Lignin as an Indicator of Algal Blooms in the Chesapeake Bay?

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Introduction

The populations of algae rapidly increase during blooms in both freshwater and marine environments. The high densities of algae during the bloom limit the depth to which light can penetrate. Plants at deeper depths start to decay due to the light limitation. As the large amount of algae die, decomposition by bacteria removes dissolved oxygen from the water. As a result, plants and animals can no longer survive, creating a dead area and deteriorating the healthy ecosystem.

Most algal blooms are the result of an excess of nutrients (particularly phosphorus and nitrogen) in water. Much of the nutrients come from terrestrial environment. Differentiating the source of nutrients, though challenging, is necessary for us to understand the mechanisms leading to algal blooms.

Lignin, the second most abundant organic compound on Earth, is a type of complex chemical compound that is present in all vascular plants. Its unique source and resistant structure makes lignin an excellent biomarker for terrestrial input to the ocean. In this study, we aim to investigate the relationship between terrestrial inputs and algal blooms via comparing lignin concentrations between bloom and nonbloom sites in the Chesapeake Bay.

Sample preparation

Lignin in marine waters from the sampling stations was analyzed in its two forms: particulate and dissolved. Briefly, seawater was filtered through 0.7um GF/F to separate organic matter into dissolved and particulate forms (DOM and POM respectively). Lignin compounds in DOM was further concentrated using a C-18 disk. Lignin compounds in both POM and DOM were analyzed using tetramethylammonium hydroxide (TMAH) thermochemolysis. This technique cleaves lignin polymer to its monomers, and further derivatives the monomers to their respective methyl esters.

Instrumentation

The lignin methyl esters were analyzed by gas chromatography coupled to a time-of-flight mass Spectrometry (GC-TOF/MS).

The GC separate the molecules based on their different chemical properties.

As the molecules come out of GC column at different retention times, they are broken down into ionzied fragments in the MS. These fragments are then detected based on their corresponding mass-to-charge ratio.

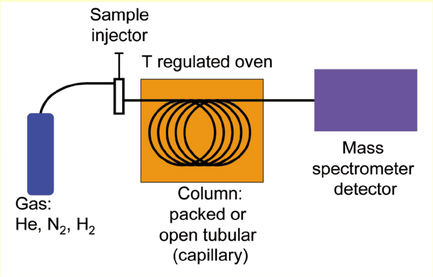

Figure 1: Diagram of GC-MS

Sampling Stations

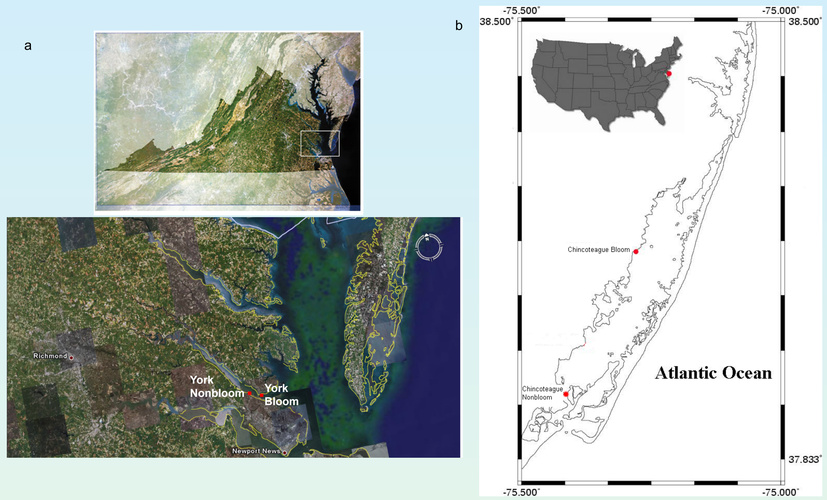

Figure 2: Nonbloom and Bloom Sampling Sites on the York River (a) and the Chincoteague Bay (b)

Results

The spectra from the GC-MS for nonbloom and bloom waters were distinctive. In DOM, the concentration of lignin compounds was much greater in bloom waters that it was in the corresponding nonbloom waters (Fig. 2). In POM, however, the concentration of lignin is comparable in bloom and nonbloom waters.

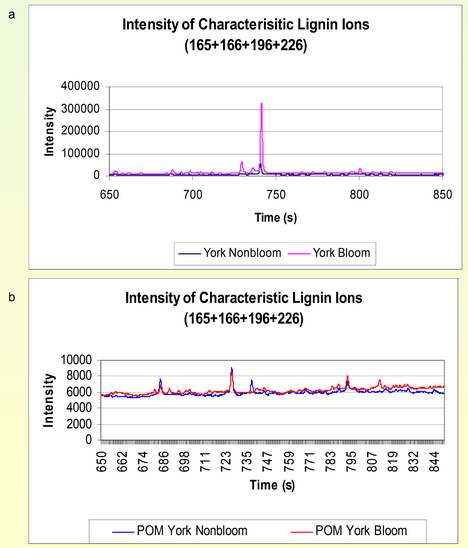

Figure 3: GC-MS Graphs Comparing Bloom and Nonbloom Waters in the York River as DOM (a) and as POM (b)

Specific lignin monomer compounds were quantified and compared between the two types of waters. Both guaiacyl and syringyl compounds were chosen, including G4, G5, G6, S4, and S6 (Fig. 3).

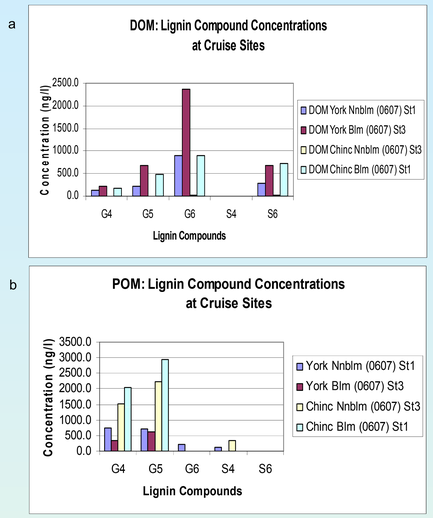

Figure 4: Specific Lignin Compound Concentrations at Bloom and Nonbloom waters in the York River and the Chincoteague Bay

G4 is a guaiacyl compound that is abundant in fresh lignin. G6, however, is an oxidized guaiacyl compound that is more evident in aged lignin (Fig. 4). The ratios of these two compounds, therefore, reveal the extent of processing for the organic matter in the water (Fig. 5), i.e., the higher the ratio, the more degraded the organic matter, and vice versa.

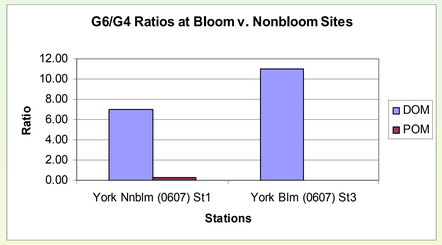

Figure 5: Comparison of G6/G4 ratios in Bloom and Nonbloom Waters of the York River

Conclusions and Future Work

In the bloom sites of the York River and the Chincoteague Bay, higher concentrations of lignin as DOM, G6 in particular, was found compared to their corresponding nonbloom sites. G4, however, was more abundant in the nonbloom sites especially as POM. This observation leads us to hypothesize that decomposition of fresher terrestrial POM can oxidize the G4 to G6, and more importantly, can also release nutrients that support algal blooms.

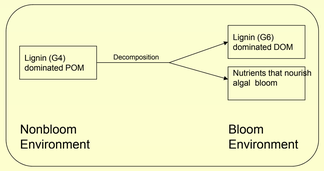

Figure 6: Conceptual Model of Lignin's Correlation in Bloom and Nonbloom Waters

The salinities in the bloom and nonbloom sites are very similar, suggesting lignin dominated POM may come from salt marsh grass or resuspended sediment. Further experimentation would need to differentiate these two possible sources.