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Subject: SFER 2009: relationships between sulfur concentrations and mercury dynamics
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Reed,

This text below is from last year's SFER mercury and sulfur Chapter (pp. 3B-45 and 3B-46)

(available at: https://my.sfwmd.gov/pls/portal/docs/PAGE/PG_GRP_SFWMD_SFER/PORTLET_SFER/TAB2236041/VOLUME1/chapters/v1_ch_3b.pdf)

and was abstracted from your report to the SFWMD.

I guess we have nothing new to say in this year's SFER, but when Cindy finishes her ACME dataset compilation and interpretation, perhaps we can conclude something new re relationships between sulfur concentrations and mercury dynamics.

Don

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RESEARCH PROGRESS

The following research needs were identified in peer-review comments regarding Everglades Consolidated Reports (ECRs) and South Florida Environmental Reports (SFERs). An update on the progress made with respect to each of the research needs is presented below.

3. Revise the Everglades Mercury Cycling Model (E-MCM) to include relationships between sulfur concentrations and mercury dynamics (2001 ECR).

Efforts to link the E-MCM to a diagenetic transport-reaction model capable of predicting the depth distribution of mercury (Hg) methylation as a function of soil biogeochemistry, are reported in Appendix 3B-3 of this volume.

Mercury cycling models have not adequately captured the complex interactions between methylmercury (MeHg) production and the sulfur cycle. In the Everglades, and in many other ecosystems, the sulfur cycle is a primary control on net MeHg production and bioaccumulation (along with inorganic mercury inputs and organic matter availability) (Compeau and Bartha, 1985; Gilmour, et al., 2007b).

As such, the SFWMD has supported efforts to capture the biogeochemical relationships between the mercury and sulfur cycles, and to link these to the E-MCM.

The mercury model supported by the Mercury Program is Tetra Tech's Everglades Mercury Cycling Model, a mechanistic simulation model that runs on Windows™-based computers (Tetra Tech, 1999, 2002). Using a mass balance approach, the model predicts time-dependent concentrations for three forms of mercury: inorganic Hg(II), methylmercury and elemental mercury. Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous, wet deposition, dry particle deposition, deposition of reactive gaseous mercury). Model compartments include the water column (dissolved and particular phases), three macrophyte species (cattails, sawgrass, water lilies), four sediment layers and a food web. The simplified food web consists of detritus, periphyton, phytoplankton, zooplankton, benthos, shrimp, mosquitofish (*Gambusia*), bluegill/warmouth sunfish (grouped together), and largemouth bass.

The E-MCM includes algorithms to represent microbial methylation of mercury, but it has been unresolved how to best link methylation in E-MCM to sulfur cycling. Once methylation in the E-MCM is linked to sulfur cycling, the model would be available to help predict how ecosystem restoration and resulting sulfate concentrations could affect MeHg production and bioaccumulation in the EPA.

To link methylation in E-MCM to sulfur cycling, a diagenetic transport-reaction model capable of predicting the depth distribution of Hg methylation as a function of soil biogeochemistry was developed. Diagenetic models are numerical simulations of the post-burial decomposition of organic matter via a sequence of microbial fermentative and respiratory processes. In these models, microbial organic matter oxidation is driven by the vertical flux of oxidants (i.e., oxygen, nitrate, and sulfate) into sediments and soils. A diagenetic transport-reaction model that is capable of predicting the depth distribution of Hg methylation as a function of soil biogeochemistry through equations based on first principals.

To explore how the diagenetic Hg and sulfur cycling model could be used to improve the ability of the E-MCM to predict responses to changing sulfate concentrations in the Everglades, the model was applied to several sites within STA-3/4 (Cells 1–3), WCA-2A (sites U3 and F1), and WCA-3A (site 3A-15) using detailed biogeochemical field data from the Aquatic Cycling of Mercury in the Everglades (ACME) study. In addition, the model was used to generate input values for E-MCM simulations of the response of site 3A-15 to decreases in sulfate input over the last 10 years (1995–2005).

The diagenetic model was first applied to sites U3 and F1 in WCA-2A, and then to site 3A-15 in WCA-3A. Site 3A-15 has been studied for over a decade through the ACME study and other programs. Surface water sulfate concentrations have dropped during that decade, along with MeHg levels in water, sediments and fish. The diagenetic model was calibrated to fit observed downcore data from 1996 through 1998, and then used to predict depth-integrated sulfate reduction rates and MeHg concentrations over the full decade. Model outputs accurately predicted the concomitant declines in sulfate reduction rate and MeHg production at site 3A-15 over time, providing mechanistic support for the hypothesis that sulfate declines are driving at least part of the observed decline in MeHg at this site. The model can now be applied to predict the distribution of MeHg across the EPA under changing sulfate loading scenarios (please

see Appendix 3B-3 of this volume).

Another goal was to create models can reproduce MeHg concentrations across the large sulfate and sulfide gradients found in the Everglades; 3A-15 is a low sulfate site where sulfide concentrations have been low throughout the study period. In order to predict MeHg concentrations at high sulfide sites, the model required empirically-fit routines for either Hg speciation and/or methylation routines, suggesting that our current understanding of Hg complexation chemistry is insufficient to model from first principals.