

Reviewer #3:

This paper uses a box model to study the controlling processes of GEM oxidation (or GOM formation) at different types of surface sites, and provides new and important information on the chemistry mechanisms of mercury that might occur in the real atmosphere. It fits well into the scope of ACP. I recommend the paper for publication after addressing the following comments.

We thank the reviewer for their thoughtful, constructive comments and suggestions. The manuscript has been revised carefully. Below we addressed the reviews point by point.

A major comment is that the box model simulation results should be compared against the measurements of PBM mixing ratios at these sites. This would help the interpretation of some controlling processes such as gas-particle partitioning in the model.

It is true that high quality GOM and PBM measurements would be of great help for modelling studies to evaluate the schemes such as gas-particle partitioning process as well as to constrain the aqueous reduction rate. However, the inlet of the Tekran speciation sampling system had an elutriator inlet with an acceleration jet to remove aerosols $> 2.5 \mu\text{m}$ so that only fine PBM was measured. The PBM calculated from the box model does not include size fractionation, thus Tekran PBM_{2.5} measurements could not be used to constrain our simulations and further constrain the reduction rate.

Another general comment is that a more detailed description of the box model set up should be given in the paper, for example the exchange of GOM between the free troposphere and the boundary layer. A schematic can be very helpful for the readers to understand which processes are discussed in the model.

We did not include a scheme to account for GOM exchange between the free troposphere and the boundary layer. Such exchange processes are highly parameterized, and location and time dependent. Including such processes could induce another major uncertainty in the model. In this study, we selected clear-sky and calm wind conditions, usually accompanied by strong stability with a strong inversion layer at the top of the daytime convective PBL layer based on measurements from the literature (e.g. Hogan et al., 2009). Minimal entrainment at the top of the boundary layer was thus expected.

The third general comment is that the paper discusses the importance of different oxidized mercury forms through their oxidation pathways. I suggest the authors also discuss the stability of these oxidized forms in the real atmosphere in the particular environment of each site.

This is a valid point. However, since properties of the oxidized forms remain largely unknown, we added a general discussion on the possible impact of different environments on speciation. The discussion added in the text is as follows in section 1 of revised manuscript:

“GOM concentrations and speciation could be impacted by meteorological conditions and chemical conditions in different environments. High solubility of GOM species, possible phase partitioning of HgO as discussed above could all be the reasons causing varying GOM speciation at different locations. For instance, the aerosol type, size distribution, and chemical composition varied largely between the MBL site and inland sites, which may lead to different gas-particle partitioning rates of GOM species.”

Specific comments: 1. throughout the paper: the use of the word “case” in this paper may confuse its readers, as it refers to both different observational days and different model simulations. For example, in page 9, section 2.2 “Case selection”, and in page 13, section 3.3 “Sensitivity analysis”.

We have changed the word “case” in sensitivity studies to “scenario”.

2. Title: it would be better if the full expression of GEM (i.e. gaseous elemental mercury) is given in the title.

Upon the reviewer’s suggestion the title was changed to “Investigation of processes controlling summertime gaseous elemental mercury oxidation at mid-latitude marine, coastal, and inland sites”.

3. Page 4, line 25. Can the authors describe which parameter is used to account for entrainment from the free troposphere?

As we responded above to a comment similar to this, we did not include a scheme to account for GOM exchange between the free troposphere and the boundary layer. Such exchange processes are highly parameterized, and location and time dependent. Including such processes could induce another major uncertainty in the model. In this study, we selected clear-sky and calm wind conditions, usually accompanied by strong stability with a strong inversion layer at the top of the daytime convective PBL layer based on measurements from the literature (e.g., Hogan et al., 2009). Minimal entrainment at the top of the boundary layer was thus expected.

4. Page 5, line 12. I do not understand why the “GEM mixing ratios ... are set to be constant mimicking GEM emission flux”. What does this mean in the model?

Revised to “the initial GEM mixing ratios along with a list of compounds (Table 2) in the model were obtained from observations in three different environments and were set to be constant during simulations”. The theory behind the fixed input concentrations of GEM among a number of other compounds is that a box model simulates the concentrations of short-lived compounds reaching an instantaneous chemical steady state, and for the time scales of such instants, the chemicals such as GEM are long-lived enough to maintain a constant level. We have added this explanation in the text.

5. Page 6, line 8. The numbers of reactions are incorrect.

Corrected.

6. Page 6, lines 11-18. The reaction constants for these aqueous Hg reactions should be given either in the main text or in the supplement. Also, I speculate these reactions are also highly uncertain. Do the authors consider the uncertainties associated with them?

A table showing aqueous Hg reactions in our model was added as Table S1.

Aqueous Hg reduction is one of the major sources of GEM in the atmosphere. Therefore, aqueous Hg reactions is supposed to be a factor controlling GEM mixing ratios, which turns out to influence GOM mixing ratios. However, aqueous Hg reduction is not an important control on GOM simulations in this study because GEM mixing ratios in the model were fixed using observed values. The uncertainties associated with aqueous Hg reactions would not influence GEM mixing ratios and therefore have minor effects on simulated GOM mixing ratios.

7. Page 12, lines 1-9. These several sentences are confusing. At first, it is mentioned that “the patterns of diurnal variation were similar at the three sites”. Then, it is said that “PM showed negligible diurnal variation”. I suggest that a statistical method is used to quantitatively detect the diurnal patterns at all the sites.

We apologize for the confusion. All three sites did show diurnal cycles, the expression of “PM showed negligible diurnal variation” were intended to suggest the daily amplitude is very small compared to that at AI and TF. We have rephrased these sentences to clarify the point. The changed wording is as follows:

“The patterns of diurnal variation were similar at the three sites with small discrepancy on the occurring time of daily peaks (~ 13:00 LT at AI, and ~14:00 LT at TF and PM), but the magnitude varied largely by site. AI had the largest GOM diurnal amplitude (i.e., daily maximum – daily minimum) ranging from 0.73 to 13.29 ppqv, TF from 0.05 to 0.57 ppqv, and PM showed a very small range from 0.05 to 0.14 ppqv.”

8. Table 2: How uncertain are the simulated [Br] at TF and PM? What is the major source of [Br]? How is the concentration of Br₂ set in the box model? In addition, are the boundary layer heights at AI and PM set to be constant? Do the authors expect any diurnal variations of the boundary layer height?

No observations of [Br] were available at the three sites. At AI, we used [BrO] observation from Saiz-Lopez et al. (2006) to constrain simulated [BrO]. However, at TF and PM, we don't have any data available to constrain Br species, so we did not give a specific source for Br and BrO. [Br₂] initial concentration was set to 1 pptv (e.g. Finley et al., 2008) but without setting it as constant. In result, Br₂ was rapidly depleted during daytime simulations with very low concentration of Br and BrO produced. Average daytime maximum of [BrO] is about 10 ppqv, and [Br] is negligible. The model simulation at TF and PM indicated that O₃ and OH were sufficient for GOM production at TF and PM.

The boundary layer heights at AI and PM were set to be constant. The major reason is we do not have diurnal cycle data of boundary layer height at AI and PM. Moreover, in the MBL, boundary layer height is usually a few hundred meters and does not vary much (Vickers and Mahrt, 2003; Angevine et al., 2006). At PM, the boundary layer height is set as averaged daytime boundary height at TF minus the elevation difference between the two sites. At night, due to its high elevation, it was above the nocturnal boundary layer.

9. Figures: The figures throughout the paper should use a consistent way of uncertainty quantification, probably being consistent with the statistical method used for the observations (Figure 1). In the current paper, min-max, standard deviation, and box-whiskers all exist making the readers difficult to compare the uncertainties among these figures.

We revised the figures and used error bars for standard deviation only.

In addition, I suggest the authors merge Figures 2, 3, and 8.

Thank you for the suggestion. We merged these three figures to Figure 2 in the revised manuscript. The merged figure was shown below (Fig. 1):

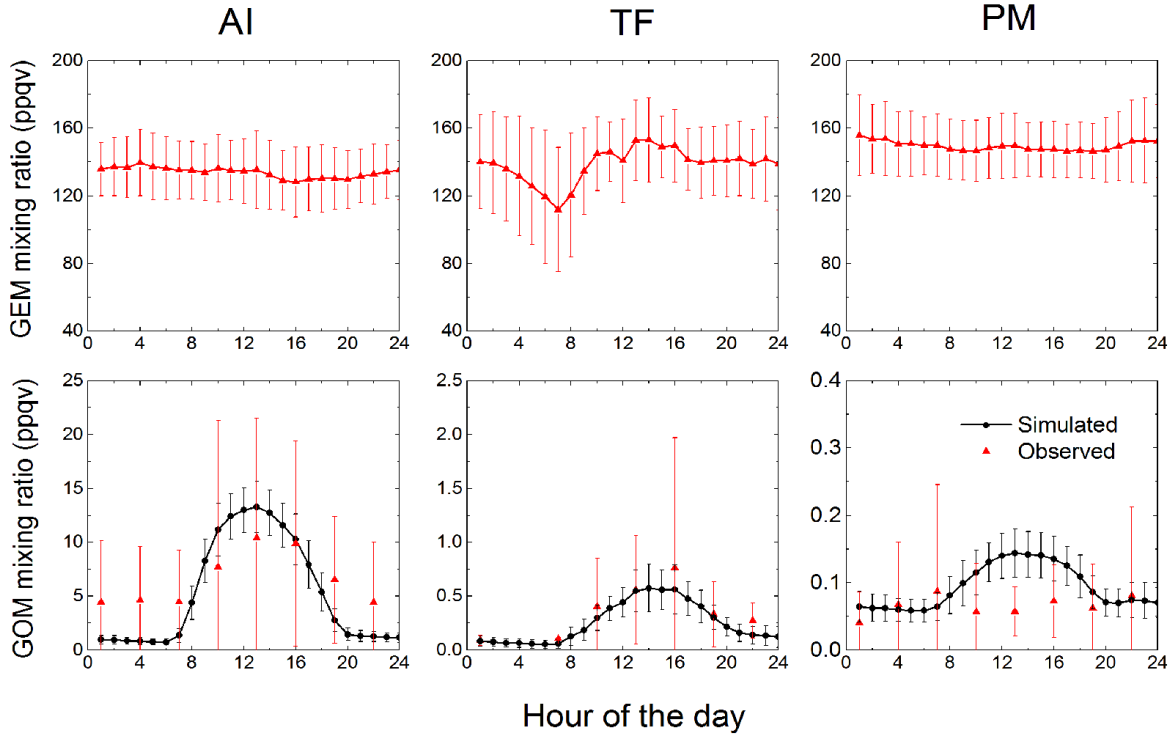


Figure 1. Average diurnal cycles of observed GEM (top panel) and simulated and observed GOM (bottom panel) averaged over the selected 50 days at Appledore Island (AI), 12 days at Thompson Farm (TF), and 21 days at Pack Monadnock (PM) from summers of 2007, 2008, and 2010. The error bars represent standard deviation.

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