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CDOM photodegradation: Implications for the oceanic methane paradox

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Photoproduction of methane (CH_4) from DOM was detected in water samples collected from peat ponds, rivers, estuaries, and coastal and open oceans. The rates of CH_4 photoproduction under solar-simulated irradiation were 259 pmol L^{-1} h^{-1} in peat pond water, 14-22 pmol L^{-1} h^{-1} in river water, 3-7 pmol L^{-1} h^{-1} in estuarine and coastal water, and 1-2 pmol L^{-1} h^{-1}in offshore water. The production rate was positively correlated to the sample's initial chromophoric DOM absorbance (A_{CDOM}) and dissolved organic carbon (DOC) concentration, whereas the ratios of CH_4 production to A_{CDOM} and DOC losses (CH_4/A_{CDOM} and CH_4/DOC) were inversely related to the initial A_{CDOM} and DOC, implying that marine DOM is more efficient than terrigenous DOM in terms of CH_4 production per unit loss of A_{CDOM} or DOC. CH_4/A_{CDOM} at the wavelength of 330 nm ranged from 0.2 to 1.5 m μmol L^{-1} and CH_4/DOC from 0.0006% to 0.02%. The CH_4/DOC translates to (0.6-24) $\times$ 10^7 mol CH_4 yr^{-1} photoproduced in global inland waters and (4.8-29) $\times$ 10^9 mol CH_4 yr^{-1} in the open ocean based on published estimates for CO_2 photoproduction in inland and open-ocean waters. The open-ocean CH_4 photoproduction term is comparable to the estimated oceanic CH_4 outgassing rates and upper-ocean microbial consumption rates and thus a potentially important contributor to maintaining CH_4supersaturation in the oxic surface ocean (i.e. the oceanic methane paradox). Several methylated compounds were identified as potential precursors of the photoproduced CH_4.