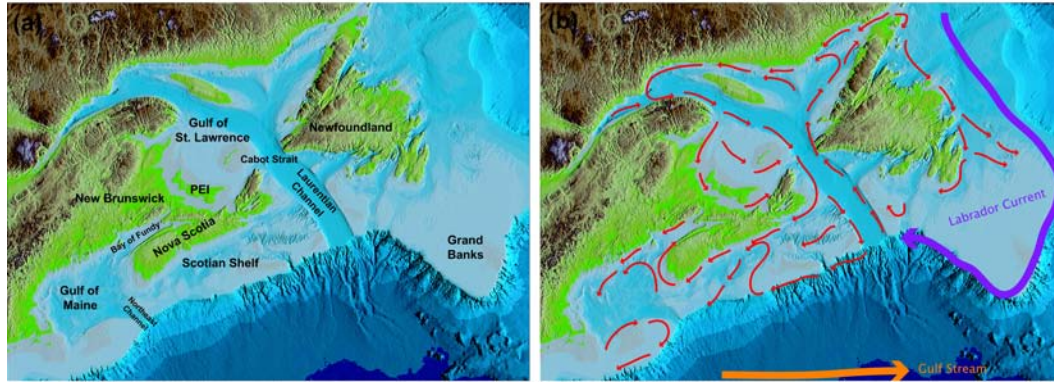


Fig. 2

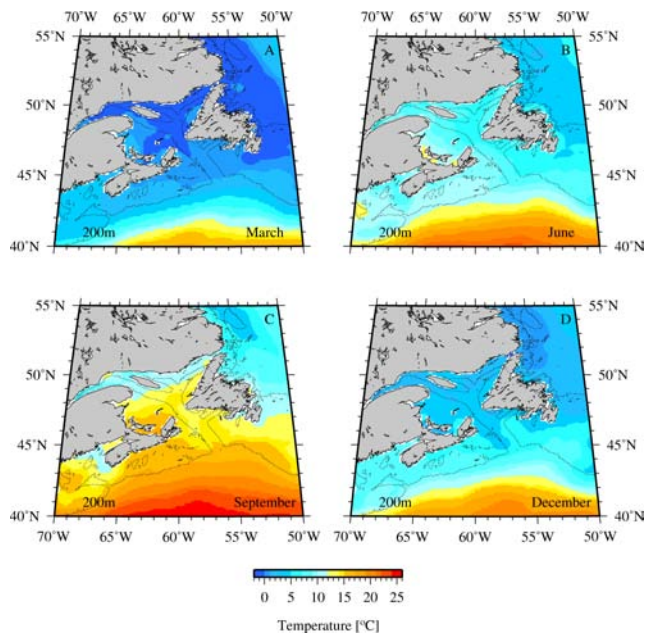
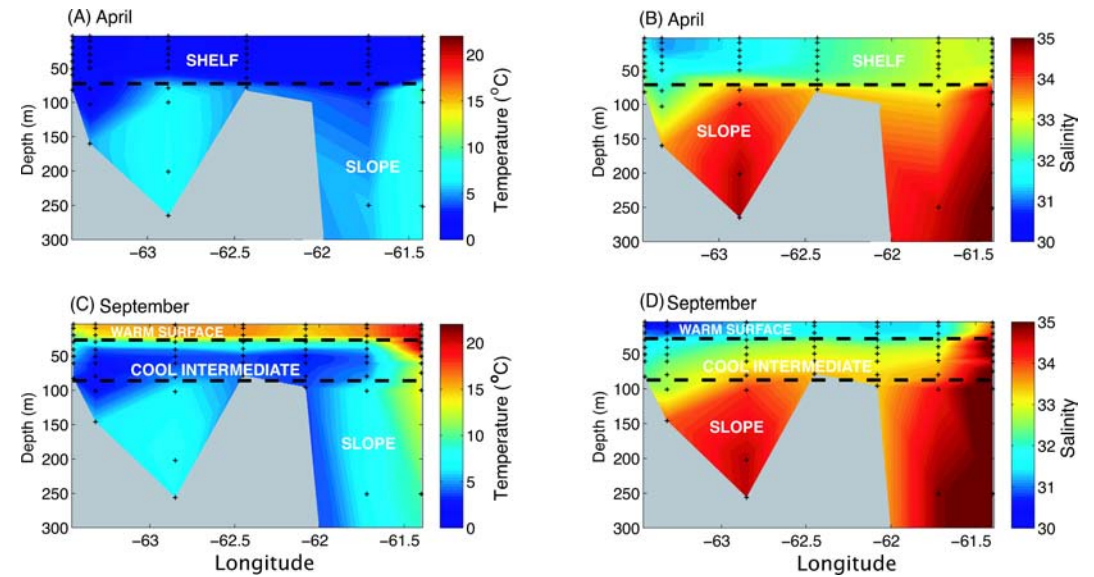


Fig. 3



Shadwick, E.H., and Thomas, H. (2011). Carbon Dioxide in the Coastal Ocean: A Case Study in the Scotian Shelf Region, in *Ocean Year Book*, 25, A. Chircop, S. Coffen-Smout, and M. McConnell, M. (eds.), Martinus Nijhoff, Leiden/Boston, 171-204.

Fig. 4

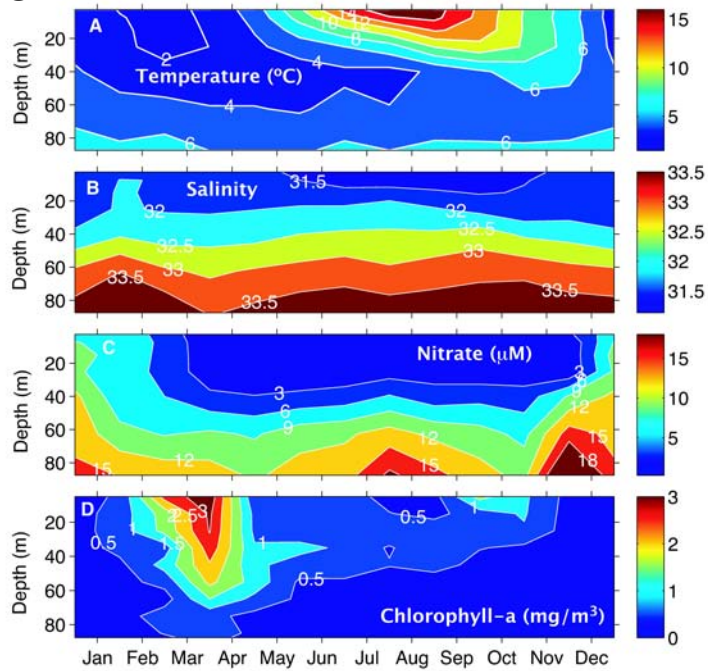


Fig. 5

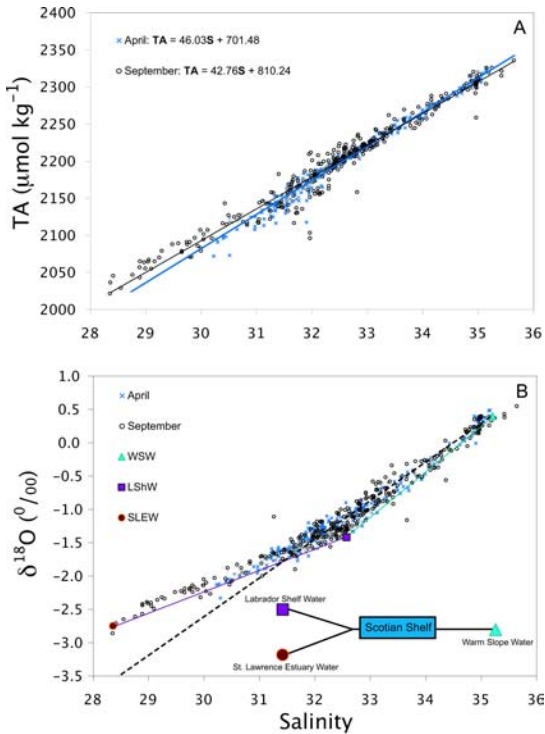


Fig. 7

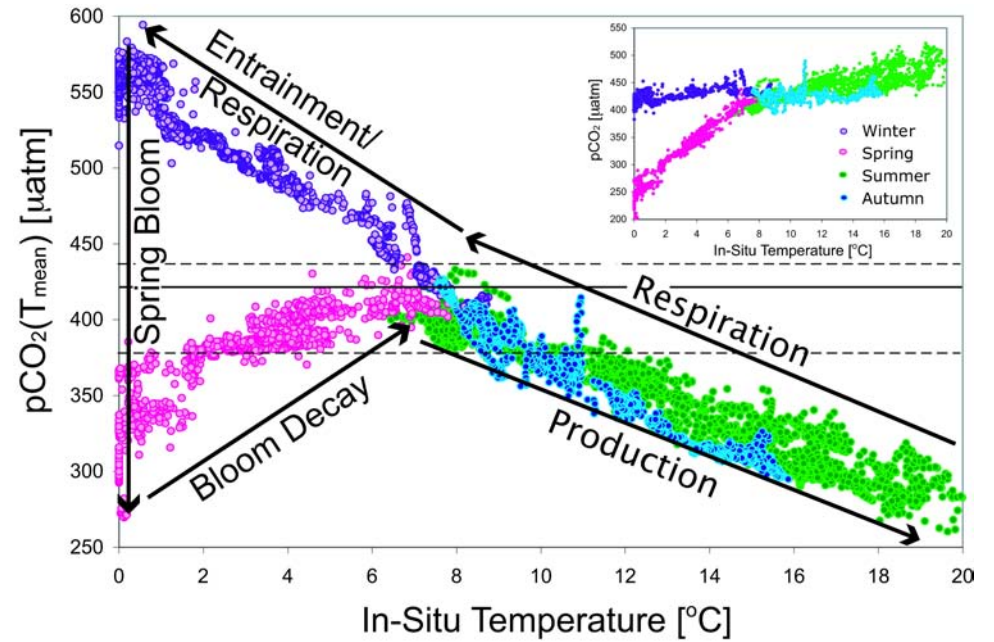
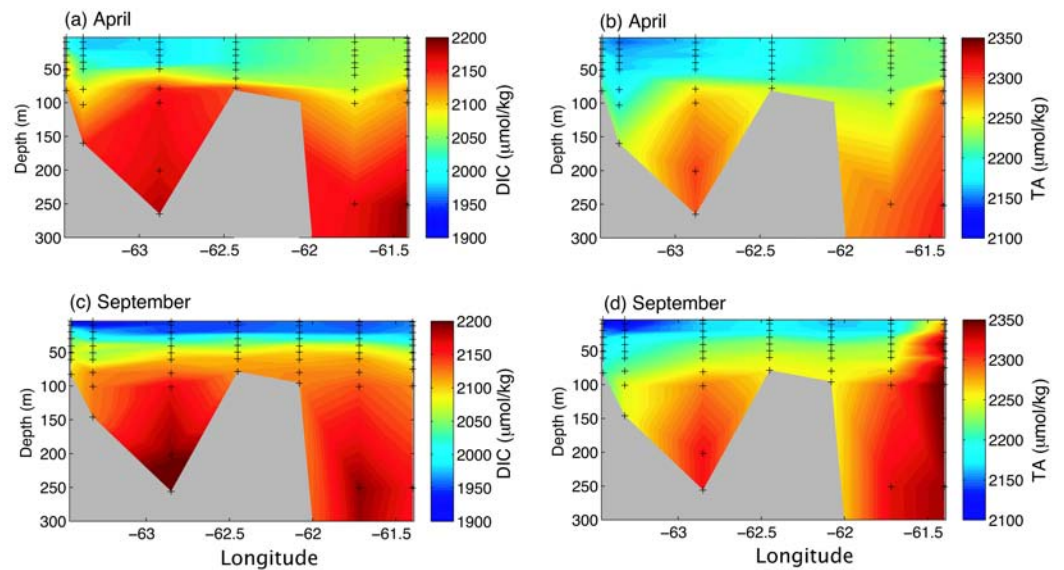
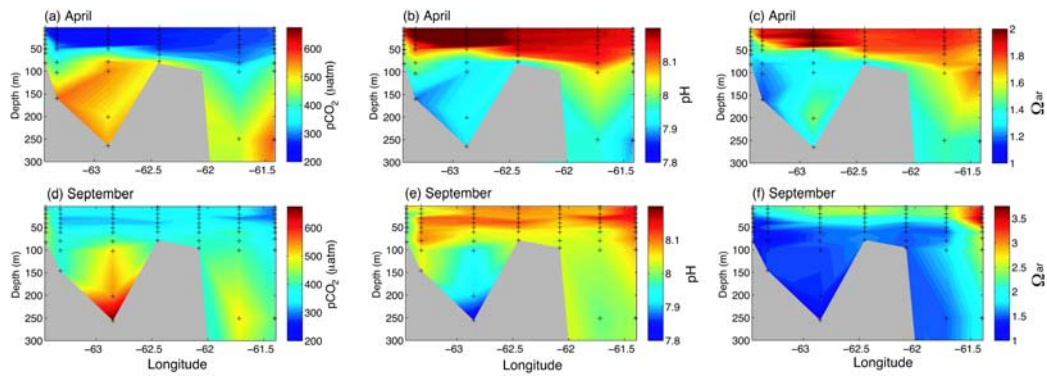


Fig. 8



Shadwick, E.H., and Thomas, H. (2011). Carbon Dioxide in the Coastal Ocean: A Case Study in the Scotian Shelf Region, in *Ocean Year Book*, 25, A. Chircop, S. Coffen-Smout, and M. McConnell, M. (eds.), Martinus Nijhoff, Leiden/Boston, 171-204.

Fig. 13



Shadwick, E.H., and Thomas, H. (2011). Carbon Dioxide in the Coastal Ocean: A Case Study in the Scotian Shelf Region, in *Ocean Year Book*, 25, A. Chircop, S. Coffen-Smout, and M. McConnell, M. (eds.), Martinus Nijhoff, Leiden/Boston, 171-204.