In Situ Chlorophyll Fluorescence Observations on NERACOOS Mooring A01: Revised Data Flagging and Changing Phenology

Massachusetts Water Resources Authority
Environmental Quality Department
Report 2016-15

Roesler, CS. 2016. ***In Situ*** **Chlorophyll Fluorescence Observations on NERACOOS Mooring A01: Revised Data Flagging and Changing Phenology**. Boston: Massachusetts Water Resources Authority. Report 2016-15. 11 p.

In Situ Chlorophyll Fluorescence Observations on NERACOOS Mooring A01: Revised Data Flagging and Changing Phenology

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Period of Performance:	1 July 2015 - 30 June 2016

Introduction

For more than a decade, hourly observations of calibrated *in situ* chlorophyll fluorescence and turbidity have been collected from Mooring A01 off Cape Ann in Massachusetts Bay. This work was first done as part of the original Gulf of Maine Ocean Observation System (GoMOOS) and more recently through 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 hourly time course of observations of calibrated chlorophyll fluorescence and turbidity at Mooring A01 are presented in this report along with a description of new flagging protocols, daily statistics and an analysis of phenology.

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 factory reported resolution of each detector is 1 digital count, which is comparable to approximately 0.012 mg/m^3 and 0.005 NTU, respectively, depending upon specific sensor calibrations. In practice the uncertainty of the sensors given the natural variability in the burst samples, combined with the uncertainty in the calibration slope (or factor scale factors), yields uncertainty levels of 0.05 mg/m^3 and 0.05 NTU, respectively.

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 for quality assurance / quality control (QA/QC) is a five step process.

Step 1. Evaluation of the offset between recovery/deployment of sensors that appear in the real-time data as step functions. These offsets are evaluated by post-recovery calibration or by identification of offset relative to prior and subsequent deployments. The offsets are flagged and the data are corrected.

Step 2. Biofouling is identified by a logarithmic increase in signal to values determined to be out of range or saturating for the sensor. Biofouling takes two forms. The first form is a smooth increase associated with biofilm growth. The second form is an increase with extreme hour-to-hour variability due to structural growth on the sensor such as seaweeds, that contaminate both the fluorescence and turbidity signals as they waft into the optical sensing volume. Biofouled data are flagged as either biofilm or structural and removed from the data stream.

Step 3. Non-photochemical quenching (NPQ) of chlorophyll fluorescence has been observed in surface waters under saturating irradiances, as demonstrated by Figure 1. Data in the figure are from a mooring, at a different location than Mooring A01, on which an irradiance sensor was deployed to enable observing the process well. The effect decreases exponentially with depth. At the surface the onset occurs as early as dawn (e.g. 7am in June) and the recovery is prior to sundown (e.g. 6pm in June). The importance and extent of this effect, and the need to correct for it, have only relatively recently begun to be recognized.

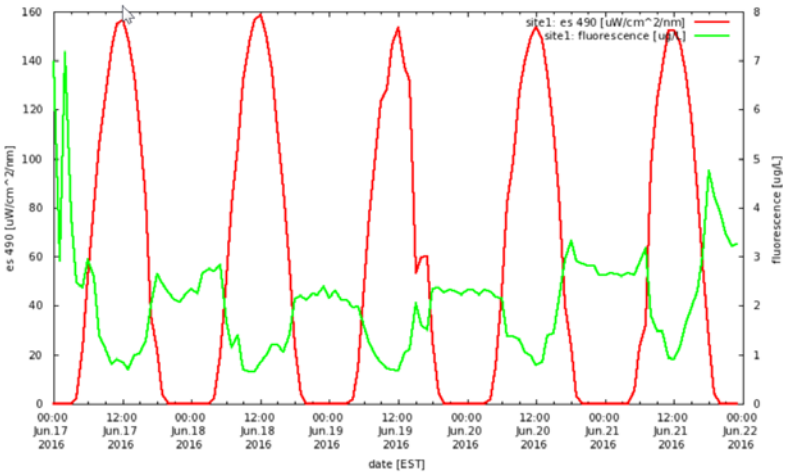

Figure 1. Graphical output of realtime irradiance (red; 490 nm) and chlorophyll fluorescence (green) data streams from the Bowdoin College LOBO mooring in Harpswell Sound, Casco Bay. Data are available at http://bowdoin.loboviz.com.

Because an irradiance sensor was not deployed on Mooring A01, in order to be conservative and limit the influence of NPQ on the dataset, all daytime chlorophyll fluorescence observations during light hours are flagged as NPQ-impacted and removed from the data stream. This is a large portion of the data, but nevertheless the nighttime data are sufficiently numerous to provide meaningful information about day to day changes in concentrations. Algorithms to correct NPQ-impacted daytime data are being developed and may be applied in future years;

such efforts will benefit strongly from inclusion of an irradiance sensor on Mooring A01, which is planned during the 2016-2017 sampling period.

Step 4. Single value outliers (SVO) are identified by quantifying the first differences that exceed 100% of the coefficient of variation and are in excess of 15 mg/m^3 or 3 NTU. SVO observations are flagged and removed from the data streams.

Step 5. The minimum detection level (MDL) of the sensors is 0.05 mg/m^3 and 0.05 NTU, respectively. Observations below -0.05 are flagged and removed. Values between -0.05 and 0, and those between 0 and 0.05 are independently flagged but not removed from the data, because removing the negative values within the accuracy of the sensor leads to positive biasing of the observed data (Thompson 1998).

In order to best track the sequences of flagging and correction and optimize for future correction schemes, the format of the hourly data arrays has changed from previous years. Chlorophyll fluorescence and turbidity are submitted as independent data arrays. The data string format for the chlorophyll fluorescence data array (BuoyA_HChl_2016_v2.mat and BuoyA_HChl_2016_v2.dat for Matlab and ASCII formats) is provided in Table 1.

Table 1. Format of the hourly observational data file for chlorophyll fluorescence.

Column	ID	Value/Range	Comment
1	Year	2005-2016	
2	Month	1-12	
3	Day	0-31	
4	Hour	0-25	
5	Minute	0-60	
6	Second	0-60	
7	Date.Time	732607 - 736575	Matlab format
8	Raw Fchl	-1.63 - 115.04	
9	Flag_Offset	0, 1	
10	Fchl_corr_offset		Corrected for offsets
11	Flag_Biofouling1	0, 1	Biofilm
12	Flag_Biofouling2	0, 1	Structural
13	Fchl_corr_biofouling	NaN	Values removed
14	Flag_NPQ	0, 1	NPQ
15	Fchl_corr_NPQ	NaN	Values removed
16	Flag_SVO	0, 1	Single value outlier
17	Fchl_corr_SVO	NaN	Values removed
18	Flag_MDL1	0, 1	<-Minimum detection level
19	Flag_MDL2	0, 1	-MDL to 0
20	Flag_MDL3	0, 1	0 to +MDL
21	Fchl_corr_MDL1	NaN	MDL1 removed
22	Deployment	15 - 36	Deployment number

The data string format for the turbidity data array (BuoyA_HNTU_2016_v2.mat and BuoyA_HNTU_2016_v2.dat for Matlab and ascii formats) is provided in Table 2.

Table 2. Format of the hourly observational data file for chlorophyll fluorescence.

Column	ID	Value/Range	Comment
1	Year	2005-2016	
2	Month	1-12	
3	Day	0-31	
4	Hour	0-25	
5	Minute	0-60	
6	Second	0-60	
7	Date.Time	732607 - 736575	Matlab format
8	Raw Turbidity	-0.60 25.95	
9	Flag_Offset	0, 1	
10	Fchl_corr_offset		Corrected for offsets
11	Flag_Biofouling1	0, 1	Biofilm
12	Flag_Biofouling2	0, 1	Structural
13	Fchl_corr_biofouling	NaN	Values removed
14	Flag_SVO	0, 1	Single value outlier
15	Fchl_corr_SVO	NaN	Values removed
16	Flag_MDL1	0, 1	<-Minimum detection level
17	Flag_MDL2	0, 1	-MDL to 0
18	Flag_MDL3	0, 1	0 to +MDL
19	Fchl_corr_MDL1	NaN	MDL1 removed
20	Deployment	15 - 36	Deployment number

Daily statistics are calculated from the final data column for chlorophyll fluorescence (column 21) and turbidity (column 19). The daily data arrays have the format provided in Table 3 (shown for chlorophyll fluorescence, same format for turbidity).

Table 3. Format of the daily observational data file for chlorophyll fluorescence.

Column	ID	Value/Range	Comment
1	Year	2005 to 2016	
2	Month	1-12	
3	Day	0-31	
4	Date	732607 to 736575	Matlab format
5	Mean Fchl	-0.01 to 25.79	Daily mean chlorophyll
6	Median Fchl	-0.01 to 25.45	Daily median chlorophyll
7	Stdev Fchl	0.00 to 5.86	Daily standard deviation
8	N	0 to 24	N^o hourly obs in daily value
9	Deployment	15 to 36	Deployment number

Results

The sequence of data processing is shown in Figure 2 from raw hourly observations (A), offset correction (B), biofouling removal (C), NPQ removal (D), and SVO and MDL removal (E).

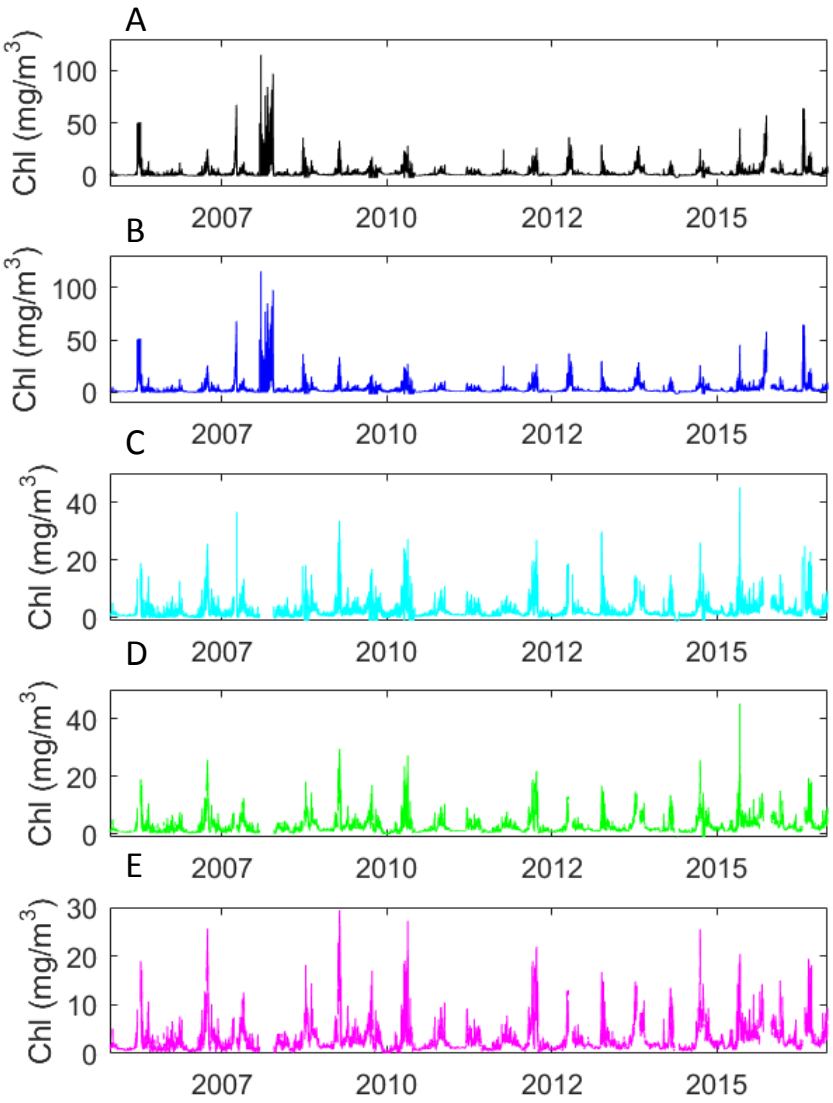

Figure 2. Time series hourly observations of chlorophyll fluorescence from 2005 to 2016 for Mooring A01 showing sequential data flagging and processing: (A) raw observations, (B) offset correction, (C) biofouling removal, (D) NPQ removal, (E) outlier and below minimum detection level removal. Part E is the final data array.

The comparable analyses for turbidity are shown in Figure 3.

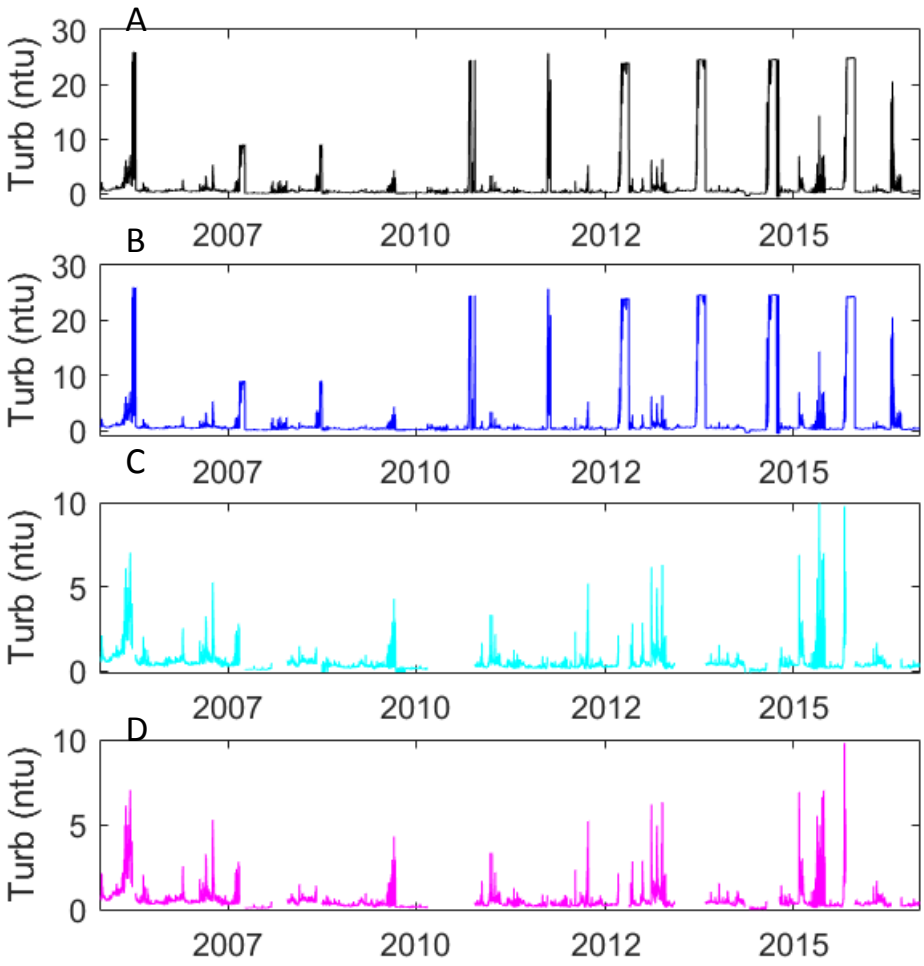

Figure 3. As in Figure 1 but for turbidity. There is no NPQ correction for turbidity.

While correcting for the offsets between deployments improves the deployment to deployment accuracy, it does not significantly impact the statistics of the time series (Table 4). However, removal of biofouled data in the time series results in significant reduction of the mean and standard deviation of the observed values. In addition, the NPQ correction raises the mean chlorophyll fluorescence value. The SVO and MDL stages do not impact the statistics of the data arrays. Of the approximately 95,000 hourly observations, almost half were removed due to NPQ flagging, a large portion as noted above. The offset correction impacts over 3,600 observations. Approximately 5,200 observations were flagged as biofouled with about 2/3 of that number due to structural biofouling and about 1/3 due to biofilm. A negligibly small portion of fluorescence observations were removed by the SVO or MDL stages. Similar patterns were observed for the turbidity time series although overall all of the processing steps impacted a larger number of hourly observations and the biofilm type of fouling dominated.

Table 4. Statistics on 2005-2016 hourly chlorophyll and turbidity observations as a function of QA/QC data processing. Columns represent sequential processing through each step. The final observational data array is the last column.

Stat	Raw	Offset (1)	Biofouling (2)	NPQ (3)	SVO (4)	MDL (5)
Chlorophyll						
N^{o} Flags		3621	1515; 3711	42,801	3	298; 38; 22
Mean	3.42	3.36	2.57	2.71	2.71	2.73
Median	1.86	1.80	1.73	1.82	1.82	1.83
Std Dev	5.44	5.44	2.71	2.74	2.73	2.72
Turbidity						
N^{o} Flags		4829	9143; 8995	Na	3	710; 266; 606
Mean	1.80	1.77	0.45	Na	0.45	0.46
Median	0.38	0.37	0.34	Na	0.34	0.34
Std Dev	5.17	5.14	0.51	Na	0.51	0.50

Phenology

Seasonal climatology is constructed by accumulating the daily fluorescence and turbidity observations for each day of the year (Figure 4). There is a clear seasonal structure in chlorophyll, with spring and fall peaks. Variability in turbidity does not exhibit a pattern similar to that in chlorophyll; higher values are observed in the spring but not at a predictable date, 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

$$chl(t) = B + P_S e^{-\frac{1}{2}((t-c_S)/d_S)^2} + P_F e^{-\frac{1}{2}((t-c_F)/d_F)^2},$$

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

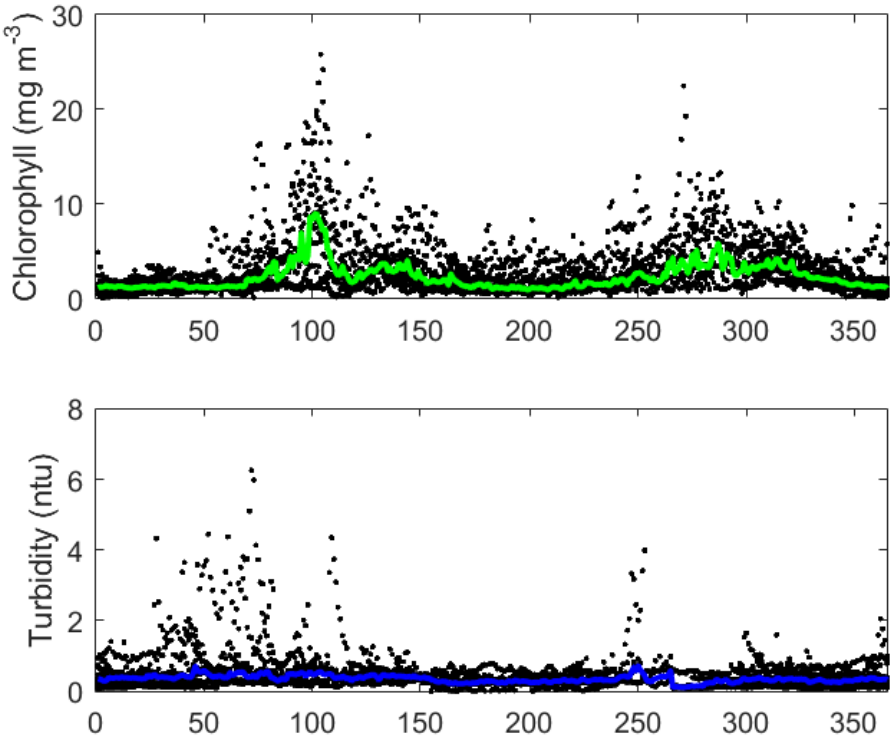

Figure 4. Observations of daily chlorophyll fluorescence (upper) and turbidity (lower) from all years at Mooring A01, shown as function of day of year (horizontal axis) to help illustrate characteristics of the seasonal climatology (shown as green in upper, blue in lower).

The decade of daily observations yields climatological amplitudes of 6.20 and 2.35 mg/m^3 for spring and fall blooms, peak timings of 101 and 291 (day numbers) and durations of 6 and 24 days, respectively. However there is a considerable amount of variability between years. Seasonal cycles in chlorophyll are variable between years (Figure 5). The spring bloom has been larger than the fall bloom for 2006, 2007, 2009, 2010, 2012 and 2015. However, the fall bloom has been larger than the spring bloom in 2008, 2013, 2014. The timing the spring bloom peak is climatologically on April 11 (Figure 4), but there is variability in the timing. The peak of the spring blooms for 2006, 2007, 2009 and 2014 were statistically equal to the climatological timing, while 2011-2013 were significantly earlier (days 80-98) and 2008, 2010, 2014-2016 were significantly longer (days 116 to 152). Previous analysis has indicated that the variability in the timing of the spring bloom is largely controlled by the intensity of river discharge (primarily from the Merrimack River, see Figure 6) and the associated salinity contribution to density stratification.

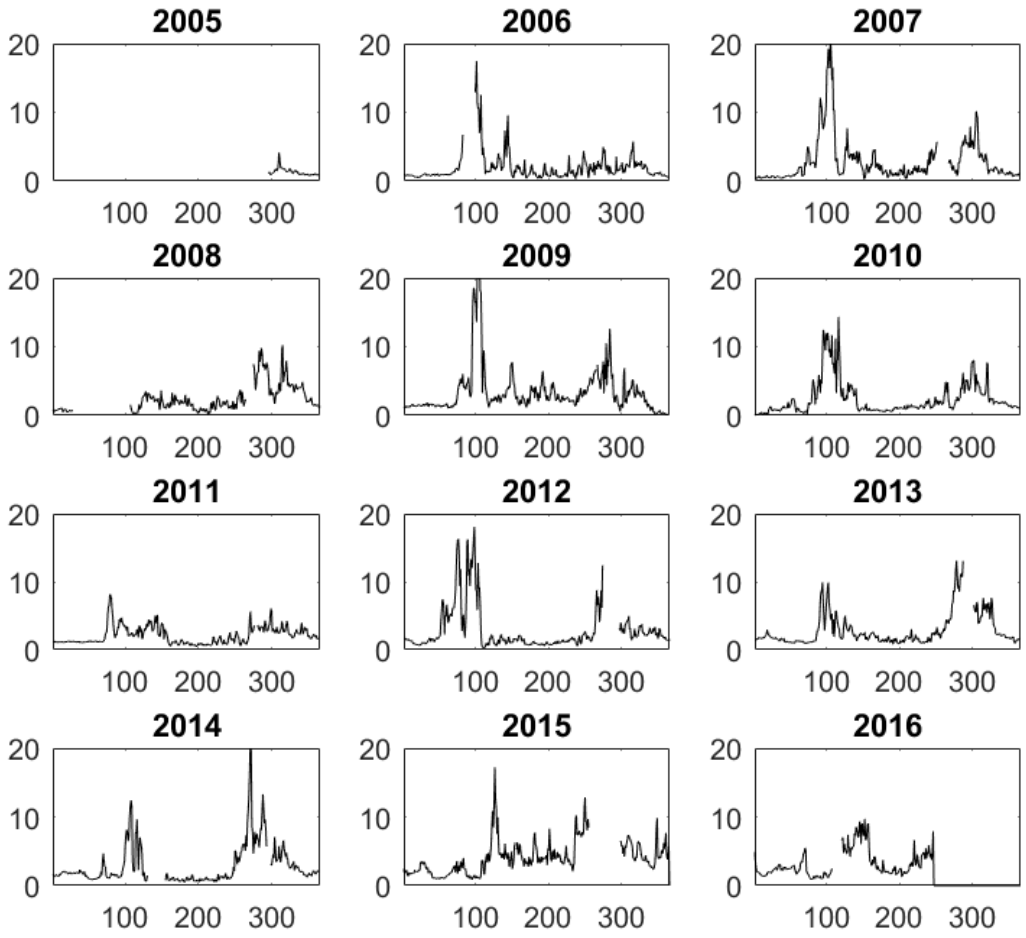

Figure 5. Annual patterns of daily chlorophyll at Mooring A01 for 2005 through 2016.

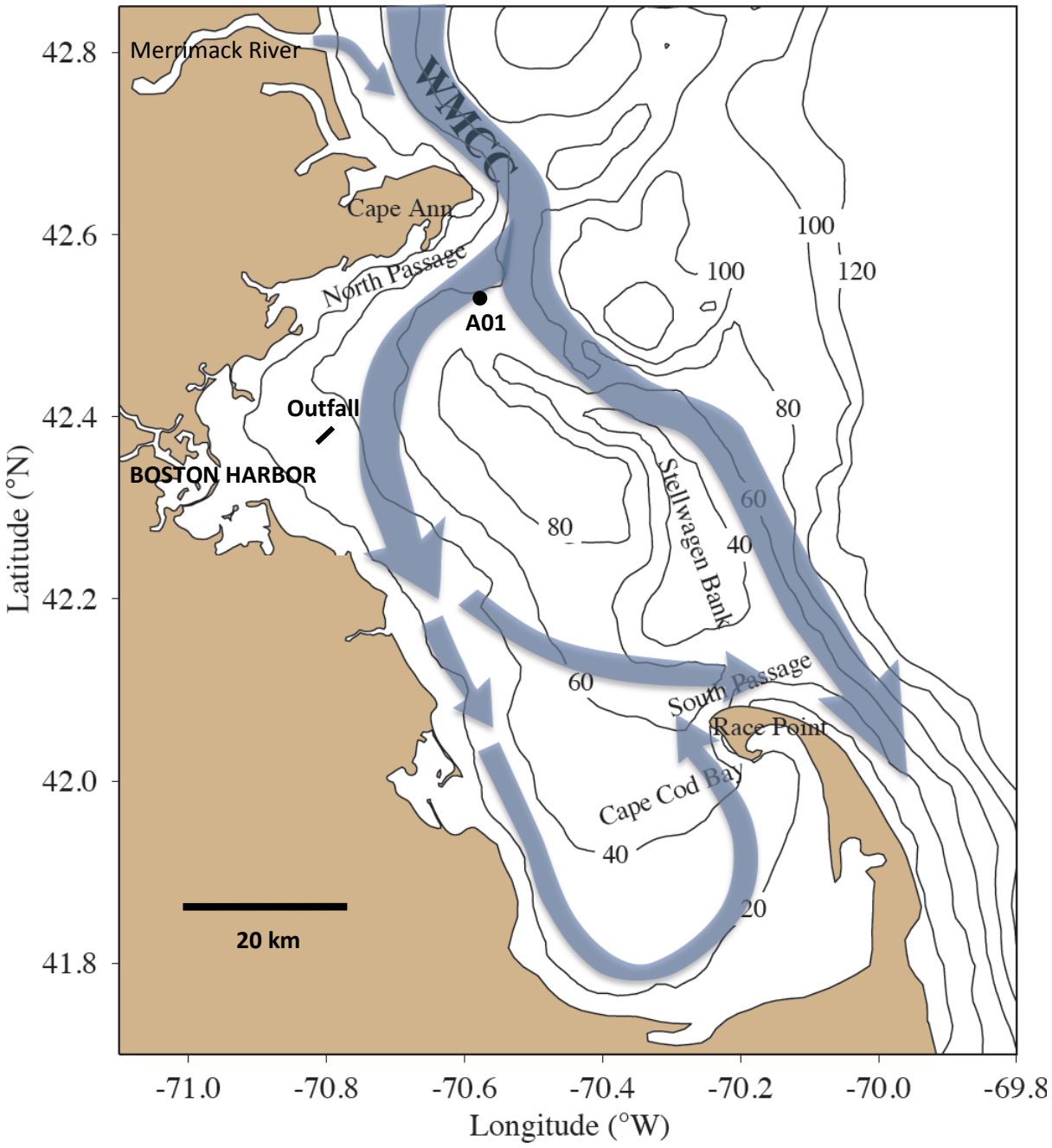

Figure 6. Location of Mooring A01 and schematic of ambient currents including influence of Merrimack River outflow. WMCC is the Western Maine Coastal Current. Adapted from Xue et al. (2014).

Summary

Over a decade of hourly bio-optical observations of calibrated chlorophyll fluorescence and turbidity collected from the NERACOOS Mooring A01 has undergone post-processing with a new protocol for flagging and data correction. The sequential analysis of flags and corrections provides insight into the impact of various instrumental and environmental factors on the retrieved observations.

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