

The molecular characterization of dissolved organic nitrogen by APPI FT-ICR MS

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Previous mass spectrometry studies of dissolved organic matter (DOM) have largely focused on the refractory carbon component [1, 2]. Dissolved organic nitrogen (DON) is largely uncharacterized at the molecular level, likely due to the inefficiency with which nitrogen species ionize in complex DOM mixtures. Water Quality Treatment Areas treat agricultural runoff and are often engineered specifically to reduce total nitrogen levels. Currently, the only parameter available to determine the effectiveness of WQTAs is total DON, which does not account for differences in the biogeochemistry of individual organic nitrogen compounds.

Tandem mass spectrometry has identified common fragments in DOM [3]. Here, we report the isolation and fragmentation of nitrogen-containing DOM ions of a single mass-to-charge ratio to elucidate structural information.

Atmospheric Pressure PhotoIonization (APPI) has advantages for FT-ICR MS characterization of dissolved organic matter (DOM) because, unlike electrospray ionization, APPI ionizes both polar and nonpolar compounds simultaneously. In this study, we were able to efficiently ionize DOM species that contain nitrogen with APPI.

Due to the efficiency of APPI to ionize N-containing DOM compounds, we were able to isolate DON ions of a single mass-to-charge ratio and fragment by infrared multiphoton dissociation. The results show neutral losses (e.g. H₂O and CO₂) similar to those from dissociation of C_xH_yO_z species. We did not observe the loss of N-containing constituents, an indication that nitrogen may be incorporated into ring structures. Work supported by NSF DMR-06-54118, OCE-07-26754, EAR-08-19811 and the State of Florida.

[1] Hertkorn *et al.* (2006) *GCA* **70**, 2990-3010. [2] Koch *et al.* (2005) *GCA* **69**, 3209-3208. [3] Stenson *et al.* (2002) *Anal. Chem.* **74**, 4397-4409.

Mercury stable isotopes fractionation in cryogenically archived specimens from the Arctic marine environment

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Mercury impacts are enhanced at high latitudes with record concentration levels in Arctic marine wildlife [1], posing a health risk for northern people who consume these subsistence resources [2]. Whereas a cascade of processes might ultimately link atmospheric Hg emissions to Hg concentrations in Arctic biota, the different temporal trend series in the Western and Eastern Arctic sectors [3] suggest that other factors may be underpinning these trends. To study these questions, we explored Hg mass dependent fractionation (MDF) and mass independent fractionation (MIF) signatures in marine mammal liver sample collections archived at the US Marine Environmental Specimen Bank. These samples were collected as part of the Arctic Marine Mammal Tissue Archival Project (AMMTAP) initiated in 1987. Mercury stable isotope measurements were conducted in beluga whale (*Delphinapterus leucas*), ringed seal (*Phoca hispida*) and polar bear (*Ursus maritimus*) liver samples collected over several years in different Alaskan regions.

Preliminary results in beluga whale showed that Alaskan Arctic and sub-Arctic regions were characterized by unique Hg MIF signatures, confirming earlier results obtained in seabird eggs collected in the same regions [4]. These results suggest that Hg-MIF may be used as a robust geographical tracer for describing habitat utilization and food webs connectivity. Significant variations in Hg MDF and MIF existed between species and between individuals at the colony, group or stock level. Since Hg concentrations and speciation in marine mammal livers tend to be influenced by several ecological factors and species-specific metabolic processes, we investigated the influence of these factors on Hg MDF and MIF variations.

[1] Lockhart *et al.* (2005) *Stoten* **351**, 391-412. [2] Choi & Grandjean, (2008). *Environ. Chem.* **5**, 112-120. [3] Wilson (2007) *AMAP Rep.* [4] Point *et al.* (2008) *GCA* **72**, A755-A755.