

1 Assessing Net Community Production in a Glaciated Alaska Fjord

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16

17 **Abstract**

18 The impact of deglaciation in Glacier Bay has been observed to seasonally impact the

19 biogeochemistry of this marine system. The influence from surrounding glaciers,

20 particularly tidewater glaciers, has the potential to greatly impact the efficiency and

21 structure of the marine food web within Glacier Bay. To assess the magnitude, spatial and

22 temporal variability of net community production in a glaciated fjord, we measured

23 dissolved inorganic carbon inorganic macronutrients, dissolved oxygen and particulate

1 organic carbon between July 2011 and July 2012 in Glacier Bay, AK. High net  
2 community production rates were observed across the bay ( $\sim 54$  to  $\sim 81$  mmol C m<sup>-2</sup> d<sup>-1</sup>)  
3 between the summer and fall of 2011. However, between the fall and winter, as well as  
4 between the winter and spring of 2012, air-sea fluxes of carbon dioxide and organic  
5 matter respiration made net community production rates negative across most of the bay  
6 as inorganic carbon and macronutrient concentrations returned to pre-bloom levels. The  
7 highest carbon production occurred within the lower bay between the summer and fall of  
8 2011 with  $\sim 1.3 \times 10^{10}$  g C season<sup>-1</sup>. Bay-wide, there was carbon production of  $\sim 2.6 \times 10^{10}$  g  
9 C season<sup>-1</sup> between the summer and fall. Respiration and air-sea gas exchange were the  
10 dominant drivers of carbon chemistry between the fall and winter of 2012. The  
11 substantial spatial and temporal variability in our net community production estimates  
12 largely reflect glacial influences within the bay, as melt-water is depleted in  
13 macronutrients relative to marine waters entering from the Gulf of Alaska in the middle  
14 and lower parts of the bay. Further glacial retreat will likely lead to additional  
15 modifications in the carbon biogeochemistry of Glacier Bay with unknown consequences  
16 for the local marine food web, which includes many species of marine mammals.  
17

1 **1.0 Introduction**

2 Glacier Bay lies within the Gulf of Alaska (Gulf of Alaska) coastal ocean and is a  
3 pristine glacially influenced fjord that is representative of many other estuarine systems  
4 that border the Gulf of Alaska (Fig. 1). Glacier Bay is influenced by freshwater input,  
5 primarily from many surrounding alpine and tidewater glaciers. The low-nutrient influx  
6 of freshwater into Glacier Bay, which is highest (up to ~40% freshwater in surface waters  
7 during the summer; Reisdorph and Mathis, 2014) along the northern regions of the bay,  
8 affects the nutrient loading and, thus, biological production and carbon dioxide (CO<sub>2</sub>)  
9 fluxes within the bay. The southern region of the bay is less affected by this runoff due to  
10 distance from the glacial influence and is more influenced by marine waters that  
11 exchange through a narrow channel with a shallow entrance sill (~25 m).

12 Over the past ~250 years, Glacier Bay has experienced very rapid deglaciation,  
13 which has likely impacted the biological structure of the bay. As the climate continues to  
14 warm, additional changes to this ecosystem and marine population have the potential to  
15 impact net community production (NCP) within the bay, with cascading effects through  
16 the food web. To better understand the seasonal dynamics of the underlying  
17 biogeochemistry in Glacier Bay, we used the seasonal drawdown of the inorganic  
18 constituents of photosynthesis within the mixed layer to estimate regional mass flux of  
19 carbon and rates of NCP along with air-sea flux rates of CO<sub>2</sub>. This approach has been  
20 used in other high-latitude regions to assess ecosystem functionality (e.g. Mathis et al.,  
21 2009; Cross et al, 2012; Mathis and Questel, 2013), including net community production  
22 and carbon cycling.

23 Previous studies have shown there is wide-ranging variability in rates of primary

1 production within other glaciated fjord systems, though NCP data within these  
2 ecosystems are sparse. Fjords within the Central Patagonia region (48°S – 51°S) are  
3 strongly influenced by glaciated terrain and freshwater runoff, similar to influences in  
4 and around Glacier Bay. A study by Aracena et al. (2011) looked at water column  
5 productivity in response to surface sediment export production in various Chilean  
6 Patagonia fjords (41-56°S). They calculated primary production rates during the summer  
7 between ~35 mmol C m<sup>-2</sup> d<sup>-1</sup> in the more southern regions (52°S - 55°S) and ~488 C m<sup>-2</sup> d<sup>-1</sup>  
8 to the north (41°S - ~44°S). In Central Patagonia, Aracena et al. (2011) estimated  
9 primary productivity at ~57 mmol C m<sup>-2</sup> d<sup>-1</sup> in the spring, a value comparable to some  
10 seasonal estimates in Glacier Bay, and found primary production rates comparable to  
11 those of Norwegian fjords (~9 to ~360 mmol C m<sup>-2</sup> d<sup>-1</sup>).

12         There have been a number of studies conducted within Glacier Bay, though  
13 conclusions of several studies are contradictory. Many of these studies had a short  
14 duration and limited coverage, missing much of the spatial, seasonal, and annual  
15 variability (Hooge et al, 2003). This lack of data leads to a significant gap in  
16 understanding of carbon cycling in Glacier Bay, as well as a lack of predictability of  
17 responses to changes in this estuarine system as climate change progresses. To capture  
18 some of the seasonal and spatial variability in the bay, we collected and analyzed  
19 monthly sampling data over a two-year period. This sampling regime, along with the  
20 variety of samples taken, has provided us with the most robust dataset collected in  
21 Glacier Bay and allowed us to elucidate the dynamic nature of NCP in a glaciated fjord.  
22 Our goal for this study was to better understand carbon cycling in Glacier Bay and how it  
23 is impacted by glacial runoff. Additionally, we wish to fill in some gaps in how these

1 processes may influence net community production within a glaciated fjord ecosystem  
2 and better understand how continued glacial melt will impact productivity in Glacier Bay,  
3 as well as in similar glaciated fjord ecosystems worldwide.

4

## 5 **2.0 Background**

6 Glacier Bay was once covered by one large icefield, the Glacier Bay Icefield, that  
7 has been rapidly retreating since the Industrial Revolution, scouring the bay and leaving  
8 behind many alpine and tidewater glaciers. Currently, the marine portion of Glacier Bay  
9 is roughly 100 km from the entrance sill to the end of the west arm, and reaches depths >  
10 400 m and > 300 m in the east arm and west arm, respectively (Fig. 2).

11 Seasonal variation in factors such as light availability, turbulent or wind mixing  
12 and freshwater input, impact physical conditions that are vital to primary production,  
13 including stratification, photic depth, and nutrient availability. These drivers of NCP vary  
14 temporally and spatially within Glacier Bay. Glacial runoff, along with glacial stream  
15 input, impart freshwater into the marine system, especially along the arms of the bay.  
16 Peak runoff has been shown to occur during the fall, though there is fairly constant flow  
17 from June to September (Hill, 2009). Low-nutrient glacial runoff is prevalent, and while  
18 it aids in stratification, its low macronutrient concentrations dilute available nutrients in  
19 the northern regions nearest tidewater outflows. In the lower parts of the bay, glacial  
20 influence is lower and macronutrients are more abundant allowing higher levels of  
21 primary production during spring and summer. Glacier Bay maintains relatively elevated  
22 phytoplankton concentrations throughout the year compared to levels observed in similar  
23 Alaskan fjords (Hooge & Hooge, 2002). However, insufficient research has been done on

1 the biological system within Glacier Bay to understand why this occurs.

2 For this paper, we have calculated seasonal NCP and air-sea carbon flux for the  
3 four regions within Glacier Bay in order to better understand ecosystem production in a  
4 glacially dominated environment, representative of much of the southern coastal AK  
5 region. This study has greatly enhanced our understanding of how glacial melt and air-  
6 sea flux impacts DIC concentrations, and thus NCP, in estuaries, like Glacier Bay, which  
7 are numerous along the Gulf of Alaska coast in Alaska, as well as other glaciated fjords  
8 worldwide.

9

### 10 **3.0 Methods**

11 Ten oceanographic sampling cruises took place aboard the National Park  
12 Service's R/V Fog Lark between July 2011 and July 2012. Water column samples were  
13 collected at six depths (2, 10, 30, 50, 100 m and near the bottom) at each station  
14 throughout the bay (Fig. 1) with a maximum depth within the west arm of ~430 m (Fig.  
15 2). Sampling depths correspond with those currently being used by the Glacier Bay long-  
16 term monitoring program and determined by the USGS in the 1990s. Each 'core' station  
17 (Fig. 1) was sampled during every oceanographic sampling cruise, while all 22 stations  
18 were sampled during the months of July and January. "Surface" water refers to water  
19 collected from a depth of 2 m. unless otherwise stated. Seasonal data was calculated by  
20 averaging each measured parameter at each depth for all cruises during the respective  
21 seasons. The summer season consists of June, July and August, fall includes September  
22 and October; winter is comprised of February and March cruises, and the spring season  
23 includes the months of April and May. Data has been averaged regionally within each of

1 the four regions of the bay (lower bay, central bay, east arm, and west arm) (Fig. 1).  
2 Regional boundaries were selected based on historical and ongoing research in Glacier  
3 Bay. Bathymetry data (Fig. 2) was retrieved from the National Geophysical Data Center.

4 Conductivity, temperature and pressure were collected on downcasts with a  
5 Seabird 19-plus CTD. Dissolved oxygen (DO) was sampled and processed first to avoid  
6 compromising the samples by atmospheric gas exchange. Samples for DO analysis were  
7 drawn into individual 115 ml Biological Oxygen Demand flasks and rinsed with 4-5  
8 volumes of sample, treated with 1 mL  $\text{MnCl}_2$  and 1 mL  $\text{NaI/NaOH}$ , plugged, and the  
9 neck filled with DI water to avoid atmospheric exchange. Dissolved oxygen was sampled  
10 and analyzed using the Winkler titrations and the methods of Langdon (2010). Samples  
11 were analyzed within 48 hours. Apparent oxygen utilization (AOU) was derived from  
12 observed DO concentrations using Ocean Data View calculations in version 4.6.2  
13 (Schlitzer, 2013).

14 DIC and total alkalinity (TA) samples were drawn into 250 mL borosilicate  
15 bottles. Samples were fixed with a saturated mercuric chloride solution (200  $\mu\text{l}$ ), the  
16 bottles sealed, and stored until analysis at the Ocean Acidification Research Center at the  
17 University of Alaska Fairbanks. High-quality DIC data was attained by using a highly  
18 precise (0.02%; 0.4  $\mu\text{moles kg}^{-1}$ ) VINDTA 3C-coulometer system. TA was determined  
19 by potentiometric titration with a precision of  $\sim 1 \mu\text{moles kg}^{-1}$ . Certified reference  
20 material, prepared and distributed by Scripps Institute of Oceanography, University of  
21 California, San Diego (Dr. Andrew Dickson's Laboratory), were run daily before sample  
22 analysis to ensure accuracy of sample values. The VINDTA 3C provides real-time  
23 corrections to DIC and TA values according to in-situ temperature and salinity.

1           Macronutrient samples (nitrate, phosphate, silicate) were filtered through 0.8  $\mu\text{m}$   
2 Nuclepore filters using in-line polycarbonate filter holders into 25 ml HDPE bottles and  
3 frozen (-20°C) until analysis at UAF. Samples were filtered to remove any particles, such  
4 as glacial silt, that had the potential to clog equipment during analysis. Samples were  
5 analyzed within several weeks of collection using an Alpkem Rapid Flow Analyzer 300  
6 and following the protocols of Mordy et al. (2010).

7           Particulate organic carbon (POC) samples were collected from Niskins into brown  
8 1 L Nalgene bottles and stored for filtering within 2 days of collection. Samples were  
9 collected at 2 m, 50 m and bottom depths. A known volume of samples was filtered  
10 through muffled and preweighed 13 mm type A/E glass fiber filters using a vacuum  
11 pump. Muffling involved using tweezers to wrap filters in aluminum foil and heating  
12 them at 450°F for ~6 hours in a muffling furnace in order to remove any residual organic  
13 material. Filtered samples were frozen for transport back to UAF where they were then  
14 dried and reweighed. Analyses were completed by OARC at UAF and were run using the  
15 methods outlined in Goñi et al. (2001).

16           The partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) was calculated using CO2SYS (version 2.0), a  
17 program that employs thermodynamic models of Lewis and Wallace (1995) to calculate  
18 marine carbonate system parameters. Seasonally averaged atmospheric  $p\text{CO}_2$  values  
19 ( $\mu\text{atm}$ ) were used (388.4, 388.9, 393.4, 393.8 and 391.8 for summer 2011 through  
20 summer 2012, respectively and were averaged from the monthly averaged Mauna Loa  
21 archive found at [www.esrl.noaa.gov](http://www.esrl.noaa.gov). For seawater  $p\text{CO}_2$  calculations in CO2SYS we  
22 used  $K_1$  and  $K_2$  constants from Mehrback et al., 1973 and refit by Dickson and Millero  
23 (1987),  $\text{KHSO}_2$  values from Dickson, the seawater pH scale, and  $[\text{B}]_{\text{T}}$  value from



1 Uppström (1974).

2 CO<sub>2</sub> fluxes were calculated using seasonally averaged seawater temperature, wind  
3 speed, and seawater and atmospheric *p*CO<sub>2</sub> data using the equation,

$$4 \text{ Flux} = L * (\Delta p\text{CO}_2) * k \quad (\text{Eq. 1})$$

5 where *L* is the solubility of CO<sub>2</sub> at a specified seawater temperature in mmol m<sup>-3</sup> atm<sup>-1</sup>  
6 and  $\Delta p\text{CO}_2$  represents the difference between seawater and atmospheric *p*CO<sub>2</sub> in  $\mu\text{atm}$ . *k*  
7 is the steady/short-term wind parameterization in cm hr<sup>-1</sup> at a specified wind speed and  
8 follows the equation,

$$9 k = 0.0283 * U^3 * (Sc/660)^{(-1/2)} \quad (\text{Eq. 2})$$

10 where *U* is wind speed in m s<sup>-1</sup>, *Sc* is Schmidt number, or the kinematic velocity of the  
11 water divided by the molecular diffusivity of a gas in water, and was normalized to 660  
12 cm hr<sup>-1</sup>, equivalent to the *Sc* for CO<sub>2</sub> in 20°C seawater (Wanninkhof and McGillis, 1999).  
13 Wind speeds were cubed using the methods of Wanninkhof and McGillis (1999) in an  
14 attempt to account for the retardation of gas transfer at low to moderate wind speeds by  
15 surfactants and the bubble-enhanced gas transfer that occurs at higher wind speeds.

16 Seawater temperatures for flux calculations were taken from surface bottle CTD  
17 data. Wind speeds were obtained from a Bartlett Cove, AK weather station (Station  
18 BLTA2) located in Glacier Bay and maintained by the National Weather Service Alaska  
19 Region.

20 NCP calculations were made using the seasonal drawdown of photosynthetic  
21 reactant DIC within the mixed layer (upper 30 m) and were normalized to a salinity of  
22 35. NCP production was calculated between each season from the summer of 2011 to the  
23 summer of 2012 (i.e. the change in concentrations between each consecutive season)

1 according to the equation (Williams, 1993),

$$2 \quad \text{NCP} = \text{DIC}_{\text{season2}} - \text{DIC}_{\text{season1}} \quad (\text{Eq. 3})$$

$$3 \quad = \Delta\text{DIC} \text{ (moles C per unit volume area)}$$

4 The influx of high-DIC waters (e.g., river discharge) can cause a dampening of the NCP  
5 signal. This effect can be accounted for by normalizing DIC to a constant deep-water  
6 reference salinity ( $S=35$ ; Millero, 2008). Since this equation only reflects the effects of  
7 DIC, freshwater influences on alkalinity were accounted for by correction of the seasonal  
8 changes in TA (Lee, 2001) using the equation,

$$9 \quad \Delta\text{DIC}_{\text{Alk}} = 0.5 * (\Delta\text{Alk} + \Delta\text{NO}_3^-) \quad (\text{Eq. 4})$$

10 and subtracting this value from the seasonal change in salinity-normalized DIC (nDIC),  
11 thus providing an NCP in which the significant process influencing seasonal changes to  
12 DIC concentrations is biological productivity (Bates et al, 2005; Mathis et al., 2009;  
13 Cross et al., 2012). Error imparted in calculating parameters, including DIC analysis and  
14 averaging of nutrient concentrations within the mixed layer, are propagated through our  
15 NCP estimates at  $\sim \pm 5\%$  of the final NCP calculation. Error propagated through each  
16 NCP estimate is listed with the NCP calculations in Table 1.

17

#### 18 **4.0 Caveats**

19 While seasonal water column DIC concentration changes can be a good  
20 approximation to determine seasonal NCP, there are several estuarine processes that we  
21 were unable to constrain that likely influenced our NCP estimates and act as additional  
22 sources of uncertainty. Some other sources of uncertainty, such as the influence of glacial

1 flour, was reduced through averaging of spatial and regional parameters as stations were  
2 reoccupied within ~30 days of one another.

3           Glacial flour can enhance DIC concentrations in seawater. Therefore, there is the  
4 possibility that the inclusion of glacial flour may have increased our DIC concentrations  
5 with respect to DIC drawdown from primary production. In this case, our estimates may  
6 underestimate NCP. However, we were not able to quantify the amount of glacial flour  
7 deposited in Glacier Bay or analyze its composition for this study. In Glacier Bay, the  
8 influence of glacial flour is limited to the northern regions (i.e. east and west arms) that  
9 are directly influence by glacial outflow, many of which enter the bay along inlets and  
10 not the main arms of the bay, possibly reducing the impact of glacial flour at many  
11 oceanographic stations in these regions.

12           Freshwater runoff that enters the bay via glacial streams flows over streambeds  
13 and can leach minerals and nutrients from bedrock, enhancing these concentrations in the  
14 surface waters of Glacier Bay. While stream water runoff in Glacier Bay was not  
15 analyzed for this study, studies of glacial runoff in southeast Alaska have shown  
16 allochthonous stream water DOC to be negatively correlated with glacial coverage  
17 (Hood, et al., 2009). Examining watersheds along the Gulf of Alaska, Hood et al. (2009)  
18 also found that the most heavily glaciated watersheds were a source of the oldest, most  
19 labile (66% bioavailable) DOM and that increased input of glacial melt was associated  
20 with increased proportions of DOM from microbial sources. As we were unable to  
21 chemically analyze glacial runoff in Glacier Bay, our NCP calculations using only  
22 changes in DIC concentrations underestimate NCP in the bay, though freshwater input is  
23 corrected to some degree by salinity normalized DIC concentrations. The quantification

1 of freshwater input into the bay is also hindered by the lack of any active gauging stations  
2 within the bay (Hill et al., 2009)

3         Some literature suggests that internal waves may form within the lower bay in an  
4 area of station 02, known as Sitakaday Narrows. This is an area of constriction with  
5 accelerated currents that can produce hydraulic instabilities, potentially causing internal  
6 waves that may influence mixing at depth as well as at a distance from this region (Hooge  
7 & Hooge, 2002). These internal waves may affect nutrient replenishment to surface  
8 waters, as well as mixing of DIC across the mixed layer. This addition of high-DIC  
9 waters from depth may also lead to an underestimation of NCP.

10

## 11 **5.0 Results**

### 12 **5.1 Spatial and seasonal salinity distributions**

13         Salinity distributions throughout the bay were generally the result of the influence  
14 of glacial runoff. During this summer season salinity ranged from 22.9 in surface waters  
15 at station 20 to 32.5 in the bottom waters of station 24 in Cross Sound. Isohalines were  
16 horizontal down to ~50 m from the upper arms through the upper portion of the lower  
17 bay then became vertical in the lower bay, intersecting the surface just north of station 01  
18 (Fig. 3).

19         Salinity was more constrained during the fall, with a full water column range  
20 between 25.3 in the surface waters at station 07 and 31.4 at depth (~130 m) at station 13.  
21 Similar to the previous summer, isohalines remained horizontal from the upper arms to  
22 the mid-lower bay near station 01 where they become vertical and intersected the surface.

1 Salinities in the lower bay near were between ~30 and 31, with the higher salinities at  
2 depth in Cross Sound.

3 During the winter salinity had a narrow range 29.6 and 31.6. The highest salinities  
4 were observed in the bottom waters at station 24, though salinity was similar at all depth  
5 at this station (~31.4). The lowest salinities (~30) were within the top 10 m of station 12  
6 with similar surface salinities throughout both arms. In the spring, salinity continued to  
7 have a narrow range, with bay-wide salinities between ~28.9 at the surface of station 12  
8 and 31.7 in the bottom water of station 24. Salinities below a depth of 50 m were  
9 relatively homogenous at ~31 (Fig. 3).

10 Returning to summer conditions in 2012, a strong salinity gradient was observed  
11 in the upper 50 m along the east and west arms. Salinities across the bay ranged from  
12 24.1 in the surface waters of station 12 to 32.2, at depth at station 24. The lowest  
13 salinities were observed in the surface waters at the head of both arms, with this low  
14 salinity signal stretching south through the through the central bay. Stations within the  
15 lower bay had the highest salinities having salinities between ~31 and 32 at all depths.

16

## 17 **5.2 Spatial and seasonal distributions of DIC and nitrate**

18 DIC and nitrate are important inorganic components that are consumed during  
19 photosynthesis at various rates throughout the year in Glacier Bay. DIC concentrations  
20 during the summer of 2011 ranged from ~1400 to 2100  $\mu\text{mol kg}^{-1}$ , with the lowest  
21 concentrations in the arms and upper-central bay. Nitrate concentrations throughout the  
22 water column ranged from ~2.5 to ~37  $\mu\text{mol kg}^{-1}$ , with slightly less variability in the  
23 surface layer (~2.5 and 24  $\mu\text{mol kg}^{-1}$ ). Surface nitrate concentrations were low, but

1 remained  $>5 \mu\text{mol kg}^{-1}$  at all stations. While there was a large drawdown of nitrate,  
2 particularly in spring and summer (as much as  $20 \mu\text{mol kg}^{-1}$  when compared to winter  
3 concentrations), surface waters were not depleted at any of the observed stations.

4 In the fall of 2011, DIC and nitrate concentrations increased in the surface waters,  
5 with DIC ranging from  $\sim 1700 \mu\text{mol kg}^{-1}$  to  $2040 \mu\text{mol kg}^{-1}$ , while below the surface  
6 concentrations reached  $\sim 2075 \mu\text{mol kg}^{-1}$ . Water column nitrate concentrations were  
7 between  $\sim 12 \mu\text{mol kg}^{-1}$  and  $32 \mu\text{mol kg}^{-1}$  with similar concentrations within surface  
8 waters ( $11 \mu\text{mol kg}^{-1}$  to  $30 \mu\text{mol kg}^{-1}$ ) and the lowest concentrations observed in the arms.  
9 DIC concentrations were much more constrained during the winter ( $\sim 1920 \mu\text{mol kg}^{-1}$  to  
10  $2075 \mu\text{mol kg}^{-1}$ ) than during previous seasons. Nitrate concentrations ranged from  $\sim 12$   
11  $\mu\text{mol kg}^{-1}$  to  $33 \mu\text{mol kg}^{-1}$ .

12 During the spring of 2012 DIC and nitrate had reduced concentrations in surface  
13 waters across the bay. Surface DIC concentrations were between  $\sim 1750 \mu\text{mol kg}^{-1}$  and  
14  $2025 \mu\text{mol kg}^{-1}$ , with water column concentrations reaching  $\sim 2075 \mu\text{mol kg}^{-1}$  (Fig. 4).  
15 Nitrate concentrations ranged from  $\sim 7 \mu\text{mol kg}^{-1}$  to  $\sim 31 \mu\text{mol kg}^{-1}$ , with an observed  
16 surface water maximum of  $\sim 20 \mu\text{mol kg}^{-1}$ . Further drawdown of DIC and nitrate in  
17 surface waters was observed during the summer of 2012. However, concentrations did  
18 not drop as low as was observed during the previous summer. DIC concentrations ranged  
19 from  $\sim 1545$  to  $2066 \mu\text{mol kg}^{-1}$ . Nitrate concentrations varied from  $\sim 13$  to  $33 \mu\text{mol kg}^{-1}$ ,  
20 with surface concentrations between  $\sim 17$  and  $31 \mu\text{mol kg}^{-1}$ . The stations with the lowest  
21 DIC and nitrate concentrations were those within the east arm and west arm (Fig. 4).

22

### 23 **5.3 Rates and Masses of NCP**

1           The seasonal transition between the summer and fall of 2011 had the largest rates  
2 of NCP observed during the year of study. Rates of NCP were positive in all regions of  
3 the bay and were highest within the east and west arms of the bay at  $70.3 \pm 3.5$  and  $81.3$   
4  $\pm 4.1$  mmol C m<sup>-2</sup> d<sup>-1</sup>, respectively. A similar NCP rate of  $68.9 \pm 3.4$  mmol C m<sup>-2</sup> d<sup>-1</sup> was  
5 observed within the lower bay, while the central bay had the lowest rate between of  $53.6$   
6  $\pm 2.7$  mmol C m<sup>-2</sup> d<sup>-1</sup> (Table 1).

7           Calculated rates of NCP became negative between fall and winter, as well as from  
8 winter to spring. Between fall and winter, the lower bay had a rate of  $-14.2 \pm 0.7$  mmol C  
9 m<sup>-2</sup> d<sup>-1</sup> followed by the central bay at  $-11.5 \pm 0.6$  mmol C m<sup>-2</sup> d<sup>-1</sup>. Rates of NCP were  
10 negative in the east and west arms ( $-0.5 \pm 0.03$  and  $-1.3 \pm 0.1$  mmol C m<sup>-2</sup> d<sup>-1</sup>),  
11 respectively. Between the winter and spring of 2012, rates of NCP remained negative  
12 within the east and west arms ( $-36.4 \pm 1.8$  mmol C m<sup>-2</sup> d<sup>-1</sup> and  $-26.6 \pm 1.3$  mmol C m<sup>-2</sup> d<sup>-1</sup>,  
13 respectively), and to a lesser degree in central bay ( $-17.5 \pm 0.9$  mmol C m<sup>-2</sup> d<sup>-1</sup>). Positive  
14 NCP rate was estimated for the lower bay of  $17.6 \pm 0.9$  mmol C m<sup>-2</sup> d<sup>-1</sup>. Between the  
15 spring and summer of 2012 NCP rates were positive across the bay, with the highest rate  
16 in lower bay ( $19.4 \pm 1.0$  mmol C m<sup>-2</sup> d<sup>-1</sup>). The central bay and the east arm had rates of  
17  $17.2 \pm 0.9$  and  $15.7 \pm 0.8$  mmol C m<sup>-2</sup> d<sup>-1</sup>, respectively, while the west arm had a lower  
18 rate at  $6.0 \pm 0.3$  mmol C m<sup>-2</sup> d<sup>-1</sup>.

19           The total mass (g C d<sup>-1</sup>) of carbon produced from NCP was also estimated  
20 between each season ( Table 1). Production occurred between the summer and fall of  
21 2011, with the greatest production in the lower bay ( $4.5 \times 10^5 \pm 1.3 \times 10^4$  kg C d<sup>-1</sup>). The  
22 central bay had a large amount of production ( $2.2 \times 10^5 \pm 1.1 \times 10^4$  kg C d<sup>-1</sup>), followed by  
23 the west and east arms ( $1.8 \times 10^5 \pm 8.8 \times 10^3$  and  $7.6 \times 10^4 \pm 3.8 \times 10^3$  kg C d<sup>-1</sup> respectively).

1            Between the fall and winter the lower bay had carbon production of  $-9.3 \times 10^4 \pm$   
2  $4.6 \times 10^3 \text{ kg C d}^{-1}$ , while the east arm had a lowest degree of production at  $-5.2 \times 10^2 \pm 2.6$   
3  $\text{kg C d}^{-1}$ . NCP masses in central bay and west arm were also negative ( $-4.7 \times 10^4 \pm$   
4  $2.3 \times 10^4$  and  $-2.7 \times 10^3 \pm 1.4 \times 10^2 \text{ kg C d}^{-1}$ , respectively). Between the winter and spring of  
5 2012 masses in the east and west arms were estimated at  $-3.9 \times 10^4 \pm 2.0 \times 10^3 \text{ kg C d}^{-1}$  and -  
6  $5.8 \times 10^4 \pm 2.9 \times 10^3 \text{ kg C d}^{-1}$ , respectively while the central bay had a value of  $-7.1 \times 10^4 \pm$   
7  $3.6 \times 10^3 \text{ kg C d}^{-1}$ . The lower bay was the only region to have a positive NCP of  $1.1 \times 10^5 \pm$   
8  $5.7 \times 10^3 \text{ kg C d}^{-1}$ .

9            Transitioning from the spring to summer the lower bay had the greatest  
10 production ( $1.3 \times 10^5 \pm 6.3 \times 10^3 \text{ kg C d}^{-1}$ ), followed by the central bay ( $7.0 \times 10^4 \pm 3.5 \times 10^3$   
11  $\text{kg C d}^{-1}$ ). The arms exhibited the lowest biomass production, with an NCP in the west  
12 arm of  $1.3 \times 10^4 \pm 6.5 \times 10^2 \text{ kg C d}^{-1}$  and  $1.7 \times 10^4 \pm 8.5 \times 10^2 \text{ kg C d}^{-1}$  in the east arm.

13

#### 14 **5.4 Spatial and seasonal distribution of POC**

15            During the summer of 2011 surface POC concentrations were between  $\sim 12$  and  
16  $\sim 55 \mu\text{mol kg}^{-1}$ . Station 20 had the highest POC concentration at all sampled depths ( $\sim 46$   
17  $\mu\text{mol kg}^{-1}$ ,  $\sim 30$ , and  $\sim 42 \mu\text{mol kg}^{-1}$ , surface to bottom), while the west arm had the  
18 highest POC concentrations below the surface ( $\sim 33 \mu\text{mol kg}^{-1}$  at 50 m and depth). The  
19 west and east arms exhibited negative AOU ( $\sim -80$  and  $\sim -64 \mu\text{mol kg}^{-1}$ , respectively).  
20 Below the surface concentrations were similar ( $\sim 9 \mu\text{mol kg}^{-1}$ ), while surface waters had a  
21 POC concentration of  $\sim 28 \mu\text{mol kg}^{-1}$ . Lower bay had relatively lower POC concentrations  
22 ( $\sim 15 \mu\text{mol kg}^{-1}$  at all depths).

23            POC concentrations decreased, especially within surface waters during the fall. A



1 maximum regional POC concentration ( $\sim 13 \mu\text{mol kg}^{-1}$ ) was observed in surface waters of  
2 the west arm. Below the surface layer POC concentrations were low, between  $\sim 5$  and  $\sim 8$   
3  $\mu\text{mol kg}^{-1}$ . A maximum regional surface AOU ( $\sim 82 \mu\text{mol kg}^{-1}$ ) was estimated for the  
4 lower bay and a minimum ( $\sim 2 \mu\text{mol kg}^{-1}$ ) in the surface waters of the central bay (Fig. 5).

5 In the winter of 2012 surface water POC concentrations were not found to exceed  
6  $20 \mu\text{mol kg}^{-1}$  and AOU across the bay were on the order of  $\sim 70 \mu\text{mol kg}^{-1}$ . Surface POC  
7 concentrations ranged from  $\sim 2$  to  $\sim 15 \mu\text{mol kg}^{-1}$ , while POC concentrations at depth  
8 varied between  $\sim 3$  and  $16 \mu\text{mol kg}^{-1}$ . The regional maximum in POC was in the surface  
9 waters in the west arm ( $\sim 11 \mu\text{mol kg}^{-1}$ ). The east arm and lower bay both had maximum  
10 POC concentrations in the bottom waters ( $\sim 14$  and  $\sim 9 \mu\text{mol kg}^{-1}$ , respectively).

11 POC concentration in the surface waters increased during the spring of 2012,  
12 primarily within northern regions of the bay. The east arm had the greatest increase in  
13 surface POC ( $\sim 62 \mu\text{mol kg}^{-1}$ ) with concentrations decreasing in the surface water to the  
14 south. The west arm and central bay had similar surface POC concentrations of  $\sim 35 \mu\text{mol}$   
15  $\text{kg}^{-1}$ , and  $\sim 30 \mu\text{mol kg}^{-1}$ , respectively. The lower bay had the lowest surface POC  
16 concentrations with  $\sim 13 \mu\text{mol kg}^{-1}$ , while having the highest rate of NCP and AOU ( $\sim 93$   
17  $\mu\text{mol kg}^{-1}$ ). The lower bay subsurface and deepwater AOU values were positive and POC  
18 concentrations,  $\sim 9 \mu\text{mol kg}^{-1}$  each, were the highest among the regions.

19 AOU values decreased in surface waters across the bay, while rates of NCP were  
20 elevated within these waters during the summer of 2012. Surface POC concentrations  
21 were highest in the east arm ( $\sim 50 \mu\text{mol kg}^{-1}$ ), while below the surface layer, POC  
22 concentrations decreased, ranging from  $\sim 4.5$  to  $\sim 7 \mu\text{mol kg}^{-1}$  at 50 m and  $\sim 5$  to  $\sim 8 \mu\text{mol}$   
23  $\text{kg}^{-1}$  at depth. The west arm and central bay regions had surface POC concentrations of

1 ~23  $\mu\text{mol kg}^{-1}$  and the lower bay exhibited the lowest surface POC concentration with  
2 ~13  $\mu\text{mol kg}^{-1}$ ..

3

#### 4 **5.5 Relationship between DIC and DO**

5        During the summer of 2011, DO concentrations ranged from ~190 to ~400  $\mu\text{mol}$   
6  $\text{kg}^{-1}$ . All samples below the surface layer, as well as surface samples within the lower bay  
7 followed the Redfield ratio, with concentrations at depth between ~190 and 280  $\mu\text{mol kg}^{-1}$   
8 (Fig. 6). Surface samples of stations within the arms and central bay had high DO  
9 concentrations and low DIC. Surface DO was higher than that at depth, ranging between  
10 ~230 and 400  $\mu\text{mol kg}^{-1}$ . However, in the lower bay DIC concentrations remained  
11 elevated (~2030  $\mu\text{mol kg}^{-1}$ ) and DO concentrations were low (~240  $\mu\text{mol kg}^{-1}$ ). During  
12 the fall, surface samples within the arms and central bay continued to deviate from  
13 Redfield. Surface DO concentrations ranged from ~210 to ~330  $\mu\text{mol kg}^{-1}$  and  
14 corresponded with reduced surface DIC concentrations. At depth, DO concentrations  
15 varied between ~200 and 280  $\mu\text{mol kg}^{-1}$  with C:O ratios close to Redfield.

16        All samples, at the surface and at depth, followed Redfield closely with surface  
17 waters having slightly higher DO and lower DIC concentrations than those at depth  
18 during the winter of 2012. Surface water DO concentrations were between 250 and ~280  
19  $\mu\text{mol kg}^{-1}$ , while deeper waters ranged from ~230 to 255  $\mu\text{mol kg}^{-1}$ .

20        In the spring, DIC was drawn down and DO concentrations increased, having a  
21 range between ~270 and 410  $\mu\text{mol kg}^{-1}$ . DO concentrations were amplified while DIC  
22 was reduced at stations in the northern-most regions of both arms. These samples  
23 deviated the most from Redfield, while the remaining samples adhered to the Redfield

1 ratio. Below the surface layer, DO concentration throughout the bay ranged from ~250 to  
2 280  $\mu\text{mol kg}^{-1}$

3 During the summer of 2012, the surface waters within the two arms and central  
4 bay continued to diverge from Redfield. DIC concentrations within the more northern  
5 regions of the bay (east arm, west arm, and central bay) were increasingly drawn down,  
6 while DO concentrations remained elevated. Surface DO concentrations ranged from  
7 ~260 to ~410  $\mu\text{mol kg}^{-1}$ , with lower DO concentrations at depth, varying from 200 - ~270  
8  $\mu\text{mol kg}^{-1}$ .

9

## 10 **5.6 Air-Sea gas flux**

11 During the summer of 2011 winds were relatively low, at  $\sim 1.6 \text{ m s}^{-1}$ , with surface  
12 waters of the central bay and the west arm were undersaturated with respect to  
13 atmospheric  $\text{CO}_2$  with  $p\text{CO}_2$  values of  $\sim 250 \mu\text{atms}$ . The central bay and the west arm  
14 acted as minor sinks ( $\sim -0.3 \pm 0.02 \text{ mmol C m}^{-2} \text{ d}^{-1}$  each). The lower bay and east arm had  
15 much higher seawater  $p\text{CO}_2$  values of  $\sim 488 \mu\text{atms}$  and  $\sim 463 \mu\text{atms}$  and acted as sources  
16 for atmospheric  $\text{CO}_2$  of  $\sim 0.2 \pm 0.01 \text{ mmol C m}^{-2} \text{ d}^{-1}$  for each region (Fig. 7).

17 During the fall of 2011, winds increased slightly to  $\sim 2.0 \text{ m s}^{-1}$  and surface waters  
18 in all regions of the bay were oversaturated with respect to the atmospheric  $\text{CO}_2$ . The  
19 lower bay experienced the highest  $p\text{CO}_2$  at  $\sim 670 \mu\text{atms}$  and acted as the largest source for  
20 atmospheric  $\text{CO}_2$  with a flux of  $\sim 1.1 \pm 0.06 \text{ mmol C m}^{-2} \text{ d}^{-1}$ . The central bay also had  
21 elevated  $p\text{CO}_2$  with  $\sim 510 \mu\text{atms}$  leading to outgassing of  $\sim 0.5 \pm 0.03 \text{ mmol C m}^{-2} \text{ d}^{-1}$ . The  
22 east arm had a  $p\text{CO}_2$  and flux values similar to that of the central bay ( $p\text{CO}_2 = \sim 514$   
23  $\mu\text{atms}$ ; flux =  $\sim 0.5 \text{ mmol} \pm 0.03 \text{ C m}^{-2} \text{ d}^{-1}$ ). Air-sea  $\text{CO}_2$  flux in the west arm was  $\sim 0.3 \pm$

1 0.02 mmol C m<sup>-2</sup> d<sup>-1</sup>, similar to the east arm and central bay, but had a slightly lower  
2 pCO<sub>2</sub> of ~482 μatms (Fig. 7).

3 Surface waters during the winter of 2012 were oversaturated in CO<sub>2</sub> with respect  
4 to the atmosphere and all regions experienced outgassing, with average wind speeds of  
5 ~2.1 m s<sup>-1</sup>. Regional pCO<sub>2</sub> values were more constrained, especially within the arms and  
6 central bay, ranging from ~400 μatms in the west arm and central bay to ~432 μatms in  
7 the east arm. Similar pCO<sub>2</sub> values and seawater temperatures (~3.5°C), led the west arm  
8 and central bay to experience comparable CO<sub>2</sub> fluxes of ~0.03 ± 0.002 and 0.06 ± 0.003  
9 mmol C m<sup>-2</sup> d<sup>-1</sup>. The east arm had a slightly higher surface temperature (~4.1°C) and flux,  
10 with ~0.18 ± 0.01 mmol C m<sup>-2</sup> d<sup>-1</sup>, while the lower bay had a slightly higher CO<sub>2</sub> flux of  
11 ~0.76 ± 0.04 mmol C m<sup>-2</sup> d<sup>-1</sup>.

12 In the spring, seawater temperatures increased slightly to ~5°C across the bay  
13 while salinity remained similar to winter values (~29 to 31). However, all regions except  
14 for the lower bay transitioned to sinks for atmospheric CO<sub>2</sub>. pCO<sub>2</sub> in the lower bay  
15 remained oversaturated with respect to CO<sub>2</sub> at ~423 μatms and had a flux of ~0.11 ± 0.01  
16 mmol C m<sup>-2</sup> d<sup>-1</sup>. Within the other three regions of the bay, surface water temperatures  
17 increased by just over 1°C. However, pCO<sub>2</sub> decreased in the surface waters and these  
18 regions acted as sinks for atmospheric CO<sub>2</sub>. The east arm had the greatest decrease in  
19 pCO<sub>2</sub>, dropping from ~432 μatms to ~167 μatms and exhibiting seasonal outgassing of ~  
20 -0.87 ± 0.04 mmol C m<sup>-2</sup> d<sup>-1</sup>. The central bay and west arm regions were also seasonal  
21 sinks for CO<sub>2</sub>, taking up ~ -0.39 ± 0.02 mmol C m<sup>-2</sup> d<sup>-1</sup> in the central bay and ~ -0.60 ±  
22 0.03 mmol C m<sup>-2</sup> d<sup>-1</sup> in the west arm.

1           During the summer of 2012  $p\text{CO}_2$  in the east arm increased to  $\sim 337 \mu\text{atms}$  with  $\sim -$   
2  $0.13 \pm 0.01 \text{ mmol C m}^{-2} \text{ d}^{-1}$  of ingassing. The central bay had a  $p\text{CO}_2$  of  $\sim 200 \mu\text{atms}$  and a  
3 flux of  $\sim -0.44 \pm 0.02 \text{ mmol C m}^{-2} \text{ d}^{-1}$ . The lower bay and west arm, acted as sources for  
4 atmospheric  $\text{CO}_2$ , having  $p\text{CO}_2$  values of  $\sim 411 \mu\text{atms}$  and  $\sim 507 \mu\text{atms}$ , respectively, while  
5 the lower bay experienced a near-neutral flux of  $\sim 0.04 \pm 0.002 \text{ mmol C m}^{-2} \text{ d}^{-1}$ . The west  
6 arm was oversaturated with respect to atmospheric  $\text{CO}_2$  with a  $p\text{CO}_2$  of  $\sim 507 \mu\text{atms}$  and a  
7 flux of  $\sim 0.26 \pm 0.01 \text{ mmol C m}^{-2} \text{ d}^{-1}$ .

8

## 9 **6.0 Discussion**

### 10 **6.1 Relationships of DIC, Nitrate, and Dissolved Oxygen**

11           DIC, nitrate and DO are important indicators of biological production in a marine  
12 ecosystem. One way they can be used as biological production indicators is through  
13 Redfield ratios. Carbon and oxygen have a C:O Redfield ratio of 106:170 (Anderson et  
14 al., 1994) and the carbon to nitrate Redfield ratio is 106:16.

15           During the summer of 2011 variability in DIC, nitrate and dissolved oxygen  
16 concentrations within the surface waters were a result of primary production, dilution  
17 from glacial discharge, or a combination of both processes. Surface waters in the arms  
18 and upper-central bay deviated from Redfield ratios for C:O and C:N (Figs. 6 and 8)  
19 Waters below this surface layer followed the Redfield ratios throughout the year. Nitrate  
20 and phosphate concentrations in the surface waters were not observed to reach depletion  
21 during the summer, indicating that they were being continuously supplied to the surface  
22 layer and that phosphate (data not shown) was not limiting. Sustained nutrient  
23 concentrations and nutrient replenishment may be the result of several physical  
24 interactions within the bay, including wind, tidal and internal wave mixing, especially

1 over shallow sills at the mouth of the bay and at the entrance to the east arm.

2           Increases in DO and the reduction in macronutrient concentrations, including  
3 DIC, within the more northern arms of the bay was due to primary production coupled  
4 with the influence of glacier runoff and salinity-driven stratification limiting mixing and  
5 nutrient replenishment in the mixed layer. In the fall of 2011, DIC and nitrate  
6 concentrations increased while DO decreased in the surface waters as primary production  
7 slowed and wind mixing increased. Due to decreasing primary production nutrient  
8 concentrations were similar within surface waters with the lowest concentrations  
9 observed in the arms where glacial runoff was still impacting surface waters. Surface  
10 water ratios for C:O and C:N deviated from the Redfield ratios, but less so than observed  
11 during summer as primary production began to decrease during the fall (Figs. 6 and 8).  
12 During the winter of 2012, increased wind mixing and the reduction of glacial input led  
13 to deeper water column mixing, with much more constrained DIC and nitrate  
14 concentrations. During the winter nitrate and DIC concentrations continued to increase,  
15 with C:O and C:N Redfield ratios indicated a decrease in primary production and  
16 increase in mixing (Figs. 6 and 8). While DIC and nitrate concentrations fell near the  
17 Redfield ratio, they deviated slightly from Redfield at the highest nitrate concentrations  
18 (Fig. 4). This may have been due to nitrification of ammonium by bacteria leading to an  
19 increase the nitrate concentration. Another possibility is ‘carbon overconsumption’, the  
20 process in which more DIC is taken up than that inferred from the C:N Redfield ratio  
21 (Voss et al., 2011). Explanations for carbon overconsumption include the preferential  
22 remineralization of organic nitrogen (Thomas and Schneider, 1999) or an increased  
23 release of dissolved organic carbon (Engel, et al., 2002; Schartau et al., 2007).

1           As temperatures began to warm in the spring of 2012, the onset of glacial melt  
2 and primary production reduced DIC and nitrate, while increasing DO concentrations in  
3 surface waters across the bay. DIC and nitrate correlated closely with the Redfield ratio  
4 except for two surface samples located at the northernmost ends of each arm (Fig. 8).  
5 This deviation may be explained by the fact that these stations were the first to be  
6 influenced by glacial runoff during the onset of the glacial melt season.

7           Further reduction in DIC and nitrate concentrations in surface waters was  
8 observed during the summer of 2012 as primary production intensified, increasing DO  
9 concentrations.. Low nutrient glacial runoff was highest at this time of year, affecting  
10 surface water DIC and nitrate concentrations within the arms. However, concentrations  
11 did not drop as low as was observed during the previous summer. Macronutrients did not  
12 reach depletion during the summer of 2012, implying they were not the limiting primary  
13 productivity, possibly due to nutrient replenishment via tidal pumping. Surface nitrate  
14 concentration continued to deviate from the C:N Redfield ratio as these macronutrients  
15 were increasingly drawn down by primary productivity and diluted by glacier runoff (Fig.  
16 8). Surface waters in several regions also deviated from the C:O Redfield ratio (Fig. 6)  
17 The stations most affected were those within the east arm and west arm, as well as upper  
18 central bay, where freshwater influence was greatest. Mixing of nutrient-rich marine  
19 waters from the Gulf of Alaska likely offset much of the drawdown from primary  
20 production and allowed these surface waters within the lower bay to fall closer to the  
21 Redfield ratio.

22

23 **6.2 NCP**

1           The seasonal transition between the summer and fall of 2011 had the largest rates  
2 of NCP observed during the year of study. During this time all NCP rates were positive,  
3 signifying enhanced primary productivity in the mixed layer. Rates of NCP became  
4 negative during the seasonal transitions from fall to winter, as well as from winter to  
5 spring. These negative NCP values indicate that air-sea fluxes (discussed in Section 5.6)  
6 and organic matter respiration were prominent, increasing CO<sub>2</sub> (DIC) concentrations in  
7 the surface waters and overwhelming any weaker signal from primary production.  
8 Between the fall and winter, the lower bay experienced the highest degree of CO<sub>2</sub> flux  
9 when compared to biological production. The biological production was overwhelmed by  
10 CO<sub>2</sub> influx in the east and west arms, but to a less degree than in regions to the south.

11           Between the winter and spring of 2012 the lower bay was the only region where  
12 biological production dominated the CO<sub>2</sub> flux with a positive NCP rate, reflecting the  
13 region's nutrient-rich marine influence from the Gulf of Alaska. The CO<sub>2</sub> flux signal  
14 exceeded NCP within the east and west arms of the bay and, to a lesser extent, the central  
15 bay. Transition from the spring to summer of 2012, primary production was evident in  
16 the NCP rates. The west arm experienced a lower rate of NCP, possibly the result of the  
17 strong low-macronutrient glacial influences along the arm, which may work to hinder  
18 production. Additionally, large volumes of glacial flour imparted into the surface waters  
19 from runoff during summer may have limited the photic depth and thus impeded some  
20 productivity in the upper arms of the bay.

21           The total mass of carbon produced between seasons via NCP was also estimated  
22 (Table 1). Between the summer and fall of 2011, we observed the greatest production of  
23 organic carbon of any seasonal transition, with the largest production signal in the lower



1 bay and decreasing to the north as glacial influence increased. Elevated production  
2 estimates within the lower could be due to continued nutrient replenishment to surface  
3 waters as a result of mixing with the more marine waters outside of the bay.

4 Despite all regions of the bay being dominated by air-sea CO<sub>2</sub> flux during  
5 between the fall and winter seasons (Table 1), there was a substantial contrast in  
6 magnitudes of estimates between the marine-dominated lower bay and the glacially-  
7 influenced east arm. These differences in magnitude were likely the result of a higher  
8 degree of wind and tidal mixing at stations outside of and near the mouth of the bay,  
9 allowing this region to have elevated air-sea flux when compared to the east and west  
10 arms (Fig. 7).

11 The production signal within the arms and central regions of the bay continued to  
12 be overwhelmed by air-sea flux between the winter and spring of 2012 (Table 1). While  
13 production estimates remained negative in the northern regions of the bay, the lower bay  
14 had a positive NCP mass signifying increased primary production and a decrease in air-  
15 sea flux in this region. This increase in NCP in the lower bay may be been the result of  
16 earlier nutrient replenishment via the more marine waters outside of the bay. Between the  
17 spring and summer there was increased production across the bay as stratification  
18 strengthen and the hours of daylight increased, with the largest production estimates in  
19 the lower bay. The east and west arms exhibited the lowest biomass production, likely  
20 hindered by the inundation of low-nutrient glacial runoff that formed a fresh surface layer  
21 and imparted glacial flour into the surface waters in these regions.

22

### 23 **6.3 Air-Sea Flux**

1           Aside from primary production, air-sea carbon dioxide (CO<sub>2</sub>) flux also impacts  
2 carbon concentrations within surface waters. In Glacier Bay, air-sea fluxes varied  
3 regionally and seasonally between the summer of 2011 and the summer of 2012. During  
4 the summer of 2011 winds were relatively low, reducing turbulent mixing, allowing for  
5 stratification and, thus, primary production. Surface waters in the lower bay and east arm  
6 acted as sources for atmospheric CO<sub>2</sub>, while the central bay and the west arm acted as  
7 sinks (Fig. 7). Drawdown of CO<sub>2</sub> in the west arm may be attributed to primary  
8 production, as well as the influx of low nutrient glacial melt. The central bay has been  
9 noted to have elevated production levels (Hooge and Hooge, 2002) that may account for  
10 the drawdown of DIC and the region's sink status. Within the east arm seawater  
11 temperatures were high, increasing the *p*CO<sub>2</sub> of these waters and, combined with  
12 influence of the reduced TA concentrations, resulted in an oversaturation of CO<sub>2</sub> in the  
13 seawater with respect to the atmosphere, overwhelming any effect from DIC drawdown  
14 via primary production and making this region a source for atmospheric CO<sub>2</sub>. Turbulent  
15 mixing across and outside the sill, as well as through Sitakaday Narrows, likely reduced  
16 stratification and enhanced air-sea flux, causing this region to be a source for atmospheric  
17 CO<sub>2</sub>.

18           In the fall of 2011, winds increased slightly and all surface waters across the bay  
19 experienced oversaturation with respect to the atmospheric CO<sub>2</sub>, with the lower bay  
20 acting as the strongest regional source (Fig. 7). The high *p*CO<sub>2</sub> values observed during  
21 fall, despite strong DIC drawdown during summer, may be the result of a variety of  
22 interactions. Reduced glacial runoff during fall increased TA concentrations (Reisdorph  
23 and Mathis, 2014) and surface water temperatures declined allowing them to hold more

1 CO<sub>2</sub> while mixing brought DIC-rich waters from depth to the surface. Increased winds  
2 also likely led to enhanced turbulent mixing across the bay.

3         During the winter of 2012 surface waters across all regions of the bay continued  
4 to experience outgassing (Fig. 7), though to a lesser degree than during fall. The lower  
5 bay experienced the largest degree of outgassing, likely due to its more turbulent mixing  
6 than other regions. Despite winter having the lowest seawater temperatures, wind mixing  
7 peaked and likely allowed for CO<sub>2</sub>-rich waters from depth and the air to enter the surface  
8 waters, increasing *p*CO<sub>2</sub> in all regions of the bay.

9         Several regions of Glacier Bay transitioned to sinks for atmospheric CO<sub>2</sub> during  
10 the spring of 2012 as primary production increased and winds slowed. The lower bay was  
11 the exception, remaining oversaturated with respect to CO<sub>2</sub> and continuing to act as a  
12 minor source for atmospheric CO<sub>2</sub>. In the more northern regions, surface waters  
13 experienced a slight increase in surface temperatures, but due to the onset of spring  
14 productivity DIC was drawn down in the surface waters, decreasing the *p*CO<sub>2</sub> and  
15 allowing them to become sinks for atmospheric CO<sub>2</sub>. The east arm experienced the  
16 largest decrease in *p*CO<sub>2</sub> and became the largest sink region within the bay, while the  
17 west arm and central bay underwent similar flux transitions as primary production  
18 increased, drawing down DIC in the surface waters. Within the arms, the onset of glacial  
19 melt may have aided in setting up stratification, also helping to lead to larger sink statuses  
20 within these regions.

21         During the summer of 2012, waters in the northern regions becoming increasingly  
22 saturated with respect to atmospheric CO<sub>2</sub>. While, *p*CO<sub>2</sub> in the east arm did increase from  
23 spring values, perhaps due to a small increase in surface water temperatures and reduced

1 in TA from glacial runoff, it was still undersaturated with respect to atmospheric  $p\text{CO}_2$ .  
2 Atmospheric  $\text{CO}_2$  uptake within the central bay strengthened slightly from spring as  
3  $p\text{CO}_2$  in this region decreased, likely due to high levels of primary production in this  
4 region, as well as high nutrient replenishment from tidal mixing between the waters of  
5 lower bay and the stratified waters within the central bay (Hooge & Hooge, 2002).  
6 Conversely, the lower bay remained a minimal source for atmospheric  $\text{CO}_2$ , while the  
7 west arm transitioned into source during the summer. The lower bay experiences the  
8 highest degree of turbulent or tidal mixing across the sill, within Cross Sounds, and  
9 through Sitakaday Narrows, inhibiting stratification and primary production and causing  
10 it act as a source for atmospheric  $\text{CO}_2$  year-round. The difference in the sink/source status  
11 of the east and west arms of the bay was likely the result of differences in glacial  
12 influences, with the west arm more influenced by low-TA glacial runoff as it has the  
13 majority of the tidewater glaciers along its length. These glaciers caused a higher degree  
14 of TA and DIC dilution than was observed within the west arm.

15

## 16 **7.0 Conclusions**

17 Glacier Bay experiences a high degree of spatial and temporal throughout the  
18 year. Environmental influences vary seasonally along a gradient from the glacially-  
19 influenced northern regions within the arms to the marine-influenced lower bay. This  
20 imparts spatial differences in stratification and macronutrient availability that effect  
21 biological processes and thus, rates of NCP within each of the four pre-defined regions of  
22 the Glacier Bay..

23 Despite Glacier Bay's limited exchange with the marine waters of the Gulf of

1 Alaska, it has been observed to support elevated primary production through most of the  
2 year (Hooge & Hooge, 2002), perhaps due to tidal pumping. However, rapid deglaciation  
3 within Glacier Bay has imparted a high volume of fresh glacial runoff, a portion of which  
4 has been from tidewater glaciers that melt directly into the bay, affecting stratification,  
5 macronutrient concentrations and influencing air-sea CO<sub>2</sub> exchange.

6 Rates of NCP were positive across the bay between the summer and fall of 2011,  
7 as well as between the spring and summer of 2012 during peak times of primary  
8 production. NCP was highest during the transition between summer and fall of 2011,  
9 with regional NCP rates ranging from ~54 to ~80 mmol C m<sup>-2</sup> d<sup>-1</sup>. Rates during the  
10 summer of 2012 were lower, between ~6 and ~20 mmol C m<sup>-2</sup> d<sup>-1</sup>.

11 Between the fall of 2011 and winter of 2012, as well as between the winter and  
12 spring of 2012, air-sea gas exchange overwhelmed any production signal across the bay,  
13 especially during the fall (Fig. 7; Table 1). The one exception was lower bay between  
14 winter and spring where NCP rates were positive, likely due to earlier replenishment of  
15 nutrients from marine waters outside the bay.

16 The impact of rapid deglaciation in Glacier Bay can be observed in the seasonal  
17 impacts on the carbon cycling and NCP in this estuarine system. This study enhances the  
18 limited biogeochemical literature regarding Glacier Bay and includes one of the more  
19 robust datasets from Glacier Bay. The influence of surrounding glaciers, especially  
20 tidewater glaciers, has the potential to significantly impact the efficiency and makeup of  
21 the marine food web within Glacier Bay in unknown ways with unknown consequences.  
22 Better understanding of the influences of NCP can help identify possible these outcomes.

23

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11 **References**

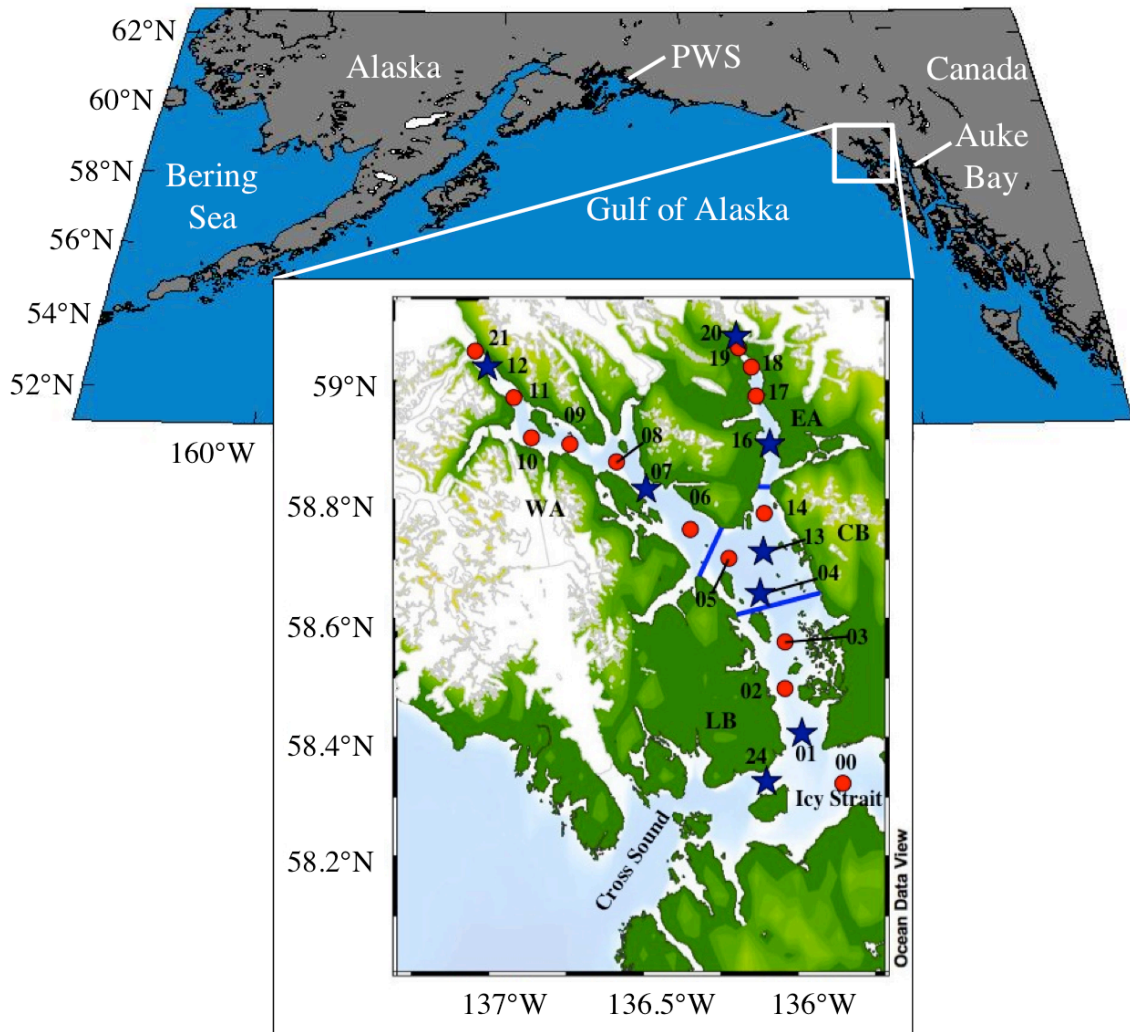
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1 **Figures and Tables**



2

3 Fig. 1: Glacier Bay location and oceanographic sampling station map - Blue lines denote

4 regional boundaries. Red dots show all oceanographic station locations with station

5 number. Blue stars represent 'core' station location. lower bay, central bay, east, west

6 arm.

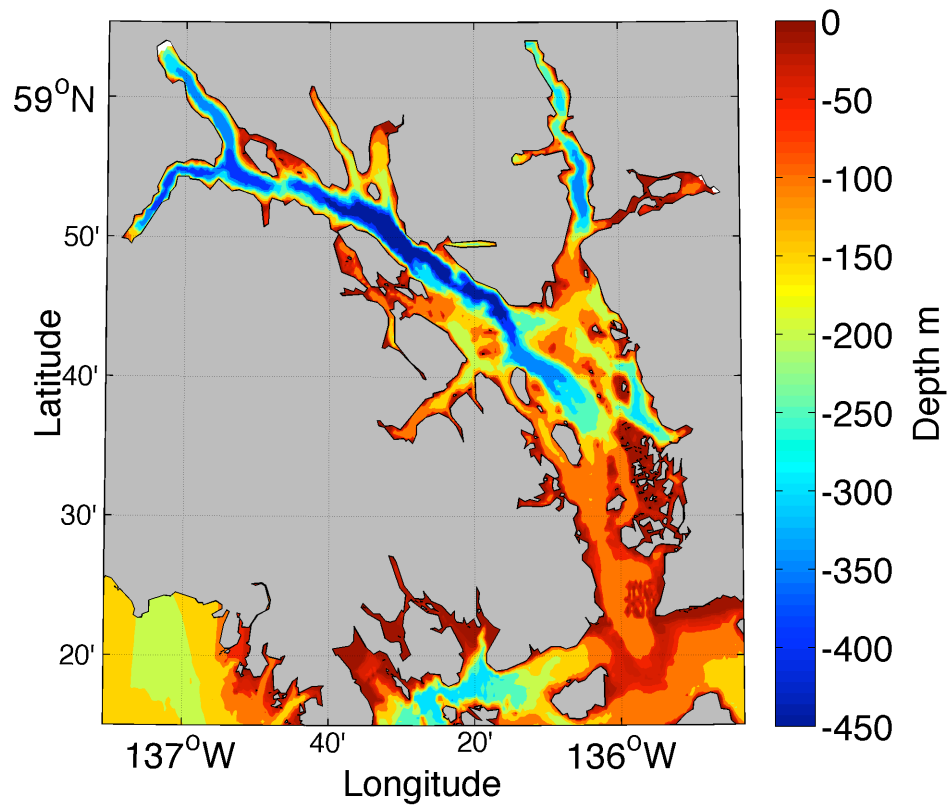
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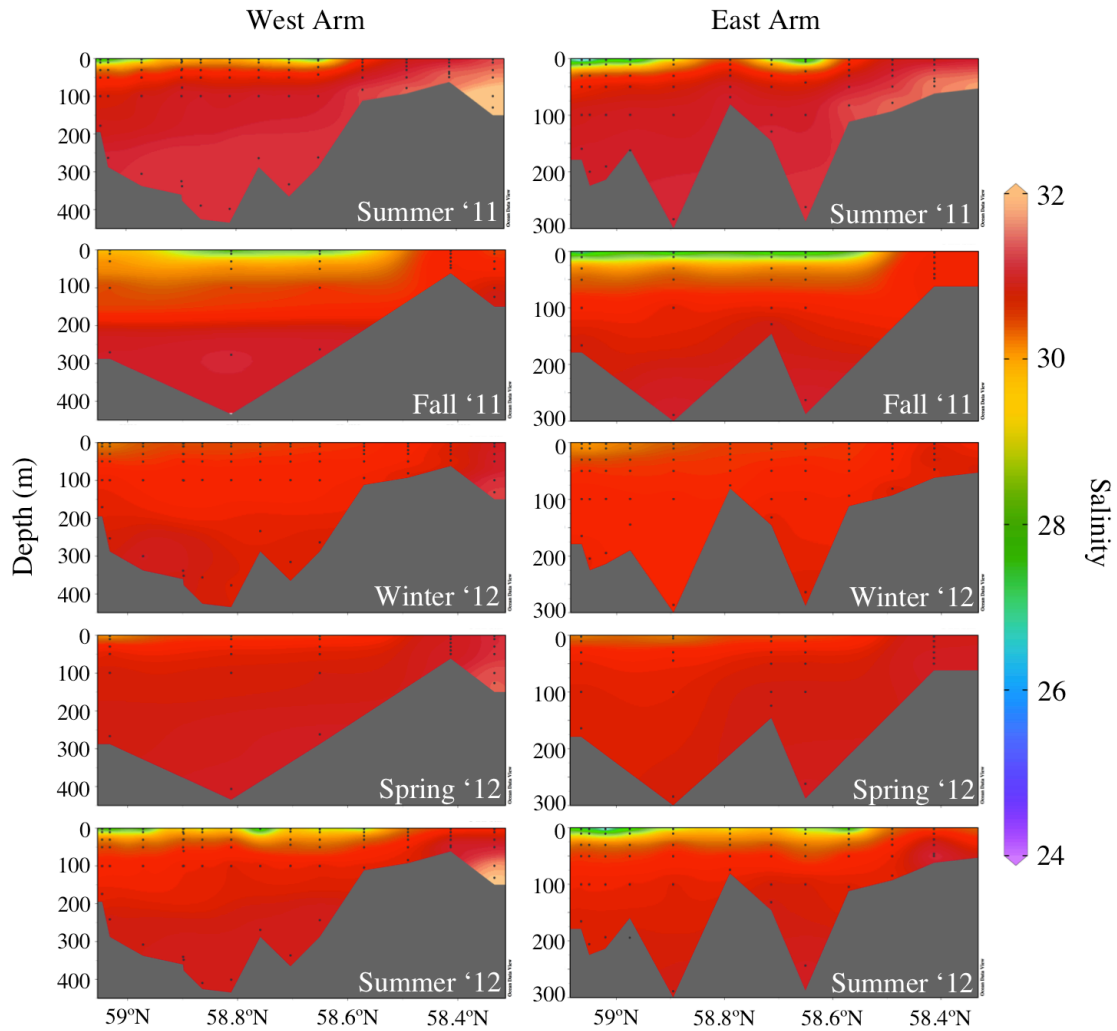
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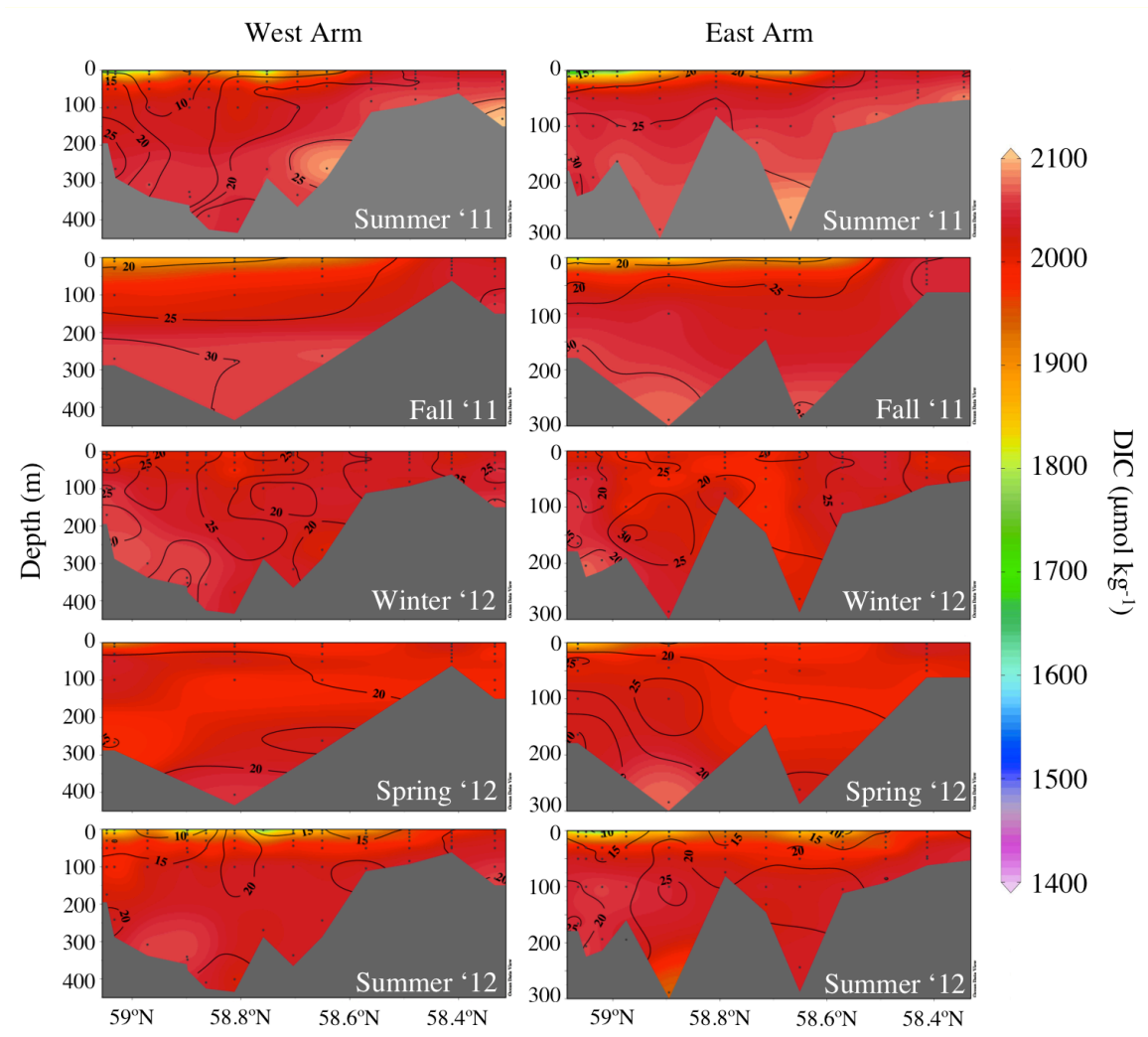
3 Figure 2: Bathymetry of Glacier Bay – Bathymetric map of Glacier Bay



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2 Figure 3: Seasonal distribution of salinity. Spatial and seasonal distribution of salinity in  
 3 the water column.

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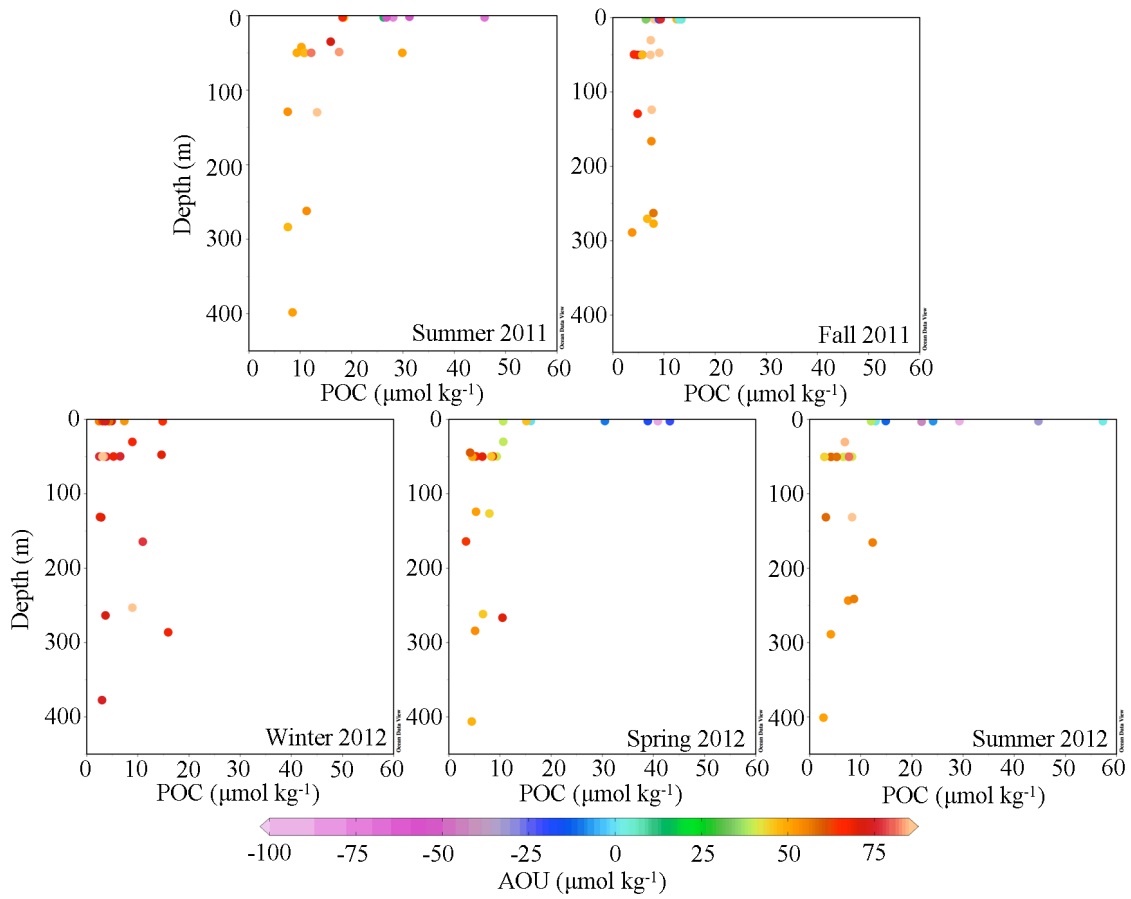
2 Figure 4: Spatial distribution of DIC and nitrate. Spatial and seasonal distribution of DIC  
 3 in the water column. Contours represent nitrate concentrations

Seasonal transition	Region	Regional Area (m <sup>2</sup> )	NCP rate (mmol C m <sup>-2</sup> d <sup>-1</sup> )	NCP mass (kg C d <sup>-1</sup> )
Summer and Fall	Lower Bay	5.44x10 <sup>8</sup>	68.9 ± 3.5	4.5x10 <sup>5</sup> ± 2.3x10 <sup>4</sup>
	Central Bay	3.40x10 <sup>8</sup>	53.6 ± 2.7	2.2x10 <sup>5</sup> ± 1.1x10 <sup>4</sup>
	West Arm	1.80x10 <sup>8</sup>	81.3 ± 4.1	1.8x10 <sup>5</sup> ± 8.8x10 <sup>3</sup>
	East Arm	9.00x10 <sup>7</sup>	70.3 ± 3.5	7.6x10 <sup>4</sup> ± 3.8x10 <sup>3</sup>
Fall and Winter	Lower Bay	5.44x10 <sup>8</sup>	-14.2 ± 0.7	-9.3x10 <sup>4</sup> ± 4.6x10 <sup>3</sup>
	Central Bay	3.40x10 <sup>8</sup>	-11.5 ± 0.6	-4.7x10 <sup>4</sup> ± 2.3x10 <sup>3</sup>
	West Arm	1.80x10 <sup>8</sup>	-1.3 ± 0.1	-2.7x10 <sup>3</sup> ± 135.7
	East Arm	9.00x10 <sup>7</sup>	-0.5 ± 0.0	-515.7 ± 25.8
Winter and Spring	Lower Bay	5.44x10 <sup>8</sup>	17.6 ± 0.9	1.1x10 <sup>5</sup> ± 5.7x10 <sup>3</sup>
	Central Bay	3.40x10 <sup>8</sup>	-17.5 ± 0.9	-7.1x10 <sup>4</sup> ± 3.6x10 <sup>3</sup>
	West Arm	1.80x10 <sup>8</sup>	-26.6 ± 1.3	-5.7x10 <sup>4</sup> ± 2.9x10 <sup>3</sup>
	East Arm	9.00x10 <sup>7</sup>	-36.4 ± 1.8	-3.9x10 <sup>4</sup> ± 2.0x10 <sup>3</sup>
Spring and Summer	Lower Bay	5.44x10 <sup>8</sup>	19.4 ± 1.0	1.3x10 <sup>5</sup> ± 6.3x10 <sup>3</sup>
	Central Bay	3.40x10 <sup>8</sup>	17.2 ± 0.9	7.0x10 <sup>4</sup> ± 3.5x10 <sup>3</sup>
	West Arm	1.80x10 <sup>8</sup>	6.0 ± 0.3	1.3x10 <sup>4</sup> ± 652.1
	East Arm	9.00x10 <sup>7</sup>	15.7 ± 0.8	1.7x10 <sup>4</sup> ± 846.9

1

2 Table 1: Regional rates and masses of NCP – NCP by region in Glacier Bay based the  
3 change in salinity-normalized DIC concentrations between seasons.

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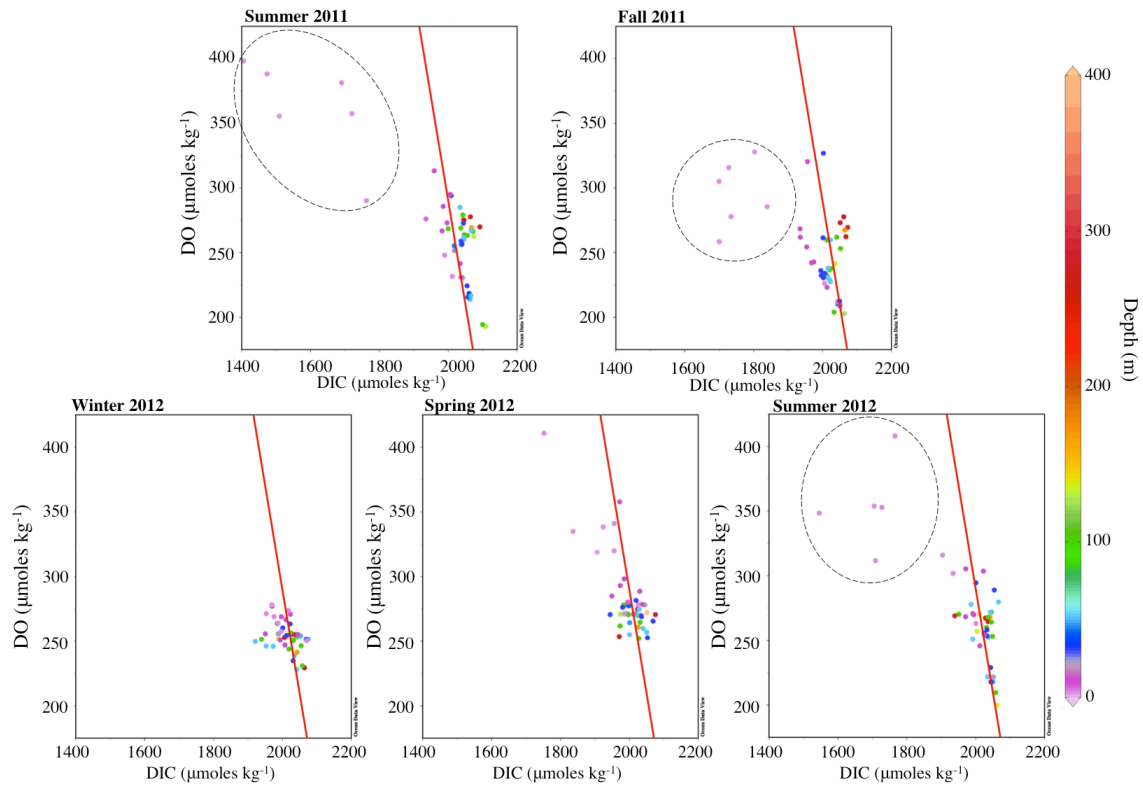
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3 Fig. 5: Seasonal POC vs. depth vs. AOU - Seasonal scatter plots of POC concentrations

4 vs. depth for each season between the summer of 2011 through the summer of 2012.

5 Color bar represents AOU in  $\mu\text{mol kg}^{-1}$ .

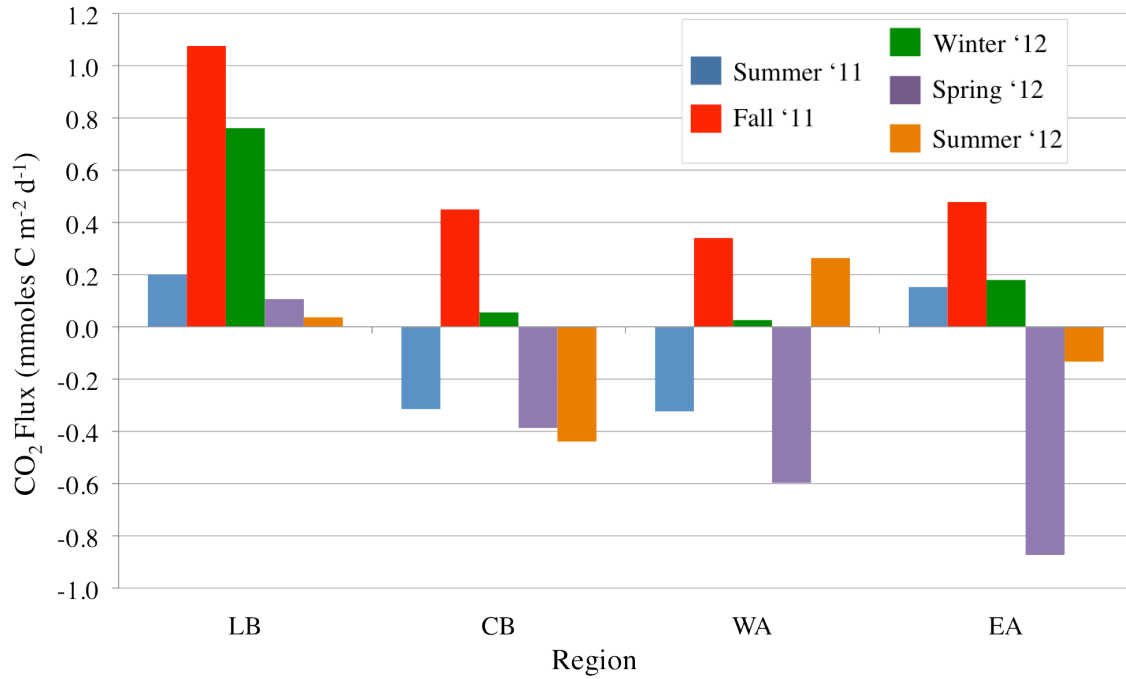
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3 Fig. 6: Seasonal DIC vs. DO vs. depth - Scatter plots of DIC concentrations vs. DO  
4 concentrations for each season between the summer of 2011 and the summer of 2012.  
5 Color bar represents depth in m. The red line depicts the C:O Redfield ratio of 106: -170.  
6 Dotted circles highlight samples that deviate from Redfield.

7

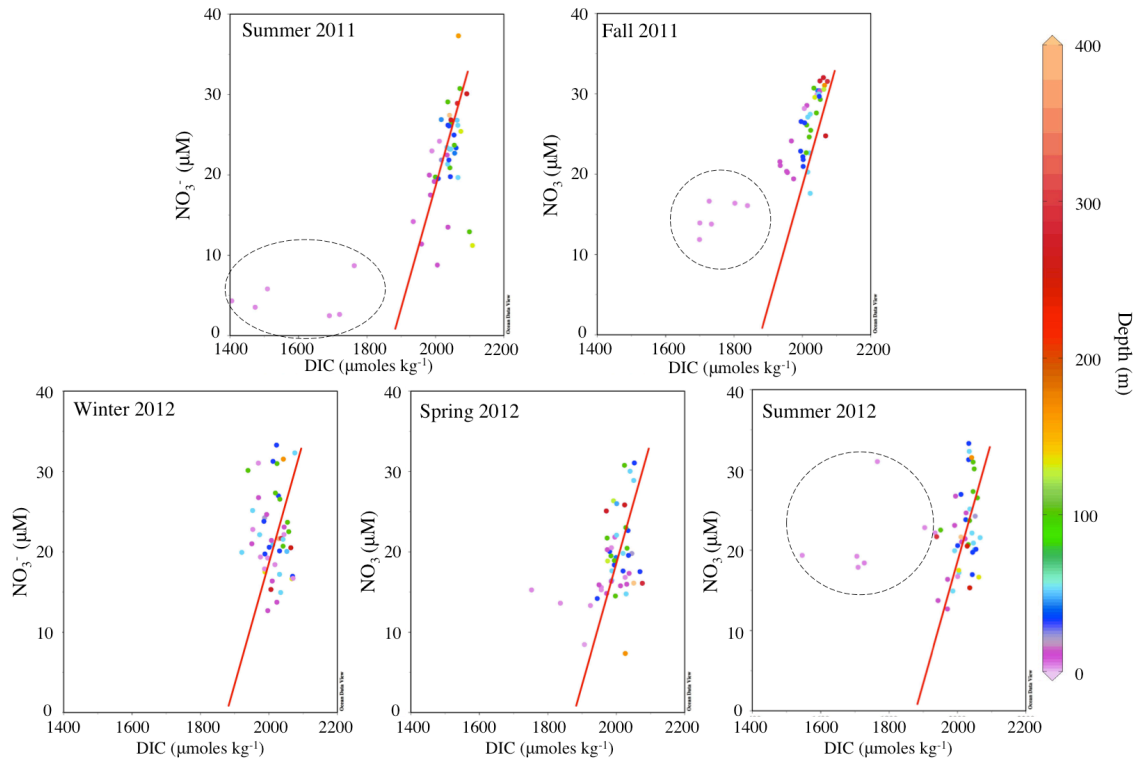


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2 Fig. 7: Air-sea CO<sub>2</sub> flux – Seasonal air-sea CO<sub>2</sub> fluxes by region in mmol C m<sup>-2</sup> d<sup>-1</sup>. Blue  
 3 represents the summer of 2011, red = fall of 2011, green = winter of 2012, purple =  
 4 spring of 2012, yellow = summer of 2012.

5





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2 Fig. 8: Seasonal DIC vs.  $\text{NO}_3^-$  vs. depth - Scatter plots of DIC concentrations vs.  $\text{NO}_3^-$   
 3 concentrations for each season between the summer of 2011 and the summer of 2012.

4 Color bar represents depth in m. The red line depicts the C:N Redfield ratio of 106:16.

5 Dotted circles highlight samples that deviate from Redfield.

6