Net Community Production and Inorganic Carbon Cycling in the Irminger Sea

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Abstract

The subpolar North Atlantic plays an outsized role in the atmosphere-to-ocean carbon sink. The central Irminger Sea is home to well-documented deep winter convection and high phytoplankton production, which drive strong seasonal and interannual variability in regional carbon cycling. We use observational data from moored carbonate system chemistry sensors and annual turn-around cruise samples at the Ocean Observatories Initiative's Global Irminger Sea Array to construct a near-continuous time series of mixed layer dissolved inorganic carbon (DIC), pCO2, and total alkalinity from summer 2015 to summer 2022. We use these carbonate system chemistry time series to deconvolve the physical and biological drivers of surface ocean carbon cycling in this region on seasonal, annual, and interannual time scales. We find high annual net community production within the seasonally-varying mixed layer, averaging 9.7 ± 1.7 mol m-2 yr-1 with high interannual variability (range of 6.0 to 13.7 mol m-2 yr-1). The highest daily net community production rates occur during the late winter and early spring, prior to the observed high chlorophyll concentrations associated with the spring phytoplankton bloom. As a result, the winter and early spring play a much larger role in biological carbon export from the mixed layer than traditionally thought.

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2 Net Community Production and Inorganic Carbon Cycling in the Irminger Sea

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6 Key Points:

We present the first multi-year, near-daily mixed layer dissolved inorganic carbon time
 series in the Irminger Sea

9 • Annual net community production within the seasonally varying mixed layer is high 10 $(9.7\pm1.7 \text{ mol m}^{-2} \text{ yr}^{-1})$ and has large interannual variability

The greatest rates of inorganic carbon removal from the mixed layer via photosynthesis
 take place prior to mixed layer shoaling

14 Abstract

- 15 The subpolar North Atlantic plays an outsized role in the atmosphere-to-ocean carbon sink. The
- 16 central Irminger Sea is home to well-documented deep winter convection and high
- 17 phytoplankton production, which drive strong seasonal and interannual variability in regional
- 18 carbon cycling. We use observational data from moored carbonate system chemistry sensors and
- 19 annual turn-around cruise samples at the Ocean Observatories Initiative's Global Irminger Sea
- 20 Array to construct a near-continuous time series of mixed layer dissolved inorganic carbon
- 21 (DIC), pCO_2 , and total alkalinity from summer 2015 to summer 2022. We use these carbonate
- system chemistry time series to deconvolve the physical and biological drivers of surface ocean
 carbon cycling in this region on seasonal, annual, and interannual time scales. We find high
- 24 annual net community production within the seasonally-varying mixed layer, averaging 9.7±1.7
- $25 \text{ mol m}^{-2} \text{ yr}^{-1}$ with high interannual variability (range of 6.0 to 13.7 mol m $^{-2} \text{ yr}^{-1}$). The highest
- 26 daily net community production rates occur during the late winter and early spring, prior to the
- 27 observed high chlorophyll concentrations associated with the spring phytoplankton bloom. As a
- result, the winter and early spring play a much larger role in biological carbon export from the
- 29 mixed layer than traditionally thought.

30 Plain Language Summary

31 The subpolar North Atlantic takes in more carbon from the atmosphere than other areas of the

- 32 ocean relative to its size. This is partially caused by photosynthesis in the surface ocean, which
- turns inorganic carbon into organic carbon that is transported into the deep ocean, a process
- 34 known as the biological carbon pump. Using measurements from sensors on moorings in the
- 35 Irminger Sea, we construct a seven-year time series of the different parts of the inorganic carbon
- 36 system. Using these, we separate out the forces that impact how much inorganic carbon has the
- 37 potential to be exchanged with the atmosphere. We find that biological processes remove
- inorganic carbon from the surface ocean in the spring, summer, and early fall, while in the winter
- 39 the surface ocean gets deeper and encompasses waters from below that have higher carbon
- 40 content. The total amount of inorganic carbon removed from the surface ocean each year by
- 41 biological process is extremely high in the Irminger Sea compared to other global ocean regions.
- 42 This research highlights the importance of long-term, full year measurements to understand
- 43 carbon cycle dynamics.
- 44
- 45
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- 47

48 **1 Introduction**

- 49 The ocean acts as a key sink in the global carbon cycle, absorbing carbon from the atmosphere at
- 50 its surface and then storing it in the deep ocean. Different biological and physical factors work in
- 51 tandem to drive this uptake. The biological carbon pump transports organic carbon produced via
- 52 photosynthesis into the deep ocean, causing a decrease in surface ocean pCO_2 that results in
- carbon dioxide moving from atmosphere to ocean (DeVries, 2022; Volk & Hoffert, 1985).
- 54 Globally, the biological carbon pump moves approximately 10 PgC yr⁻¹ into the ocean interior
- and is the main contributor to the 40-fold difference between the ocean and atmosphere carbon
- reservoirs (Caldera et al., 2018; Friedlingstein et al., 2022; Siegel et al., 2023). The North
- 57 Atlantic accounts for a disproportionately large share of this global export relative to its size,
- 58 with estimates ranging from 0.55 to 1.94 PgC yr⁻¹ (average 1.27 PgC yr⁻¹; Sanders et al., 2014).
- 59 While extensive study has taken place in the North Atlantic on the myriad of pathways
- 60 contributing to the region's biological carbon export, there is still high uncertainty in total flux
- 61 values and the underlying mechanistic controls (Sanders et al., 2014).
- 62 Organic carbon meanders on its path from the surface to the deep ocean. It can be repeatedly
- aggregated, disaggregated, consumed, and respired by different classes of organisms, and is
- 64 transported via sinking of particles, physical injection of high organic carbon waters, and vertical
- migration of heterotrophic grazers (Boyd, 2015; Boyd et al., 2019; Huang et al., 2022; Siegel et
- al., 2023; Stemmann & Boss, 2012). While known as the biological carbon pump, the physical
- 67 processes involved in removing organic carbon from the surface cannot be siloed. In the North
- Atlantic, large spring phytoplankton blooms are thought to be the primary driver of high carbon export (Martin et al., 2011), however physical processes like deep convection have the potential
- export (Martin et al., 2011), however physical processes like deep convection have the potential
 to counterbalance this export by entraining previously exported carbon (Kortzinger et al., 2008;
- 70 to counterbalance this export by entraining previously exported carbon (Kortzinger et al., 2008,
 71 Palevsky & Nicholson, 2018; Quay et al., 2012, 2020). These dynamics are especially strong in
- ratevský & Nicholson, 2018, Quay et al., 2012, 2020). These dynamics are especially strong in
 the subpolar North Atlantic, which contains the deepest winter convection on Earth (de Jong et
- al., 2018; de Jong & de Steur, 2016; Holte et al., 2017) and high primary productivity (Boss &
- 74 Behrenfeld, 2010; Henson et al., 2006, 2009).
- 75 To investigate the intertwined roles of biology and physics on carbon export, we use carbonate
- 76 chemistry system measurements of dissolved inorganic carbon (DIC) and total alkalinity (TA)
- 77 which provide mechanistically agnostic tracers of the removal and addition of carbon from the
- surface ocean. Net community production (NCP) is a measure of the net biologically produced
- 79 organic carbon in the upper ocean. It can be determined using inorganic carbon measurements
- 80 and when integrated throughout the year represents the biological pump on an annual basis
- 81 (ANCP, Emerson, 2014). Marine carbon cycling has been studied around the globe by making
- 82 inorganic carbon system measurements at regular intervals throughout the year since the early
- 83 1980's (Bates et al., 2014). However, these historic discrete shipboard measurements have not
- 84 provided adequate temporal resolution to constrain the full seasonal and interannual variability
- 85 influencing ANCP using carbonate chemistry (Bates et al., 2014; Racapé et al., 2013).

- 86 Technological advances since the turn of the century have increased observational capacity,
- 87 providing high frequency time series measurements (more than once a day) for a number of
- 88 chemical and physical parameters on both stationary mooring arrays and mobile floats and
- 89 gliders. These have enabled the construction of DIC and TA mass balance budgets in the
- 90 Northeast Atlantic, North Pacific, and Southern Ocean, and the subsequent disentanglement of
- 91 biological and physical forcing on carbon cycling and quantification of annual net community
- 92 production (Fassbender et al., 2016, 2017; Haskell et al., 2020; Huang et al., 2022; Knor et al.,
- 93 2023; Kortzinger et al., 2008; Sauvé et al., 2023; Yang et al., 2021).
- 94 The Irminger Sea is an area of particular interest within the North Atlantic and is the location of
- 95 the Global Irminger Sea Array (operated by the NSF's Ocean Observatories Initiative, OOI). The
- 96 location was selected in order to provide sustained atmospheric, physical, and biogeochemical
- 97 observations at a high latitude site, with a focus on the critical influences that affect the global
- 98 ocean-atmosphere system (Fig 1., Ocean Observatories Initiative Science Prospectus, 2007;
- 99 Smith et al., 2018). Fast moving currents bring water southward along the eastern coast of
- 100 Greenland, and warm waters move northward along the eastern boundary as part of the North
- 101 Atlantic current, forming the central Irminger Gyre where the array is located (de Jong et al.,
- 102 2018). A 19-year time series (2002-2020) using OOI and nearby mooring data finds extreme
- 103 variability in the depth of winter convection (285-1480 m, de Jong et al., 2024). Prior work in the
- 104 region has used oxygen production as a tracer of photosynthesis and respiration (Palevsky &
- 105 Nicholson, 2018) and the carbonate system seasonal cycle has been generally characterized
- 106 (Bates et al., 2014; Racapé et al., 2013). As with many sites, there has not been sufficient data in
- 107 the Irminger Sea to resolve full year-round net community production until now. Understanding
- 108 the controls on the biological pump in subregions like the Irminger Sea contributes to our overall
- 109 understanding of the North Atlantic's current carbon export and the potential changes it may
- 110 undergo as a result of climate change, including changes in primary productivity, surface and
- 111 deep ocean respiration, and physical transport. Here, we use seven years of high temporal
- 112 frequency mooring data from the OOI Irminger Sea Array to provide the longest near-continuous
- 113 daily carbonate chemistry dataset to date in this region. We leverage these data to determine the
- biological and physical forcing on carbon cycling and quantify net community production over
- seasonal, annual, and interannual time scales in the subpolar North Atlantic.





117



- 119 Irminger Array (red star). The colored shading is the mean sea surface currents and the black
- 120 contours are the mean sea surface height in millimeters for 2015-2022. Data are from E.U.
- 121 Copernicus Marine Service Information, <u>https://doi.org/10.48670/moi-00148</u>.

122 **2 Data**

- 123 2.1 Ocean Observatories Initiative Global Irminger Sea Array
- 124 The Ocean Observatories Initiative (OOI) is a 25-year, NSF funded program that began
- 125 collecting data in 2014, after nearly a decade of proposals and planning (Cowles et al., 2010;
- 126 Isern & Clark, 2003; Smith et al., 2018). Our primary data source is the OOI Global Irminger
- 127 Sea Array, which is comprised of 4 moorings, triangularly arranged and spaced approximately
- 128 20 km apart, and profiling and open ocean gliders (Fig. 2). Repeat hydrography at the mooring
- 129 locations is also available from annual turn-around cruises. Our analysis focuses on the pH and
- 130 pCO_2 sensors, all of which are located in the upper 130m of the water column, as well as their
- 131 co-located CTDs.



133 Figure 2. Schematic showing locations of the autonomous biogeochemical sensors and co-

located CTDs on the OOI Irminger Array used in this analysis. Contour lines on the map showlocal bathymetry (m).

- 136 All carbonate system sensors, except at the surface, are Submersible Autonomous Moored
- 137 Instruments (SAMI) made by Sunburst Sensors; both the pH and pCO₂ versions utilize
- 138 spectrophotometry and a pH sensitive indicator dye (Álvarez et al., 2020; Lai et al., 2018). The
- 139 surface pCO_2 sensor is a Pro-Oceanus CO_2 -Pro, which operates above and below the water,
- 140 making air and seawater measurements using infrared detection (Jiang et al., 2014). The pH and
- 141 pCO_2 sensors below the surface make a measurement every 2 hours and the surface pCO_2 sensor
- 142 makes a measurement every hour, though occasionally measurements are further apart due to
- battery limitations. Shallow sensors (pH sensors at 20m & 30m; *p*CO₂ sensors at 0m, 12m, &
- 144 40m) are in the mixed layer for the majority of the annual cycle, while deeper sensors (pH 100m,
- 145 pCO_2 80m & 130m) are only in the mixed layer in the winter. The 20m and 100m pH sensors
- 146 have very little usable data and have been excluded from this analysis.

147 pH and pCO_2 data were quality controlled using gross range and spike tests based on Quality

- 148Assurance / Quality Control of Real Time Oceanographic Data (QARTOD) recommendations,
- 149 followed by a moving median filter (Palevsky et al., 2023; U.S. Integrated Ocean Observing
- 150 System, 2020; Table S1). We also remove data deemed suspect based on OOI operational
- annotations (for further detail, see the OOI Biogeochemical Sensor Data Best Practices and User
- 152 Guide; Palevsky et al., 2023). The fixed asset data within the mixed layer for pH, pCO_2 ,
- temperature, salinity, and pressure are at times sparse, with different depths and locations
- available across the time series (Fig. S1 and S2). This sparsity is primarily due to infrastructure
- 155 and instrument failures, which tend to occur during the late winter when seas are extremely 156 rough and power becomes limited due to low sun angle. As a result, we have opted to combine
- 157 all carbonate system sensor data within the mixed layer in order to create the most complete time
- series possible. Previous work has shown that the horizontal spatial variability is low enough to
- 159 analyze sensors across the array as one data stream (de Jong et al., 2018; Palevsky & Nicholson,
- 160 2018).

161 Beyond the upper ocean carbonate system chemistry and CTD sensors, we use calibrated oxygen

- 162 data from the wire-following profiler on the Apex profiler mooring (200-2000m, one cycle every
- 163 20 hours) and gliders (0-200m and 0-1000m, varying temporal coverage). These are corrected
- 164 using repeated stable deep oxygen measurements on the 3.1θ isotherm (~1800-2000m), based on
- 165 the approach previous applied at the Irminger Sea Array by Palevsky & Nicholson (2018). These
- 166 oxygen data are used for carbonate system predictions below the mixed layer using the
- 167 CONTENT model (Bittig et al., 2018). We also use chlorophyll-*a* data from Sea-Bird/WETLabs
- 168 fluorometers deployed on the OOI moorings at 1m, 12m, and 30m during periods they are within
- 169 the mixed layer. These data are presented for qualitative rather than quantitative interpretation, as
- 170 end-user quality control and calibration of the fluorometer data are beyond the scope of this
- 171 work.
- 172 2.2 Cruise Data
- 173 During the turn-around cruise each summer, discrete dissolved inorganic carbon (DIC), pH, and
- total alkalinity (TA) samples are collected at depths corresponding to the deployment depths of
- moored pH and pCO_2 sensors (Palevsky et al., 2023). In addition to the discrete samples
- 176 routinely collected and analyzed by the OOI program, we collected and analyzed additional DIC
- and TA samples from the 2018 and 2019 turn-around cruises (Palevsky et al. 2023b). Quality
- 178 control of the discrete DIC, pH, and TA samples provided by the OOI program identified
- 179 inconsistencies among these three carbonate system chemistry variables that indicate data quality
- 180 issues with a subset of the TA samples. We therefore rely primarily on directly-measured
- 181 discrete DIC data rather than on other measured or calculated carbonate chemistry variables in
- 182 calibrating and validating the sensor-based time series. Our analysis also uses calibrated salinity,
- temperature, and oxygen depth profiles from sensors on the CTD rosette (Fogaren et al., 2023;
- 184 McRaven, 2022a-d).

185 **3 Methods**

186 3.1 Carbonate System Time Series

187 We synthesize the fixed mooring assets to construct a near-continuous mixed layer carbonate 188 system chemistry time series over the seven year period from summer 2015 through summer 189 2022. The mixed layer depth fluctuates significantly throughout the year, which results in the carbonate system sensors below the nominal 12m sensor alternating being in the mixed layer and 190 191 below it, depending on their deployment depths and the current depth of mixing. For our mixed 192 layer time series, we use only sensors deployed at nominally 40m and shallower; the process 193 used to determine when sensors are in the mixed layer is described in Section 2 of the 194 Supplementary Information (Fig. S3).

195 3.1.1 Total Alkalinity

196 Due to the close co-varying relationship between total alkalinity (TA) and salinity, regressions

between the two have long been used to estimate total alkalinity for carbonate system

198 calculations (Millero et al., 1998), with other variables having been incorporated in more recent

work. We use the Locally Interpolated Alkalinity Regression (LIAR) model to predict TA from
 mixed layer sensor data, using temperature, salinity, and location as predictors (Carter et al.,

201 2018).

202 3.1.2 Dissolved Inorganic Carbon

203 For each pCO_2 and pH sensor, DIC was calculated from daily averages of the sensor 204 measurements and estimated total alkalinity (described above) using CO2SYS, with temperature, 205 pressure, and salinity from co-located CTDs (Lewis & Wallace, 1998; Orr et al., 2018; van 206 Heuven et al. 2011). Silicate and phosphate are also calculation inputs as they contribute to the 207 acid-base system, however DIC outputs are very insensitive to these inputs (< 1 μ mol kg⁻¹ 208 difference calculated using the minimum and maximum values ever recorded in the region). As a 209 result, we use mean nutrient values from regional GLODAPv2_2021 data (Lauvset et al., 2021; 210 Olsen et al., 2016). We used the dissociation constants of Lueker et al. (2000), the KSO₄ constant 211 of Dickson (1990), and the total boron constant of Uppström (1974). Days with fewer than 2 212 measurements of pCO_2 or pH values are excluded. There are several short gaps in the time series 213 where no carbonate system data is available. In the later part of the time series (summer 2018 -214 summer 2022) we fill these gaps using DIC predicted using CONTENT from the calibrated 1m 215 and 12m moored oxygen sensors, with the longest gap being about 2 months in summer 2019

and all others being less than two weeks (Fig. S4).

217

219 3.1.3 Calibrating the DIC time series

220 Our use of a multitude of carbonate system chemistry sensors requires confirmation that these 221 sensors are accurately measuring our parameters of interest. Once calibrated, the DIC time series 222 calculated from individual sensors in the mixed layer match well with validation data from 223 deeper moored assets as well as discrete cruise samples. The SAMI pCO_2 sensors show 224 significant offsets from one another and from the Pro-Oceanus pCO_2 sensor during some 225 deployments, but follow the same seasonal, weekly, and daily patterns when in the mixed layer 226 (Fig. S5a). The SAMI pH sensors also show offsets, though much less substantial. The offsets 227 between the SAMI sensors are not consistent annually, and there is no offset seen in the 228 temperature data of the co-located CTDs, which indicates a known sensor calibration issue that 229 require correction rather than a true signal (DeGrandpre et al., 2004; Kortzinger et al., 2008). The 230 shallower pCO_2 and pH sensors (12-40m) used in the mixed layer time series are generally 231 within a steep thermocline during turn-around cruises in summer, precluding aligning the 232 moored sensor data with the discrete samples collected from co-located CTD casts as a

233 calibration approach itself.

234 Unlike the SAMI sensors, when the Pro-Oceanus surface pCO_2 sensor measures for the entire

235 deployment, the newly deployed sensor matches the previously deployed sensor while both are

236 operational, which instills confidence in the accuracy of the surface Pro-Oceanus (summer 2020

and 2021, Fig. S1). The Pro-Oceanus, however, fails after only weeks to months in five out of

the seven deployments used in this analysis. In order to create a complete mixed layer time

series, we leverage the strengths of both carbonate chemistry sensor systems on the array,
namely the longevity of the SAMI sensors and the accuracy of the Pro-Oceanus. We correct for

offsets in the DIC time series calculated from the shallow (12-40m) SAMI pH and pCO_2 sensors

by aligning them with the available DIC time series calculated from the Pro-Oceanus, after

which we average all DIC data in the mixed layer (Supplementary Information Section 4, Fig.

244 S5).

245 While we do not use the 80m and $130m pCO_2$ sensor data as part of our mixed layer time series,

they provide a useful check on our calibration process. The final mixed layer DIC time series

shows good agreement with these deeper sensor DIC data, calibrated using predicted DIC from

turn-around cruise CTD dissolved oxygen measurements, once they reenter the mixed layer (Fig.

249 S5c, Bittig et al., 2018; Palevsky et al., 2023b). This agreement with the independently calibrated

250 deep sensors, as well as with the available discrete cruise data points, further instills confidence

251 in the choice to align the 12-40m DIC time series with the DIC time series from the Pro-Oceanus

252 (Fig. S5c). A detailed explanation of the calibration processes can be found in Section 4 of the

253 Supplementary Information.

254

256 3.1.4 *p*CO₂

- 257 We fill in the gaps in the surface pCO_2 record directly measured by the Pro-Oceanus using pCO_2
- calculated from the mixed layer DIC time series, mixed layer estimated total alkalinity, salinity
- at 30m, and the fifth generation European Centre for Medium-Range Weather Forecasts
- atmospheric reanalysis (ERA5) sea surface temperature (Fig. S8, Hersbach et al., 2020). Salinity
- 261 at 30m is used because there are frequent gaps in the surface pCO_2 record due to surface mooring
- 262 platform failures, which also affected the co-located CTDs.
- 263 3.2 Mixed Layer Budget
- 264 Seasonal changes in the observed mixed layer DIC concentration are driven by physical
- transport, gas exchange, evaporation and precipitation, and biological processes, namely net
- 266 community production and calcium carbonate production and dissolution (eq.1, Fassbender et
- al., 2016, 2017; Haskell et al., 2020; Kortzinger et al., 2008; Palevsky & Quay, 2017; Yang et
 al., 2021). Changes in total alkalinity are driven by the same processes as DIC, with the
- exception of gas exchange (eq. 2). The time rate of change terms for each tracer (left hand side of
- eq. 1 and 2, respectively) are determined from the DIC and TA time series data. Observational
- 271 data allows us to calculate the non-biological drivers ($dDIC/dt_{Gas Exchange}$, $dDIC/dt_{EP}$, and
- dDIC/dt_{Entrainment}; dTA/dt_{EP}, and dTA/dt_{Entrainment}) and subtract from the weekly overall change
- 273 (dDIC/dt; dTA/dt), leaving the biological drivers (dDIC/dt_{Biology}; dTA/dt_{Biology}), as the remainder.
- The sections below describe how each of the right hand side terms in these equations are
- calculated. All right-hand side terms in both budgets are calculated at weekly resolution. We
- smooth the observed carbonate system time series used in the budget with a three week running mean to remove high-frequency variability.

278
$$\frac{dDIC}{dt} = \frac{dDIC}{dt}_{|Gas \ Exchange} + \frac{dDIC}{dt}_{|EP} + \frac{dDIC}{dt}_{|Entrainment} + \frac{dDIC}{dt}_{|Biology}$$
(1)

279
$$\frac{dTA}{dt} = \frac{dTA}{dt}_{|EP} + \frac{d(TA}{dt}_{|Entrainment} + \frac{dTA}{dt}_{|Biology}$$
(2)

280 3.2.1 Gas Exchange

The rate of DIC change due to gas exchange is calculated from the measured partial pressure of carbon dioxide (pCO_2) in the atmosphere and surface waters, wind speed, temperature, and salinity, with positive values indicating a flux from the atmosphere into the ocean (eq. 3).

284
$$\frac{dDIC}{dt}_{|Gas Exchange} = \mathbf{k} * \mathbf{K}_{H} * (\mathbf{pCO}_{2_{Air}} - \mathbf{pCO}_{2_{Seawater}}) * \boldsymbol{\rho}$$
(3)

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- 285 The piston velocity (k) is calculated using the Ho et al. (2006) wind speed-dependent gas transfer
- 286 parameterization, implemented in the MATLAB gas_toolbox (Manning and Nicholson, 2022)
- and the Schmidt constant (Wanninkhof, 1992). Of the OOI moored assets, the surface buoy faced
- the most challenges with continuous data collection, limiting the ability to use directly-measured
- 289 meteorological data. Therefore, ERA5 products from the nearest grid cell (60°N, 39.5°W) are
- used for hourly sea surface temperature and 10m wind speeds (calculated from v- and u-winds at
- 10m, Hersbach et al., 2020). The ERA5 winds match well with the OOI 10m measured wind
- 292 speeds, when available (Fig. S9).
- 293 The solubility of CO_2 is calculated using the temperature and salinity dependent constant (K_H)
- from Weiss (1974). The mixed layer seawater pCO_2 data is calculated as described in section
- 295 3.1.4. The air pCO_2 data is from NOAA's Global CarbonTracker gridded daily average product
- at 59°N, 40.5°W using CO₂ mole fraction, humidity, and barometric pressure (CT_2022 and CT-
- 297 NRT.v2023-4, Jacobson et al., 2023, comparison with Pro-Oceanus air *p*CO₂, Fig. S10).
- 298 Multiplying by the density (ρ) leaves us with the amount of carbon exchanged in units of mmol
- 299 $m^{-2} d^{-1}$.
- 300 3.2.2 Physical Transport

301 The fixed nature of moored sensors necessitates a Eurlerian approach in order to account for the

- 302 influence of horizontal and vertical transport on mixed layer DIC. The primary physical
- 303 influence is entrainment, whereby the mixed layer increases in depth and adds water from below
- 304 into the mixed layer. When the mixed layer shoals (detrainment), the mixed layer DIC
- 305 concentration is not impacted. Given that this study site is in the center of the Irminger Gyre
- 306 where there are low horizontal velocities, we exclude horizontal transport from our budget (Fig.
- 3071). We also exclude estimating the budget contributions of vertical diffusion and vertical
- 308 velocity. Although these have been shown to be significant in mixed layer mass balance budgets
- 309 in other regions (such at North Pacific and North Pacific subtropical gyre, Fassbender et al.
- 310 2016; Knor et al. 2023), measured values for these terms have been shown to be low in the
- 311 Irminger Sea and exceptionally deep winter convection at this site means that entrainment
- dominates over these second-order processes (Fratantoni, 2001; Painter et al., 2014; Våge et al.,
- 313 2008).

314 In order to calculate the rate of physical entrainment, we use weekly mixed layer depths. There 315 has been extensive discussion within the literature regarding how to define the mixed layer depth 316 with respect to timescales of mixing and biological processes (Carranza et al., 2018; Carvalho et 317 al., 2017; Lacour et al., 2019). We use a combination of methods including temperature 318 thresholds and bio-optical methods to determine the mixed layer depth depending on the time of 319 year and availability of both OOI and external data (Table S2), a full explanation of which can be 320 found in the Supplementary Information, Section 6. We determine the effects of entrainment on 321 mixed layer DIC, TA, and salinity using a one-dimensional model that accounts for the influence 322 of mixing between the prior mixed layer and newly-entrained waters, calculated at weekly time 323 steps. This model uses the mixed layer time series to calculate physical entrainment rates and 324 accounts for the salinity, DIC, and TA of waters being entrained into the mixed layer using DIC 325 and TA estimated from OOI glider and wire-following profiler oxygen, temperature, and salinity 326 using the CONTENT model (Bittig et al., 2018). The entrainment model tracks closely with

observed DIC concentrations in the fall, showing that the increase in mixed layer DIC during this
 period of time is primarily the result of the entrainment of high DIC waters (Fig. S12).

329 3.2.3 Evaporation and Precipitation

330 To account for dilution and concentration effects on DIC and TA due to evaporation and

331 precipitation, we find the difference between the observed change in salinity over time and the

entrainment-modeled change in salinity over time (Fassbender et al., 2016; Haskell et al., 2020).

We attribute the difference between the observations and the modeled change to evaporation and precipitation, as any change in salinity not due to entrainment is the result of these surface

processes in our model, again assuming minimal horizontal advection. We multiply the

difference in the two by the ratio of DIC (and TA) to absolute salinity on the first day of each

deployment, working under the assumption that the ratio that salinity changes due to evaporation

and precipitation is the same for DIC and TA (eq. 4). The same process is followed for TA.

339
$$\frac{d(DIC,TA)}{dt}_{|EP} = \left(\frac{dSal}{dt} - \frac{dSal}{dt}_{Entrainment}\right) * \frac{(DIC,TA)}{Sal}_{t=1}$$
(4)

340 3.2.4 Biological Processes

341 The biological drivers are calculated as the residual terms of equations 1 and 2. These drivers are

342 net community production (NCP) via photosynthesis and respiration and calcium carbonate

343 (CaCO₃) formation and dissolution (eq. 5).

$$344 \qquad \frac{d(DIC,TA)}{dt}_{|Biology} = \frac{d(DIC,TA)}{dt}_{|NCP} + \frac{d(DIC,TA)}{dt}_{|CaCO_3}$$
(5)

- 345 In order to separate the soft tissue processes (photosynthesis and respiration, which influence
- NCP) from calcium carbonate production and dissolution, we leverage the known production
- ratio of CO₂ and H⁺ (117 to -17) from respiration using 1 mole of phosphate (HPO₄²⁻) (Anderson
- & Sarmiento, 1994; Fassbender et al., 2016). This formation and precipitation of CaCO₃
- influences TA and DIC in a 2:1 ratio. This allows us to calculate the influence of NCP on the
- 350 mixed layer DIC budget (eq. 6). We also calculate weekly and annual NCP within the
- 351 seasonally-varying mixed layer by integrating to the weekly mixed layer depth.

352
$$\frac{dDIC}{dt}_{|NCP} = \frac{\left(\frac{dTA}{dt}_{|Bio} - 2*\frac{dDIC}{dt}_{|Bio}\right)}{-2*\frac{-17}{117}}$$
 (6)

353 3.3 Uncertainty

Here we present the calculated uncertainties of the calibrated DIC, TA, and pCO_2 time series, as

- 355 well as uncertainties of terms in the DIC budget (Table 1). The uncertainties of the measured
- 356 parameters propagated through to calculate these values can be found in the Supplementary
- 357 Information (Table S3). Temperature and salinity measurement errors are slight but do factor
- into all of the calculated parameter uncertainties.
- 359 The uncertainty of the mooring DIC time series is estimated using the CO2SYS error
- 360 propagation, with temperature, salinity, pressure, pH, pCO_2 , and estimated TA uncertainties as
- 361 inputs (Orr et al., 2018). Uncertainty for estimated TA is generated from the LIAR model (Carter
- 362 et al., 2018). A limitation of deriving total alkalinity from salinity is that mixed layer TA can
- 363 change independent of salinity when biological formation of calcium carbonate occurs. Remote
- 364 sensing shows calcification rates exceeding 1 mmol C m^{-2} and very high interannual variability
- in calcification rates in the Irminger Sea, which could lead to our DIC estimates being slightly
- high in late summer (Hopkins et al., 2015). Despite this, the close agreement between the surface
- 367 sensor pCO_2 and surface pCO_2 calculated from DIC and TA suggest that the impact of this
- 368 uncertainty in TA is small (Fig. S8).

There is uncertainty in each of the terms of the mass balance budget (eq. 1 & 2, Table 1). The 95% confidence bounds of entrainment are calculated by taking the minimum and maximum values from the entrainment model runs with a combination of systematically over- and under-estimated mixed layer depths and the lower and upper uncertainties of the DIC concentration below the mixed layer. The evaporation-precipitation uncertainty is estimated using a Monte Carlo simulation iterated 5000 times with the salinity and DIC entrainment uncertainty and the uncertainty of the DIC concentration on the first week of each deployment. The gas exchange uncertainty is also calculated using a Monte Carlo simulation to account for the uncertainties in temperature, salinity, pCO_2 of air and seawater, and a 20% assigned uncertainty in the gas transfer coefficient to account for uncertainty in the wind speed data as well as in the parameterized relationship between wind speed and gas transfer (Ho et al., 2006; Wanninkhof, 2014; Yang et al., 2021). Calculating the biological processes as the remainder from the mass balance budget means that the biological term contains the accumulation of the uncertainties from all the other budget terms. We use a wrap-around Monte Carlo containing all the previously discussed uncertainties (Table 1) in which we subtract the physical transport, EP, and gas exchange terms from the overall change in DIC in order to determine the uncertainty in the biological processes.

399 Table 1.

400 Uncertainties of analyzed parameters

Time series	Uncertainty	Primary sources of error
Calibrated DIC $(\Delta DIC_{Observed})$	11.2-11.6 mmol m ⁻³	Measurement of pH and pCO_2 , calibration of DIC time series
TA ($\Delta TA_{Observed}$)	9.7-10.2 mmol m ⁻³	Estimate from LIAR model, measurement of salinity
pCO ₂	2 µatm	Measurement of surface pCO_2 , calculation from DIC and TA
$\Delta DIC_{Entrainment}$	8.7-10.3 mmol m ⁻³	DIC concentration below the mixed layer, mixed layer depth
ΔDIC _{EP}	1.1-2.0 mmol m ⁻³	entrainment salinity model from MLD and glider/WFP salinity measurements, ratio of DIC/TA to salinity on first day of deployment
ΔDIC_{GE}	0.02-0.05 mmol m ⁻³	air and sea pCO_2 , wind speed, gas transfer coefficient
ΔDIC _{NCP}	14.7-16.0 mmol m ⁻³	Combined uncertainty of all other budget terms, stoichiometry of photosynthesis-respiration and calcium carbonate formation-dissolution
ΔDIC _{CaCO3}	28.5-30.5 mmol m ⁻³	Combined uncertainty of all other budget terms, stoichiometry of photosynthesis-respiration and calcium carbonate formation-dissolution

401

Note. Values shown are the range of yearly means over all seven years in the time-series.

402 **4 Results and Discussion**

- 403 4.1 Mixed layer time series
- 404 Here we present mixed layer carbonate system variables (DIC, TA, and pCO_2) as well as their
- 405 potential drivers (mixed layer depth, temperature, and chlorophyll-*a*) in the central Irminger Sea
- 406 (Fig. 3). The carbonate system variables follow a similar annual cycle of highs and lows, with
- 407 the minimums occurring in late summer at the end of the productive season, then
- 408 climbing throughout the fall to a maximum in winter, after which they are drawn down again in
- 409 the spring (Fig. 3).
- 410





- 414 In the Irminger Sea, sea surface temperatures vary significantly, from around 3°C in the winter
- 415 up to 12° C in the summer. The partial pressure of CO₂ (*p*CO₂) is significantly affected by
- 416 temperature (Weiss, 1974); if there were no biological processes reducing the pCO_2 , we would
- 417 expect to see the highest pCO_2 in the summer and the lowest pCO_2 in the winter, as solubility
- 418 declines as temperature increases (Takahashi et al., 2002). Instead, as has been well documented
- 419 in prior literature, the greatest pCO_2 are recorded in the winter and lowest are found in the
- 420 summer due to biological drawdown, indicating that biophysical effects, rather than temperature,
- 421 are the primary drivers of pCO_2 at our site (Bates et al., 2014; Landschützer et al., 2018;
- 422 Takahashi et al., 2002).
- 423 The influence of vertical mixing and primary productivity can be clearly seen on the other,
- 424 temperature-insensitive, carbonate system parameters (DIC and TA). In the spring and summer,
- 425 the mixed layer is strongly stratified and high chlorophyll concentrations are recorded. At the
- 426 same time, DIC concentrations reach their minimum in the annual cycle, ranging from 2074±8 to
- 427 $2110\pm8 \,\mu\text{mol kg}^{-1}$ during our period of observation (Fig. 4). It is important to note that while
- 428 chlorophyll concentration does indicate primary productivity, the amount of inorganic carbon
- 429 being utilized is not directly reflected, as widely varying chlorophyll to carbon ratios occur at
- 430 different global locations, depths in the water column, and times of year (Sathyendranath et al.,
- 431 2009). Due to infrastructure failures, the sensors are not always successful in capturing the entire
- 432 spring bloom; however, in situ chlorophyll measured by fluorometry and satellite chlorophyll
- 433 data confirm annual spring and fall blooms at the Irminger site (Painter et al., 2014).

In the fall, convection begins and the mixed layer starts deepening. The Irminger Sea's uniquely 434 435 deep mixed layers are not observed until later in the season, with mixed layer depths rarely 436 exceeding 100m before mid November. Most of the interannual variability in mixed layer depth 437 occurs in the winter, both in the timing of deepening and the maximum depth reached. Some 438 years, such as 2015-2016, experience early and rapid deepening, but the deepest sustained winter 439 mixing is usually reached in mid to late March, ranging from ~400 to ~1300m. The patterns 440 observed here match previous analysis of MLDs in this region (de Jong et al. 2024). Shoaling in the spring begins gradually and then intensifies, going from near maximum depths to less than 441 442 100m over the span of a few weeks from early April to mid-May (Sterl and de Jong, 2022). 443 During this time, we observe repeated shoaling and deepening, a process previously observed in 444 the North Atlantic (Lacour et al., 2019). After the final shoaling, increased chlorophyll 445 concentrations are observed again. It should be noted that the seven year OOI time series 446 captures a period of time in which there is particularly strong winter convection (3 winters 447 deeper than 1000m), even for the Irminger region. Before the OOI time series, winter mixed 448 layer depths for only one year between 2002 and 2013 (2011-2012) were close to 1000m (de 449 Jong et al., 2024).

- 450 The mixed layer DIC signal generally increases and decreases in concert with the seasonal
- 451 changes in mixed layer depth. The increase in mixed layer DIC coincides with mixed layer
- deepening (Fig. 3). It is rapid in mid-September through mid-November and then continues to
- 453 rise with a less significant slope between mid-February to late March, when it reaches the
- 454 maximum annual concentration. The DIC concentration begins to decrease moderately in the late
- 455 winter and then decreases more rapidly in late April to mid-May, coinciding with high
- 456 chlorophyll concentrations.





462 series. Gaps less than 2 weeks have been filled via linear interpolation.

463 The amount of fall-winter increase and spring-summer decrease of mixed layer DIC varies from

464 year to year. While there is a broad interannual range in the amplitude of the DIC seasonal cycle

465 (mean 68 ± 11 , range 54-81 µmol kg⁻¹), the range of the winter maximum weekly DIC

466 concentration is only 14 μ mol kg⁻¹ (Fig. 4). This is almost within the uncertainty of the mixed

467 layer DIC time series (~11 μ mol kg⁻¹), making the annual maximum DIC effectively

468 indistinguishable from year to year. The summer minimum is far more variable, reflecting more

469 variability in the impact of biological DIC drawdown than winter convection on the mixed layer

470 DIC annual cycle. The DIC seasonal cycle amplitude is similar to previous measurements in the

- 471 Irminger Sea (~60 μ mol kg⁻¹, Bates et al., 2014) and other high latitude regions including the
- 472 North Pacific (~56 \pm 7 µmol kg⁻¹ at Ocean Station Papa, 73 \pm 2 µmol kg⁻¹ in the Kuroshio
- 473 Extension, Fassbender et al., 2016, 2017) and Western Antarctic Peninsula (~55 μmol kg⁻¹, Yang
- 474 et al., 2021), however the interannual variability observed in the Irminger Sea is higher.

476 4.2 Mixed Layer Carbon Mass Balance

- 477 To investigate the specific drivers of the annual carbonate system chemistry cycle and its
- 478 interannual variability, we use a mass balance approach. Comparison among each of the terms
- 479 influencing the DIC seasonal cycle (eq. 1) shows that entrainment of deep waters and biological
- 480 processes have the greatest impact on the DIC seasonal cycle, with gas exchange and
- 481 evaporation-precipitation playing relatively minor roles (Fig. 5).
- 482

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487

488 Figure 5. Influences of each term in the mixed layer DIC mass balance budget (eq. 1) on a) the 489 observed change in DIC concentration since Aug. 15 over each of the seven years in the time 490 series. Changes in mixed layer DIC are driven by: b) the change in DIC concentration due to 491 entrainment, c) the change in DIC concentration due to biological processes, d) the change in 492 DIC concentration due to gas exchange, and e) the change in DIC concentration due to 493 evaporation and precipitation, each presented as the cumulative change since August 15 in each year of the time series. Each of these terms is calculated within the seasonally-varying mixed 494 495 layer depth at weekly resolution (f). Note that the y-axes are scaled differently on each plot.

- 496 While gas exchange has very little impact on the overall mixed layer DIC concentration, the 497 average total addition of DIC to the mixed layer due to CO₂ influx from the atmosphere is 2.1 $mol \pm 1.1 mol m^{-2} yr^{-1}$ over our seven year period. A recent *p*CO₂ climatological product reports 498 a mean of 3.0 ± 0.7 mol m⁻² yr⁻¹ during our study period (range 2.1-3.8 mol m⁻² yr⁻¹, Landschützer 499 500 et al. 2020). This matches our observations within the uncertainty, and the somewhat higher 501 values can likely be attributed to our differing choice of gas transfer parameterization 502 (Atamanchuk et al., 2020). From our observational data, the years with the lowest annual carbon 503 uptake via gas exchange are also the years when the maximum mixed layer depth exceeds 1000m (2015-2016 and 2017-2018), potentially indicating that the continued entrainment of high 504 505 DIC waters suppresses winter uptake driven by cooling waters. Gas exchange occurs at the 506 surface and therefore has the highest potential to impact DIC concentration when the mixed layer 507 is shallowest (has the least volume). The most significant stratification occurs during the summer 508 when the difference between air and seawater pCO_2 is greatest. These conditions would support 509 strong influx; however the winds tend to be slow this time of year and do not drive vigorous gas 510 exchange. In the winter when extremely high winds occur, the volume of the mixed layer has 511 expanded by almost two orders of magnitude, so even the fastest gas exchange has very little 512 impact on overall mixed layer DIC concentration, making gas exchange (dDIC/dt_{GE}) the least
- 512 impact on overall mixed layer DIC concentration, making gas exchange (dDIC/dt_{GE}) the le
- 513 impactful driver of changes in mixed layer DIC (Fig. 5d).

514 The impact of evaporation and precipitation on DIC concentration ($dDIC/dt_{FP}$) is also low 515 throughout the year, and, as with gas exchange, has the greatest impact when the water column is 516 stratified due to its influence occurring only at the air-sea interface. The impact of evaporation 517 and precipitation varies from year to year but, on average, mild dilution occurs in the summer months, reducing DIC concentration by $6.4 \pm 4.3 \text{ mmol m}^{-3} \text{ yr}^{-1}$ (Fig. 5e). The dominant driver of 518 DIC increase in the mixed layer is entrainment (dDIC/dt_{Entrainment}), which increases mixed layer 519 520 DIC by $64\pm17 \text{ mmol m}^{-3} \text{ yr}^{-1}$. The DIC concentration rises concurrently with an increase in 521 mixed layer depth as high DIC waters from below mix with the DIC-depleted surface waters. 522 The concentration rises rapidly even though the mixed layer does not deepen extremely quickly 523 because of the outsized role of the addition of water into the shallow end-of-summer mixed layer 524 and the very low summer DIC concentration. A mixed layer of 20m with DIC of 2080 mmol m⁻³ that entrains 80m of 2170 mmol m⁻³ DIC waters then has a DIC concentration of 2152 mmol m⁻³, 525 an increase of 72 mmol m⁻³ and roughly the amplitude of the seasonal cycle. Alternatively, a 526 100m mixed layer with DIC of 2152 mmol m⁻³ that entrains 200m of 2170 mmol m⁻³ DIC waters 527 results in a DIC concentration of 2164 mmol m⁻³, only increasing the overall concentration by 8 528 mmol m⁻³. The total amount of carbon added via entrainment varies based on each year's 529 maximum mixed layer depth, but brings the surface concentration close to the same value each 530 winter (~2220 mmol m^{-3}). While we have primarily considered the extremely deep winter 531 532 convection for its role in returning carbon to the surface ocean in the winter, the subsequent 533 springtime shoaling of the mixed layer detrains water that contains both inorganic and organic 534 carbon in a process known as the seasonal mixed layer pump (Dall'Olmo et al., 2016). The intraseasonal and seasonal mixed layer pump has been shown to significantly contribute to 535 536 carbon export in the subpolar North Atlantic, a process which is likely occurring at our study site

537 (Lacour et al., 2019).

538 Biological processes (dDIC/dt_{Biology}) lead to a net drawdown of DIC on an annual basis (Fig. 5c), 539 with photosynthesis and calcium carbonate formation outpacing respiration and calcium 540 carbonate dissolution. In the fall, the influence of biology is near zero, with slight heterotrophy in 541 some years and autotrophy in others; however, the uncertainty crosses zero most years, 542 obscuring any definitive fall trend. Each winter shows the same pattern: from February to May 543 there is a slow but persistent decrease in DIC concentration due to biological processes. Once the 544 mixed layer shoals, there is much more rapid drawdown, which comprises the bulk of the change 545 in concentration due to biology over the annual cycle. While we cannot quantitatively relate the 546 measured chlorophyll to DIC drawdown, the chlorophyll data clearly supports the rapid

547 reduction due to primary productivity in the late spring (Fig. 3).

548

549

551 4.3 Annual Net Community Production

552 The annual net community production (ANCP) within the mixed layer is the upper bound on the amount of carbon removed from the surface ocean by the biological pump each year (NCP = -553 554 ΔDIC_{NCP}). The choice of depth of integration for calculating ANCP varies depending on the 555 method of export research. This can lead to discrepancies when intercomparing ANCP rates, 556 particularly in high latitude regions with deep winter convection, where a significant fraction of 557 the carbon removed from the mixed layer during spring and summer is subsequently respired 558 within the seasonal thermocline and re-entrained into the mixed layer during winter (Palevsky & 559 Doney, 2018). Here, we leverage our mixed layer DIC budget to determine the seasonal cycle 560 and interannual variability of NCP and ANCP integrated to the seasonally varying mixed layer 561 depth. While not all of this NCP will lead to long-term carbon sequestration at depth, this value is of particular interest as the surface ocean pCO_2 , and in turn the influx of carbon from the 562 563 atmosphere to the upper ocean, is strongly influenced by NCP-driven changes in mixed layer

564 DIC concentration.

565 We find net autotrophy in the Irminger Sea for most of the year, with the highest NCP rates 566 occurring in the early spring prior to mixed layer shoaling (Fig. 6). NCP rates in this paragraph 567 are the mean and standard deviation across all 7 years. In the late summer into the late fall, we observe NCP from near neutral to mildly heterotrophic ($-5\pm17 \text{ mmol m}^{-2} \text{ d}^{-1}$ from Aug. 15 to 568 Nov. 15). In January, there is a transition to autotrophy with an NCP of 24 ± 43 mmol m⁻² d⁻¹ until 569 the end of February. By April, shoaling has begun and the mixed layer is strongly autotrophic, 570 with an NCP of 77 ± 26 mmol m⁻² d⁻¹ from the beginning of April to mid-May. From then until 571 August 15th, the mixed layer is relatively shallow and continues to be autotrophic at a much 572 lower NCP of 28 ± 24 mmol m⁻² d⁻¹. 573



575 **Figure 6.** Net community production (NCP) rates integrated to the seasonally-varying mixed

576 layer depth. The colored lines show each individual year, the thick black line shows the mean

- 577 across all years, and the gray shading is one standard deviation of the interannual mean. The bar
- 578 chart shows total annual net community production (ANCP). ANCP error bars are the
- 579 uncertainty as calculated through Monte Carlo analysis (details in Section 3.3).

580 We find that the central Irminger Sea has high ANCP as well as high interannual variability, with an annual mean of 9.7 \pm 1.7 mol C m⁻² yr⁻¹ (\pm signifies propagated error, not standard deviation, 581 Fig. 6). The highest ANCP recorded during our study period was 13.7 ± 2.3 mol C m⁻² yr⁻¹ during 582 583 2017-2018. This year had a later-than-average onset of mixed layer deepening, resulting in a 584 shallow fall mixed layer that caused the high fall chlorophyll concentration without a high depth-585 integrated rate of NCP. This is the only year with a decrease in DIC due to entrainment, likely 586 indicating photosynthesis below the mixed layer during the large fall bloom. There is a late fall 587 respiration signal, potentially fueled by sinking organic carbon from the fall bloom. 2017-2018 had very deep winter convection, as well as a decrease in DIC due to NCP from early March to 588 mid-April that outpaced the time series mean (12 mmol m⁻³ reduction in DIC over this time 589 period compared to the time series mean of 5 mmol m^{-3}), which together resulted in high 590 591 integrated NCP over this time period and for the yearly total. The lowest ANCP recorded occurred during 2021-2022 ($6.0\pm1.3 \text{ mol m}^{-2} \text{ yr}^{-1}$), which also had the earliest spring shoaling of 592 the observed period (Fig. 3). DIC increased in the late fall due to both entrainment and 593 594 respiration and there were relatively low NCP rates in the winter and early spring. These findings 595 indicate that the depth and timing of winter mixing substantially impacts the overall annual net 596 community production; however the rate of DIC drawdown by biology prior to mixed layer 597 shoaling is also an important control on ANCP.

598 This study adds to a growing body of research using DIC and TA as mass balance tracers to

599 quantify ANCP within the seasonally varying mixed layer depth. The majority of sites have vielded lower ANCP than we find in the Irminger Sea $(2\pm1 \text{ mol C m}^{-2} \text{ vr}^{-1} \text{ at in the North})$ 600 Pacific, $1.2\pm2.8 \text{ mol C} \text{ m}^{-2} \text{ vr}^{-1}$ in the North Pacific subtropical gyre, and $2.8\pm2.4 \text{ mol C} \text{ m}^{-2} \text{ vr}^{-1}$ 601 602 on the West Antarctic Peninsula shelf; Fassbender et al., 2016; Knor et al., 2023; Yang et al., 2021). However, in the Kuroshio extension in the North Pacific, ANCP was 7 ± 3 mol C m⁻² yr⁻¹ 603 604 (Fassbender et al., 2017). The Kuroshio site has the deepest winter mixed layer depths of other 605 sites where these methods have been used (up to 300m), and similarly to the Irminger Sea, there 606 are extremely high NCP rates seen in early spring as a result. A mixed layer carbon budget in the eastern subpolar North Atlantic (Porcupine Abyssal Plain site, 49°N, 16.5°W) found NCP within 607 the seasonally-varying mixed layer of 6.4 ± 1.1 mol m⁻² yr⁻¹, with over two thirds of the 608 609 production occurring prior to the spring shoaling of the mixed layer, a similar seasonal 610 partitioning and annual magnitude as at our site (Kortzinger et al., 2008). Kortzinger et al. also 611 found that 40% of the carbon exported from the seasonally-varying mixed layer was 612 subsequently offset by entrainment of respired carbon during deep winter mixing. Reduced 613 ANCP when integrating to the winter mixed layer depth as compared to ANCP within the seasonally-varying mixed layer has been corroborated by oxygen budgets using data from across 614 615 the subpolar North Atlantic (Quay et al., 2012, 2020). Given the uniquely deep winter mixing in the Irminger Sea, it will be important for future work to contextualize our ANCP results by 616 617 determining what fraction of this NCP contributes to long-term carbon sequestration, as well as 618 the mechanistic relationship between NCP-driven DIC-drawdown in the mixed layer and air-sea 619 CO₂ flux.

620 Our chemical tracer approach cannot provide insight into the complex ecosystem level dynamics 621 that likely contribute to the observed high interannual variability in ANCP, however there is a clear connection between strong convection and high ANCP. Prior work investigating 622 623 interannual variability of phytoplankton productivity in the Irminger Sea based on satellite chlorophyll data (which therefore does not capture early spring NCP discussed here) found that 624 625 the onset of elevated chlorophyll concentrations varies by as much as 30 days (Henson et al., 2006). Their analysis found that timing of spring mixed layer shoaling influenced the timing and 626 magnitude of the spring bloom; stormier winters with a high number of days with gale-force 627 628 winds in turn delayed spring stratification, corresponding to later onset of elevated chlorophyll 629 and lower peak chlorophyll concentrations (Henson et al., 2006). However, our work shows 630 significant DIC drawdown by NCP within the deep late winter-early spring mixed layer, prior to 631 mixed layer shoaling and increase in surface chlorophyll concentrations. Our finding of elevated 632 NCP during deep winter mixing is consistent with the disturbance-recovery spring bloom 633 hypothesis, in which the decoupling of zooplankton predator and prey during deep mixing 634 enables enhanced primary productivity due to relief of grazing pressure (Behrenfeld & Boss, 635 2014). Historically, increased light availability with a shoaling mixed layer has been thought to 636 be the catalyst of increased phytoplankton growth (Sverdrup 1953), however more recent work has demonstrated that though high chlorophyll concentrations may be driven by this critical 637 638 depth hypothesis, a combination of more complex ecosystem interactions caused by winter 639 mixing are at play (Behrenfeld & Boss, 2014 and references within; Mignot et al., 2018). Our results suggest that deeper mixed layers in the later winter and early spring may actually drive 640 higher ANCP, potentially the result of inhibition of grazing due to mixing. 641 642 643 644 645 646 647

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652 **5. Conclusions**

653 This work constructs the first long term time series of the inorganic carbon system in the 654 subpolar North Atlantic using daily measurements of the carbonate system. Strong biological 655 drawdown is the primary removal mechanism of inorganic carbon from the mixed layer. 656 Increases in mixed layer DIC are primarily controlled by entrainment of high DIC waters as the 657 mixed layer deepens due to winter convection. Similar maximum DIC concentrations are found 658 each winter despite interannual variability in winter mixing, implying that variations in the depth 659 of winter convection do not drive wintertime mixed layer DIC concentrations. While previous 660 analysis at this site has emphasized the role of deep winter mixing reintroducing respired carbon to the mixed layer that has been previously exported (Palevsky and Nicholson, 2018), we find 661 that strong NCP in the late winter and early spring begins reducing DIC concentration prior to 662 shoaling in all years, such that years with extremely deep convection actually drive higher ANCP 663 664 from the seasonally-varying mixed layer than those with shallower convection. The highest rates 665 of NCP occur prior to the appearance of high chlorophyll concentrations, highlighting the utility 666 of in situ sensing of carbonate parameters rather than relying on chlorophyll measurements as a 667 proxy for biological productivity in the mixed layer. It is probable that the detrainment of water 668 containing freshly produced organic carbon in the spring contributes to a high magnitude of

669 carbon export, a subject which warrants further exploration.

The average annual net community production within the seasonally-varying mixed layer is 670 $9.7\pm1.7 \text{ mol C} \text{m}^{-2} \text{vr}^{-1}$ and ranges from 6.0 to 13.7 mol C m⁻² vr⁻¹ over the 7-year study period. 671 Sparsity of data often leads to averaging across multiple years in ocean biogeochemistry and 672 673 specifically when determining ANCP, however doing so can blur the important differences from 674 year to year in both the drivers and magnitude. Averaging across multiple years does not 675 sufficiently capture the complex carbonate system dynamics in the central Irminger Sea, driven 676 by high interannual variability of winter convection and primary productivity. Collecting observational data is both costly and challenging, however if only one year of data is collected or 677 multiple years are averaged together, ANCP in areas with high interannual variability like the 678 679 Irminger Sea will be misrepresented. This is highly relevant in the context of efforts to detect the 680 emerging impacts of ongoing anthropogenic climate change on biogeochemical cycles relative to 681 baseline natural variability (Henson et al. 2016). The intended 25-year time series of the OOI 682 Irminger Array will provide more information about the interconnected physical and 683 biogeochemical controls on interannual variability in ANCP, as well as potential long-term 684 trends.

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- have collected and disseminated this time-series dataset. Our work with these data, and
- 694 collection and analysis of ancillary measurements during OOI turn-around cruises, was
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696 **Open Research**

- 697 Data Availability
- 698 Ocean Observatories Initiative mooring and glider data used in this analysis are all from the
- 699 THREDDS Gold Copy catalog
- 700 (https://thredds.dataexplorer.oceanobservatories.org/thredds/catalog.html).
- 701 Reference designators for each depth and deployment can be found in the OOI Data Explorer
- 702 (https://oceanobservatories.org/knowledgebase/how-to-decipher-a-reference-designator/,
- 703 <u>https://dataexplorer.oceanobservatories.org/</u>). OOI DIC and TA bottle samples were accessed
- through the OOI Alfresco portal
- 705 (https://alfresco.oceanobservatories.org/alfresco/faces/jsp/browse/browse.jsp).
- 706
- 707 DIC and TA bottle samples run at Boston College can be accessed on the Biological and
- 708 Chemical Oceanography Data Management Office Database (BCO-DMO, <u>https://www.bco-</u>
- 709 <u>dmo.org/dataset/904722</u>). ERA5 Reanalysis hourly sea surface temperature and 10m wind speed
- 710 data, used for mixed layer calculations and air-sea gas exchange, are from
- 711 https://doi.org/10.24381/cds.adbb2d47. Sea surface height and current data used in Figure 1 are
- from E.U. Copernicus Marine Service Information, <u>https://doi.org/10.48670/moi-00148</u>.
- 713 NOAA's CarbonTracker data, used in air-sea gas calculations, are from
- 714 <u>https://doi.org/10.15138/ffxv-2z26</u>. Nutrient mean values at our site are from GLODAPv2_2021,
- 715 accessible at <u>https://www.ncei.noaa.gov/data/oceans/ncei/ocads/data/0237935/</u>.
- 716
- 717 Software Availability
- All analyses were conducted in MATLAB from MathWorks. Basic physical oceanographic
- conversions were done using the Gibbs SeaWater (GSW) Oceanographic Toolbox of TEOS-10,
- available at <u>http://www.TEOS-10.org</u>. Calculations within the carbonate chemistry system used
- 721 CO2SYS.v2.1, available at <u>https://zenodo.org/records/3952803#.X0kReGdKhTa</u>. Predicted DIC
- and TA were determined using the CONTENT model, accessible at
- 723 <u>https://github.com/HCBScienceProducts/CANYON-B</u>. Gas transfer parameterizations were
- calculated using the Gas_Toolbox, accessible at <u>https://zenodo.org/records/545858</u>.
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