

## Molecular level characterization of methyl sugars and other carbohydrate compounds in marine high molecular weight dissolved organic matter (HMWDOM)

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Dissolved organic matter (DOM) is an active component of the carbon cycle however its chemical composition, fate, and sources are poorly understood. Approximately 30% of surface DOM can be sampled by ultrafiltration, and thereby concentrates the high molecular weight DOM fraction (HMWDOM > 1kDa)[1]. Previous studies have shown that most HMWDOM is comprised of carbohydrates (acylated carbohydrates or APS), but only a minor fraction of the carbohydrate has been identified at the “molecular level” (as monosaccharides after hydrolysis, *i.e.* fucose, rhamnose, arabinose, galactose, glucose, mannose, and xylose). The discrepancy between NMR derived estimates of HMWDOM carbohydrate (50-70% C) and molecular level analyses (10-20% C) has not been explained, and no new sugars have been identified in HMWDOM in about 10-15 years[2].

Here using ultrafiltration, silver cation preparative chromatography, and GC-MS we identified 50 novel sugar compounds after hydrolysis of the HMWDOM. Sugars were identified using chemically synthesized sugar standards and mass spectra data available in literature. Our results showed that mono- and di- methylated hexoses; mono- and di- methylated pentoses; mono- and di- methylated 6-deoxysugars, as well as heptoses, methylated heptoses, 3,6-dideoxysugars and 1,6 anhydrosugars (*i.e.* levoglucosan, galactosan, and mannosan) are components of HMWDOM, which may explain in part the low apparent yields of sugars recovered by molecular level (HPLC) analyses compared to NMR estimates.

Our results also indicated that the above compounds accounted 2-3% of the APS in surface/deep waters and their diversity decreased with depth. The high diversity of mono- and di- methylated hexoses in the surface sample most likely suggests an algal and/or bacterial source, while the high abundance of methylated 6-deoxy hexoses in the deep sample points toward a important bacterial contribution.

[1] Benner *et al* (1992) *Science* **255**, 1562-1564. [2] Aluwihare *et al* (1997) *Nature* **387**, 166-167.

## Multiple pools of reduced carbon can be released during hyperthermals

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Numerous transient hyperthermals have been identified in Earth history, and most are associated with a sharp negative carbon isotope excursion (CIE). The CIEs indicate that rapid global warming was at least partly caused by the release of reduced carbon, with methane hydrates, peat deposits and permafrost all being proposed as sources. Much work on hyperthermals, and especially the Paleocene-Eocene Thermal Maximum (PETM), illustrates that rapid global warming caused dramatic changes in the hydrological, erosional and weathering regime. These changes were associated with a marked increase in the mobilisation and transport of soil and terrestrial vegetation, and it is likely that under a warmer climate state at least some of this OM was oxidised, providing a positive feedback on global warming. Here, we present evidence that even reduced carbon reservoirs that are generally perceived as recalcitrant (*i.e.* kerogen) are also mobilised during such events.

Kerogen inputs to marginal marine sediments increased dramatically during both OAE1a and the PETM. This is documented by a shift in biomarker (sterane and hopane) assemblages from thermally immature to mature signatures over short stratigraphic scales. This is indicative of mixing of two distinct organic matter sources, most likely a source contemporaneous with sediment deposition and another older, reworked source. These observations confirm that an increase in hydrological energy during hyperthermals was sufficient to markedly and widely increase sedimentary rock erosion. We suggest that this strong response was particularly due to rapid deviation from steady state conditions. Moreover, erosion and chemical weathering are generally coupled and even ancient kerogens have been shown to be highly oxidisable during shale weathering; thus, these events were likely associated with kerogen oxidation. Although unlikely to have been a major source of additional reduced carbon (<10% of the CIE), this work highlights the potential lability of all organic matter pools during rapid climate change events.