

Interactive comment on “Measurement-based modeling of daytime and nighttime oxidation of atmospheric mercury” by Maor Gabay et al.

Anonymous Referee #1

Received and published: 14 March 2017

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

C1

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? 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? 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.

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? 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.

Lines 58-68: This section discusses only O₃ and OH. Are there any laboratory kinetics

C2

studies pointing out the uncertainties on GEM oxidation by Br and NO₃? If so, these studies should be discussed here as well.

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?

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

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?

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

C3

Line 155: The strong correlation between RGM and NO₃ doesn't necessarily imply GEM oxidation by NO₃. It's essential to eliminate other possibilities that can lead to similar RGM and NO₃ trends at night. Could the peak in RGM at night be due to the sampling of the free troposphere?

Line 159: The model assumes that O₃, OH, NO₃, and H₂O₂ are the only oxidants of GEM. I don't understand why the Hg reactions with Br and BrO are listed in Table S1.

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?

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).

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.

Figure 2: Observed RGM should be plotted here to compare model results with observations. Lines 262, Fig. 3: I'm not quite sure what is the significance of the gas-particle 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 NO₃+Hg⁰ reaction in the model?

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?

Line 338-340: Why were the k[OH+Hg⁰] increased to 6.5E-13 and 9E-13? Where are

C4

these numbers from? From Fig. a and b, it appears that increasing $k[\text{OH}+\text{HgO}]$ to these values overestimated the observed RGM. I was wondering why you didn't use the $k[\text{OH}+\text{HgO}]$ values calculated in the supplement. The lower rate constants might be able to reproduce the observed RGM.

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

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?

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

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

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?

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.

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

C5

LWC ranges to see if the simulations match up with the observations for different levels of LWC.

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?

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?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-39, 2017.

C6