**An Ultrahigh-Resolution Mass Spectrometry Index to Estimate**

**Natural Organic Matter Lability**

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**Results and Discussion**

Determining the chemical constituents of natural organic matter (NOM) by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) remains the ultimate measure for probing OM source material, evolution, and transport. However, lability and the fate of OM in the environment remains a controversy. FT-ICR MS-derived elemental compositions are presented in this study to validate a new interpretative method to determine the extent of NOM lability from various environments. FT-ICR MS data including 35 samples analyzed over the last decade from the same 9.4 tesla instrument was used to validate the application of a NOM lability index incorporating marine, freshwater, and glacial ecosystems. A molecular lability boundary (MLB) was developed from the FT-ICR MS molecular data, visualized from van Krevelen diagrams, dividing the data into more and less labile constituents. The concept of an FT-ICR MS molecular lability boundary (MLB) is based on our current understanding of van Krevelen diagrams, incorporating chemical information depicted by various H/C and O/C ratios and the relative boundaries of each chemical class region. Chemical NOM constituents above the MLB at H/C ≥ 1.5 correspond to more labile material (shaded region of Figure 1), whereas NOM below the MLB, H/C < 1.5, exhibits less labile, more recalcitrant character.



**Figure 1.** van Krevelen diagrams for OM isolated from (a) the Apalachicola River, (b) marine algae before passage through a laboratory engineered sand column, (c) the mixture of algal marine-derived and Apalachicola River OM after passage through the sand column, and (d) Gulf of Mexico brine fluid seep, hydrocarbon and oil seep (Bush Hill), and bottom water. Heterogeneous molecular character is depicted in Figure 1a-c for molecular constituents containing CcHhNnOoSs when n = 0, 1, 2 and s = 0 or 1. Percentages of molecular species above and below the MLB are provided for each sample. More labile material from Apalachicola was reported for the marine algal derived OM (Figure 1b) and OM extends to varying labilities for different Gulf of Mexico benthic features (Figure 1d).

Of all marine, freshwater, and glacial environments considered for this study, glacial ecosystems were calculated to be the most labile. The MLB extends our interpretation of FT-ICR MS NOM molecular data to include a metric of lability and generally ranked the OM from most to least labile as glacial>marine>freshwater. The MLB distinguishes between more and less labile OM and its contribution to the overall ecosystem, providing a further advance in the interpretation of molecular data derived from FT-ICR mass spectra. Applying the MLB is useful not only for individual NOM FT-ICR MS studies, but also provides a lability threshold to compare and contrast molecular data with other FT-ICR MS instruments that survey NOM from around the world.

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**References**

[1] D’Andrilli, J. *et al*., Rapid Communications in Mass Spectrometry, **29**, 2385-2401 (2015).