Final Thesis

Inorganic Carbon Cycling in Scotian Shelf Waters

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1.0 Introduction

1.1 Motivation

Coastal oceans play an important role in the biogeochemical cycling of carbon, as they sustain disproportionately high biological activities given their small surface area compared to the open sea (Shadwick & Thomas, 2014). However, the biogeochemical signals and properties such as the concentration of dissolved inorganic carbon (DIC) in coastal ocean remains largely unstudied in comparison to the open ocean (Shadwick, 2010). Shadwick et al. (2010) studied the CO_2 system on the Scotian Shelf and found that the Scotian Shelf acts as a source of atmospheric CO_2 at the annual scale, in contrast to many other coastal regions, which absorb CO_2. Another study carried out by Gledhill et al. (2015) claimed that Scotian Shelf is vulnerable to coastal acidification due to the freshwater input from St. Lawrence. These findings attracted my interests to study Scotian Shelf waters, and explore their biogeochemical characteristics and status.

In order to assess the current situation of Scotian Shelf waters in the ocean carbon cycle, a proper baseline must be set. However, studies have yet to be conducted on the biogeochemical signals such as fraction of $^{13}C/^{12}C$ ($DI^{13}C$) of the Scotian Shelf waters. In this research, I will examine the seasonal and spatial distribution of stable carbon isotopes with depth in Scotian Shelf waters, as well as their governing processes. The results of this study will provide more details on the seasonality of the carbon cycle on the Scotian Shelf, and provide a baseline of data from which further studies can be carried out, for example investigations into ocean acidification on the Scotian Shelf.

1.2 Background

The Scotian Shelf is a broad (~200 km wide, 700 km long) continental margin off the Eastern coast of Canada and is located at the boundary between the subpolar and subtropical gyres (Loder et al., 1997) (see fig. 1). It is characterized as a rich ecosystem that supports a diversity of marine life communities and habitats (Atlantic Coastal Zone Information Steering Committee, 2016). It also supports important fisheries and other human activities (Fisheries and Oceans Canada, 2014; Gulf of Maine Census, 2016). As a result, the Scotian Shelf is essential to local communities both economically and environmentally. A better understanding of the Scotian Shelf will be beneficial to local communities and species living in this habitat.

The Gulf of St. Lawrence provides the major freshwater input to the Scotian Shelf water system from the North via the Cabot Strait (Burt et. al, 2013a) (fig. 1). The Nova Scotia Current flows from the northeast to the southwest and is influenced by the Gulf Stream and the Labrador Current (Gulf of Maine Census, 2016) (fig. 1). Water exiting the Cabot Strait feeds the Nova Scotia current and generates minimum salinities on the Scotian Shelf in late summer (Gledhill et al., 2015). River input further plays an important role in the Scotian Shelf biogeochemistry due to the surface water dilution (Gledhill et al., 2015).
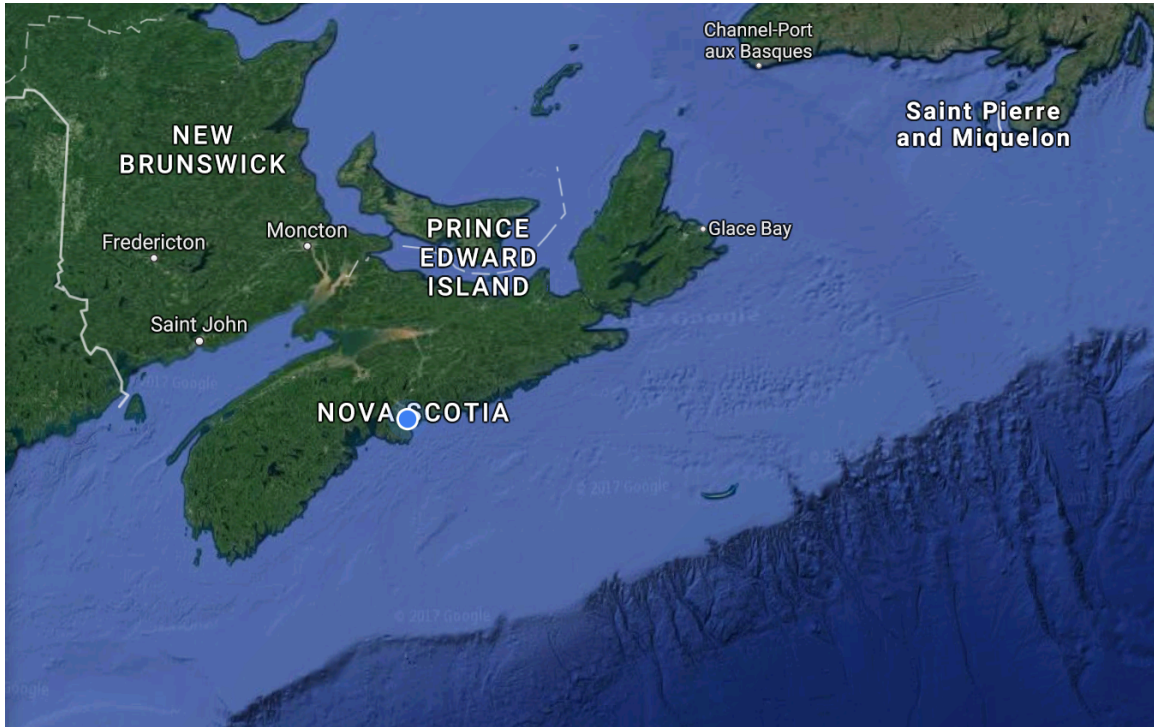
Fig. 1. Scotian Shelf.

Biological processes also change inorganic carbon signals significantly. The increase of biological production changes biogeochemical signals in the Scotian Shelf waters by altering the isotopic carbon ratio (denote as $DI^{13}C$), concentrations of dissolved inorganic carbon (DIC), alkalinity, as well as salinity in both surface (0 to 50 m depth) and subsurface water (50 to 100 m depth). Phytoplankton removes carbon from water column through photosynthesis, as it prefers to uptake light carbon (^{12}C) than heavier carbon (^{13}C) during photosynthetic carbon fixation (Hoins et al., 2016). The $DI^{13}C$ signal of the left behind thus becomes heavier due to this process. This leads to the surface water containing low concentrations of DIC with a heavy $DI^{13}C$ signature. In subsurface water, the organic carbon in sinking particles is remineralized into DIC, thus the water will be isotopically light due to the release of light carbon (^{12}C), and the $DI^{13}C$ signal will be decreased. According to these mechanism, the increase or decrease of DIC and $DI^{13}C$

signals show where the biological processes occur and where the river input is. The patterns of seasonal and spatial variations of the carbon isotopes can also be demonstrated from the signals. Thus, using stable carbon isotopes can access the seasonality and spatiality of inorganic carbon system in Scotian Shelf waters, and can also identify their governing processes.

1.3 Summary of Literature

Numerous studies have been conducted on Scotian Shelf showing large temporal and spatial variations in biogeochemical properties include alkalinity, salinity, DIC and temperature. Umoh and Thompson (1994) studied the seasonal cycle of sea-surface temperature on Scotian Shelf has been studied and found out that the temperature ranges from 0°C to 20°C in Scotian Shelf waters, and it is the largest range in comparison to other ocean waters in the world. A research carried out by Shadwick and Thomas (2014) stated that a seasonal decrease in surface DIC (up to 70 μmol kg−1), and an increase of pH in surface water (~0.2 units), along with changes in alkalinity, salinity and net community production (NCP) were found in Scotian Shelf waters, in the spring and winter of 2007.

The Scotian Shelf also has large spatial variations in selected properties, due to its unique location at the downstream of the Gulf of St. Lawrence, as well as at the junction between the subpolar and subtropical gyres (Loder, 1997; Umoh & Thompson, 1994; Shadwick et al., 2011a). Studies unravelled large spatial variations in temperature, salinity and DIC in Scotian Shelf waters. For example, the maximum DIC and TA concentrations are found offshore of the Scotian Shelf (Shadwick and Thomas, 2014), and the maximum salinities are found in the deeper waters (Shadwick and Thomas, 2014;

Shadwick, 2010)

However, temporal and spatial variations of $DI^{13}C$ in Scotian Shelf waters have yet to be uncovered. In this research, the distribution of $DI^{13}C$ in Scotian Shelf and its seasonal-spatial variations will be studied. The use of $DI^{13}C$ helps to further describes the biological processes (photosynthesis and respiration). It can reveal clear signals and trends of where biological processes occur in Scotian Shelf waters and help unravel the relationship between biological processes and the selected biogeochemical parameters.

1.4 Study Introduction

This project focuses on studying the seasonal and spatial patterns of stable carbon isotopes distribution with depth along with other biogeochemical parameters including salinity and alkalinity in Scotian Shelf waters. The result of this study will deepen the understanding of seasonality of the carbon cycle on the Scotian Shelf and provide a baseline of the data from which further studies can be carried out, for example with respect to ocean acidification.

The research question is "what were the seasonal and spatial patterns of stable carbon isotopes distribution of dissolved inorganic carbon with depth in Scotian Shelf waters in 2014, and what were the governing processes?" The hypothesis is that there are seasonal decreases in surface DIC and increases in subsurface DIC as a result of a combination of biological production and surface dilution due to river input.

There are three objectives in this research: 1) Present baseline for the biogeochemical characteristics including concentration of DIC and fraction of $^{13}C/^{12}C$ ($DI^{13}C$) of Scotian Shelf waters. 2) Unravel and attempt to identify the role of river input

on these biogeochemical parameters. 3) Study the biogeochemical processes such as photosynthesis and respiration taking place in Scotian Shelf waters.

1.5 Summary of Approach

The research question will be addressed by plotting data with Matlab (version 2016a), Excel and Ocean Data View (ODV). The data plots exhibit the spatio-seasonal patterns of biogeochemical parameters distributions. The spatio-seasonal variability of the carbon system parameters are evaluated based on full water column sampling along four primary transect lines throughout the Scotian Shelf region during April and October in 2014. The $DI^{13}C$ data on the Scotian Shelf is also used to unravel the effects of river runoff and biological processes, i.e. photosynthesis and respiration, as well as their seasonal and spatial variability on the observed DIC concentrations.

2.0 Literature Review

2.1 Introduction

This literature review focuses on previous studies, which have studied the carbon cycling processes in ocean waters from the last several decades, with an emphasis on Scotian Shelf waters. Key objectives of this project are addressed and demonstrated in the literature review. This review helps illuminate the current understanding of the biogeochemical properties and governing processes of the Scotian Shelf water and also draw attention to important knowledge gaps on this topic.

2.2 Scotian Shelf Water

The Scotian Shelf is a highly productive area, which hosts active fisheries and aquaculture, and it is also impacted by oil and gas exploration (Shadwick, 2010). Its abundant productivity makes it both economically and environmentally essential to local communities and species.

The Scotian Shelf is uniquely located at the downstream of the Gulf of St. Lawrence, as well as at the junction between the subpolar and subtropical gyres, thus leads to the large temporal and spatial variations in its hydrographical properties (Loder, 1997; Umoh & Thompson, 1994; Shadwick et al., 2011a). Since the Scotian Shelf plays an important role in the ocean carbon cycling system, Shadwick et.al (2010; 2011a) have conducted a number of studies on the seasonal and spatial variability in the CO_2 system on the Scotian Shelf. In 2010, Shadwick et al. found that the Scotian Shelf acts as a source of atmospheric CO_2 at an annual scale, with a reversal of this trend occurring only during the spring phytoplankton bloom. The reasons are that the photosynthesis occurred in spring bloom rapidly decreases DIC in the waters; however, it is out-weighted by the thermodynamic increase due to warming (Shadwick and Thomas, 2014).

Many studies have been conducted on Scotian Shelf waters in order to have better understanding of this region. Based on the economic value and its importance on ocean carbon cycle, more research is needed to be conducted on Scotian Shelf waters to keep the data updated, and provide a baseline of DIC and $DI^{13}C$ from which further studies can be carried out, for example with respect to ocean acidification.

2.3 Biogeochemical Parameters

For the purpose of assessing current status of the Scotian Shelf waters, several biogeochemical parameters include fraction of stable carbon isotopes ($DI^{13}C$), dissolved

inorganic carbon (DIC), total alkalinity (TA), salinity (S) and in-situ temperature (I.S.T) are selected.

DI^{13}C is a ratio of ^{13}C over ^{12}C, as the phytoplankton prefers to uptake lighter carbon, DI^{13}C is able to give clear signals of where biological processes pass by. In 2004, Keeling et al. conducted a research study at Station ALOHA near Hawaii, using DIC, DI^{13}C, and alkalinity to unravel seasonal and long-term dynamics of the upper ocean carbon cycle in the area. Shadwick et al. (2010) used DIC, TA, and partial pressure of CO_2 (pCO$_2$) parameters to assess the biological processes in Scotian Shelf waters. Shadwick and Thomas (2014) also used DIC, TA and nitrate measurements to assess the spatio-temporal variability of inorganic carbon system in Scotian Shelf waters. In 2016, Burt et al. provided a detailed assessment of carbon cycling processes within Hudson Bay, using basin-wide measurements of dissolved inorganic carbon (DIC) and total alkalinity (TA), and isotope tracers (δ ^{18}O and DI^{13}C). Although these biogeochemical parameters such as DIC, TA, S and DI^{13}C are widely used in studying ocean waters, studies have yet to be conducted on DI^{13}C in Scotian Shelf waters.

2.3.1 Seasonality

Scotian Shelf has large temporal variations in selected hydrographical and biogeochemical properties, include temperature, alkalinity, salinity and DIC. In 1994, Umoh and Thompson conducted studies on the seasonal cycle of sea-surface temperature on Scotian Shelf, and found out that the temperature varies from an annual minimum 0°C to an annual maximum 20°C. They concluded that this temperature range is the largest range, in comparison to the other ocean waters in the world. Shadwick (2010) also concluded same result, and stated that in autumn the surface temperature is the warmest

in the central Scotian Shelf, while in spring, it is the coldest. In 1997, Loder et al. found

that from June to October, the surface salinity of Scotian Shelf is decreases from roughly

30.5 to 29.5, due to the freshwater input from St. Lawrence. A research study carried out

by Shadwick and Thomas (2014) stated that a seasonal decrease in surface DIC (up to 70

μmol kg-1), and an increase of pH in surface water (~0.2 units), along with changes in

alkalinity, salinity and net community production (NCP) were found in Scotian Shelf

waters, in the spring and winter of 2007.

2.3.2 Spatiality

Scotian Shelf also has large spatial variations in selected hydrographical and

biogeochemical properties, due to its unique location at the downstream of the Gulf of St.

Lawrence, as well as at the junction between the subpolar and subtropical gyres (Loder,

1997; Umoh & Thompson, 1994; Shadwick et al., 2011).

Spatiality alongshore (from Gulf of St. Lawrence toward Gulf of Maine)

In 2010, Shadwick found the strong linear relationship between salinity and

alkalinity in the Scotian Shelf suggests a two end-member system in the region: 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.

Spatiality offshore

The selected biogeochemical parameters show clear signals of spatial variability

offshore. In Shadwick and Thomas's study (2014), the maximum DIC and TA

concentrations are found offshore of the Scotian Shelf. Shadwick (2010) also claimed

that the salinity increases further offshore due to the northward transport of warm, saline, Gulf Stream waters; the surface temperature follows the same pattern.

Spatiality in surface and deep water

The spatial variability in Scotian Shelf waters is also shown in surface water and deep water. For instance, the maximum salinities are found in the deeper waters (Shadwick and Thomas, 2014; Shadwick, 2010). Shadwick (2010) also mentioned that from spring bloom to autumn, the surface DIC decreases to an annual minimum due to phytoplankton uptake and freshwater dilution; subsurface DIC increases to an annual maximum due to respiration and remineralisation in Scotian Shelf waters.

The spatiality of distributions of the selected biogeochemical parameters is studied in three aspects. Studies unravelled large spatial variations in temperature, salinity and DIC in Scotian Shelf waters. However, the spatial variations in DI^{13}C have yet to be uncovered.

2.4 Governing processes

2.4.1 Biological processes

Burt et al. (2013) and Shadwick et. al (2011a) claimed that biological processes are the dominant control on mixed-layer DIC. Photosynthesis carried out by phytoplankton uses light carbon to give a decrease signal in DIC and an increasing signal in DI^{13}C. As mentioned before, the Scotian Shelf acts as a source of atmospheric CO_2 at an annual scale, with an out-gassing of 1.4 mol C m^{-2}yr^{-1}, and a reversal of this trend occurring only during the spring phytoplankton bloom (Shadwick et. al, 2011a;

Shadwick, 2010; Shadwick & Thomas, 2014). The reasons are that the photosynthesis occurred in spring bloom rapidly decreases DIC in the waters, however, it is out-weighted by the thermodynamic increase due to warming. The region also emits CO_2 during autumn and wintertime due to wind-driven and other influences (Shadwick & Thomas, 2014, Shadwick 2010).

2.4.2 River input

The freshwater input plays an important role on the carbon cycling processes. Gledhill et al. (2015) stated that the supplied amounts of DIC, dissolved and particulate organic carbon, and nutrients from riverine and estuarine sources, as well as total alkalinity (TA), can all significantly affect the local carbonate chemistry of the receiving water mass. Since the DIC: TA ratio largely determines the buffering capacity of the water; the river input has significant influence on the buffer capacity of the receiving water, due to variations of DIC and TA concentrations in rivers (Gledhill, 2015). They also concluded that Scotian Shelf waters are more vulnerable to coastal acidification due to a reduced buffering capacity, which results from larger river input. Ji et al.'s study (2008) also shows important role of river input on Scotian Shelf waters. They found that the river input in surface water can slow vertical nutrient exchange between surface and deep waters, thus reducing the overall spring primary productivity throughout the region.

The importance of river input is not only found in Scotian Shelf waters, but also in other regions. In Baltic Sea, the carbonate system of the Baltic Proper is strongly influenced by the input of waters (Thomas & Scheneider, 1999); in North sea, soil respiration and dissolution of carbonate minerals in the drainage basin of the river leads to a decreasing signal of $DI^{13}C$ (Burt et al., 2016b); in Hudson Bay, the river input can

directly reduce the buffering capacity of the seawater, and dilute carbonate ions, which decreases the concentration of DIC (Burt et al., 2016a).

In conclusion, the river input can impact the carbon cycling processes by decreasing the DIC concentration in surface water, impeding vertical mixing between surface water and deep water, and decreasing the buffer capacity of receiving water. As a result, the river input can affect the spring primary production throughout the region. Soil respiration and carbonate minerals dissolution can also influence the $DI^{13}C$ signal in a small range.

2.4.3 Air-sea equilibrium

Air-sea exchange also governs the carbon cycling process in the ocean waters and this is in turn is being influenced by burning fossil fuels. As fossil fuel burning gives out isotopically light CO_2 gas, and the anthropogenic CO_2 emission inputting huge amount of ^{12}C over hundreds of years, the proportion of ^{12}C, ^{13}C and ^{14}C in both the atmosphere and the ocean has been shifted (Quay et al., 2003). Consequently, the global oceans were experiencing a mean change in surface waters $DI^{13}C$ of -0.160 ‰ (Quay et al., 2003). This annual decrease of $DI^{13}C$ in surface ocean water caused by an addition of anthropogenic CO_2 to the atmosphere is referred as Suess effect (Keeling, 1979). As a result, air-sea flux influences carbon cycling processes in a small but significant way.

2.5 Knowledge gaps

Various studies have carried out in Scotian Shelf waters using biogeochemical parameters such as DIC, TA and nitrate measurements, which provide historical characteristics and information for Scotian Shelf Waters. This information also includes

net community production and salinity variations. However, the relationships between the distribution of the biogeochemical parameters and the biological processes have not been thoroughly researched, and their implications have not been fully established. In this research, a unique parameter, $DI^{13}C$, is used to help further describe these biological processes. It will show clear signals and trends of where biological processes (photosynthesis and respiration) occur in Scotian Shelf waters.

The study will also deepen the understanding of spatio-temporal variability of the carbon cycle in 2014 on the Scotian Shelf, and provides a baseline of the data in 2014 from which further studies can be carried out.

2.6 Conclusion

This literature review covered various studies on carbon cycling processes in ocean waters, with a focus on Scotian Shelf waters, from the last several decades. Based on the previous studies, key objectives and their definitions are identified and elaborated. The existing knowledge gap will be filled by this research, which will help further our understanding of carbon cycling on the Scotian Shelf and its implications for specific marine problems, such as ocean acidification. Also, the newest baseline that exhibits the current status of Scotian Shelf will be established.

3.0 Methods

3.1 Sample Collection and Analysis

Discrete bottle samples were collected on April and October cruises in 2014, as part of the Atlantic Zone Monitoring Program (AZMP) at stations distributed along four transects throughout the Scotian Shelf shown in Fig. 2 (Shadwick & Thomas, 2014). The

four transects include the Browns Bank Line (BBL), Halifax Line (HL), Louisburg Line (LL) and Cabot Strait Line (CSL) (see fig. 2). There are 9 stations along BBL, 12 stations along HL, 7 stations along LL and 6 stations along CSL. Samples were collected throughout the water column with a 10 m vertical resolution within the euphotic zone at all stations.

In a study performed by Shadwick and Thomas (2014) a detailed sampling procedure is described as follows. 12-L Niskin bottles mounted on a General Oceanic 24-bottle rosette fitted with a SeaBird CTD are used for tapping DIC, DI^{13}C and TA samples. In this way, high precision in-situ temperature, and salinity data is associated with the chemical data. Mercury chloride solution is used for poisoning the samples and to halt any biological activity. The samples are stored in dark at 4 °C to await analysis (Shadwick & Thomas, 2014).

The samples were sent to Dalhousie and Yale University for analysis. DIC and TA were analysed at Dalhousie lab by coulometric and potentiometric titration respectively. A VINDTA 3C (Versatile Instrument for the Determination of Titration Alkalinity by Marianda) was used for analysing DIC and TA, following by standard procedures (Dickson et al. 2007). The uncertainties of DIC and TA measurements are 2 μmol kg^{-1} and 3 μmol kg^{-1} respectively (Shadwick & Thomas, 2014).
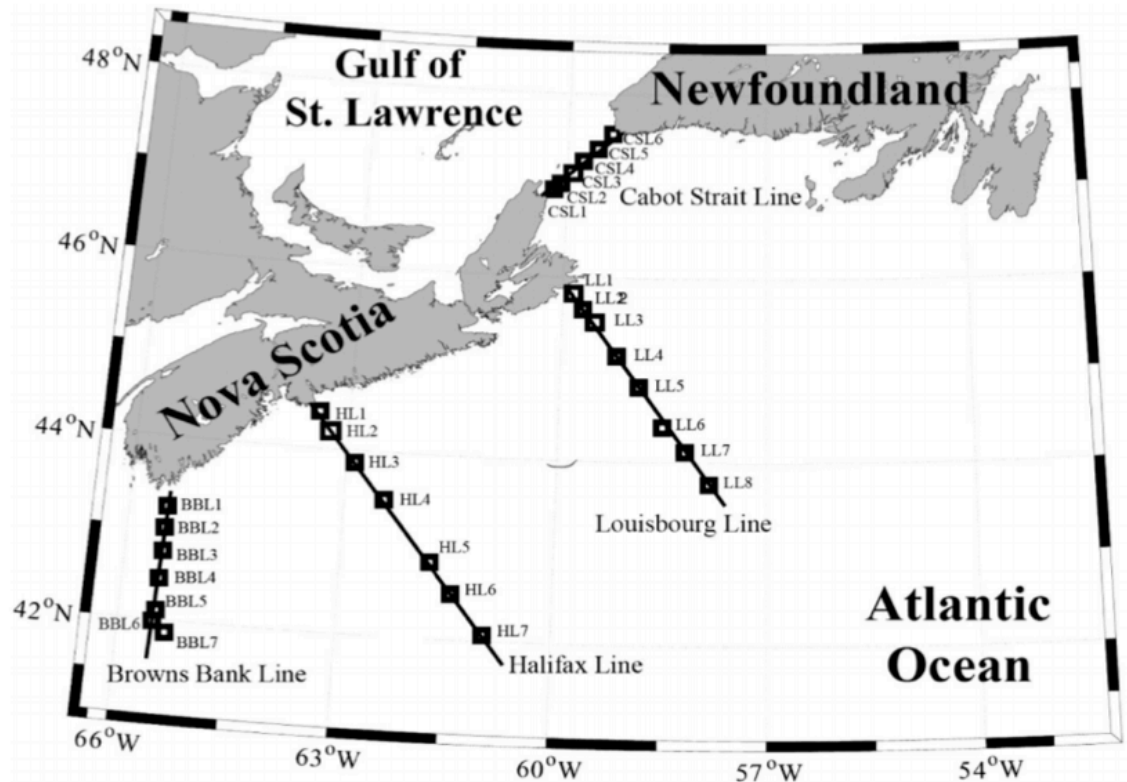
Fig. 2. Locations of station sampled along four primary transect lines in the Scotian Shelf region on AZMP cruises in spring and autumn 2007. Reprinted from "Seasonal and spatial variability in the CO_2 system on the Scotian Shelf (Northwest Atlantic)," by E. H. Shadwick, 2014, *Marine Chemistry*. *160*, 43. Copyright [2014] by the Elsevier B.V. Reprinted with permission.

The most common source of acidity in water is dissolved carbon dioxide. Carbon dioxide enters seawater undergoes several chemical reactions shown in equations 3.1.1 - 3.1.3.

$CO_{2(g)} \leftrightarrow CO_{2(aq)}$ **Equation 3.1.1**

$CO_{2(aq)} + H2O \leftrightarrow H^+ + HCO_3^-$ **Equation 3.1.2**

$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$ **Equation 3.1.3**

The dissolved inorganic carbon (DIC) is thus calculated as the sum of concentrations of

CO_2, CO_3^{2-}, and HCO_3^- shown in equation 3.1.4.

$DIC = [CO_2] + [HCO^{3-}] + [CO_3^{2-}]$ **Equation 3.1.4**

Phytoplankton uptake light carbon through photosynthesis to produce organic matter, once the organic matter sinks down and gets remineralized, light carbon is released into water, shown in equation 3.1.5 and 3.1.6.

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ **Equation 3.1.5**

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6\ H_2O$ **Equation 3.1.6**
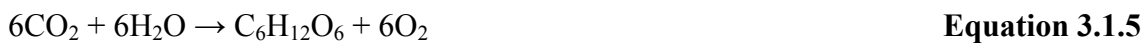
Total alkalinity (TA) is the quantitative capacity of water to neutralize an acid. It expressed as excess of bases (proton acceptors) of weak acids (pka>4.5) over strong acids (proton donator) (pka<4.5 at 25 °C), shown in equation 3.1.7.

$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] +$ minor components **Equation 3.1.7**

Measurement of $DI^{13}C$ was conducted at Yale University using continuous-flow isotope-ratio-monitoring mass spectrometry (CF-irmMS) on Thermo Finnigan MAT 253 gas mass spectrometers coupled to a Thermo Electron GasBench II via a Thermo Electron Conflo IV split interface (Burt et al., 2016a). The $DI^{13}C$ is calculated by relating it to the isotopic composition of Pee Dee Belemnite (PDB) standard, with an uncertainty of ±0.1 ‰, Shown in equation 3.1.8 (Burt et al., 2016a).

$$DI^{13}C = 1000 \left\{ \frac{\left(^{13}C/^{12}C_{sample}\right) - \left(^{13}C/^{12}C_{standard}\right)}{\left(^{13}C/^{12}C_{standard}\right)} \right\}$$ **Equation 3.1.8**

3.2 Data Analysis

Key variables (DIC, DI^{13}C, total alkalinity, salinity and temperature) are plotted against depth for each station of all transects, with same scale for all the plots. Selected stations for each transects are stations near shore to offshore. Same number of the stations' plots for both spring and fall are chosen in order to compare the seasonality of each transects, as well as their spatial variability. These plots are plotted by using Matlab. Scatter plots for DIC and DI^{13}C relationship are plotted by Excel. DIC and DI^{13}C relationship provide an indication of the relative effect of biological process (biological production and respiration) and river input, as well as air-sea CO_2 exchange. By colouring the data points based on the different water mass, river input signal can be seen. Use ODV to generate contour plots for DI^{13}C of all stations throughout HL, a better image of where the biological production and respiration occurs can be illustrated.

3.3 Limitation

A main limitation in this research is the limited data coverage due to the short period of time to collect samples. Due to the high cost of offshore work needed to collect samples for this type of data, researchers have to choose between temporal coverage and spatial coverage. The research is conducted on a large spatial range (from the east to the west of Scotian Shelf), thus the time of data coverage is limited.

4.0 Results and Discussion

4.1 The Browns Bank Line (BBL) section

Seven stations (BBL1 to BBL7) are distributed on the browns bank transect shown in Fig. 2. In spring, the surface and subsurface water temperature of all stations varies from 1.75 °C to 12.07 °C. The mean surface DIC concentration is 2057 μmol kg^{-1}, with a minimum value of 2036 μmol DIC kg^{-1} found in BBL3. In the subsurface (50 m to 100 m), the minimum value of DIC is 2064 μmol kg^{-1} found at station BBL1 where is the closest to the coast. Value of 2100 μmol kg^{-1} DIC is found at 100 m depth at stations BBL3 and BBL4. Values of DIC are approaching 2172 μmol kg^{-1} at depth greater than 100 m at the offshore stations BBL6 and BBL7. The mean surface DI^{13}C value is about 0.83, with a minimum value of 0.65 at nearshore station BBL1 (see Table 1). The surface DI^{13}C concentrations increase along the BBL transect and reach to 1.14 at offshore station BBL6. Minimum DI^{13}C values are found in subsurface, with recoveries at depth greater than 100 m exhibited by all the stations (examples are shown in Fig. 3).

In autumn, the water temperature varies from 8.9 °C to 21.03 °C. The mean surface DIC concentration is 2009 μmol kg^{-1}, with a minimum value of 1973 μmol DIC kg^{-1} found in BBL1 (see Table 1). The surface DIC is increasing along the Browns Bank transect, from 1973 μmol kg^{-1} at station BBL1 to a value of 2024 μmol kg^{-1} at offshore station BBL6 (see Table 1). A slight decrease in surface DIC is found at BBL7. Comparing to spring conditions, the surface DIC is reduced in autumn by 48 μmol kg^{-1}. In the subsurface, the values of DIC vary from a minimum of 2041 μmol kg^{-1} at station BBL1, to 100 m values on the order of 2108 μmol kg^{-1} DIC at stations BBL3 and BBL4

and the values are approaching 2174 μmol kg^{-1} DIC at depth greater than 100 m at the offshore station BBL6. A slight decrease in subsurface DIC is again found at BBL7. The subsurface DIC in fall is 2084 μmol kg^{-1}, which is about 15 μmol kg^{-1} lower than spring value (see Table 1). The mean surface DI^{13}C value is 1.23, with a minimum value of 1.08 at offshore station BBL7. DI^{13}C concentrations decrease along the BBL transect and reach 1.08 at offshore station BBL7. Minimum DI^{13}C concentrations are found in subsurface (examples are shown in Fig. 3). An increase (about 0.4 and 0.15 respectively) in mean DI^{13}C value is found in both surface and subsurface in autumn relative to spring conditions (see Table 1).

4.2 The Halifax Line (HL) section

In spring, the mean value of surface DIC is 2059 μmol kg^{-1}, with minimum mean surface DIC value (2016 μmol kg^{-1}) found in nearshore station HL1 (see Table 1). The surface DIC values also increase along the transect further offshore, and reach 2096 μmol kg^{-1} at HL 2096 μmol kg^{-1}. The mean surface DIC value and the mean subsurface DIC in spring between HL and BBL are similar (see Table 1). The mean DIC value in subsurface is 50 μmol kg^{-1} higher in subsurface than in surface (see Table 1). The surface DI^{13}C is 0.938, with a maximum surface DI^{13}C value found in HL1. The surface DI^{13}C decreases along the transect further offshore, which follows the opposite trend of surface DIC. The minimum DI^{13}C is found in subsurface, with a minimum value of 0.45 at offshore station HL11. The mean DI^{13}C values in both surface and subsurface of HL are both larger than the mean DI^{13}C values of BBL accordingly.

In fall, the surface DIC value is about 76 μmol kg^{-1} lower comparing to spring, however, the mean DIC values in subsurface in spring and fall are about the same (see Table 1). The lowest surface DIC is 1935 μmol kg^{-1} found in station HL1. The mean DIC value is higher in subsurface by 124 μmol kg^{-1} than in surface (see Table 1). This difference in fall is about 74 μmol kg^{-1} larger than the difference in spring. The surface DIC in HL in fall is about 26 μmol kg^{-1} lower than the value in BBL, however, the subsurface DIC is 23 μmol kg^{-1} higher (see Table 1). The mean DI^{13}C in surface and subsurface are 1.175 and 0.56 respectively (see Table 1). The highest DI^{13}C value reaches 1.95 found in station 4 and 5. This is the highest value in all the stations through out the 4 transects in fall.

4.3 Louisbourg Line (LL) section

In spring, the mean surface DIC is 2035 μmol kg^{-1}, with a minimum surface DIC found in nearshore station LL1, which is 1998 μmol kg^{-1} (see Table 1). The surface DIC is increasing along the transect further offshore and reaches maximum value at 2053 μmol kg^{-1} at offshore station LL8. The mean subsurface DIC is 2077 μmol kg^{-1}, with a minimum value found in station LL1 (2064 μmol kg^{-1}), and a maximum value found in station LL6 (2123 μmol kg^{-1}). The mean values of surface DIC and subsurface DIC in Louisbourg transect are lower than the values in both Halifax transect and Browns Bank transect accordingly. The mean surface DI^{13}C is 1.04, with a minimum value found in LL4 as 0.76 and a maximum value (1.32) found in offshore station LL9.

In fall, the mean surface DIC is 1981 μmol kg^{-1}, varies from a minimum value of 1935 found in LL1 to a maximum value of 2041 μmol kg^{-1} found in LL9. The mean surface DIC value is decreased by 54 μmol kg^{-1} relative to spring value. The mean subsurface DIC is 2104 μmol kg^{-1}, which is increased by 123 μmol kg^{-1} compared to surface mean value, and increased by 27 μmol kg^{-1} compared to subsurface DIC value in spring (see Table 1). The mean DIC values of Louisbourg Line in surface and subsurface are both similar to the values in Halifax Line accordingly. The surface DI^{13}C value (1.26) is higher than the surface DI^{13}C value (1.04) in spring (see Table 1). The minimum DI^{13}C is found in subsurface at station LL2, and the maximum value of subsurface DI^{13}C is found at offshore station LL9.

4.4 Cabot Strait Line (CSL) Section

The CSL has the lowest mean surface DIC value (2006 μmol kg^{-1}) in spring compared to other transects (HL,LL, and BBL) (see Table 1). The surface DIC is again increasing along the CSL transect, with a minimum value of 1971 μmol kg^{-1} found in nearshore station CSL1 and a maximum value of 2044 μmol kg^{-1} at offshore station CSL6. This is consistent with the observations along the Browns Bank, Halifax Line and Louisbourg Line sections which indicate increasing surface DIC concentrations with distance from the coast. The mean value of subsurface DIC is 2077 μmol kg^{-1}, and the maximum value of 2107 μmol kg^{-1} is found at CSL2 (see Table 1). The mean value of DI^{13}C is surface and subsurface are 1.04 and 0.72 respectively (see Table 1). The minimum DI^{13}C is found in subsurface at station CSL1, and the values increase along the transect further shore, which leads to a maximum value of 0.87 found at station CSL6.

The mean subsurface DI^{13}C of CSL in spring is the largest value relative to the according values other transects, as well as the mean surface DI^{13}C in spring (see Table 1).

In fall, the mean surface DIC is 1991 μmol kg^{-1}, with a minimum value found in stations CSL2 and CSL3. An increase about 87 μmol kg^{-1} surface DIC is shown at the nearby station CSL4, and CSL5. The mean subsurface DIC value is 2118 μmol kg^{-1}, with the maximum value of 2133 μmol kg^{-1} is found in nearshore station CSL2 (see Table 1). The values of mean subsurface DIC is decreasing along the transect further offshore, and a minimum value is found at CSL6 at 2097 μmol kg^{-1}. The surface DI^{13}C is 0.97, the minimum value is found at CSL2, the maximum value of 1.12 is found at CSL5. The minimum value of DI^{13}C found in subsurface is 0.17, again found at station CSL2. The subsurface DI^{13}C is increasing along the transect further offshore, and the maximum value of 0.58 is found at station CSL6. CSL has distinct properties compare to other transects, since it has the lowest DIC values in its surface waters and highest DIC values in deep waters. The lowest DI^{13}C values in all the stations through out the 4 transects in fall are also found in CSL deep waters.

Table 1 Mean values of surface DIC in µmolkg^{-1}, subsurface DIC in µmolkg^{-1}, surface DI^{13}C and subsurface DI^{13}C of 4 transects (BBL, HL, LL and CSL) in spring (S) and fall (F) in 2014.

Tra-nsec-ts	Avg. surf. DIC-S µmolkg^{-1}	Avg. surf. DI^{13}C S	Avg. Subsurf. DIC-S µmolkg^{-1}	Avg. subsurf. DI^{13}C S	Avg. surf. DIC-F µmolkg^{-1}	Avg. surf. DI^{13}C F	Avg. Subsurf. DIC-F µmolkg^{-1}	Avg. subsurf. DI^{13}C F
BBL	2058	0.831	2099	0.555	2010	1.235	2090	0.698
HL	2060	0.938	2105	0.630	1984	1.175	2108	0.568
LL	2035	1.042	2077	0.768	1981	1.265	2105	0.645
CSL	2006	1.037	2077	0.726	1992	0.972	2119	0.403
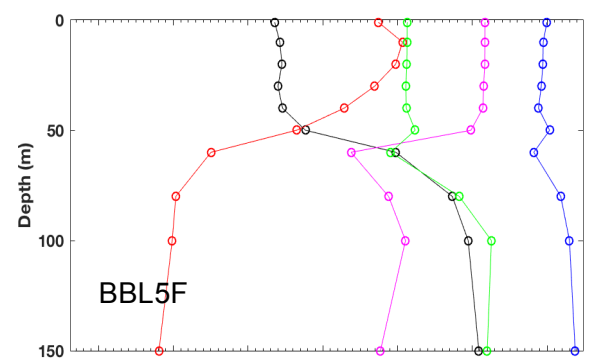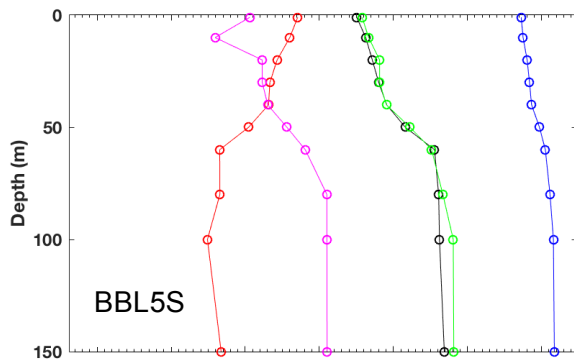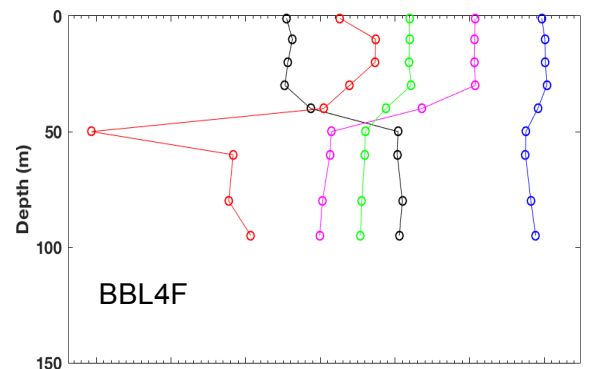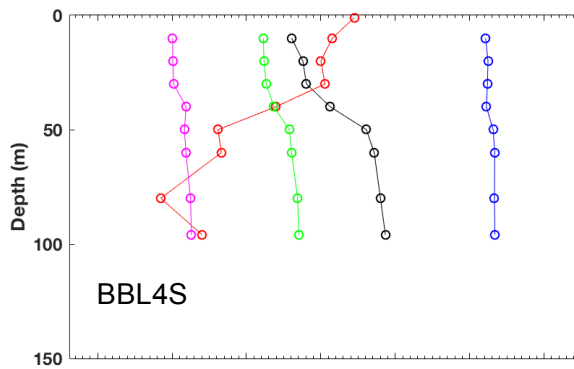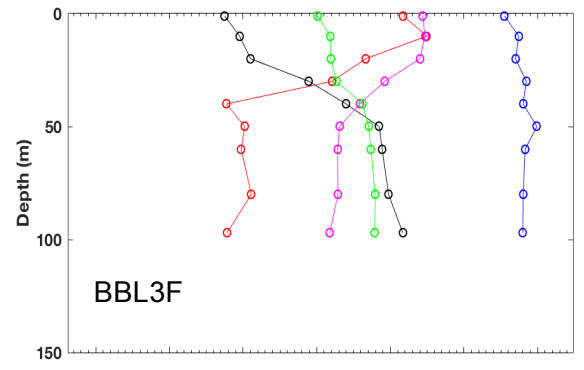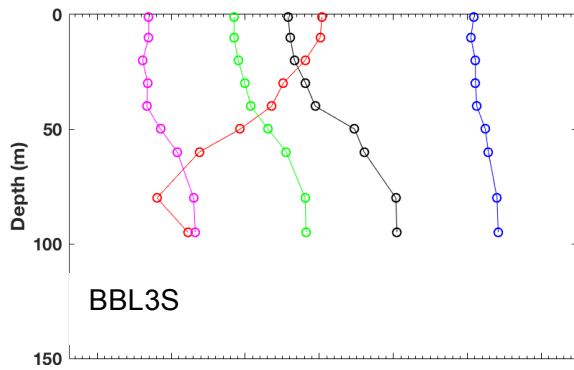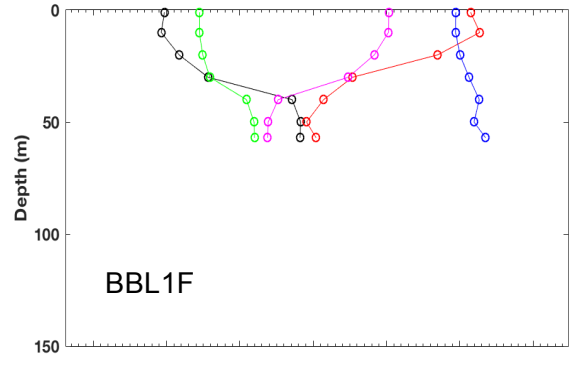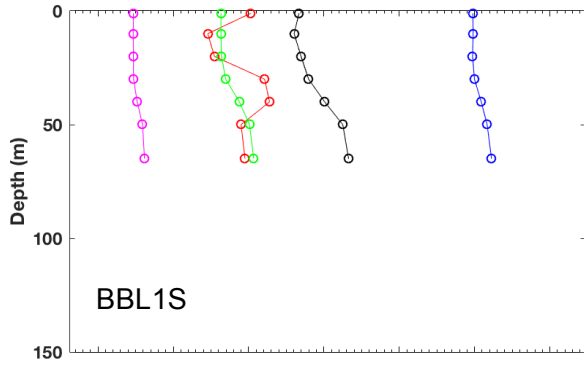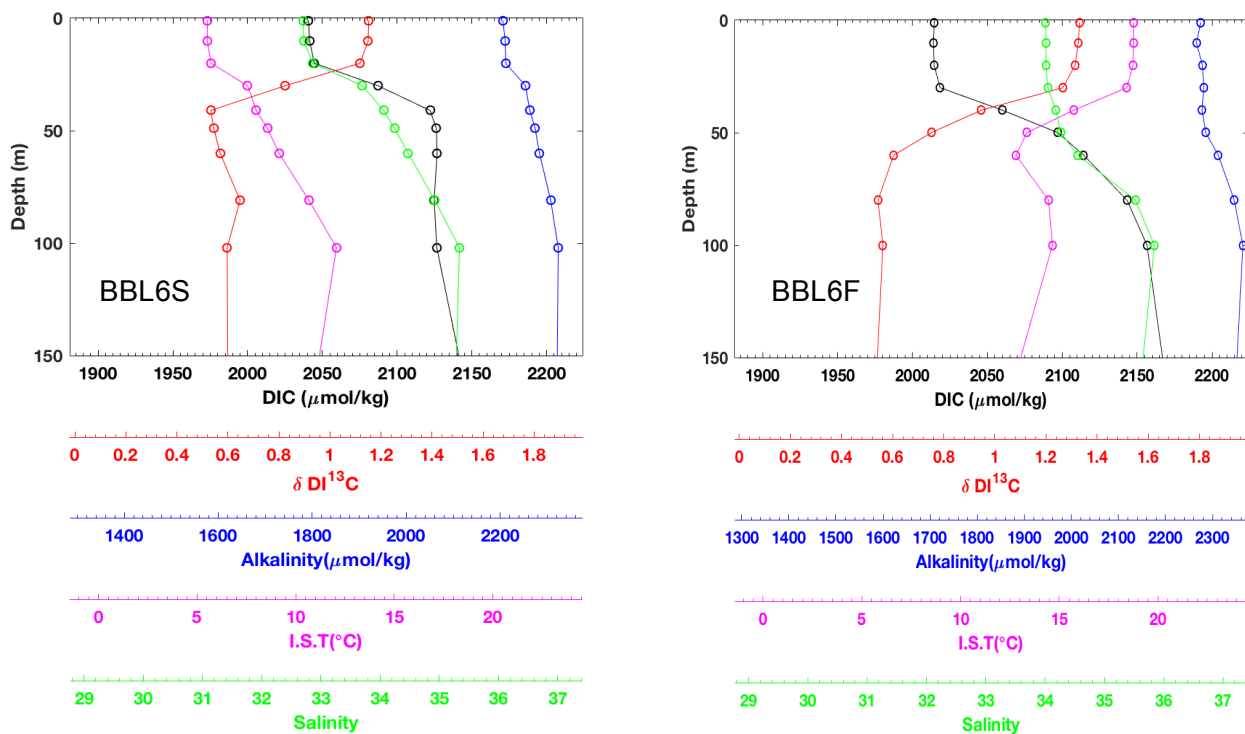
Fig. 3. Seasonal profiles of DIC, DI¹³C, alkalinity, in-situ temperature and salinity   along Browns Bank Line at stations 1, 3, 4, 5 and 6
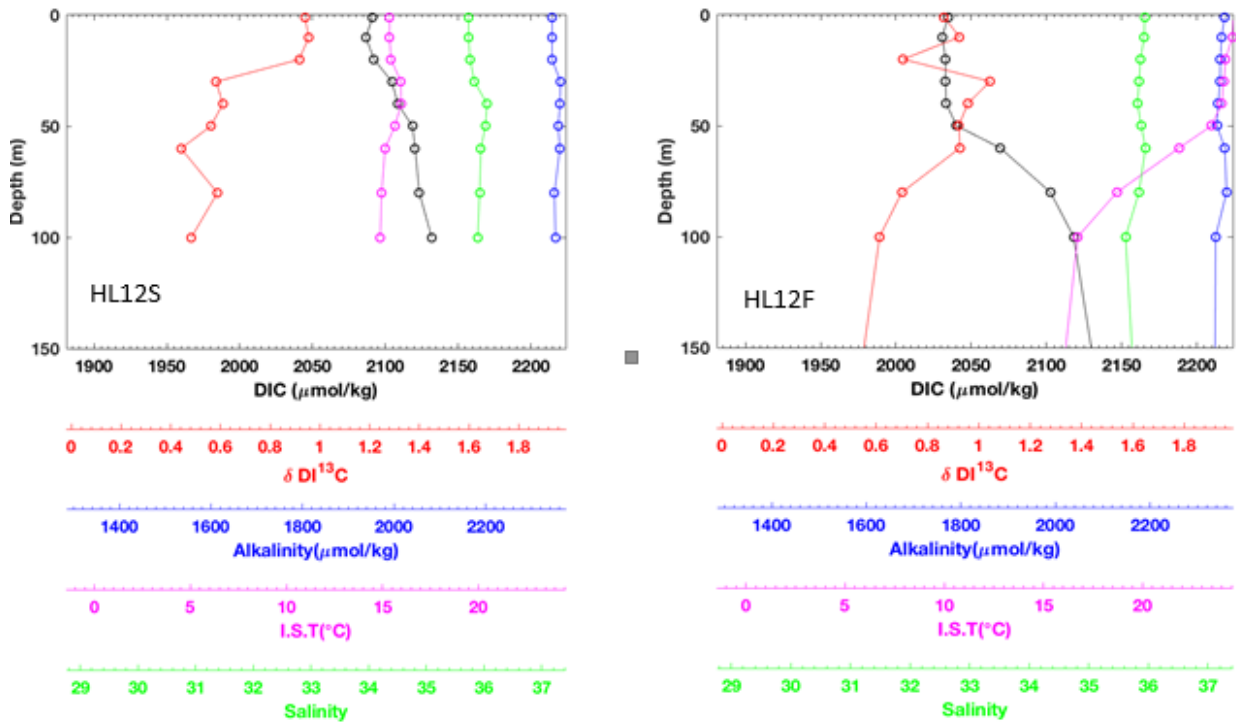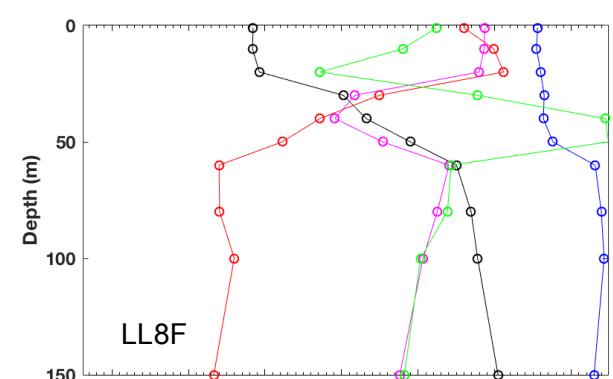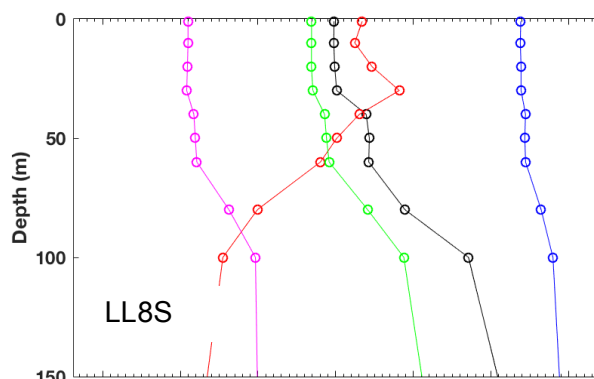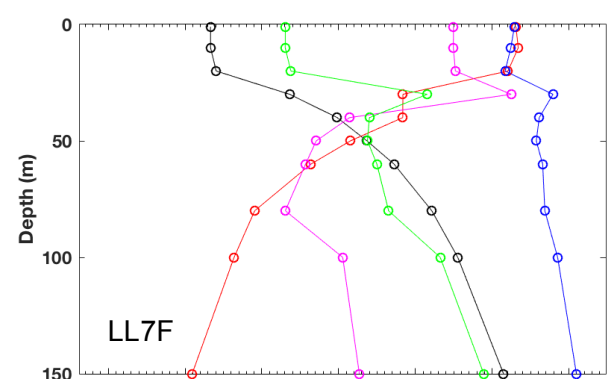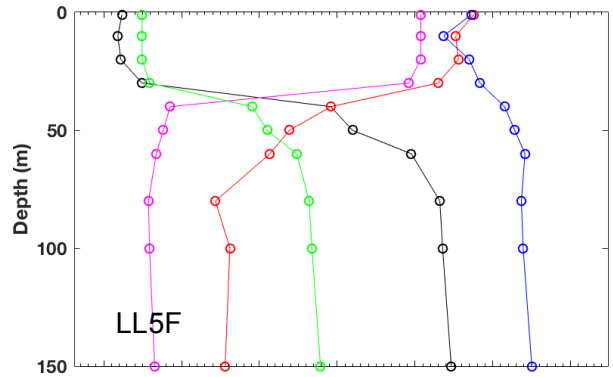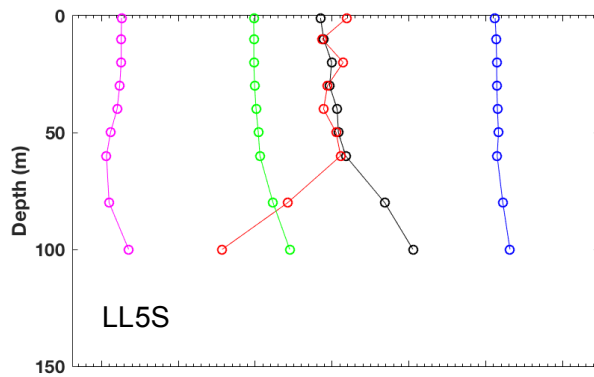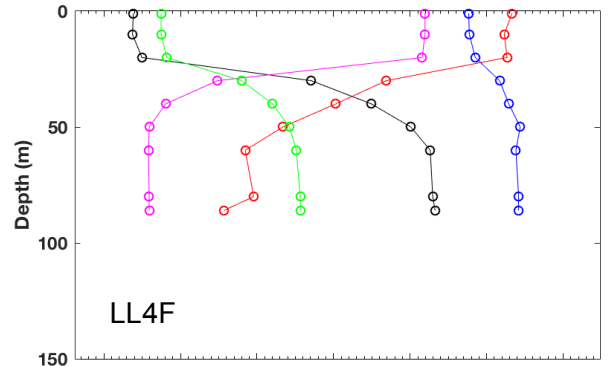
HL1S

HL1F

HL2S

HL2F

HL6S

HL6F

HL10S

HL10F
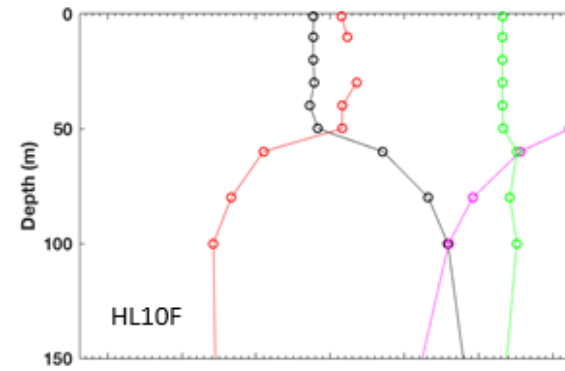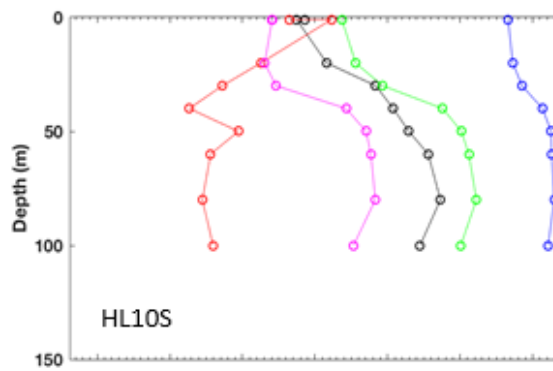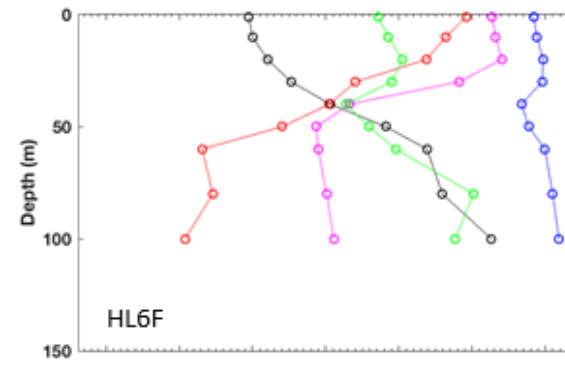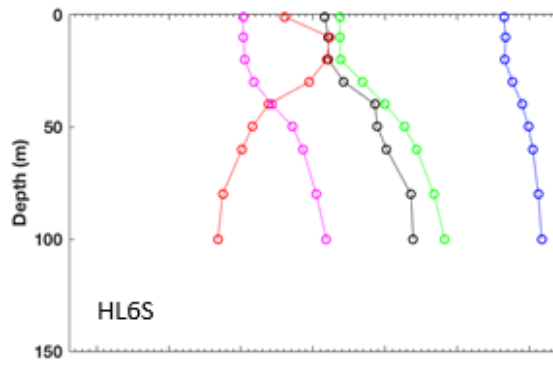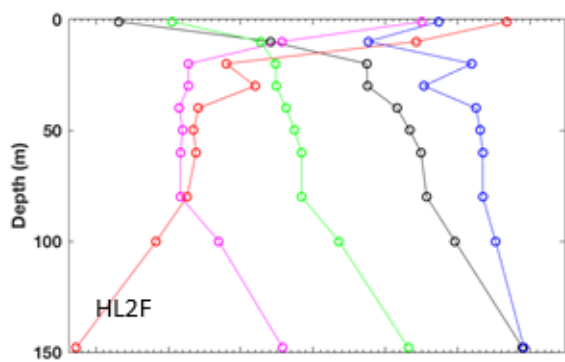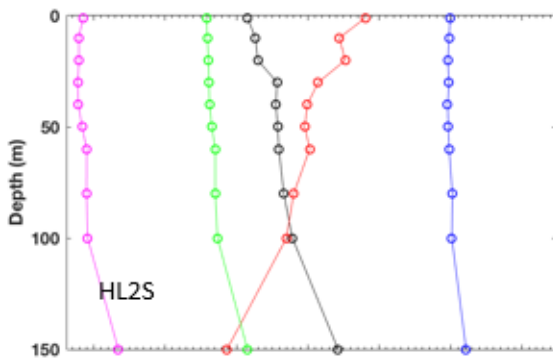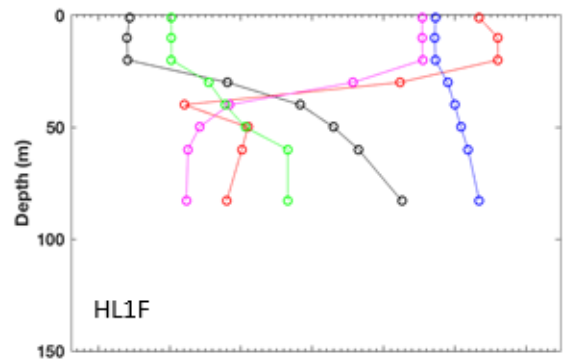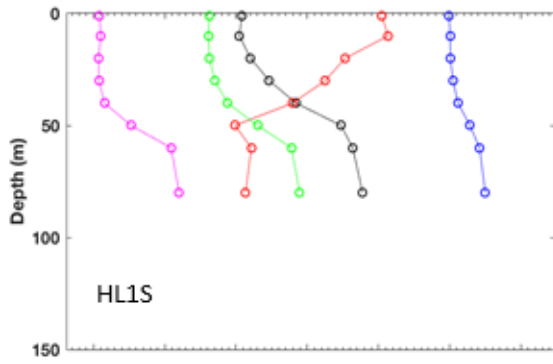
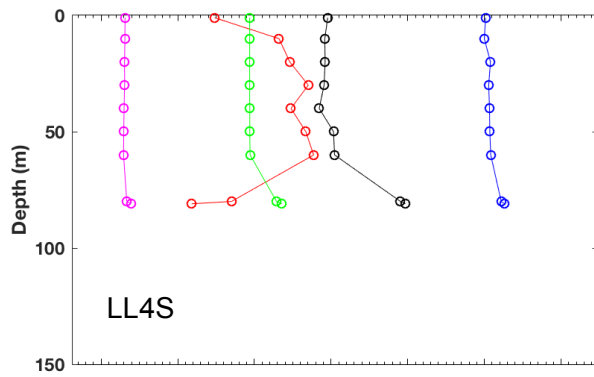**Fig. 4.** Seasonal profiles of DIC, DI¹³C, alkalinity, in-situ temperature, and salinity along Halifax Line at stations 1,2,6,10 and 12.
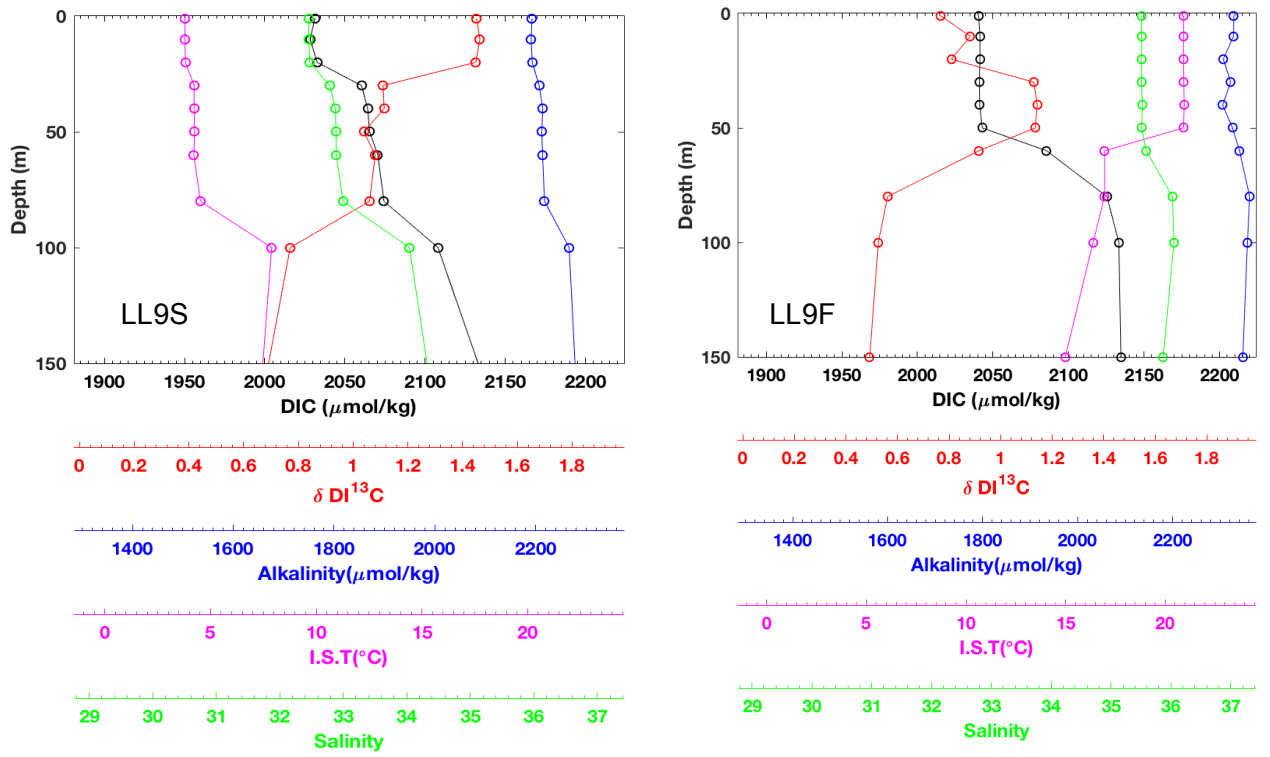
LL4S

LL4F

LL5S

LL5F

LL7S

LL7F

LL8S

LL8F
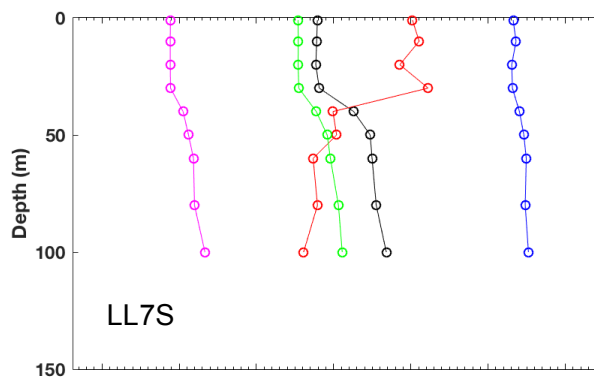
Fig. 5. Seasonal profiles of DIC, DI^{13}C, alkalinity, in-situ temperature, and salinity along Louisbourg Line at stations 4,5,7,8 and 9.
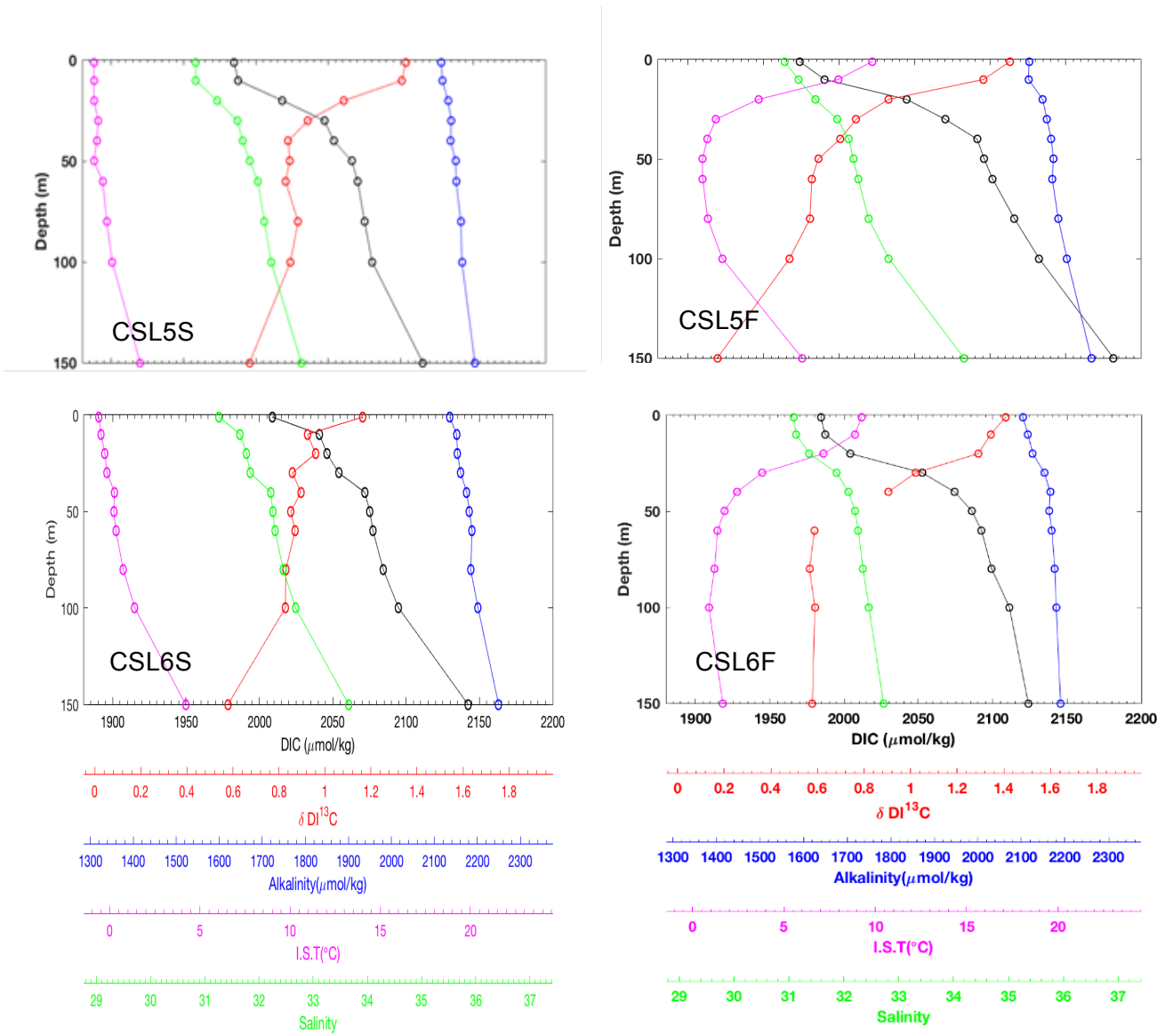
Fig. 6. Seasonal profiles of DIC, DI¹³C, alkalinity, in-situ temperature, and salinity along Cabot Strait Line at stations 1,3,4,5 and 6.

4.5 Seasonality

All transects show strong seasonal variability on the DIC and DI^{13}C values. In figure 8, a wider range of values in fall than in spring is seen. The reasons for this difference are surface water inflow and biological processes. Additional explanation for more clustered data properties in spring is that the surface water are well mixed in winter, due to wind driven and other influences (Shadwick and Thomas, 2014). In fall, the photosynthesis dominants, thus DIC decreases with DI^{13}C increases (see in Fig. 8). However, in spring, respiration results in increase of CO_2, which increases the DIC signal and decreases the DI^{13}C signal (Fig. 8).

In Browns Bank Line, the surface DIC decreases about 48 µmolkg^{-1} from spring to fall, because the ongoing process of photosynthesis consuming the light carbon, which also leads to the increase of DI^{13}C signal by the order of 0.404 (Table 1).

In Halifax Line, the seasonal decrease of surface DIC is 76 in µmolkg^{-1} and the surface DI^{13}C increases 0.237. The highest DI^{13}C value in all the stations through out the 4 transects in fall reaches 1.95, which is found in Halifax Line station 4 and 5. The outstanding value of high DI^{13}C indicates intense photosynthesis occurred at the time. This is because the surface water current brings in nutrient and enhances the photosynthesis processes, and this is a signal of outer shelf flow. This surface water current signal can be seen in figure 7, where the alkalinity is relatively low at places when DI^{13}C values are around 1.9 (compare to other sample points in HL). The low alkalinity indicates that river inflow dilution has occurred.

The Louisbourg Line shows similar patterns as Halifax Line. Its seasonal decrease in surface DIC is around 54 µmolkg^{-1}, with an increase of DI^{13}C signal of 0.223. The reason for their similarities is that they share the same water masses.

In Cabot Strait Line, the seasonal decrease is relatively light compare to other transects. The seasonal surface DIC decreases only 14 µmolkg^{-1}, and a slight DI^{13}C increases is found around 0.065. The slight decrease in surface DIC is also found in Shadwick and Thomas's paper (2014), and their value of the seasonal surface DIC decrease in CSL is 5 µmolkg^{-1}. The slight difference in surface DI^{13}C is result in similar biological production amount in spring and fall in CSL.

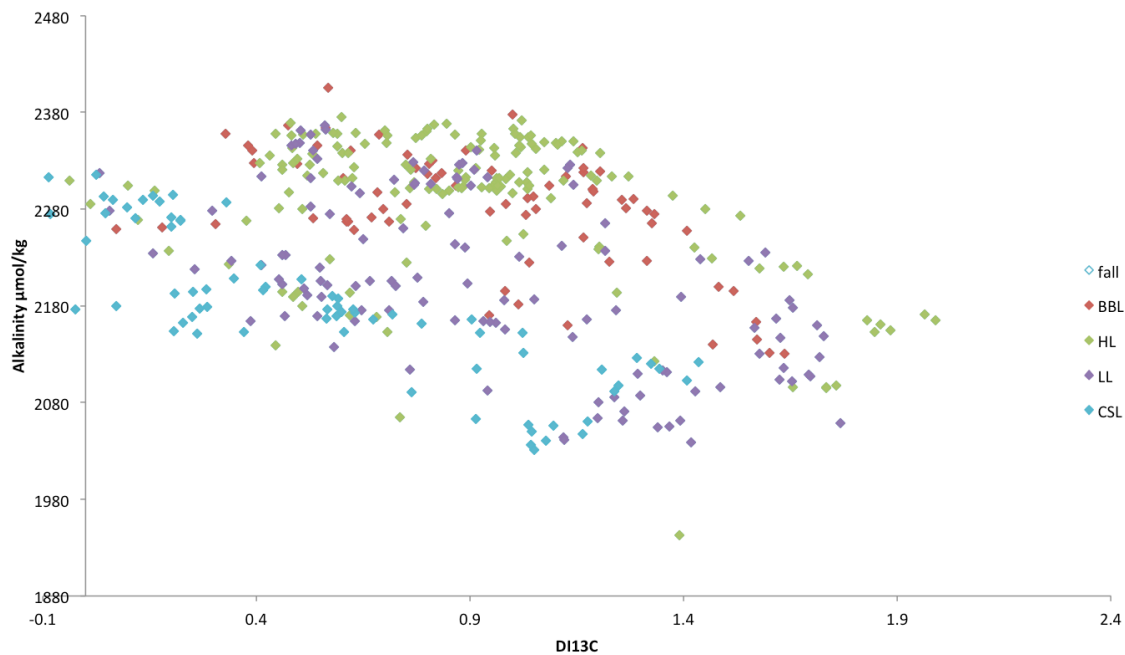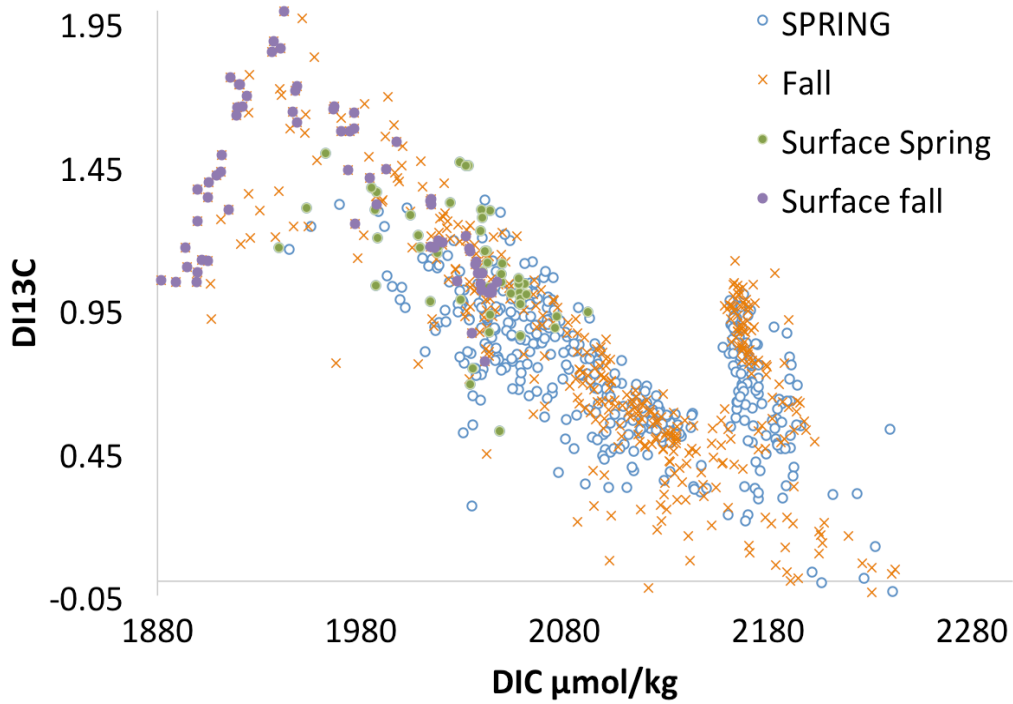**Fig. 7.** Alkalinity (µmol/kg) v.s DI^{13}C of all the sample data through out 4 transects profile.

Fig. 8. DI^{13}C v.s DIC profile of full data samples in spring and fall.
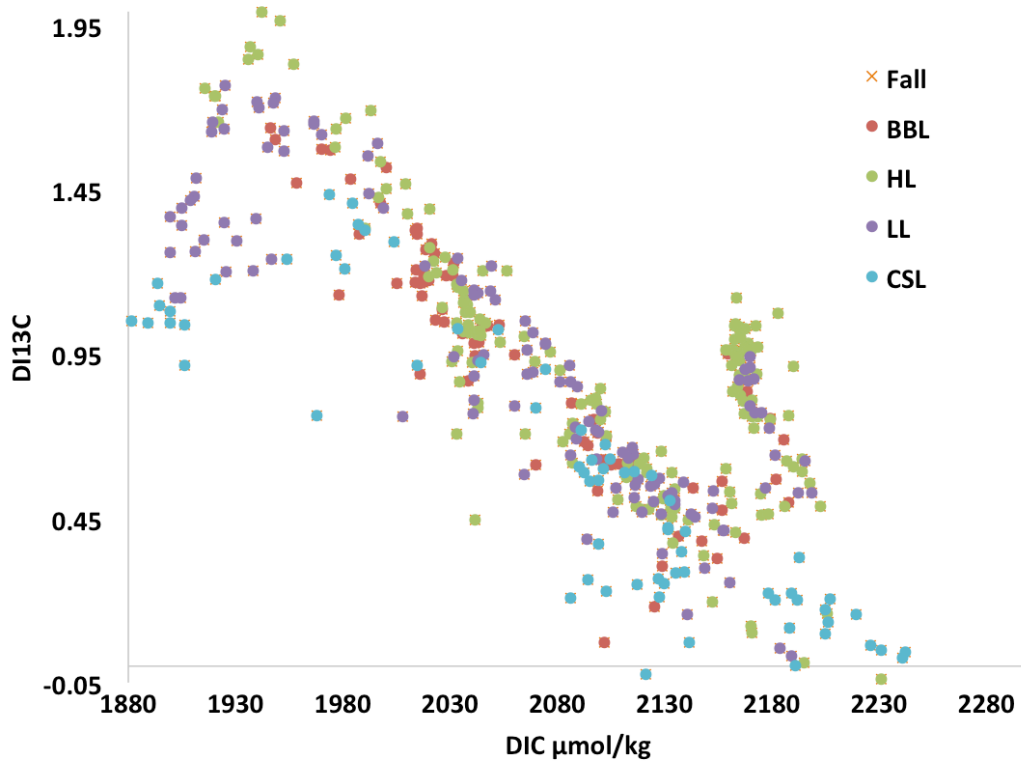

Fig. 9. DI^{13}C v.s DIC distribution in 4 transects in fall.

4.6 Spatiality

Spatial variability is illustrated by comparing properties of waters near shore to offshore, surface water to deep water, and properties along shore. The spatial variability of DIC and $DI^{13}C$ parameters are found in all transects (see fig. 9-14). Here we focus on the patterns in fall for better illustration, due to its large variability.

Halifax Line is used to show the spatial variability from near-shore to offshore. Surface DIC increases with distance further offshore and $DI^{13}C$ on the other hand, decreases in offshore waters (shown in fig. 4 fall term plots). This result is also represented in fig. 10. Orange and red colors are seen in the surface water from station 1 to station 5, with red color shown at station 4 and 5. This means stronger photosynthesis occurred in surface water near shore, with the most intense photosynthesis occurred at station 4 and 5, thus this shelf break signal can be seen clearly. This result is again showing inner shelf flow and outer shelf flow influences with different level. Blue color in subsurface represents the occurrence of respiration processes.
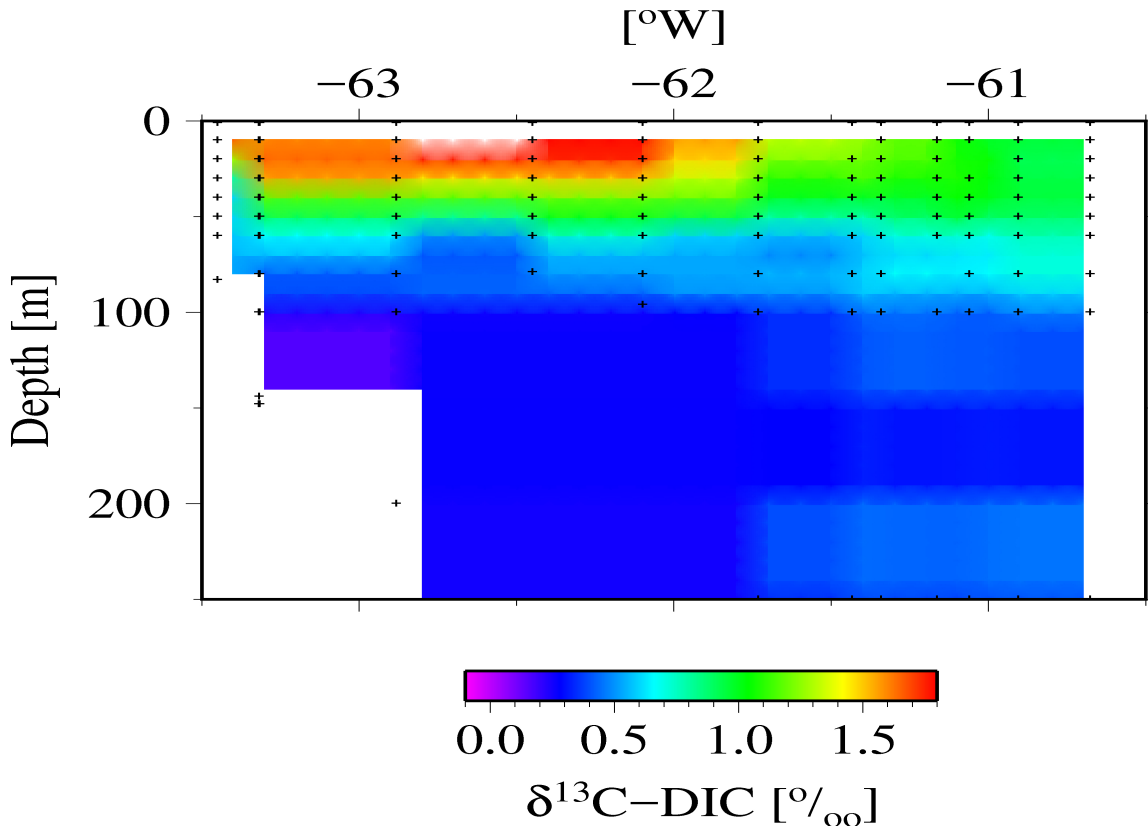
Fig. 10. DI^{13}C of shallow water along Halifax line section in fall.

DIC and DI13C in the Scotian Shelf waters also vary with depth. With photosynthesis occurs in surface water, DIC decreases and DI^{13}C increases. As organic matters sink down, respiration occurs to increase DIC and weaken the DI^{13}C signals (fig. 9 and fig. 10, see also fig. 11). However, after certain depth (around 500 m), shown in fig. 11 and fig. 12, the DI^{13}C signal starts to increase with depth, and hits the maximum value around 1 at depth approximately at 2500 m, and then stay consistent with depth after that (see fig. 11, fig 12 and figure 9). The reason for this variability in deep waters is still unknown, however, the water mass deeper than 3500 m is considered to be a signal of Deep Western Boundary Current (DWBC). The DWBC contains water masses such as Denmark Strait Overflow Water, North Atlantic Deep Water and Labrador Sea Water ("The Deep Western Boundary Current on the Scotian rise", 2016).
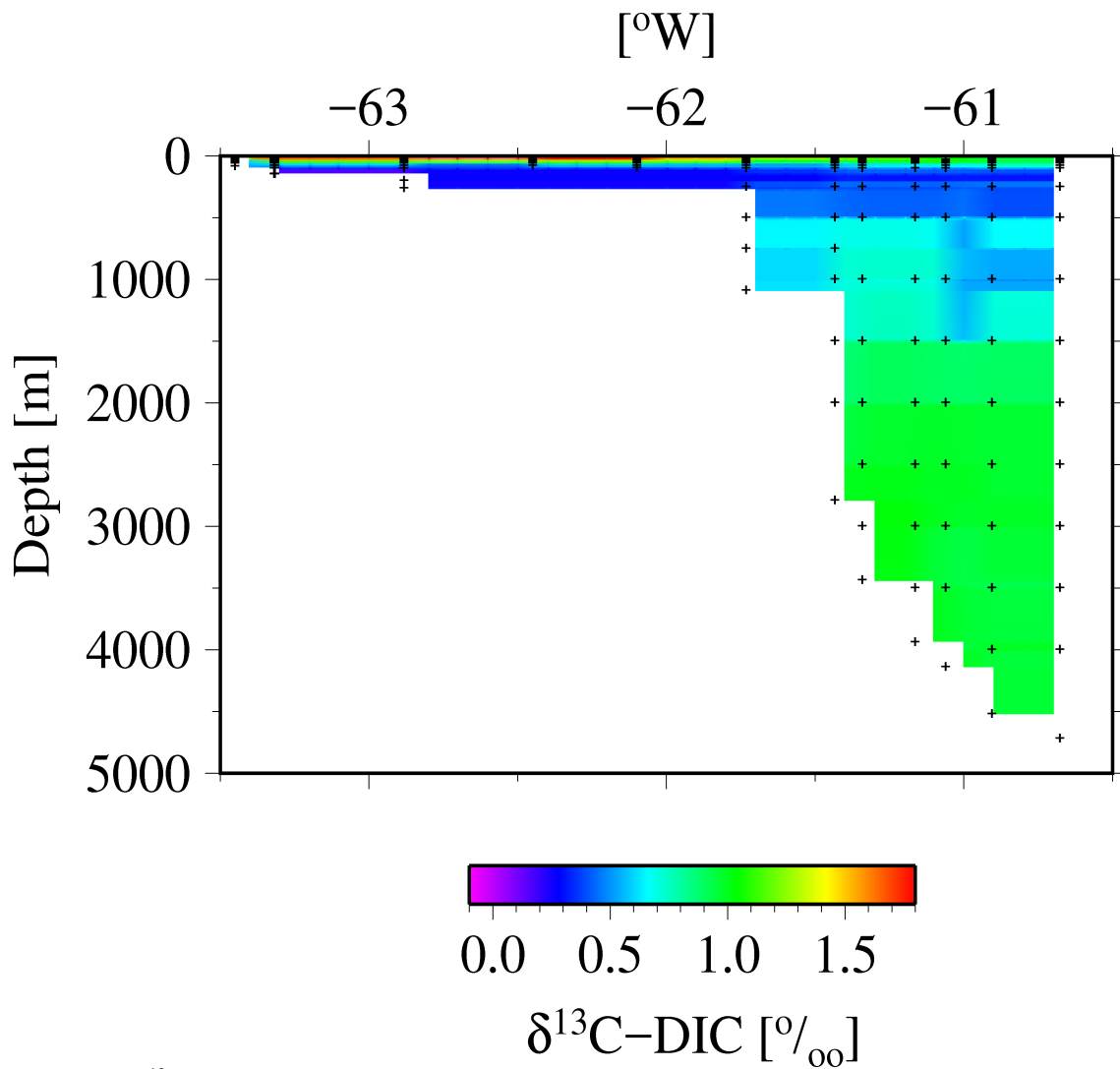
Fig. 11. DI^{13}C of deep water along Halifax line section in fall.
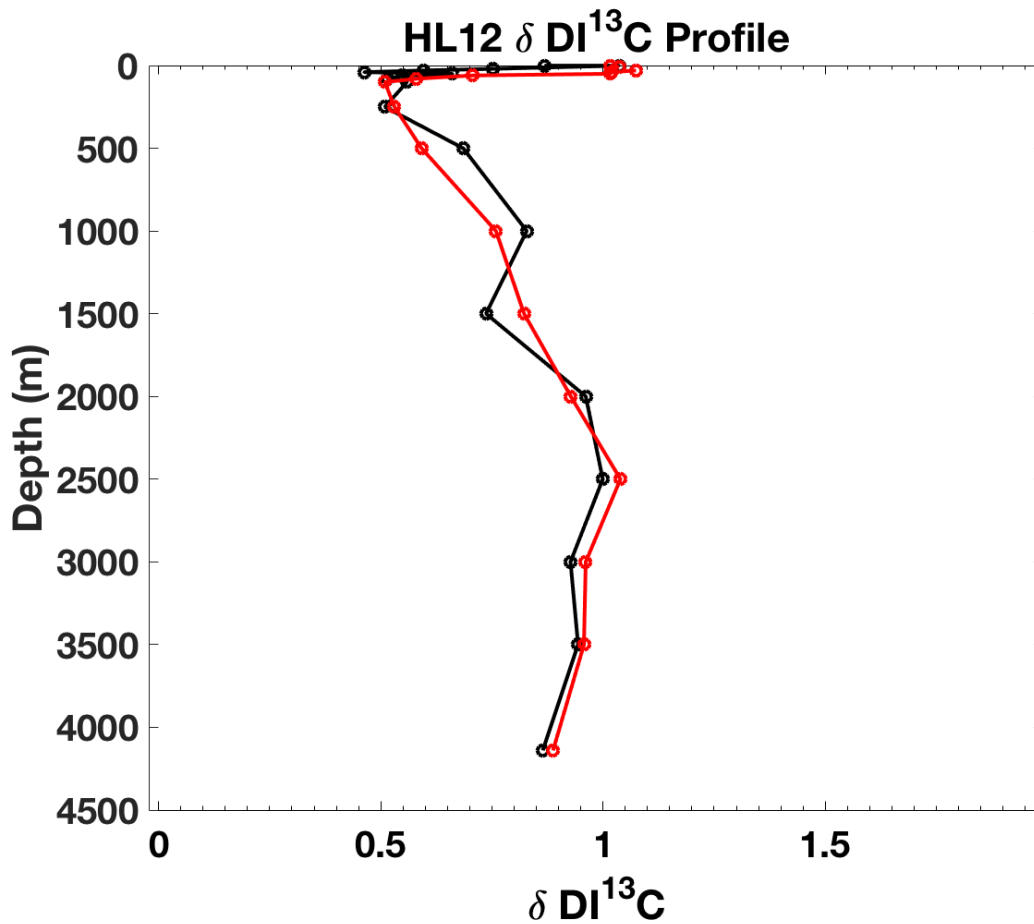
Fig. 12. DI^{13}C profile for Halifax Line Station 12 in spring (black line) and fall (red line).

Comparing spatial variability along shore, CSL shows the most distinctive characteristics relative to other sections. The surface DIC in CSL is the lowest comparing to the surface DIC in other transects, as well as its DI^{13}C, due to surface water dilution effect (fig. 9). CSL also contains the lowest DI^{13}C value with the highest DIC value in deep waters relative to other transects (see fig. 9 and fig. 14), which exhibiting strong respiration processes occurred in the water.

Fig. 13. DI^{13}C profile of CSL at station 3 in spring (black line) and fall (red line).

Fig. 14. DI^{13}C of mid-depth water along Cabot Strait section in fall.
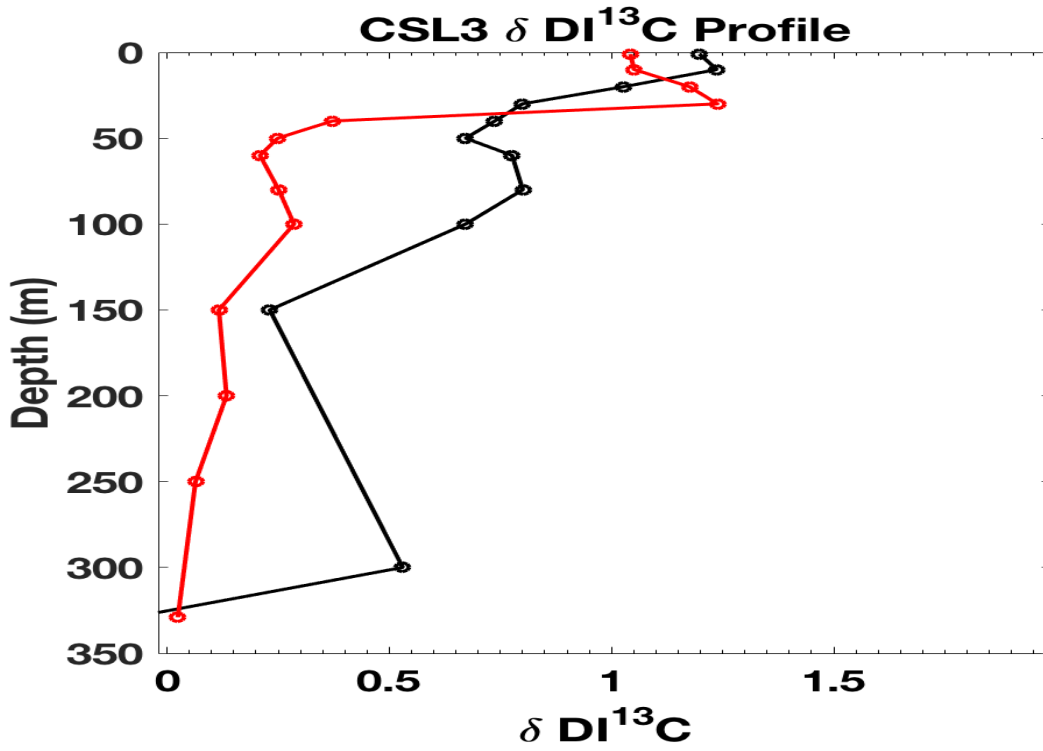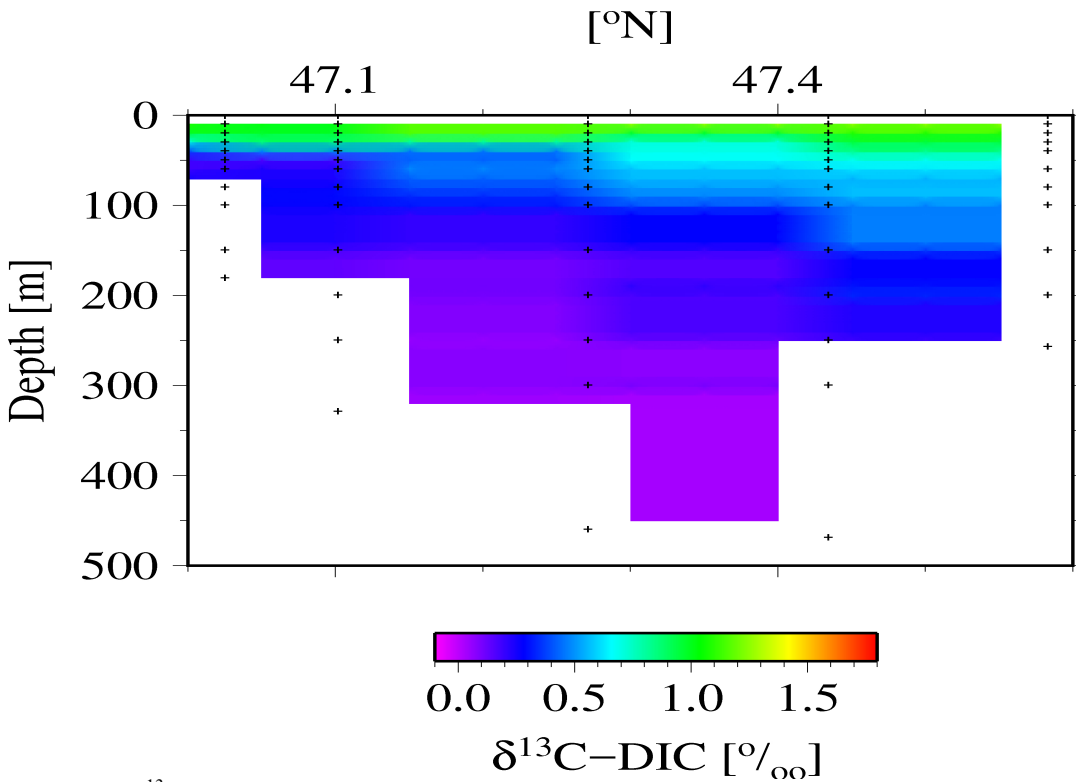
4.7 Governing processes

The governing processes exhibited in the results are river inputs and biological processes (fig. 15). St. Lawrence Estuary water and water from Labrador Sea enters Scotian Shelf via Cabot Strait, thus surface water of Cabot Strait Line gives a river input signal, and detected as inner shelf flow (the input slope is shown as blue line in fig. 15). Water comes out from Cabot Strait mix with the Labrador Current and creates an outer shelf flow on Scotian Shelf. The outer shelf flow presents in the LL and HL at station 4 and 5, shown as the red line in fig. 15, gives the highest value of $DI^{13}C$ in HL4 and HL5 and indicating intense biological production. As a result, it is clear that the river inputs are able to change inorganic carbon system by different level. Cabot Strait deep water is presented inside the blue circle in fig.15. This water is originated from South, which is rich in DIC, poor in oxygen with old biological process history (Mucci et. al, 2011). Thus it gives the highest DIC signal with the lowest $DI^{13}C$ values, indicating strong respiration processes, comparing to other transects (see fig. 15 and fig.14). The deep water (deeper than 3500m) in BBL, LL, and HL is exhibited in the purple circle in fig. 15. This signal indicates the cold DWBC with young biological history. The reason for increasing $DI^{13}C$ signal without decreasing DIC signal currently remains unknown, however, further research will be carried out and focusing on this phenomena.
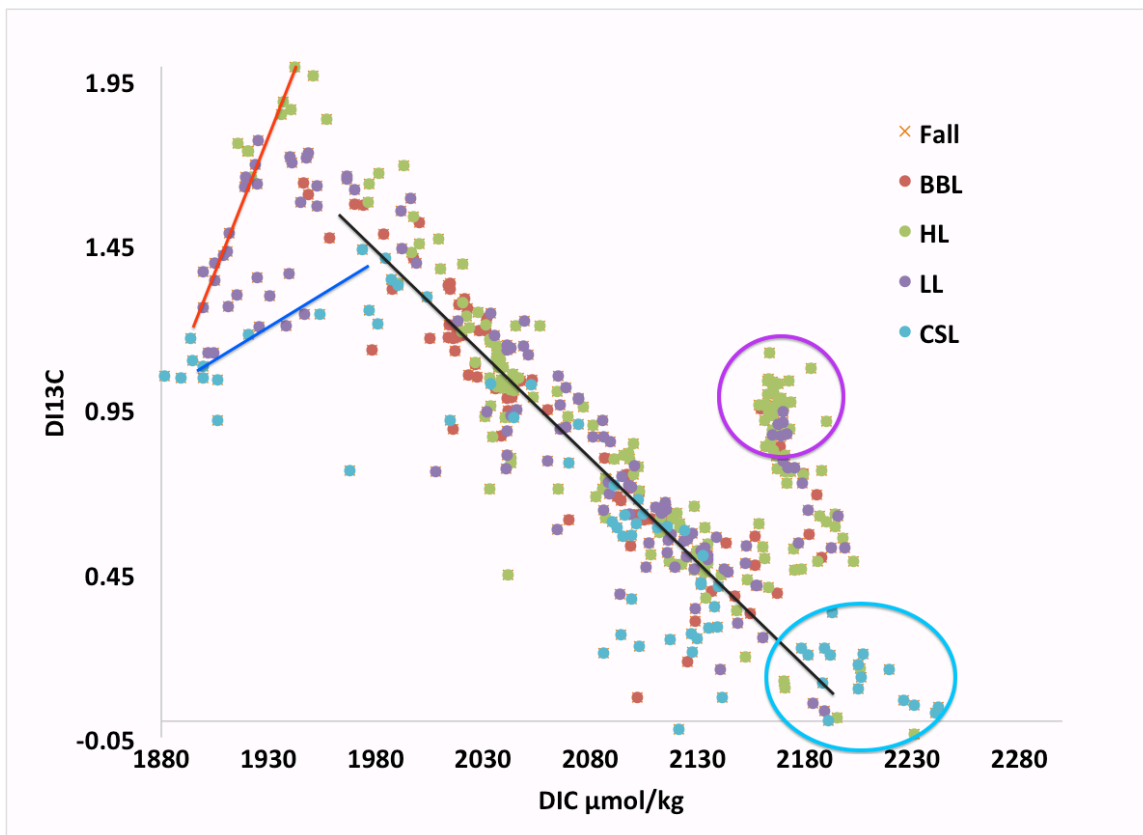
Fig. 15. DI^{13}C v.s DIC distribution in 4 transects in fall. Black line represents biological signal; blue and red lines are inner shelf inflow and outer shelf inflow respectively; sample data in purple circle are deep waters with depth deeper than 3500m; data in blue circle are deep waters of CSL.

The biological process is the dominant governing factor of the inorganic carbon system in Scotian Shelf waters. Phytoplankton uptake light carbon isotope through photosynthesis, which decreases DIC and increases DI^{13}C in surface water. In subsurface waters, respiration gives out CO_2, which increases DIC and decreases DI^{13}C. In fig. 15, the black line shows the negative linear relationship between DIC and DI^{13}C, and indicates a strong effect of biological processes on DIC and DI^{13}C signals.

5.0 Conclusion

The study is carried out to focus on inorganic carbon cycling in Scotian Shelf waters, the goal of this research is to study the seasonal and spatial variability of selected

paramters such as DIC, $DI^{13}C$, alkalinity, salinity and temperature, with a focus on DIC and $DI^{13}C$. The research is also aiming at identifying the governing processes of the inorganic carbon system. The results of this study will provide more details on the seasonality of the carbon cycle on the Scotian Shelf, and provide a baseline of the data from which further studies can be carried out, for example investigations into ocean acidification on the Scotian Shelf.

The inorganic carbon system in Scotian Shelf waters exhibits large variability in both seasonal and spatial scale. A seasonal decrease of surface DIC and a subsurface increase of DIC are found in inner shelf. Highest biological production is found in Halifax Line surface water near shore area and the lowest biological production in surface water is found in Cabot Strait Line. Lower $DI^{13}C$ signal are shown in subsurface waters further offshore, with a rebound occur in deep waters, however, Cabot strait line deep waters exhibits the lowest $DI^{13}C$ values (in the order of 0) due to its old biological history. Governing processes indicated by the results are biological processes and river inputs. The biological process is the dominant control over inorganic carbon system in the Scotian Shelf waters. Inner shelf waters and outer shelf waters are also seen in the research and they are able to change the inorganic carbon signals in different levels. Suess effect might also influence the inorganic carbon system in Scotian Shelf waters; however, the interpretation of Suess effect signal has not been studied in this research due to the time limit.

Other than Suess effect signal detection, the quantification of biological production and river input in Soctian Shelf waters, and the deep water signal interpretation go beyond the limits of the methods presented in this research, and they will be the focus of future work in the region.

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