IDENTIFICATION OF THE ORIGINS OF ELEVATED ATMOSPHERIC MERCURY EPISODES USING A LAGRANGIAN MODELLING SYSTEM

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Abstract: We report the application of a receptor-oriented transport model, the Stochastic Time-Inverted Lagrangian Transport (STILT) model, to the interpretation of hourly total gaseous mercury (TGM) concentrations at three monitoring sites in Southern Ontario during four episodes of high TGM. STILT is a Lagrangian modelling system (Lin, J.C. et al. 2003) that simulates the transport of ensembles of air parcels backward in time from an observation point to upstream locations where surface inputs of target species occurred. A complete inventory of anthropogenic and natural mercury sources were used to compute the emissions.
The study was initiated by simulating the mercury concentrations in a North American domain using CMAQ-Hg, a regional Eulerian chemical transport model (CTM). The STILT model was applied to several short episodes (usually lasting for 1-4 days) in which the TGM measurements at four air quality measurement stations in Southern Ontario significantly exceeded the predictions of the CTM. The STILT analysis compared the origins of air parcels arriving during the elevated TGM episodes with those of air parcels arriving at proximal times when the measurements and the CTM predictions were both low.
The results consist of the STILT–predicted hourly concentrations at the measurement site as well as the surface footprint where the mercury responsible for the episode was emitted. The temporal STILT prediction is in better agreement with the measured time series than that of CMAQ-Hg. We believe this is partly due to the superior ability of STILT to capture near-field influences and partly due to the spatial averaging inherent in Eulerian modelling. Also, the predicted footprint locations were reasonable, coinciding with known locations of large mercury sources during the high episodes and with cleaner areas otherwise.

1. INTRODUCTION

In the atmosphere, the predominant form of mercury is the elemental gas Hg(0) (Schroeder et al., 1991). This species has a residence time of around one year (Lindqvist and Rodhe, 1985). Mercury is a true global pollutant. Due to the high vapour pressure of Hg(0), atmospheric transport is the primary mechanism by which it is distributed throughout the environment. Because of this ubiquity, long range transport and long atmospheric lifetime, it is important to limit mercury emissions into the atmosphere. Extensive monitoring and stringent regulations have reduced mercury emissions during the past few decades but further reductions are possible. The ability to identify the largest sources will assist in this effort. We present here a direct method to pinpoint the locations of large mercury sources through a combination of measurement and modelling. The present report concerns the modelling element of this approach. In the past, many different modelling approaches have been developed for this purpose. These use either Eulerian or Lagrangian techniques, depending on the spatial and temporal scales involved. We will propose a combination of these methods.

Eulerian models calculate the pollutant's fate and transport everywhere in a modeling domain using a fixed coordinate system that defines a set of stationary grid volumes. Air is viewed as a fluid that is being carried by the wind past a stationary observer in the domain. The Eulerian model is ideal for complex chemical interactions of the atmospheric constituents and much of the atmospheric mercury model development is moving to Eulerian models (Bullock, 2000, Bullock and Brehme, 2002). Eulerian models have been widely applied to the investigation of mercury emission, transport, chemistry and deposition (Petersen et al., 2001; Christensen et al., 2004;). Eulerian models, however, have limitations. The primary drawback is their inability to simulate subgrid scale processes, which results in their exclusion of near-field influences in simulations. Their requirement to average the processes over an entire grid volume limits their ability to explore nonlinear source-receptor relationships.

Lagrangian models, on the other hand, follow the trajectories of an ensemble of air parcels (sometimes called particles), allowing them to simulate turbulence and capture subgrid scale transport with high accuracy. This extra detail, however, limits the number of sources they can simulate and prevents their use with complex nonlinear chemistry. Lagrangian particle models have been used by numerous researchers (Stohl et al., 1998) to model atmospheric transport from source to receptor (forward modelling) but few studies to date have used backward or time-reversed trajectories, which attempt to identify the sources contributing to a given receptor. The backward approach is most efficient when the number of unknown source elements exceeds the number of measurements. This is especially important because measurements are almost always made at a point or along a line (aircraft) and Eulerian models cannot use such data efficiently without the application of near-source sub-grid models.

In this presentation, we will report the predictions of hourly TGM concentrations at three monitoring sites in Ontario, Canada (Point Petre, Egbert and Burnt Island) using the STILT Lagrangian modeling framework. The concentrations obtained with STILT results are compared with observations and with previously modelled concentrations using Eulerian modeling framework CMAQ-Hg (Gbor et al., 2007). Both simulations employed the same input dataset. The comparison will focus on episodes in which the concentrations predicted by CMAQ-Hg differed significantly from the measurements. In this way we explore the ability of CMAQ-Hg to simulate Hg(0) transport and chemistry and also attempt to identify the source locations responsible for the anomalous concentrations.

2. MODEL CONFIGURATION

Eulerian Model

The Eulerian model used in this work was based on the CMAQ-Hg V4.3 model, which was developed by Bullock (Bullock and Brehme, 2002). In previous work (Gbor et al., 2006), we modified this model by including the dry deposition of Hg(0) and RGM. We also developed a model that calculates natural mercury emissions from soil, water and vegetation canopies and added it to the CMAQ-Hg model. Details of these modifications and the natural mercury emission model are provided in (Gbor et al., 2006) and (Gbor et al., 2007).

This model system was used to simulate the year 2002 in a domain covering most of North America with 132x90 horizontal 36km grid squares and 15 vertical layers. The PSU/NCAR MM5 V3.6 meteorological model was used with the PX LSM land surface model (LSM). The 1999 National Emissions Inventory (NEI) version 3 IDA Files was used for emissions of anthropogenic criteria pollutants in the United States. The 1995 inventory for criteria anthropogenic sources in Canada was obtained from the Ontario Ministry of Environment (OMOE) (Chtcherbakov, 2003) for use in this project. Emissions of Criteria pollutants from biogenic sources were processed using the BEIS3 program in SMOKE and a gridded land use file for North America. Anthropogenic Hg emission data for the US and Canada were obtained from the USEPA (2004). Natural mercury emission and anthropogenic mercury were merged with criteria emissions using SMOKE. Mercury boundary conditions, which varied from January to December, were taken from the global mercury simulation work of Seigneur et al. (2004), which included both natural and anthropogenic emissions of Hg. The results of these simulations were used in the present work.

Lagrangian Model

The STILT model was developed from the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model system. The STILT model uses the mean advection scheme from HYSPLIT but employs a different turbulent module in order to satisfy the well-mixed criterion in the strongly inhomogeneous environment of the PBL, where the simple drift correction does not work. The model simulates the transport of air parcels with ensembles of fictitious particles advected with mean wind velocities as well as stochastic velocities parameterized to capture the effects of turbulent transport. The particle ensemble is released at a receptor location and transported backward in time, representing the air parcels arriving (in the forward-time sense) at the receptor. Thus the particles represent influence, marking out the upstream regions affecting the receptor. STILT provides the capability to represent near-field influences, transforming this noise to signal that is useful in diagnosing surface emissions. Significant computational savings are realized because the influence of upstream emissions at different times is modelled using a single particle simulation backward in time, starting at the receptor and sampling only the portion of the domain that influences the observations. The backward-time formulation yields the same information as the forward-time alternative, generating the spatial and temporal dependence of the upstream source with a single particle simulation rather than numerous forward simulations from all potential upstream regions, thus reducing computational time significantly.

For the purposes of the present study, wet and dry Hg deposition processes were added to the basic STILT advection model. Dry deposition is only computed when the particle center position is within the surface layer. The time constant for dry deposition is calculated from the dry deposition velocity, which is calculated in the MCIP model, a part of the CMAQ-Hg simulation. The wet deposition was defined using the Henry's Law constant (H) in an expression that defines a wet deposition velocity: $V_{wet} = HRTP$, where R, T and P are respectively the universal gas constant and the temperature and precipitation rate in the grid volume.

Measurements

Surface concentrations of TGM were measured at the three sites shown in red in Figure 1. These rural sites, which are part of the Canadian Atmospheric Mercury Measurements Network (CAMNet)of Environment Canada, were chosen to eliminate the possibility of contamination from local sources. The TGM concentrations are based on one-hour sample integration periods using the Tekran Model 2537A Ambient Mercury Vapour Analyser.

Modelling

The measured values for the entire year (2002) were compared with the CMAQ-Hg simulations for the same time period. In general, the agreement was very good. The correlation coefficients (R) between modelled daily average total gaseous Hg concentrations and measurements for Point Petre, Egbert and Burnt Island are between 0.74 and 0.82. For these rural sites the natural emissions (emissions from soil, water and vegetation) were very important. If the natural emissions are neglected, the R values decrease to the range between 0.22 and 0.51. This shows that there are no strong local anthropogenic sources.

Despite the excellent agreement with daily averages, there were many cases where the (hourly) measurements and simulations differed significantly for short periods of time that varied from a few hours to a few days. We identified these episodes as the arrival of mercury plumes from non-local sources. Examples of such cases are shown in Figure 2 as time series covering the period from 20 to 30 July 2002 for each of the monitoring sites. The measured values are shown in red. In each case an episode of high measured TGM is indicated by a pair of vertical dashed lines and labelled “H”, while another pair of dashed lines and the label “L” indicates a period that occurs shortly before or after the high episode in which the measured value of TGM is low. Also plotted are the corresponding TGM values

simulated by the CMAQ-Hg Eulerian model (green) and the STILT Lagrangian model (blue). The estimated error bars for the STILT calculation are superimposed in light blue.

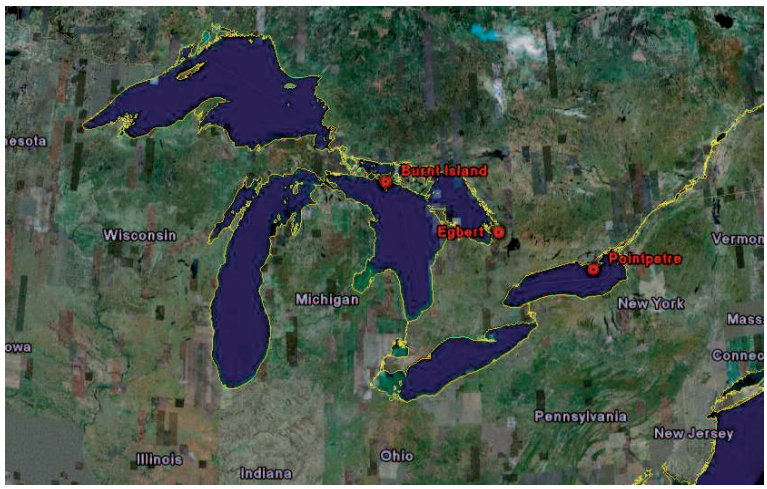

Figure 1. Sites where surface concentration measurements were made for comparison with the predictions of the Eulerian and Lagrangian models.

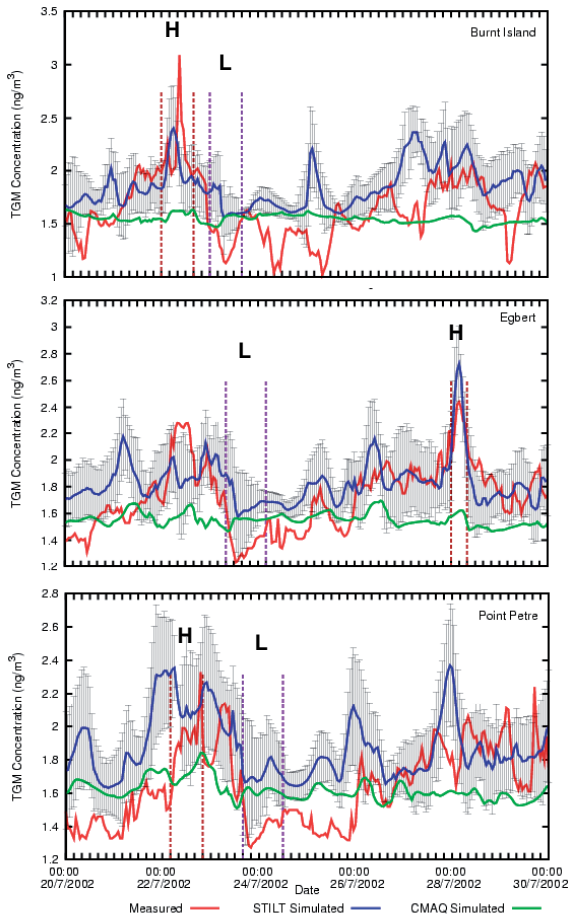

Figure 2. Comparison between observed and modeled TGM concentrations for20 to 30 July.

These results confirm the point made above that the CMAQ-Hg simulation is reasonably accurate on a long term average basis. It is not, however, capable of reproducing rapid concentration variations that occur over a period of a few hours. The STILT simulation, on the other hand, shows much more short term structure and in general this structure corresponds – at least qualitatively - to that in the measured values.

In the STILT simulation, an ensemble of 3000 particles and a six-day evolution period were used. The hourly concentrations are determined by averaging the concentrations carried by all particles arriving at a receptor after the period of evolution. The particle concentrations were determined by adding the emission into the particle and subtracting the deposition from the particle that occur during the period of evolution. Depositions were calculated as described above. Increases in concentration due to surface emissions are added when the parcel dips below an altitude z*, which is equal to one half of the height of the PBL. The magnitude of the change in concentration is determined by vertically diluting the surface flux over z*. This assumes rapid mixing in the PBL. For emission sources above the PBL, we used a similar approach in which the emission fluxes are diluted downward to the grid volume in which the particle is located. Thus STILT maps the spatiotemporal distribution of source influences on the composition at the receptor as a footprint. The spatial location and extent of the footprint are deduced from the transport calculation. The contribution to the observed concentration at a receptor is determined for each location by multiplying the footprint area times a surface emission flux, which was calculated using the Sparse Matrix Operator Kernel Emissions processor (SMOKE) to process the emission inventories used for the CMAQ-Hg simulation. Six-day back-trajectories were used to include possible distant source regions. The boundary conditions for particles whose endpoint locations after six days are within the domain are set according to the global mercury simulation work of Seigneur et al. (2004).

3. RESULTS

Figure 3 shows the source footprints resulting from the STILT simulations for the time periods indicated by the dashed lines in Figure 2. The periods of low measured mercury are shown in the top row and the episodes of high measured TGM concentrations are shown in the bottom row. For example, the top left panel shows the source footprint for the TGM arriving at the Burnt Island station between 0:00 and 16:00 on 23 July, while the bottom left panel shows the source footprint for the TGM arriving between 0:00 and 16:00 on 22 July.

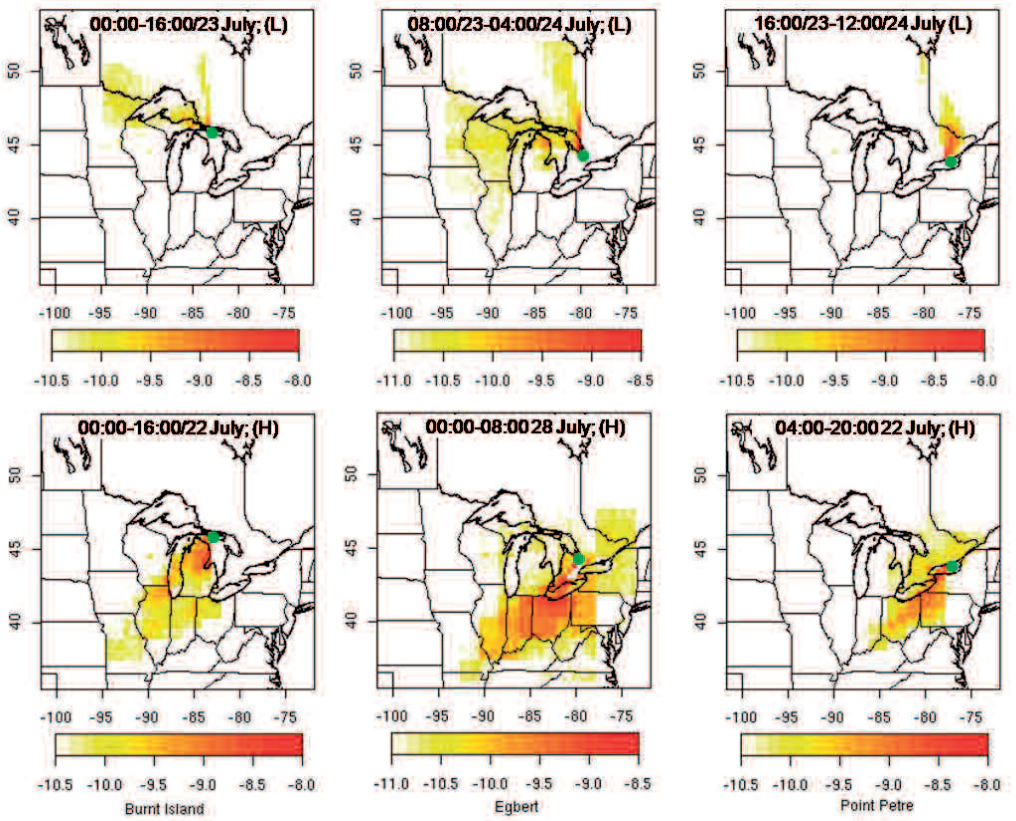

Figure 3. Source footprints for measured TGM episodes shown in Figure 2 The source footprint is the sum of the TGM content of all air parcels arriving during the indicated time period. The TGM content is the difference between the TGM emitted into and lost from the air parcel during the trajectory, as explained above.

4. CONCLUSION

The results presented above, which are typical of the episodes examined during the model simulation year, 2002, illustrate the power of the combination of Eulerian and Lagrangian modelling when applied to the identification of the source regions of measured pollutants. The high resolution of the Lagrangian approach identifies source footprint regions for air parcels with a precision that is limited only by the resolution of the available meteorology. (A basic resolution of 36 km was used for this study, but much higher resolutions, down to 4 km in many cases[1], are used routinely in current simulations). A Lagrangian model alone, however, is not capable of distinguishing between episodes in which high concentrations are due to transport from specific sources and concentration variations that have meteorological causes such as shifts in the boundary layer height or the arrival of a weather system.

The addition of an Eulerian model, however, removes this uncertainty. The ability of the Eulerian model to simulate complex nonlinear chemistry ensures that its results reproduce faithfully the chemistry and physics (dissolution, photochemistry, etc.) of all trace atmospheric species. When operated at moderate resolution (*e.g.* 10-40 km) the Eulerian simulation accounts for the average or background pollutant levels very accurately. Except in unusual cases, however, Eulerian models are not capable of identifying pollutants emitted from a specific source region or separating them from those originating elsewhere. Comparing Eulerian and Lagrangian simulations of the same time period with measurements, however, can achieve this separation. Large deviations of the Eulerian simulation from the measured concentration of a pollutant indicate that the pollutant is not simply part of the general background, but has a specific origin that can be identified. The Lagrangian model can then be applied to determine the source region.

This combined modelling approach has applications in matters relating to both local and trans-boundary transport of pollutants. The Lagrangian techniques embodied in the current version of STILT can be used over distances of a few tens of km to a few thousand km, and with accuracies limited only by the meteorology. Development work that is currently under way will improve these parameters, which the result that these tools will become even more valuable in the future.

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[1] The Waterloo Centre for Atmospheric Sciences produces a 48 hour weather forecast on this domain with a maximum resolution of 4 km. (*http://www.forecast.uwaterloo.ca*)