Phototransformation of dissolved organic matter to ammonium and new forms of nitrogen-containing organic compounds: the biogeochemical implications

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Photochemical transformation of dissolved organic matter (DOM) has been well recognized as an important process impacting carbon cycling and nutrient dynamics across aquatic environments. Photo-degradation of DOM can release ammonium, termed as photoammonification, which is increasingly observed and reported from earlier studies in lakes, rivers, coastal and oceanic waters. This photoammonification process potentially can shape the remineralisation of organic nitrogen, although the molecular-level pathway is unclear. In this study, a DOM-rich blackwater sample from the Dismal Swamp, VA was subjected to photodegradation in the laboratory for an extended period of time (up to 60 days). Bulk analysis of carbon, nitrogen, and nutrients were conducted at multiple time points to track their dynamic changes during photo-irradiation. We have applied an array of advanced analytical techniques to examine the molecule evolution of DOM and photo-flocculated particulate organic matter through ultra-high resolution mass spectrometry, NMR, and x-ray adsorption spectroscopy. Besides photo-production of ammonium, we also observed neoformation of nitrogen-containing molecules that are associated with both aliphatic proteinaceous organic compounds (e.g., amide, peptides) and condensed aromatic compounds (e.g., black nitrogen). It is suggested that the photo-product ammonium and the intermediate products, e.g., small peptides, may promote the incorporation of nitrogen to DOM. We will propose the underlying pathways for this incorporation, which have important biogeochemical implications to the fate of organic nitrogen.