What does chlorophyll variability tell us about export and CO2 flux variability?

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Abstract

Export is used to quantify the importance of biology to the ocean carbon sink. Satellite images of sea surface chlorophyll provide observations of variability in biological production, but how these variations affect export and carbon fluxes is poorly understood. We investigate this in the North Atlantic using a general circulation model coupled to a medium-complexity ecosystem model and satellite data. We find that biological production is significant on the mean and dominates the seasonal cycle of pCO2, but that variations in annual CO2 flux and export are not significantly correlated. Large year-to-year variability in bloom-period pCO2 is due to changing bloom timing. Integrated bloom strength and associated carbon uptake and export do not vary substantially. The model indicates that small biological variability, quantitatively consistent with SeaWiFS (1998-2006), is not sufficient to be a first-order control on annual subpolar CO2 flux variability.
Introduction

Although we can quantify the amount of carbon dioxide pumped into and remaining in the atmosphere each year, we are currently unable to fully explain why the relative magnitude of terrestrial and oceanic sinks appears to be decreasing [Raupach et al., 2007; Canadell et al., 2007]. The difficulty of distinguishing trends from interannual variability is one confounding factor. In order to understand the current and future trajectory of the oceanic carbon sink, the mechanisms that control its strength and year-to-year variations must be understood. Currently, direct observations at the global scale can only provide the climatological seasonal cycle and mean of the oceanic sink [Takahashi et al., 2002].

Ocean biology is critical to maintaining the mean sink of atmospheric carbon dioxide into the ocean. Photosynthesis reduces oceanic pCO2 by converting dissolved inorganic carbon (DIC) into organic carbon, and grazing by zooplankton and death of phytoplankton create a sinking mass of carbon that remineralizes back to DIC at depth. This biological cycle causes a net movement of DIC from the surface to depth and is often referred to as the “biological pump.” Behrenfeld et al. [2006] estimate that more than one million tons of carbon are fixed into organic matter as CO2 each day by ocean biology. Sarmiento et al. [1988] estimate that the current atmospheric pCO2 would be two to three times its current value today if it were not for the biological control of the gradient of DIC in the ocean. It is reasonable to hypothesize that in regions of large biological production, interannual fluctuations in biological productivity may alter the annual sink of carbon dioxide. The subpolar North Atlantic is one such region, with a pronounced spring bloom and a large annual mean flux of carbon dioxide into the ocean. Sabine et al. [2004] estimate the North Atlantic has taken up 23% of the total anthropogenic CO2, even
though it is only 15% of the global ocean. Recent studies suggest this important sink may be changing. Schuster and Watson [2007], based on their analysis of pCO2 data, conclude that the North Atlantic sink between 20°N and 65°N is rapidly declining.

Coupled ocean-atmosphere model results suggest that a future increase in ocean temperatures and stratification will alter chlorophyll and export production [Sarmiento, 1999; Bopp et al., 2001]. Increases in export production in the subpolar region [Bopp et al., 2001] and decreases in the subtropical region are anticipated. Behrenfeld et al. [2006] investigate recent (1999-2006) satellite data and suggest that global biological productivity within the subtropics has already declined, but they are unable to make any conclusions about trends in the high latitudes.

To better address these ideas we need to understand to what extent biological variability impacts the oceanic carbon sink in the present day subpolar North Atlantic.

Satellites, such as the Sea-viewing Wide Field-of-view Sensor (SeaWiFS), provide estimates of chlorophyll at fine spatial and temporal resolution, but we are currently uncertain what these year-to-year variations in satellite observations mean in terms of oceanic carbon sink variability. Chlorophyll is not a direct measurement of biomass and is dependent upon temperature, light, and nutrients [Geider et al., 1998]. Biomass itself is also not a direct measurement of export, as the sinking velocities of particulate matter is dependent upon size. Do larger peak chlorophyll observations indicate more biomass and export for the entire year? Are years of greater daily average chlorophyll years of a greater oceanic carbon sink? What can these satellite estimates of chlorophyll tell us about interannual export variability?
We use an ocean general circulation model coupled to an ecosystem-biogeochemical component to determine whether biology is a first order control of interannual CO2 flux variability in the North Atlantic subpolar gyre. We seek to understand how year-to-year variations in biological production affect the annual sink of carbon dioxide in the region and to learn what satellite observations can tell us about a year’s anomalous sink. We also consider controls of North Atlantic bloom variability \cite{Follows and Dutkiewicz, 2002; Ueyama and Monger, 2005} and the lack of a significant trend in production in observations in the subpolar North Atlantic \cite{Behrenfeld et al., 2006}.

This paper is organized as follows. The next section will describe the model used, experimental setup, and model verification. The third section will discuss model results, and the final section includes discussion and conclusions.

**Section 2: Model Description**

We use a medium-complexity ecosystem model coupled to a three-dimensional North Atlantic regional ocean circulation model.

**Section 2.1: The Physical Model**

We use the MIT general ocean circulation model \cite{Marshall et al., 1997a, 1997b} reconfigured to the bathymetry of the North Atlantic with a horizontal resolution of 0.5° x 0.5°. The model uses a z-coordinate system of 23 vertical layers. The uppermost layers have finest resolution, with layer depths of 10 meters, becoming coarser with depth to 500 meters below 2500 meters. The Gent-McWilliams \cite{Gent and McWilliams, 1990} eddy parameterization and KPP vertical mixing
scheme [Large et al., 1994] are used to simulate the effects of sub-grid scale processes. The bathymetry extends from 20° South to 81.5° North. At the southern boundary, there is a sponge layer in which tracers are rapidly restored to climatology, and the Mediterranean, Labrador and Norwegian Seas have closed boundaries. Temperature and salinity are relaxed to climatology at the Strait of Gibraltar. Model tracers have a time step of 40 minutes, and momentum is integrated more rapidly with a time step of 200 seconds. The physical model is forced with daily winds, heat, freshwater, and radiation data taken from the National Centers for Environmental Protection (NCEP) Reanalysis I between 1980 and 2006 [Kalnay et al., 1996]. The physical model is spun up for eighty years while relaxing sea surface temperature and salinity to monthly climatology [Boyer et al., 2004] with timescales of 2 weeks and 1 month, respectively. The relaxation forcings during spin up are saved out of the model, and during model experiments discussed here, the relaxations are turned off, but the climatological relaxation forcings are added to interannually varying forcing terms. This increases modeled physical variability. For more physical model details and verification, refer to Ullman [2008].

Section 2.2: Ecosystem Model

The ecosystem model is an updated version of the Dutkiewicz et al. [2005] model that includes the cycles of carbon, alkalinity, and oxygen. The cycles of iron, phosphorous, and silica are explicitly modeled throughout the entire water column. There are a total of nineteen ecosystem tracers: phosphate (PO$_4$), silicic acid (Si), total dissolved inorganic iron (FeT), phosphorous in small phytoplankton (Phy1), phosphorous in large phytoplankton (Phy2), phosphorous in zooplankton, dissolved organic phosphorous, particulate organic phosphorous, particulate organic silicate, iron in zooplankton, dissolved organic iron, particulate organic iron, dissolved
organic carbon, dissolved inorganic carbon, particulate organic carbon, particulate inorganic 
carbon, carbon in zooplankton, oxygen, and alkalinity. Model diagnostics quantify the effect of 
advection, diffusion, air-sea gas exchange, precipitation/evaporation, and biological production 
on DIC and ALK concentrations. Figure 1 is a schematic of the ecosystem model.

Nutrients are taken up by two classes of phytoplankton: a small class and a large diatom class. 
The model allows biological productivity to be affected by light, nutrients, and temperature. The 
two phytoplankton classes have separate maximum growth rates, modified by the most limiting 
nutrient according to a Michaelis-Menten parameterization, by temperature according to Eppley 
[1972], and by light availability. The ratio of carbon to phosphorous in the model is a constant 
120, and the ratio of silicate to phosphorous is 25 in diatoms. Both small and large 
phytoplankton create 170 moles of oxygen for every one mol of phosphorous they uptake 
[Anderson and Sarmiento, 1994]. Forty percent of incoming shortwave radiation is assumed to 
be photosynthetically active radiation (PAR). Fractional ice coverage is prescribed with daily 
resolution from NCEP Reanalysis I data, and its presence blocks the same fraction of incoming 
radiation. The model allows for self-shading, so light penetration is dependent upon the 
chlorophyll concentration, 

\[ I = I_0 \times \exp(-(k_w + k_c Chl)z) \]  

where \( I_0 \) is the daily averaged PAR incident on the surface, \( k_w = 0.04 \) (m\(^{-1}\)) is the attenuation 
coefficient for water, and \( k_c = 0.05 \) (m\(^2\) mg Chl\(^{-1}\)) is the attenuation coefficient for chlorophyll, 
Chl is the chlorophyll concentration (mg m\(^{-3}\)), and \( z \) is the depth.
Chlorophyll is computed at each model time step, dependent upon phytoplankton populations and allowing for photo adaptation and nutrient stress in a technique similar to Doney et al. [1996].

\[
Chl = Phy_1 \times (B_{max} - (B_{max} - B_{min}) \times \min(I_*,1)) \times \min\left(\frac{PO_4}{P_0} + Kp1, \frac{FeT}{FeT + Kf1}\right)
+ Phy_2 \times (B_{max} - (B_{max} - B_{min}) \times \min(I_*,1)) \times \min\left(\frac{PO_4}{P_0} + Kp1, \frac{FeT}{FeT + Kf1}, \frac{Si}{Si + Ks}\right)
\]

where \(I_*\) is the critical irradiance for photo adaptation, \(Kp1\) and \(Kp2\) are the half-saturation constants of phosphate for small and large phytoplankton, \(Kf1\) and \(Kf2\) are the half-saturation constants of iron for small and large phytoplankton, \(Ks\) is the half-saturation constant of silicic acid, and \(B_{min}\) and \(B_{max}\) are the maximum and minimum ratios of chlorophyll to phosphorous in phytoplankton.

The one zooplankton class preys upon both classes of phytoplankton, but feeding preference is given to small phytoplankton because of the diatom’s protective silica shell. Grazing is not perfectly efficient, and fifty percent of the prey biomass is lost to the particulate and dissolved pools. When small phytoplankton die, fifty percent of this loss enters the dissolved pool. Diatoms are more efficient exporters, and eighty percent of their mass enters the particulate pool when they die. The particulate pool of phosphorous remineralizes with a timescale of 70 days and sinks due to gravitational forces at a rate of 2900 meters per year. For the purpose of this analysis, export is defined to be the rate of removal of particulate organic carbon from through 100 meters, as done by Bopp et al. [2001].
Carbon in several forms (dissolved inorganic, dissolved organic, particular organic and particulate inorganic), alkalinity, and oxygen are active tracers in the model. DIC is modified by biological uptake, remineralization of dissolved organic carbon, and the air-sea exchange of carbon. Oxygen is exchanged across the air-sea interface, created by photosynthesis, and used during remineralization. Changes in particulate inorganic carbon and nutrient concentrations alter alkalinity. Seawater alkalinity, temperature, salinity, DIC, PO4, and silicate concentrations are used to determine pH according to Follows et al. [2006], using the constants of Millero [1995] and Weiss [1974]. The pH and DIC are used to determine the concentration of CO2 gas and H2CO3, which determine pCO2. Atmospheric pCO2 increases according to Mauna Loa observations [Keeling et al., 2001] during the model run and includes the seasonal cycle. The flux of carbon dioxide between the ocean and atmosphere is parameterized as the difference in partial pressure across the air-sea interface multiplied by the piston velocity, which in turn is a square function of wind speed [Wanninkhof, 1992]. The Schmidt number coefficients are from Weiss [1974]. We define a positive flux as one directed into the ocean.

The biogeochemical model spin up begins in winter and is initialized with GLODAP [Key et al., 2004; Lee et al., 2006] DIC and ALK climatology, World Ocean Atlas 2005 [Garcia et al., 2005a, 2005b] nutrients and oxygen, and very low values of phytoplankton and zooplankton. The ecosystem component is turned on after the eighty-year physical model spin up, and the coupled model is spun up for twenty years. The coupled model is then run for twenty-seven years with daily forcing between 1980 and 2006. The years 1980 and 1981 are ignored in model analysis to allow for adjustment.
Section 2.3: Model-Data Comparisons

Climatological modeled and observed chlorophyll and standard deviation of June chlorophyll in the model and eight years of observations are shown in Figure 2. The depth to which SeaWiFS is retrieving ocean color varies in both space and time. For the model, the surface chlorophyll concentration is considered to be the depth-weighted average in the top 5 meters. Results and patterns are robust with differing selections of the depth to which model chlorophyll is integrated. The model replicates the pattern and cycle of observed chlorophyll well, but overestimates the magnitude of peak chlorophyll in the subpolar region by a factor of two to three. The model underestimates chlorophyll in the subtropical region, a problem common in models that do not explicitly model eddies [McGillicuddy et al, 2007; Oschlies and Garçon, 1998]. One additional potential reason for our underestimation of production is that we neglect nitrogen fixation. However, satellite retrieval of surface chlorophyll does have an error on the order of 30% (http://oceancolor.gsfc.nasa.gov).

Surface ocean pCO2 is affected by temperature (SST), alkalinity (ALK), salinity (SSS), and dissolved inorganic carbon (DIC). In order to understand how biology affects the pCO2, we separate the temperature-driven pCO2 (pCO2-T) from the effects of alkalinity, salinity, and DIC (pCO2-nonT) according to the equations of Takahashi et al. [2002], based upon experimental results of Takahashi et al. [1993]. This separation is valuable in the study of the subpolar North Atlantic because DIC and temperature are the two dominating controls on pCO2 in the region [Ullman, 2008]. pCO2-nonT can be understood primarily as the effect of DIC.

\[
pCO_2 - T = pCO_2 \times \exp(0.0423 \times (SST - SST)) \tag{3}
\]
\[
pCO_2 - nonT = pCO_2 \times \exp(0.0423 \times (SST - SST)) \tag{4}
\]
The bar represents a time averaged mean value. Although the equations are not linear, using daily model output to calculate these results in pCO2-T and pCO2-nonT that sum to within a couple µatm of total pCO2.

We can compare these components of the model’s carbon cycle to observations. In Figure 3, the seasonal cycle of total pCO2 and each of the pCO2 components are shown compared to the climatology of Takahashi et al. [2002]. The seasonal cycle is defined as the mean over the late summer/early fall months (August, September, October) minus the three-month winter mean (January, February, March). The model does well capturing the observed pattern of the seasonal cycle of pCO2, clearly illustrating the dominance of temperature to the cycle in the subtropics and the dominance of DIC cycling in the subpolar region. The cycle of pCO2-nonT is slightly stronger than observed in the subpolar region due to the large model bloom there. The weak bloom in the subtropical region causes a weaker seasonal cycle of pCO2-nonT than observed. The seasonal cycle of pCO2-T is a bit strong in the subtropical region.

In summary, the coupled model does a good job capturing the pattern of the spring bloom and the seasonal cycle of pCO2 throughout much of the North Atlantic basin. The primary deficiency is that mean biological productivity is too low in the subtropical region. Despite this, variability in chlorophyll (Figure 2) is consistent with data across the basin, and thus we conclude the model is an adequate tool for understanding the effect of biological variability on CO2 fluxes.
Section 3: Results

Section 3.1: Bloom Dynamics

Timing of the bloom is dependent upon both the physical and chemical state of the ocean and may affect the annual biomass and export. For example, blooms that begin later in the subpolar gyre may be limited by the length of the growing season, and those years may have reduced net biomass and export. Timing of modeled bloom peak dates is verified using SeaWiFS satellite data from 1998-2006. To isolate bloom peak dates, SeaWiFS, 8-day chlorophyll data and daily model chlorophyll were smoothed using a four week median filter as in Ueyama and Monger [2005], and the peak was defined as the first day between December 1 and November 1 of the maximum chlorophyll value. Figure 4 shows the agreement between the climatological calendar day of peak chlorophyll in the model and the satellite data. Bloom start dates (not shown) are determined using the cumulative variance technique as in Ueyama and Monger [2005]. We fit a sigmoidal curve to the cumulative variance of the chlorophyll time series in each model grid cell. The start of the bloom is determined as the first day the slope of the curve reaches twenty percent of its maximum value. We find that the bloom begins in the fall in the lower latitudes and progresses northward through the spring and summer, similar to that found by Ueyama and Monger [2005].

We would like to understand whether interannual variations in the magnitude of the North Atlantic spring bloom have an effect on yearly export and CO2 fluxes. In Figure 5a, we show the standard deviation of 25 years of monthly-averaged June pCO2-nonT from the model. The subpolar region shows large variability in the magnitude of June pCO2 during the height of the bloom due to interannual variability in DIC changes from biological activity. Zooming in on the
boxed region near Iceland shown in Figure 5a, we show the seasonal cycle of weekly pCO2 and its standard deviation (black dashed) in Figure 5b. The largest variability in total pCO2 occurs during June and is due to change in the pCO2-nonT component, which is due to bloom timing and magnitude variability. This maximum in variability occurs during the time of maximum change in the seasonal cycle of total pCO2. This suggests that variability in the bloom timing might impact yearly CO2 fluxes.

The importance of the bloom to the seasonal cycle of pCO2 is shown in Figure 6a, where the significant correlations between the bloom peak date and the date of minimum oceanic pCO2 are shown. Positive correlations north of 45°N indicate that bloom timing affects the date of the annual minimum pCO2. Earlier blooms shift this minimum earlier, and later blooms shift the minimum pCO2 later. Between 30°N and 45°N, minimum pCO2 occurs when the water is coldest and mixing most vigorously. Productivity peaks at the same time, because the mixing supplies nutrients to the surface (Figure 6b), but it is the cold that causes the pCO2 minimum, not productivity.

Section 3.2: Export and CO2 Fluxes

Ocean biology controls summertime pCO2 in the subpolar region, but does this summertime control of pCO2 exert a first order control on the annual CO2 fluxes in the region? SeaWiFS provides satellite-derived estimates of year-to-year variations in ocean chlorophyll. It is expected that years with larger chlorophyll peaks and integrated chlorophyll are years of greater export of particulate organic carbon, even though chlorophyll is not a direct measurement of biomass. We test this expectation.
We define export as the flux of particulate organic carbon through 100 meters, as done in Bopp et al. [2001]. The correlation between modeled integrated annual biomass in the top 55 meters (December – November) and integrated export over the same time period is significantly correlated almost everywhere in the North Atlantic (Supplementary Figure 1). Thus, greater biological productivity does result in more export, but do larger blooms create an anomalous influx of CO2 for the year? We consider this by correlating the annual CO2 flux (positive into ocean) and annual export (Figure 6c). Large-scale correlation between annual CO2 fluxes and annual export exists in the subtropical region, but not in the subpolar region.

As with the seasonal cycle (section 3.1), the large-scale correlation between annual CO2 fluxes and annual export in the subtropical region does not indicate a first order control of biology in that region; instead it indicates an indirect relationship via temperature. Years of increased mixing bring both cold and nutrient rich waters to the surface. Increased nutrient supply fuels increased biological production and export in this highly nutrient limited region. However, oceanic pCO2 in the subtropical North Atlantic is largely controlled by temperature and alkalinity [Ullman, 2008], and it is the anomalously cold temperatures that lead to a reduced pCO2. Colder years are therefore years of greater biological production and (indirectly) lower pCO2 and in the region, in agreement with the findings of Bopp et al. [2001] and Sarmiento et al. [2004]. Annual temperatures and maximum winter mixed layer depth, as defined as the depth at which the potential density differs from the surface by 0.125 kg/m3, are significantly anti-correlated almost everywhere (not shown).
We find that years of greater biological production in the subpolar region are years of greater export, but not necessarily years of a greater influx of CO2. In the subpolar region, where light is seasonally limiting, export is positively correlated to annual SST (Supplementary Figure 2), indicating that years of greater warmth and greater stratification provide more light and less bloom-time mixing, and thus greater biological productivity [Folke and Dutkiewicz [2002]; Ueyama and Monger [2005]]. These are also years of lower supply of DIC to the upper layers, and Figure 6d illustrates the first order control of the CO2 fluxes by DIC in the high latitudes, as found by Ullman [2008]. Years of lower surface DIC are years of increased CO2 influx in this region, but is it the lower DIC due to less deep winter mixing or greater biological productivity? Using the model, we can quantify the change in DIC created by biological production above or below the 25-year daily mean (Supplementary). We find the day-to-day change in pCO2 created by the anomalous biological activity amounts to a summer daily average change in pCO2 on the order of 2 µatm or less in the subpolar gyre, in agreement with the findings of Le Quéré et al. [2003]. Changes in pCO2 caused by anomalous winter mixing in the model are larger than those caused by anomalous biological productivity (not shown, on the order of 10 µatm), and increased wind speeds in winter also cause larger winter fluxes, so winter mixing must be controlling the annual CO2 flux variability. These factors combine such that winter flux variability is significantly larger than summer flux variability in the subpolar gyre (Supplementary Figure 3).

The small area within the subpolar gyre to the southwest of Iceland that shows a significant correlation between export and CO2 flux variability (Figure 6c) is a region of very deep winter mixing. In this region, anomalous biological production is not a first order control of flux variability, but mixing is highly correlated to biological production here. Deeper mixing in this
region increases surface DIC concentrations and decreases the magnitude of the spring bloom by keeping phytoplankton mixed away from the light [Dutkiewicz et al., 2001]. In this way, years of decreased mixing are also years of increased export in this small region. The correlation is indirect.

Years of increased integrated chlorophyll are indeed years of greater export, but years of greater export are not necessarily years of an increased CO2 sink. Export and CO2 fluxes are correlated in the subtropics, but biology does not control pCO2 in this region. Anomalies in export do not correlate with CO2 flux anomalies in the subpolar region, suggesting that biology is not a first order control on CO2 flux variability anywhere in the North Atlantic.

Section 3.3: Biological Variability

We have shown that biological productivity in the subpolar region determines the seasonal cycle of pCO2 (Figure 3,5), so why is it not a first order control of CO2 flux variability (Figure 6c)? DIC controls the annual pCO2 and CO2 fluxes in the subpolar region, but anomalous summertime biological production does not create anomalous annual CO2 fluxes (Figure 6c,d).

We define integrated bloom strength as the annually integrated chlorophyll. In this section, we illustrate that large variability in June pCO2 (Figure 5) is driven by bloom timing, not integrated magnitude of the bloom.

The ratio of the standard deviation in daily chlorophyll to the mean between 1998 and 2006 is shown for the model and SeaWiFS in Figure 7a,b. Since the model is unable to produce the magnitude of the bloom observed in the subtropical region (Section 2.3), percent variations in
less productive regions are unrealistically large, and so areas in which the model integrated
annual average chlorophyll is less than 150 mg m\(^{-3}\) are masked. We consider here only the
variability in the subpolar North Atlantic. The model does very well at capturing the percent of
biological variability throughout the subpolar region, even capturing specific regions of observed
greater variability, such as along 30°W. The average percent variability is 13.5% in the data and
15.3% in the model. Percent variability also agrees with Levy et al. [2005] who find annually
integrated chlorophyll varies by 10% of its mean in a region of the subpolar North Atlantic (16°-

The box in Figure 7b corresponds to the near-Iceland region introduced in Figure 5, and Figure
7c depicts the 25 years of model chlorophyll in that region. Though large year-to-year variations
in bloom timing exist, the variability in integrated bloom strength (the area underneath each
curve) and export are small. Thus, the variations in timing that drive the large variability in June
pCO\(_2\) (Figure 5) do not translate to significant anomalies in integrated biomass or export over
the course of the year. The percent variation of modeled annual export at Iceland (4.8%) is even
less than the percent variation in modeled yearly chlorophyll (10.9%); chlorophyll is not a direct
measurement of biomass and does not take into account the community structure. Between 1998
and 2006, integrated chlorophyll varied by 18% of its mean in SeaWiFS data. In the subpolar
gyre of the North Atlantic, we find that blooms that start earlier also end earlier, an unexpected
result for a light-limited region. Further model analysis indicates that tight ecosystem coupling
limits interannual variability of integrated bloom strength. An initial diatom bloom begins to
reduce silicate and phosphorous availability. At the same time, zooplankton concentrations
increase. When silicate is limited, the diatom bloom subsides and small phytoplankton begin to
dominate the biomass. When light and nutrients limit growth, the phytoplankton concentrations decrease. The water is again suitable for growth in the late fall, but often zooplankton are at too high a population to allow another bloom. Such a cycle was observed by Sieracki et al. [1993] and discussed by Lochte et al. [1993] during the North Atlantic Bloom Experiment. Since the integrated bloom magnitude does not vary dramatically, there is a limited variability in the annual strength of the biological pump, and this is not sufficient to be a first order control of the CO2 flux variability in the region.

Section 4: Discussion and Conclusions

We have used a basin scale ocean general circulation model coupled to a medium complexity ecosystem to determine whether variations in biological productivity can be a first order control of the annual CO2 fluxes in the subpolar North Atlantic. We have shown that large variability in summer pCO2 exists in the subpolar region and is due to the bloom’s control of the seasonal cycle of pCO2. However, upon closer inspection, the large variability present in summer is due to bloom timing and not integrated bloom strength. Although no significant causal relationship was found between variations in subpolar biological production and annual subpolar CO2 fluxes, biology does determine the timing of the seasonal cycle of pCO2 within the region and is an important driver of the mean flux [Behrenfeld et al., 2006]. Further, biological activity is critical to the mean carbon uptake. The maximum annual mean CO2 flux due only to solubility, estimated using the technique of Keeling et al. [1993], is only 0.1 PgC/yr into the North Atlantic. Including biological production increases this flux to 0.34 PgC/yr. The pattern of annual mean CO2 fluxes also matches the pattern of annual export (Supplementary Figure 4).
The model replicates the percent chlorophyll variability observed in SeaWiFS in the subpolar gyre, and the small percent variability in modeled annually integrated export (5-10%) suggests that it is not sufficient to be a first order control of annual CO2 flux variability. Modeled biological variability alters summertime daily average pCO2 on the order of a couple µatm. Our findings agree with Le Quéré et al. [2003] who found that biological interannual variability only altered pCO2 by a couple of µatm. Light summer winds over the subpolar gyre further ensure that biologically-controlled flux variability is limited.

In the subtropical region, yearly biological production and export are significantly correlated to annual CO2 fluxes, but the relationship is not causal. Here, SST controls pCO2 but is related to biology through the vertical supply of nutrients. Colder SSTs decrease oceanic pCO2, increase vertical mixing, and enhance the bloom. Our results agree with Behrenfeld et al. [2006] who find a strong correlation between biological production and climate within the permanently stratified regions of the ocean. However, we do not anticipate any effect on the CO2 fluxes due to the changes in biological production. Modeled biological variability in the subtropical region exceeds 100 percent but still does not control pCO2, because SST controls pCO2 in the region [Ullman, 2008]. Therefore, we conclude that biology has not been a first order control on the interannual variability of CO2 fluxes anywhere in the North Atlantic in recent years, barring changes in ecosystem structure that would not be captured in this model.

Despite biology not controlling CO2 flux interannual variability, interpretation of in situ observations of oceanic pCO2 need to carefully consider bloom timing in order to properly understand CO2 cycling, variability, and trends. Model results show that changes in bloom
timing can alter monthly pCO2 values by tens of µatm (Figure 5), so sparse observations should be extrapolated to annual timescales with great care.

Recent studies have used SeaWiFS data to understand year-to-year variations and trends in biological productivity on a global scale. Our results suggest SeaWiFS may be very useful for estimating variability in export out of the ocean surface on short timescales, but cannot directly elucidate CO2 flux variability on annual timescales. Sarmiento et al. [2004] and Bopp et al. [2001] both suggest that increased stratification with a warming climate may lead to an enhanced subpolar bloom. In agreement with Behrenfeld et al.’s. [2006] data analysis, modeled chlorophyll in the subpolar gyre does not exhibit an increasing trend between 1982 and 2006. Furthermore, our results suggest that because the integrated bloom strength is relatively insensitive to the timing of bloom initiation, changes in the timing and amplitude of biological production during the bloom that may be driven by future climate warming may not substantially modify annually integrated CO2 fluxes.
Figure 1. Ecosystem model schematic [Dutkiewicz et al., 2005] showing movement of iron, phosphorous, silicon, and carbon through the nutrient, plankton, particulate, and dissolved matter pools. The figure also shows the ecosystem’s contribution to the air-sea exchange of carbon dioxide and oxygen, and the use and production of oxygen within the water column.
Figure 2. Model surface (55 meters) and SeaWiFS climatology and standard deviation of June chlorophyll mg/m$^3$. Modeled climatology and standard deviation between 1998 and 2006. SeaWiFS data from 1998-2006.
Figure 3. Maps of the seasonal amplitude (ASO – JFM) of pCO$_2$, pCO$_2$-T, and pCO$_2$-nonT in the North Atlantic for the model and observational data of Takahashi et al. [2002]. The dark line is zero seasonal change.
Figure 4. Climatology of bloom peak day in SeaWiFS satellite data (1998-2006) and in the model (1982-2006).
Figure 5. (a) Standard deviation of 25 years of June pCO2-nonT in µatm. The large variability in June pCO2 (not shown) in the subpolar region is due to pCO2-nonT variability. The boxed region corresponds to the Icelandic region depicted in b. (b) Twenty-five year climatology of the pCO2 seasonal cycle and root mean square of weekly pCO2 and each of its components near Iceland (57.5°N 17.5°W). Summertime variability in pCO2 is driven by variability in pCO2-nonT.
Figure 6. (a) Significant correlations between the day of the year of the bloom peak and the day of the year of the minimum oceanic pCO₂ value. (b) Significant correlations between the annual maximum mixed layer depth and surface DIC concentrations. (c) Significant correlations between annual surface DIC concentrations and the annual CO₂ flux. (d) Significant correlations between annual export and detrended annual CO₂ flux.

All correlations presented take into account the temporal autocorrelation between the two time series as in [Bretherton et al., 1999] and are considered significant at the 95% confidence level. Dashed contour lines indicate a negative correlation. The thick black lines are lines of zero correlation.
Figure 7. (a,b) The percent the standard deviation is of the mean daily chlorophyll between fall 1998 and 2006 in SeaWiFS (a) and the model (b). Eight-day weeks 10 through 37 of the year are used in this analysis, because SeaWiFS data in the subpolar region is too sparse during the omitted weeks. To compare the model to SeaWiFS satellite data, a daily average chlorophyll value for each year was calculated in both the data and model. Due to cloud cover and other satellite issues, not all grid points have observational data every 8-day period, so area-weighted averages for 5° x 5° regions were used with observational data. Within a 5° x 5° area, the available data for each 8-day record is assumed representative of the entire area and an area-weighted average is created, ignoring missing data points. The model is able to capture the percent variability observed and much of the pattern of variability magnitude.
(c) 25 years of modeled chlorophyll at region near Iceland boxed in (b). Thick black line is modeled climatology. Annually integrated chlorophyll varies by only 10.9% of the mean, and annual export varies by only 4.8% of the mean between 1982 and 2006. SeaWiFS daily average chlorophyll (1998-2006) varies by 18% of its mean in this region.


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Supplementary

The net effect of anomalous biological production is defined as the difference between anomalous drawdown of DIC by phytoplankton and the anomalous remineralization of organic carbon to DIC. The model outputs DIC daily, so DIC resulting from the total biological production (mean + anomaly) is known. We calculate the 25-year mean effect of biology (drawdown-remineralization) on DIC concentration for each day of the year. The change in DIC due to anomalous biological activity is calculated as the difference between the total effect on DIC and the daily mean effect on DIC. We add this DIC to the model output DIC to determine the DIC and pCO2 that would have resulted from mean biological activity on that day.

Anomalous biological activity results in a daily average change in pCO2 of 2µatm.
**Supplementary Figures**

**Figure 1.**

Significant correlations between anomalous annual biomass (D-N) and anomalous annual export (D-N).
Figure 2. Significant correlations between anomalies of annually averaged SST and export. Colder years in the subtropics are years of greater production and export. Warmer years in the subpolar region are years of greater export.
Figure 3. Winter (Dec-Apr) (top) and summer (May-Sep) (bottom) average wind speed, RMS of pCO₂, and RMS of CO₂ flux. Winter has significantly faster winds and greater flux variability than summer.
Figure 4. Modeled 25-year mean annual (D-N) export and mean annual (D-N) CO₂ flux. Positive fluxes are ones into the ocean.
Figure Captions

Figure 1. Ecosystem model schematic [Dutkiewicz et al., 2005] showing movement of iron, phosphorous, silicon, and carbon through the nutrient, plankton, particulate, and dissolved matter pools. The figure also shows the ecosystem’s contribution to the air-sea exchange of carbon dioxide and oxygen, and the use and production of oxygen within the water column.

Figure 2. Model surface (55 meters) and SeaWiFS climatology and standard deviation of June chlorophyll mg/m³. Modeled climatology and standard deviation between 1998 and 2006. SeaWiFS data from 1998-2006.

Figure 3. Maps of the seasonal amplitude (ASO – JFM) of pCO2, pCO2-T, and pCO2-nonT in the North Atlantic for the model and observational data of Takahashi et al. [2002]. The dark line is zero seasonal change.

Figure 4. Climatology of bloom peak day in SeaWiFS satellite data (1998-2006) and in the model (1982-2006).

Figure 5. (a) Standard deviation of 25 years of June pCO2-nonT in µatm. The large variability in June pCO2 (not shown) in the subpolar region is due to pCO2-nonT variability. The boxed region corresponds to the Icelandic region depicted in b. (b) Twenty-five year climatology of the pCO2 seasonal cycle and root mean square of weekly pCO2 and each of its components near Iceland (57.5°N 17.5°W). Summertime variability in pCO2 is driven by variability in pCO2-nonT.
Figure 6. (a) Significant correlations between the day of the year of the bloom peak and the day of the year of the minimum oceanic pCO2 value. (b) Significant correlations between the annual maximum mixed layer depth and surface DIC concentrations. (c) Significant correlations between annual surface DIC concentrations and the annual CO2 flux. (d) Significant correlations between annual export and detrended annual CO2 flux.

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