Molecular-Level Characterization of Reactive and Refractory Dissolved Natural Organic Nitrogen Compounds by Atmospheric Pressure Photoionization Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Results and Discussion

Dissolved organic nitrogen (DON) represents a significant fraction of the total dissolved nitrogen pool in most surface waters and serves as an important nitrogen source for phytoplankton and bacteria. As with other natural organic matter mixtures, ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is the only technique currently able to provide molecular composition information on DON. Although electrospray ionization (ESI) is the most commonly used ionization method, it is not very efficient at ionizing most DON components. Positive- and negative-mode atmospheric pressure photoionization (APPI) coupled with ultrahigh resolution FTICRMS at 9.4 T were compared for determining the composition of DON before and after bioassays. Toluene was added as the APPI dopant to the solid-phase DON extracts, producing a final sample that was 90% methanol and 10% toluene by volume. Positive-mode (+) APPI proved significantly more efficient at ionizing DON; 62% of the formulas that could be assigned in the positive-ion spectrum contained at least one nitrogen atom vs. 31% in the negative-ion spectrum. FTICR mass spectral data indicated that most of the refractory DON compounds (i.e. nonreactive during the 5 days of the incubation) had molecular compositions representative of lignin-like molecules, while lipid-like and protein-like molecules comprised most of the small reactive component of the DON pool. From these data we conclude that (+) APPI FTICRMS is a promising technique for describing the molecular composition of DON mixtures. The technique is particularly valuable in assessing the bioavailability of individual components of DON when combined with bioassays.

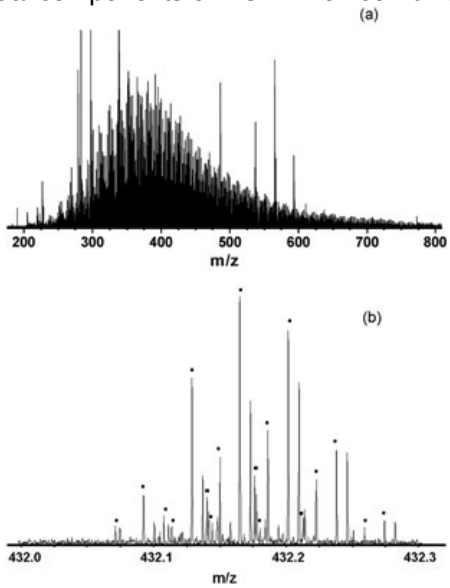

Figure 1. (a) Broadband positive-ion atmospheric pressure photoionization FT-ICR mass spectrum of the Caloosahatchee River sample and (b) 0.3 *m/z* unit window from that spectrum with the N_1 and N_3 class peaks labeled.

Acknowledgements

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References

[1] Osborne, D.M., *et al.,* Rapid Commun. Mass Spectrom., **27**, 851-858 (2013).