Photolysis and the dimethylsulfide (DMS) summer paradox in the Sargasso Sea

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ABSTRACT: Apparent quantum yields and rates of dimethylsulfide (DMS) photolysis were determined from Sargasso Sea seawater with the goal of assessing the extent to which photoreactions affect the unusually elevated upper ocean concentrations of DMS during the summer, the so-called DMS summer paradox. Apparent quantum yields determined with monochromatic radiation decrease exponentially with increasing wavelength and indicate that DMS photolysis is driven by ultraviolet (UV) radiation. The relative spectral partitioning differs between samples collected from the surface mixed layer (15 m) and from the chlorophyll a maximum (80 m), presumably because of differences in chromophoric dissolved organic matter (CDOM) quality (e.g., apparent degree of bleaching). Quantum yields are also temperature dependent, and an approximate doubling of photolysis rates occurs for a 20° C increase in temperature. The significance of DMS photolysis to upper ocean sulfur budgets is explored using a multiyear (1992- 1994) DMS time series, concurrent irradiance determinations and temperature profiles, and estimates of CDOM absorption. Depth-integrated, mixed-layer DMS photolysis rates peak in the summer (15-25 μmol m^{-2} d^{-1}) and decline to ,1 μmol m^{-2} d^{-1} in the winter. These rates correspond to specific turnover rates of ~0.29 d^{-1} in the summer and < 0.02 d^{-1} in the winter. Seasonal changes in solar radiation, temperature, and DMS concentrations drive the 30-fold differences in photolysis rates, overshadowing differences caused by photosensitizer (CDOM) quantity or quality (21-35%). These results demonstrate that although photolysis is not the primary driver of the summer paradox, it makes an important contribution to the time-depth pattern of DMS concentrations observed in the Sargasso Sea.