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The Vinylguaiacol/Indole or VGI ("Veggie") Ratio: Assessing Relative Contributions of Terrestrial and Aquatic Organic Matter to Sediments

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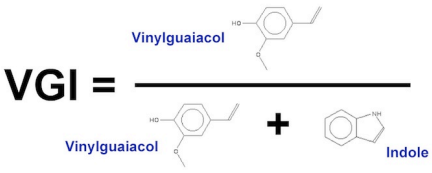
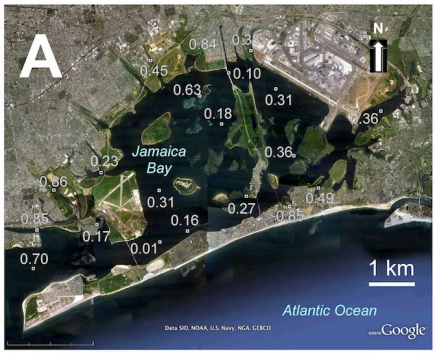


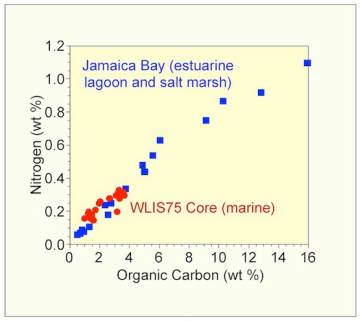
(1) The organic matter (OM) fraction of estuarine sediments is often distinctive and thus diagnostically useful in determinations of sedimentary provenance. Among the most fundamental distinctions to be made is that between **terrestrial and aquatic OM**. To supplement the parameters commonly used for this purpose (e.g., C/N and stable isotope ratios), we proposed the **Vinylguaiacol/Indole or VGI ("Veggie") ratio**, defined as [vinylguaiacol / (indole + vinylguaiacol)] using data produced by analytical **pyrolysis**-gas chromatography/mass spectrometry of dried, homogenized sediment samples. The ratio employs the peak areas of these two compounds on the mass chromatograms of their molecular ions (m/z 150 and 117).

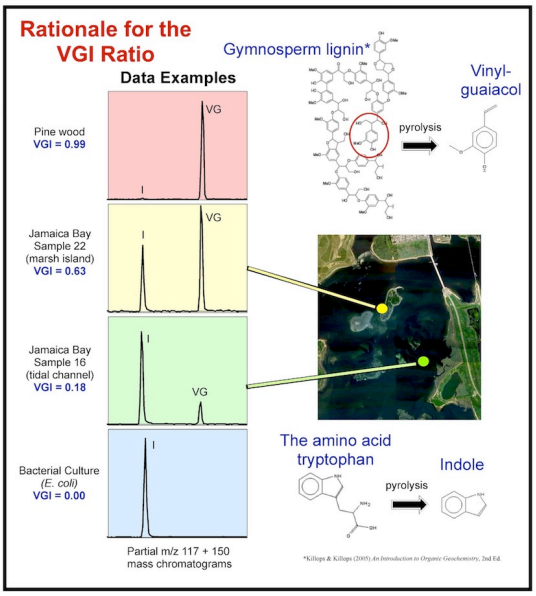
(3) Vinylguaiacol and indole are commonly detected in Recent sediment pyrolyzates. We hypothesized that their relative quantities therein should be proportional to the relative contributions of land plant and microbial OM, respectively.

(2) Major pyrolysis products of **terrestrial plant lignin** include a variety of methoxyphenols, notably **4-vinylguaiacol**. In contrast, **aquatic algae and bacteria** characteristically produce distinctive organonitrogen compounds upon pyrolysis, particularly **indole**, derived from the amino acid tryptophan. The end member VGI ratio value of about 1.00 is obtained for reference land plant matter, including the marsh plants *Phragmites* and *Spartina*, as well as maple and pine wood. The end member value of 0.00 is obtained for cultured microbes, including *Escherichia coli* and the cyanobacterium *Anacystis*.



VGI Ratio Values for Sediments of Jamaica Bay, New York

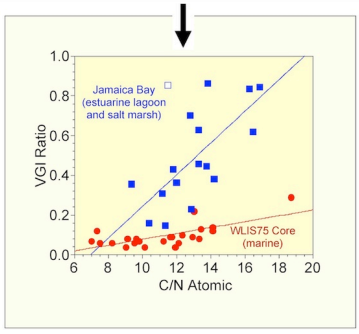




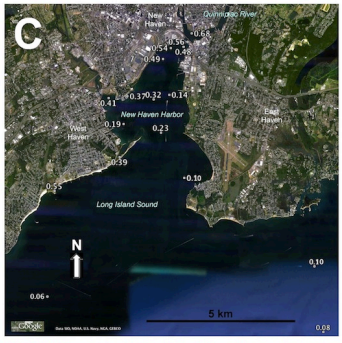
(4) For both the estuarine/marsh and marine samples, nitrogen contents increase as TOC increases, with a wider range for the former (**above**). VGI values generally increase with increasing C/N, but the VGI can distinguish between estuarine/marsh and marine samples (**below**).

(6) Jamaica Bay (NY), behind an Atlantic barrier island and with marsh islands and multiple urbanized tidal creeks, displays a very wide VGI range, affected by proximity to stands of marsh vegetation, bathymetry, and sediment grain size (**Rationale & Map A**).

Conclusion - The VGI ratio provides a simple and effective molecular parameter useful in determining the relative contributions of terrestrial and aquatic organic matter to estuarine and near-shore marine sediments, supplementing traditional bulk chemical and isotopic indicators.



Index Map - New York metropolitan area and southern New England, USA

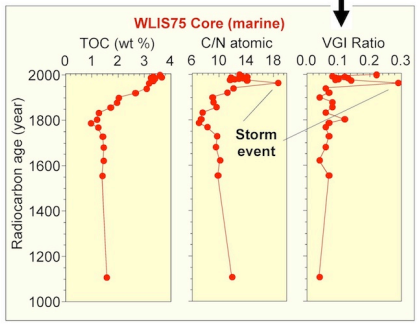


VGI Ratio Values in the Vicinity of New Haven Harbor (Connecticut)

(5) The Long Island Sound core shows to an increase in TOC in recent decades, likely due to seasonal hypoxia. Shifts in C/N and VGI are also evident at the top of the core. Both C/N and VGI show a spike in terrestrial OM input likely due to a major storm event in the mid-1950's (**below**).

(7) Deep water Long Island Sound sediments show a strong predominance of aquatic OM (VGI about 0.05), while nearshore sediments collected 2 km from the mouth of the Housatonic River and in embayments near the Connecticut and Thames River mouths have a greater terrestrial OM component (VGI of 0.15 to 0.23). Samples taken from *Spartina* peat marshes at the mouths of major rivers (Housatonic and Connecticut) entering Long Island Sound have high (*ca.* 0.9) VGI ratio values. The results demonstrate a precipitous decrease in the relative amounts of unaltered land plant OM in the offshore direction, but also that a minor fraction persists in deeper water environments (**Map B**).

(8) Sediments from New Haven (CT) harbor show a diminution in VGI values from 0.66 at the mouth of the Quinnipiac River to 0.08 at the entrance to the harbor over a distance of only 4 km, as terrestrial influences wane moving towards open water (**Map C**).



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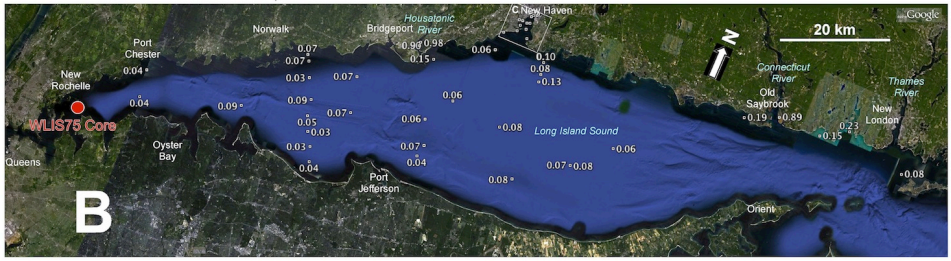

VGI Ratio Values for Long Island Sound Sediments