J3.2 A MERCURY RE-EMISSIONS MODEL (MREM) FOR NATURAL SURFACES

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1. INTRODUCTION

The processes leading to atmospheric mercury dispersion are governed by the industrial use of elemental mercury (Hg^0) in anthropogenic emissions and the emissions from natural surfaces. The emissions of Hg^0 from contaminated surfaces have long been known. However, elemental mercury is readily re-emitted from natural surfaces due to its high vapor pressure (Lindberg et al, 1998). Recent studies have shown that the contribution of natural Hg emissions to the global Hg pool is roughly equal to the anthropogenic emissions. A natural Hg emissions database must be developed to accurately model atmospheric Hg.

2. METHODS

Natural Hg emissions were modeled using fifth-generation NCAR / Penn State Mesoscale Model (MM5) meteorological data and the EPA's Biogenic Emissions Inventory Version 2 (BEIS2) land cover data.

Natural mercury emissions were categorized into the following three sources based on the mechanism of the emissions for the given land cover types.;

1. Air/water fluxes
2. Emissions from vegetation canopies
3. Air/soil fluxes

2.1 Air/water Fluxes

The air water flux of mercury is driven by the equilibrium between the vapor and aqueous phases of Hg^0, which is governed by the concentration gradient, ΔC (*ng m*$^{-3}$), and the transfer velocity, K (*m s*$^{-1}$).

$$F_w = K\Delta C \quad (1)$$

Where

$$\Delta C = C_l - C_g / H \quad (2)$$

Where C_l and C_g are the Hg^0 concentrations of water and air respectively and *H* is Henry's law coefficient.

The transfer velocity is calculated for two wind regimes. For stable conditions where breaking waves are not present, $u^* \leq 0.3$ *m s*$^{-1}$, *K* is estimated from the friction velocity, *u**, and the Schmidt number, Sc, according to Mackay and Yeun (1983).

$$K = 1.0x10^{-6} + 144x10^{-4}(u^*)^{2.2} Sc^{-0.5} \quad (3)$$

For higher wind velocities where breaking waves are present, the transfer velocity is estimated according to Xu et al (1999) to account for bubble plumes and the enhanced rate of gas-water transfer.

$$K = 2.778x10^{-8}[(69.8U - 236.4) + wc(115436.4 - 69.8U)]Sc^{-0.5} + 2.778x10^{-8}(\frac{-37}{\alpha} + 6120\alpha^{-0.37}Sc^{-0.18})wc \quad (4)$$

Where U is the wind speed in m s^{-1}, *wc* is the fractional white cap coverage calculated according to Asher and Wanninkhof (1996), and α is the Ostwald solubility coefficient for dissolved Hg^0.

2.2 Canopy Emissions

Recent studies have shown that Hg^0 in soil water is taken in by vegetation during the transpiration processes, transported through the xylem stream and emitted into the atmosphere along with the water vapor (Lindberg et al. 1998). Thus, emissions from vegetation are modeled as a linear function of evapotranspiration.

$$F_c = E_c C_s \quad (5)$$

Where F_c is the emission rate in *ng m*$^{-2}$ *s*$^{-1}$, E_c is the rate of evapotranspiration in *m* (H_2O) *s*$^{-1}$ and C_s is the soil water Hg^0 concentration in *ng m*$^{-3}$.

Evapotranspiration was modeled using the Penmann-Monteith model as described in Campbell and Norman (1998). Canopy conductance was modeled according to Stewart (1988).

2.3 Air/soil Fluxes

Emissions of Hg^0 from soil surfaces are believed to be dependent on the soil water content, surface temperature, and solar radiation (Capri and Lindberg, 1998). However, insufficient measurements have been made to determine an analytical relationship of Hg^0 emissions from soils. Some empirical correlations have been found between some environmental parameters and the soil Hg^0 flux (Xu et al, 1999).

The net soil flux was modeled as a function of soil temperature according to a linear relationship

between the log of the net emission rate and the surface temperature, as described in Capri and Lindberg (1998).

$$Log(F_s) = aT_s + b \quad (6)$$

Where F_s is the net flux of mercury from the soil in *ng* m^{-2} h^{-1}, T_s is the absolute surface temperature in *K*, and a and b are regression coefficients.

3 RESULTS

Water surface fluxes ranged from 20 *ng* m^{-2} h^{-1} in warm areas under high wind speeds during midday to 0.1 *ng* m^{-2} h^{-1} under cool and calm nighttime conditions for a mid summer day.

The modeled soil surface fluxes are completely dependent on surface temperature and ranged form 0.18 *ng* m^{-2} h^{-1} around Hudson Bay early in the morning to 1.7 *ng* m^{-2} h^{-1} in the southwestern corner of the model during late afternoon local time.

Foliar emissions ranged from 0 *ng* m^{-2} h^{-1} during the nighttime when transpiration had ceased to a maximum of 70 *ng* m^{-2} h^{-1} during mid day in heavily forested areas with plentiful incoming solar radiation.

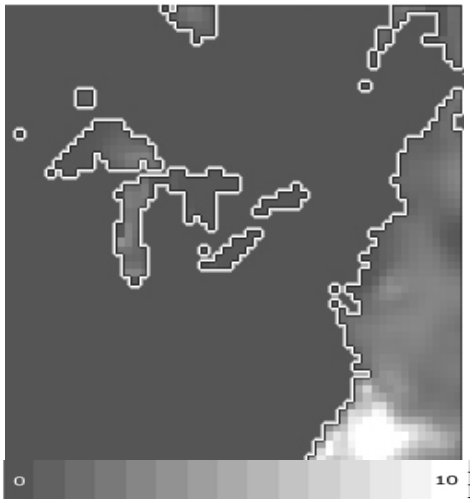

Figure 1, Natural Hg emissions in *ng* m^{-2} h^{-1} at 12:00 AM EST July 9, 1996

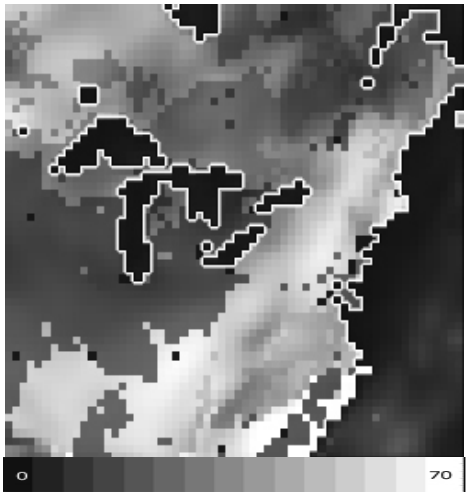

Figure 2, Natural Hg emissions in *ng* m^{-2} h^{-1} at 12:00 PM EST July 9, 1996

During a typical summer nighttime run, MREM shows that the Hg^0 flux is dominated by low emissions from water surfaces. This response is due to the lack of transpiration and the low magnitude of soil emissions. However during daylight hours foliar emissions are roughly twice the magnitude of the water flux and half an order of magnitude higher than the soil fuxes.

4 REFERANCES

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