# Phytoplankton and nitrate in Harpswell Sound: A multi-scale investigation

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# Phytoplankton and nitrate in Harpswell Sound: A multi-scale investigation

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**Introduction:**

Phytoplankton require certain essential nutrients for growth. The Redfield ratio (Redfield, 1934) dictates an ideal element proportion of 106 carbon: 16 nitrogen: 1 phosphorus in order to maintain balanced phytoplankton growth through photosynthesis (Li et al., 2008). Under typical conditions, the concentration of nutrients present in the water directly controls the attainable phytoplankton yield. When phytoplankton are able to grow to their full potential, the number of nitrogen molecules that exist in the water in inorganic nutrient form will equal the number of nitrogen molecules that ultimately end up in phytoplankton cellular material.

While plankton that are starved of nutrients tend to die off quickly, plankton that are simply nutrient limited can adjust to constant but low levels of nutrient concentration (Cullen et al., 1992), often by adjusting their Redfield ratio. As an essential nutrient, nitrogen is a limiting factor for phytoplankton growth (Dugdale, 1967). In oceanic and coastal ecosystems, nitrogen is most commonly available in the form of dissolved nitrate ($NO_3^-$) (Zielinski et al., 2011). The formation of nutrients through microbial processes such as denitrification in deep water creates a source of nitrogen in the deep ocean (Arrigo, 2005). Phytoplankton growth is limited by both light and nutrients: therefore, the transport of nitrate into the euphotic zone controls the rate of primary production. In the Gulf of Maine, nitrate concentration varies with depth and season from approximately 0 to 20 µm (*Figure 1*). Water properties such as temperature and salinity determine the density structure, thereby controlling the depth and rate of mixing. In conjunction with phytoplankton uptake in surface waters, the depth of the seasonal nitracline evolves, which signifies a transport of nutrients from depth to surface waters (Townsend, 1998).

**Background:**

For the past four years, an *In Situ* Ultraviolet Spectrophotometer (ISUS) has been deployed on the Bowdoin Buoy in Harpswell Sound, Maine. The ISUS has been collecting hourly observations of nitrate concentration concurrent with sensors collecting hourly observations of water temperature, salinity, and chlorophyll fluorescence (which can be used as a proxy for phytoplankton biomass). The goals of this study are twofold. First, we examine the relationship between nitrate concentration and the co-occuring hydrographic properties of temperature and salinity in the Gulf of Maine (and specifically in Harpswell Sound) in order to determine the qualities of the source water masses for nitrate in these regions. Second, we investigate the utilization of nitrate via the correlation between nitrate concentration and phytoplankton biomass on timescales that are relevant to phytoplankton growth and bloom dynamics.

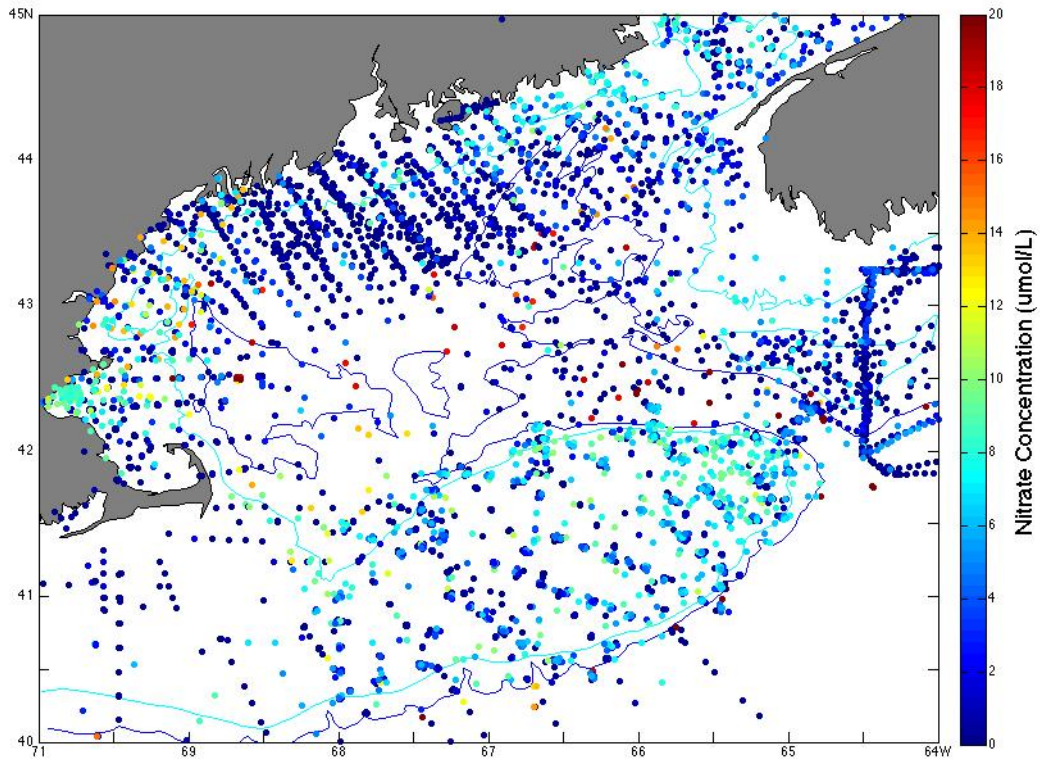


**Figure 1.** Measured nitrate ($NO_3^-$) concentration (umol/L) in the Gulf of Maine, 1990-2012. *(Data from Rebuck et al., 2009).*

Using historical nutrient and water quality data for the Gulf of Maine gathered by Rebuck et al. (2009), in addition to 7 years of CTD observations of temperature and salinity and *In Situ* Ultraviolet Spectrophotometer (ISUS) observations of nitrate collected from the Bowdoin Buoy (also GoMOOS Buoy D) in Harpswell Sound, Maine, this study aims to determine: the relationships between nitrate and temperature and nitrate and salinity in the Gulf of Maine and in Harpswell Sound; the similarities between ISUS-measured nitrate to nitrate measured in lab; and the relationship between ISUS measured nitrate and chlorophyll concentration.

**Approach:**

The *In Situ* Ultraviolet Spectrophotometer (ISUS by Satlantic, Inc.) offers the ability to quantify nitrate concentrations based on optical properties (*Figure 2*). The instrument measures the magnitude of absorption of ultraviolet light by dissolved nitrate molecules in the water.

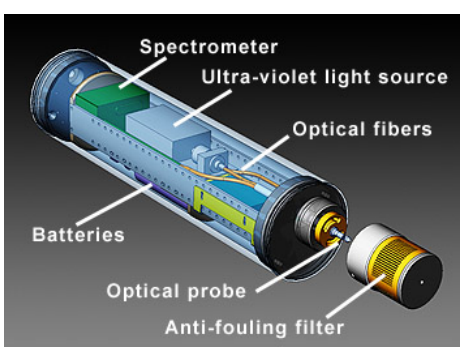


**Figure 2.** The ISUS sensor includes a sample probe, a UV light source, and a spectrophotometer that continuously measures the absorption of nitrate directly in the water. (*Image © Monterey Bay Aquarium Research Institute, 2001*).

The concentration is determined from the ratio of the measured absorption coefficient to the molar specific absorption coefficient of nitrate. The ISUS is placed directly into the water at a site of specific interest—it measures the absorption and computes the nitrate concentration at this site every hour. This method of analysis gives superior stability, precision, and accuracy in data compared to a typical water sample analysis in a laboratory setting (Johnson & Coletti, 2002). A timeseries of ISUS-measured nitrate concentration is available for Harpswell Sound from 2007-2012 (*Figure 3*). This timeseries was compared to nitrate concentration measured in lab from discrete water samples over the same time period. While the overall patterns and ranges are coherent, point-by-point validation is weak. One source of uncertainty is the extreme temporal and spatial variation in the Sound, which serves to drive uncertainty in the synopticity of sampling.

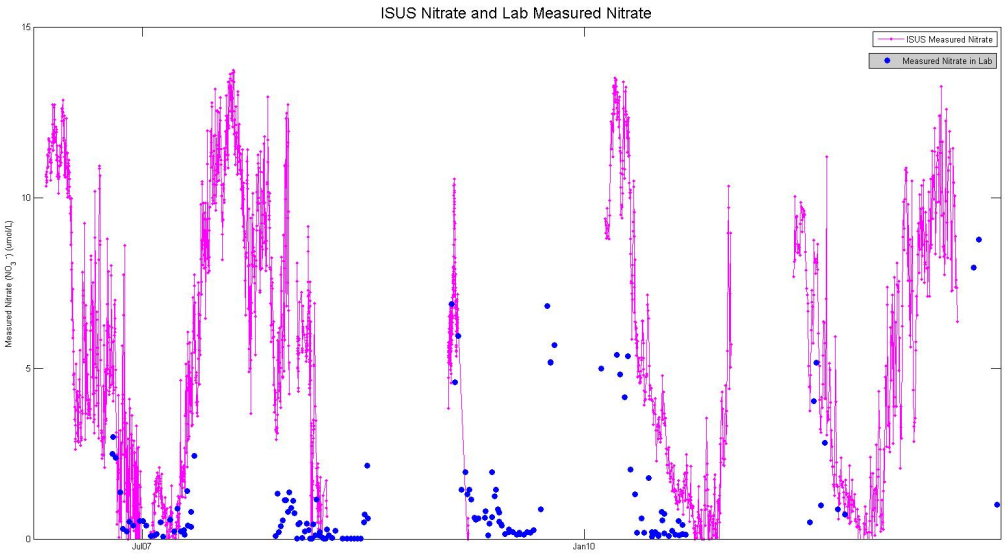


**Figure 3.** Measured nitrate in lab (blue dots) from summer 2007 to summer 2012 compared to ISUS- measured nitrate from winter 2007 to winter 2012 (pink). ISUS data is separated by deployment and shifted by subtracting the minimum value of each deployment from the total values in the deployment (assuming a summertime low of about zero).

A second source of uncertainty is the variability in salinity and river-borne dissolved organic matter (the latter of which gives Maine rivers their characteristic brown color) in coastal areas similar to Harpswell Sound. These factors may complicate the measurement of nitrate concentration, as both salt and dissolved organic matter absorb light in the same wavelength range as nitrate (Anderson, 2012). There are methods of correction that can be applied to the data in order to secure a more accurate final reading (Zielinski et al., 2011; Anderson, 2012). As a first step, the offset correction for each deployment was based upon a climatological mid-summer (high stratification) validation value of zero.

During summer 2014, further sampling occurred: once per week between May 21, 2014 and June 18, 2014, measurements of the depth distribution of salinity, temperature, density, chlorophyll fluorescence, and dissolved oxygen content were taken at the Bowdoin Buoy.

Water samples were collected at five discrete depths each week, and were returned to the lab for analysis of chlorophyll concentration on the Turner fluorometer and nutrient concentration on the SmartChem discrete wet chemistry analyzer (by WESTCO). These laboratory analyses were used to calibrate and validate the buoy- and boat-based optical observations.
In order to compare the trends in water quality and nitrate concentration in Harpswell Sound to the general patterns in the Gulf of Maine, the ISUS data and discrete nitrate analyses data were compared to data presented in Rebuck et al. (2009). The study compiles an eighty-five year dataset including measured nitrate, temperature, and salinity around the Gulf of Maine. For the purpose of this study, only the data from 1990-2009 were examined, in addition to previously unpublished data from 2010-2012.

The analysis of nitrate observations was performed in two phases. First, the variability in nitrate measured on the buoy since 2007 along with co-located discrete water samples was compared to the historical dataset (Rebuck et al., 2009) in order to place Harpswell Sound in the broader spatial and temporal context of the Gulf of Maine. Second, the time series buoy observations of nitrate and chlorophyll were analyzed to determine temporal covariability.

**Results:**

The data from Rebuck et al. 2009 (*Figure 4*) shows clear variation in nitrate over the course of the year, with an annual high in the winter and annual low in the mid-summer. Salinity holds a more stable pattern over the course of the year. Temperature varies seasonally, with the coldest water in January and February and warmest water in late August and early September. Harpswell Sound shows similar dynamics (*Figure 5*): nitrate falls to a summertime low of zero each year, salinity varies frequently but not dramatically, and temperature is highest in summer and lowest in winter.

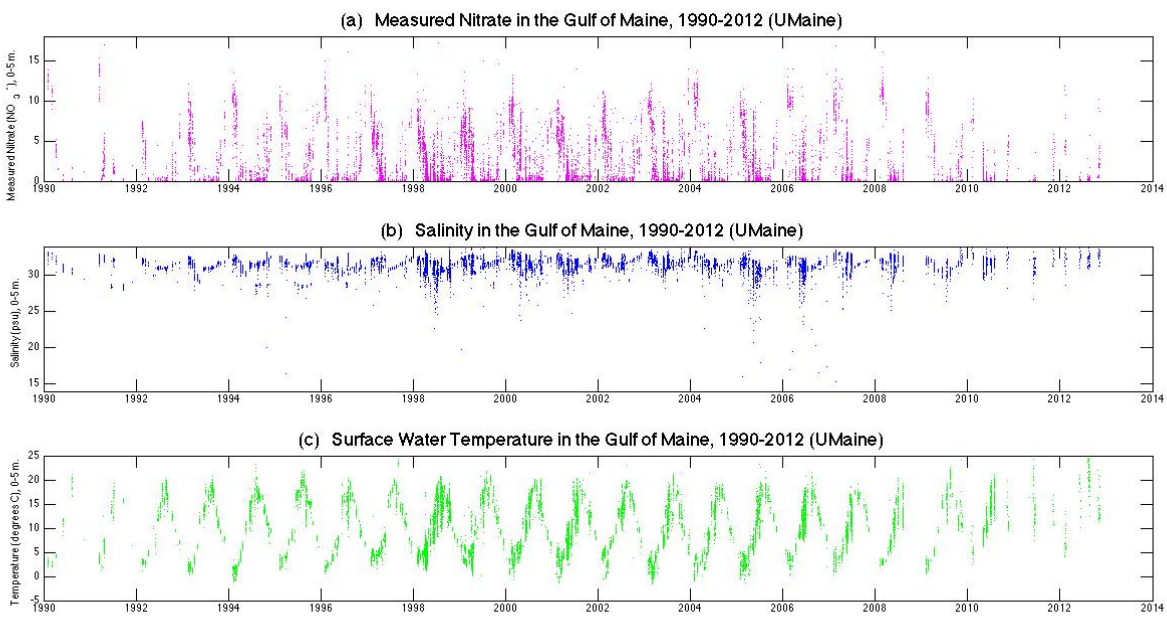


**Figure 4.** Time series of (a) lab-measured nitrate, (b) salinity, and (c) water temperature in the Gulf of Maine (all sites) from 1990-2012). (*Data from Rebuck et al., 2009*).

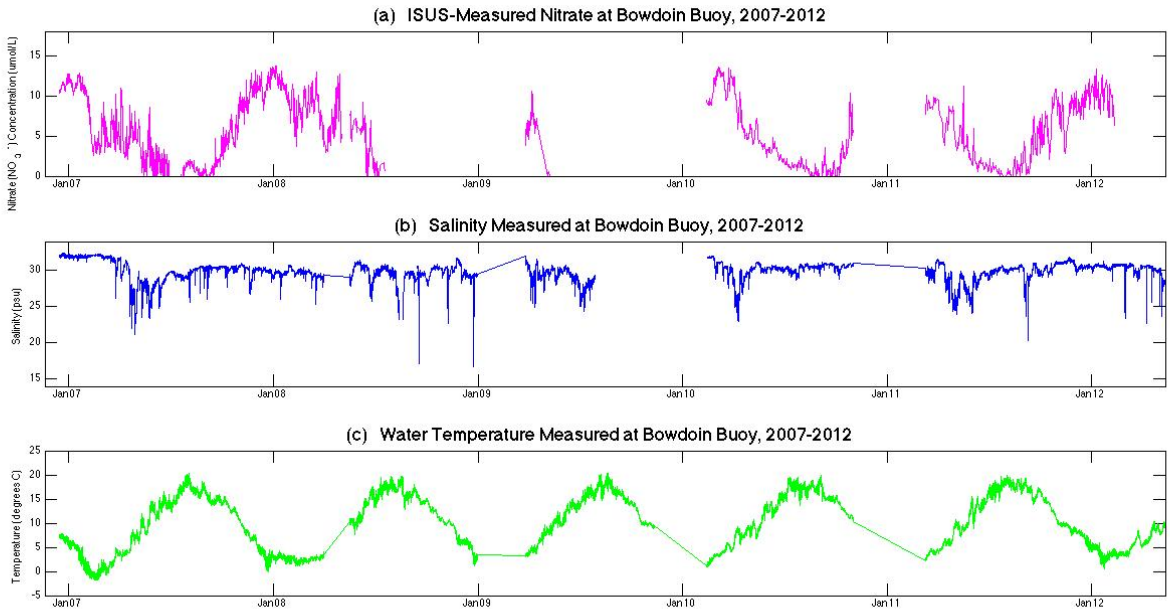


**Figure 5.** Time series of (a) ISUS-measured nitrate, (b) salinity, and (c) water temperature measured at ~1.5 m. on the Bowdoin Buoy from 2007-2012.

Next, a clear relationship between nitrate concentration and salinity and nitrate concentration and water temperature for both the Gulf of Maine and Harpswell Sound emerged (*Figure 6*). The highest concentrations of nitrate are found in the saltiest water (between 30-34 psu) and in cold water (between 3 and 12 degrees Celsius).

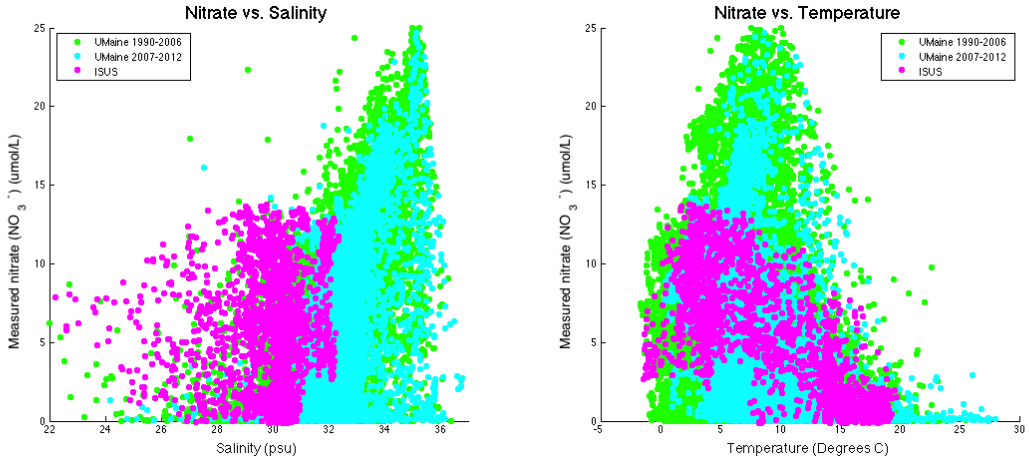


**Figure 6.** (a) Nitrate vs. salinity and (b) nitrate vs. temperature. Gulf of Maine 1990-2006 green and 2007-2012 cyan, and Harpswell Sound 2007-2012 magenta, measured with ISUS deployed on the Harpswell Sound mooring. (*Rebuck et al., 2009*).

The temperature ands salinity ranges observed in Harpswell Sound fell within the broader range in the Gulf of Maine data set. The associated nitrate concentrations determined with the ISUS are commensurate with the Gulf of Maine values, which were resolved analytically in the lab. While there are relatively few match-ups for validation, these points did show the correlation between the two methods. The similarity of the distribution of measured nitrate from water samples in lab and the *in situ* temperature and salinity characteristics of the sampled waters were very coherent with those measured by the ISUS, providing some quantitative validation.

The five-year time series of ISUS-measured nitrate and calibrated chlorophyll fluorescence (*Figure 7*) clearly demonstrates both the strong seasonality in nitrate and the variable patterns in phytoplankton blooms. In 2010, as an ideal example (*Figure 8*), there is a clear draw down of nitrate, with isolated replenishments. However, there is no single associated spring bloom, but rather many smaller blooms throughout the season. Despite the apparent lack of large-scale convergence in the time series, a statistically significant inverse relationship was observed (*Figure 9*).

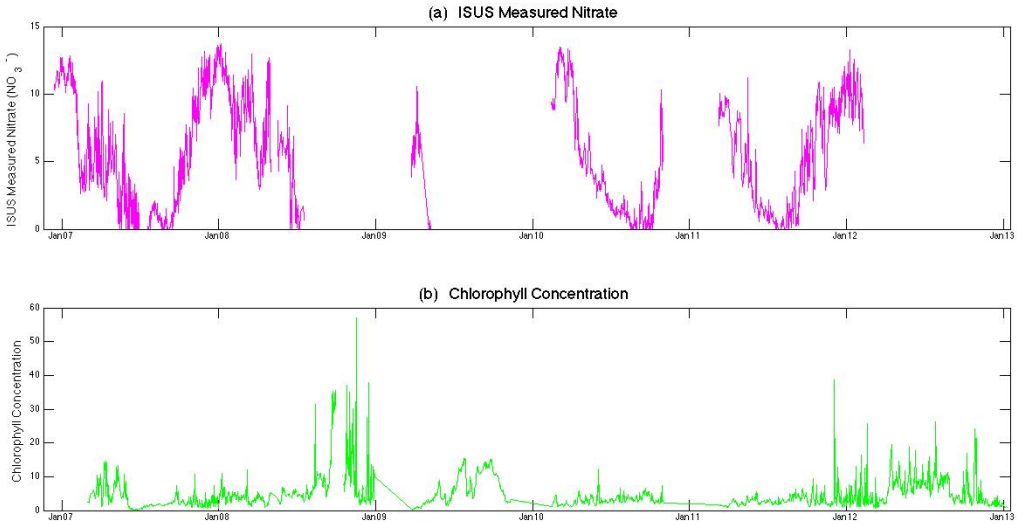


**Figure 7.** Timeseries of (a) ISUS-measured nitrate and (b) calibrated chlorophyll fluorescence measured at the Bowdoin Buoy, 2007-2012.

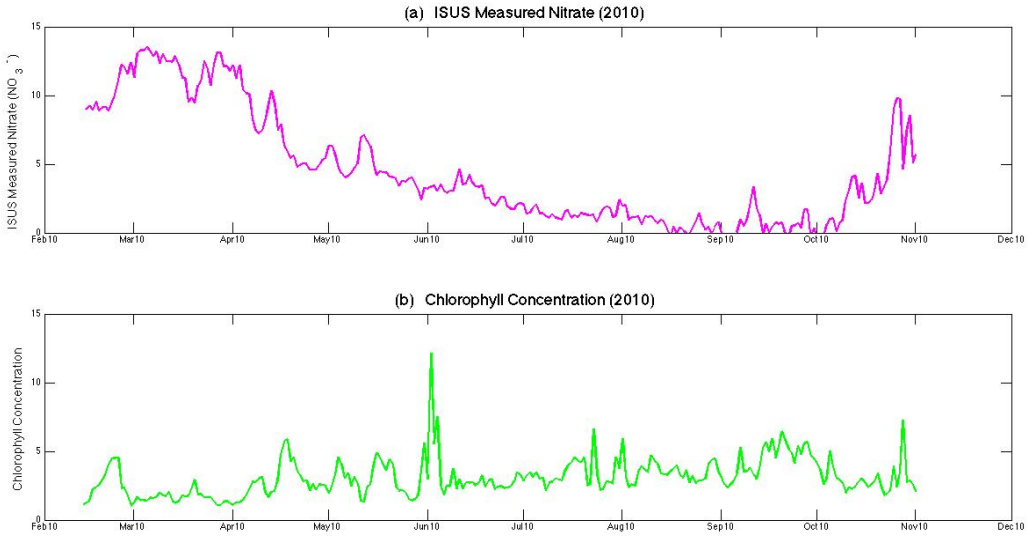


**Figure 8.** Timeseries of (a) ISUS-measured nitrate and (b) calibrated chlorophyll fluorescence measured at the Bowdoin Buoy for the 2010 deployment.

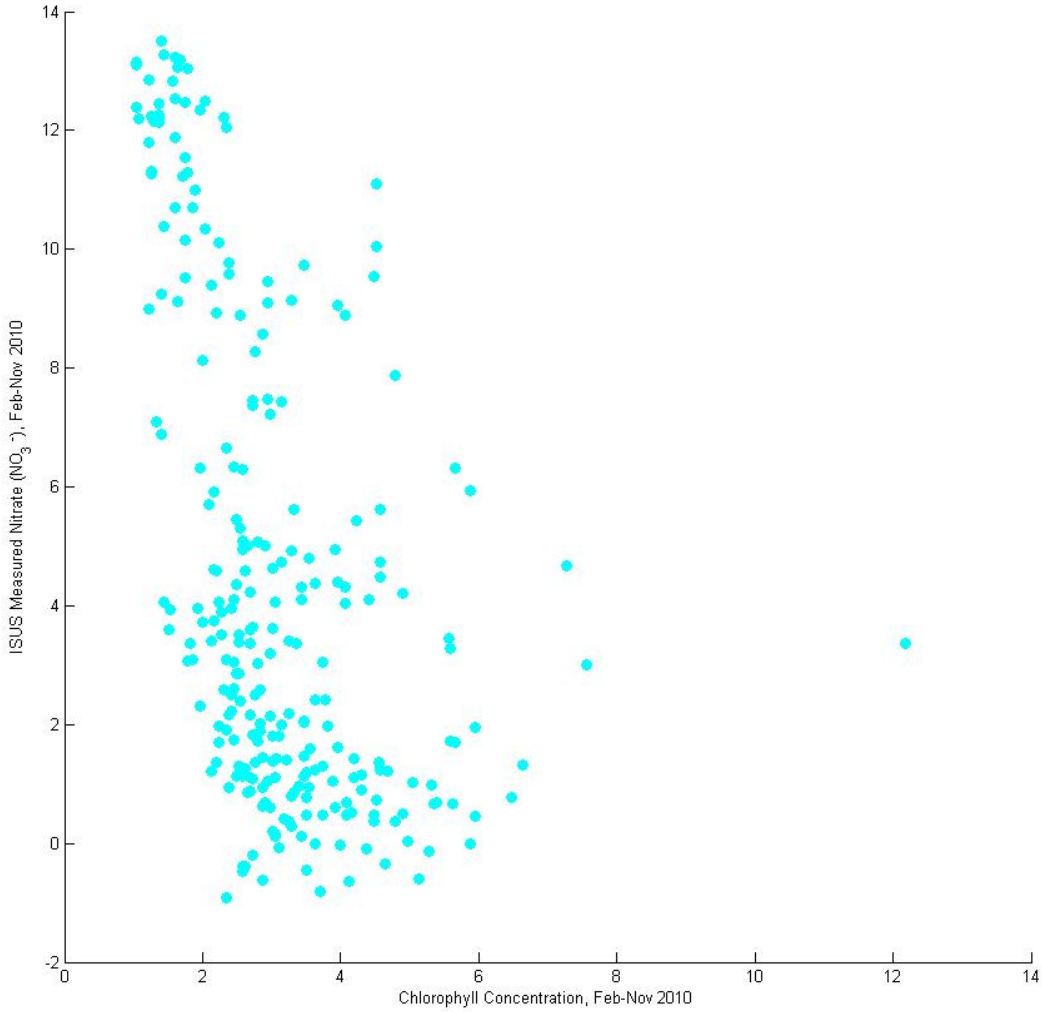


**Figure 9.** Chlorophyll concentration vs. ISUS-measured nitrate concentration, February-November 2010.

**Discussion:**

*Temporal patterns in nitrate, temperature, and salinity*

Nitrate, temperature, and salinity varied seasonally as well as annually for both the Gulf of Maine and Harpswell Sound. The extensive data set from Rebuck et al. 2009 shows a clear variation in nitrate over the course of the year, featuring an annual high in the winter and annual low in the mid-summer. Salinity is higher in winter and lower in summer, but the changes in salinity are less drastic than the changes in other water qualities. Temperature varied most dramatically, with the coldest water developing in January and February and warmest water occurring in late August and early September. While the data set from Harpswell Sound shows a smaller range, similar dynamics emerge: nitrate falls zero each summer and climbs to its peak in winter, salinity changes often but stays within a smaller range, and water temperature reaches a high in summer and low in winter. Future work on the Harpswell Sound data set, plus the addition of data from summers 2012, 2013, and 2014, could allow for a better comparison between the nitrate, salinity, and water temperature levels in Harpswell Sound and the levels throughout the Gulf of Maine.

*Nitrate in the context of water masses in Harpswell Sound & the Gulf of Maine*

The highest concentrations of nitrate are found in cold, salty water, between 30-34 psu and between 4 and 12 degrees Celsius. This water matches the profile for deep water, which is a rich source of nutrients (Townsend, 1998). While the coldest water over the course of the year (<4°C) is found at the surface, surface water is not a source of nitrate. This pattern was observed both generally in the Gulf of Maine and more specifically in Harpswell Sound, indicating that processes observed in Harpswell Sound are closely connected to broader scale oceanographic processes. Harpswell Sound is a reverse estuary that is flooded with fresh water from the Kennebec River, which outflows slightly north of the mouth of Harpswell Sound. Due to the Coriolis effect, this water flows south and to the right, towards the shore and into the mouth of Harpswell Sound, creating the saltiest environment at the most inland point (Wolovick et al., 2008). Therefore, the flow dynamics and water quality in Harpswell Sound are potentially very different than the rest of the Gulf of Maine, which encompasses hundreds of square kilometers of diverse coastline and open ocean (*Figure 1*). These results also indicate that nutrients generated by deep ocean processes are dominant in Harpswell Sound and river sources are negligible, a result that is not found in most areas, but which is consistent with the recorded cycling of nutrients in the Gulf of Maine (Townsend, 1998).

*Chlorophyll and nitrate*

The relationship between nitrate and chlorophyll as a proxy for phytoplankton biomass showed a strong inverse correlation over an annual cycle. At the beginning of the growth season, low levels of phytoplankton consume the high levels of nitrate and therefore, as the bloom grows, the concentration of nitrate decreases proportionally to the growth of phytoplankton. Over the course of the summer, the nitrate decreases until it reaches zero, while phytoplankton reach maximal concentrations. After this low point in nutrient levels, the bloom begins to decline, as the phytoplankton are starved of nutrients. Low nitrate is associated with low phytoplankton biomass (the wedge of data points in Figure 9). While this expected interaction is not as clear on the timeseries of the data, which includes more significant variability driven by smaller-scale

changes in the ecosystem, the relationship becomes incredibly clear when comparing nitrate and chlorophyll levels directly. The expected dependence of phytoplankton on nutrients is evident through these results, similar to the results presented in Li et al., 2010. The ISUS-measured nitrate data for Harpswell Sound from 2007-2012 requires further processing, which will show variations in year-to-year yield. This data is necessary in order to fully explore the relationship between chlorophyll and nitrate concentration on all pertinent timescales to bloom growth dynamics.

*Further analysis*

On an hourly or daily basis, the relationship can determine how the dissolved nutrient is incorporated from seawater into cell physiology via uptake. On a seasonal scale, it would detail the dynamics of phytoplankton populations, which are controlled on a daily basis by nutrient injection from deep, cold, salty waters. Finally, on an inter-annual scale, it could highlight year-to-year differences in cumulative phytoplankton biomass and describe net changes in biomass over time (Li et al., 2010).

The next step in analysis of the dataset would continue to resolve the differences in general phytoplankton biomass. Li et al. (2010) propose that the slope of the relationship between nitrate and chlorophyll varies based on the species of phytoplankton. On a weekly or monthly scale, this difference in slope between nitrate and chlorophyll concentrations could show the progression of species over the duration of a typical bloom. At the beginning of the bloom, smaller species (such as diatoms) might uptake fewer particles. As the bloom develops, the cell size of the phytoplankton would increase, and the nitrate uptake would vary.

Future analyses would include the ISUS data from summers 2013 and 2014, which would continue to justify the validity of the ISUS values in comparison to nutrient data from the water samples taken over the course of these summers. In cultures and in the preliminary comparison of the ISUS data with chlorophyll data (*Figure 8*), chlorophyll concentration and nitrate concentration vary inversely as dissolved inorganic nitrogen becomes dissolved organic nitrogen via phytoplankton uptake. To examine the data on an inter-annual scale, it would be necessary to integrate the chlorophyll data and find the area under the curve, yielding the total concentration of nitrate over the course of a year. Then it would be possible to determine the changing phytoplankton concentration each year based on nitrate concentration, which could lead to further analysis of the differing conditions in Harpswell Sound during years with large phytoplankton blooms versus small phytoplankton blooms.

This data could eventually demonstrate a correlation between nutrient concentration and harmful algal blooms (HABs), which affect both the Gulf of Maine and Harpswell Sound each year and can impact vital industries such as fisheries. If a certain nitrate concentration can be easily matched to a peak in phytoplankton biomass in Harpswell Sound, and further correlated with historical records of HABs, then it could potentially become easier to predict when these blooms might affect the Gulf of Maine, or more specifically when they might affect Harpswell Sound.

**Conclusions:**

- ISUS-measured nitrate is consistent with historical data sets, signifying validity for the instrument
- Water masses in Harpswell Sound fit into the broader context of the water masses in the Gulf of Maine based on the concentration of nitrate at certain salinities and temperatures
- Time series of nitrate and chlorophyll show strong seasonal trends, and when resolved over the course of a year yield expected inverse relationship

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