The carbon cycle of Glacier Bay, Alaska: primary productivity, the importance of terrestrial inputs and the air-sea carbon dioxide exchange

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Abstract

Understanding the carbon cycle of Glacier Bay is important for examining future effects of climate change on a highly productive, estuarine fjord. To accomplish this analysis, three main factors will be addressed: the air-sea gas exchange of carbon dioxide (CO_2), the extent of terrestrial sources of organic carbon and the quantification of primary productivity. Water samples, vertical net tows, and wind data were collected throughout the Bay to measure total DIC, carbon isotope ratio, alkalinity, and particulate organic carbon content. pCO_2 levels throughout the bay ranged from 187µatm and 301µatm and wind speed averaged 14.4 knots. Combining these numbers with atmospheric CO_2 levels of 385ppm (374µatm), gas flux from atmosphere to ocean was 0.60g/m^{2}day, which is inline with coastal Artic and Antarctic winter gas flux rates and about 8 times higher than global open ocean basin yearly average flux rates. It was also determined that about thirty percent of the organic carbon in the bay comes from a terrestrial source. This value is low for a system like Glacier Bay, but probably typical due to the cold time of year and therefore low freshwater input from streams and rivers. DIC at depth is largely influenced by DIC rich waters from outside of the bay, which is contrary to the expectation that most of the excess DIC below the mixed layer usually comes from respiration. Extremely low winter runoff conditions, vigorous tidal flushing and the earliest stages of the spring phytoplankton bloom were responsible for the interesting results of this study.

Introduction

Coastal zone carbon cycles are driven mostly by atmospheric CO_2 levels, sediment delivery from rivers and shore activity, as well as human sewage inputs (Ver et al. 1999). While coastal sections account for a very small fraction of the world's ocean, they are incredibly important to fisheries, the global carbon cycle and primary production. Ninety percent of the fish catch, eighty percent of organic burial and fourteen to thirty percent of the ocean's primary productivity occurs where saltwater meets the land (Gattuso et al. 1998). Understanding the impacts of river input and increasing atmospheric CO_2 levels is of great concern for coastal regions throughout the world.

Coastal areas act as filters of organic matter, nutrients and pollutants between the land and sea (Ver et al. 1999). Glacier Bay is an estuarine fjord consisting of long basins with high river input and a sill at the mouth. The bay has only one, narrow entrance and a prominent sill that causes traditional estuary circulation to be replaced by turbulent mixing. This type of mixing is driven by the vigorous flushing of the bay due to significant tidal variation (Etherington et al. 2007). Because of the high nutrient input from freshwater sources and the strong 'filtering' effect of the sill, primary productivity is high here and limited almost exclusively by light penetration (Hooge & Hooge 2002). This unique combination of geography, physical forcing and nutrient availability make this region of southeast Alaska a particularly important habitat to whales, harbor seals, halibut and salmon (Mathews & Pendleton 2006; Carlson et al. 2005). The goal of this project was to increase the awareness of the carbon cycle of Glacier Bay, Alaska, which is one of the most essential nutrient structures to its ecosystem.

The delicate nature of marine ecosystems is easily disturbed by natural and human influences. Over the past three decades, an extensive network of CO_2 monitoring has been set up. In addition, thousands of field measurements have been taken and elaborate mathematical models have been created to look at how the sea buffers atmospheric CO_2 (Jacobson et al. 2007). The ocean is the primary buffer for CO_2 in our atmosphere, and as concentrations of atmospheric CO_2 increase, the pH of the buffering surface ocean drops. If pH drops far enough, organisms with calcium carbonate shells will not be able to survive (Caldeira & Wickett 2003). Determining the rate of gas exchange and the current concentration of CO_2 in the surface water will allow for a prediction to be made about potential ecosystem impacts in the future.

This research attempted to define a relationship between organic carbon, primary productivity and air to sea CO_2 gas exchange in Glacier Bay, Alaska. In addition to establishing these connections, the report examines the importance of terrestrial organic carbon inputs, and looks for potential future impacts of CO_2 concentration increase. The dominant source of organic carbon to the bay will be terrestrial, due to high amounts of river input and restrictive nature of a high sill. Flux of CO_2 from atmosphere to ocean will be evident, but the impacts will be minimal due to the rapid flushing of surface water from the bay.

Methods

Shipboard collection

Dissolved inorganic carbon samples were collected in 250 mL glass bottles, poisoned with 100 µL of mercuric chloride ($HgCl_2$) and grease sealed. These samples were placed in crates for laboratory analysis after the cruise.

Alkalinity samples were collected in 300 mL glass oxygen titration bottles to ensure that there is no air contamination. These samples were then placed in the ship laboratory to allow their temperatures to equilibrate to ambient levels. Then, the samples were measured for pH and analyzed by the Gran titration method in batches of 8 using an auto titrator.

Particulate organic carbon was collected at stations 00, 03, 05, 07, and 22 from 1m diameter, 100 micron vertical net tows. The net tows were cast to a depth of 30 meters. Water was drained away from the samples before they are transferred to 100 mL glass bottles. Samples were dried and stored for elemental analysis after the completion of the cruise.

Table 1 lists the sampling depths of the stations to be tested. DIC is measured at all stations and all depths, while alkalinity and POC are measured only in the surface. At station 00, 04 and 07 alkalinity was measured at all depths.

Laboratory Measurements

Total dissolved inorganic carbon and DIC stable isotope ratios were assessed by acidifying the poisoned seawater sample and extracting it via the method defined in Quay et al. 1992. Total

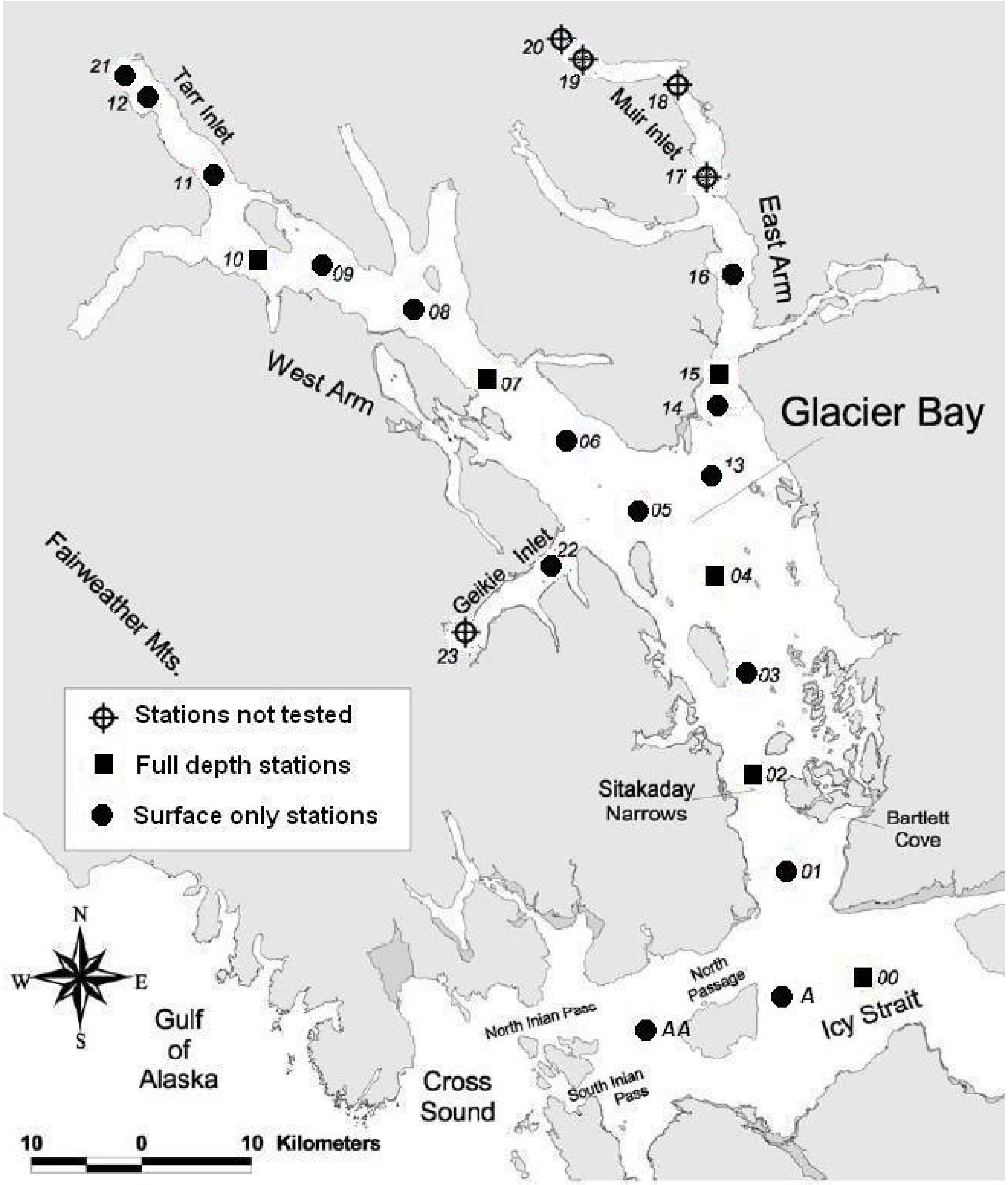


Figure 1: Showing NPS stations in Glacier Bay cruise. Some stations will be sampled for full depth profiles down to the mixed layer, some will be sampled in the surface layer only, and others will not be sampled at all. Locations chosen to achieve wide spatial distribution. Squares indicate stations where water was sampled below the surface layer, circles represent stations where only surface stations were sampled.

USGS station	DIC collection depths (m)	Alkalinity col. depth (m)	Plankton col. depth (m)
00	0,5,10,25,50,100	0,5,10,25,50,100	0 to 5
01	0	0	
02	0,5,10,25,50,100	0	
03	0	0	0 to 30
04	0,5,10,25,50,100	0,5,10,25,50,100	
05	0	0	0 to 30
06	0	0	
07	0,5,10,25,50,100	0,5,10,25,50,100	0 to 30
08	0	0	
09	0	0	
10	0,5,10,25,50,100	0	
11	0	0	
12	0	0	
13	0	0	
15	0,5,10,25,50,100	0	
16	0	0	
21	0	0	
22	0	0	0 to 30
A	0	0	
AA	0	0	

Table 1: The locations and depths of sampling for each type of sample taken.

Basin	(g m^{-2} day^{-1})
Pacific	0.026
Atlantic	0.13
Indian	0.081
Southern	0.15
Global	0.073
Glacier Bay	0.60

Table 2: Global yearly averages for other ocean basins. Note, that the Glacier Bay basin only represents a 4 day average in March.

DIC was calculated by measuring temperature and pressure in a known volume after the CO_2 had been isolated from all other gasses. The extracted CO_2 was then run on a Finnigan 252 mass spectrometer and compared to an internal standard. This provided the $^{13}\delta C/^{12}\delta C$ ratio of the inorganic carbon.

Dried POC samples were ground in a mortar and pestle and loaded into sterilized aluminum sample boats and weighed. The samples were then combusted in an elemental analyzer to determine the $^{13}\delta C/^{12}\delta C$ ratio of the organic carbon.

Calculations

Wind speed was recorded constantly throughout the cruise. The anemometer of the *Thompson* is 20.42 meters from the surface of the water. The following logarithmic transform was performed to average this wind speed measurement to a height of 10 meters.

$$W_{10m} = W_{20.42m} \left(\frac{\log\left(\frac{10}{z_0}\right)}{\log\left(\frac{W_{20.42m}}{z_0}\right)} \right) \tag{1}$$

Where W_{10m} is the corrected wind speed, $W_{20.42m}$ is the measured wind speed, and z_0 is the roughness height of 0.005m. Wind speeds were converted from knots to meters per second. Next, Schmidt coefficients and piston velocities were calculated using the following equations (Nightingale 2000).

$$S_c = A - (B \cdot T) + (C \cdot T^2) - (D \cdot T^3) \quad (2)$$

Where coefficient A is 2073.1, B is 125.62, C is 3.6276, and D is 0.043219 from Wanninkhof 1992. T is the absolute temperature of seawater in Kelvin and S_c is the Schmidt number. Then, using the Schmidt number from equation 2 and wind values from equation 1, the piston velocity (K_n) is calculated.

$$K_n = \left(0.222 W_{10m}^2 + 0.333 W_{10m}\right)\left(\frac{600}{Sc}\right)^{\frac{1}{2}} \quad (3)$$

Next, volumetric solubility of CO_2 was calculated from seawater temperature (T) and salinity (S). Equation 4 was used to calculate the solubility (F) for each station where DIC measurements were taken based on solubility parameters A_1, A_2, A_3, A_4, B_1, B_2, and B_3 (Sarmiento & Gruber 2006).

$$\begin{aligned} \ln F = A_1 + A_2\left(\frac{100}{T}\right) + \\ A_3 \ln\left(\frac{T}{100}\right) + A_4\left(\frac{T}{100}\right)^2 + \\ S\left(B_1 + B_2\left(\frac{T}{100}\right) + B_3\left(\frac{T}{100}\right)^2\right) \end{aligned} \quad (4)$$

We are able to calculate the pCO_2 of seawater from temperature, salinity, alkalinity and total DIC. To perform this calculation, a Matlab script was used, which was developed using the relationships defined by Lueker et al. 1999. Finally solubility calculated from equation 4, piston velocity from equation 3, pCO_2 of seawater and the pCO_2 of the atmosphere were combined into an equation that will gives an average flux rate for CO_2 between the surface ocean and atmosphere (Dickson & Goyet 1994).

$$Flux = K_n \times F \times \left(pCO_2^{atm} - pCO_2^{ocean}\right) \quad (5)$$

The inorganic $^{13}\delta C/^{12}\delta C$ ratios found at depth and in the surface will be related to the total DIC and particulate organic $^{13}\delta C/^{12}\delta C$ ratio to determine how much of the respired carbon comes from terrestrial inputs.

Station (NPS#)	Carb. / Nit. (ratio)	$^{13}\delta C/^{12}\delta C$ (‰)	Confidence (+ / -)
22	8.97	-22.97	0.614
03	9.34	-23.79	0.854
05	9.12	-23.28	1.551
07	6.27	-21.18	0.307

Table 3: Showing the POC data for each of the 4 stations tested. Carbon to nitrogen ratio tests for closeness to Redfield ratio.

Results

First, we examined how certain parameters vary with distance from the mouth of the bay. Station 00 was set as the ‘zero distance,’ since it is located in an area that is effected by water exiting Glacier Bay, but less so than any other NPS station. Surface salinity ranged from a high of 31.46 practical salinity units (psu) at the mouth to about 30.2 psu at the back of the west arm of Glacier Bay (Figure 2a). The surface $^{13}\delta C/^{12}\delta C$ ratio along the same transect ranged from -6‰ at the mouth to a peak value of 34‰ at station

Station	13/12	Dominant Process
00	-0.06	Respiration
2	0.01	Balanced
4	0.10	Photosynthesis
5(CS2)	0.34	Photosynthesis
22	0.31	Photosynthesis
6	0.23	Photosynthesis
7	0.27	Photosynthesis
8	0.24	Photosynthesis
10	0.06	Photosynthesis
11	0.13	Photosynthesis
21	0.03	Balanced
16	-0.13	Respiration
15	-0.11	Respiration

Table 4: The $\delta 13/\delta 12$ ratio and which process is dominating at each station. Depleted levels mean respiration is dominating, enriched levels indicate photosynthesis

05. Further into the west arm, northwest of station 05, the ratio decreased back to around 0‰ (Figure 2b). A depleted value means that respiration is dominating photosynthesis and an enriched value indicates the opposite. DIC in most basins is linked positively with salinity, so DIC data was plotted against distance from station 00 to ensure that it compared in a similar manner, and increase the confidence in these DIC results (Figure 3a).

Comparing general water properties, like salinity and temperature to one another is also necessary for us to analyze the accuracy of the carbon data. Using data from the Seabird conductivity, temperature and depth instrument (CTD) casts and calculated results based on measurements, depth profile and mixed layer plots were constructed for the following: water temperature versus salinity (Figure 4a & 4b), DIC versus salinity (Figure 5), $^{13}\delta C/^{12}\delta C$ ratio versus salinity (Figure 6), and alkalinity versus salinity (Figure 7a & 7b). Alkalinity, temperature and DIC all had close correlation to salinity. As the salinity decreased further into the bay, so did the alkalinity, temperature and total DIC. The $^{13}\delta C/^{12}\delta C$ ratio showed inverse proportion to total DIC. The mixed layer was defined as the depth at which the density had increased by 0.125 kg/m^3. These trends and correlations were close to the expected outcomes and increased our confidence in the accuracy of measuring, sampling and calculating techniques.

Throughout the duration of the cruise, wind speed in the park ranged from 0.5 to 30.7 konts and averaged 14.4 knots.

The partial pressure of carbon dioxide in seawater in Glacier Bay ranged between 187µatm and 301µatm in the surface and from 239µatm to 300µatm at depth. The pCO_2 of the surrounding atmosphere in Glacier Bay is 385ppm according to the NOAA Earth System Research Laboratory monitoring network (Peters et al. 2007). By applying equations 3, 4, and 5 to our data, we find a net CO_2 flux from atmosphere to ocean ranging from 0.32 grams / m^2 *day(g/m^{2}day) to 0.87g/m^{2}day and averaging to 0.60g/m^{2}day (Table 3).

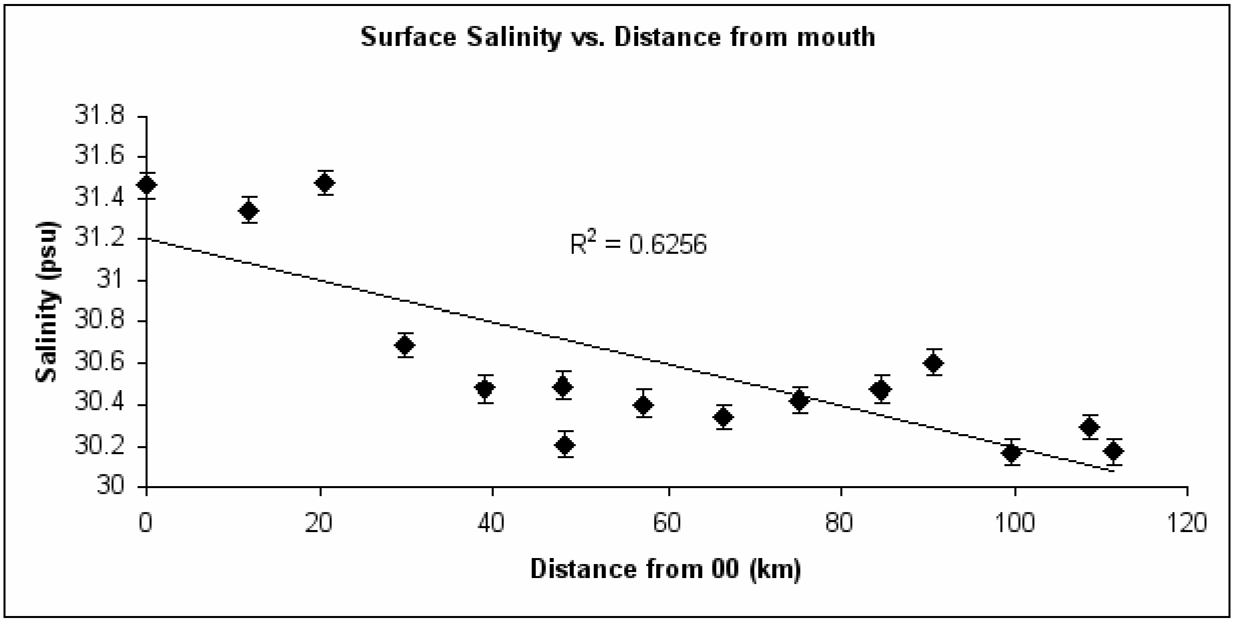
Particulate organic carbon-13 isotope ratios range from stations 03, 05, 07, and 22 range between -21.12 and -24.98‰ (Table 4). To test for accuracy, isotope ratio was plotted against the carbon to nitrogen ratio to look for trends and adherence to Redfield ratios. All data points were close to Redfield, with a slight abundance of carbon (Figure 8).

A Keeling plot was created to estimate the extent of the influence of biological respiration on the CO_2 present in the water column at station 07 (Figure 9). The intercept of the linear regression is -13.8, which corresponds to -13.8‰ $^{13}\delta C/^{12}\delta C$ ratio at depth.

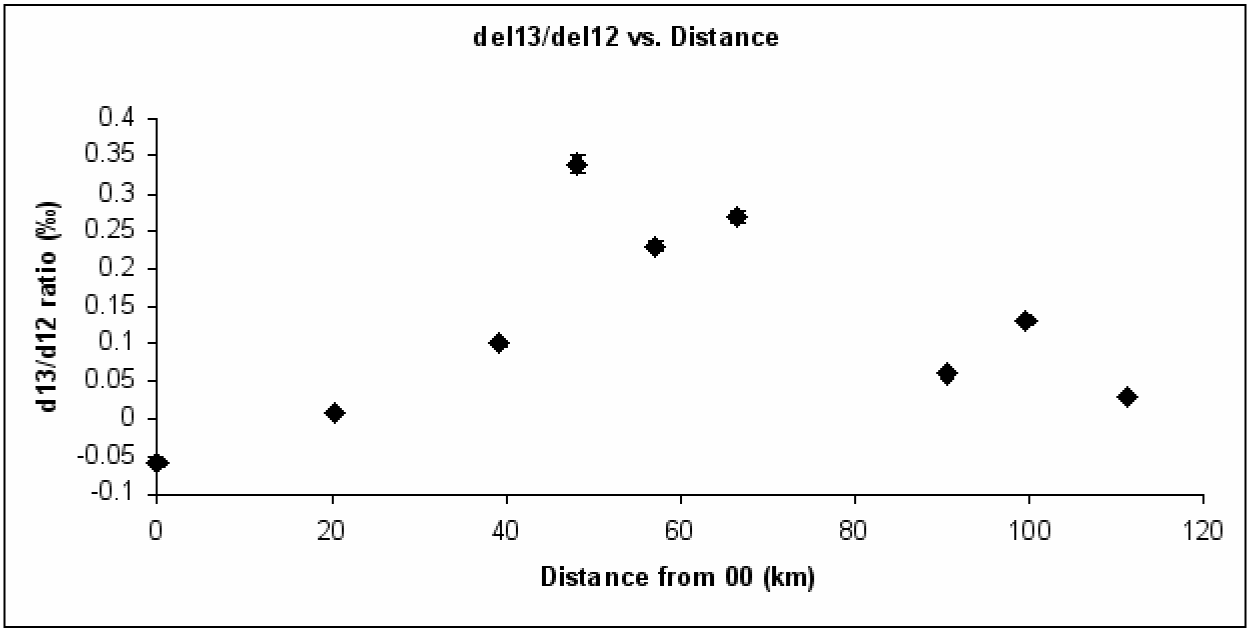
Discussion

CO_2 flux between ocean and atmosphere

CO_2 concentration in the atmosphere is cur-



(a)



(b)

Figure 2: a.) Salinity vs. distance from the mouth of the bay. The mouth of the bay is given a 0 distance at station 00. The salinity measurements are all from the surface and ranged over a three day sampling period. b.) d13/d12 ratio vs. distance from mouth. Highest values found occurred near the middle of the bay with the most depleted water occurring at the mouth and slightly depleted water present in the back of the west arm of Glacier Bay.

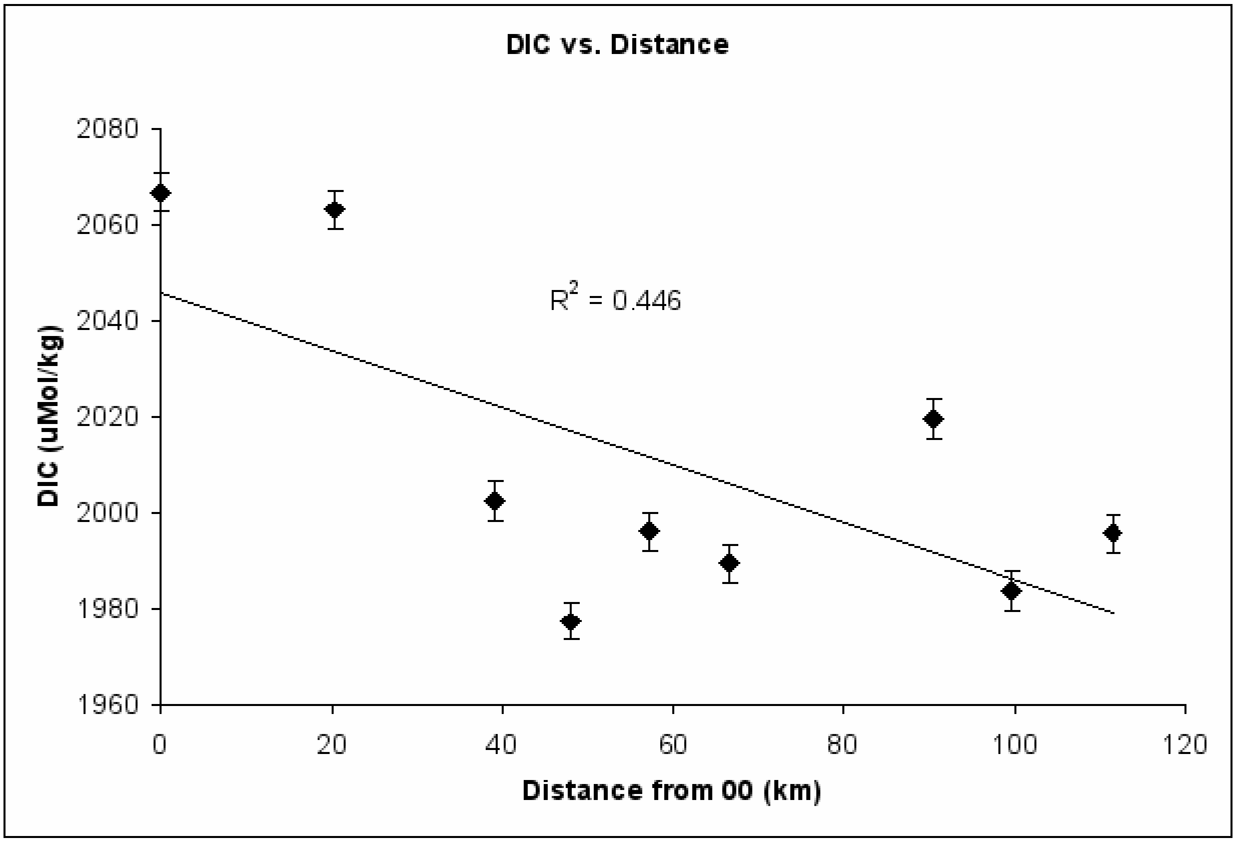
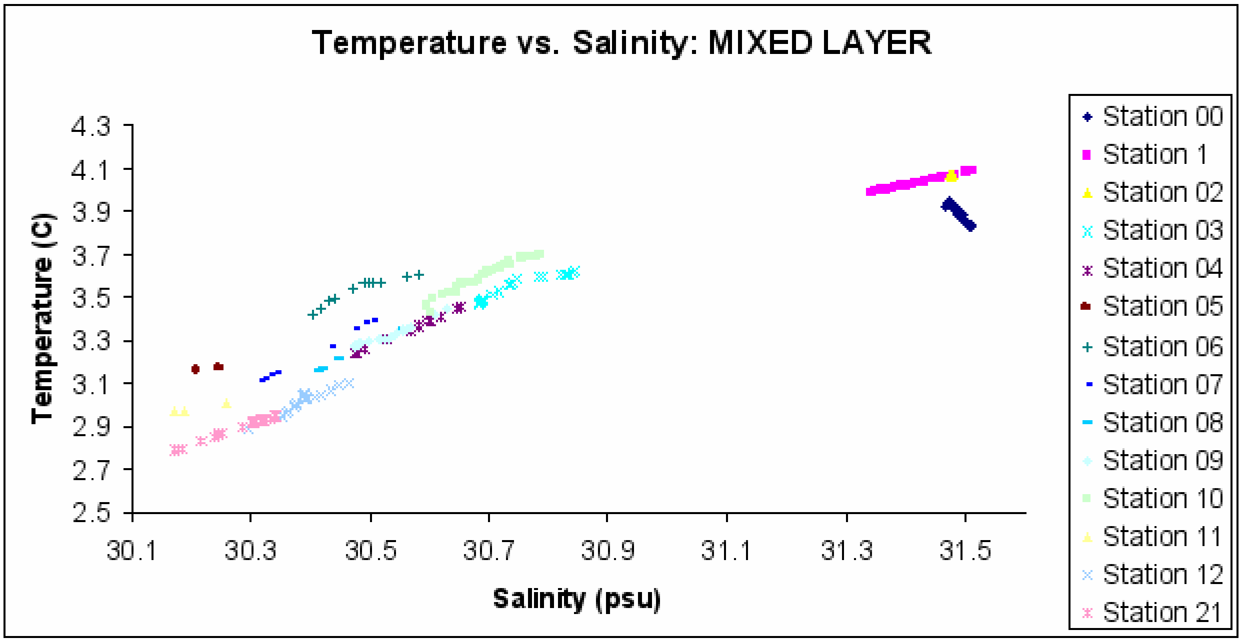


Figure 3: DIC vs. distance from the mouth. The mouth of the bay is given a 0 distance at station 00.

rently about 385ppm globally and can be compared to the pCO_2 levels measured in the ocean to determine the gas flux rate. The range of surface pCO_2 levels was between 187µatm and 301µatm. These values were low when compared to average, open ocean levels of CO_2, which range between 330ppm to 450 ppm annually (Peters et al. 2007). The average wind speed value of 14.4 knots during our time in Glacier Bay was close to annual averages measured in open ocean basins, which are about 16 knots. 385ppm in dry air atmospheric reading translates to about 374 µatm (Takahashi 2002). The $0.60g/m^2$day average gas transfer rate of CO_2 from the atmosphere to the water in the bay is extremely high when compared to global averages of open ocean basins which is about $0.08g/m^2$day. However, the winter gas flux in North Atlantic and southern ocean coastal regions is 0.4 to $0.7g/m^2$day due to the rapid down welling in these regions. During the winter, CO_2 gas flux in Glacier Bay is comparable to fluxes in artic and antarctic zones (Takahashi 2002).

Isotope ratio and photosynthesis vs. respiration

In general, depleted values of $^{13}\delta C/^{12}\delta C$ ratio suggest that respiration is dominating photosynthesis and enriched values suggest the opposite (Quay et al. 1992). $^{13}\delta C/^{12}\delta C$ ratio peaked around the middle of the bay and reached minimums in the east arm, at the top of the west arm and at the mouth of the bay (Table 5). Due to the time of year, this likely shows that phytoplankton are just beginning to bloom at the central stations and have not yet started blooming at stations in the east arm and back



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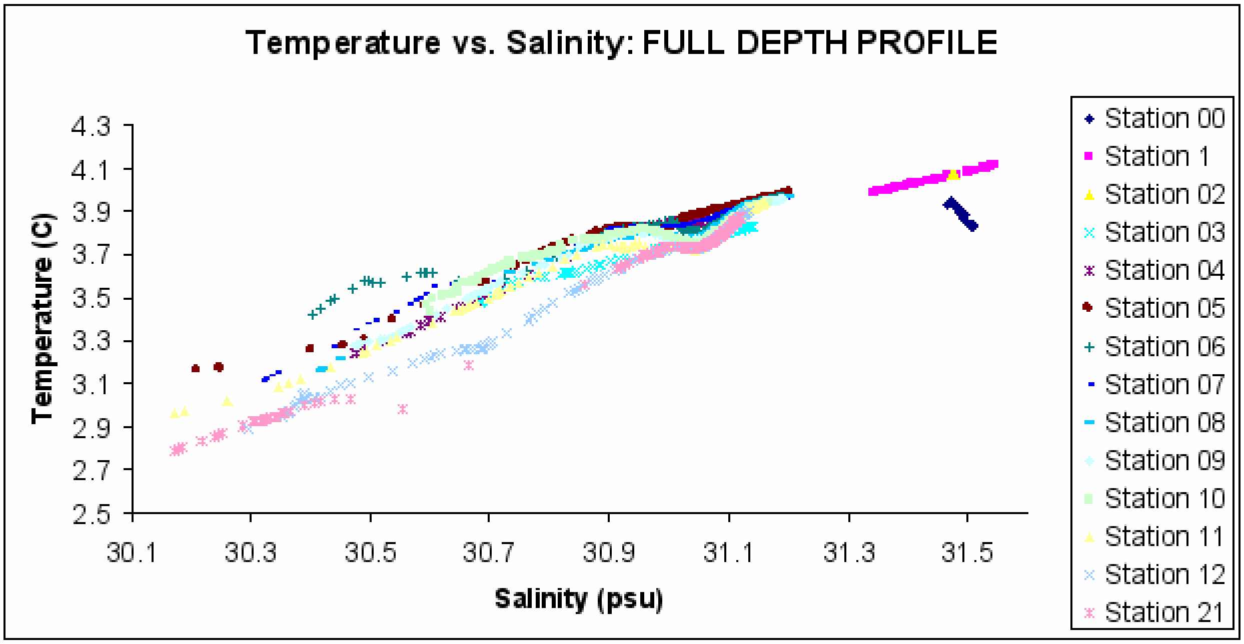


(b)

Figure 4: a.) Temperature vs. salinity in the mixed layer. Grouping to right represents three stations close to or just outside of the bay. b.) Temperature vs. salinity in the entire water column. Grouping to right represents three stations close to or just outside of the bay.

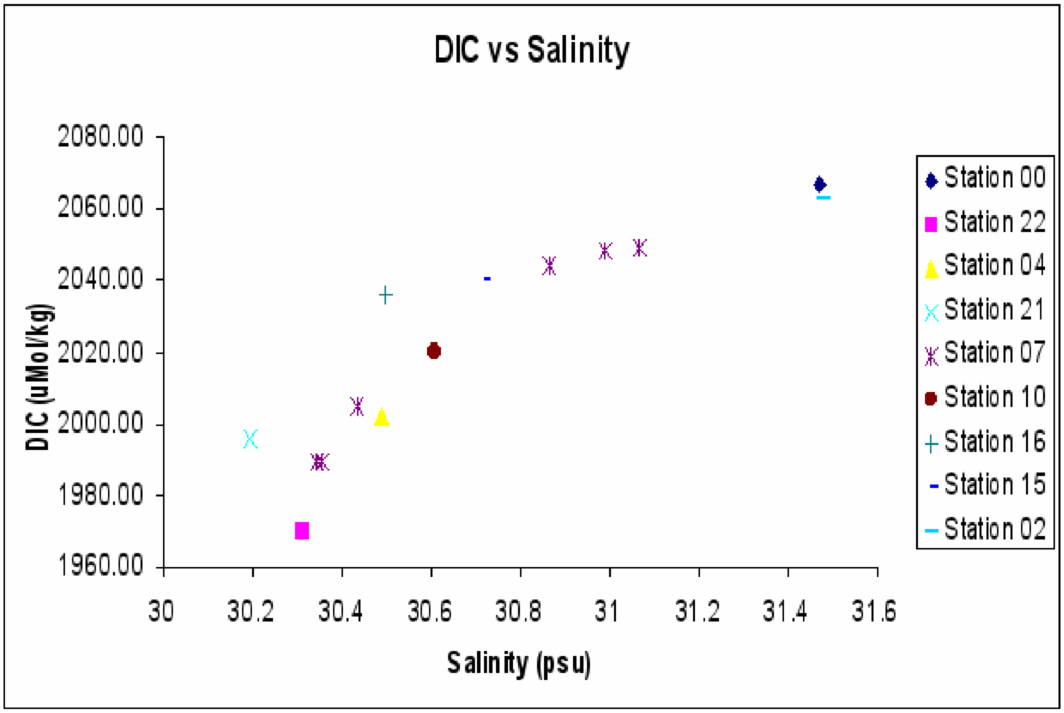


Figure 5: DIC vs. salinity. Total DIC at each surface station with several depths at station 07.

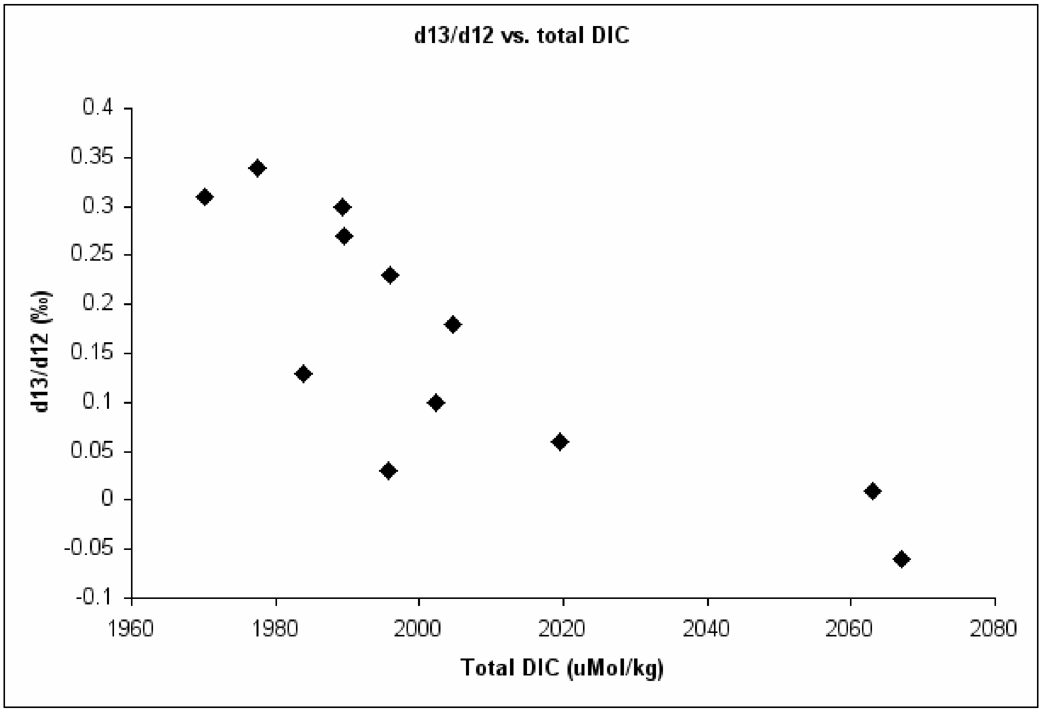
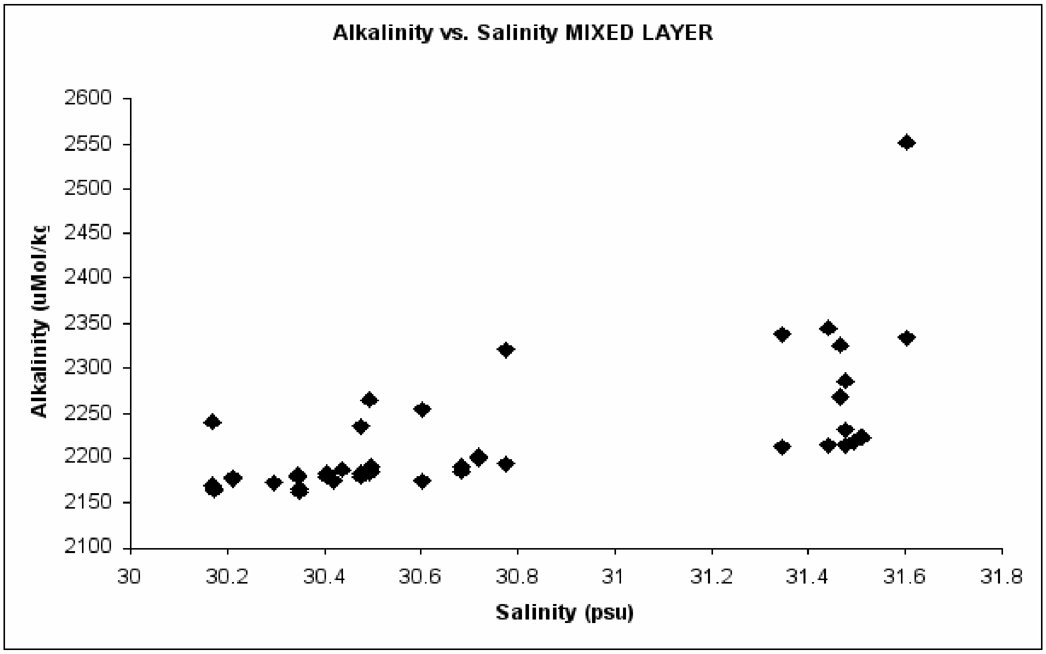


Figure 6: $^{13}\delta C/^{12}\delta C$ ratio vs. the total DIC. Inverse correlation is typical.



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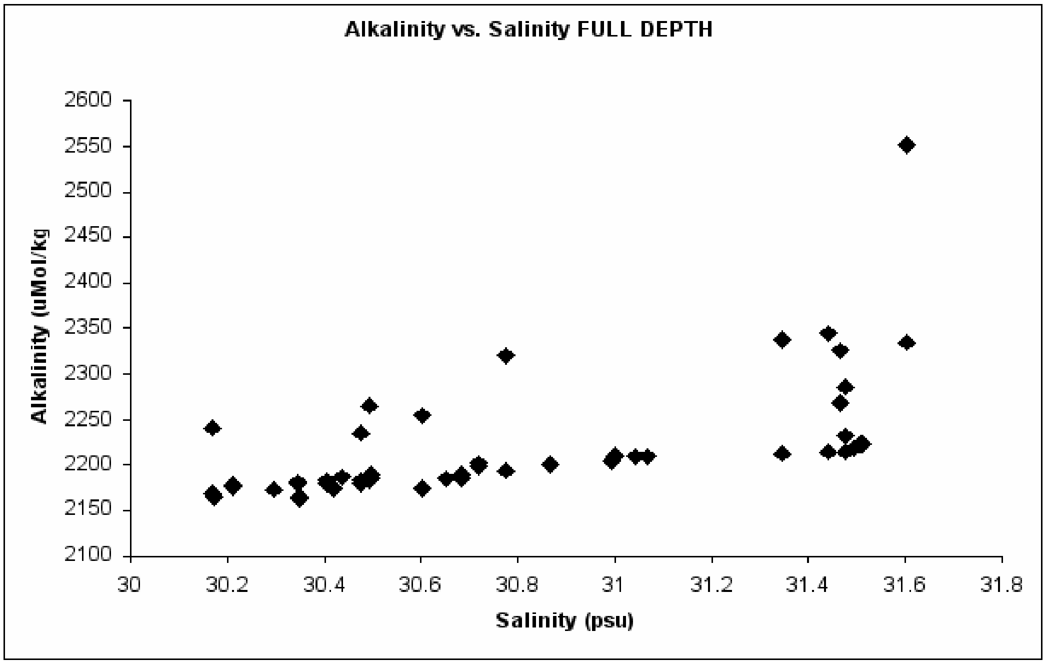

(b)

Figure 7: a.) Alkalinity vs. salinity in the mixed layer. b.) Alkalinity vs. salinity in the full depth profile.

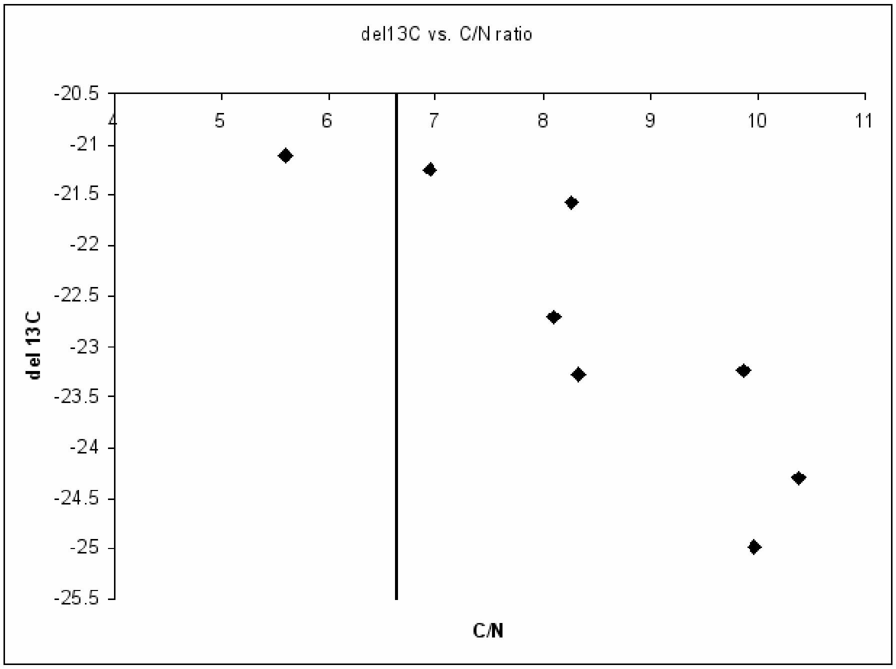

Figure 8: Verifies validity of POC data. The vertical line represents the typical Redfield ratio found in the ocean. The y-axis is the carbon to nitrogen ration measured in the organic samples.

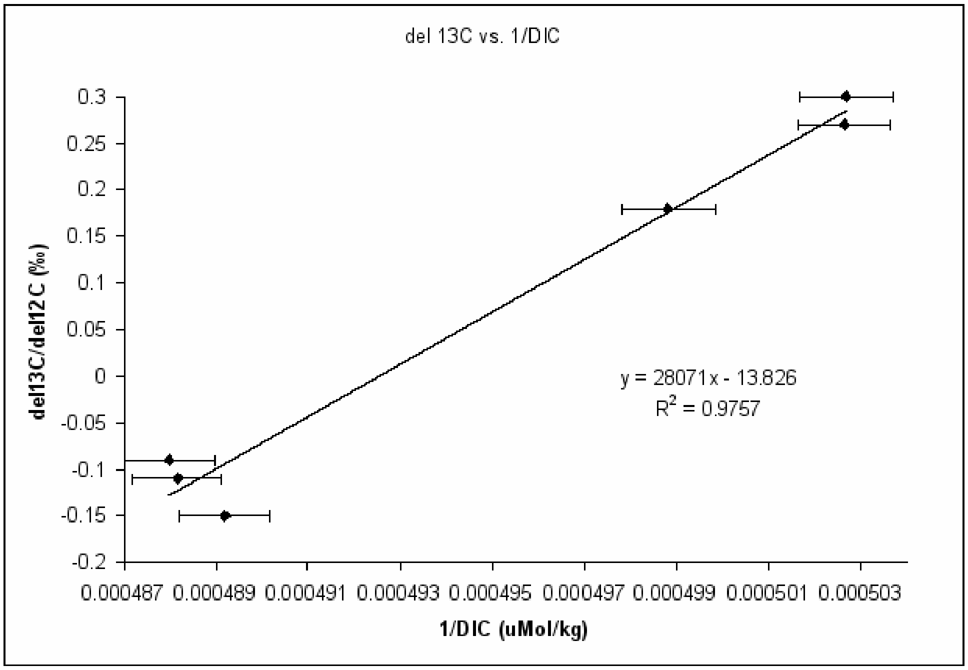

Figure 9: $^{13}\delta C/^{12}\delta C$ ratio vs. 1/total DIC. Linear regression plotted and intertercept used to make estimation of $^{13}\delta C$ signature of the CO_2 respired biologically.

of the west arm.

Source of organic carbon to the bay

River input was minimal during the time we were in Glacier Bay; which caused a serious impact on my hypothesis regarding nutrient sources. Depending on the year, freshwater input to the bay reaches its lowest volume between February and March (Etherington et al. 2004). This year, the winter season was extended in Glacier Bay and river runoff volume was still at a minimum; as evidenced by the modest surface salinity drop of only 1.2 psu from the entrance of the bay (station 00) to the back of the west arm (station 21). The low presence of freshwater from river and stream runoff means that the organic carbon source to the system is mostly oceanic. This idea is further supported by the POC $^{13}\delta C/^{12}\delta C$ ratio that averages -22.8‰ between 4 stations in the central part of the bay, which is closer to the standard -21‰ ratio of ocean based organic carbon than the -27‰ ratio we expect from terrestrial organic carbon. If we plot 22.8 between 21 and 27, we can assume that only about 30% ±5% of the organic carbon in the central part of Glacier Bay came from terrestrial sources.

A Keeling plot was utilized to estimate the isotopic signature of the respired CO_2. Under normal circumstances, water from below the mixed layer contains more total dissolved inorganic carbon due to high respiration, biological degradation and lack of photosynthesis. Additionally, one would expect the isotope ration of respired carbon to roughly match the ratio of POC measured from the same locations. At station 07, we see a typical pattern of carbon: lowest DIC at the surface that increases with depth and enriched $^{13}\delta C/^{12}\delta C$ at the surface that decreases with depth. Ordinarily, the difference between surface DIC and deep DIC is entirely attributed to respiration and biological decomposition. By plotting the $^{13}\delta C/^{12}\delta C$ ratio on the y-axis and 1/total DIC on the x axis, we can extrapolate via linear regression to find the signature of just the CO_2 that was respired (Pataki et al. 2003). In Figure 8, the Keeling plot derived value -13.8‰ is much higher (less depleted) than expected. The value of -13.8‰ does not closely match the station 07 measured POC signature of -21.2‰ (Table 4). This must mean that the source of additional DIC at depth is not just due to respiration. This is likely due to a sub-mixed layer intrusion of water from an area of higher DIC. With the vigorous tidal mixing found in the bay, this DIC loaded water likely came from outside of the bay.

Limitations of this study, and future research

Although measurement techniques proved to be very accurate, there are several limitations and areas where future improvements can be made. The most valuable improvement to this study would be the creation of a time series of DIC, alkalinity, POC and wind speed measurements that spanned at least one full year. Sampling for only a few days out of the year gives us a small glimpse, or ‘snapshot in time’ of the full picture of the Glacier Bay carbon cycle. Sampling periodically throughout the year would give us a yearly CO2 flux average and enable us to see changes in the source of carbon to the system. Additionally, sampling organic carbon from the entire water column and from every station where DIC and alkalinity samples were collected would allow for a higher resolution view of the entire carbon cycle.

Conclusions

- Measured CO_2 flux rates were almost 8 times higher than the global yearly average; $0.60 g/m^2$day vs. $0.08 g/m^2$day.

- CO_2 flux was, however, inside the range of fluxes for both arctic and southern ocean basins during the winter months.

- Organic carbon was, at most, 30% composed of terrestrial organic matter, the rest coming from the ocean, which indicates strong mixing with water outside the bay.

- When attempting to estimate the isotope ratio of the respired CO_2, a value of -13.8‰ was found, which must mean that the larger total DIC at depth is due to an intrusion of DIC rich deep water from outside of the bay. We are able to make this assumption since we know that there must be high mixing in the bay due to tidal flushing and because most of the organic carbon is composed of an oceanic source.

- Sampling throughout a year long period or more, is necessary to learn about the entire carbon cycle of a productive, sub-arctic, estuarine-fjord like Glacier Bay, Alaska.

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