A semi-empirical kinetic-thermodynamic framework for assessing methylmercury productivity and expression in aquatic sediments

DIMITRI VLASSOPOULOS[1], STEFANIE HELMRICH[2], AND PEGGY A. O'DAY[3]

[1]Anchor QEA, Portland, OR, USA
(dvlassopoulos@anchorqea.com)
[2] [1]Univeristy of California Merced, Merced, CA, USA
(shelmrich@ucmerced.edu, poday@ucmerced.edu)

A biogeochemical framework was developed and applied to interpreting and ranking the expressed methylmercury productivity of sediments across multiple aquatic systems using a limited set of sediment analytical data (bulk Hg, MeHg and TOC concentrations). The underlying geochemical model accounts for equilibrium sediment-porewater partitioning (aqueous speciation, organic matter sorption, and nano/micro-HgS precipitation) and kinetic methylation-demethylation processes. A sensitivity analysis was performed to identify limitations in quantitative application of the conceptual framwork. The framework defines theoretical upper limits for MeHg as a function of total Hg concentrations in sediments. Deviations below this maximum are primarily related to the activity of methylating microbes and biogeochemical redox processes that enhance MeHg demethylation. The general validity of the framework was established in extensively characterized systems including data on aqueous speciation, selective sequential extraction, X-ray absorption spectroscopy, and voltammetric redox profiling. Comparison of MeHg productivity in sediments from marine, estuarine, and freshwater systems across the United States highlights the universal importance of local redox status in moderating MeHg expression despite a range of Hg sources (industrial, mining and atmospheric deposition) and concentrations.