A novel method for characterizing dissolved organic matter (DOM) in subsurface sediments for anaerobic degradation processes using FT-ICR-MS and induction-based nano-spray technique

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Marine subseafloor holds a substantial amount of living biomass (the deep biosphere). These microbes might drive a slow but extensive carbon flow and play an important role in the carbon cycle within the deep Earth and geochemical processes in the upper hydrosphere. It is not clear how the microbes could survive on old and recalcitrant organic matter (ROM) in subsurface sediments. Dissolved organic matter (DOM) encompasses the analytical window for the initial degradation of ROM, while there is no suitable method to characterize the DOM of volume-limited pore water in deep subsurface sediments. Moreover, conventional pretreatments of pore water via solid phase extraction induce selective loss of DOM.

We have developed a novel analytical technique for DOM from subsurface sediment using ultra-high-resolution mass spectrometry (FT-ICR-MS) coupled with nano-electrospray ionization (nano-ESI). This technique enables better ionization and signal detection of rapidly-cycled DOM with small sample volumes and reduces the depressive effect of ionization. By incorporating FT-ICR-MS coupled with induction-based nanospray ionization, we were able to meticulously dissect the composition of DOM within interstitial waters. The level of detail achieved uncovered nearly 10,000 distinct DOM species from less than 10 µL of sample, which is only 0.1% of the sample size required by the conventional method. These insights reveal that current models may vastly underestimate the heterogeneity of DOM. Soil DOM was not dominated by ligninlike or CRAM compounds, as determined using the conventional method. The novel method revealed more peptide/carbohydratelike compounds, highly condensed aromatics, and more than double the number of CHNO compounds. A more complete understanding of DOM will allow us to elucidate the biogeochemical processes of DOM. The new method expands our comprehension of DOM diversity and contributes a new analytical window of carbon cycling for volume-limited samples, especially the rapidly-cycled DOM and the largely unknown initial step of the degradation process in subsurface sediments.