



Reading the molecular signature of ecosystems in dissolved organic matter

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To make forecasts about the behavior, origin and fate of dissolved organic matter (DOM) in the environment, we need further insights into the molecular composition of this complex mixture. The development of soft ionization procedures and mass spectrometers capable of ultrahigh resolution (Fourier-Transform Mass Spectrometry, FTMS) have opened important new horizons in this regard. However, the application of such systems is restricted due to high purchase and maintenance costs. The introduction of the improved version of the Orbitrap FTMS analyzer (“Elite”) in 2011 could open new perspectives for the molecular-level investigation of DOM, as it combines high performance with lower overall costs. We compared the Orbitrap with an established FT-ICR-MS (ion cyclotron resonance, 15 Tesla) to assess the potential of this analyzer on a broad set of 17 terrestrial and aquatic DOM samples prepared by solid phase extraction (SPE-DOM, Dittmar et al. 2008). The dataset included groundwater, soil water from different depths and vegetation covers (forests, grassland), as well as bog, river, lake and marine waters. We here show that the Orbitrap analyzer is able to detect hard-to-resolve nitrogen and sulfur containing compounds (triplet signal $[\text{CHO}]\text{N}_2\text{O}_2$, $[\text{CHO}]\text{C}_5$, $[\text{CHO}]\text{C}_2\text{H}_4\text{S}$) up to a mass-to-charge ratio of ~ 430 and well retrieves the intensity information of the FT-ICR-MS. Both points have been recently reported as major obstacles in the detailed molecular-level analyses of DOM by Orbitrap systems (Hawkes et al. 2016). In our data, slight deviations in intensity representation were only found in samples characterized by stronger aromaticity, and especially in the lower mass range (below m/z 250). A subset of > 6000 formulae detected in both sets was used to further characterize the sample set on a molecular level. The derived ecological information, as assessed by ordination and post-ordination gradient fitting, was highly consistent among both datasets. A dominating first coordinate (65% of variation) described a gradient of saturation/ aromaticity, going along with contribution changes of the respective molecular groups. This gradient was also linked to allover spectrum intensity. The second coordinate represented a gradient in contribution of heteroatoms and allover number of formulae per sample. Interestingly, the third coordinate separated the relatively strongly reworked groundwater and marine DOM samples based on intensity-weighted average mass and number of C and O atoms per sample. About 150 formulae were only detected in one or two samples of the set, and could possibly contain further ecosystem-specific information. Ongoing research using mass spectrometric fragmentation analysis aims to identify these and previously reported (Roth et al. 2014) ecosystem-specific molecules.

References

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