Observations of pigment and particle distributions in the western North Atlantic from an autonomous float and ocean color satellite

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Abstract

   Profiling floats with optical sensors can provide important complementary data to satellite ocean color determinations by providing information about the vertical structure of ocean waters, as well as surface waters obscured by clouds. Here we demonstrate this ability by pairing satellite ocean color data with records from a profiling float that obtained continuous, high-quality optical data for 3 yr in the North Atlantic Ocean. Good agreement was found between satellite and float data, and the relationship between satellite chlorophyll and float-derived particulate backscattering was consistent with previously published data. Upper ocean biogeochemical dynamics were evidenced in float measurements, which displayed strong seasonal patterns associated with phytoplankton blooms, and depth and seasonal patterns associated with an increase in pigmentation per particle at low light. Surface optical variables had shorter decorrelation timescales than did physical variables (unlike at low latitudes), suggesting that biogeochemical rather than physical processes controlled much of the observed variability. After 2.25 yr in the subpolar North Atlantic between Newfoundland and Greenland, the float crossed the North Atlantic Current to warmer waters, where it sampled an unusual eddy for 3 months. This anticyclonic feature contained elevated particulate material from surface to 1000-m depth and was the only such event in the float's record. This eddy was associated with weakly elevated surface pigment and backscattering, but depth-integrated backscattering was similar to that previously observed during spring blooms. Such seldom-observed eddies, if frequent, are likely to make an important contribution to the delivery of particles to depth.

   Upper ocean processes have long been known to regulate the vertical distribution of phytoplankton and the dynamics of blooms and primary production (e.g., Riley et al. 1949; Sverdrup 1953; Denman and Gargett 1983; Smetacek and Passow 1990) through their influence on nutrient and light availability. Unfortunately, estimating primary production (PP) from shipboard observations at the temporal and spatial scales relevant to quantify the oceans' role in global elemental cycling and climate is not practical.

   Efforts have therefore been directed toward estimating PP from remotely observed ocean color. At this time, however, remotely sensed ocean color alone cannot provide sufficiently accurate estimates of phytoplankton standing stocks and PP in the upper ocean. The primary limitations are (1) no consensus exists regarding appropriate algorithms for calculating PP and associated uncertainties, (2) ocean color data provide only surface observations, so that

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estimates of subsurface distributions must rely on poorly constrained assumptions, (3) satellites chronically undersample cloudy regions, and (4) the atmosphere provides nearly 95% of the signal retrieved by the satellite, so very accurate atmospheric correction schemes are required for reliable estimates of water-leaving radiance. Since any biases in estimated PP and algal standing stock directly affect downstream estimates of oceanic carbon budgets and fluxes, reducing uncertainties in ocean-color-based algorithms will directly improve quantitative characterizations of global biogeochemical processes.

Profiling floats measuring physical parameters such as temperature and salinity have been in operation since the late 1990s and are part of an international observation network (Argo, e.g., Gould et al. 2004). However, very few profiling floats have been fitted with sensors that monitor the ocean's biogeochemistry. Recent effort has been devoted to pushing for the addition of oxygen sensors to the Argo floats (Körtzinger et al. 2006). The float described in this paper was equipped with optical sensors capable of providing estimates of the standing stock of particles and phytoplankton chlorophyll *a* (Chl *a*) pigment.

Optical properties such as the diffuse attenuation coefficient and beam attenuation have been previously measured with profiling floats (Mitchell et al. 2000; Bishop et al. 2002, 2004) to investigate the dynamics of phytoplankton and particulate organic materials in the upper ocean for periods of up to 18 months (Bishop et al. 2004). Bishop et al. (2002) used dusk-to-dawn changes in beam attenuation to estimate growth rates of phytoplankton in the upper ocean and related those rates to dust deposition events in the North Pacific.

Here we showcase the use of a profiling float to routinely obtain observations of upper-ocean hydrographical and optical properties that can be linked to ocean color measurements, as would be possible if such sensors were incorporated into an Argo-like program. In addition to measuring algal and particulate carbon parameters throughout the year, such floats provide measurements in cloudy conditions and can be used to interpolate missing remotely sensed data. The floats also provide distributions of biogeochemical parameters as a function of depth. Together with physical data collected by float and satellite sensors, some links between upper ocean dynamics and biogeochemistry are studied.

Materials and methods

A Webb Research APEX float was fitted with a Sea-Bird Electronics SBE41 conductivity–temperature–depth (CTD) and a single-prototype, flat-faced digital WET Labs hockey-puck-sized sensor package that included two sensors: one measuring side scattering at 880 nm (WET Labs light-scattering sensor [LSS], e.g., Baker et al. 2001) and the other measuring Chl *a* fluorescence (470 nm excitation, 680 nm emission, analogous to the commercially available WET Labs ECO fluorometer). The LSS was chosen because it was deemed to be the most sensitive single-faced scattering sensor available at the time and it had the ability to provide estimates of mass concentration

of particles in the deep ocean with an accuracy similar to that of beam transmissometers (Baker et al. 2001). Chlorophyll fluorescence provides a proxy for chlorophyll concentration and standing stocks of phytoplankton biomass (Cullen 1982), and scattering provides a proxy for total particulate mass and particulate organic carbon (Baker et al. 2001; Stramski et al. 2008).

The CTD was mounted at the top of the float and the optical package was mounted near the bottom, facing approximately 45° outward from the downward direction to avoid reflections from the float and sedimentation of particles onto the sensor face. An oxygen sensor was also deployed on the float but failed within 6 months of launch; hence, O_2 data are not reported here. Sensors were integrated into the float using a Sea-Bird Electronics Apf9a controller. Before launch, the float and sensors were tested for pressure effects and endurance in a pressure tank simulating 50 dive cycles to 1200 m, with data recorded throughout.

Fluorometer calibration—The chlorophyll fluorescence sensor was calibrated in the lab by the manufacturer with a suspension of spinach chloroplasts and by us with a diatom culture at the University of Maine. Two vicarious field calibrations were also performed. The float's first 70 d of chlorophyll data were compared with those from three similar optical sensors deployed on a Labrador Sea mooring in June 2004 (simultaneous with float deployment) and calibrated with chlorophyll extracted from local waters. Three years of float chlorophyll data were vicariously calibrated against the National Aeronautics and Space Administration's (NASA's) moderate resolution imaging spectroradiometer (MODIS) chlorophyll product.

Calibration provides two parameters for converting measured fluorescence counts to estimated chlorophyll concentration: a dark signal measured in the absence of fluorescence and a slope parameter describing a linear fit of fluorescence to chlorophyll. The dark signal was established by following the manufacturer's recommendation to cover the detector with black tape and to immerse the instrument in water while recording the output signal. During simulated dives in a pressure tank, dark counts varied between 24 and 28 counts (with a minimum of 19 and a maximum of 31 counts). The dark count value reported by the manufacturer was 28, and the minimum we measured in the field was 23 counts. Given this variability, we used a dark count of 25 in the calculations presented below, and we propagated an uncertainty of 6 counts in the estimates of uncertainties. (For comparison, 1 mg m^{-3} chlorophyll equals 500 counts.)

The slope relating measured fluoresced intensity (minus the dark signal, in counts) to chlorophyll concentration (in mg m^{-3}) is inherently variable because of biological variability in chlorophyll-normalized absorption and fluorescence quantum yield (Cullen 1982). Further uncertainty was introduced into our fluorescence-to-chlorophyll conversions by the fact that the 470-nm excitation band associated with our sensor is not at the peak of chlorophyll absorption but rather that of accessory pigments that are passing electrons to the chlorophyll (Perry et al. 2008).

The manufacturer's regression slope for our fluorometer (9.2×10^{-3} mg chlorophyll m^{-3} count^{-1}), on the basis of spinach chloroplasts as the calibration standard, differed from the slope obtained at the University of Maine (10.8×10^{-3} mg chlorophyll m^{-3} count^{-1}) with a diatom culture. Vicarious calibration against the mooring sensors resulted in a lower slope (4.2×10^{-3} mg chlorophyll m^{-3} count^{-1}, 40 match-ups, correlation coefficient $R = 0.76$), and regression with NASA's MODIS chlorophyll product (see below) resulted in an even lower slope (2×10^{-3} mg chlorophyll m^{-3} count^{-1}, 221 match-ups, $R = 0.88$). We elected to use the MODIS slope in the calculations presented here but suggest that these values may be biased low by as much as a factor of 2, with a minimal absolute uncertainty of ± 0.03 mg chlorophyll m^{-3} (NASA reports their product to have an average global uncertainty of 30%; *see* also discussion in Perry et al. 2008).

LSS calibration—The LSS was calibrated by the manufacturer with both a turbidity standard (formazine) and polystyrene calibration beads (Duke Scientific) while taking simultaneous measurements with a spectral beam transmissometer (WET Labs ac9). The LSS was designed to provide a robust estimate of mass concentration of particles (turbidity); as such, it does not have a well-defined sampling volume or well-defined scattering angle but instead collects light scattered from all angles, with maximal response to sidescattered photons (Baker et al. 2001).

The LSS calibration provides two parameters: a dark signal measured in the absence of a scattering substance and a slope parameter that relates the counts measured by the instrument (minus the dark counts) to the concentration of the calibration standard (expressed in nephelometric turbidity units, when calibrated against formazine or in m^{-1} when calibrated against a beam attenuation meter or a backscattering sensor). The dark counts were estimated by the manufacturer to be 41.8, and in our pressure tests they varied between 50 and 54. The lowest value measured in the field was 59 counts. Since the pressure tests were done just before deployment, we used the lab average of 51.8 counts as the dark count in the calculations presented here, and we propagated an uncertainty of 10 counts.

The slope parameter determined using a beam transmissometer measuring attenuation at 650 nm differed by a factor of 3 for the formazine (1.30×10^{-4} m^{-1} count^{-1}) and calibration bead (3.21×10^{-4} m^{-1} count^{-1}) solutions. Two vicarious field calibrations were also performed. The slope derived from calibration against three near-surface, bead-calibrated 440-nm backscattering sensors (i.e., providing an estimate of $b_{bp}[440]$) on the Labrador Sea mooring (1.48×10^{-5} m^{-1} count^{-1}; 40 match-ups, $R = 0.64$) differed by less than 10% from a regression with inversion-derived estimates of satellite-measured backscattering (1.64×10^{-5} m^{-1} count^{-1}; 213 match-ups; see below for details of the ocean color processing). For our calculations of mass concentrations of particles, we elected to use the MODIS (satellite) slope.

Theoretical considerations—i.e., Mie calculations using a Fournier–Forand analytical phase function (Fournier and
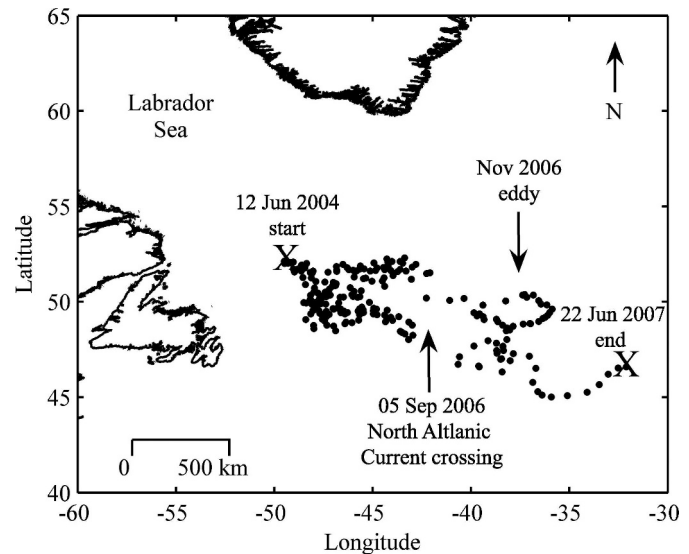

Fig. 1.   Float trajectory.

Jonasz 1999); indices of refraction, n, varying from 1.05 to 1.15; and a particulate size distribution with differential power-law slopes varying from 3.5 to 4.5 (slopes from Stramski and Kiefer 1991)—suggest that the ratio of particulate backscattering at 440 nm to the scattering measured by the LSS at 880 nm can vary from 0.2 to 0.56. This range of ratios would be much smaller for samples in which the particle composition varies less widely than in the theoretical calculations (e.g., for a population of near-surface organic particles). On the basis of the factors detailed above, we estimate the uncertainties in the backscattering coefficients reported here to be on the order of a factor of two, with an absolute uncertainty in the backscattering coefficient at 440 nm of 3×10^{-4} m^{-1}. To put this in perspective we note that the backscattering coefficient of pure seawater at 440 nm is 5.0×10^{-3} (Twardowski et al. 2007).

Float deployment and mission—The float, deployed at 51.84°N, 48.43°W on 12 June 2004 (Fig. 1), was programmed to collect data every 5 d on an upward trajectory from 1000-m depth to the surface. Data were collected at 50 depths during each profile, with larger sampling intervals at depth and smaller intervals close to the surface. (Approximate data-collection intervals were: over depth range 1000 to 450 m, every 50 m; over 400 to 325 m depth, every 25 m; over 35 to 15 m depth, every 5 m; and at 7 m below the sea surface.) At the surface, the CTD was turned off and in-water measurements of chlorophyll fluorescence and backscattering were taken while the float broadcast data to the Argos satellite.

To ensure that Chl *a* fluorescence measurements were not biased by nonphotochemical quenching (e.g., Loftus and Seliger 1975; Sackmann et al. 2008), the float was programmed to surface close to midnight local time at the launch location. As the float drifted approximately 17° westward over the course of its mission, the surfacing time was always within 2 h of the float's local midnight. After each profile, the float spent approximately 10 h at the
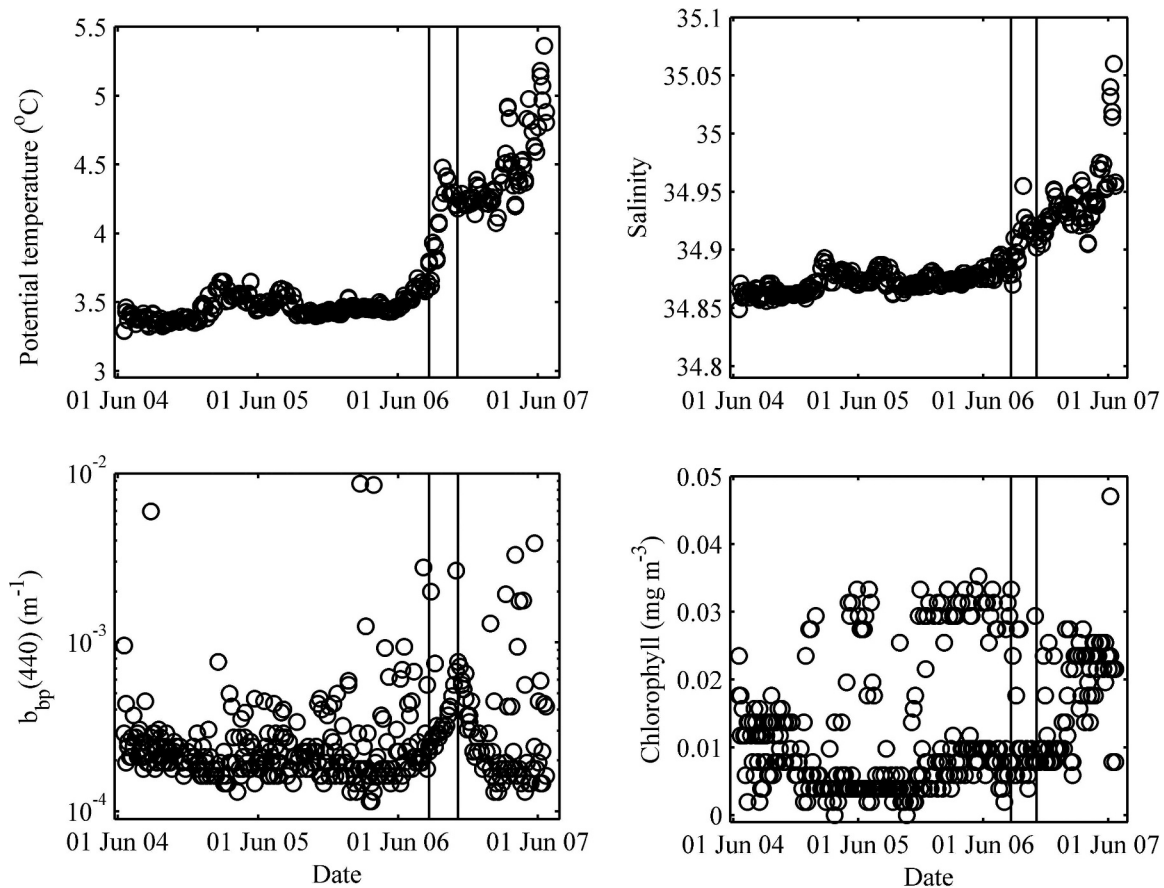
Fig. 2.   Potential temperature, salinity, particulate backscattering at 440 nm, and chlorophyll at depths deeper than 970 m. The two vertical lines denote crossing of the North Atlantic Current (left) and the center of a particle-rich anticyclonic eddy (right). Chlorophyll values lower than 0.04 mg m^{-3} are not significantly different from zero.

surface, sending data to the Argos satellite (using an algorithm that ensured that at least 95% of the data would be transferred) and collecting optical surface data before returning to its parking depth at 1000 m.

Satellite ocean color—Ocean color remote sensing products were obtained from http://oceancolor.gsfc.nasa. gov/PRODUCTS/. For remotely sensed chlorophyll concentrations, we used NASA's OC3 standard chlorophyll product for the MODIS. For the remotely sensed particulate backscattering coefficient at 440 nm (b_{bp}[440]), we used normalized water-leaving radiances and the inversion algorithm outlined in Maritorena et al. (2002). Level 2 data were processed as follows: all satellite passes within a 6-h period (which amount to all data collected within a daylight period) were averaged into a single scene. The data were subsequently median-averaged over all nonmasked data pixels within 7.5 km of the float's most recent location. (The 7.5-km scale was based on a spatial decorrelation analysis [not shown] and agrees with the local baroclinic radius of deformation [e.g., Smith et al. 2000].) For vicarious calibration of the float's two sensors (described above), the ocean color data were interpolated to the time of the float's surfacing (with slightly fewer match-ups for backscattering than for chlorophyll: n = 213 for b_{bp} and n = 221 for chlorophyll).

We tested for contamination of pixels adjacent to clouds by applying a dilation operator. Cloud-masked regions were enlarged by a binary dilation operation with a disk-shaped kernel (two-pixel radius) to remove cloud edge effects (Gonzales and Woods 1992). This operation reduced the number of available remotely sensed spectra obtained for 12 June 2004 to 1 May 2007 from 233 to 150 without significantly changing either the correlation coefficient or the calibration slope between in situ data and those inverted from satellite. We thus elected not to apply the dilation procedure in the analyses that follow.

Sea surface height—Sea surface height anomaly data with ¼° resolution were obtained from the Colorado Center for Astrodynamics Research at the University of Colorado, Boulder. Data were processed as in Leben et al. (2002).

Results

Sensor stability and general oceanographic consistency—Float 0005 accomplished 221 profiles of the upper 1000 m of the western North Atlantic Ocean, one every 5 d, between its launch on 12 June 2004 and its disappearance on 22 June 2007. The float spent most of its mission in the subpolar gyre before crossing the North Atlantic Current in
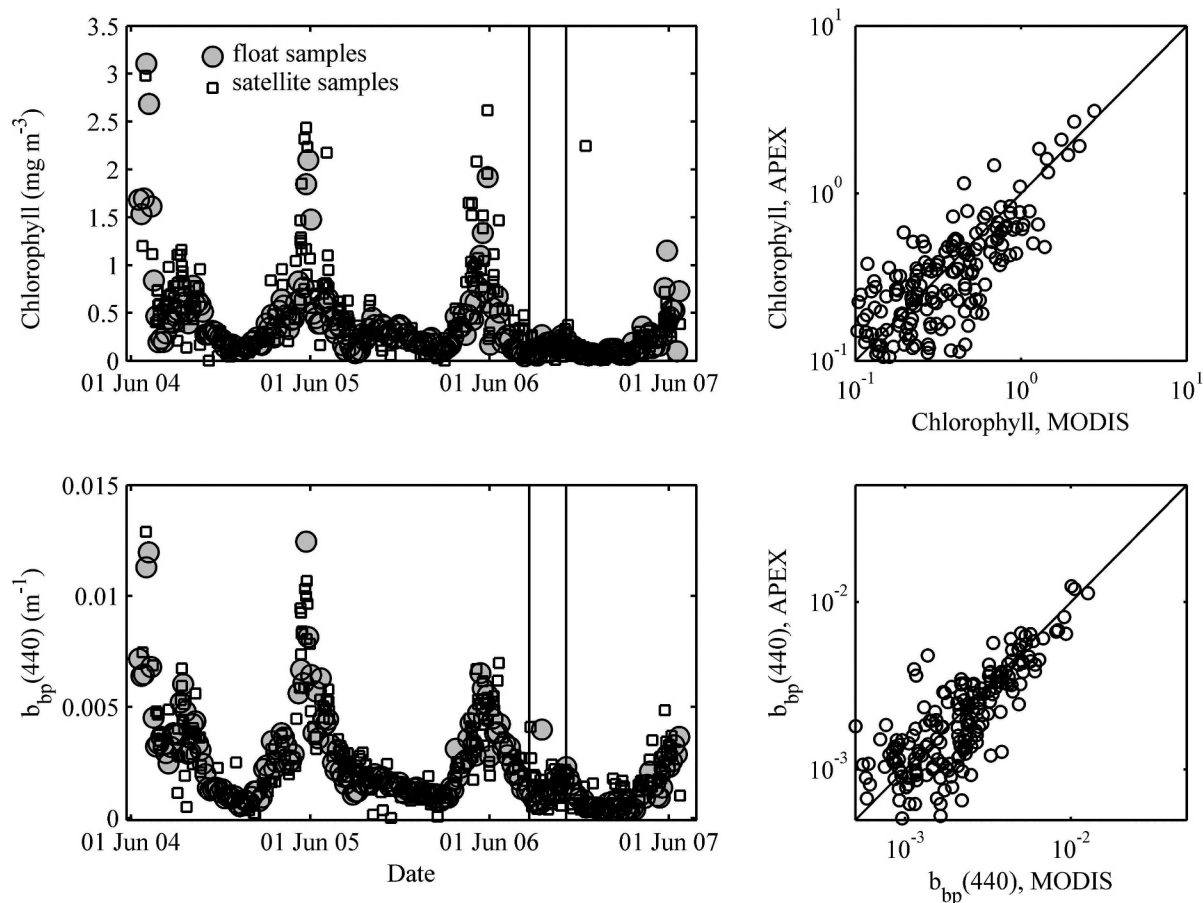
Fig. 3.   Time series and comparison of the particulate backscattering coefficient at 440 nm and chlorophyll concentration as measured by the float and satellite ocean color sensors.

September 2006 and drifting into warmer waters to the south (Fig. 1). The float then spent approximately 3 months within an anticyclonic eddy with highly elevated backscattering values (see below).

For one assessment of sensor stability, we examined data from depths greater than 970 m, with the expectation that in the absence of sensor drift, these deep-water values should remain approximately consistent throughout the float mission. Except for rare spikes in the backscattering coefficient (probably associated with occasional large particles entering the field of view of the sensor) and the higher values associated with passage through an eddy, the deep values are approximately constant ($b_{bp}[440] \sim$ 0.00015 m^{-1}), suggesting that the float sensors were stable over the course of the 3-yr mission (Fig. 2). The variability of the deep-water backscattering is on the order of 10% of the backscattering by pure seawater. Ultimately this is the uncertainty when using the float data as validation for satellite-derived backscattering values.

As a second assessment of sensor stability, we compared the float data to concurrent satellite data. Although the remotely sensed data were earlier used to define the (single) slope parameter we used to convert digital counts to estimates of chlorophyll and backscattering (*see* Methods), the consistent long-term correlation between surface

estimates of these quantities obtained from the satellite and from the float over 3 yr supports our hypothesis of little drift in the optical sensors (Fig. 3, $R = 0.88$ for chlorophyll and 0.90 for backscattering, independent of the slope value chosen). If the float's sensors had experienced significant instrumental drift, the satellite and float estimates of chlorophyll and backscattering would have been expected to diverge over time.

The float data were also assessed in terms of their consistency with the relationships between particulate backscattering and chlorophyll (Fig. 4) found in careful shipboard measurements of in situ chlorophyll concentration and backscattering in the Antarctic Polar Frontal Zone (APFZ), the Ross Sea (Reynolds et al. 2001), and the South Pacific (Huot et al. 2007). To convert $b_{bp}(555)$ reported in these studies to $b_{bp}(440)$ for this comparison, we assumed a λ^{-1} spectral functionality for b_{bp} and hence applied a multiplicative factor of 1.25 to the $b_{bp}(555)$ values. Remotely sensed (satellite ocean color) estimates of backscattering and chlorophyll are also included (Fig. 4; Behrenfeld et al. 2005). The float-based ratios of backscattering to chlorophyll are consistent with those observed in these other studies.

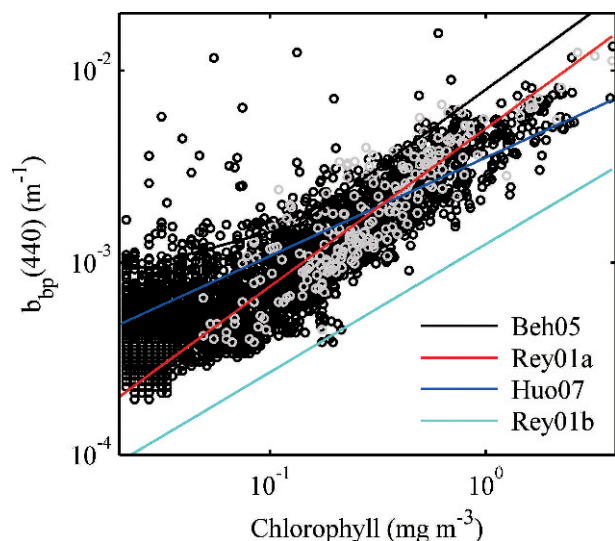Previous measurements were also available for suspended mass in the deep North Atlantic (Jacob and Ewing

Fig. 4. Particulate backscattering coefficient at 440 nm vs. chlorophyll, as measured by the float within the upper 10 m (gray circles) and upper 300 m (black circles) of the water column. Four published relationships are also shown: Beh05, Behrenfeld et al. 2005; Rey01A, Reynolds et al. 2001, AFPZ; Huo07, Huot et al. 2007, South Pacific; and Rey01R, Reynolds et al. 2001, Ross Sea. Values of chlorophyll smaller than 0.04 mg m^{-3} are not significantly different from zero.

1968). For this comparison, we relied on a regression between LSS-determined turbidity and suspended matter (mg L^{-1}; Baker et al. 2001) that is accurate to within 5%. On the basis of the manufacturer's LSS turbidity calibration translated in terms of backscattering, suspended mass (in units of mg L^{-1}) in our data set is estimated to be approximately $20b_{bp}(440)$. Applying this conversion factor to the float's measurements of backscattering in deep clear waters (where $b_{bp}[440] \sim 2 \times 10^{-4}$ m^{-1}, Fig. 2) provides an estimate of suspended mass of 0.004 mg L^{-1}. This value is consistent with a previous report of 0.0045 mg L^{-1} for clear deep North Atlantic waters (Jacob and Ewing, 1968).

Upper ocean dynamics—To quantitively describe variability in the waters encountered by the float, we calculated decorrelation timescales (a measure of how well-correlated through time are successive measurements of a given quantity) for both optical and physical float measurements. Phytoplankton surface distributions are known to be spatially patchy (the local baroclinic deformation radius and local spatial decorrelation scale of chlorophyll are O [10 km]) and to have the potential to be highly variable temporally because of rapid growth rates (O [1 d]), grazing dynamics, and mesoscale eddy dynamics. Thus one may expect chlorophyll data to be highly uncorrelated between subsequent vertical profiles. Contrary to this expectation, however, we find chlorophyll to have an unexpectedly long e-folding time of nearly 2 weeks (Fig. 5). The near-surface optical properties (and thus biogeochemistry) have shorter decorrelation timescales than do the physical properties (Fig. 5), with chlorophyll's being the shortest.
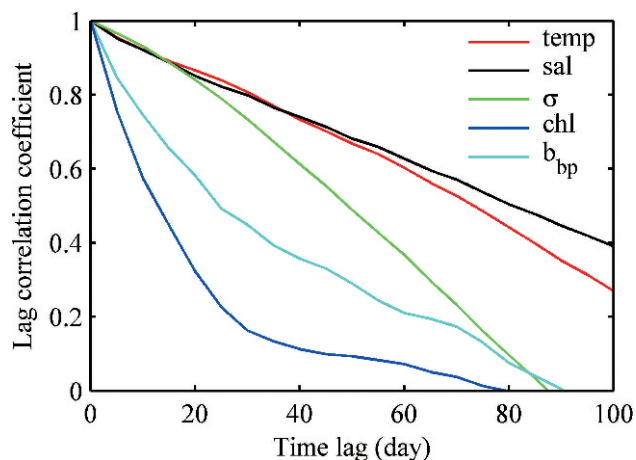

Fig. 5. Lag correlation for near-surface chlorophyll, backscattering, density, salinity, and temperature measured from the profiling float. Temporal averages were removed from all variables before computing the lag correlation.

The float spent a little more than 2 yr in the subpolar western North Atlantic (Fig. 1). The annual cycle dominates the variability in the sensor record, with surface waters warming (decreasing in density) between February and late August, followed by subsequent cooling (Fig. 6). The near-surface chlorophyll and backscattering coefficients, which are always higher than the same measurements at depth, exhibit a rapid rise in the spring and a slower decrease in the fall and winter. The chlorophyll and backscattering coefficients are well correlated ($R > 0.86$) in the upper 300 m, consistent with backscattering being dominated by phytoplankton and particles that covary with phytoplankton (Fig. 4).

Significant variations in the chlorophyll/b_{bp} ratio are observed in the course of the annual cycle (Fig. 6). Below the mixed layer in the summer, a significant increase in chlorophyll/b_{bp} is evident, consistent with photoacclimation of cells to low light or availability of nutrients (Fig. 6). This ratio also increases near the surface in the winter, possibly due to an increase in pigmentation associated with short daylength and deeper mixing. When converting the upper 50-m water column $b_{bp}(440)$ to phytoplankton carbon using the conversion of Behrenfeld et al. (2005), we find the chlorophyll/carbon ratio to have a median of 0.02 mg chl mg C^{-1} (10th percentile = 0.01, 90th percentile = 0.36), consistent with values observed in phytoplankton cultures (e.g., Cloern et al. 1995).

At greater depths, no significant pigment concentration is observed at any time of year (Fig. 7). In contrast, the seasonal modulation in backscattering is observed all the way to the deepest-depth bin (750–1050 m), though with an amplitude two orders of magnitude smaller than at the surface and with a maximum that is shifted later in the year relative to the surface's particle concentration maximum.

Effects of clouds—To assess the usefulness of the float's ability to sample under clouds, we compared the temporal coverage provided by the float (five to six surfacings per month) to that of the MODIS satellite (Fig. 8) within the
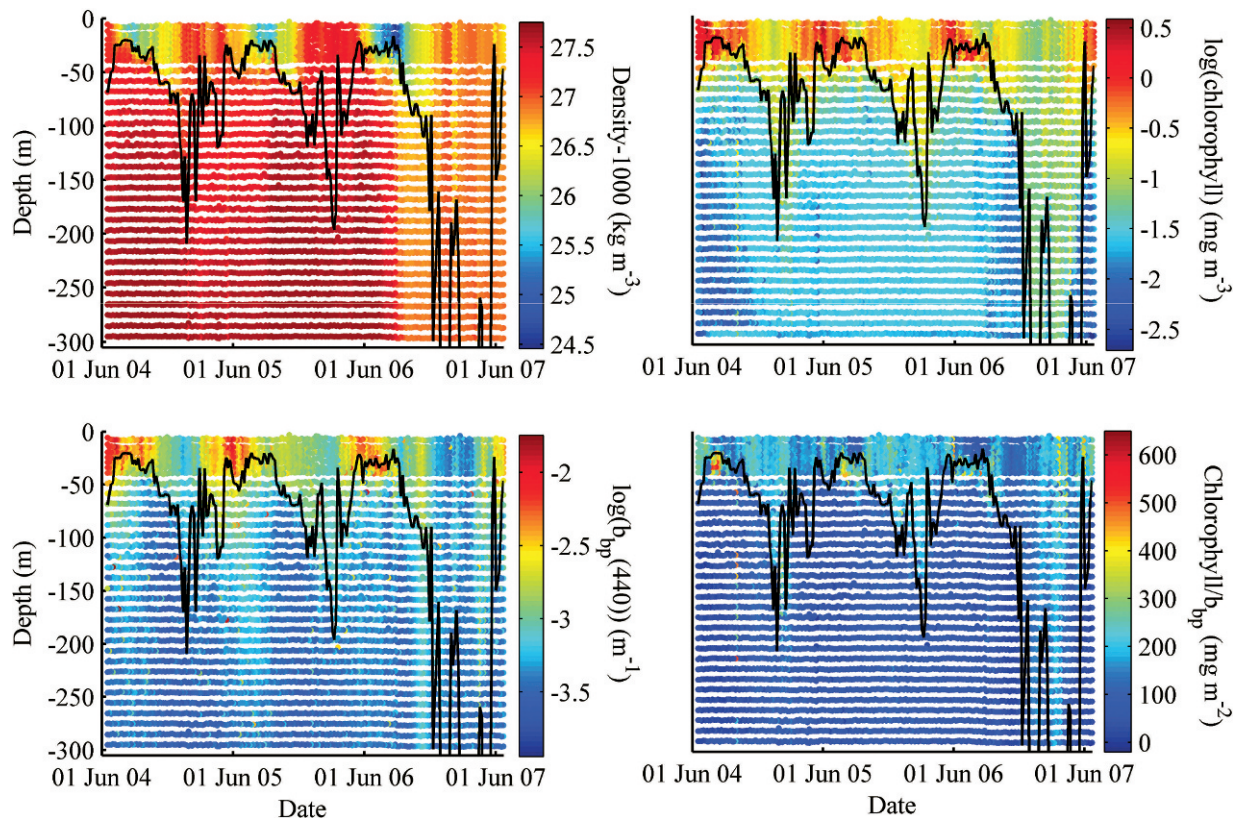
Fig. 6. Evolution of density, chlorophyll, and backscattering at 440 nm and the ratio of chlorophyll to backscattering at 440 nm as a function of time and depth in the upper 300 m. The black line denotes the mixed layer depth (defined as the depth where density is 0.125 kg m^{-3} greater than near the sea surface).

7.5-km radius around the float's latest position. In summer months, we obtained denser sampling with the remote sensing data; during the cloudy North Atlantic winters, the float data density was superior.

To determine whether the greater winter data density from the float translates to significantly different monthly mean values, we computed the coefficient of variation (C.V.) (the ratio of the monthly standard deviation to the monthly mean) for the float chlorophyll data (Fig. 8). During cloudy periods (when the number of satellite samples is low), the C.V. in optical properties is usually also low, indicating little change in upper ocean chlorophyll over the course of the month. Sunny periods, associated with many remote observations, are usually associated with a large C.V. in upper ocean chlorophyll. This variance, however, is often resolved by the more frequent satellite ocean color measurements.

The eddy event—An unusual eddy was sampled in the fall of 2006, following the float's crossing of the North Atlantic Current. This eddy was quasistationary from September to mid-November (not shown), had a small expression in remotely sensed chlorophyll concentration (relative to measurements before and after its encounter, Fig. 3), and was observed well in altimetry data (Fig. 9). While circling with the eddy, the float recorded the only occasion of deep (>970 m) scattering significantly elevated above background levels (Fig. 2). Depth-integrated chlo-

rophyll values show little signal associated with the eddy; however, integrated b_{bp} values show a signal comparable in magnitude with that observed during the spring bloom (Fig. 10).

Discussion

We have demonstrated the ability to reliably measure optical variables—specifically, chlorophyll concentration and particulate backscattering—for a period of 3 yr with a profiling float. Data quality was maintained with no apparent evidence of fouling, possibly due to the mission profile, which included a large fraction of time in the dark, cold, deep ocean and relatively short stays at the surface (about 10 h every 5 d, mostly at night; *see* also Bishop et al. 2002). The vicarious calibration approach performed here provides a chlorophyll-to-b_{bp} relationship consistent with those observed in other studies (Fig. 4). Average suspended mass was also consistent with that previously observed in the deep North Atlantic.

Good temporal correlation between float-based and remotely sensed observations showcases the potential for using similar in-water sampling platforms for validation or interpolation of ocean color data. In addition, these data can be used to test for potential biases in monthly mean satellite values during times of cloudy conditions. Here we find that within the subpolar gyre, periods of
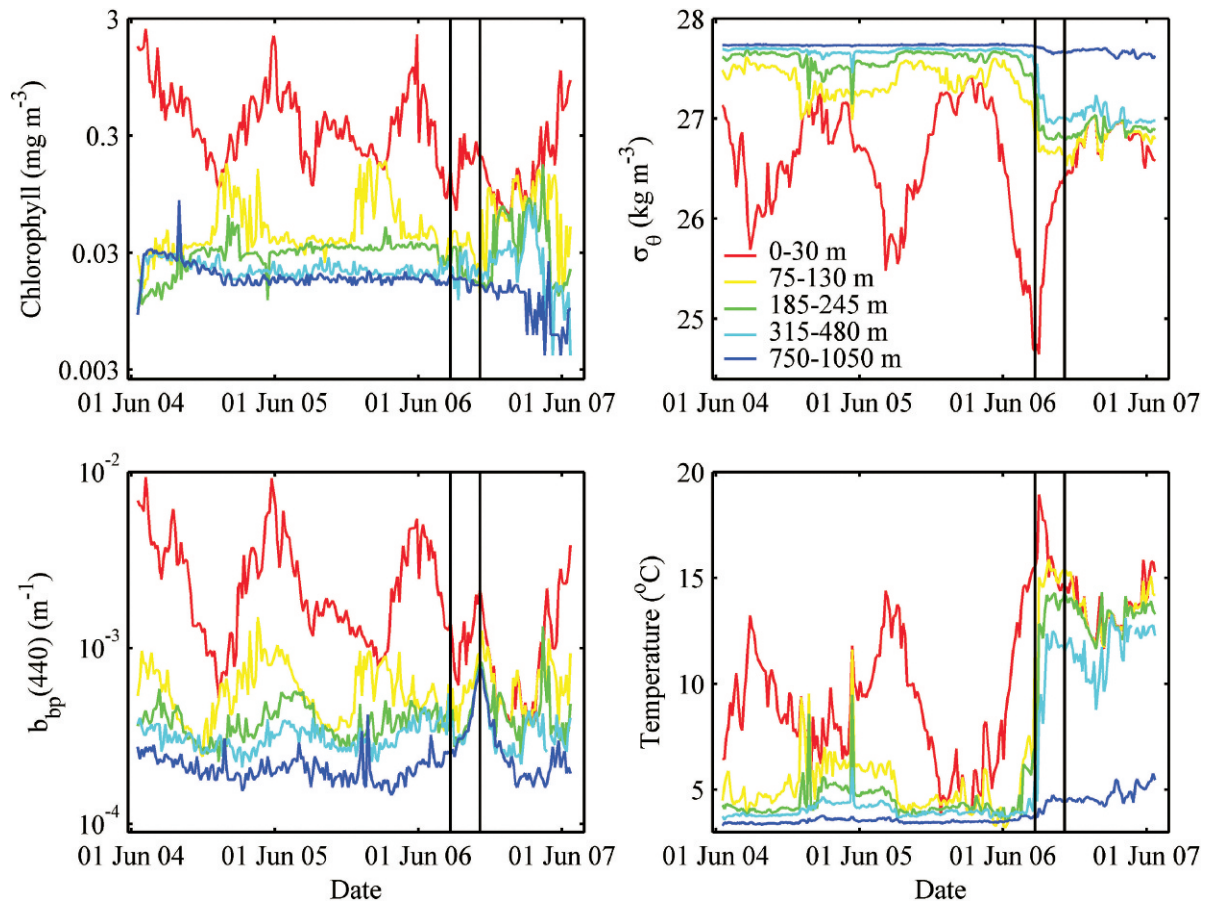
Fig. 7. Evolution of chlorophyll, density, particulate backscattering, and temperature as a function of time for five depth bins. Lines represent the median of the property values for data in the following depth bins: 0–30 m, 75–130 m, 185–245 m, 315–480 m, and 750–1050 m. Each bin contains approximately five sampling depths. The vertical black lines denote crossing of the North Atlantic Current (left) and the center of a highly backscattering anticyclonic eddy (right).

sparse satellite coverage (i.e., winter) are correlated with low variability in chlorophyll, suggesting that at high latitudes winter clouds do not significantly bias remotely estimated monthly means. This result may be explained by the fact that the winter period is associated with low temperatures and lower average mixed-layer light levels, both of which are likely to decrease phytoplankton growth rates.

Autocorrelation analysis of the whole data set shows chlorophyll to have a shorter decorrelation timescale than backscattering. This difference is likely due to the ability of phytoplankton to rapidly (within a generation timescale) alter their intracellular chlorophyll concentration in response to changes in light and nutrients, whereas other phytoplankton components (phytoplankton carbon, for example) vary more slowly. The longer decorrelation timescale for backscattering may also suggest that the scattering sensor is detecting slowly varying material that does not covary with phytoplankton (e.g., non-photosynth bacteria).

The chlorophyll decorrelation timescales observed by the float (O[20 d]) are significantly longer than the O(2 d) decorrelation timescales calculated for equatorial Pacific chlorophyll from ocean color data (Strutton and Chavez

2003) and the O(4 d) decorrelation timescale calculated for California Current in situ chlorophyll from drifters (Abbott and Letelier 1998). This result may seem surprising given the shorter deformation radius in the North Atlantic, but can be explained by the significantly larger seasonal signal there. This signal dominates the observed variability.

In comparing decorrelation timescales for optical variables and hydrographic variables, we found shorter decorrelation timescales for all of the optical variables. Denman and Abbott (1994) and Abbott and Letelier (1998), in contrast, observed equal decorrelation timescales for temperature and chlorophyll in the California Current. Strutton and Chavez (2003) interpret covariation in decorrelation timescales as being a sign of causality. Under that interpretation, our observation suggests that phytoplankton concentration in the western North Atlantic is significantly modulated by processes other than those responsible for variability in the upper ocean's hydrography.

One distinctive event captured by the float was a particle-rich eddy sampled in the late fall of 2006 just south of the North Atlantic Current. This eddy's particle load was observed coherently throughout the upper 1000 m of the water column, suggesting that it may be responsible for a large flux of particles to depth. This event, which had
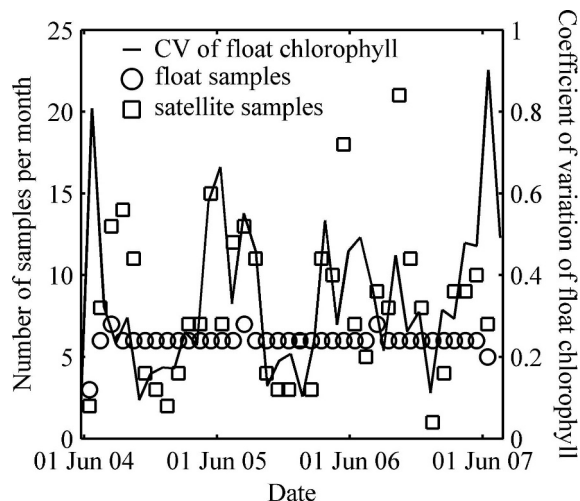
Fig. 8.   Number of data points per month provided by the float and satellite sensors, and C.V. of chlorophyll (on the basis of float data) as a function of time.
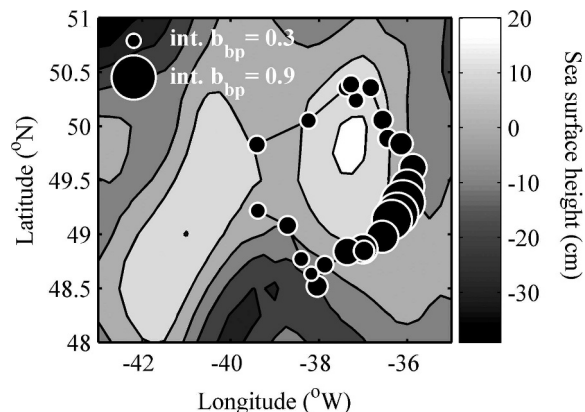

Fig. 9.   Float trajectory and backscattering coefficient from 5 September (49.8°N, 39.4°W) to 29 December 2006 (49.2°N, 39.4°W) overlain on contours of sea-surface anomaly (in cm) for 18 October 2006. Note the anticyclonic eddy centered at 50°N, 37°W. This feature was quasistationary at this location for longer than 2 months.

little expression in surface ocean color, is reminiscent of observations at the Bermuda Atlantic Time Series (BATS) station (Conte et al. 2003) where, during some winters, large fluxes of biogenic materials were collected in 3000-m sediment traps in association with an eddy feature with little surface expression in chlorophyll.

Currently we do not have a mechanism to explain the processes that formed or concentrated the particulate material within the eddy. Settling velocities of micron-size particles such as coccoliths cannot explain the temporal coherence in signal between near-surface measurements and those at 1000 m (B. Balch 2007 pers. comm.). Additionally, no anomalous atmospheric transmission values, possibly associated with a dust deposition event, occurred during that time.

Eddies such as that sampled by the float and those observed at BATS could be very important (even dominant) in the global biogeochemical inventory of carbon and its flux to depth (e.g., Sweeney et al. 2003). However, we cannot currently account for such contributions because of the faint ocean color signal of such eddies, our inability to sample the subsurface ocean from space, and the limited space and timescales observable using shipboard observations or single-point moorings, which cannot capture many realizations of such eddies.

In terms of methodological considerations, we found that care must be taken to ensure that floats surface at nighttime. We had programmed midnight surfacings so as to avoid the confounding effects of nonphotochemical quenching in the chlorophyll fluorescence data. Indeed, we often observed reductions in fluorescence through time after sunrise. A similar effect has often been observed with fluorometers deployed on other autonomous vehicles such as gliders (Perry et al. 2008).

In future deployments of optical floats, we would recommend replacing the sidescattering sensor with a backscattering or attenuation sensor. The LSS, although excellent for quantifying particles, has an optical geometry

that is not very well constrained; this means that an LSS and another optical sensor calibrated with the same calibration particles will likely give different estimates of concentration in field samples where particle size and composition differ from those of the calibration particles (e.g., Gibbs 1974). In recent years, backscattering sensors that sample a small, well-defined volume have been developed, providing an opportunity to measure an inherent optical property that is rather well understood and can be directly related to remotely sensed quantities (Stramski et al. 2004). Backscattering is also a good proxy for particulate organic carbon (e.g., Stramski et al. 2008).

Attenuation is another good proxy for particulate carbon (e.g., Bishop 1999; Stramski et al. 2008), but our eddy experience points to a need for caution in field calibrations of beam transmissometers. These instruments are often calibrated against the clearest deep waters in a deep cast (e.g., Bishop et al. 2002; Stramski et al. 2008, and references therein). If, however, such a procedure had been used in this North Atlantic study, the particle-signal increase associated with the 2006 eddy would have been greatly reduced.

For future deployments, we would also recommend replacing the chlorophyll fluorometer with a sensor to directly measure chlorophyll absorption (if a stable sensor could be developed). Here we used chlorophyll fluorescence as a proxy for chlorophyll concentration, which, for many processes and modeling studies, must in turn be converted to phytoplankton absorption. The relationship between chlorophyll fluorescence and chlorophyll concentration is inherently variable because of biological variability in chlorophyll-normalized absorption (a function of cell size and accessory pigments) and fluorescence quantum yield (a function of species, nutritional status, and light history). For example, calibration of a fluorescence sensor with the same excitation and emission characteristics as ours found that calibration slopes (chlorophyll : F) for a marine diatom species and for a marine cyanobacterium differed by a
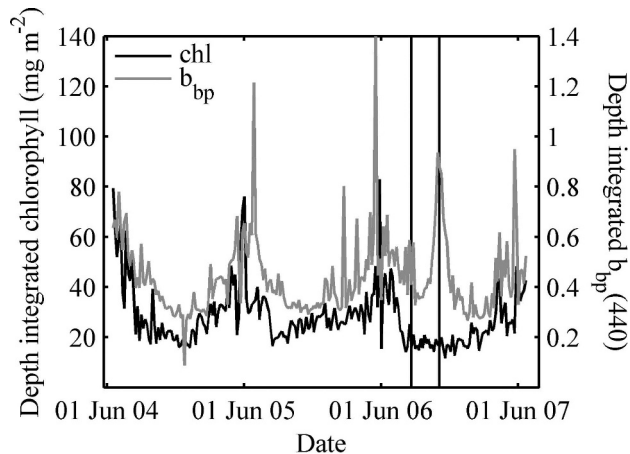
Fig. 10. Integrated chlorophyll and particulate backscattering from the surface to 300-m depth.

factor of 7 (L. Karp-Boss unpubl.; *see* also Schubert et al. 1989). As a result, fluorescence—although a very useful proxy for chlorophyll concentration, given that quantity's large dynamic range in oceanic waters—does not give a very accurate measure of that concentration (Cullen 1982; ACT 2005).

If a chlorophyll fluorometer is to be used, it is advisable to perform the instrument's prelaunch calibration using chlorophyll extracted from phytoplankton populations local to the float's mission area. Better yet would be local-assemblage calibrations conducted at intervals throughout the mission as often as possible. Even these extra-effort calibrations will fall short of ideal because phytoplankton assemblages change with time and depth, but the more closely the calibration standards can be matched to the local assemblage, the better. In addition, a recent study using a novel optical sensor with multiple excitation–emission bands suggests the possibility to significantly improve the accuracy of retrieved chlorophyll concentration (Proctor 2008).

For future deployments of optical and biogeochemical sensors on floats or other platforms, we also recommend that rigorous, quantitative error analysis and propagation be a standard part of the calibration and data analysis procedures. We devoted considerable effort to this undertaking (*see* Methods), demonstrating that the fluorometer and LSS measurements are accurate but imprecise. Fluorescence is an inherently noisy proxy for chlorophyll, but, again, because of chlorophyll's large dynamic range in oceanic environments, even an imprecise measurement is a useful one.

The quantification of analytical precision (*see* Methods section) is not commonly undertaken for optics-based methods used to characterize biogeochemical quantities—but it is critically important. Ecosystem and biogeochemical ocean modelers are starting to use optical variables to better model the underwater light field (e.g., for rate calculations of photosynthesis and photo-oxidation) and to constrain biogeochemical variables (e.g., Fujii et al. 2007). Data such as those collected by the float discussed here can provide these models with much-needed groundtruth,

resulting in increased model skill. Such exercises require, in addition to the basic data set, accompanying estimates of methodological and data uncertainties. Otherwise, the propagation of errors throughout the model calculations and "goodness of fit" between model output and observations cannot be quantitatively assessed.

In the very near future, O(5 yr), increasing numbers of biogeochemical modelers will undoubtedly begin assimilating and testing against optical and other biogeochemical data sets. However, the accompanying demand for high temporal and spatial high-quality optical data will not be met by existing programs and platforms. In this study, we have demonstrated the significant contribution that could be made by autonomous profiling floats (*see* also Uz 2006). If a fleet of biogeochemical profiling floats were to operate throughout the world's oceans, the contribution of the mesoscale band to important biogeochemical fluxes could be constrained.

Such a fleet (Argo) already exists for measurements of temperature and salinity. A coordinated effort by the oceanographic community, analogous to the current effort to add oxygen measurements, could make a complementary biogeochemical fleet a reality. All these future float missions will benefit considerably from newer communication technologies such as satellite cell phones (e.g., iridium), which allow for significantly shorter stays at the surface (less than 10 min), two-way communication (allowing for adaptive sampling), and higher vertical sampling resolution per unit power.

It is our hope that the success and results demonstrated here and in previous optics-based studies of ocean biogeochemistry (e.g., Bishop et al. 2002, 2004) will encourage the addition of biogeochemical sensors to the existing and planned fleet of autonomous platforms in the world's oceans. Such a fleet could provide required inputs and constraints for the ocean-scale models needed to improve our understanding of the oceans' roles in biogeochemical cycling in general and of recent climate processes in particular.

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