PRELIMINARY

Aquatic Cycling of Mercury in the Everglades (ACME) Project: Synopsis of Phase I Studies and Plans for Phase II Studies

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In 1994, a consortium of agencies lead by the U.S. Geological Survey began a multi-investigator study of the factors contributing to the high levels of mercury (Hg) in Everglade's biota, the Aquatic Cycling of Mercury in the Everglades (ACME) project. The overall objective has been to understand Hg cycling well enough to create management strategies that will minimize methylmercury (MeHg) bioaccumulation in the Everglades, while fulfilling other management objectives such as nutrient reduction and natural hydroperiod restoration.

Mercury contamination of the Everglades ecosystem is one of the most severe cases in the published literature. Currently, no human consumption of any Everglades' sport fish is recommended due to high Hg levels in fish tissues. Because virtually all Hg contained in edible fish is MeHg, a complete understanding of the processes controlling the environmental fate of MeHg is requisite to making responsible ecosystem management decisions. Information necessary to meet the project objectives includes, the precise locations and rates of MeHg production and destruction, environmental factors (such as water chemistry) that either exacerbate or mitigate MeHg production, and food-web bioaccumulation pathways.

Results of Phase I Studies (1995-1998)

The precise underpinnings of why wetlands, such as the Everglades, are susceptible to methylmercury production and bioaccumulation are not completely understood. High rates of microbial MeHg production in anaerobic, organic-rich sediments and advective flows of nutrient bearing water are probable causes. Previous work by the ACME project has revealed that Hg and MeHg distributions in water, sediment and biota show complex seasonal and spatial trends, and that the cycling rates of Hg and MeHg are so rapid that many measurements need to be conducted on a diel basis. In addition, *in situ* microbial processes and photochemical processes control MeHg levels at the ecosystem level. Mercury loads to the Everglades are dominantly derived from atmospheric sources, but toxicity is largely controlled by the relative rates of conversion to methylmercury, which in turn appears to be intimately associated with other complex biogeochemical cycles, such as the sulfate/sulfide cycle.

Specific key findings of Phase I of the ACME project are the following:

- (1) MeHg bioaccumulation is driven by internal MeHg production, mainly in surface sediments;
- (2) MeHg concentrations in all matrices (sediment, surface water, pore water, and biota) are maximal in the central Everglades (southern WCA2A, WCA2B and north-central WCA3);
- (3) MeHg is somewhat lower in more pristine areas like Everglades National Park and WCA1, and much lower in the most eutrophic areas of WCA2A and the constructed nutrient-retention wetlands;
- (4) The spatial MeHg pattern is not driven primarily by inorganic Hg concentration, although there is weak but significant relationship between Hg and MeHg concentrations in surface sediments;
- (5) Photochemical reduction and photo-demethylation are important mechanisms for removal of mercury and destruction of MeHg, respectively, over much of the Everglades;
- (6) Sulfur inputs from areas north of the Everglades have a large impact on MeHg production, but the magnitude and even direction of the impact varies with the sulfate and sulfide concentration;
- (7) Phosphate and nitrate generally have no direct effect on MeHg production rates in sediment cores;
- (8) Anaerobic microbial processes, including sulfate reduction, are key components of microbial organic carbon decomposition in Everglades sediment;

- (9) Microbial dissimilatory sulfate reduction (rather than assimilation by plants) appears to be the most important mechanism for reduced sulfur storage in Everglades peat;
- (10) Natural fires and extended periods of peat exposure can greatly exacerbate MeHg production (for example 10x increases in sediment MeHg levels), and this phenomenon appears to be driven by sediment oxidation and release of sulfate after re-inundation;
- (11) Bioaccumulation of MeHg in Gambusia appears to be facilitated by the movement of benthic invertebrates (insects and zooplankton) into the water column, and less importantly by direct grazing on surface sediments and periphyton;
- (12) Methylation occurs only in periphyton "mats" where microbial sulfur cycling occurs, and is most common in the less-calcareous periphyton found in eutrophic areas.

Plans for Phase II Studies (1999-2003)

To provide predictive capabilities of the potential effects of restoration efforts on Hg cycling in the Everglades, the complex relationships between loadings of Hg, sulfur, and nutrients on MeHg production and bioaccumulation need to be better understood. In the next phase of this research, we will better quantify these individual relationships, and the interactions among these three key parameters, through amendments to *in situ* mesocosms. Short-term addition experiments are useful in examining processes, but may not predict long-term responses, for a number of reasons. Response of plant growth to nutrients is the obvious example, but other changes, like changes in Hg speciation and bioavailability over time, or development of microbial communities, are also important. An understanding of the relationship between Hg, S or nutrient loading and MeHg production and bioaccumulation requires a long-term, large-scale approach because there are many steps between the entry of "new" Hg to the ecosystem, its conversion to MeHg, and bioaccumulation in the food web.

We will use stable Hg isotope amendments to examine the relationship between Hg loading and MeHg production and bioaccumulation. This new approach will allow us to track the fate of newly deposited Hg separately from the larger existing pools, and to track the bioavailability of new Hg over time. The use of individual stable Hg isotopes will allow us to follow the cycle of new Hg added to the system, from initial partitioning, accumulation in vegetation, MeHg production and accumulation in sediments, fluxes and accumulation in the food web. We will also be able to trace burial, post-depositional reworking of Hg through sediments and plants, and Hg⁰ formation.

Important unknowns that stable isotopes will allow us to address are the availability of Hg in decaying plant material relative to newly deposited Hg adsorbed to sediments for methylation; and the recycling of buried Hg to the sediment surface through plant growth and decay. We also plan to make sulfur amendments as either a stable or radioisotope for the same reason. Sulfur isotope additions will allow us to find out how fast sulfide is turned over in sediments and made available again for sulfate reduction (through photosynthetic re-oxidation of sulfide), a key variable in modeling the relationship between sulfate load, sulfate reduction rate and sulfide accumulation in the oligotrophic Everglades. Isotopes will also allow us to track what fraction of newly added sulfate is retained in sediments.