

**Calibration and correction of the
chlorophyll fluorometer on
GoMOOS Buoy A01:
November 2005-June 2013**

Massachusetts Water Resources Authority
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Calibration and Correction of the Chlorophyll Fluorometer on GoMOOS Buoy
A01: Nov 2005 – Jun 2013

Principal Investigator: Dr. Collin Roesler

Institution: Bowdoin College
Department of Earth and Oceanographic Science

Address: 6800 College Station
Brunswick, ME 04011

Phone/Fax: 207-725-3842 / 207-798-7037
Email: croesler@bowdoin.edu

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Introduction

The Gulf of Maine Integrated Coastal Ocean Observing System is administered by the Northeast Regional Association of Coastal Ocean Observing Systems (NERACOOS; <http://gyre.umeoce.maine.edu/buoyhome.php>). It has completed its twelfth year of real-time hourly observations in the Gulf of Maine (Table 1). Initial funding for the system supported optical sensor packages on 4 buoys (B, E, I, M and N). Buoy A was instrumented (in 2005) through support from MWRA; Buoy F (Penobscot Bay) through support from NASA, and Buoy D02 (Harpwell Sound) through support from NSF and NASA (Pettigrew and Roesler 2005).

Table 1. Gulf of Maine Integrated Coastal Ocean Observing System (GoMICOOS, formerly GOMOOS) Buoy Network Operated by N. Pettigrew (University of Maine, Physical Oceanography Group) and integrated with bio-optical sensors operated by C. Roesler (Bowdoin College, Environmental Optics Lab).

Site	Location	Start Date	Latitude	Longitude	End Date
A01	Massachusetts Bay	2001-07-10	42° 31.39' N	070° 33.93' W	-
B01	Western Maine Shelf	2001-07-09	43° 10.84' N	070° 25.67' W	-
D02	Harpwell Sound	2006-12-14	43° 45.70' N	069° 59.30' W	2013-01-09
E01	Central Maine Shelf	2001-07-09	43° 42.89' N	069° 21.47' W	-
F01	Penobscot Bay	2001-07-08	44° 3.33' N	068° 59.89' W	-
I01	Eastern Maine Shelf	2001-07-24	44° 6.34' N	068° 6.50' W	-
M01	Jordan Basin	2001-07-12	43° 29.44' N	067° 52.79' W	-
N01	Northeast Channel	2004-06-03	42° 20.08' N	065° 54.23' W	-

The Buoy A optical sensor package consists of a WETLabs combination chlorophyll fluorometer/turbidity sensor (ECO FLNTU) and a DH4 data handler that provides the mean values of 30-second burst sampling each hour to the buoy data logger for real time transmission. The time course observations of calibrated chlorophyll fluorescence and turbidity at buoy A is presented in this report from the perspective of the interannual variations in the seasonal phytoplankton cycle, the timing of the spring bloom and the associated specific growth rates.

Methods

The two FLNTU sensors are serviced and calibrated by the factory in between each deployment. Additionally, the fluorometers are calibrated in Roesler's lab using a monospecific culture of the diatom *Thalassiosira pseudonana* grown under constant irradiance (to minimize diel variations in pigment concentration and photosynthetic parameters), in replete nutrients and light levels that maximize growth rates (i.e. $\sim 300 \mu\text{E m}^{-2} \text{s}^{-1}$) and minimize pigment packaging due to low light acclimation. These fluorescence efficiencies of the culture have been shown to be

repeatable over years (Proctor and Roesler 2010). This approach to calibration thus provides not only a consistent fluorescence response between deployments; it also provides a more realistic estimate of *in vivo* chlorophyll concentrations from *in situ* fluorescence. Drift and biofouling are assessed in two ways. Instrumental drift is quantified as the difference in dark reading of sensors, which were calibrated using laboratory diatom cultures, before and after each deployment. Over the lifetime of the sensors, this instrumental drift continues to be negligible. Biofouling is an additional source of signal drift and takes two forms, biofilms on the sensor optical heads, and growth of macroalgae and invertebrates on the buoy infrastructure that can obscure or interfere with optical readings (frondular biofouling). The former leads to slowly increasing signal intensity, particularly in the turbidity reading. The latter leads to

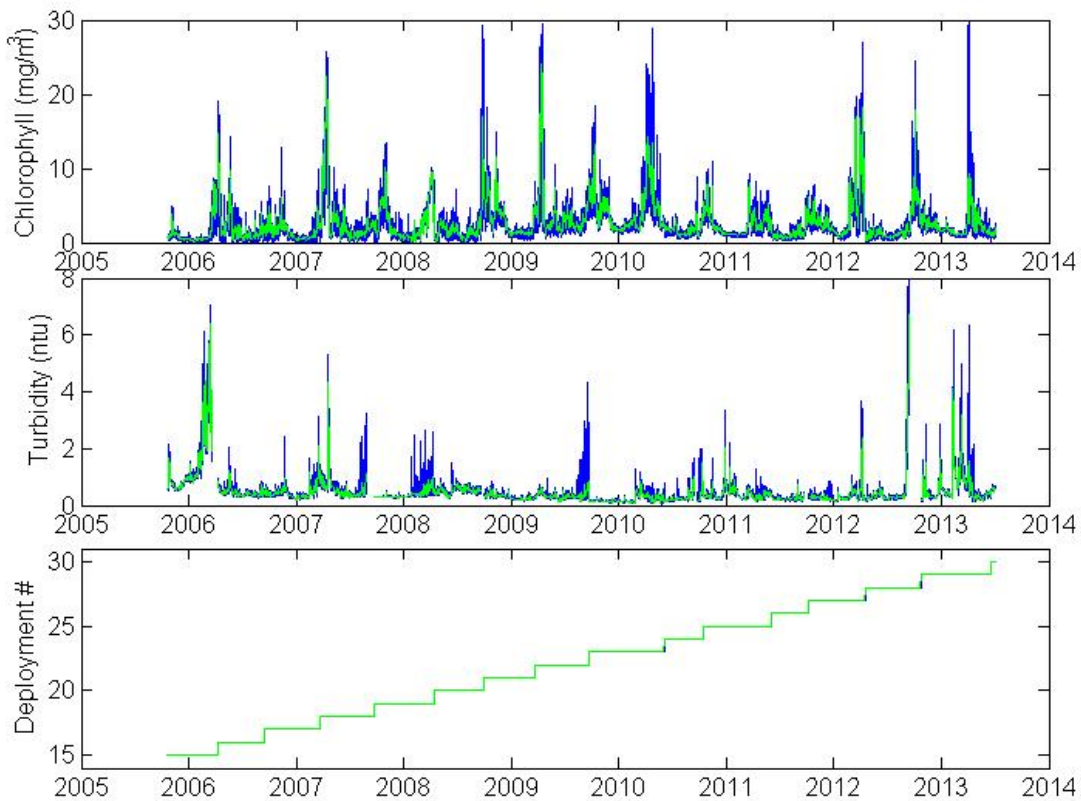


Figure 1. Time series observations of (*top panel*) calibrated chlorophyll fluorescence, (*middle panel*) turbidity, and (*bottom panel*) deployment number for GoMICOOS Buoy A measured at 2.5 m from December 2006 = June 2013. Hourly observations are shown in blue, daily median values in green.

increased variability as fauna and flora waft into the optical path. Fouling by biofilms is quantified by the difference in observations collected on the last day of a deployment and the first day of the subsequent deployment. The offset is then projected backward in the prior deployment to the time point when the offset trend first appears. For example, if there is an offset at both the beginning and the end of the deployment, suggesting an erroneous dark value, the entire deployment is corrected for the offset. If, however there is a linear or

exponential rise in background fluorescence, a best fit line or exponential function is fit to data to identify the approximate date of biofouling onset (Roesler and Boss 2008). The offset can then either be used to flag data subject to biofouling or can be used to compute a first order correction. Towards the end of many deployments, as macroalgae or invertebrates grow on the buoy infrastructure, increased variability in the detected signals are observed, particularly in the turbidity reading. In processing the turbidity data, saturating and unrealistic hourly observations are removed but within the constraints of realistic values, high variations remain

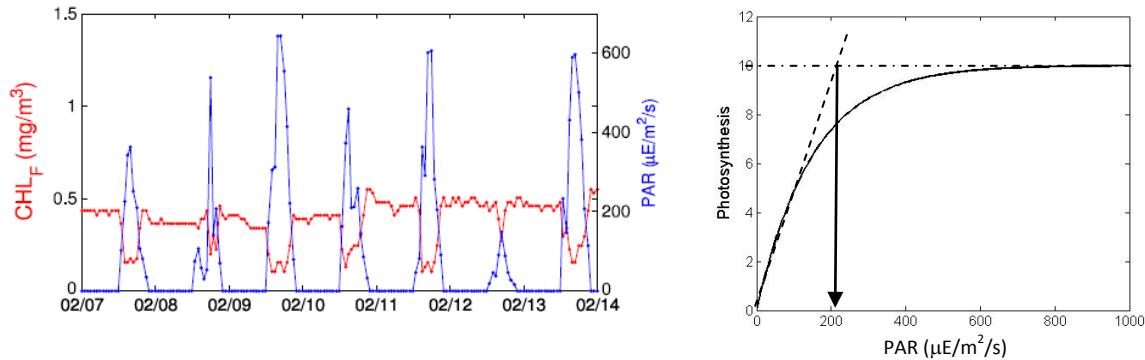


Figure 2. (left panel) Time course of hourly observations of *in situ* chlorophyll fluorescence (red symbols) and incident irradiance (PAR, blue symbols) measured at 2.5 m depth from NERACOOS buoy I located in 100m water depth southeast of Mt Desert Island (showing non-photochemical quenching of fluorescence under high irradiances). (right panel) Example of a photosynthesis versus irradiance curve for phytoplankton showing the linear dependence at limiting irradiances (dotted line) and the independence at saturating irradiances (dash-dot line). The intersection of these two provides an estimate of the saturating irradiance, E_k , which can be estimated from the time course of irradiance and fluorescence at left.

in the hourly observations (Figure 1). Daily median values are generally more well-behaved, yielding much lower variability than the hourly data.

Results

The complete hourly time series of calibrated chlorophyll fluorescence and turbidity are shown in Figure 1. Spring and fall blooms are apparent each year with lower chlorophyll concentrations evident in winter due to light limitation and in summer due to nutrient limitation. Substantial diel variations are due to non-photochemical quenching (NPQ) of fluorescence (shown in detail in Figure 2). This time series was taken from buoy I and shows the simultaneous measurement of photosynthetically available radiation. It is clear that there is a critical irradiance that induces NPQ of fluorescence. This irradiance value similarly induces quenching of photosynthesis. The irradiance level that NPQ occurs is called E_k or the irradiance at which the dependence of photosynthesis on incident irradiance departs from the linear relationship under light limitation to the maximal photosynthesis values at light saturating

conditions (Figure 2B). The value of E_k is a very useful parameter for analytically modeling *in situ* photosynthesis. It is important to note that biomass is not changing but the fluorescence yield

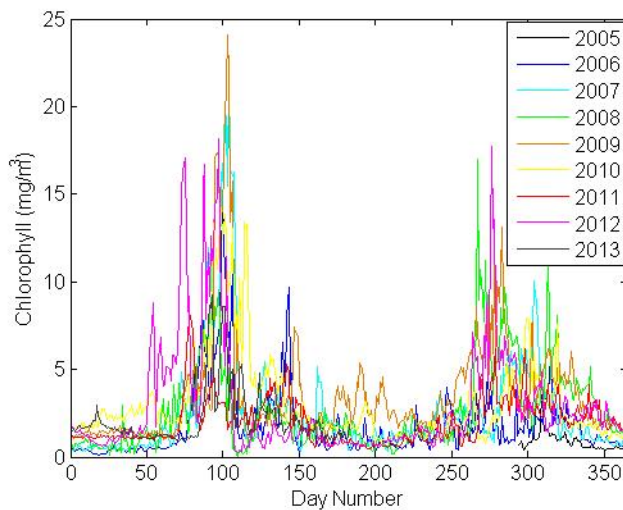


Figure 3. Annual patterns of daily median chlorophyll observed at Buoy A.

(fluorescence per chlorophyll) is. Thus under conditions of NPQ, *in situ* fluorescence is not a good proxy for phytoplankton biomass as the fluorescence per chlorophyll yield can vary 10 fold due to NPQ. The times of day for which NPQ decreases the yield appear to be approximately 0900 to 1500 depending upon cloudiness. Thus a simple, direct comparison between discrete samples collected at the buoy site and the simultaneous fluorescence values is likely to exhibit large discrepancies.

Variations in the seasonal cycle of phytoplankton are apparent in the daily median chlorophyll observations (Figure 3). It is clear that there is substantial variability in both the timing and intensity of the spring and fall blooms at the Cape Ann buoy location. Spring blooms initiate as early as February (e.g. 2012) or as late as April (e.g. 2013) depending upon the timing and mechanism for stratification. The peak concentrations vary from approximately 10 to 25 mg/m^3 . There also appears to be a substantial secondary bloom in May most years. 2009 exhibited a substantial set of mini-blooms throughout the summer. Autumn blooms typically initiate in mid-September to mid-October and last until destratification is complete in December. The magnitude of the fall blooms is much more variable compared to spring blooms due to the dependence on the intensity of mixing and re-injection of nutrients into the euphotic zone.

In the previous report (Roesler 2011), the timing and mechanism for the initiation of spring blooms on the shelf in the Gulf of Maine was discussed, in particular the role of hydrologic forcing on early salinity stratification compared to the more predictable and less variable thermal stratification. One implication of the variation in timing of the spring bloom appears to be variations in the specific growth rates during the spring bloom (Figure 4). The daily biomass-

specific growth rates, μ (d^{-1}), were computed from the best fit exponential slope of the form $Chl(t_2) = Chl(t_1) \exp(\mu * (t_2 - t_1))$ fit to daily chlorophyll fluorescence observations and time during the exponential growth phase of the spring bloom. The first observed exponential increase in chlorophyll concentration was considered the first bloom of the season ([Behrenfeld and Boss 2014](#)). Spring bloom growth rates varied from a low of 0.02 d^{-1} to a high of 0.23 d^{-1} (a

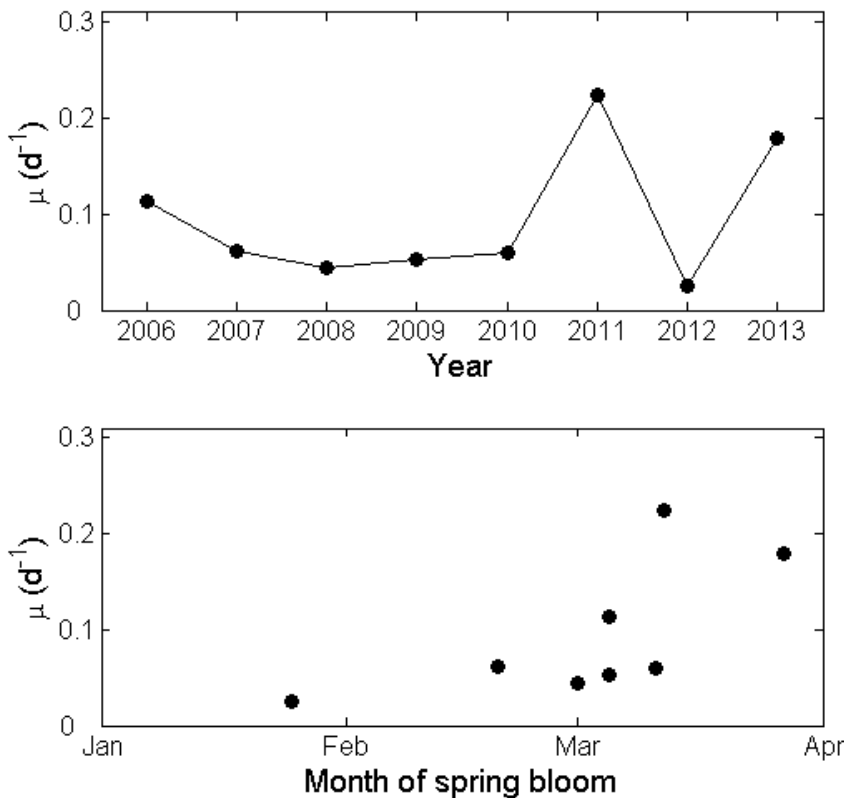


Figure 4. (top panel) Estimated value of the specific growth rates during the spring bloom for each year. (bottom panel) Dependence of the specific growth rate on the time of year.

specific growth rate of 0.65 d^{-1} represents a doubling per day, a value obtained in the laboratory under ideal conditions for fast-growing species of diatoms). Growth rates exhibited an exponential increase with the month of the onset. Phytoplankton growth rates typically exhibit a Q_{10} of two for temperature dependence, meaning that for every ten degrees (C) increase in temperature, growth rates will double. The temperature of the upper water column is highly seasonally dependent. Thus the implication for blooms occurring earlier in the year is that they will occur at colder temperatures and thus will exhibit lower growth rates. This observation warrants further investigation as the predictions for the Gulf of Maine are earlier ice out and increased and earlier precipitation events, both of which will induce earlier salinity-initiated stratification and hence earlier but slower-growing blooms

Conclusions

The estimation of chlorophyll concentration from *in situ* fluorometry is complicated by both physiological sources of variation (NPQ) and natural variations in the fluorescent yield due to species-specific variation (discussed in prior report). However, a well calibrated and well understood time series of chlorophyll fluorescence yields not only robust estimates of chlorophyll biomass, but also physiological characteristics of the phytoplankton such as the saturating irradiance for photosynthesis (if paired with an irradiance sensor) and *in situ* specific growth rates for the population.

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Massachusetts Water Resources Authority
Charlestown Navy Yard
100 First Avenue
Boston, MA 02129
(617) 242-6000
www.mwra.com