

We thank the reviewer for the high level of attention given to our paper and for the thorough review and comments that are very helpful in improving the paper. Several of the reviewer comments indicate that a number of key points presented in our paper were not entirely clear, and we will address these concerns in a revised manuscript. In the following all the reviewer's comments (in italic font) are followed by our detailed answers.

General comments: This study determined the reaction rates for the gas-phase oxidation of GEM by OH and NO₃ radical using gaseous elemental mercury (GEM) and reactive gaseous mercury (RGM) measurements in Jerusalem. HgO was simulated using the CAABA/MECCA box model using different sets of reaction kinetics from previous studies and in this study, ozone and liquid water content conditions, and dry deposition velocities. The modeled HgO were compared with observed diel variation in RGM. The results suggest that OH and NO₃ radical are important daytime and nighttime oxidants, respectively, at this site. The topic presented in this study is very interesting and attempts to gain a better understanding of mercury chemistry using a modeling and measurement approach. While the approach is novel compared to previous atmospheric mercury modeling studies and only a few modeling studies have tried to simulate the diel variations of RGM, I have a few major concerns. First, the assumptions made to derive the rate constants for the oxidation of GEM by OH and NO₃ radical are not very realistic, e.g. absence of gas-particle partitioning, dry and wet deposition of RGM, impact of anthropogenic sources, boundary layer mixing, and oxidation of GEM by BrO or Br.

It's impossible to rule out the impact of these factors on the observed RGM variation. Is there a way to account for these processes in the rate constant calculations?

Answer:

Our reply regarding each of the points which were raised by the reviewer is given below:

- Gas-particle partitioning: CAABA/MECCA does take into account gas-aerosol partitioning. Gas-aerosol partitioning is performed based on Henry's law and kinetic limitations for accumulation soluble aerosol modes (Sander and Crutzen, 1996; Sander et al., 2011). This is described in line 140 and lines 170-173. We will try to edit these sections for clarity in the new manuscript.

- RGM dry and wet deposition: Both dry and wet deposition of RGM are accounted for by the model. We also included sensitivity analyses to investigate the impact of dry deposition on our results as described in Sect. S4 of the supplement. Wet deposition is accounted for in MECCA module: first stage is RGM uptake by aerosols and second stage includes scavenging of the aerosols (page 7, line 141). As is mentioned below we will evaluate the errors that are associated with uncertainties / biases of these processes.

- Impact of anthropogenic sources – it is unlikely that measured RGM is significantly and directly influenced by anthropogenic emission sources at the measurements site (see lines 90-98; The reader is referred to read more about this point in Peleg et al., 2015 (page 5, lines 98-100)). This working hypothesis is based on knowing the

emission sources at this area and the lack of correlation between RGM and different measured parameters, including trace gases (except O₃ and NO₃), and wind direction and speed. It should be emphasized however that the model configuration was based on rigorous representation of photochemistry in the model (pages 9-10, lines 182-195). One of the most important related issues is the representation of OH in the model which is discussed and investigated extensively (lines 125-133, pages 6-7; Sect. S1 of the supplement).

Boundary layer mixing: Boundary layer mixing is not included in the model. We use a box model, which is aimed at representation of the chemistry at the measurement point. Note that in the case of NO₃ the measurements were performed by applying non-point measurement by using an LP-DOAS, but still a correlation of NO₃ with RGM could be obtained as is demonstrated by Peleg et al. (2015). We don't expect that variation in the boundary layer height could significantly affect our calculated rate constants, because the calculations are based on RGM peaks during nighttime and around noontime, at time when the boundary layer height is quite stable. However, in case that significant variations in the boundary layer height occurred around noontime, we expect that it will be associated with underestimation of the calculated rate constants, because we expect decrease in RGM concentrations with increasing boundary layer height.

Oxidation of GEM by BrO and Br: GEM oxidation by Br, and to a lesser extent by BrO, has been indicated as playing a major role globally and in large portion of the atmosphere (i.e., upper troposphere and in the marine boundary layer). As described in our reply to the next general comment, just below, Br and BrO are expected to play only a minor role at the measurement site. We will evaluate the potential bias associated with incorrect implementation of bromine-induced mercury oxidation in the model and with respect to the calculation of the rate constants, as suggested by the reviewer.

Second, the oxidation of GEM by Br is considered in many atmospheric Hg models; however the model simulations in this study assumed the only oxidants of GEM are O₃, OH, NO₃, and H₂O₂. While you discussed that Br is not an important oxidant at this site because it is not in a marine environment or the free troposphere, does this argument apply to other surface continental sites? Should future atmospheric Hg models exclude Br when simulating continental sites?

Thank you for this comment. While gaseous Br may be the main viable GEM oxidant on a global scale, particularly over marine regions and the free troposphere (Holmes et al., 2010), bromine contribution to GEM oxidation in the non-marine boundary layer is much smaller. At these areas its relative contribution to GEM oxidation depends on the level of photochemical pollution, aerosol properties, humidity and reaction rate with volatile organic compounds. We realize that the arguments that were given by us in the manuscript, for not including Br and BrO as GEM oxidants in the model, were not strong enough. With BrO lifetime of few minutes under sunlight, its concentrations over land surface are generally below 0.1ppt (e.g., Yang et al., 2005), and the concentrations of Br should be significantly lower than this. In the following, we describe model simulations that we performed in order to study the potential

contribution of Br and BrO to the overall oxidation rate of GEM at the measurement site.

The used chemical mechanisms and kinetics of reactive halogen species, and Br-Hg interaction are the same as described in Obrist et al. (2011). The model was ran with the same configuration as described in the manuscript for the BASE simulation (see Table 1 in the main text), with reaction rate constant of GEM with OH of $6.5\text{E-}13 \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. This model configuration led to a relatively good agreement between simulated and measured HgO (see Fig. 4 in the manuscript). We included in the model a Br₂ flux as a source for the reactive bromine species and set its magnitude such that the maximum BrO concentrations reached 0.1ppt, which we assume were the maximum BrO concentrations at the site (e.g., based on Yang et al., 2005). To simulate the nighttime GEM oxidation we ran the model according the BASE* simulation (see Table 1 in the main text), with reaction rate constant of GEM with NO₃ of $3.0\text{E-}15 \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. We would estimate that the maximum Br concentrations should be around 0.01ppt during daytime. This estimation is based on reported [Br]/[BrO] ratios (e.g., Fig. 4 in Fernandez et al., 2014; Figs. 1,2 and in Tas et al., 2012; Fig. 2 in Tas et al., 2008) and taking into consideration the sharp decrease of [Br]/[BrO] ratio with O₃ together with the relatively high O₃ concentrations at the measurement site. However, the simulations indicated [Br]/[BrO] of between ~0.36-0.133 and 0.04-0.45 during daytime and nighttime, respectively (panel b in figures 1 and 2 below).

We ran the simulation described above with and without including the Hg-Br interaction. Figures 1 and 2 below compare the HgO obtained by these two runs. It is shown that the maximum differences in HgO concentrations for the two run types were ~7.1% and ~4.0%, at time when HgO reached its daytime and nighttime maximum concentrations, respectively. For comparison, note that the lower limit rate constant $k[\text{OH}+\text{Hg}^0]$ that we evaluated in this study is larger by a factor of ~7 than the conventional value suggested by Sommar et al. (2001). We attribute the relatively low impact of gaseous Br and BrO on GEM oxidation at the measurement site to remoteness from the sea, high photochemical activity and dry conditions. Our analyses indicate that there are several parameters, including LWC, deposition velocities and oxidation by Br and BrO, that are associated with uncertainties with respect to the evaluated GEM oxidation rate constants. We will follow, the reviewer's advice and will take into account all of these uncertainties in the evaluation of the rate constants. We will include corresponding sensitivity analyses in the revised manuscript and will extend the discussion on the evaluated rate constant values, accordingly.

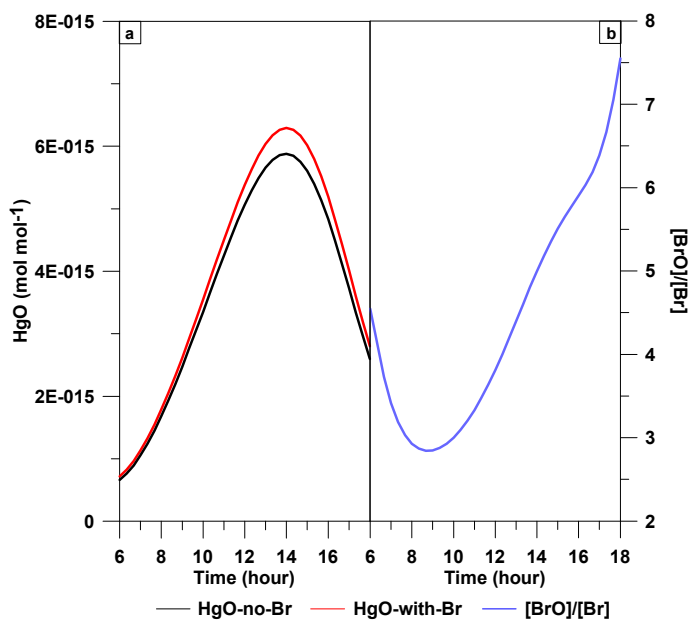


Figure 1. The role of bromine chemistry in daytime GEM oxidation. The figure presents the daytime profile of HgO which was obtained with and without inclusion of the Hg-Br interaction in the model (a) and the corresponding [BrO]/[Br] ratio (b).

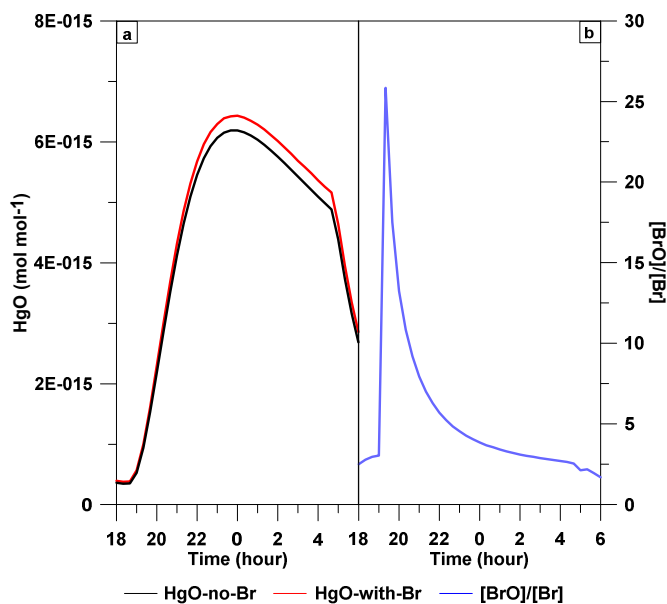


Figure 2. The role of bromine chemistry in nighttime GEM oxidation. The figure presents the nighttime profile of HgO which was obtained with and without inclusion of the Hg-Br interaction in the model (a) and the corresponding [BrO]/[Br] ratio (b).

Third, the nighttime oxidation of GEM by NO₃ radical has not been accounted for in previous modeling studies. The paper can be improved by providing more details on the formation of the NO₃ radical, how it reacts with GEM, kinetics data, atmospheric lifetime, ambient air concentrations, geographical distribution of this oxidant, etc

Answer:

Thank you for this comment. In the new manuscript we will add more information about the formation and chemistry of ambient NO₃, including all the factors which are mentioned here.

Specific comments: Line 51-57: The discussion on uncertainties in mercury modeling need to be expanded, particularly the uncertainties on which oxidants dominate the oxidation of GEM and uncertainty magnitudes associated with the reaction kinetics. Many mercury modeling studies focus on O₃, OH and/or Br, but haven't focused much on the NO₃ radical. More details on the reaction between GEM and the NO₃ radical should be included here, e.g. results from Peleg et al. (2015) or other work, how the NO₃ radical is formed and why it's only present at night, kinetics data, etc. Also, what are the current uncertainties regarding removal via dry deposition that you mention in line 54?

Answer:

We will expand the discussion on uncertainties regarding GEM oxidants in the introduction, including NO₃, and we will provide more details about its formation, chemical pathways and available kinetic information. We will also expand the discussion on the current uncertainties in RGM removal via dry deposition.

In lines 56-57, are you referring to uncertainties in gas-particle partitioning or incomplete knowledge on mercury species in air? There are also uncertainties in Hg emissions inventory and atmospheric oxidized Hg measurements (used in model validation) which should be discussed.

Answer:

We refer here to incomplete knowledge about speciation in the gas phase in general, which to some extent results from incomplete knowledge about gas-particle partitioning. We will make this clearer in the new manuscript. We will refer also to uncertainties in emission inventory in the revised manuscript.

Lines 58-68: This section discusses only O₃ and OH. Are there any laboratory kinetics studies pointing out the uncertainties on GEM oxidation by Br and NO₃? If so, these studies should be discussed here as well.

Answer:

We agree that the discussion should include all relevant oxidants, and we will add information on laboratory kinetics study of GEM oxidation by Br. Note that currently there are no available experimental-based information about the oxidation of GEM by NO₃ (lines 147-157).

Lines 100-102: Please include how high the typical NO₃ levels were and explain how NO₃ forms. If its formation is driven by photochemical activity, why is NO₃ only present at night? I'm also surprised by the high ozone concentrations at this site because the 60 ppb concentration seems to be more common in large cities. Is the high ozone mainly from local vehicular traffic or transported from the rest of Europe?

Answer:

We will include information about NO₃ concentrations at the measurement site in this section. We will explain in a clearer way the relation between strong photochemical activity in the site and high nighttime NO₃ concentrations, which are induced by the relatively high nighttime NO₂ and O₃ concentrations (e.g., Asaf et al., 2009, 2010). We will also mention the impact of the relatively dry conditions on NO₃ concentrations. We will mention the fast photolysis of NO₃ during daytime, and expand our discussion about NO₃ chemistry as is described in our reply to the reviewer comment on lines 51-57. Air masses originated in Europe impact the ozone concentrations mainly in western Israel, but the relatively high ozone concentrations in inland Israel, including the measurement site in Jerusalem, are induced by local emissions from transportation and industry, which take place mostly in western Israel. Together with the dry and warm meteorological conditions these emission sources lead to the relatively strong regional ozone formation.

Lines 108-109: Please mention the sampling duration for RGM and FPM.

Answer:

We will add this information.

Lines 115-117: Suggest revising this sentence to, "A meteorological station (Met One Instruments, location??) was situated on the same rooftop to measure basic meteorological parameters, e.g. wind speed, wind direction, temperature, pressure, and relative humidity (RH) with LODs of 0.5 m s⁻¹, 5_, 0.4 K, 0.2 torr and 3%, respectively."

Answer:

We will correct this sentence accordingly.

Supplement, Sect. S1 and Equation S2: The equations for determining the rate constant of the OH+Hg⁰ and NO₃+Hg⁰ are based on many assumptions that cannot be validated. It assumes no dry and wet deposition of RGM, no anthropogenic emissions impact on RGM, and no gas-particle partitioning. These assumptions are not realistic. More analysis needs to be done to rule out the impact of these processes on RGM at this site. For example, please confirm whether there was any precipitation during the entire sampling period to eliminate the possibility of wet deposition. Is there a possibility of local or regional transport of RGM to this site considering that the daytime peak RGM concentration of ~38 pg/m³ (Fig. 1) is quite high? Could the changes in mixing height also impact the diurnal variation of RGM? It was mentioned that the rate constants would be underestimated if dry deposition of RGM is ignored. What would be the combined effect on the rate constants if other processes were not considered and the magnitude of the uncertainties?

Answer:

Thank you for this comment. It is true that the equations used to calculate the rate constant of GEM with OH, O₃ and NO₃ are based on several assumptions as mentioned by the reviewer. Nevertheless, we believe that these evaluated rate constants can use as a lower rate estimation based on the following arguments:

- a) The kinetic calculations were based on selected measurement days (27) which showed a definite daytime RGM peak, while we don't expect that these peaks were significantly affected by either gas-aerosol partitioning or local anthropogenic emissions, based on the arguments in b and c below, respectively.
- b) All selected days, which were used for the kinetic calculations (27 days for the daytime calculations and 19 days for the nighttime calculations) showed a definite RGM peak and no corresponding sharp RH decrease (which may have led to a shift in the gas-aerosol partitioning; Sect. S1 of the Supplement).
- c) No correlations were observed across the entire measurement periods between RGM concentration and other atmospheric chemical species (e.g., CO: R₂ < 0.01; SO₄: R₂ < 0.01; SO₂: R₂ < 0.1; lines 97-98), or between RGM and meteorological parameters (R₂ < 0.01 both for wind speed and wind direction). It is therefore unlikely that measured RGM concentrations were significantly influenced directly by anthropogenic emissions, as is further discussed by Peleg et al. (2015).
- d) Removal processes for RGM were not taken into account in the calculations.
- e) In general, changes in the mixing height should not positively correlate with RGM concentrations, because daytime RGM peaks tend to occur around noontime, at time when the boundary layer height is either quite stable or increases.

We will extend the discussion on the uncertainties associated with the measurement-based calculated rate constants. It is difficult to evaluate the magnitude associated with uncertainties, based on the measurements alone, mainly due to uncertainties in removal processes by wet surfaces. Therefore, we will use the measurement-based simulations as a complementary tool, for this evaluation.

We confirm that there wasn't any precipitation during the entire sampling period.

Sect. S1: How do the rate constants of the OH+Hg⁰ and NO₃+Hg⁰ compare with previous studies?

Answer:

This is discussed in the main manuscript (see below) and we will refer the reader to the related sections.

“The k[OH+Hg⁰] value calculated based on the measurement results (see Sect. S1 of the Supplement) was found to be 2.8(±0.5)E-13 and 1.1(±0.5)E-13 cm³ molecule⁻¹ s⁻¹, using the Hall (1995) and Pal and Ariya (2004b) k[O₃+Hg⁰] values, respectively, with errors representing the standard deviations of the mean. These rate constants are higher by a factor of only 1.2 and 3.2, respectively, than the commonly used k[OH+Hg⁰]. Note, however, that these calculated k[OH+Hg⁰] values do not take into account RGM-removal processes, which would cause the total formed RGM to be much higher than the concentrations used for the kinetic calculations. This can result in significant underestimation of k[OH+Hg⁰] by the kinetic calculations.” (lines 448-456).

” The calculated $k[\text{NO}_3+\text{Hg}^0]$ based directly on the measurement results was found to be $2.8(\pm 0.5)\text{E-}15$ and $1.9(\pm 0.5)\text{E-}15 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ using the $k[\text{O}_3+\text{Hg}^0]$ values from Hall (1995) and from Pal and Ariya (2004b), respectively.” (lines 469-471). Just before this section we refer the reader to the only available reference for the reaction rate of GEM with NO_3 :

“To the best of our knowledge, no published information regarding the rate of GEM oxidation by NO_3 is currently available except for a suggested upper limit of $4\text{E-}15 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Sommar et al., 1997). “(lines 460-462).

Line 155: The strong correlation between RGM and NO_3 doesn't necessarily imply GEM oxidation by NO_3 . It's essential to eliminate other possibilities that can lead to similar RGM and NO_3 trends at night. Could the peak in RGM at night be due to the sampling of the free troposphere?

Answer:

We agree about this point. The possibility of positive RGM- NO_3 correlation due to other factors, mainly uptake by dew and intrusion from the upper troposphere is discussed in Peleg et al. (2015). Peleg et al. (2015) demonstrated that NO_3 -RGM correlation occurred independently on these factors. We will mention in the new manuscript the potential dependence of NO_3 -RGM correlation on these factors. Below we cite the discussion about the possibility that the correlation is due to intrusion from higher altitudes.

“A second possibility for the observed RGM and NO_3 correlations could be advective transport and subsidence from higher altitudes. In a previous paper,...Asaf et al., 2009... it was suggested that the presence of very high levels of NO_3 (above $500 \mu\text{g m}^{-3}$) could possibly be explained by the entrainment of fresh O_3 from the upper atmosphere. Similarly, high RGM levels observed at night in Jerusalem might be from intrusion of RGM present in the higher troposphere (Lyman et al., 2012) down to the surface,...Selin et al., 2008... as has been observed in semiarid and mountainous regions of the western U.S. during high pressure subsidence events....Fain et al., 2009..., Weiss-Penzias, et al., 2009. In the present study, no extreme concentrations of NO_3 were observed (maximum noted was 430 ng m^{-3} in contrast to an average of almost 900 ng m^{-3} noted by Asaf et al., 2009, 2010) and no sharp nighttime elevations in O_3 levels occurred as in a previous study; in fact, O_3 concentrations generally decreased at night. Most importantly, boundary layer tracers such as CO showed no decreases in concentrations during nighttime as would be expected during tropospheric influenced subsidence events (e.g., Figures 3 and 4). In regards to transport events, it is important to note that wind directions originated from a narrow range from the west and northwest throughout the campaign, and that observed concentration enhancements of NO_3 and RGM were unrelated to changes in wind speeds or directions. We therefore propose that it is unlikely that advection processes caused the observed correspondence of NO_3 and RGM concentrations, and that no major intrusions of RGM and O_3 (leading to NO_3 formation) occurred during our measurement period.”

Line 159: The model assumes that O_3 , OH, NO_3 , and H_2O_2 are the only oxidants of GEM. I don't understand why the Hg reactions with Br and BrO are listed in Table S1.

Answer:

We suggest keeping the rate constants of Hg-Br chemistry in the table and indicate that these were used only for sensitivity analyses.

Line 162-165: Br needs to be considered in addition to BrO. If GEM oxidation by Br is being used in global models, why would it not apply to this site?

Answer:

As is mentioned in our response to the general comments, Br and BrO are included in global models due to their importance as GEM oxidants in the free troposphere and the MBL. Their contribution to GEM oxidation in the non-marine boundary layer is much smaller. At these areas its relative contribution to GEM oxidation will depend on the level of photochemical pollution, aerosol properties, humidity and reaction rate with volatile organic compounds. We don't expect that bromine chemistry plays significant role in the boundary layer of the measurement site considering the expected low concentrations of these species at this area and based on the sensitivity analysis we performed. As we mentioned above, we will present the sensitivity analysis in the new manuscript. We will evaluate the associated uncertainty in the calculated GEM oxidation rates, which are related to uncertainties in Hg-Br interaction, and will add it to the discussion on the calculated rate constants.

Line 167: How long is the lifetime of GEM in this study? I'm surprised that its lifetime is shorter than a few days estimated for GEM+BrO (Wang et al., 2016). If that's the case, GEM oxidation by Br should be considered because the rate constant for GEM+Br is larger than GEM+BrO (Subir et al., 2011, Atmos Environ).

Answer:

Thank you for this comment. We realize that this is wrong (GEM lifetime under the studied conditions is ~2-3 days). As we mentioned above we realize that the arguments that were given by us in the manuscript, for not including Br and BrO as GEM oxidants in the simulation, need to be edited. In the new manuscript we will change this section and include discussion on the sensitivity analyses of different factors (including oxidation by Br and BrO), with respect to the calculated rate constants.

Lines 220-221: GEM oxidation by Br is considered in many Hg models which simulate Hg concentrations across the globe. It doesn't seem right to exclude these reactions only because the site is distant from the ocean.

Answer:

As we mentioned above we realize that the arguments that were given by us in the manuscript, for not including Br and BrO as GEM oxidants in the model, were not strong enough. Nevertheless, we expect that the contribution of Br and BrO to GEM oxidation in the non-marine boundary layer is relatively small. In these areas their relative contribution to GEM oxidation will depend on the level of photochemical pollution, aerosol properties, humidity and reaction rate with volatile organic compounds. In the new manuscript we will change this section and include discussion on the sensitivity analyses, instead. We will follow the reviewer's advice and will take into account these uncertainties in the evaluation of the rate constants, and associated discussion.

Figure 2: Observed RGM should be plotted here to compare model results with observations.

Answer:

We will add the average observed RGM diurnal profile and will indicate the average over the maximum RGM levels in a similar way to figures 4-6 (see our explanations for this issue in our reply to the comment on line 325 below).

partitioning results. It was mentioned earlier in the paper that gas-particle partitioning was not important at this site considering the low FPM concentrations.

Line 266-268: Why is the agreement between simulated and measured gas-particle partitioning better during nighttime than daytime? Is it due to the inclusion of the NO_3+Hg^0 reaction in the model?

Answer:

Our simulations indicate that removal of measured RGM is significantly higher during nighttime compared with daytime. Accordingly, the results presented in Fig. 3 obtained by applying a higher removal rate for RGM during nighttime (see lines 196-205) compared with daytime. It may be possible that the uptake of RGM by aerosols was underestimated more significantly during daytime than during nighttime. The underestimation of RGM uptake by aerosols is one of the reasons why we believe that the simulation-based calculated reaction rates of GEM were underestimated by our modeling-based analyses (e.g., lines 350-353).

Lines 325: I'm confused why the dashed line inside the box is the average RGM maximum while the diurnal variation of RGM shown in the same plot is much lower than this average maximum RGM?

Answer:

This is because the two magnitudes were computed differently. The average diurnal profile doesn't show the real (average) maximum RGM peak, considering that the maximum RGM timing was changed from day to day. Therefore in order to better account for the peak magnitude we present also the average (daytime in this case) RGM maximum (see lines 256-261). We will improve the explanation about this issue. Note that average RGM diurnal profile indicates the timing of the measured RGM peaks, and therefore we included it in the figure.

Line 338-340: Why were the $k[\text{OH}+\text{Hg}^0]$ increased to $6.5\text{E}-13$ and $9\text{E}-13$? Where are these numbers from? From Fig. a and b, it appears that increasing $k[\text{OH}+\text{Hg}^0]$ to these values overestimated the observed RGM. I was wondering why you didn't use the $k[\text{OH}+\text{Hg}^0]$ values calculated in the supplement. The lower rate constants might be able to reproduce the observed RGM.

Answer:

The reason for that is related to our previous reply (comment on line 325). The average (daytime) RGM maximum is indicated by the horizontal dashed line in the box, rather than by the average diurnal profile, which significantly underestimates the RGM daytime peak magnitude. Therefore, the RGM was not overestimated by the specified rate constants. We will improve the explanation provided in the figure caption, and in the text, regarding the reasoning for including both the average diurnal profile and the

average peak concentrations. The rate constants that were calculated in the supplement are lower than the rate constants evaluated by the model, because they were calculated without taking into account any of the removal processes.

Line 342: Please explain why a higher LWC would lead to earlier peaks in HgO (i.e. the timing of the peak).

Answer:

Thank you for this comment. The RGM peak is roughly controlled by GEM oxidation rate and concurrent uptake by aerosols, and can be defined as the point in time for which the formation rate of RGM due to oxidation becomes lower than the rate of decrease in RGM due to its uptake by aerosols. Higher LWC is associated with higher uptake rate by aerosols and therefore associated with earlier peak timing.

Line 344: Is the LWC value of 5 $\mu\text{g m}^{-3}$ comparable to the observed LWC at this site? I'm interested in whether this LWC value is realistic considering the semiarid conditions at this site. Although this LWC value predicted HgO concentrations that are in good agreement with the observed RGM, the LWC needs to be representative of the conditions at this site. Also, what is the diurnal variation like for LWC? I'm guessing it is drier during daytime, so is it appropriate to use a higher LWC value?

Answer:

Note that the LWC used by us for the BASE simulation is $1.08\mu\text{g m}^{-3}$, but we have no solid indication that this is accurate enough. Therefore, we performed sensitivity analysis in order to investigate the potential impact of significantly lower and higher LWC values, ranging $0.5\text{-}5\mu\text{g m}^{-3}$. We estimate that a value of $5\mu\text{g m}^{-3}$ may be too high to represent the LWC at the measurement site, while being more typical to more polluted (e.g., see Fig. 5 in Liu, 2012) and humid areas (e.g., see Fig. 3 in Guo et al., 2015). Note that the rate calculation was performed by applying a value of $1.08\mu\text{g m}^{-3}$ for LWC in the model.

Line 346: Should it be “observed RGM” instead of “simulated RGM”?

Answer:

Thank you. We will fix this mistake.

Line 377: What is the significance of this finding? Are you suggesting that the rate constant by Hall (1995) should not be used?

Answer:

Our results point out that the rate constant suggested by Hall (1995) is too small in agreement with other studies (e.g., Calvert and Lindberg, 2005). However, we think that we cannot suggest not using this value based on our study alone, at time when there is still much uncertainty regarding the kinetics of atmospheric mercury oxidation.

Line 382: It was mentioned earlier in the paper that there is a second peak sometime in the afternoon that is likely due to GEM oxidation by O₃. Doesn't the simulation suggest that is the case?

Answer:

Thank you for this comment. It is indeed possible that the HgO peak, which was obtained with a rate constant of $1.8\text{E-}18 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, accounts for the second (/latter) daytime measured RGM peak (e.g., Fig.1). However, this simulated peak cannot explain the first (/former) observed RGM peak, because it occurred several hours later. This points out that the observed noontime RGM peaks can be better reproduced by increasing more significantly the reaction rate constant of GEM with OH than the reaction rate constant of GEM with O₃.

Figure 5: Please change "Pall & Ariya" to "Pal & Ariya" in the legend of part a. The figure captions for parts a and b should be switched. Also, the concentrations on the y-axis that are shown in purple are hard to read.

Answer:

These will be changed in the revised manuscript.

Line 387: Please explain why a lower LWC causes a large delay in the simulated HgO peak.

Answer:

The RGM peak is roughly controlled by uptake by aerosols and GEM oxidation and can be defined as the point in time for which the formation rate of RGM due to oxidation becomes lower than the decrease in the rate of RGM removal due to its uptake by aerosols. Higher LWC is associated with higher uptake rate by aerosols and therefore associated with earlier peak. Therefore, a lower LWC should be associated with a delay in the HgO peak.

Line 406: Why were the simulations only compared with the peak in RGM (the horizontal line) instead of the observed RGM variation? Also since you are varying the LWC in the simulations, I suggest plotting the observed nighttime RGM variation for different LWC ranges to see if the simulations match up with the observations for different levels of LWC.

Answer:

The nighttime RGM profile was highly scattered across different nights, such that there is no representative nighttime profile of RGM during the measurements period (see Fig. 1). Therefore we only referred in this figure to NO₃ peak value, regardless of the peak timing. The NO₃ peak value represents the average over measured NO₃ peaks at night, with relatively high peak NO₃ concentrations (>60 ppt) that were associated with simultaneous RGM peaks. The average concentrations of these RGM peaks equals 6.17 ppq, as indicated by the dashed horizontal lines in Fig. 6 (lines 403-407). We don't have available measurements of LWC and therefore it will be difficult to compare the simulated and measured RGM for different LWC values. Because LWC tends to positively correlate with relative humidity (RH) we will try to compare the measured

and simulated RGM for different RH. Note however that considering that removal of both RGM and NO₃ is strongly affected by water vapor availability, adds additional level of complexity to such analysis (e.g., see Fig. 7 and relate discussion in Peleg et al. (2015)).

Line 409: What is the relative humidity for the simulation that best agreed with RGM observations (the LWC in Fig. 6 is 1.08)? Is this in line with the nighttime relative humidity conditions observed on average at this site?

Answer:

Nighttime RH at the measurement site averaged 65%. At this RH and considering the level of air-pollution at the site we estimate that LWC could reach higher than 1.08 μg m⁻³ (e.g., see Fig. 5 in Liu, 2012 and Fig. 3 in Guo et al., 2015), and 5 μg m⁻³ can be considered as a realistic value. However, our approach was conservative, trying to provide a lower rate constant for the oxidation of GEM by NO₃. Nevertheless, we will evaluate the potential value of the uncertainties that are associated with the calculation of the rate constants and will include it in the discussion on their evaluated values.

Supplement, Sect. S4, Fig. S2: Which of the dry deposition velocities best simulate the conditions at this site given the dependency of dry deposition on surfaces?

Answer:

Unfortunately it is impossible to state which of the deposition velocities is most representative of the conditions at the measurement site, based on the currently available knowledge. Reported values for sub-urban areas fall into wide range (e.g., 0.03 ± 0.02 cm s⁻¹-1.52 ± 0.58 based on Zhang et al., 2009). We will use the reviewer suggestion to include the related uncertainty in the evaluated rate constants of GEM oxidation.

References:

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