

Effects of molecular structure and functional groups of organic ligands on photochemical transformation of mercury and methylmercury

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Photochemical reduction of mercury (Hg) and photo-degradation of methylmercury (MeHg) are among important pathways of elemental Hg(0) production and demethylation in natural and contaminated open surface waters. This transformation is affected by aqueous ionic species, among which aromatic moieties and thiolate functional groups in naturally dissolved organic matter (DOM) are thought to be the most important because of their light-absorbing and Hg-complexing characteristics. However, exact mechanisms by which DOM and organic ligands mediate transformation of Hg or MeHg is not clear owing to our incomplete understanding of the structural arrangement and stoichiometry of reactive functional groups in DOM. In this study, various DOM isolates and naturally-occurring S- or O-containing model ligands were used to systematically investigate the role of various functional groups and their steric arrangements in photochemical transformation of Hg or MeHg. We show that, for O-containing ligands, the photochemical reduction rates of Hg(II) are driven primarily by the secondary reaction and influenced not only by the neighboring functional groups but also their positioning on the aromatic benzene ring structure. On the other hand, photoreduction of Hg(II)-thiolate complexes is driven largely by the direct photolysis (or primary reaction). The presence of dissolved oxygen decreases the photoreduction of Hg(II) but increases reoxidation of Hg(0), in which singlet oxygen rather than hydroxyl radicals formed by the photolysis of thiols drives the photooxidation. We also show that photodegradation of MeHg is enhanced by the presence of DOM isolates and various S- or O-containing ligands in both fresh and saline solutions. However, this enhanced demethylation depended on the chemical structure, concentration, and redox state of the organic ligands. Photodegradation rates of MeHg in ambient water collected from East Fork Polar Creek at Oak Ridge, Tennessee, are estimated to range from 7.8 to 78 ng m⁻² d⁻¹ at 35°C, suggesting that photodegradation could be an important sink for MeHg in this natural ecosystem. Our findings are thus of critical importance for constructing the mass balance and for improved understanding of the fate of Hg and MeHg in this contaminated environment.