

EPRI Comments: Lagrangian Modeling of Mercury Transport

Issue Brief

Recent releases of slide presentations on the internet have displayed results using Lagrangian (trajectory-tracking) source-receptor models that appear to demonstrate the dominance of power plant mercury emissions on deposition into nearby waterways. This has led to statements that power plants within 60 miles or so of a watershed are primarily responsible for all the mercury depositing there. In fact, any such conclusions are based on modeling methods that are sensitive to the selection of the particular trajectories used, the limitations in data on contributing mercury source strength, and reliance on uncertain inventory.

Background

A number of recent statements on the contribution of power plant-emitted mercury to mercury deposition have cited results of source-receptor modeling carried out by NOAA in collaboration with other agencies and institutions. The cited results have relied on Lagrangian models such as the NOAA HYSPLIT model to derive the contributions of individual mercury sources to deposition in two hydrologic basins, the Great Lakes basin and the Chesapeake Bay watershed. With a single exception, the sources cited have been unpublished material not subject to scientific peer review or public comment: slide show presentations, private briefing material, conference talks, etc. Yet the supposed findings have been used as the basis for regulatory and operational decisions by state and federal officials.

EPRI has reviewed these “modeling exercises”¹ to illuminate their assumptions, input data, model structure and limitations, model verification, and other aspects that impact the modeling results. The comments below reflect EPRI’s evaluation.

EPRI Comments

The modeling ignores the contribution of global mercury sources to U.S. deposition.

The paper on Great Lakes mercury deposition states that “...only sources in the United States and Canada were included.” The authors go on to cite two other modeling exercises² reporting that non-North American contributions to deposition in the Great Lakes region range from about 13% to 20% of total deposition. Since the authors ignore these non-North American contributions, the error introduced in computed deposition is at least 15% to 25% (since the deposition due to U.S. and Canadian mercury sources alone is assumed to represent the total deposition). This problem arises again in trajectories used for the EPA Steubenville study; the computed trajectories include rainfall events that progress from the southwest U.S., but are not tracked further back beyond the U.S.-Mexican border. The modeling thus

¹ Cohen, M., R. Artz, R. Draxler, P. Miller, L. Poissant, D. Niemi, D. Ratté, M. Deslauriers, R. Duval, R. Laurin, J. Slotnick, T. Nettesheim, J. McDonald, 2004, “Modeling the atmospheric transport and deposition of mercury to the Great Lakes,” *Envir. Res.* 95, 3, 247-65, (2004).

² Cohen, M., Modeling the fate and transport of atmospheric mercury in the Chesapeake Bay region, presentation at the NOAA Chesapeake Bay Office, May 17, 2004, Annapolis, MD.

fails to incorporate the very large mineral recovery and power plant mercury sources in northern Mexico.

But the error introduced by ignoring non-North American sources of mercury may be substantially larger, since the contribution of global sources may be larger than that estimated by Cohen et al. (2004). Modeling work by Seigneur et al.³ found that, when all global sources (both anthropogenic and background) were incorporated into their model, non-North American emissions contributed 40 to 70% of the total deposition of mercury in the Great Lakes area. So restricting emissions to North American sources may underestimate Great Lakes deposition by up to 70%.

Since the presentation of Chesapeake Bay results by Cohen appears to use the same model in the same manner, those calculations relating deposition to particular sources are similarly flawed. The omission of non-North American sources will tend to drive these deposition estimates downward from what a full global inventory would yield and thus inflate the relative contribution from the power plants modeled.

Further evidence that the modeled values under-predict total mercury deposition (and thus overestimate the contribution from modeled power plants) can be seen in a presentation given at a meeting in Florida in May 2006 (see <http://www.arl.noaa.gov/ss/transport/cohen.html#item45>). Results presented there showed total modeled deposition for various locations. Total modeled deposition for Mobile Bay was ~3.5 µg/m²-year. Data from the national Mercury Deposition Network (MDN) show measured wet deposition there ranging from 16 to 27 µg/m²-year. Similarly, modeled total deposition in the Great Lakes area show ~2.5 to 9 µg/m²-year while MDN shows measured wet deposition of ~5 to 14.5 µg/m²-year.

³ Seigneur, C., K. Vijayaraghavan, K. Lohman, P. Karamchandani and C. Scott, "Global source attribution for mercury deposition in the United States," *Environ. Sci. Technol.*, **38**, 555-569 (2004).

An inconsistent set of mercury chemical reactions is included in the modeling.

Mercury is emitted primarily in three forms: elemental mercury, Hg⁰; divalent mercury, Hg^{II}; and particulate-bound mercury, Hg_p. The first two forms may undergo reduction and oxidation reactions in the atmosphere, converting Hg^{II} into Hg⁰ and vice-versa. Eventually some of the Hg^{II} will be removed either by dry deposition or by precipitable water.

In order to accurately simulate the fate of atmospheric mercury, models should account for the most important chemical reactions that may occur. One reaction that reduces Hg^{II} to Hg⁰ in "heterogeneous" microenvironments (cloud droplets, aerosols, etc.) involves the hydroperoxyl radical HO₂. Pehkonen and Lin⁴ determined the rate of mercury reduction involving this radical, allowing its inclusion in model chemical mechanisms. However, Garfeldt and Jonsson⁵ questioned the earlier experiments and provided a substantially lower reaction rate for this mechanism. Cohen et al. ignore the reaction completely, thus omitting a potentially important reduction reaction. However, Cohen et al. retained two gas-phase oxidation reactions of Hg⁰ to Hg^{II}, involving ozone and hydroxyl, respectively. Thus, they minimize the reduction of easily-deposited Hg^{II} to the insoluble Hg⁰ while retaining the oxidation of Hg⁰ to Hg^{II}. This noninclusive selection of chemical mechanisms favors the deposition of mercury relatively closer to its sources.

The mechanisms included, however, are not consistent with the global mercury cycle. Bergan and Rodhe⁶ simulated the global mercury cycle without the hydroperoxyl reaction; however, they also

⁴ Pehkonen, S.O. and C.J. Lin. Aqueous photochemistry of divalent mercury with organic acids, *J. Air Waste Manage. Assoc.*, **48**, 144-150 (1998).

⁵ Gårdfeldt, K. and M. Jonsson. Is bimolecular reduction of Hg(II)-complexes possible in aqueous systems of environmental importance? *J. Phys. Chem.*, **107**, 4478-4482 (2003).

⁶ Bergan, T. and H. Rodhe. Oxidation of elemental mercury in the atmosphere; constraints imposed by global scale modeling, *J. Atmos. Chem.*, **40**, 191 (2001).

omitted the rapid oxidation of Hg^0 by the hydroxyl radical (which Cohen et al. keep in their mechanism). Seigneur et al.⁷ recently tested the mechanism of Cohen et al. in the EPRI/AER global chemical transport model. It was concluded that the Cohen et al. mechanism led to unrealistically low mercury concentrations, even accounting for uncertainties in global emissions and removal rates. Bullock⁸ evaluated the effect of the hydroxyperoxyl reaction on North American simulations using the CMAQ regional model and concluded that eliminating this reaction degraded model performance vs. data. Therefore, the chemical mechanism of Cohen et al. is inconsistent with current understanding of the behavior of atmospheric mercury at global and regional scales *when all mercury sources are taken into account*. Use of this mechanism in isolation accounts for the apparent ability of the Cohen approach to derive a source-receptor mass balance involving only relatively nearby sources.

The model has never been tested against the full set of observational data.

The work by Cohen et al. on mercury deposition in the Great Lakes and Chesapeake Bay compares modeled wet deposition and data from the Mercury Deposition Network (MDN). Those comparisons show that the model of Cohen et al. tends to underestimate mercury wet deposition in the Great Lakes basin (by up to a factor of three)⁹, consistent with their simulations ignoring non-North American sources. These underestimates would be even greater if a chemical mechanism consistent with the global mercury cycle were used.

Moreover, no results have been published of model

performance against the national network of MDN wet deposition data. For each modeling “exercise” presented or published, results are compared with MDN data for the immediate study region only. Since the sources for each exercise are chosen only from the region under study without extending beyond North America, there is no general validation test of the model results or method. No measure of model goodness-of-fit is evident from the limited validation that has been performed.

Conclusions

There are three primary shortcomings in the recent applications of the HYSPLIT Lagrangian model to mercury deposition in the Great Lakes basin and the Chesapeake Bay. First, mercury sources outside of North America are ignored in the modeling. Second, the mercury chemistry mechanism used in the modeling omits several key reactions, biasing the results toward faster deposition. Third, no general model performance statistics have been derived.

The first factor, incomplete source inventory, tends to bias modeled deposition low unless the model is calibrated using deposition data. Global-scale simulations, as well as recent data, indicate that oxidation during long-range atmospheric transport of mercury leads to significant contributions of these distant sources to wet deposition within the United States. Thus ignoring those sources will have significant consequences for modeled U.S. deposition patterns and source attribution.

The second factor, incomplete mercury chemistry, tends to bias modeled regional deposition results high. The lack of one potentially significant heterogeneous reduction mechanism will lead to a higher proportion of Hg^0 due to North American mercury sources (the only sources included in the model). This will increase the wet deposition values calculated relative to what a more complete chemistry would yield.

⁷ Seigneur et al., "Atmospheric mercury chemistry: sensitivity of global model simulations to chemical reactions" *J. Geophys. Res.*, in press.

⁸ Bullock, O.R. 7th International Conference on Mercury as a Global Pollutant, 27 June – 2 July 2004, Ljubljana, Slovenia; *RMZ – Materials and Geoenvironment*, **51**, 1527-1530 (2004).

⁹ Figure 8 of Cohen et al., op.cit

The first two shortcomings tend to counter one other, with fewer sources lowering the estimated deposition rates and exclusion of one reduction reaction increasing it. The combined effect of these two factors is to overstate the importance of local sources relative to distant sources, because the Hg^{II} fraction of atmospheric mercury from local sources is overestimated and contributions from distant sources are omitted. Although it is impossible to tell *a priori* which factor will dominate, the work by Cohen et al. shows a close match between model calculations of wet deposition from nearby sources and observed wet deposition in the Chesapeake Bay. This finding indicates that the chemical mechanism factor outweighs the source factor. Since no test of model fit to a set of national deposition data has been carried out, there is no way to tell if the model would predict deposition throughout the U.S. But the three limitations described in this analysis combine to lessen confidence in the statistical strength of this model in simulating reality.

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