Hourly, Daily and Seasonal Climatology of *In Situ* Chlorophyll Fluorescence Observations on NERACOOS Mooring A01 and Comparison with Satellite-derived Chlorophyll Estimates

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Hourly, Daily and Seasonal Climatology of *In Situ* Chlorophyll Fluorescence Observations on NERACOOS Mooring A01 and Comparison with Satellite-derived Chlorophyll Estimates

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Introduction

Nearly a decade of hourly observations of calibrated *in situ* chlorophyll fluorescence and turbidity have been collected from the NERACOOS Mooring A01 as part of the original Gulf of Maine Ocean Observation System (GoMOOS) and more recently the NorthEast Regional Association of Coastal and Ocean Observing Systems (NERACOOS). The Mooring A01 bio-optical observing equipment consists of a WETLabs ECO FLNTU combination chlorophyll fluorometer and turbidity sensor, an ECO battery pack, and a DH4 data handler. The DH4 provides power to the sensor, records a 30-second burst sample hourly, and sends resulting mean values to the mooring's central Campbell data logger for real-time transmission. Hourly observations are provided in near real-time by the University of Maine Physical Oceanography Group via the web portal (http://gyre.umeoce.maine.edu/data/gomoos/buoy/html/A01.html). The time course of observations of calibrated chlorophyll fluorescence and turbidity at Mooring A01 are presented in this report along with results and statistics of post-processing steps, and computation of daily estimates and seasonal climatologies. As a part of the analysis, *in situ* observations of calibrated chlorophyll fluorescence are compared to estimates of chlorophyll concentration derived from the MODIS Aqua ocean color satellite, to assess closure between the two methods of time series observations.

Methods

As has been previously published (Roesler 2014a, b), the two FLNTU sensors are serviced and calibrated by the WET Labs factory in between deployments. The fluorometers are calibrated in the lab prior to deployment using ten dilutions of a monospecific culture of the diatom *Thalassiosira pseudonana* (Proctor and Roesler 2010). The culture is grown in nutrient replete L1 media at an irradiance that maximizes growth rates (i.e. ~300 μEin m^{-2} s^{-1}) and minimizes pigment packaging due to low light acclimation. The culture is harvested in exponential growth with maximal extracted chlorophyll concentrations between 20-50 mg m^{-3}. This approach to calibration provides a transfer function between sensors and between a single sensor over time, accounting for variations in sensor gain, and also provides conversion of the signal from digital counts (millivolts) to biogeochemical units (mg m^{-3}). Because the excitation wavelength (470 nm) does not directly stimulate chlorophyll fluorescence, it is not possible to calibrate with a standard dilution of purified pigment. In vivo fluorometers take advantage of the energy transference between accessory pigments in the light harvesting complexes to chlorophyll *a* by stimulating accessory pigment absorption at 470 nm. While the fluorescence yield (fluorescence per extracted chlorophyll) varies between species, as a function of environmental acclimation, growth phase, and non-photochemical quenching, each of these sources of variability can be assessed on long-term time scales of observations and thus the impacts can be minimized or exploited for further information (Roesler and Barnard 2013).

Post-processing of the real-time data includes evaluation of changes between recovery/deployment operations to assess biofouling, drift and calibration offsets. The raw hourly observations are mean values of hourly 30-second burst samples. Corrected hourly

values are generated by removing biofouled values and correcting remaining values for calibration drift. Specific definitions of quality flags are given in the data files associated with this report. The negative chlorophyll and turbidity values are no longer systematically removed from the data set, as done in prior processing of these data. Rather, the calibration uncertainties suggest that the resolution of the optical observations is of order 0.1 mg chl/m^3 and 0.1 NTU (non-dimensional turbidity units), respectively. Thus an observed value of -0.09 mg m^{-3} cannot be distinguished from 0.01 mg m^{-3}; it is within the uncertainty of zero concentration. Removing the negative values within the accuracy of the sensor has now been deiscontinued because it leads to positive biasing of the observed data (Thompson 1998).

Results

The raw and processed time series observations of chlorophyll and turbidity for the entire data set are shown in Figure 1. Much of the post processing involves removal of observations suspected contaminated by biofouling. This is particularly apparent in the turbidity time series for which the end of each deployment is typically biofouled. These flagged biofouled observations represent approximately 5% and 12% of the total hourly observations for chlorophyll fluorescence and turbidity respectively.

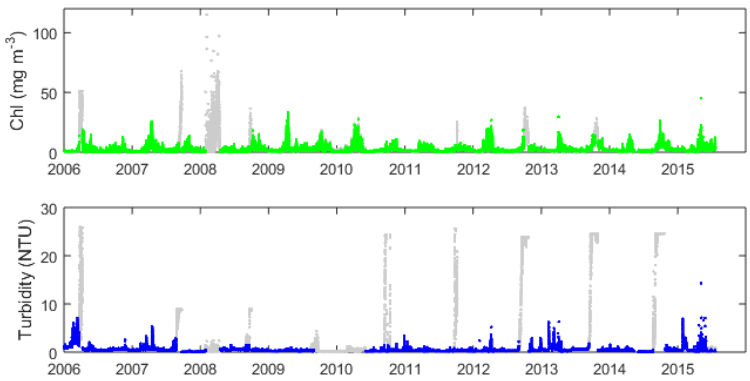

Figure 1. Hourly observations of raw (grey) and post-processed (colored) time series of calibrated chlorophyll fluorescence (upper) and turbidity (lower).

Removal of biofouled data in the time series results in reduction of the mean, median and standard deviation of the observed values (Table 1). As expected, the mean values of the corrected data exhibit much larger reductions than the median values, consistent with the observation that biofouled observations are infrequent and of large magnitude. The negative or saturated offset flags represent approximately 8% and <1% of the total observations for chlorophyll fluorescence and turbidity, respectively. Instrument drift, which is correctable, accounts for approximately 1% and 2.5% of chlorophyll fluorescence and turbidity, respectively.

Table 1. The mean ± standard deviation, median and mode values of the raw and post-processed observations of chlorophyll and turbidity from the moored package, and from the satellite derived chlorophyll estimates (see text for details).

		Raw Observations			Processed Observations		
Observation	units	Mean ± Std	Median	Mode	Mean ± Std	Median	Mode
Moored Chlorophyll	mg m^{-3}	3.20 ±5.15	1.75	1.17	2.45 ± 2.67	1.61	1.17
Satellite Chlorophyll	mg m^{-3}				2.63 ± 2.85	1.73	1.03
Moored Turbidity	NTU	1.61 ± 4.81	0.38	0.24	0.48 ± 0.50	0.37	25.54

A histogram of the raw and corrected observations (Figure 2) indicates that while the shapes of the histograms appear similar, the post-processing does remove the negative observations as well as the infrequent but very large observations associated with saturated values and biofouling; the mean and median values for both chl and turbidity are lower but within the observed standard deviations. For turbidity in particular, large rare observations are more common than for chlorophyll fluorescence.

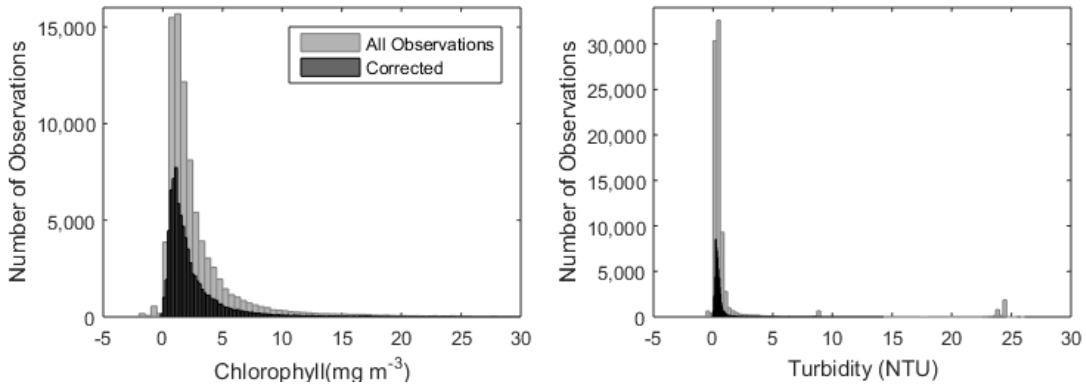

Figure 2. Histogram of raw (gray) and corrected (black) hourly observations of chlorophyll (left panel) and turbidity (right panel) at Mooring A01 2005 – 2015.

Daily median calibrated chlorophyll and turbidity observations for the 2005 to 2015 time series are shown in Figure 3. Annual spring and fall phytoplankton blooms are evident in the chlorophyll time series with peak bloom values exceeding 10 mg m^{-3} each year, although these occurrences are relatively rare (Figure 2) compared with modal concentrations of approximately 2.45 mg m^{-3} (Table 1). The seasonal cycle in turbidity is less distinct with a single maximum per year occurring in the springtime.

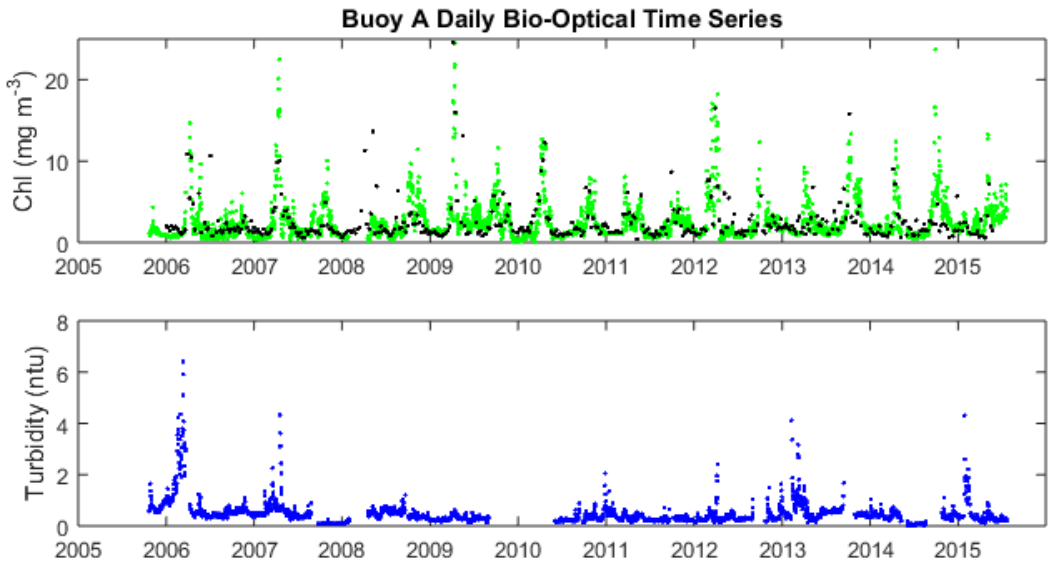

Figure 3. Time series hourly observations of calibrated chlorophyll fluorescence (upper) and turbidity (lower) from Mooring A01 over the bio-optical deployment period. In the upper frame the 8-day estimates of chlorophyll concentration obtained from MODIS 4km Standard Product Chlorophyll for a 0.1 degree square centered on Mooring A01 are shown by black dots.

Validation of the *in situ* bio-optical observations is quite limited due to the relatively few visits to the mooring. Thus we look to alternative data sources for validation. The MODIS ocean color sensor on the AQUA satellite provides estimates of near surface chlorophyll concentration (http://observationaloceanography.com/satellite-data/ocean-color-modis-aqua/). The 8-day composite, 4-km resolution data are available at the Giovanni online data system, developed and maintained by the NASA GES DISC (Acker and Leptoukh 2007). Satellite chlorophyll time series data were obtained from January 2006 through June 2015 for a 0.1 by 0.1 degree square centered on Mooring A01's location. This area includes more than the nearest individual 4-km pixel nearest to the mooring, and was selected in order to increase the number of cloud-free pixels found in the time series. Chlorophyll estimates from *in situ* fluorescence and by satellite retrieval are similar in both magnitude and temporal pattern (Figure 3). The satellite even replicates the infrequent large values that are at times questioned because they exceed the average peak chlorophyll concentrations by up to a factor of 5 and are not commonly sampled by shipboard due to their rare and patchy occurrences. Validation of this sort is powerful because of the very different theoretical basis of measurement. Ocean color is sensitive to absorption by all phytoplankton pigments, while *in situ* fluorescence is an optical property specific to the chlorophyll molecule. The comparison is also powerful because of the differences in temporal (8-day composite vs. daily) and spatial sampling regimes (composite of 0.1 degree square area vs. point observation). Descriptive statistics show comparable mean, median and standard deviations from the satellite and *in situ* fluorometry (Table 1; Figure 4).

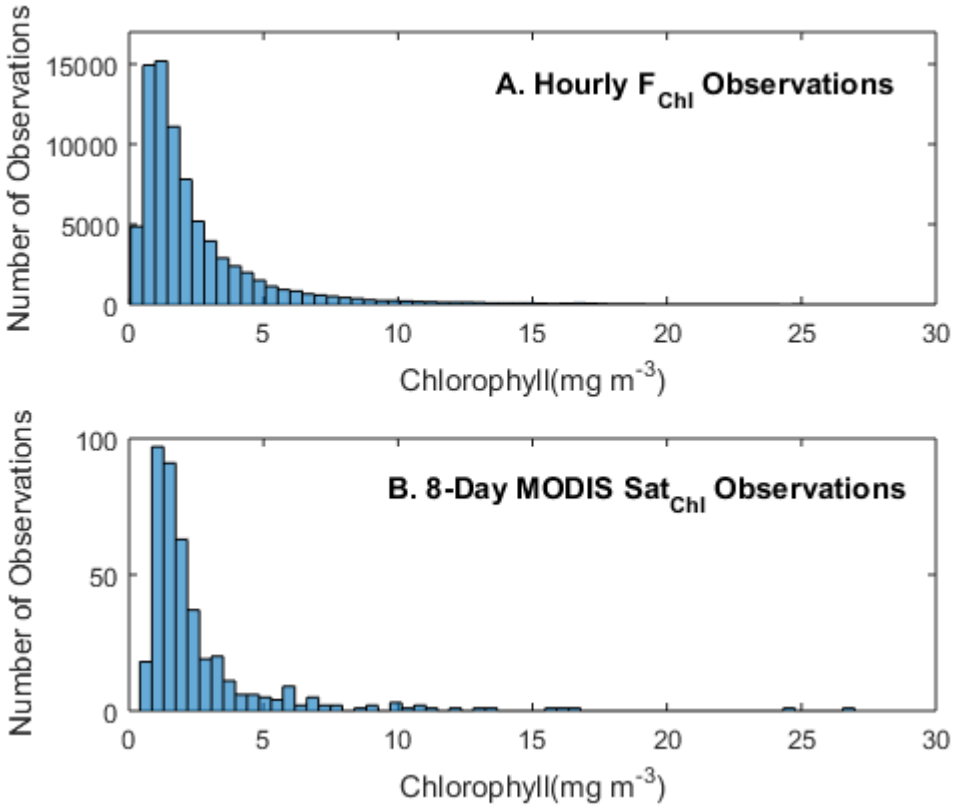

Figure 4. Histogram representations of daily *in situ* calibrated chlorophyll fluorescence obtained from the Mooring A01 bio-optical sensor package (A) and the 8-day estimates of satellite-derived chlorophyll concentration obtained from MODIS observations (B).

Seasonal climatology information is constructed by accumulating the daily fluorescence and turbidity observations for each day number (Figure 5). There is a clear seasonal structure in chlorophyll, with spring and fall peaks. Variability in turbidity does not follow a pattern similar to that in chlorophyll; a single maximum in turbidity appears to occur between February and April, likely due to suspended sediments carried by rivers during the spring freshet.

The seasonal pattern in chlorophyll is modeled by computing daily median values and performing non-linear least squares fits (results in Table 2) to the analytic function of time *t*

$$chl(t) = B + P_S e^{-\frac{1}{2}((t-t_p)/t_d)^2} + P_F e^{-\frac{1}{2}((t-t_p)/t_d)^2},$$

where B is the background chlorophyll and the two Gaussian terms represent the spring and fall blooms, with each bloom characterized by a peak concentration *P* (mg m^{-3}) a central date t_p (day of year) of peak concentration, and a duration parameter t_d (days).

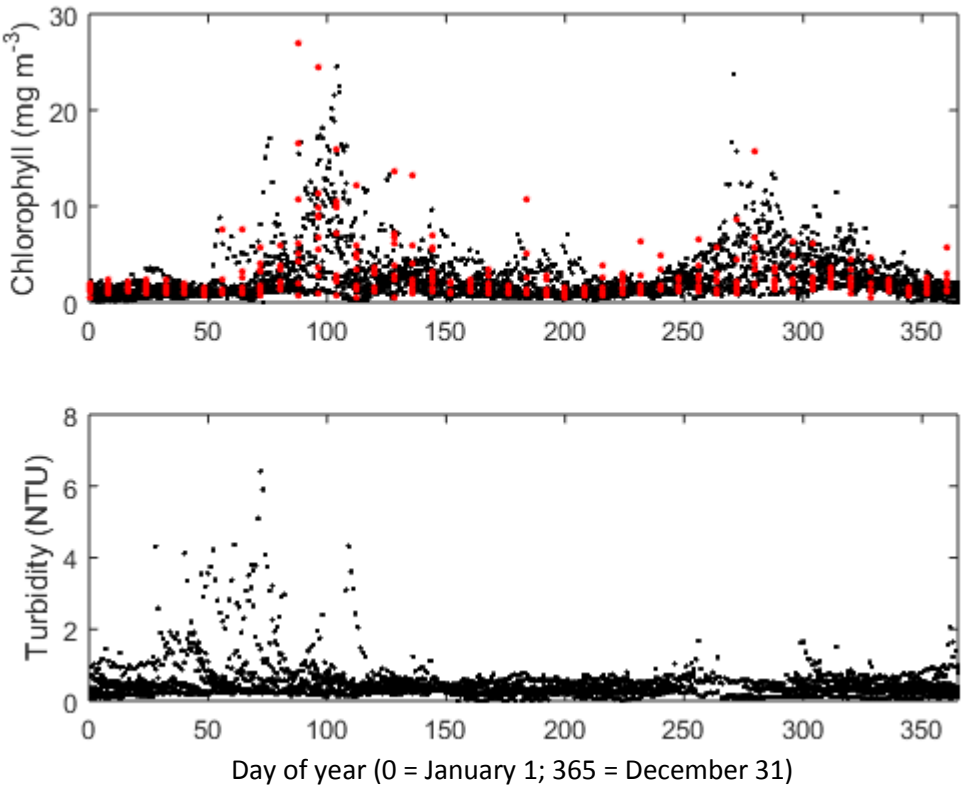

Figure 5. Observations of hourly chlorophyll fluorescence (upper) and turbidity (lower) from all years at Mooring A01, shown as function of day of year (horizontal axis) to help illustrate characteristics of the seasonal climatology. In upper frame, 8-day MODIS chlorophyll observations are shown in red.

Table 2. Statistics of the timing, intensity and duration of the spring and fall blooms observed at NERACOOS Mooring A01, all years, with four other NERACOOS moorings shown for comparison.

	Spring bloom			**Fall Bloom**			**Background**
NERACOOS Mooring	Peak (mg m^{-3})	Central day	Duration (d)	Peak (mg m^{-3})	Central day	Duration (d)	Concentration (mg m^{-3})
A01	10.2	100	8	2.9	289	24	1.7
B01	4.8	107	19	3.6	287	19	1.3
M01/M02	1.8	119	29	2.2	275	18	0.8
E01/E02	4.0	126	41	3.5	265	40	0.2
I01	3.9	201	74	N/A	N/A	N/A	0.4

The Mooring A01 peak concentration is more than double that found at the other mooring locations (Table 2). The background chlorophyll concentration decreases along the shelf from Mooring A01 to Mooring I01. The typical spring bloom at Mooring A01 occurs on April 10, one week prior to the bloom at NERACOOS Mooring B01 (off Cape Elizabeth) and more than 3 months before the peak at NERACOOS Mooring I01 upstream of Penobscot Bay in the Eastern Maine Coastal Current. The Mooring A01 bloom durations are shorter than at other mooring locations by weeks to a month. Fall bloom peaks are much less variable in timing (occurring within about a three-week range at all sites) and weaker in magnitude, but with more comparable durations at all sites.

Results from analytical fits (not shown) to satellite-estimated chlorophyll near A01 (discussed above) are similar to those in Table 2.

The years 2005, 2007, 2008 and 2010 are noteworthy as they are associated with early ice out in the rivers, earlier gulf-wide stratification and earlier nearly synoptic blooms. Although the spring blooms at Mooring A01 are relatively unchanged in these years, those at Mooring I01 are significantly earlier and shorter lived. The bloom statistics for the years 2005-2010 (the last for which there is processed data for moorings B-N) are shown in Table 3. While the timing of the spring bloom peaks at moorings A01 and B01 are not statistically earlier than for the entire time series, they are significantly earlier at the upstream moorings E01-M01 by weeks to months, with peak timing nearly the same as that observed at A01.

Table 3. Same as Table 2 but for 2005-2010.

	Spring bloom		
Mooring	Peak (mg m^{-3})	Central day	Duration (d)
A01	9.1	100	9
B01	3.9	120	18
M01/02	6.9	104	12
E01/E02	4.6	117	11
I01	2.5	102	8

Summary

Nearly a decade of hourly bio-optical observations of calibrated chlorophyll fluorescence and turbidity collected from the NERACOOS Mooring A01 has undergone post-processing. Flags have been applied to the data to indicate instrumental offset (dark reading) corrections, anomalous negative readings below the detection limits (after offset corrections), and biofouling impacted data. Specific definitions of quality flags are given in the data files associated with this report.

Daily calibrated chlorophyll fluorescence observations compare well both in magnitude and temporal pattern with the satellite-derived estimates of chlorophyll concentration from 8-day composite 4-km resolution values from a 0.1 degree square area centered on the mooring location. These comparisons support the large but rare high values observed during the spring and fall blooms over the time series that are rarely validated by water samples. The seasonal climatology for mooring A01 indicates two main blooms, spring and fall, which precede those observed at upstream moorings farther to the north in the Gulf of Maine. The seasonal pattern in turbidity is more variable and appears more linked to the spring freshet.

Acknowledgments

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