TEMPORAL VARIATION IN SURFACE WATER MYCOSPORINE-LIKE AMINO ACIDS (MAAs) IN THE WESTERN GULF OF MAINE

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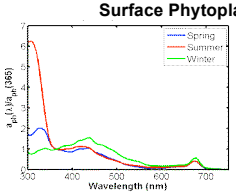
Phytoplankton in the upper water column experience a dynamic light field including high-energy ultraviolet (UV) radiation. Mycosporine-like amino acids (MAAs), protective pigments induced by UV-B light (280 – 320nm), may shield cells from structural and physiological damage. While MAAs have been studied in Antarctic waters, the Southern Ocean, Bermuda and the United Kingdom, research on these pigments has not previously occurred in coastal temperate waters of the United States. MAAs extracted from filtered water samples are identified using high-resolution reverse-phase liquid chromatography, UV absorbance, and co-chromatography with known MAA standards. This study summarizes a seasonal survey, taken over eleven months, of phytoplankton MAAs from surface waters (one to ten meters) in the western Gulf of Maine. Cycles of MAA production are related to concentrations of photosynthetic pigments and solar irradiation levels.

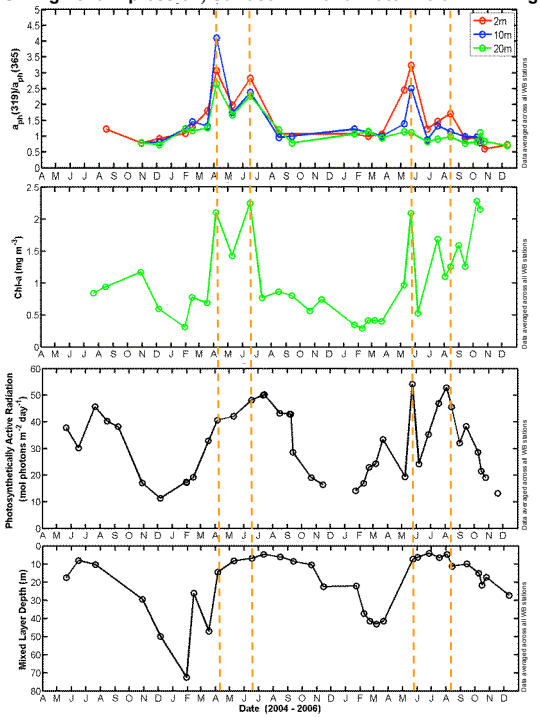
Seasonal Trends at Wilkinson Basin Stations

Surface Phytoplankton Absorption Spectra



Surface phytoplankton absorption coefficient values (a_{ph}) exhibited seasonal variations in the UV range. Absorption peaks between 310 and 340 nm observed during spring and summer months were much smaller or absent in the fall and winter. These peaks were likely caused by UV-absorbing compounds such as MAAs. Example spectra from WB3 at left.

UV Pigment Expression, Surface PAR and Water Column Mixing

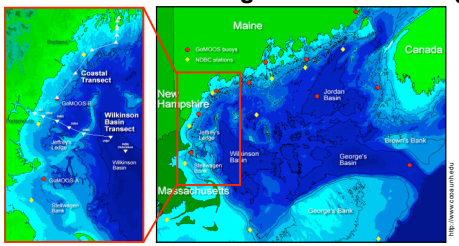


- UV-absorbing pigment expression exhibited distinct variation with both time of year and depth. Interannual variability was also observed, particularly at 20 m.
- Peaks were correlated with increased surface irradiance (PAR) and stronger water column stratification during spring and summer months.
- Gulf of Maine patterns are similar to those found in studies of phytoplankton UV absorption in the Sargasso Sea (Morrison & Nelson, 2004) and MAAs in the English Channel (Llewellyn & Harbour, 2003).

Morrison, J.R. & N.B. Nelson. 2004. Seasonal cycle of phytoplankton UV absorbance at the Bermuda Atlantic Time-series Study (BATS) site. Limnology and Oceanography 49: 215-224.

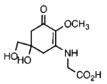
Llewellyn, C.A. & D.S. Harbour. 2003. A temporal study of mycosporine-like amino acids in surface water phytoplankton from the English Channel and correlation with solar irradiation. Journal of the Marine Biology Association of the United Kingdom 83: 1-9.

UNH Coastal Observing Center Monitoring



The University of New Hampshire's (UNH) Coastal Observing Center has undertaken a monthly sampling program in coastal and offshore waters of the western Gulf of Maine for the past several years, including the collection of samples for MAA assessments since February 2006. Field work aboard the research vessel R/V *Gulf Challenger* examines different coastal water types, from rivers and near shore areas to the deep Wilkinson Basin (WB), in order to monitor the state of the pelagic ecosystem. The work presented here focuses on samples gathered from surface waters at stations along the WB transect.

MAAs comprise a cyclohexenone ring with amino acid or imino alcohol substituents. They present a single absorption band in the UV, with maxima ranging from 310 to 360 nm. More than 20 structurally distinct MAAs are fully characterized; novel mycosporine-like compounds have been observed but not identified. In many phytoplankton, MAA synthesis can be induced by increased irradiance or UVR exposure. Often, multiple MAAs with different absorption maxima are found within one organism, increasing protection across a range of wavelengths although one compound typically accounts for most of the absorbance.



Mycosporine-Glycine (λmax=310nm)

Data Collection and Methods

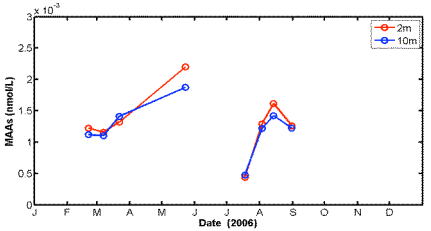
- Water samples were collected via Niksin bottles on a CTD profiler at 2 and 10 m depths, then concentrated on 25 mm glass-fiber filters and stored in liquid nitrogen until analyzed.
- In-water light field measured with Satlantic Hyperpro profiling radiometer. Phytoplankton absorption was calculated as the difference between total and detrital particle absorption using the Quantitative Filter Technique (QFT, after Mitchell et al., 2000).
- Surface Photosynthetically Active Radiation (PAR) data was extracted from 8-day composite SeaWifs images.
- MAAs were extracted for 24 hours from finely-chopped filters in 2.0 mL 100% methanol at -20°C. Centrifuged supernatant used for MAA and protein analyses. MAAs separated by reverse-phase isocratic HPLC on C-8 column with mobile phase of 40% methanol and 0.1% glacial acetic acid (v:v) in water at 0.6 mL/minute flow rate (modified from Shick et al., 1992). MAA peaks detected by UV absorbance at 313 nm and co-chromatography with primary and secondary standards.
- Soluble protein determined by measuring extraction absorbance at 235 and 280 nm (HP8453 UV-VIS spectrophotometer, 1 cm path) following Whitaker and Granum (1980).

Shick, J.M, et al. 1992. Survey of ultraviolet radiation-absorbing mycosporine-like amino acids in organs of coral reef holothuroids. Marine Ecology Progress Series 90: 139-148.

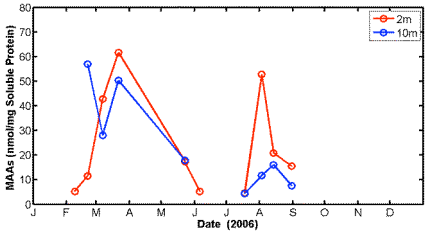
Whitaker, J.R. & P.E. Granum. 1980. An absolute method for protein determination based on difference in absorbance at 235 and 280 nm. Analytical Biochemistry 109: 156-159.

Mitchell, B.G., et al. 2000. Determination of spectral absorption coefficients of particles, dissolved material, and phytoplankton for discrete water samples. In: *Ocean optics protocols for satellite ocean color sensor validation, Revision 2.* NASA Technical Manual 2000 – 209966. SIMBIOS Project, Goddard Space Flight Center, NASA.

MAAs at Wilkinson Basin Stations



Preliminary analyses found MAAs in samples from all Wilkinson Basin stations through most of 2006. MAA concentrations (above) increased rapidly during spring and declined later in the summer. Low levels of these compounds were present even in winter. The most common MAA was mycosporine-glycine; other identified MAAs include shinorine and porphyra-334. MAAs levels normalized to protein concentration (below) also showed seasonal and depth variations.



Conclusions and Future Work

- In the highly variable marine environment of the Gulf of Maine, fluctuations in phytoplankton assemblage may have significant impacts. Our initial MAA analysis indicates that these UV-absorbing compounds are present through most of the year, peaking in the late spring and summer months while exhibiting a complex seasonal signal and interannual variability, both of which may correlate to a number of different factors. For instance, as solar radiation levels increase and the mixed layer depth gets shallower, surface phytoplankton require photo-protective mechanisms such as MAAs.
- Some bloom-forming species of phytoplankton that are best able to produce MAAs in order to survive higher levels of UV radiation may also generate harmful algal blooms in coastal areas (ex. *Alexandrium fundyense* in the eastern Gulf of Maine). Long-term monitoring of MAA concentrations on regional and global scales may offer one of the best ecological measures of increasing UV levels in the marine environment as well as a means of assessing the pelagic ecosystem's response.
- Next steps include continued sampling and MAA analyses throughout the Gulf of Maine as well as efforts to quantify unknown MAAs using additional standards and continued evaluation of surface light dynamics. A closer look at the phytoplankton assemblage present at each sampling time is also planned.

Acknowledgments

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