Characterization of IHSS Pony Lake Fulvic Acid Dissolved Organic Matter by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry and Fluorescence Spectroscopy

J.D'Andrilli (Montana State U., Engineering); C.M. Foreman (Montana State U., Engineering); A.G. Marshall (FSU, NHMFL, Chemistry); D.M. McKnight (U. Colorado, Arctic Research)

Results and Discussion

We present the extensive characterization of Antarctic Pony Lake (PL) dissolved organic matter (DOM), an International Humic Substance Society (IHSS) fulvic acid (FA) reference standard, by use of electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) and excitation/emission matrix fluorescence spectroscopy (EEMS). PLFA is the first reference standard available through IHSS derived solely from a microbial source. A number of factors differentiate PLFA from other IHSS standards, including source material, geographic location, sunlight exposure, freeze-thaw conditions, and other *in situ* environmental influences. ESI FT-ICR MS and EEMS were used to compare the PLFA microbial DOM compositional signature to the IHSS Suwannee River (SR) FA, a standard frequently studied for environmental DOM analysis. Although $C_cH_hO_oN_nS_s$ (n = 0, 1, or 2 and s = 0 or 1) constituents were present in both IHSS samples, PLFA contained more N and S molecular species; whereas SRFA was dominated by $C_cH_hO_o$ compounds (see Figure 1). Proteinaceous character was detected with both methods, in greater abundance for PLFA, which we attributed to its microbial source material and labile, potentially more reactive nature than SRFA. Characterization by both analytical techniques resulted in complementary data that reinforce the importance of PLFA as an IHSS reference standard that should be utilized for other microbiological environmental DOM comparisons.

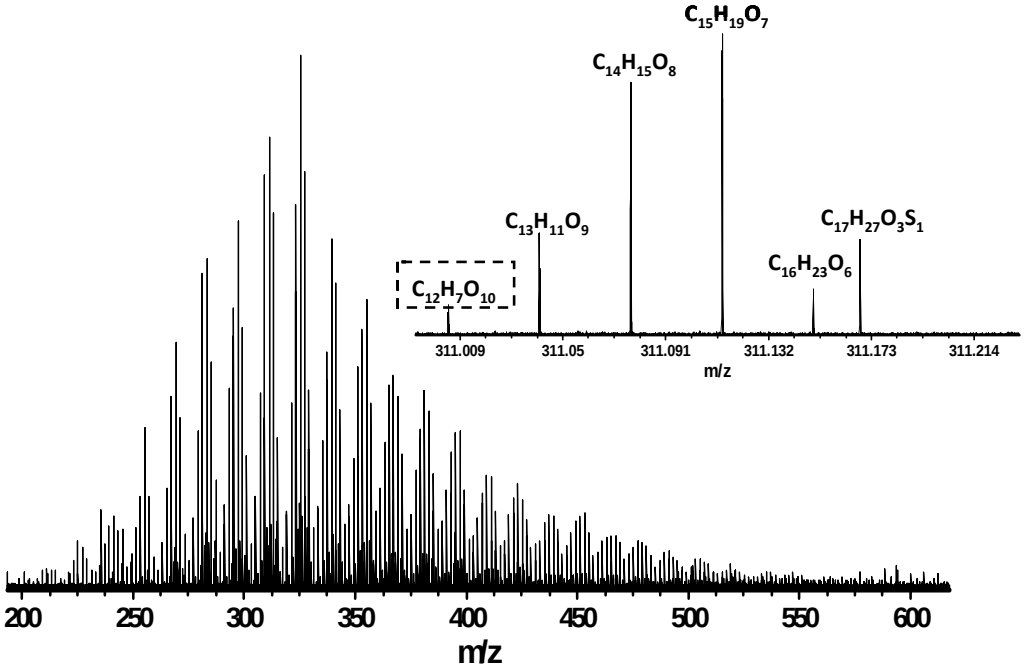

Figure 1. Negative ESI FT-ICR mass spectrum for Sewaunee River fulvic acid. SRFA. The inset shows molecular formula assignments for each SRFA peak with the unique molecular formula not observed for Pony Lake fulvic acid highlighted.

Acknowledgments

This work was supported by the NSF Division of Antarctic Sciences through ANT-0338342 and ANT-0838970, by the NSF Division of Materials Research through DMR-11-57490 and the State of Florida.

References

[1] D'Andrilli, J., *et al*., Org. Geochem., **65**, 19-28 (2013)