Critical review of mercury methylation and demethylation rate laws for biogeochemical reaction modeling

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Methylmercury (MeHg) in the environment poses a significant threat to human and ecological health and is a major contaminant of concern for water quality. Mechanistic computational models that simulate the net production of MeHg in anoxic sediments are an emerging tool to extend basic knowledge and to support management or remediation decisions. Simulation modeling has the advantage of investigating responses of a system to various perturbations, such as different management strategies or the effect of climate change. Application of a mechanism-based model requires building the model using thermodynamic and kinetic constraints and testing its sensitivity to variations of model parameters. A biogeochemical reaction model using the PHREEQC program was modified from prior studies to improve the model description of net MeHg production in sediments. Rate equations to describe different pathways of methylation and demethylation were implemented and coupled to biogeochemical redox reactions. A comprehensive literature review was conducted to: determine ranges of (de)methylation rate constants derived from mercury isotope assay measurements; estimate the relative contribution of different pathways for (de)methylation; and estimate the rate of organic matter degradation under different environmental conditions. Different mathematical formulations for rate laws and constants were critically reviewed and evaluated for experimental conditions. Sensitivity analysis and the comparison of simulation output with field data sets was used to verify the model formulations. The coupling of (de)methylation reactions and redox processes provides valuable insight into which pathways dominate methylation and demethylation under specific environmental conditions thus contributing to our basic understanding of mercury cycling in sediments.