

Identification of reactive and refractory components of dissolved organic Nitrogen by FT-ICR mass spectrometry

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The composition of the individual components that comprise dissolved organic nitrogen (DON) are largely unknown, primarily due to the inefficiency with which nitrogen species ionize by electrospray ionization (ESI) prior to mass spectral analyses. Unlike ESI, atmospheric pressure photoionization (APPI) can ionize a broad range of molecules through electron detachment or charge transfer between a photoionized dopant (e.g. toluene) and a DOM analyte of interest [1]. APPI also exhibits less ion suppression from matrix effects. Here we show the unique ability of APPI coupled to ultrahigh resolution mass spectrometry to identify the reactive and refractory components of DON.

Figure 1 is an isolated 0.30 Da window from an ultrahigh resolution APPI FT-ICR mass spectrum of DON in surface waters draining an agricultural area in South Florida.

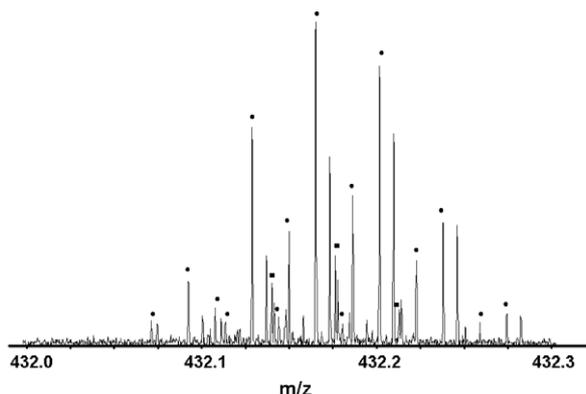


Figure 1: Isolated 0.30 Dalton window at nominal mass 432 from negative-ion APPI FT-ICR mass spectrum of DON. Nitrogen-containing compounds labeled.

Using this optimized, negative-ion APPI strategy we have been able to identify the reactive and refractory components of DON in these nitrogen-rich waters. Surprisingly, microbial attack on DON does not release much nitrogen.

[1] D'Andrilli *et al.* (2010) *Rap. Commun. Mass Spectrom.* **24**, 643–650.

Partitioning peatland gas production: Determining the fraction of CO₂ produced from methanogenesis

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We developed isotope mass balance equations quantify the amount of carbon being remineralized in a peatland. As carbon is remineralized, it generates CO₂ (in the form of DIC) and CH₄. The CO₂ is produced in one of two ways: organic matter fermentation and methanogenesis. We assume that with fermentation, organic carbon produces CO₂ only, with no isotopic fractionation. That is, the CO₂ has the same δ¹³C as the organic material, -26‰. CH₄ is produced solely from methanogenesis. We assume and equimolar production of CO₂ with CH₄ production. By collecting porewater samples and analyzing them for ¹³C-CO₂ and ¹³C-CH₄ isotope signatures and concentrations of both CO₂ and CH₄, we were able to calculate the proportion of CO₂ formed from organic matter fermentation and methanogenesis. The ¹³C-CO₂ we measure in porewater represents a mixture between the ¹³C-CO₂ from organic matter decomposition and ¹³C-CO₂ from methanogenesis. Based on the amount of CO₂ formed from methanogenesis, we were able to calculate how much methane should be present in the porewater based on the understanding that methanogenesis forms equal net amounts of CO₂ and CH₄. Knowing how much CH₄ should be present and how much was actually measured, we can get an estimate of how much CH₄ has bubbled out of our porewater at a certain depth. Using values obtained from porewater sampling, we found that at 0, 154, and 261cm depth. The percent CO₂ from methanogenesis was 55.8%, 88.1%, and 91.4%, respectively. The percent CH₄ loss due to obullition was 68.9, 78.7, and 84.4, respectively. Fractionation factor values were 1.0975, 1.0850, and 1.0835, respectively. These findings indicate that with increasing depth both the percent CO₂ formed from methanogenesis and the percent CH₄ lost increased while the fractionation factor value decreased.