Illuminated darkness: Molecular signatures of Congo River dissolved organic matter and its photochemical alteration as revealed by ultrahigh precision mass spectrometry

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ABSTRACT: Congo River water was filtered and then irradiated for 57 d in a solar simulator, resulting in extensive photodegradation of dissolved organic matter (DOM). Whole-water (i.e., unfractionated) DOM was analyzed pre- and post-irradiation using ultrahigh resolution Fourier transform ion cyclotron mass spectrometry (FT-ICR MS), revealing the following three pools of DOM classified based upon their photoreactivity: (1) photo-resistant, (2) photo-labile, and (3) photo-produced. Photo-resistant DOM was heterogeneous, with most molecular classes represented, although only a small number of aromatics and no condensed aromatics were identified. The photoproduced pool was dominated by aliphatic compounds, although it included a small number of aromatics, including condensed aromatics. Aromatic compounds were the most photoreactive, with > 90% being lost upon irradiation. Photochemistry also resulted in a significant drop in the number of molecules identified and a decrease in their structural diversity. The FT-ICR MS signatures of two classes of refractory organic matter, black carbon and carboxylic-rich alicyclic molecules (CRAM), were present in the sample prior to irradiation, indicating that the Congo River could be a significant exporter of recalcitrant DOM to the ocean. All black carbon-like molecules identified in the initial sample were lost during irradiation. Molecular signatures consistent with CRAM were also highly photo-labile, demonstrating that environmental solar irradiation levels are capable of removing these refractory compounds from aquatic systems. Irradiation also shifted the molecular signature of terrestrial DOM toward that of marine DOM, thereby complicating the task of tracking terrestrial DOM in the ocean.

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