

Photolytic redox transformation of mercury and degradation of methylmercury as influenced by complexing organic ligands

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Photochemical reduction of mercurial [Hg(II)] species is one of the important pathways of producing elemental Hg(0) in open waters and contributing to Hg cycling in the environment. This redox transformation is affected by aqueous and surface species, among which the naturally dissolved organic matter (DOM) is thought to play a major role because of its aromatic moieties that pertain light-absorbing characteristics. However, how DOM mediates the photochemical reduction of Hg(II) is not yet clear. In this study, we systematically investigated effects of the structural arrangement and stoichiometry of reactive functional groups in DOM on photochemical reduction of Hg(II), by using analogs including salicylic acid, 4-hydrobenzoic acid, anthranilic acid, 4-aminobenzoic acid, and phthalic acid. Photochemical reduction of Hg(II) is influenced not only by the neighboring functional groups but also their positioning on the aromatic benzene ring. The rates were found to increase in the order of anthranilic acid > salicylic acid > phthalic acid by varying neighboring functional groups from amine, hydroxyl, to carboxyl on benzoic acid. The substitution position of the functional groups affected reduction rates in the order: anthranilic acid > 4-aminobenzoic acid and salicylic acid > 4-hydroxybenzoic acid. Analyses of ultraviolet (UV) light absorbance of these DOM analogs indicate that the Hg(II) reduction rate is positively correlated to their UV absorption. Quantum chemical calculations suggest that upon photoexcitation, a $\pi\sigma^*$ transition localized at the -NH₂ or -OH groups of the benzoic acid leads to the formation of a -NH· or -O· radical respectively, via the H-atom detachment. The calculations also indicate that in the presence of DOM, the Hg(II) reduction rate may be enhanced through a radical channel. Various organic ligands including DOM were also studied for their influences on photodegradation of monomethyl mercury (MeHg) in fresh and saline waters under anaerobic conditions. Our results indicate that, under UV irradiation, organic ligands can enhance MeHg photodegradation, depending on the chemical and structural properties of the ligands. Thiol functional groups and aromaticity are among the most important factors affecting MeHg photodegradation, as thiol group binding of MeHg and the UV absorption by aromatic moiety jointly resulted in fast MeHg degradation. Photodegradation of MeHg in ambient water collected from East Fork Polar Creek (EFPC), Oak Ridge, TN occurred at relatively high rates, suggesting that photodegradation could be a major sink for MeHg in this ecosystem. The daily photodegradation fluxes of MeHg in EFPC were estimated to in the range of 11.7 to 117 ng m⁻² d⁻¹ during the summer and these values are useful for constructing mass balance of MeHg (and Hg in general) and understanding the role of DOM in Hg photochemical transformation and geochemical cycling in the environment.