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Estimation of direct emissions and atmospheric processing of reactive mercury using inverse modeling

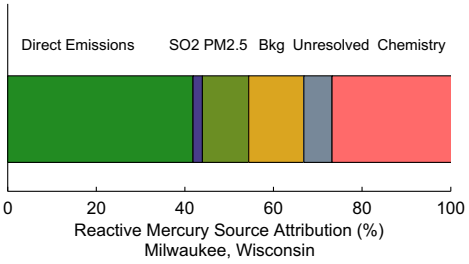
Benjamin de Foy [a,b,*], Jongbae Heo [c], James J. Schauer [c]

[a] Department of Earth and Atmospheric Sciences, Saint Louis University, USA
[b] Earth and Life Institute, Université catholique de Louvain, Belgium
[c] Civil & Environmental Engineering, University of Wisconsin–Madison, USA

HIGHLIGHTS

- 50–70% of reactive mercury in Milwaukee is from direct emissions.
- Direct emissions are much higher than in most current chemical transport simulations.
- 15% of reactive gaseous mercury is estimated to be due to free tropospheric transport.
- Ozone oxidation of GEM is better represented in models than OH and Br oxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

There are large uncertainties in the estimation of sources of reactive mercury in current photochemical models, with many models suggesting that three quarters or more of reactive mercury in the atmosphere is due to secondary oxidation of the gaseous elemental mercury present in the global background. An inverse model is used to estimate the sources of mercury at an urban site in Wisconsin based on a year long time series of hourly measurements. The model combines high resolution backtrajectories simulated with WRF and WRF-FLEXPART, forward simulations of passive tracers using a transport model (CAMx), hourly time series of atmospheric pollutant concentrations and time series from a chemical box model for oxidation of elemental mercury by ozone, the hydroxyl radical and bromine. The hybrid formulation provides an estimate of the mercury concentrations on a polar grid surrounding the site along with emission scaling factors for emissions from forest fires and lake surfaces. In addition, the model estimates the impact of oxidation of gaseous elemental mercury from the three pathways. The inverse model identified direct emissions of reactive mercury, defined as the sum of reactive gaseous mercury and particle-bound mercury, that are associated with regional sources and with forest fires. The results suggest that oxidation by ozone is adequately characterized in existing chemical mechanisms, but that oxidation by the hydroxyl radical and by bromine may be underestimated. The results suggest that between 50 and 70 percent of the reactive mercury at the measurement site is due to direct emissions and hence suggest the importance of developing emission inventories for reactive mercury species.

1. Introduction

Mercury is a powerful neurotoxin that is globally present in the atmosphere (Mergler et al., 2007). Despite its relevance to human and ecosystem health, significant uncertainties remain in its

* Corresponding author. Department of Earth and Atmospheric Sciences, Saint Louis University, USA. Tel.: +1 314 977 3122.
E-mail address: bdefoy@slu.edu (B. de Foy).

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emissions inventories and its atmospheric reactions (Gustin and Jaffe, 2010; Lindberg et al., 2007). Common measurements distinguish between mercury in three forms: Gaseous Elemental Mercury (GEM), Reactive Gaseous Mercury (RGM), and Particle-bound mercury (PHg), with Reactive Mercury (RHg) being the sum of RGM and PHg. Although most of the mercury in the atmosphere is in the form of GEM, deposition of RGM and PHg is much faster (Zhang et al., 2012a). The deposited mercury reacts to form methylmercury which leads to bio-accumulation and adverse health effects.

There are significant discrepancies between simulated and measured levels of RHg (Holloway et al., 2012; Bullock et al., 2008, 2009), which are thought to be mainly due to limitations in our understanding of the chemical mechanisms (Sillman et al., 2007; Lin et al., 2006, 2007), to uncertainties in the parameterization of deposition (Baker and Bash, 2012) and to measurement uncertainties (see Section 2.2). Both aqueous (Subir et al., 2011) and heterogeneous (Subir et al., 2012; Rutter et al., 2012) reactions play a significant role in these uncertainties leading to the potential for compensating errors (Lin et al., 2006). The lifetime of GEM was estimated to be approximately 1 year (Lindberg et al., 2007), but Holmes et al. (2010) suggests that it could be as low as 6 months due to oxidation by bromine.

RGM has been found to correlate with ozone, suggesting secondary formation, as well as with sulfur dioxide, suggesting direct emissions (Lindberg and Stratton, 1998). A combination of measurements and simulations suggest the importance of RGM transport events in the free troposphere (Huang and Gustin, 2012). In addition to the uncertainty about the oxidation of mercury, there is uncertainty about the reduction of RGM to GEM, either specifically in power plant plumes (Zhang et al., 2012b) or in the general atmosphere (Pongprueksa et al., 2008) which can introduce excessive simulated RHg if in-stack emission factors are used and near field chemical transformations are not addressed (Lohman et al., 2006). In current models, most of the RGM is due to photochemical oxidation of GEM. This leads to very high estimates of the impact of the global background on local deposition (Holloway et al., 2012; Zhang et al., 2012b; Lin et al., 2012; Selin and Jacob, 2008; Seigneur et al., 2004).

This study uses an inverse model to estimate direct emissions and chemical formation of reactive mercury based on a year-long time series of hourly speciated mercury concentrations. As an alternative to the use of Eulerian models using mercury chemical mechanisms, we develop a method that uses backtrajectories, forward simulations of passive tracers, surface concentrations of tracer species and simulations of RGM formation from GEM oxidation from a chemical box model. By developing an approach that does not rely on a full chemical simulation, we seek to provide constraints on mercury sources and reactions that are complementary to existing studies. The inverse method is based on de Foy et al. (2012b) who used it to estimate GEM emissions from forest fires, lakes, regional and local sources. We have expanded the method in order to be able to estimate emissions and chemical formation of reactive mercury.

2. Methods

2.1. Inverse model

The inverse model estimates emissions due to sources surrounding the receptor site by using backtrajectories of passive tracers that have been mapped onto a polar grid. This is combined with forward Eulerian simulations of passive tracers from selected source groups, in a manner similar to the two-step method (Rigby et al., 2011; Roedenbeck et al., 2009). The inverse model produces emission scaling factors for each source term included in the forward transport simulations. When multiplying the a priori emissions by the emission scaling factor we obtain the a posteriori emissions estimate. Fig. 1 shows a flowchart of the inverse model process.

The inversion generates an estimate of "gridded emissions" on a grid that stretches out 1000 km from the receptor site. These gridded emissions are a posteriori estimates based on a priori emissions set to zero. They do not include emissions that are better

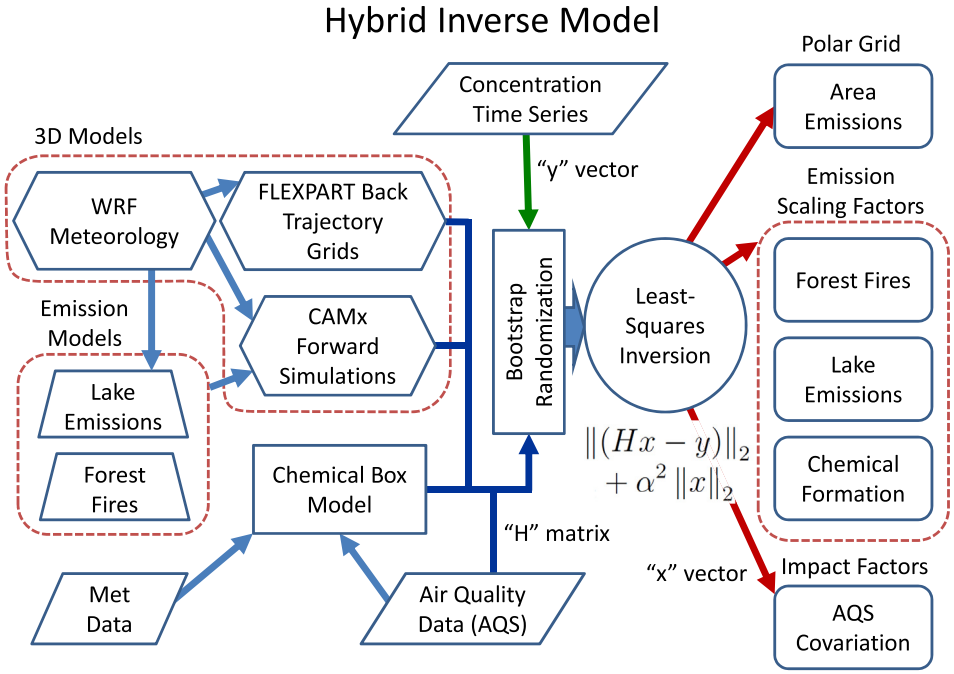

Fig. 1. Flowchart of the inverse model showing the combination of inputs from backtrajectories, forward simulations, chemical box model and air quality data (AQS) into the matrix *H*. The output vector *x* of the inversion is a hybrid containing area emissions, emission scaling factors for forest fires, lake emissions and chemical formation as well as impact factors for air quality data.