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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Quantitative assessment of upstream source influences on total gaseous mercury observations in Ontario, Canada" *by* D. Wen et al.

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Interactive Comment

Comment: However, there appears to be no treatment for the chemical conversion of one form to the other. Chemical transformation of mercury between Hg0 which is slowly deposited and various oxidized forms that are rapidly deposited is poorly understood and remains a primary source of error and uncertainty for all atmospheric mercury models. I fear this failure to address chemical transformation detracts greatly from the information to be gained by this work.

Response: While we do not include the atmospheric chemistry of mercury, we believe that this is not a serious omission for three reasons: (1) the majority of TGM (>90%) is elemental Hg (Hg0) and the chemical conversion of Hg0 in the atmosphere is very slow (rate constants: 2.11×10^{-18}exp(-1256.5/T) for Hg(0)+O_3, 2.6×10^{-18} for Hg(0)+Cl, 8.5×10^{-19} for Hg(0)+H_2O_2, and 7.7×10^{-14} for Hg(0)+OH. (Bullock and Brehme, 2002, 2006), (2) Although the chemical conversion of RGM is fast, RGM only accounts for less than 3% of TGM, in general, and (3) the particle simulation period (six days) is quite short compared to the residence time of TGM, which is more than one year (Lamborg et al., 1999; Sommar et al., 2001; Slemer et al., 1985). Thus the chemical conversion of TGM does not affect its mixing ratio very much during the time of the simulation. The following text will be added after line 6 on page 28764 to clarify this point.

"The chemical transformation of TGM is assumed to be unimportant and is not considered in the STILT modeling. This assumption is based on: (1) gas phase reactions of elemental Hg, which constitutes more than 90% of the Hg in the atmosphere (Slemr et

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al., 1985; Schroeder et al., 1991), are very slow; (2) although its chemical conversion is fast, RGM generally only accounts for less than 3% of TGM (Lindberg and Stratton, 1998; Poissant et al., 2005); and (3) the six-day particle simulation period is quite short compared to the atmospheric residence time of TGM."

Comment: The modified STILT model has been applied here to estimate the sources of TGM for three locations in southern Ontario. Four 10-day time periods are analyzed, each having been chosen for season coverage (winter, spring, summer, autumn), but also to cover periods where another model (CMAQ) proved inaccurate. The authors suggest that the poor accuracy from CMAQ was mostly due to errors in simulated near-field transport that are inherent in all Eulerian-type models and that the Lagrangian transport analysis of STILT provides improved accuracy in this regard. If near-field sources are a major influence on TGM concentrations, the obvious remedy for Eulerian-type modeling is to use a finer horizontal grid. If I understand correctly, both STILT and CMAQ used the same emissions and meteorological data resolved at 36 km on the horizontal scale. In this case, the only real advantage STILT would have over CMAQ is a precise location for the receptor site. The errors in transport simulation due to horizontal smoothing of the wind data would be similar for both models, would they not? The same is true for errors related to the definition of emission sources. A common argument for Lagrangian transport modeling over Eulerian techniques is that it eliminates numerical diffusion. The use of finer grid sizes and non-dispersive advection schemes can well address this difficulty in Eulerian modeling.

Response: We are not suggesting that all Eulerian models are subject to the same kinds of near-field errors. Here, we are reporting on what was observed in this study. We agree with the Reviewer that finer grid spacing or the use of different advection schemes can address some of these errors. The use of meteorological fields with the same grid sizes is more of an "apples-to-apples" comparison, however, because both

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kinds of models are subject to the same limitations using windfields with the same resolution as the starting point. Also, it has been pointed out at the end of the paper that the two approaches are complementary, and that a combined Eulerian-Lagrangian approach would be highly fruitful.

Comment: The authors' results do show superior agreement to observed TGM air concentrations with STILT. However, as the manuscript explains, the simulation periods were chosen to include instances where CMAQ exhibited poor performance in reproducing observed TGM air concentrations. As mentioned above, STILT does not address chemistry. CMAQ simulates chemical transformations of mercury between Hg0 and RGM and physical transformations of mercury between gaseous and aerosol forms. CMAQ may have provided an inaccurate simulation of these mercury transformations during the test periods selected. I do not believe the evidence provided here should be used to conclude that Lagrangian trajectory modeling as applied in STILT has a fundamental advantage over Eulerian-type modeling in the assessment of source influences on TGM air concentrations. This sort of conclusion could only be drawn by applying these models over a long period of time that is not chosen to put either model at a disadvantage.

Response: For the reasons mentioned above, neglecting chemical transformation of TGM is not a major limitation for short-term simulations (six days here). This is also supported by simulation results that show TGM concentrations simulated by STILT (without chemistry) are quite close to those of CMAQ (with chemistry) for all autumn and winter test periods. The difference in the simulated TGM concentrations of the two models is very small when near-field emissions (especially natural emissions) are small (winter and autumn test periods) and is quite large when near-field emissions (especially natural emissions) are strong (spring and summer test periods). In view of this, we conclude that upwind emissions play a more important role than chemical

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transformation in TGM simulations during the test periods. We agree with the reviewer that general conclusion may only be drawn from a long time series comparison and we will add the following modification to address the reviewer's concern.

We have acknowledged the value of Eulerian models in the final paragraph of the paper. We note, however, that we did not know whether STILT would have a better or worse performance than CMAQ before selecting the simulation periods. Also, STILT has an obvious disadvantage (without chemistry of atmospheric Hg), we do not feel there is an issue of putting CMAQ at a disadvantage.

Modifications to the manuscript regarding this point will include:

1) lines 15-19 on page 28756
"STILT captures high frequency concentration variations better than the Eulerian CTM, due to its ability to account for near-field influences that are not resolved by typical grid size in Eulerian CTMs. Thus it is particular valuable for the interpretation of plumes (short-term concentration variations) that requires complex sub-grid treatment in Eulerian models "

will be modified to
"In these comparisons STILT captures high frequency concentration variations better than the Eulerian CTM, likely due to its ability to account for the sub-grid scale position of the receptor site and to minimize numerical diffusion. This is particularly valuable for the interpretation of plumes (short-term concentration variations) that require the use of finer mesh sizes or controls on numerical diffusion in Eulerian models "

2) lines14-24 on page 28767
"This shows that STILT has better skill than CMAQ in reproducing short term variations, such as occur in plumes. This simply reflects the fact that an Eulerian model such as CMAQ calculates one spatially-averaged value in each grid volume, thus smoothing out sub-grid scale processes and leading to the exclusion of near-field or sub-grid influences in the simulations. STILT models the near-field processes that influence

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tracer concentrations at high spatiotemporal resolution by simulating turbulence and capturing sub-grid scale transport (Lin et al., 2003). This is important because measurements are almost always made at a point rather than averaged over a grid cell, so near-field or sub-grid scale influences on the concentration at the measurement point (e.g., near-by sources/sinks) can cause significant deviations between the simulations and the observed values (Gerbig et al., 2003)."

will be modified to
"This shows that STILT has better skill than CMAQ in reproducing short term variations, such as those occurring in plumes. Because the same wind and emission fields were used by STILT and CMAQ, we believed that the difference stemmed from numerical diffusion is minimized in the Lagrangian model, preventing dilution of the footprint that dampens fluctuations in tracer concentrations. The artificial dilution is also reduced by the Lagrangian model by advecting particles backward in time from the receptor point rather than an entire gridcell."

3) lines 26-27 on page 28770
"STILT-modeled air concentrations of Hg generally agreed well with observations and, on average, exhibited better performance than the Eulerian CTM CMAQ."

will be modified to
"While a comparison over longer time periods than the limited episodes in this study is necessary to establish unequivocal results, STILT-modeled air concentrations of Hg generally agreed well with observation and, on average, exhibited better performance than the Eulerian CTM CMAQ for the examined episodes."

4)lines 3-4 on page 28771
"the better performance of STILT can be ascribed to its ability to capture near-field influences"

will be modified to
"the better performance of STILT can likely be ascribed to its ability to capture near-field

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influences by treating the receptor as a point rather than a gridcell and by minimizing numerical diffusion.

Comment: I am also concerned about the modification made to STILT to account for deposition. Once deposition comes into play, how does that affect the theoretical demonstration of time-reversibility in Thomson (1987)?

Response: The reversibility of air parcel transport has been demonstrated in STILT for mass-conserving windfields in Lin et al. (2003). In this study the backward-time simulations were carried out only for the air parcels (i.e., Lagrangian particles). The depositional processes were carried out in the forward-time direction.

Comment: For mercury, wet deposition is brought about by more than just sub-cloud scavenging by precipitation. In addition to water solubility, reduction-oxidation chemistry in cloud droplets is also important. For dry deposition, especially that of RGM, definition of the surface layer depth is very important. Rapid dry deposition of RGM to the surface leads to rapid depletion when the surface layer is shallow. It appears that a constant surface layer depth of approximately 75 meters was used in the STILT modeling. If so, I would expect the dry deposition flux for RGM to be overestimated for nighttime conditions when the true surface layer depth is less than 75 meters and underestimated in daytime where convective mixing extends much higher than 75 meters.

Response: The Reviewer may be referring to the daytime mixed layer rather than the surface layer (Zs). While the daytime mixed layer can reach altitudes on the order of 1 km, Zs is only a fraction of that height. Stull [1988] roughly defined Zs as “the bottom 10% of the boundary layer”, which means Zs = 100 m for a daytime mixed layer height

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of 1 km. Hence the daytime underestimation would be much smaller than envisioned by the Reviewer. As for the nighttime, modeling nighttime turbulence is widely acknowledged as being extremely difficult, so we did not attempt to determine nighttime Zs.
In CMAQ, dry deposition is assumed to take place in the lowest model layer and this layer is set as the surface layer for dry deposition calculations. In the CMAQ-Hg simulation, the depth of the surface layer has been set to approximately 75 meters. In order to be consistent with CMAQ-Hg modeling and because of the reasons mentioned above, we assumed a constant surface layer of approximately 75 meters in the STILT modeling. Thus, uncertainties in surface layer depth affect not only STILT simulations; they affect CMAQ simulations as well. Smaller and variable surface layer depths can be used in the STILT modeling if they are available in the meteorological data. The following lines will be modified to make this clear.

lines 15-16 on page 28762
"Since dry deposition is only computed when the particle is within the surface layer (approximately 75m), Zs defaults to the depth of the surface layer"

will be modified to
"Dry deposition is assumed to occur from the lowest model layer in CMAQ, which is 75 m. In order to be consistent with the CMAQ modeling, we set the surface layer depth Zs in STILT to 75 m for dry deposition calculations."

Comment: Besides the shortcomings mentioned above, the ecological and human health risks from mercury contamination are very weakly associated with air concentrations of TGM. It is the atmospheric deposition of mercury to sensitive aquatic systems that is important. Most of this deposition occurs specifically from RGM air concentrations. TGM is much easier to measure than its rather small and elusive RGM fraction. For this reason, TGM measurements are much more available. However, TGM air concentrations, whether measured or simulated, provide little useful information for risk

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assessment or risk mitigation related to mercury exposures.

Response: While this is true, the TGM measurements are readily available to be compared against models, as the Reviewer has pointed out. The same cannot be said for RGM Hence in this paper the comparisons against model simulations were carried out using TGM, as the specific purpose of this study was not for risk assessment nor for risk mitigation.

Specific Comments (referenced to the printer-friendly PDF format of the manuscript)
Comment: p. 28758, lines 7-10: The text states that the particles simulated in STILT are not tied to grids, so they can resolve sub-grid scale influences. However, the wind data used to define their transport are certainly gridded since the same wind data used by CMAQ were also used in STILT. How is it that particles traveling between discrete points offer any advantages when the wind information used to define their movement is gridded? Explain how STILT can resolve influences below the length scale of the meteorological data used to define transport and diffusion, especially when the emissions across the derived "footprint" and the precipitation driving wet deposition are also gridded to that same scale.

Response: We thank the Reviewer for this comment. This point has not been stated clearly. The statements made in the identified lines are of a general nature, in that Lagrangian models have the potential to resolve sub-grid scale influences by transporting particles using wind vectors interpolated down to their sub-grid scale locations. Thus the footprint can be of higher resolution than the meteorological grids and hence *can* make use of higher resolution emission data. However, as the Reviewer has correctly pointed out, in this specific study the Lagrangian and Eulerian models use the same meteorological and emission fields. Even in this case, though, the Lagrangian models are not subject to numerical diffusion and can treat the sub-grid scale location of the receptor site (as also acknowledged by the Reviewer earlier).

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The identified lines (lines 7-10 on page 28758) will be changed to the following:
"Since the particles are transported by wind vectors interpolated down to their sub-grid scale point locations they have the potential to resolve sub-grid scale influences, which are particularly important in cases where strong and variable sources/sinks are found in the near-field of a measurement site. Advection by Lagrangian particles is also known to minimize numerical diffusion, which is often found in Eulerian advection schemes (Odman, 1997)."

All of the other references to these points in the revised paper will be modified to include these clarifications.

Comment: p. 28759, lines 14-15: The text states that the authors modified CMAQ V4.3 to include dry deposition of Hg0 and RGM. However, CMAQ has always treated dry deposition of RGM since it was originally adapted for atmospheric mercury simulation. Did you simply add a treatment for Hg0 dry deposition? Maybe the treatment for RGM dry deposition was modified. Please explain.

Response: In CMAQ V4.3, dry deposition of Hg0 was assumed to be negligible in comparison to that of RGM and PHg, and was not included. Although its dry deposition velocity is small, Hg0 is the most abundant Hg species in the atmosphere, so we have included its dry deposition in our simulations. This was done by modifying the Meteorology Chemistry Interface Processor (MCIP) program. For Henry's law constant and diffusivity of Hg0 we chose 0.11M/atm (Lin and Pehkonen, 1999) and 0.1194 cm^2/s (Massman, 1999), respectively. A leaf mesophyl resistance was added for Hg0 using an empirical relationship in Du and Fang (1982) because ignoring the leaf mesophyl resistance leads to a significant over prediction of Hg0 dry deposition velocity (Lindberg et al. 1992). In CMAQ V4.3, dry deposition of RGM was referenced to that of nitric acid, but we used the deposition properties of $HgCl_2$ instead. We assumed a Henry's law constant of 1.4106M/atm (Lin and Pehkonen, 1999) and a diffusivity of 0.05 cm^2/s

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(Scholtz et al.,2003).

Comment: p. 28765, lines 19-21: The small subset of particles that did not reach the boundary should not be used to estimate boundary influences. Extrapolating to the boundary regardless of how far the particle endpoint is from that boundary seems dreadfully haphazard.

Response: Simulating the background contribution requires the particles that did not reach the boundary to be initialized with levels generated by a global simulation. The particles' endpoints in this small subset (about 9% of total number) were found on average to be 430 km away from the boundary at the end of transporting them for six days. Thus they are mostly found within the coarse output gridded at 8° latitude $\times$ 10° longitude from the global model output used for initializing their TGM concentrations. Thus the extrapolation does not significantly affect simulated concentrations. The following lines will be modified to make this clear:

Lines 19-21 on page 28765:
"For the small subset of particles that did not reach the lateral boundary, we assigned Hg background concentrations at locations determined by extrapolating a line connecting the receptor to the particles."

will be modified to:
"For the small subset (approximately 9% of total number) of particles that did not reach the lateral boundary, we assigned Hg background concentrations at locations determined by extrapolating a line connecting the receptor to the particles based on the fact that these particles' endpoints were close to the boundary (430 km away, on average). Thus, even if extrapolated, they are still mostly found within the same coarse-grained gridcell of the global model (8° latitude $\times 10°$ longitude). Assigning the background concentrations for all particles was also necessary to establish the background contri-

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bution in this study to be compared against the natural and anthropogenic contributions (see below)."

Comment: Section 3.1 and Figure 2: Upon first glance, Fig. 2 appears to show a very strong reduction in sampling error from 50 to 1000 particles, with little improvement offered from additional particles. However, the vertical scale for sampling error does not extend to zero. This gives the false impression that the adopted particle number of 3000 offers a nearly complete reduction of sampling error. This figure should either show the sampling error scaled all the way to zero or provide a secondary scale on the right showing the fraction of error reduction from the worst case (50 particles).

Response: this figure will be modified.

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