Continuous hourly observations of chlorophyll fluorescence, turbidity, and irradiance in Massachusetts Bay (2005 – 2022) reveal earlier and stronger fall phytoplankton blooms

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Continuous hourly observations of chlorophyll fluorescence, turbidity, and irradiance in Massachusetts Bay (2005 – 2022) reveal earlier and stronger fall phytoplankton blooms.

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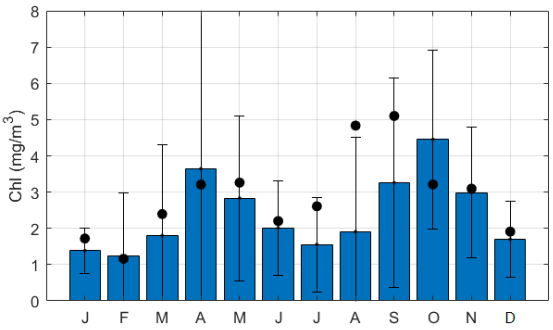
SUMMARY

Since late 2000, the Massachusetts Water Resources Authority (MWRA) has discharged treated wastewater from its Deer Island Treatment Plant in Boston through a 15 km (9 mi) tunnel into Massachusetts Bay. To help ensure that nutrients in the discharge do not contribute to excess growth of phytoplankton (marine algae), MWRA monitoring includes research vessel surveys to measure phytoplankton conditions approximately monthly. The surveys reveal strong seasonal variations with consistent levels year-to-year, including near the outfall.



Monthly median values of chlorophyll fluorescence: median of 2005-2022 (blue bars; error bars represent one standard deviation) and median of 2021-22 sampling, covered in this report (black circles). The 2021-22 annual mean was typical but the timing, or phenology differed: chlorophyll peaks were earlier and longer in spring and earlier, higher and longer in the fall compared to typical year.

MWRA augments the monthly surveys with nearly continuous hourly observations from a buoy in northeastern Massachusetts Bay off Cape Ann. University of Maine maintains the buoy, which collects oceanographic observations, and reports the data in real time online (www.neracoos.org) with support from the Northeast Regional Association of Coastal Ocean Observing Systems and MWRA. Since 2005 MWRA has contracted with Bowdoin College researchers to provide estimates of chlorophyll and turbidity. Chlorophyll is a pigment unique to phytoplankton, providing a robust estimate of concentration. Turbidity is an indicator of water cloudiness due to suspended particles such as sediments and bacteria.

Bowdoin configures and calibrates the bio-optical sensors, works with University of Maine to deploy and recover them at sea, arranges manufacturer repair and maintenance, and interprets results in the context of oceanographic conditions. The chlorophyll fluorometer measures the red light emitted (fluoresced) by the phytoplankton chlorophyll in response to a stimulating blue light flash. The turbidity sensor measures the red light scattered back to the sensor in response to an emitted red light flash. As of 2016, Bowdoin has added two additional sensors to the bio-optical package, a second chlorophyll fluorometer and an above-surface spectral irradiance sensor. The second fluorometer has an automated wiper that reduces biofouling and additional colors of stimulating light flashes to identify different types of phytoplankton. Maintaining the two fluorometers provides required overlap for time series integrity and data redundancy to reduce measurement uncertainty and provide insurance against instrument failure. The irradiance sensor measures the intensity of sunlight and is used to improve the estimate of chlorophyll concentrations derived from fluorescence measurements.

Results of the 2021-22 observations were generally within the ranges of earlier years and did not indicate unusual water quality with respect to chlorophyll concentrations. For all years of data, there is a recurring seasonal pattern with spring and fall chlorophyll increases (blue bars in figure) due to phytoplankton blooms. For 2021-22 (black circles in figure), the annual average phytoplankton concentration was similar to earlier years, while the phenology, or timing of the seasonal progression, included slightly earlier and longer spring bloom and a much earlier,

longer and larger fall bloom. Turbidity, on the other hand, has remained relatively constant, both seasonally within each year and in the long term over 2005-22. This indicates modest seasonal variations and no detectable change over the years in suspended biological particles, such as bacteria or other plankton.

Introduction

This report describes work and results from the July 2022 through June 2023 contract period, which covers all deployments recovered within the contract period, in this case deployment 45, for MWRA's continuous biological monitoring in Massachusetts Bay performed by Bowdoin College researchers. The program focus is real-time monitoring of water quality conditions, with emphasis on marine algae (phytoplankton) through chlorophyll measurements and other suspended particles through turbidity measurements. The goal of the retrospective analysis is to establish seasonal benchmark values against which to evaluate changing values and timing of annual cycles, thereby improving MWRA's ability to detect critical changes in marine algae or suspended particles and respond if necessary. MWRA's Ambient Monitoring Plan, attached to its National Pollutant Discharge Elimination System permit to discharge treated effluent from the Deer Island Wastewater Treatment Plant into Massachusetts Bay, requires this monitoring.

The program consists of bio-optical observations made at a depth of 3 m on the moored buoy off Cape Ann (Figure 1) operated by University of Maine with support from the Northeast Regional Association of Coastal and Ocean Observing Systems (NERACOOS) and MWRA, referred to as Buoy A01 or Mooring A01. When founded in 2005 it comprised a two-channel sensor measuring chlorophyll fluorescence and turbidity. Chlorophyll fluorescence, the red light emitted by phytoplankton in response to their absorption of light, is an indicator of their concentration in seawater. Turbidity is a measure of cloudiness due to suspended particles. It is used to monitor for the presence of other biological particles such as bacteria that might respond directly to changing nutrient loads. Observations began on October 22, 2005, and there now are approximately seventeen years of hourly observations. In 2016 Bowdoin added two additional bio-optical sensors to improve the quality and quantity of the chlorophyll estimates: a second chlorophyll fluorometer and an above-surface irradiance sensor. The second fluorometer solved one observational challenge and provided an additional piece of information about the marine algae community. Previously, a portion of measurements at the end of each deployment was observed to be impacted by biofouling films or branching organism growing on the optical faces of the sensor. The second chlorophyll fluorometer has an integrated wiper that effectively prevents growth on the windows, thereby increasing the usable portion of retrieved data. Second, the fluorometer employs three LEDs (blue, blue-green and green colors) to stimulate fluorescence. The differing fluorescence responses to these three colors provide qualitative information about the composition of phytoplankton. The irradiance sensor, which measures the intensity and color of the solar spectrum, solved a second challenge to estimating chlorophyll concentration from the fluorometer. Under high light levels, the magnitude of the chlorophyll fluorescence signal is damped (quenched) and might be misinterpreted as a decrease in chlorophyll concentration. By knowing the magnitude

of the solar spectrum the mid-day fluorescence readings are corrected, thereby providing improved accuracy in chlorophyll concentration for the hourly observations.

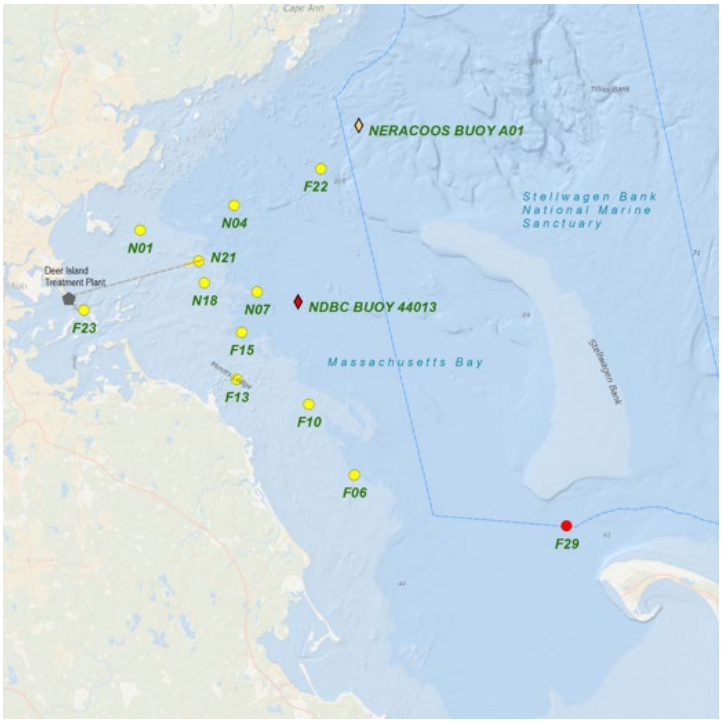


Figure 1. Data in this report are from sensors deployed and operated by Bowdoin College on Buoy A01 (yellow diamond). The buoy is operated by the University of Maine for the Northeast Regional Association for Coastal and Ocean Observing Systems (NERACOOS). For reference, Deer Island Treatment Plant (gray pentagon), outfall tunnel (dashed gray line), outfall (purple line under station N21), MWRA ship survey monitoring stations (yellow circles), and Boston Buoy 44013 (red diamond) operated by the National Data Buoy Center (NDBC) are annotated.

The focus of this report is presentation of the data from deployment A0145, the 45th deployment of the mooring A01, covering the dates 2 November 2021 to 9 September 2022. It is the only A01 deployment recovered within the 2021-22 contract year. The data have been added to the dataset and this report includes brief descriptions of the quality assurance and analysis methods, and bio-optical interpretations of all years of data.

Sensors

The WETLabs ECO FLNTU two-channel sensor is the standard bio-optical device that has been deployed on the mooring since 2005 (e.g., Roesler 2016). In order to provide continuous observations with no gaps between deployments, we dedicate two such sensors to the program and swap them on/off the mooring at the start of each deployment, so at all times one is in the field and the other is on shore. The WETLabs facility (a subsidiary of SeaBird Electronics) services and calibrates the sensors when they are on shore in between deployments in the field. On the mooring the sensors are integrated into a WETLabs DH4 data handler that provides power to the sensors, controls sampling, archives the raw observations of each hourly burst sampling, and provides hourly mean values to a Campbell Scientific data logger (Table 1). The logger incorporates the optical observations, together with those from all other buoy sensors, into a real-time data stream that is sent via cell phone modem or satellite communications to University of Maine. There, the data stream from the FLNTU is parsed,

calibrations are applied, and data products are made available at the online data portal http://gyre.umeoce.maine.edu/data/gomoos/buoy/html/A01.html and sent to NERACOOS, which also presents the data online in real time at their website www.neracoos.org. Since 2016 (deployment A0136), the second fluorometer (F3WB) and the spectral irradiance sensor (OC507-ICSA) have been deployed in a stand-alone configuration integrated into the same DH4. Only a subset of their data is transmitted in real time due to limitations on the DH4 and Campbell logger.

Table 1. Components of the optical sensing package on the buoy, bolded text to indicate how instrument is referred to in text.

INSTRUMENT	PURPOSE
WETLabs ECO **FLNTU**	Optical sensor, measures chlorophyll fluorescence (470 nm excitation) and turbidity, at 3 m depth.
WETLabs ECO **FL3-WB** ("F3WB")	Optical sensor, measures chlorophyll fluorescence (3 excitation wavelengths), at 3 m depth.
Satlantic **OC507**-ICSA	Optical sensor, measures solar irradiance; mounted on the buoy tower.
WETLabs **DH4**	Data logger, collects and stores data from optical sensors; computes mean FLNTU data; transmits means to Campbell Scientific Data Logger, which transmits it in real time to the University of Maine where it is relayed to NERACOOS and posted online.

Each sensor collects set of measurements for approximately one minute every hour. Depending upon the sampling rate of the sensor (approximately once per second), this burst sample consists of approximately 60 measurements. The complete set of measurements in each burst sampling is stored on the DH4. Only the mean value of the burst samples is transmitted in real time due to limitations of the Campbell software. The full data set is retrieved from the DH4 after the mooring is recovered and the sensors removed from its infrastructure, transported to Bowdoin, cleaned, downloaded and post-processed. These individual measurements within each burst sampling are analyzed to ensure the mean values reported in real time are robust estimates of the bursts, by comparison to their median and standard deviation, and to process the data streams from the remaining optical sensors. The result is robust hourly mean values of each optical data stream. Description of the sensor data streams, and the information derived from them is detailed in Roesler (2021).

Instrument Calibration. Recent work has concluded that the factory calibrations of the WETLabs ECO model chlorophyll fluorometers are biased by a factor of 2 globally, with regional patterns in the specific values of the bias (Roesler et al. 2017). For this reason, the laboratory calibration for the chlorophyll fluorometer has always been implemented for sensors on Buoy A01, instead of factory calibrations. Details of the calibration are outlined in Roesler (2021).

Should further improvement to calibration results be desired, Bowdoin researchers now have the capability to measure the full suite of phytoplankton pigments using high performance liquid chromatography (HPLC) following protocols established by the NASA Goddard Space Flight Center Field Support Group (Van Heukelem and Thomas 2005). This is the state-of-the-art method for pigment identification and quantitation. Such analyses could be performed on water samples collected on the ship survey program at the sampling station closest to Mooring A01 (Figure 1), in order to further improve calibrations and to support and validate pigment-based phytoplankton taxonomy.

The 7-step post-processing protocol for the real-time data for quality control

As explained in detail in prior reports (e.g., Roesler 2020, 2021), a series of processing steps are necessary to maintain the high quality of the dataset.

Step 1. Quality assurance on times recorded by the irradiance sensor.

Step 2. Calibration comparison and correction between sensors.

Step 3. Correction for sensor drift.

Step 4. Identification of and removal of biofouled data.

Step 5. Identification, flagging, and correction of chlorophyll fluorescence observations impacted by non-photochemical quenching (NPQ).

Step 6. Removal of single value outliers (SVOs).

Step 7. Identification of values below minimum detection levels (MDLs) and within MDL of zero.

Details and examples for all steps other than #2 can be found in Roesler (2020); details and examples for step #2 can be found in Roesler (2021).

Data products provided. In order to give a clear sequence of observations, flagging and correction steps, we provide hourly data arrays including each stage of the post-processing. These are also helpful for optimization of correction schemes for biofouling and NPQ.

Separate data files are submitted for:

- the chlorophyll (Chl) and turbidity (NTU) sensors of the FLNTU,
- each channel of the calibrated ECO F3WB chlorophyll fluorometer (F1 through F3),
- the 7-channel irradiance (ED7).

The Appendix provides data string formats:

Table A1 provides the data string for hourly chlorophyll fluorescence data obtained from the FLNTU and F3WB sensors.

Table A2 provides the data string format for the hourly turbidity.

Table A3 provides the data string format for the hourly downwelling irradiance and upwelling radiance data files.

Table A4 provides a list of the data file names, descriptions, units and array sizes.

The data arrays provided have the Matlab binary storage “mat” file format.

Results and Discussion

Time series bio-optical observations. The time series bio-optical observations from the FLNTU span October 2005 through September 2022 (deployments A0115-A0145), while the observations from the F3WB and irradiance sensors span from July 2016 to September 2022 (deployments A0137-A0145). *Measurements from the most recent deployment exhibits higher variability in both chlorophyll and turbidity, compared to most previous years, but are within the range of observed variations over the whole data record (Figure 2).*

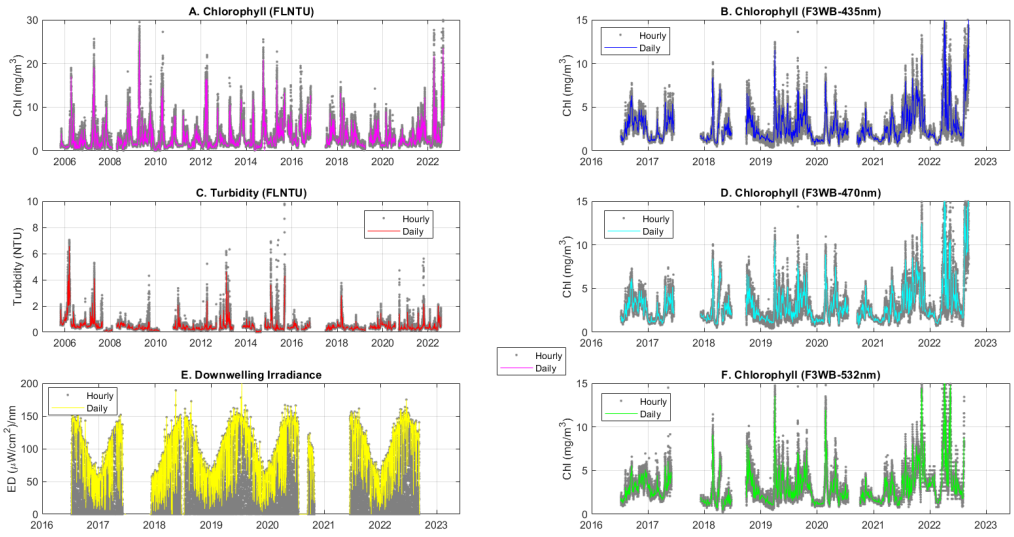


Figure 2. Time series of hourly (gray symbols) and daily (colored lines) observations of chlorophyll fluorescence (A: FLNTU, 2005-2022; B, D, and F: F3WB, 2016-2022), turbidity (C: FLNTU, 2005-2022), and solar irradiance (E: 2016-2022). Daily values are medians for all but irradiance, which is the daily maximum.

Long-term annual climatology. The daily climatological values for the chlorophyll time series originating in 2005 (Figure 3A) clearly shows a distinct spring bloom that peaks in early April and lasts about two weeks. Climatologically, the magnitude of the bloom is about 8 mg Chl/m^3. This is followed by a summer interval of lower chlorophyll, followed by a slowly increasing fall bloom beginning in August, peaking in early October at a value of approximately 5 mg Chl/m^3, and declining through the end of December. The lowest chlorophyll concentrations are in the winter months of January through mid-March. The pattern in chlorophyll observations over the last 6 years as measured with the F3WB, which exhibits the same values as the FLNTU chlorophyll sensor over that time interval, indicates the emergence of an earlier spring bloom at the end of February, lasting about 2 weeks, with a peak value of about 3 mg Chl/m^3. This is followed by the April bloom observed in earlier years. Since 2016, the fall bloom has increased in magnitude from about 5 mg Chl/m^3 to 7 mg Chl/m^3. The fall bloom is also peaking a month earlier, in September compared to October, still declining by the end of December.

There is not a strong seasonal signal in turbidity (Figure 3C). Values are typically of order 1 NTU. However, some years there are larger values occurring in late winter, with rare events in fall. These events correspond to storms when stratification is weakening in the fall or at a minimum in the winter. There does not appear to be a biological signal in the turbidity.

The seasonal pattern in the daily maximal solar radiation clearly demonstrates the effect of latitude (Figure 3E) as the dominant source of variation. Within that framework, variations are associated with clouds; spring and early summer months show significant cloud impacts, as does November. The clearest months are August – October, and December – January, associated with high pressure systems at this latitude.

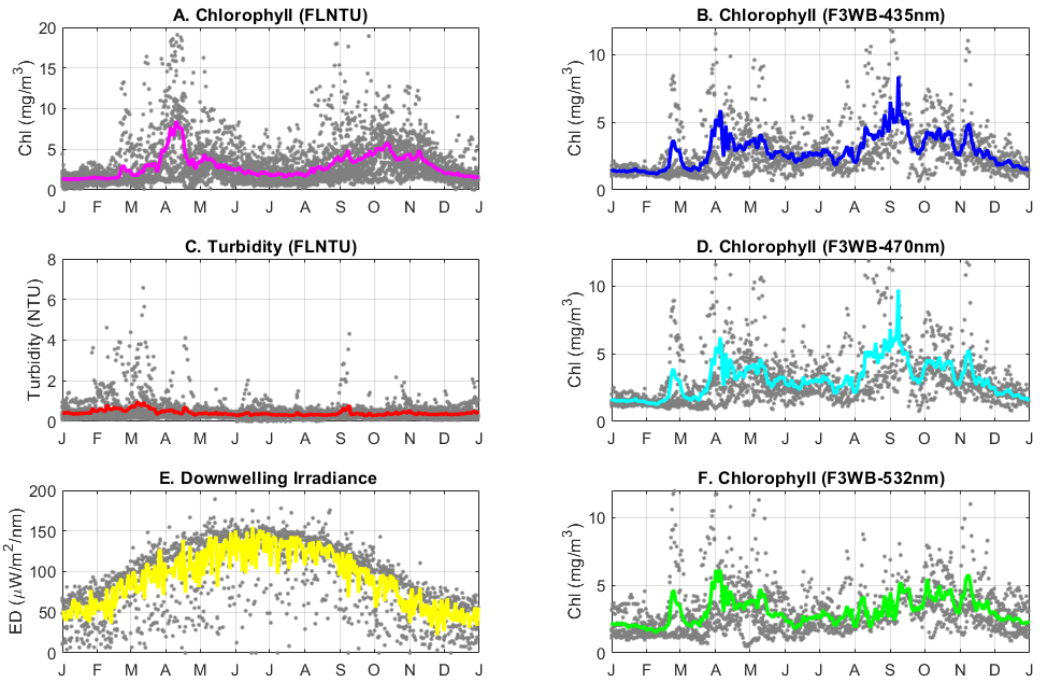


Figure 3. Daily observations (gray symbols) and climatological means (colored lines) for the complete bio-optical time series for chlorophyll fluorescence (A: FLNTU, 2005-2022; B, D, and F: F3WB, 2016-2022), turbidity (C: FLNTU, 2005-2022), and solar irradiance (E: 2016-2022).

Monthly climatological means for the bio-optical time series are shown in Figure 4. The spring bloom chlorophyll peak occurs in April and the fall bloom peak in October. The mean value of the April bloom is smaller than the fall bloom, partly due to the division of data between April and May, and its standard deviation is larger (Figure 4A). The 2021-22 monthly mean observations indicate the earlier onset of the spring bloom in March, the extended spring bloom over April and May and the summer low value in June. Unlike the long-term climatology, the fall bloom initiated in July, peaked in August and September at value nearly twice that of the spring bloom and more than twice the value as the long-term mean since 2005. The F3WB time series originating in 2016 looked very similar to the climatology originating in 2005 with the exception of the onset of the spring bloom in March, and the early onset of the fall bloom in July and the higher peak value.

The seasonal pattern in turbidity in 2021-22 was essentially flat through the year (Figure 4C), however, there is substantial variability January through April when winter storms drive events in increased turbidity. September continues to be a month of higher variability.

The monthly pattern in solar irradiance in 2021-22 (Figure 4E) reveals a pattern nearly identical to the climatology with the exception of December in which the irradiance was significantly lower that the climatology.

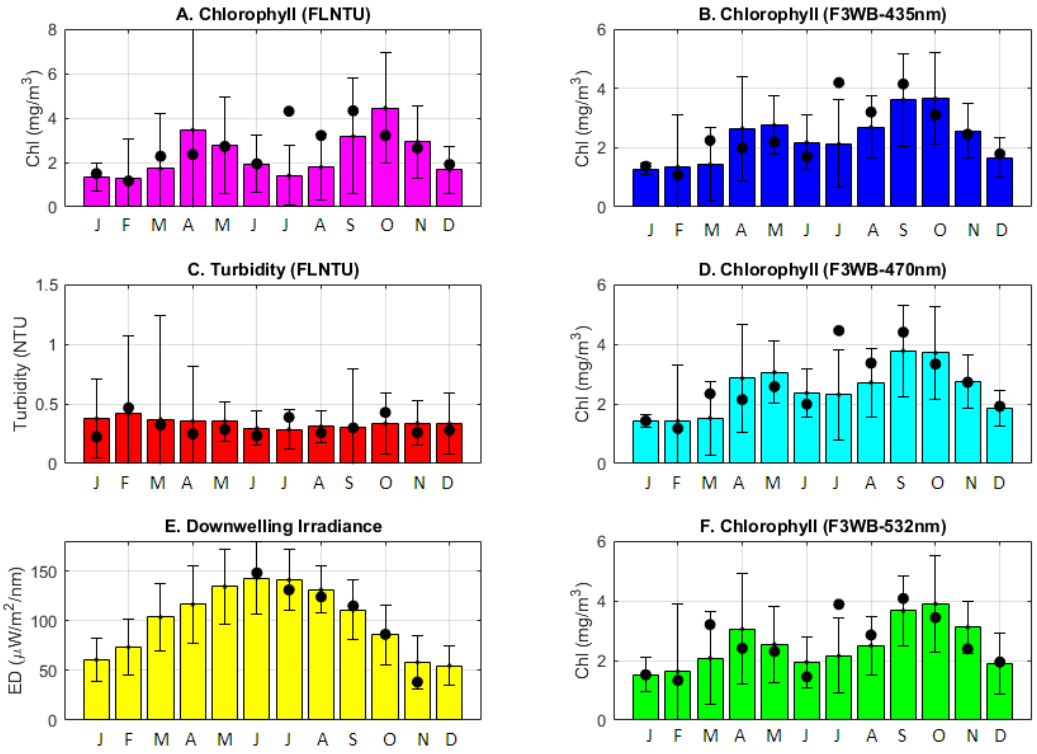


Figure 4. Monthly median (bars; all years) values of chlorophyll fluorescence (A: FLNTU, 2005-2022; B, D, and F: F3WB, 2016-2022), turbidity (C: FLNTU, 2005-2022), and solar irradiance (E: 2016-2022). Error bars indicate standard deviation. Observed monthly median values for the 2021-22 data (A0145) are shown as black symbols.

Overall, there is not a significant trend in the annual median values of chlorophyll or turbidity at Mooring A01 over the last 17 years. Annual median values of chlorophyll reveal an increasing period from 2005-2009, relatively constant interval from 2010-2014, a peak in 2015, slight decrease in 2016, and relatively constant values from 2017 - 2022 (Figure 5A). A consistent pattern appears in the F3WB chlorophyll time series (Figure 5 B, D, and E). What is notable about the 2021-2022 data is the increase in variability compared to previous years since 2009. The annual mean pattern in turbidity exhibits a decrease from 2005-2009 followed by more uniform mean values over the past decade (Figure 5C). Three years (2006, 2013 and 2015) have exhibited the strongest variability. In 2021 turbidity was slightly lower (clearer water), but more variable. Irradiance has generally increased since 2017, with the 2022 peak likely an artifact of missing wintertime observations during the later part of the year (this was observed in the 2021 data as well, which is now rectified with the complete year of observations).

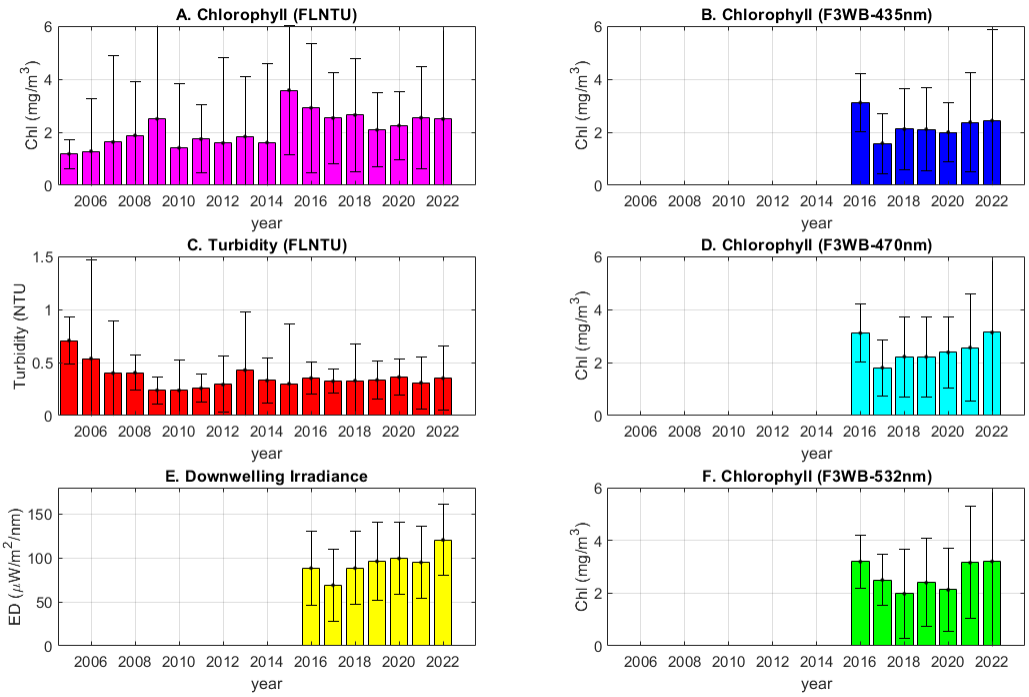


Figure 5. Annual medians of daily values of chlorophyll fluorescence (A, B, D, F), turbidity (C), and solar irradiance (E); error bars indicate standard deviation.

The lack of a significant long-term trend contrasts with a recent study that proposes significant decreases in phytoplankton standing stock across the Gulf of Maine based on an independent ship-based dataset (Balch et al., 2022). Both datasets show clear multiyear, nearly decadal, cycles that cannot yet be statistically resolved with the 15-20 years of available data, particularly when there are sampling gaps.

Changing phenology. The continuous observations from A01 clearly demonstrate a change in the timing, or phenology, of the phytoplankton blooms. While the overall concentration of phytoplankton does not exhibit a trend, there is a significant redistribution of *when* phytoplankton bloom. Changing phytoplankton phenology will have significant consequences for organisms that depend upon them as a food source and who time their reproductive cycles based upon bloom timing. Variability in annual median chlorophyll concentrations can be driven by high peak concentrations during blooms, longer blooms or overall higher sustained concentrations. A Hovmöller diagram of the chlorophyll concentration (Figure 6) is used to identify the trends in the peak timing, intensity and duration of the phytoplankton blooms. From 2006 through 2010 a dominant spring bloom occurred in April with a minor secondary bloom in June. In 2011 and 2012 the spring bloom was 2-4 weeks early. From 2013 through 2016, the major spring bloom occurred increasingly later in the spring, to nearly late May by 2016. 2018 and 2020 both exhibited late February blooms, of much higher magnitude than that observed in 2012. Secondary blooms occurred in April and May. A later and lower magnitude

spring bloom was observed in 2021 followed by an early and more intense bloom in 2022, which was followed by a significant bloom in May. The fall blooms have exhibited a trend from November to late August (the apparent exception in 2020 is due to missing data from July through September). Clear evidence of the early and extended fall bloom, starting in July, appears in 2021 and was even more intense in 2022.

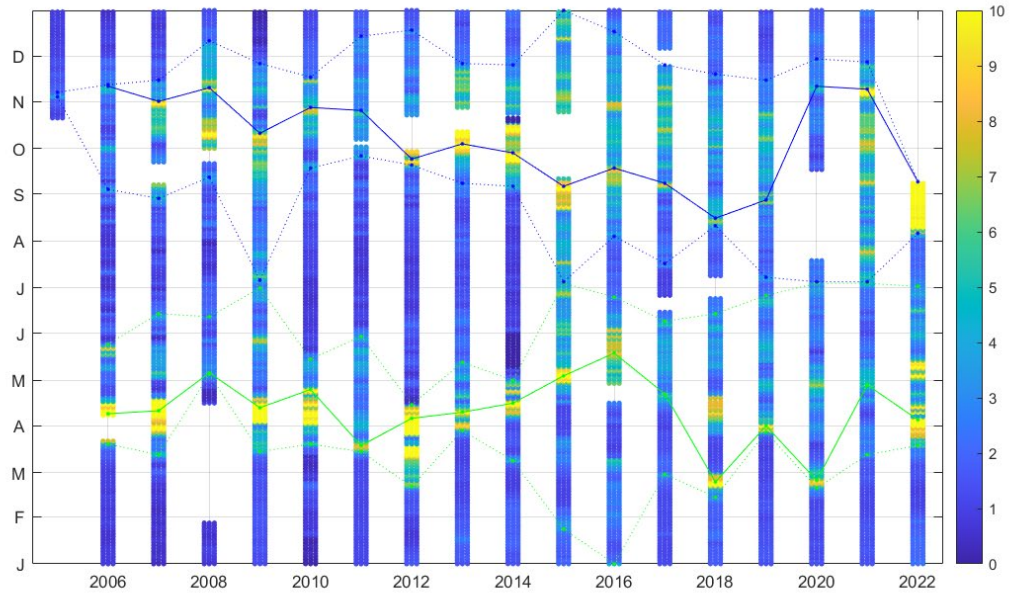


Figure 6. Hovmöller diagram chlorophyll concentration over the entire bio-optical times series at Buoy A01. Green line identifies the timing of the peak of the spring bloom, the blue line identifies the timing of the peak of fall bloom. Dotted lines indicate when the chlorophyll concentration exceeded 3 mg/m^3 at both the initiation and decline of each bloom and thus represents the time span of the bloom.

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Appendix. Data file formats.

Table A1. Format of the hourly observational data file for chlorophyll fluorescence data arrays, including those derived from FLNTU and FL3-WB sensors.

Column	ID	Value/Range	Comment
1	Year	2005-2020	
2	Month	1-12	
3	Day	0-31	
4	Hour	0-25	
5	Minute	0-60	
6	Second	0-60	
7	Date.Time	732607 – 738773	MATLAB® format, decimal local standard time (EST)
8	Raw Fchl	-3.42 – 230.91	Raw hourly mean
9	Flag_Offset	0, 1	Between deployments
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	-1.58 - 45.19	Values corrected (Carberry et al. 2019)
16	Flag_SVO	0, 1	Single value outlier
17	Fchl_corr_SVO	NaN	Values removed
18	Flag_MDL1	0, 1	< - Method detection level (MDL)
19	Flag_MDL2	0, 1	-MDL to 0
20	Flag_MDL3	0, 1	0 to +MDL
21	Fchl_corr	-0.04 to 29.47 /NaN	Cumulative removal/correction
22	Deployment	15 – 44	Deployment number
23	ECO-FLNTU S/N	001-9999	Sensor serial number, FLNTU

Table A2. Format of the hourly observational data file for Turbidity.

Column	ID	Value/Range	Comment
1	Year	2005-2021	
2	Month	1-12	
3	Day	0-31	
4	Hour	0-25	
5	Minute	0-60	
6	Second	0-60	
7	Date.Time	732607 - 738773	MATLAB® format, decimal local standard time (EST)
8	Raw Turbidity	-0.59 to 25.95	
9	Flag_Offset	0, 1	
10	Turb_corr_offset		Corrected for offsets
11	Flag_Biofouling1	0, 1	Biofilm
12	Flag_Biofouling2	0, 1	Structural
13	Turb_corr_biofouling	NaN	Values removed
14	Flag_SVO	0, 1	Single value outlier
15	Turb_corr_SVO	NaN	Values removed
16	Flag_MDL1	0, 1	< - Method detection level (MDL)
17	Flag_MDL2	0, 1	-MDL to 0
18	Flag_MDL3	0, 1	0 to +MDL
19	Turb_corr	-0.05 to 9.81 /NaN	Cumulative removal/correction
20	Deployment	15 - 44	Deployment number
21	ECO-FLNTU S/N	001-9999	Sensor serial number, FLNTU

Table A3. Format of the hourly observational data file for downwelling irradiance (ED) and upwelling radiance (LU).

Column	ID	Value/Range	Comment
1	Year	2005-2022	
2	Month	1-12	
3	Day	0-31	
4	Hour	0-25	
5	Minute	0-60	
6	Second	0-60	
7	Date.Time	732607 - 738773	MATLAB® format, decimal local standard time (EST)
8-14	Raw Ed(7)	-33.32 - 240.31	
15	Flag_Offset	0, 1	
16-22	Ed(7)_corr_offset		Corrected for spectral and intersensor offsets
23	Flag_Biofouling	0, 1	Biofouling
24-30	Ed(7)_corr_biofouling	NaN	Values removed
31	Flag_SVO	0, 1	Single value outlier
32	Flag_MDL1	0, 1	< - Method detection level (MDL)
33	Flag_MDL2	0, 1	-MDL to 0
34	Flag_MDL3	0, 1	0 to +MDL
35	Flag Cal	0, 1	Indicates multiplicative scaling
36-42	Ed(7)_final	-0.05 – 229.45/NaN	Cumulative removal/correction
43	Deployment	15 – 44	Deployment number
44	OCI_507_SN	001-9999	OCI 507 sensor serial number

Table A4. List of submitted data arrays (.mat files) for chlorophyll fluorescence (from FLNTU sensor and each of the three channels of the F3WB sensor), turbidity, spectral irradiance, and central wavelengths of irradiance sensor.

Array Name	**Description**	**Units**	**Array size (row x columns)**	**Format**
H_Chl_45	hourly chlorophyll fluorescence, FLNTU for full time series and each deployment	mg/m3	7454x23	Table A1
H_NTU_45	hourly turbidity from FLNTU for full time series and each deployment	NTU	7454x21	Table A2
H_F1_45	Hourly chlorophyll fluorescence response from 435 nm excitation (F3WB) for full time series and each deployment	mg/m3	7454x23	Table A1
H_F2_45	Hourly chlorophyll fluorescence response from 470 nm excitation (F3WB) for full time series and each deployment	mg/m3	7454x23	Table A1
H_F3_45	Hourly chlorophyll fluorescence response from 532 nm excitation (F3WB) for full time series and each deployment	mg/m3	7454x23	Table A1
H_ED_45	Hourly spectral irradiance, 7 channels for full time series and each deployment	μW/cm2/nm	7454x44	Table A3
H_ED_45_wave	Irradiance central wavelength	nm	7x1	n/a

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