Ecosystem Controls on Methylmercury Production by Periphyton Biofilms in a Contaminated Stream: Implications for Predictive Modeling

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Periphyton biofilms in freshwater aquatic environments can be a net source of monomethylmercury (MMHg), as has been shown in East Fork Poplar Creek (EFPC) in eastern Tennessee, USA. Using enriched stable mercury (Hg) isotopes, we quantified Hg methylation and MMHg demethylation in periphyton biofilms from EFPC across seasons, creek location, and under different light exposure. Methylation and demethylation rate potentials were estimated using a transient availability model ($k_{m,trans}$ and $k_{d,trans}$, respectively) and compared to rate potentials estimated from a conventional full availability model ($k_{m,full}$, $k_{d,full}$). The transient availability model accounts for competition for Hg and MMHg among sorption, desorption, oxidation, reduction, methylation and demethylation reactions. Rate potentials assuming transient availability averaged 15× and 9× times greater for k_m and k_d, respectively, for the transient versus full availability models. Significant predictive relationships were obtained between environmental variables (season, location, light) and $k_{m,trans}$ and $k_{d,trans}$. Additionally, ambient MMHg concentration in biofilms was significantly correlated with $k_{m,trans}$. Light exposure and season were significant predictors of $k_{m,trans}$ with greater values in full light exposure and in the summer. Season, light exposure, and location were significant predictors of $k_{d,trans}$, which was highest in dark conditions, in the spring, and at the upstream location. In contrast, no significant predictive relationships were derived for $k_{m,full}$ or $k_{d,full}$ and there was no relationship between ambient MMHg and $k_{m,full}$. These results underscore the importance of applying transient availability kinetic models to MMHg production data when estimating MMHg production potential and flux.