

Environmental Controls on Methylmercury Production and Degradation in Everglades Sediments

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The net production of toxic methylmercury (MeHg) by sediment bacteria is arguably the most critical step in the chain of events leading to mercury (Hg) contamination of Everglades wildlife. Our understanding of the opposing microbial processes involved (for example, Hg-methylation and MeHg degradation) has progressed over the last decade, although, the specifics regarding what mediates these processes are still largely unknown. This study attempts to directly quantify the effect of a suite of environmental parameters thought to be important in controlling microbial Hg-transformation rates. These parameters include: temperature, sulfur chemistry, organic matter, and sediment oxidation/reduction (redox) conditions. Controlled laboratory experiments were conducted on homogenized surface sediment (0-4 cm) collected from five sites along the north-south eutrophication gradient. Sampling locations included two sites in the nutrient enriched ENR, two sites in the transitional WCA-2A, and one site in comparatively pristine WCA-3A. Radiolabel techniques (that is, $^{203}\text{Hg}(\text{II})$ and ^{14}C -MeHg amendments) were used to measure potential rates of Hg-methylation and MeHg-degradation, respectively, in parallel sets of sediment slurries subject to specific temperature or geochemical treatments. There was a general increase in Hg-methylation potentials going from north to south (nutrient enriched to pristine sites), in unamended anaerobic samples incubated at 20 °C. In contrast, MeHg degradation rates varied little among sites. The positive influence of temperature on Hg-methylation rates also generally increased from north to south. While the temperature affect on MeHg degradation was also positive, among-site differences were minimal. The activation energy (E_a) parameters calculated from these temperature-dependent experiments may be used to refine the existing Everglades Hg-model. Single high-level amendments with oxygen, sulfide and solid phase FeS generally inhibited Hg-methylation, while added acetate had little impact. Similar trends, albeit less consistent or pronounced, were observed for MeHg-degradation.

An expanded set of multi-level amendment experiments was subsequently conducted with the aim of determining concentration-dependent relationships between Hg-transformation rates and sulfate, sulfide, FeS and oxygen (sediment redox). The strongest and most consistent relationships were found for added solid-phase FeS and with sediment redox. The inhibitory effect of these parameters on Hg-methylation increased from north to south. Similar negative concentration-dependent relationships were found for added sulfate and sulfide, but not at all sites. As with calculated E_a values, the concentration-response coefficients generated in this project may be used to refine the Hg-model. Further studies are pending regarding the influence of humic acid concentration on microbial Hg-transformations. Results from these experiments indicate that sulfur chemistry as a whole, and solid-phase reduced-S in particular, plays a critical role in regulating net MeHg production in the Everglades. Further, net MeHg production appears to be primarily a function of gross Hg-methylation, as rates of microbial MeHg degradation are largely constant over a wide range of geochemical variables.