Bio-optical observations of the 2004 Labrador Sea phytoplankton bloom

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[1] A unique time series of moored bio-optical measurements documented the 2004 spring-summer bloom in the southern Labrador Sea. In situ and satellite chlorophyll data show that chlorophyll levels in the 2004 bloom were at the upper end of those typically observed in this region. Satellite chlorophyll and profiling float temperature/salinity data show that the main bloom, which typically peaks in June/July, is often preceded by ephemeral mixed layer shoaling and a lesser, short-lived bloom in May; this was the case in 2004. The particulate backscatter to beam attenuation ratio \((b_{bp}[470 \text{ nm}]/C_{p}[660 \text{ nm}])\) showed peaks in the relative abundance of small particles at bloom initiation and during the decline of the bloom, while larger particles dominated during the bloom. Chlorophyll/C\(_{p}\) and \(b_{bp}/\text{chlorophyll}\) were correlated with carbon export and dominated by changes in the pigment per cell associated with lower light levels due to enhanced attenuation of solar radiation during the bloom. An NPZ (nutrients, phytoplankton, zooplankton) model captured the phytoplankton bloom and an early July peak in zooplankton. Moored acoustic Doppler current profiler (ADCP) data showed an additional mid-June peak in zooplankton biomass which was attributed to egg-laying copepods. The data reported here represent one of the few moored time series of \(C_{p}\), \(b_{bp}\) and chlorophyll extending over several months in an open ocean region. Interpretation of data sets such as this will become increasingly important as these deployments become more commonplace via ocean observing systems. Moreover, these data contribute to the understanding of biological-physical coupling in a biogeochemically important, yet poorly studied region.


I. Introduction

[2] The Labrador Sea, located between Greenland and Canada, has a disproportionately large impact on global ocean physics and biogeochemistry relative to its size. It is an important region of deep water formation, and experiences an intense phytoplankton bloom that peaks most years in June or July. This bloom makes the region a significant sink of atmospheric \(\text{CO}_2\), while deep water formation efficiently transfers the anthropogenic \(\text{CO}_2\) to the deep ocean [DeGrandpre et al., 2006]. The biological activity and air-sea \(\text{CO}_2\) exchange at the surface determine the chemical properties of waters that are sequestered for millennia, in contrast to other sink regions which return sequestered inorganic carbon to the surface on decadal time scales.

[3] Despite its biogeochemical significance, the Labrador Sea has been the topic of relatively few biological studies. Cota et al. [2003] investigated the link between bio-optical properties and satellite chlorophyll observations during fall and spring, and discovered that global algorithms tend to underestimate chlorophyll at high latitudes. In a modeling study, Tian et al. [2004] showed that during the intense spring/summer bloom, \(C\) export was almost entirely due to sinking particulate organic carbon (POC). This was in contrast to the period of deep winter convection, when the model showed that the dissolved organic carbon (DOC) pool contributed significantly to the annual export flux of carbon. While Tian et al. [2004] did not discuss the relationship between biogenic export and air-sea \(\text{CO}_2\) exchange, Martz et al. [2009] calculated that during the bloom, 47 mmol C m\(^{-2}\) d\(^{-1}\) was assimilated into biomass and was rapidly exported, and that all of the exported carbon was likely replaced with atmospheric \(\text{CO}_2\) prior to the onset of deep mixing in autumn and winter.

[4] This paper describes the biological component of a moored process study designed to understand the air-sea
flux of CO\textsubscript{2}, and the surface processes controlling it, during
the Labrador Sea spring/summer bloom of 2004. Moored
measurements of fluorescence-based chlorophyll (F\textsubscript{chl})
and particulate organic carbon (POC, from beam attenuation
(C\textsubscript{p}) and particulate backscatter (b\textsubscript{bp})), and a biological
model describe the bloom dynamics. With these data, the
goals of the paper are to (1) quantify bloom dynamics
(2) determine whether bio-optical data can be used to
describe changes in the phytoplankton community over the
course of the bloom, and (3) compare the in situ data to their
satellite equivalents. Goal 1 is important because of the
region’s status as a globally significant carbon sink that has
received relatively little attention in terms of focused pro-
cess studies. It addresses interannual variability and factors
limiting the bloom at its peak. Goal 2 is relevant to nascent
ocean observing systems, because it provides an example of
interpreting changes in pigments and particle size spectra.
Goal 3 quantifies the accuracy of satellite measurements for
high latitude systems. The carbon budget of the mixed layer,
including particulate export and air-sea CO\textsubscript{2} exchange, is
described in detail by Martz et al. [2009].

2. Methods

2.1. Climatological Chlorophyll Variability
and the Timing of the Deployment

From its initiation at about 40°N in March, the North
Atlantic spring bloom migrates northward at approximately
20 km d\textsuperscript{−1} [Siegel et al., 2002], reaching the Labrador Sea in
May or June (Figures 1 and 2). The deployment occurred
at 53°N 49°W, at the southern edge of what is commonly
referred to as the Labrador Sea, but in a region of active
convection and therefore deep water formation. In their
analysis of 2023 Argo float profiles from the Labrador Sea,
Irminger Sea and the region south of Greenland, Vage et al.
[2009] observed their deepest mixed layer depth (1800 m)
at a location 60 km from where our mooring deployment
ended (see below), near the location of Ocean Weather
Station Bravo. The deployment was timed to capture the peak
of the bloom and its impact on ocean chemistry and air-sea
gas exchange (Figure 2). Satellite data summarized by
Siegel et al. [2002, Figure 1] suggest that the mean timing of bloom
onset at the mooring location in this study is approxi-
mately May 31. Our summary of satellite observations from
Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and
Moderate Resolution Imaging Spectroradiometer (MODIS)
agrees with this date within the uncertainties associated with
interannual variability, but an earlier, smaller bloom pre-
ceding the June–July bloom is common (Figure 2).

2.2. Mooring Deployment

The deployment consisted of two moorings: a tether
float that was anchored to the seafloor to which instruments
were attached at 9, 15, 20 and 35 m, and the air-sea inter-
geraction spar (ASIS) buoy [Graber et al., 2000], attached to
the tether buoy with 60 m of wire rope, on which the 3
and 5 m instruments were mounted. The moorings were
deployed on June 12 and 13 2004. On June 30 both the tether
buoy and ASIS began to drift for unknown reasons (Figure 1)
[see also Martz et al., 2009, Figure 1]. The buoys remained
connected and drifted together in a northerly direction ending
up at 55°N 49°W, about 250 km from the deployment site,
where they were recovered on August 25 2004.

The suite of bio-optical and chemical instruments
deployed on the moorings was as follows (see also Table 1
adapted from Martz et al. [2009]). At 3, 9 and 15 m, chlo-
orphyll fluorescence and particulate backscatter (b\textsubscript{bp}) were
measured with WETLabs ECO-FLR (optical sensor for
measuring fluorescence) and ECO-VSF (optical sensor for
measuring backscatter at three angles) sensors, respectively.
The ECO-FLR excitation and detection wavelengths were
470 and 695 nm, respectively, and the ECO-VSF light
source was 470 nm. Fluorescence at 5 and 20 m was measured

Figure 1. (a) The 2004 summer (June 21 to September 20)
MODIS chl (mg m\textsuperscript{−3}) for the North Atlantic, showing the
trajectory of the ASIS mooring and the ‘in bloom’ CTD sta-
tion that was performed on the homeward leg of the deploy-
ment cruise. (b) As in Figure 1a but showing the 2004
summer chl as an anomaly calculated relative to the 2002
to 2009 summer climatology.
with Chelsea fluorometers (excitation 430 nm, detection 685 nm), while beam attenuation \((C_p)\) at 9 and 35 m was measured with WETLabs 0.25 m path length CStar (WET Labs optical sensor for measuring beam attenuation) transmissometers (660 nm). A 300 kHz ADCP (Teledyne RDI) was mounted at 9 m on the foot of ASIS, looking downward. This frequency is very close to the maximum backscatter intensity for copepods \([\text{Lavery et al.}, 2007]\), and the data were used to qualitatively assess zooplankton dynamics.

Argo profiles that occurred within 300 km of the mooring were extracted and used to quantify the mixed layer depth \((Z_{\text{mld}})\). The \(Z_{\text{mld}}\) was calculated using two criteria: (1) the depth at which temperature was 0.2°C cooler than the shallowest (surface) temperature and (2) the depth at which density \(\left(\sigma_t\right)\) was 0.03 kg m\(^{-3}\) greater than the surface value. For the duration of the deployment (June 12 to 25 August 2004) there were 18 profiles that satisfied the distance from mooring criterion and for these profiles, the two \(Z_{\text{mld}}\) criteria differed by 2 m or less, except for one profile in June for which the difference was 10 m. The average of the two \(Z_{\text{mld}}\) values is plotted in Figures 2 and 3.

### 2.3. Optical Measurements of Chlorophyll and Particulate Organic Carbon

Conductivity-temperature-depth (CTD) profiles were performed at the mooring location before and after deployment. Chlorophyll fluorescence and \(C_p\) data from the instruments on the CTD were compared with the same data from the mooring, and discrete samples for chlorophyll (chl) and POC were taken from up to 12 depths in the upper 100 m. Discrete chl samples were filtered and extracted in 90% acetone according to standard techniques \([\text{Holm-Hansen et al.}, 1965; \text{Lorenzen}, 1966]\), then analyzed in a Turner 10 AU fluorometer that had been previously calibrated with chl standards from Turner Designs (Sunnyvale, California). There was significant daytime inhibition of fluorescence in the mooring time series, so the conversion from fluorescence to fluorescence-based chlorophyll \((F_{\text{chl}})\) was done using the mean fluorescence from 23:00 to 01:00, local time each night, to produce one \(F_{\text{chl}}\) measurement per day. Profiles of extracted chl at 1, 10, 15 and 20 m (and deeper but these are the important depths for \(F_{\text{chl}}\) calibration) were obtained before and after deployment (June 12 and 13 2004). These two profiles were averaged and compared with the 23:00–01:00 fluorescence value for the first night of each fluorometer’s deployment. That is, the \(F_{\text{chl}}\) calibration is essentially a one point calibration, which is the standard factory technique (http://www.wetlabs.com) except that our calibration was performed with in situ chl concentration, not a synthetic solution intended to mimic chl. We acknowledge that the one point calibration is not ideal, but the two chl profiles (June 12 and 13 2004) were similar and the mooring fluo-

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**Figure 2.** (a and b) The annual cycle of chl in the vicinity of the mooring deployment based on SeaWiFS (8 day, 9 km spatial resolution) and MODIS Aqua (8 day, 4 km spatial resolution) data from 2003 to 2008. In Figures 2a and 2b the shaded envelope represents the mean seasonal cycle plus and minus one standard deviation. The solid line with filled circles represents the time series for 2004, the year of the mooring deployment. In Figures 2a and 2b the mean annual envelope and the 2004 time series were calculated from a region surrounding the mooring that was \(16 \times 16\) pixels for SeaWiFS and \(32 \times 32\) pixels for MODIS Aqua (i.e., \(1.3^\circ \times 1.3^\circ\) in each case). (c and d) The effects of changing the size of the averaging box around the mooring. The legend defines the size of the averaging box in units of pixels. Also plotted is the time series of mixed layer depth from nearby Argo floats, see text for details. The error bars represent the range of mixed layer depths calculated from the temperature and density criteria, and the value plotted is the mean of the two. Vertical lines indicate the deployment and recovery of the mooring.
rescence data for the first few days of deployment showed little variability. The use of the near-midnight fluorescence data to derive Fchl has minimized the effect of the strongest variability in the fluorescence/chl ratio, but it must be acknowledged that cellular pigment concentrations, cell division and nutrients, among other factors, can influence this ratio [Cullen, 1982], which could impact the accuracy of our Fchl estimates. Thus, it is probably more realistic to interpret our Fchl time series as a relative index of chlorophyll rather than an accurate measurement.

\[ C_p = \frac{-\ln(Tr)}{x} \]

where x is the instrument path length (0.25 m) and Tr (transmittance) = \( \frac{V_{sig} - V_{dark}}{V_{ref} - V_{dark}} \). In this equation, \( V_{sig} \) is the voltage measured by the instrument and \( V_{ref} \) and \( V_{dark} \) are calibration coefficients supplied by the factory. Discrete samples for POC were filtered and preserved using methods similar to those used by Gardner et al. [2003]. The samples were analyzed postcruise by the Marine Sciences Institute Analytical Lab at the University of California Santa Barbara. POC and \( C_p \) were related by the linear equation

\[ \text{POC (mmol m}^{-3}\text{)} = 34.96 \times C_p \text{ (mmol m}^{-2}\text{)} \] with a correlation, \( r = 0.92 \). This slope compares favorably with those obtained by Gardner et al. [2003] for the Joint Global Ocean Flux Study North Atlantic Bloom Experiment (JGOFS NABE; 25.39 mmol m\(^{-3}\)) and the equatorial Pacific JGOFS (36.97 mmol m\(^{-3}\)).

[11] Calibration samples were not obtained from the recovery cruise so no postdeployment calibration was attempted. In coastal mooring deployments, we routinely use two criteria to diagnose biofouling: (1) increased variability in fluorescence and (2) failure to return to a baseline fluorescence value after a bloom event. Neither of these features were apparent in our fluorescence data, and the same was true for the \( C_p \) and bbp data. Moreover, no biofouling was present on the instruments when they were recovered. We therefore conclude that the data were not compromised by biofouling.

[12] Particulate backscatter (bbp) was calculated as follows. The raw counts from each of the three ECO-VSF instruments in the mixed layer and the 9 m transmissometer (Table 1) were compared in property versus property plots and time series. This comparison revealed that the factory dark offset for two of the three ECO-VSF instruments was about 10 counts too high (approximately 7%, or in terms of backscatter, 0.0035 m\(^{-1}\)). We adjusted the offsets and all three instruments were in better agreement with each other and with the 9 m transmissometer. The raw data from the ECO-VSF instruments were converted to the volume scattering function, \( \beta(\theta) \), at each of the three angles (100°, 125° and 150°) using the factory scale and adjusted offset (pure water) values. These corrected \( \beta(\theta) \) values were then multiplied by \( 2\pi \sin \theta \) to convert to a polar steradian area. A third order polynomial was fit to the three measured points and extrapolated in each direction to \( \pi/2 \) and \( \pi \) radians. The area under the polynomial curve was calculated and then multiplied by 1.013 according to the WET Labs manual. This calculation included a correction for pure water, but not salinity. We accounted for salinity according to Buiteveld.

Figure 3. Time series of (a) Fchl from the fluorometer on the mooring and chl from MODIS and SeaWiFS, (b) POC from the mooring, phytoplankton carbon (Cphyto multiplied by 3.33) derived from SeaWiFS data (the MODIS Cphyto data were almost identical) and mixed layer depth from the PWP model (ordinate axis inverted), (c) Fchl to beam attenuation ratio (Fchl/Cp) from the mooring and (d) particulate backscatter to beam attenuation ratio (bbp[470 nm]/Cp[660 nm]), also from the mooring. All mooring data are for the instruments at 9 m, almost always in the mixed layer.
et al. [1994] and M. Twardowski (WET Labs, unpublished application note, 2005). The resulting data represent only scattering due to particles, denoted bsp. This process is the same as that summarized by Boss et al. [2004], except that Boss’ salinity correction was based on Morel [1974].

[13] The mooring pCO2 data [Martz et al., 2009] and the satellite chl data (Figure 2) suggest that a small bloom occurred in May, before the more intense bloom that we observed at the mooring location in June–July (subsequently referred to as the ‘main bloom’). On the return transit southwards from the deployment in June, a CTD station was performed in the peak (as determined by underway chlorophyll fluorescence) of the northward advancing main bloom to obtain an estimate of the chlorophyll concentrations that might be expected at the mooring when the bloom arrived there. The near-surface CTD chlorophyll concentrations in the bloom and the FChl mooring measurements at the peak of the bloom (Figure 3) were both between 8 and 9 mg m\(^{-3}\). Both of these in situ measurements at the peak of the bloom are significantly higher than the corresponding SeaWiFS and MODIS chl in the region around the mooring (2 mg m\(^{-3}\); Figure 2). This means that (1) SeaWiFS and MODIS observations underestimated chl for our mooring deployment or (2) the bloom was more widespread than observed on the return transit (approximately 49°W, 51°N) than when it reached the mooring location at approximately 49°W, 53°N. The latter of these options is refuted by the satellite, mooring and in situ data. We extracted SeaWiFS and MODIS satellite chl data from the region surrounding the ‘in bloom’ CTD and there was no difference between the values observed there as the bloom passed and those observed when the bloom reached the mooring location. Archival data from Fisheries and Oceans Canada, Newfoundland (P. Pepin and G. Maillet, personal communication, 2004), confirm that chl concentrations approaching 10 mg m\(^{-3}\), as measured during the cruise and by the moored fluorometers, do occur during the peak of the bloom. The discrepancy between the satellite and in situ measurements is not due to a vertical gradient in chl. The first optical depth (the part of the water column observed by satellite ocean color sensors) is shallower than 10 m for chl greater than about 1.0 mg m\(^{-3}\) (our entire data set), and chl in the upper 10 m is uniform, or if anything, higher at the surface than at 9 m, for which the data are presented in Figure 3. Thus we conclude that the satellite sensors underestimated chl in this high latitude region, perhaps due to taxon-specific bio-optical properties. Cota et al. [2003] showed that diatoms in the Labrador Sea had ~1.5 times lower chl-specific absorption due to pigment packaging, related to growth at low irradiance and/or sun angle. This low absorption could lead to satellite underestimation of chl.

[14] Time series of the 8 day mean chl surrounding the mooring location were constructed from MODIS 4 km and SeaWiFS 9 km level 3 data using a variable box around the mooring location (4 \times 4, 16 \times 16 and 64 \times 64 pixels for SeaWiFS; 8 \times 8, 32 \times 32 and 64 \times 64 pixels for MODIS; Figure 2). There was very little difference between these time series, indicating that spatial resolution and the spatial averaging window do not significantly affect calculated mean chl. For comparison of satellite data with surface data from a profiling float, Boss et al. [2008] found the best agreement for a radius of about 7 km (very close to 0.1° longitude at this latitude). The size of the averaging box in that case was likely more important because the profiling float data are more sporadic in space and time. The distance between the ‘bloom’ and ‘mooring’ locations (Figure 1) was approximately 275 km and the time difference between the initiation of the bloom at the two locations was about 2 weeks, consistent with the 20 km d\(^{-1}\) northward propagation speed of the bloom described by Siegel et al. [2002]. Note that this propagation is not an advective process. It is a northward migration of the bloom concomitant with the changing seasons.

2.4. Biological Model

[15] The nutrient-phytoplankton-zooplankton (NPZ) model of Marra and Ho [1993] was integrated into the Price-Weller-Pinkel (PWP) mixing model [Price et al., 1986]. The PWP-NPZ mixing was identical to the PWP-CO2 model described by Marra et al. [2009]. All biological forcing parameters were taken directly from Marra and Ho [1993], as follows. Phytoplankton growth followed a cell quota model [Caporion, 1968] with a maximum phytoplankton growth rate, μmax = 1.0 day\(^{-1}\) and a minimum cell quota for N, KQ = 0.2 mmol. Nutrient uptake followed Michaelis-Menten kinetics with a half saturation for nitrate uptake, K\(_n\) = 0.2 mmol m\(^{-3}\) and a maximum uptake rate, V\(_m\) = 0.9 mmol m\(^{-3}\) d\(^{-1}\). Zooplankton grazing was parameterized according to the Ivlev function [Franks et al., 1986] with a maximum grazing rate, R\(_{mg}\) = 0.5 day\(^{-1}\) and an Ivlev constant, A = 0.9 mmol m\(^{-3}\). Phytoplankton growth was light dependent with an irradiance for maximum growth rate, E\(_{max}\) = 50 μEin m\(^{-2}\) s\(^{-1}\). The remaining necessary constants were the zooplankton regeneration coefficient (γ = 0.3 day\(^{-1}\)), the zooplankton loss coefficient (g = 0.15 day\(^{-1}\)) and the phytoplankton loss coefficient (m = 0.15 day\(^{-1}\)). The model was initiated with the following mixed layer averaged concentrations: 6.0 μM nitrate, 0.5 μM N phytoplankton and 0.04 μM N zooplankton.

3. Results

[16] The results and discussion are structured around the three major themes from the introduction: (1) Bloom dynamics, (2) the efficacy of bio-optical data for describing changes in the phytoplankton community over the course of

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*Adapted from Martz et al. [2009]. PAR stands for photosynthetically active radiation. Yes means successful operation and No means instrument failure/ unreliable data.*

\(^a\)Data until year day (YD) 225.

\(^b\)Data until YD 222.

\(^c\)Questionable data replaced.

\(^d\)Data until YD 231.

\(^e\)Data until YD 213. Deployment and recovery were year days 164 and 239, respectively.
the bloom, and (3) comparison of in situ data with satellite equivalents.

3.1. Bloom Dynamics

F_{chl} started increasing on about June 15, several days after the mooring deployment, concomitant with a shoaling of the mixed layer (Figure 3). Analysis of satellite data and mixed layer depths from Argo floats in the vicinity (Figures 2c and 2d), show that the mixed layer first shoaled to about 35 m in early May. This earlier shoaling also coincided with a smaller spring bloom that is visible in the 2004 satellite chl time series data in Figure 2. The satellite chl climatologies also suggest that an earlier spring bloom before June is common for the region. Therefore, we conclude that the mooring deployment captured the majority of the spring bloom, but not its initial onset. Unlike Siegel et al. [2002], we are not attempting to pinpoint the precise date of bloom initiation so we do not adopt a quantitative definition of bloom onset. We simply refer to the bloom as the initiation of an obvious rapid increase in F_{chl}.

In the model, a decline in observed POC inventory after about July 3 occurs within a few days of the exponential increase in zooplankton (Z), which begins on July 5 and continues for one week, suggesting that zooplankton grazing of phytoplankton is responsible for the declining POC inventory observed by our sensors (Figure 4). Note that Martz et al. [2009] found that the POC standing stock represents only a small fraction of the total carbon (see their Table 2). That is, over the course of the deployment, the modeled POC inventory increased by only 38 mmol C m$^{-2}$. In their Figure 9, remineralization of all of the accumulated POC accounts for only a small increase in DIC, relative to the DIC drawdown during the bloom. Modeled phytoplankton biomass continues to increase for about 5 days following the onset of the zooplankton increase. This increase is not evident in the observed F_{chl} concentrations, indicating that the in situ zooplankton response and/or nutrient depletion occurred much faster than in the model. Comparison of the POC and F_{chl} inventories (compare the shape of the curves in Figures 3a and 3b after July 2) [also see Martz et al., 2009, Figure 7a] reveals a more rapid decrease in the F_{chl} inventory during this period, indicative of a decrease in F_{chl}/C_{p} due to photoadaptation. After July 28, the model projects that zooplankton and phytoplankton reach near steady state, and this is reflected in the POC inventory. As the bloom is ramping up, the time series of modeled phytoplankton tracks observed POC and F_{chl} (Figures 3 and 4). Therefore, we conclude that the POC pool is dominated by phytoplankton biomass during the second half of June, after which heterotrophs make an increasing contribution.

The model was also run with 5.0 $\text{mM}$ initial nitrate, cf 6.0 $\text{mM}$ initial nitrate depicted in Figure 4. The purpose of this run was to test the sensitivity of the model to initial conditions and to account for the possibility that more N drawdown than we anticipated had occurred prior to mid-June. This extra drawdown seems likely given the small May bloom seen in the satellite data (Figure 2) and the relatively low pCO$_2$ concentrations (325 $\mu$atm) at the beginning of the mooring deployment. The effect of this lower initial N on the timing and magnitude of the modeled phytoplankton bloom and the zooplankton response was minimal. The maximum standing stock (in units of N) changed by less than 10% and the timing of the bloom was delayed by a day.

The ADCP acoustic backscatter (ABS (dB)) data are interpreted as indicative of zooplankton biomass [Wade and Heywood, 2001], and as mentioned in the methods, the 300 kHz frequency of the ADCP instrument is well suited to detecting copepods. The modeled and observed zooplankton biomass data are compared in Figure 5. The most significant features of these data are (1) elevated then decreasing zooplankton biomass prior to and during the rise of the bloom,
followed by (2) increasing zooplankton biomass after the peak of the bloom, and (3) strong diel vertical migration throughout.

3.2. Bio-optics and Phytoplankton Community Composition

[21] The time series of $F_{\text{chl}}$ and POC (Figure 3) are correlated ($r = 0.92$), documenting the rise and decline of the bloom. We have included the time series of $F_{\text{chl}}/C_p$ (Figure 3c) because of its proposed relationship to phytoplankton physiology [Behrenfeld and Boss, 2003] (also see section 4). Since $C_p$ is linearly related to POC, and assuming that $C_{\text{phyto}}$ can be approximated as a constant proportion of POC (30%) [Behrenfeld et al., 2005], the $F_{\text{chl}}/C_p$ time series is an indicator of changes in the chl to carbon ratio of the phytoplankton community. Likewise we have shown the time series of $\text{b}_{\text{bp}}[470 \text{ nm}]/C_p[660 \text{ nm}]$ (Figure 3d) to investigate the temporal variability in particle composition. The $\text{b}_{\text{bp}}[470 \text{ nm}]/C_p[660 \text{ nm}]$ time series shows variability that is the inverse of $F_{\text{chl}}/C_p$, an initial increase then a decrease near the initiation of the bloom and an increase as the bloom declines, but the postbloom peak occurs earlier compared to the corresponding minimum in $F_{\text{chl}}/C_p$. The information that these dynamics convey regarding particle size and bloom dynamics will be explored in the discussion.

[22] We compared our $\text{b}_{\text{bp}}/F_{\text{chl}}$ data with a recent compilation of similar measurements spanning a wide range of productivity regimes from the South Pacific, Bering Sea and the Benguela upwelling system (Figure 6) [Huot et al., 2008]. The thick solid line is the linear fit to our data, while the thin solid line is the linear fit to the Huot et al. [2008] data set and the dashed lines are an approximate envelope of their data. This shows that our data are within the bounds of previous measurements, or slightly on the high end for $\text{b}_{\text{bp}}$ during the decline of the bloom (the data points that lie roughly along the upper bound line in Figure 6a are from July 15 to 29). The slope of the relationship is the same for the onset and decline of the bloom, but the intercept is different. In the discussion these data are used to investigate whether they may convey information on particle size distribution and species composition or serve as a proxy for export (Figure 6c).

3.3. Remotely Sensed Versus In Situ Measurements

[23] There was significant disparity between $F_{\text{chl}}$ and satellite chl estimates during the peak of the bloom, as described above, yet they agreed well at the beginning and end of the data set (Figure 3a). In contrast, the satellite and in situ estimates of carbon agree well. The $C_{\text{phyto}}$ data (Figure 3b) are derived by the Behrenfeld group at Oregon State University, using the Garver–Siegel–Maritorena (GSM) algorithm [Maritorena et al., 2002] applied to SeaWiFS observations. The values have been multiplied by 3.33 before plotting with the mooring POC data to account for the assumption that $C_{\text{phyto}} = 30\%$ of total POC [Behrenfeld et al., 2005].

4. Discussion

[24] The most detailed bio-optical observations to date of the spring–summer bloom in the Labrador Sea have been presented. Despite the regional focus, these data have implications for future observations and interpretation in the context of ocean observing systems. Here, using the same
of presentation as the results, we elaborate on the bio-optical data, and discuss their importance in the context of satellite observations and global productivity algorithms. We compare the NPZ model with the bio-optical and ADCP time series and explain the temporal variability in these data. The mixed layer carbon budget, including particulate export and air-sea CO₂ exchange, complements these analyses and is described with both observations and a model by Martz et al. [2009].

4.1. Bloom Dynamics

[25] When discussing the bloom we are referring to the spring-summer increase in chl, but note that Behrenfeld [2010] and Boss and Behrenfeld [2010] have recently suggested an alternative interpretation based on both carbon and chl variability prior to spring stratification. Our in situ data show that the 2004 bloom in the southern Labrador Sea was characterized by chl concentrations at the upper end of previous in situ observations by Fisheries and Oceans Canada, Newfoundland (P. Pepin and G. Maillet, personal communication, 2004). The satellite data suggest that 2004 chl briefly exceeded the mean +1 standard deviation (Figure 2). Despite the fact that the satellite data seem to have underestimated chl (see section 4.3), they provide important information on the timing of the peak chl concentrations. In the Labrador Sea, based on the entire SeaWiFS and MODIS data sets, the spring bloom peaks in June or early July, and in this regard 2004 was typical (Figures 2 and 3; in one year the main bloom peaked as late as the end of July). There are instances in the data record, including 2004, of prebloom peaks as early as April. The satellite data for the entire North Atlantic for 2004 (data not shown) indicates that the timing of the bloom elsewhere was similar to the climatology presented by Siegel et al. [2002]. Comparison of the 2004 North Atlantic summer chl image with the MODIS Aqua summer climatology (2002 to 2009; Figure 1) shows that in 2004, satellite chl was above average by more than 1 mg m⁻³ in Davis Strait and the Labrador Sea.

[26] Since POC is derived from C_p in a linear fashion, Fchl/C_p (Figure 3c) is also an index of the chl to carbon ratio, and it suggests variability in photoacclimation of the phytoplankton population. That is, as the bloom developed, the

Figure 6. The relationship between particulate backscatter, Fchl and carbon export. (a) Particulate backscatter as a function of Fchl for daily averaged data. Shading is date, 2004, to depict changes in the relationship as the bloom progressed. The thick solid line is the linear fit to the data. The thinner solid line is the fit from Huot et al. [2008] and the dashed lines represent the approximate envelope of their data. Note the log-log scale. (b) Time series of b_bp/Fchl and Fchl, to show changes in the ratio in the context of the bloom development and demise. (c) The 7 day running average of combined POC and PIC export as calculated by Martz et al. [2009, Figure 7c]. Positive values indicate net export of particulate carbon from the upper 35 m.
attenuation of incoming solar radiation increased. In order to capture sufficient light for photosynthesis, the pigment content of mixed layer phytoplankton cells increased, while we assume that the carbon per cell did not change significantly. This phenomenon has previously been well documented in situ and in cultures [e.g., Geider, 1987]. Variability in the carbon to chl ratio of the phytoplankton community caused a twofold increase in $F_{\text{chl}}/C_p$ from about 5 to 10 mg m$^{-2}$ as the bloom developed, followed by a decrease to about 2.5 mg m$^{-2}$ at the termination of the bloom and then a return to a relatively stable value around 5 mg m$^{-2}$. Changes in $F_{\text{chl}}/C_p$ could also be due to phytoplankton accounting for a variable proportion of POC. For instance, the decreased $F_{\text{chl}}/C_p$ after the bloom could be caused by either reduced self shading or an increase in the population of microheterotrophs. There is some evidence for the latter in both the model results [Martz et al., 2009] and in the comparison between satellite C$_{\text{phyto}}$ and in situ POC. Using the 30% assumption, satellite C$_{\text{phyto}}$ is multiplied by 3.33 for comparison with in situ POC in Figure 3b. Before the peak of the bloom, there is very close correspondence between the two time series suggesting that this assumption is valid. After the peak of the bloom, the satellite data underestimate POC, indicative of a greater contribution from heterotrophs and a $<$30% contribution by phytoplankton to total POC. [27] The term microheterotrophs is used above to refer to small grazers such as dinoflagellates. We use the temporal variability in acoustic backscatter (ABS) shown in Figure 5 to document the variability in larger zooplankton such as copepods. The observed ABS can be explained in the context of previous observational studies of zooplankton dynamics in the North Atlantic. A detailed time series of observations from weather station M in the Norwegian Sea in 1997 [Niehoff et al., 1999] documented a large increase in female copepods (Calanus finmarchicus) prior to the spring phytoplankton bloom. In that location, the 1997 spring bloom began on about May 10 and peaked in late May. The abundance of female Calanus peaked on three separate occasions during April prior to the beginning of the bloom, but egg production was low. Approaching the beginning of the bloom, the abundance of females as a proportion of the copepod population increased slightly and egg production also increased. At the peak of the bloom and thereafter, females became rare, egg production decreased and the zooplankton population was dominated by copepodite stage V, which is the stage that commences diapause, prior to the reproductively capable copepodite stage VI. [28] While Niehoff et al. [1999] studied copepod dynamics on the opposite side of the North Atlantic basin from this study, the zooplankton populations and their dynamics are very similar. Planque and Batten [2000], using continuous plankton recorder data from 1958 to 1997 showed that the southern Labrador Sea and the region off Norway are the two areas in the North Atlantic with the highest abundance of Calanus finmarchicus. Head et al. [2003] showed that Calanus finmarchicus accounted for 80% of the abundance of large copepods in spring and summer in the Labrador Sea and Wiebe [2001] described this region as a center of distribution for the species in the western North Atlantic. Planque and Batten [2000] also described the temporal variability in Calanus for the Labrador Sea, with a small peak in abundance before the phytoplankton bloom, and a larger peak coinciding with the bloom. Therefore, the peak in zooplankton biomass that was observed prior to the bloom (June 15; Figure 5) was probably due to females coming to the surface to spawn after emerging from diapause at several hundred meters. As the phytoplankton bloom matured, and based on the previous studies cited above, the population structure of the copepods likely transitioned to almost exclusively copepodite stage V, which dominated the second peak in biomass around July 8 and 9 and grazed on the bloom. We suggest that as the phytoplankton food source for these copepods declined, so did their numbers. Note that within this general pattern of abundant spawning females followed by the onset and decline of a copepodite population feeding on the phytoplankton bloom, there are periods of ephemeral decline in copepod biomass, notably on July 18 and 30. At least some of this is likely caused by horizontal advection of a patchy distribution. [29] The NPZ model (Figure 4) described the peak in phytoplankton biomass very well, and also captured the postbloom increase in zooplankton, with some discrepancy in the event timing based on comparison with the ADCP record (Figure 5). The prebloom increase in zooplankton was not observed at all in the zooplankton model output, because the model only represents consumers, not breeding females, and was initialized with very low zooplankton initial concentrations (0.04 $\mu$M N zooplankton). Note also that the model does not predict a complete depletion of nitrate (Figure 4). Körtzinger et al. [2008] did observe exhaustion of nitrate, and a much slower recovery in nitrate concentrations than suggested by the model. The DIC observations from our deployment [Martz et al., 2009] do not suggest any significant, rapid remineralization, so we conclude that export dominated the removal of POC from the mixed layer [see Martz et al., 2009, Table 2]. [30] Martz et al. [2009] calculated DIC consumption of approximately 2000 mmol C m$^{-2}$ during the development of the bloom. For Redfield consumption of N and C, this would be accompanied by a concomitant drawdown of 302 mmol N m$^{-2}$. However, Körtzinger et al. [2008] documented departure from Redfield behavior in their observations such that the C:N uptake ratio was 11, equivalent to 181 mmol N m$^{-2}$ drawdown for 2000 mmol C m$^{-2}$. For a mixed layer of 35 m, depletion of our initial 6 mmol m$^{-3}$ nitrate equates to a consumption of 210 mmol N m$^{-2}$ within the bounds of the two extremes just cited. So while the NPZ model provided some insight into the timing, it underestimated the magnitude of the bloom and may have incorrectly suggested that grazing pressure rather than nutrient limitation was the cause of bloom demise. 4.2. Bio-optics and Phytoplankton Community Composition [31] Mooring and CTD transmissometer $C_p$ data from the first few days of deployment were compared with each other and with discrete POC samples. The correlation between $C_p$ and extracted POC was 0.92, and the correlation between the high resolution (15 min) colocated 10 m $C_p$ and b$_{bp}$ data was 0.95 (not shown). However, there exists small variability in the ratio $b_{bp}[470 \text{ nm}]/C_p[660 \text{ nm}]$ (Figure 6), which can be interpreted in the context of the biogenic particle size spectrum. Interpretation of this kind is hampered by our lack of floristic samples, and it is likely that
particle morphology contributes to changes in $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$, but here we focus on size. To overcome this limitation, future deployments could include automated water samplers.

[32] We measured $b_{bp}$ at 470 nm and $C_{p}$ at 660 nm. The backscattering ratio, $b_{br}$, is the ratio of total to particulate only backscatter ($b_{bp}/b_{bp}$). If we assume that $b_{bp}$ is constant as a function of wavelength (as observed in both field and laboratory studies [e.g., Whitmire et al., 2007, 2010]), and that CDOM absorption is negligible at 660 nm, then it follows that $b_{br} = b_{bp}[470\text{ nm}]/b_{bp}[470\text{ nm}] = b_{bp}[660\text{ nm}]/b_{bp}[660\text{ nm}] = b_{bp}[660\text{ nm}]/C_{p}[660\text{ nm}]$, from which: $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}] = b_{br} \times b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$.

[33] Changes in $b_{br}$ in the ocean are often dominated by compositional changes. Low values are associated with organic material while high values with inorganic material [Twardowski et al., 2001]. Changes in $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}] \sim C_{p}[470\text{ nm}]/C_{p}[660\text{ nm}]$ are most influenced by the mean size of the underlying particle population [Boss et al., 2001], increasing with decreasing size (ignoring second order effects due to changes in the relative contribution of absorption to attenuation at 470 nm). Assuming that composition changes are small near the surface, consistent with open ocean observations of $b_{br} \sim 0.01$ [Whitmire et al., 2007], size dynamics will dominate the variability of $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$.

[34] This concept is broadly consistent with the variability observed in the time series of $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$ (Figure 3d). The $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$ decreased rapidly at the beginning of the time series indicating an increasing fraction of diatoms that dominated the bloom. During the first half of July as the bloom was declining, there was a peak in modeled export, presumably of large diatoms, and a corresponding increase in $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$ as these large algal cells were removed. This period also corresponds with a decrease in zooplankton biomass (Figure 5b). In mid-July, $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$ decreased sharply and remained low for the rest of the deployment. This transition around July 18–20 also corresponded to a small increase in zooplankton biomass, which lends support to the idea that the large particles during this period of the record include zooplankton fecal material.

[35] It is also possible that changes in the particle index of refraction were responsible for the temporal variability in the $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$ time series. To definitively attribute the patterns to particle size distribution or refractive index would require more detailed spectral information, such as $b_{bp}$ at wavelengths in the red, in addition to our observations at 470 nm. This is an important point in the context of emerging bio-optical measurements from ocean observatories. Significant progress could be made in this area with further work on laboratory cultures [e.g., Whitmire et al., 2010] and bio-optical time series coupled to in situ sampling for floristics.

[36] Another desirable outcome from this data set would be a relationship between optical parameters and carbon export. Figure 6 shows the time series of 7 day running average modeled export flux (POC + particulate inorganic carbon (PIC)) from Martz et al. [2009] on the same time axis as the time series of $b_{bp}/F_{chl}$. To test for correlations with the optical data, we regressed the export data against $F_{chl}/C_{p}$ (Figure 3c), $b_{bp}/F_{chl}$ (Figure 6b) and $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$ (Figure 3d). Note that $F_{chl}/C_{p}$ and $b_{bp}/F_{chl}$ are almost the reciprocal of each other because of the close relationship between $b_{bp}$ and $C_{p}$. The correlation between export and $b_{bp}[470\text{ nm}]/C_{p}[660\text{ nm}]$ was very poor ($r = 0.12$). There was evidence of a linear correlation between export and both $F_{chl}/C_{p}$ and $b_{bp}/F_{chl}$, except for a subset of data from July 15 to 29 where export was relatively constant while $b_{bp}/F_{chl}$ increased and then decreased. This corresponds to the data in the plot of $b_{bp}$ versus $F_{chl}$ (Figure 6a) that lie almost on the maximum dashed line. If these data are excluded from the analysis, the correlation between export and $F_{chl}/C_{p}$ was 0.76 and the correlation between export and $b_{bp}/F_{chl}$ was −0.74. We interpret this as increases in the chl to carbon ratio, that is increased attenuation of solar radiation due to a dense bloom, are correlated with increased export. This relationship could be further explored using mooring deployments that include both surface bio-optics and sediment traps in a range of ocean provinces.

[37] The peak POC concentrations observed during the 2004 Labrador Sea bloom were about 35 mmol m$^{-3}$, 50% higher than the maximum of approximately 23 mmol m$^{-3}$ observed during JGOFS NABE in 1989. The Labrador Sea 2004 $F_{chl}$ concentrations were about 3 times higher than NABE. Figure 1 indicates that 2004 was an above average year in terms of satellite chl, but the magnitude of the chl anomaly translates to very high chl:C ratios. To convert total POC to phytoplankton C, Behrenfeld et al. [2005] used a factor of 0.3 (i.e., $C_{phyto} = 0.3 \times \text{POC}$), based on field studies suggesting that phytoplankton account for 24 to 37% of total POC. Applying this correction to the JGOFS NABE data gives $C_{phyto}$ ratios that range from 0.03 to 0.04. These are in the middle of the range of laboratory-derived $C_{phyto}$ values summarized by Behrenfeld et al. [2005, Figure 3], and at the upper end of the range for their satellite derived chl:$C_{phyto}$, which are closer to 0.01 for irradiance and temperature values typical of the North Atlantic. For our data set, $F_{chl}/C_{phyto}$ increased from 0.045 to 0.068 as the bloom peaked, before dropping to as low as 0.025 in late July. These values are extremely high given the ambient temperatures (6 to 12°C), but still lower than the highest observed in culture (0.13 to 0.16 for temperatures >25°C). The main cause of high chl:$C_{phyto}$ is increasing pigments per cell to compensate for increased attenuation that occurs in dense blooms. The extremely high $F_{chl}/C_{phyto}$ values observed here are again consistent with an anomalously intense 2004 Labrador Sea bloom.

[38] Behrenfeld and Boss [2003] introduced $C_{p}\cdotchl$, denoted $c_{p}^{*}$, as a potential diagnostic for phytoplankton physiology. This is the inverse of $F_{chl}/C_{p}$ plotted in Figure 6. They observed a positive correlation between $c_{p}^{*}$ and $P_{opt}^{\text{BB}}$ (the optimal biomass-normalized productivity) in their analysis of data sets from the Hawaii Ocean Time series (HOT), the Bermuda Atlantic Time Series (BATS), JGOFS Equatorial Pacific and JGOFS NABE. For JGOFS NABE, $c_{p}^{*}$ and $P_{opt}^{\text{BB}}$ were well correlated, but $c_{p}^{*}$ and chl did not covary as closely as they did in our data set (Figure 3). Again, it seems that the $F_{chl}/C_{p}$ time series is dominated by changes in pigment per cell as the bloom intensified, hence the high values during the onset and peak of the bloom, followed by a decrease as the bloom ends. In terms of magnitude, the $c_{p}^{*}$ numbers suggested by, or equivalent to, our $F_{chl}/C_{p}$ time series (Figure 3) are less than half the cor-
responding (midbloom) values reported by Behrenfeld and Boss [2003]. Hence, there is likely not a consistent relationship between chl/Cp and PB opt across the North Atlantic basin. However, the coherent relationships between Fchl, POC, b_{bp}[470 nm]/C_p[660 nm] and F_{ch4}/C_p depicted in Figure 3 suggest that these physiological proxies could be used for short-term prediction of bloom dynamics. For example, note the rapid changes in b_{bp}[470 nm]/C_p[660 nm] and F_{chl}/C_p just prior to the bloom onset.

4.3. Remotely Sensed Versus In Situ Measurements

[39] As described above, the satellite chl retrievals for this region can be significant underestimates compared to in situ data. Cota et al. [2003] suggested that the SeaWiFS OC4V4 algorithm underestimated chl by more than 1.5-fold for chl <10 mg m\(^{-3}\), and attributed this problem to pigment packaging and phytoplankton species composition. When the time series data in Figure 3a are plotted against each other, the in situ F_{chl} is approximately 2.6 times the satellite estimates. This argues for the development of regional algorithms where sufficient in situ validation data exist.

[40] Finally, the relevance of these data to recent carbon-based (as opposed to chl-based) satellite primary productivity algorithms should be discussed. Figure 7 shows the relationship between C_p and b_{bp} for our data set, with the data points shaded by F_{chl} concentration. C_p has been used for some time to obtain estimates of POC (for a review see Gardner et al. [2003]), but satellite ocean color is proportional to b_{bp}, not C_p. Carbon-based satellite productivity algorithms [Behrenfeld et al., 2005; Westberry et al., 2008] rely on accurate retrievals of C_{phyto} from b_{bp}, yet few validation data sets exist, and for the most part C_{phyto} is estimated simply as 30% of total POC. Using this assumption to convert satellite-based estimates of C_{phyto} to POC resulted in good correlation between the two time series (Figure 3b). The discrepancy during the demise of the bloom (C_{phyto} < POC) suggests that during that period, C_{phyto} accounts for less than 30% of POC, consistent with our assertion of an increased heterotrophic community. The correlation between C_p and b_{bp} for the daily average data in Figure 7 was 0.96 (compare 0.95 for the full resolution, 15 min data described in section 4.2), the slope was 75.57 and the intercept not significantly different from zero. This verifies that b_{bp} can be used as a proxy for POC, yet the variability around this linear fit provides information on particle size distribution and species composition (Figure 6 and section 4.2).

5. Conclusions

[41] This paper has presented a detailed mooring time series of bio-optical properties from the Labrador Sea, an important biogeochemical province which has received relatively little attention with regard to biological and bio-optical dynamics. The data show that the 2004 bloom was characterized by high chl compared to other years, which was reflected in the derived optical proxies such as F_{chl}; C_{phyto} and F_{ch4}/C_p. Temporality in these ratios and in b_{bp}[470 nm]/C_p[660 nm] was correlated with modeled carbon export and expected changes in phytoplankton community structure during the progression of the bloom. The high productivity for 2004, and the implied magnitude of carbon drawdown and export [Martz et al., 2009] should be taken into account when considering the interannual variability in the Labrador Sea carbon sink. As ocean observatories develop, the biological oceanography community needs to become more adept at the interpretation of bio-

Figure 7. Relationship between C_p and b_{bp} from the two instruments deployed together at 9 m. The equation of the linear fit is C_p = 75.57 \times b_{bp}, correlation, r = 0.96. The points are shaded by F_{chl} concentration (mg m\(^{-3}\)).


References


