Measurement-based modeling of daytime and nighttime oxidation of atmospheric mercury

Maor Gabay1, Mordechai Peleg2, Erick Fredj3, Eran Tas1*

1The Department of Soil and Water Sciences, The Robert H. Smith Faculty of Agriculture, Food and Environment, Hebrew University of Jerusalem, Rehovot, Israel
2Institute of Earth Sciences, Edmud Safra Campus, Givat Ram, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
3Department of Computer Science, Jerusalem College of Technology, Jerusalem 91160, Israel

*Correspondence to: Eran Tas, The Department of Soil and Water Sciences, The Robert H. Smith Faculty of Agriculture, Food and Environment, Hebrew University of Jerusalem, Rehovot, Israel.
eran.tas@mail.huji.ac.il.
Abstract. Accurate characterization of gaseous elemental mercury (GEM) chemical oxidation pathways and their kinetics is critically important for assessing the transfer of atmospheric mercury to bioaquatic systems. Recent comprehensive field measurements have suggested that the nitrate radical (NO$_3$) plays a role in efficient nighttime oxidation of GEM, and that the role of the hydroxyl radical (OH) as a GEM oxidant has been underestimated. We used the CAABA/MECCA chemical box model and additional kinetic calculations to analyze these measurement results, in order to investigate the nighttime and daytime oxidation of GEM. We assumed a second-order reaction for the NO$_3$ induced nighttime oxidation of GEM. Our analysis demonstrated that nighttime oxidation of GEM has to be included in the model to account for the measured variations in nighttime reactive gaseous mercury (RGM) concentration. A lower limit and best-fit rate constant for GEM nighttime oxidation are provided. To the best of our knowledge, this is the first time that a rate for nighttime oxidation of GEM has been determined based on field measurements. Our analysis further indicates that OH has a much more important role in GEM oxidation than commonly considered. A lower-limit rate constant for the OH–RGM reaction is provided.

1 Introduction

Over 90% of atmospheric mercury is in the form of gaseous elemental mercury (GEM) (Schroeder and Munthe, 1998). With a lifetime of 6 to 24 months, it is considered a global pollutant (Cole et al., 2013). GEM oxidation to Hg$^{2+}$ is associated with the formation of more reactive and soluble species, either in the gaseous phase (reactive gaseous mercury, or RGM) or as particulate matter (fine
particulate-bound mercury, or FPM). RGM and FPM are deposited from the atmosphere much more rapidly than GEM, by both dry and wet deposition.

Oxidation of GEM is therefore a critical stage in the process of transferring atmospheric mercury to aquatic systems, where it can be further converted into the highly toxic biocumulative methyl mercury (MeHg) (Schroeder and Munthe, 1998). Accurate characterization of GEM chemical oxidation pathways and their kinetics is therefore highly important in assessing the transfer of atmospheric mercury to bioaquatic systems. Even though many computer-modeling studies in recent years have focused on investigating the oxidation and deposition of GEM, our understanding of the related mechanisms is still far from complete (Subir et al., 2011). Uncertainty in mercury modeling arises from several sources (Ariya et al., 2009, 2015), including incomplete information on chemical reaction pathways and their kinetics (e.g., oxidation of GEM by NO$_3$; Peleg et al., 2015), poor characterization of removal and recycling via heterogeneous processes (e.g., reduction of Hg(II) by aqueous hydroperoxyl radical (HO$_2$); Lin and Pongprueksa, 2007), and removal via dry deposition (Bergan and Rodhe, 2001; Lin and Pongprueksa, 2007). Uncertainties are also associated with inaccurate mercury speciation (e.g., mercury oxide (HgO) speciation between the gas and particulate phases; Hedgecock et al., 2005; Jaffe et al., 2014; Lu and Schroeder, 2004).

A major source of uncertainty in simulating the GEM oxidation pathway is inaccuracy in oxidation-rate determinations. For instance, a sensitivity study by Bergan and Rodhe (2001) indicated that the rate constant suggested by Hall (1995) for GEM oxidation by ozone (O$_3$) is too slow to account for the major portion of GEM removal from the atmosphere. A different kinetics study, using the Pal and Ariya (2004b) O$_3$–GEM rate constant showed that the oxidation rate of GEM is too fast,
leading to unrealistically low GEM concentrations (Seigneur et al., 2006). Calvert and Lindberg (2005) pointed out that direct oxidation of GEM by O$_3$ is unlikely in the atmosphere, and HgO formation may occur via initial formation of HgO$_3$. Whereas a laboratory study by Sommar et al. (2001) suggested that the lifetime of GEM against oxidation by OH ranges from 4 to 7 months, other studies have suggested that GEM removal by OH is probably unimportant in the atmosphere (Calvert and Lindberg, 2005; Goodsite et al., 2004). These cardinal results reinforce the current uncertainty with respect to GEM oxidation kinetics, and the need for further study. Disagreements in evaluated oxidation rates are common across kinetics studies performed by different methods – experimental, theoretical calculations, or computerized global or detailed chemical models (e.g., the rate constant of GEM oxidation by OH; Bergan and Rodhe, 2001). Different experimental conditions may also cause differences in oxidation rates from one study to the next (e.g., Hall, 1995; Pal and Ariya, 2004b). Furthermore, in many cases, experimentally based determinations of oxidation rate are performed at much higher reactant concentrations and lower pressures than found in the atmosphere, leading to increased uncertainty when extrapolated to typical atmospheric conditions (Subir et al., 2011).

In the present study, we applied a chemical box model to study the nighttime and daytime pathways and oxidation rates of GEM based on recent field measurements performed by Peleg et al. (2015). Those field measurements included simultaneous NO$_3$ and speciated mercury quantification, which allowed reinforcing the assumption that NO$_3$ can significantly oxidize GEM as originally suggested by Platt and Heintz (1994) and Sommar et al. (1997). Peleg et al. (2015) further suggested underestimation, in previous studies, of daytime GEM oxidation by OH as compared to GEM oxidation by O$_3$. 
2 Methods

2.1 Field measurements

The model simulations were based on measurements performed in Jerusalem, Israel (31°47′N 35°13′E, 760 m above sea level) from 24 Jun to 2 Aug 2012. The measurements and their results are briefly discussed below; more detailed information can be found in Peleg et al. (2015). The measurement area can be characterized as an urban area under semiarid conditions, and the major source of air pollution is transportation emissions. Possible Hg pollution sources are two major power plants located some 80 km to the NW and 65 km to the SW. Note that no correlations were observed across the entire measurement periods between RGM concentration and other atmospheric chemical species (e.g., CO: $R^2 < 0.01$; $SO_4$: $R^2 < 0.01$; $SO_2$: $R^2 < 0.1$), or between RGM and meteorological parameters ($R^2 < 0.01$ 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). As shown previously, high NO$_3$ levels are formed in Jerusalem, driven by relatively strong photochemical activity (e.g., typical daylight O$_3$ levels are ~60 ppb; Peleg et al., 2015) and dry conditions (average 42% during the day and 65% at night; Asaf et al., 2009). Typical mercury levels in the area are 0.2 ppt, in agreement with typical rural and remote sites in the northern hemisphere (Valente et al., 2007). All instrumentation was situated on a building rooftop at the Hebrew University campus at Givat Ram. Measurements included quantification of GEM using
a Tekran model 2537B instrument (Tekran Inc., Toronto, Canada), and the same instrument was used
in conjunction with Tekran 1130 and 1135 instruments to quantify RGM and FPM, respectively. The
reported 5 min limit of detection (LOD) for the 2537B is <0.02 ng m\(^{-3}\), with some potential
reservations for RGM and FPM (Peleg et al., 2015). A long-path differential optical absorption
spectrometer (LP-DOAS; Platt, 1994; Platt and Heintz, 1994; Sigrist, 1994) was used to quantify NO\(_3\)
with an average LOD of 8.7 ± 5.2 ng m\(^{-3}\).

Trace gases, including carbon monoxide, sulfur dioxide, and ozone, were measured using
models 48i, 43i, and 49C, respectively (all from Thermo Environmental Instruments Inc., Waltham,
MA, USA), with manufacturer-reported LODs of 4.0 ppb, 2.0 ppb and 1.0 ppb, respectively. A
meteorological station (Met One Instruments, was situated on the same rooftop to measure basic
meteorological parameters (wind speed, wind direction, temperature, pressure, relative humidity
(RH)) with LODs of 0.5 m s\(^{-1}\), 5°, 0.4 K, 0.2 torr and 3%, respectively. Solar radiation data were
available for Jerusalem from the Israel Meteorological Service.

2.1.1 Field measurement-based kinetic calculations
The field measurement results were used to estimate the rate constants of GEM with OH
(k[OH+Hg\(_0\)]) and NO\(_3\) (k[NO\(_3\)+Hg\(_0\)]), based on 27 selected measurement days, as explained in more
detail in Sect. S1 of the Supplement. Note that these calculated rate constants may be specifically
valid for the specific research area. The calculations, as well as additional analyses (see Sect. 3.2 and
3.3), make use of OH concentrations. Because OH concentrations were not available for the
measurement site, a theoretical diurnal OH profile was constructed for the respective days, based on
the assumed correlation between OH concentration and UV intensity (Smith et al., 2006; von Glasow et al., 2002) and assuming that maximal OH concentration was 0.5 ppt, which is among the highest concentrations reported for semi-polluted areas (see Sect. S1 of the Supplement; Stone et al., 2012).

The diurnal OH concentration was then calculated accordingly for 7 Jul 2012 based on the measured UV intensity. The UV data were taken from a nearby weather station (Nayot, Jerusalem). Figure 1 presents the constructed diurnal profile of OH, as well as the average measured diurnal profiles of O₃ and RGM.

2.2 Model simulations

The CAABA/MECCA chemical box model (Sander et al., 2005, 2011) was used for the research analyses. CAABA/MECCA uses explicit chemical mechanisms of gas- and aqueous-phase reactions, as well as photochemical reactions and heterogeneous reactions for aerosols and clouds. Gas–aerosol partitioning is based on Henry's law, subjected to kinetic limitations (Sander and Crutzen, 1996). Formation and scavenging of aerosols are both included in the MECCA module. The chemical mechanism accounts for species containing O, H, C, N, S, Cl, Br, I and Hg, with a total of 664 equations (186 gas phase, 266 aqueous phase, 154 heterogeneous, 58 photolysis). The default chemical mechanism of MECCA is available at http://www.mecca.messy-interface.org/. MECCA was used to study the oxidation of GEM in the troposphere by Obrist et al. (2011), Tas et al. (2012), and Xie et al. (2008). The oxidation pathways of mercury are shown in Tables S1–4 (see Sect. S2 of
the Supplement). The reaction of GEM with NO$_3$ was added to the chemical mechanism, taking into account the study by Sommar et al. (1997), and based on preliminary simulations (not shown).

The possibility of direct oxidation of GEM by NO$_3$, however, is in contrast to recent computational results presented by Dibble et al. (2012), which indicated that the bond energy of Hg-ONO$_2$ is far too low to support direct oxidation by NO$_3$. However, recent findings by Peleg et al. (2015) suggest that NO$_3$ is directly involved in GEM oxidation. Therefore, while NO$_3$ may not act as initiator of the GEM oxidation, it may play a role in a secondary addition to the first step of Hg oxidation (XHg$^+$. Because the mechanism by which NO$_3$ leads to GEM oxidation is currently unknown, and taking into account the relatively strong correlation between RGM and NO$_3$ observed by Peleg et al. (2015), as a first approximation we incorporated the nighttime oxidation of GEM by NO$_3$ as a second-order rate according to the reaction:

$$Hg^+ + NO_3 \rightarrow HgO + NO_2$$

(R1)

We assumed that O$_3$, OH, NO$_3$, and H$_2$O$_2$ are the only GEM oxidants. While gas-phase bromine atom (Br) may be the main viable GEM oxidant on a global scale, particularly over marine regions and the free troposphere (Holmes et al., 2010), we assumed that its contribution to GEM oxidation at the measurement site is relatively small. This assumption was based on previous measurements performed at the Dead Sea basin, which indicated that no RGM is present when BrO levels decrease to below the detection limit of the DOAS setup (~3 ppt; Obrist et al., 2011), combined with the fact that no BrO was observed during DOAS measurements performed in Jerusalem (unpublished results). Furthermore, Wang et al. (2016) indicated a lifetime of a few days for GEM with BrO concentrations of a few parts per trillion, whereas the lifetime of GEM based on our study is much
shorter, reinforcing the notion that Br-induced oxidation of GEM does not play a significant role at the measurement site.

The specific model simulations used for this study are summarized in Table 1. For the BASE simulation, we used the model with one aerosol mode, representing sulfate aerosols. We configured the model to account for a sulfate aerosol concentration of 8 µg m$^{-3}$, based on a previous study in the region (Andreae et al., 2002; Formenti et al., 2001; Wanger et al., 2000). Note, however, that the low FPM concentrations observed at the measurement site suggest that only a relatively small portion of the mercury species partitioned into the aerosol phase (Peleg et al., 2015). The relatively small effect of aerosols in the studied area may result from the relatively low RH in the region. Simulations were configured to represent typical meteorological conditions in the measurement area for temperature (293 K), daytime boundary layer height (1000 m) and RH (42%). The GEM level was kept constant at 210 ppq (the average measured concentration). A realistic representation of the photochemistry in the model is highly important considering its direct impact on the daytime GEM oxidants OH and O$_3$, and the impact of O$_3$ concentrations on nighttime NO$_3$ concentrations (Asaf et al., 2010). Therefore, special attention was given to ensure realistic representation of photochemistry in the model by verifying that NO$_3$, NO, NO$_2$ and O$_3$ concentrations agree with the corresponding measured concentrations and volatile organic compounds (VOC) concentrations agree with typical suburban concentrations (Finlayson-Pitts and Pitts Jr, 1999; see Figs. S3–S5 of the Supplement). This was achieved by using adequate fixed values for the fluxes of NO, NO$_2$ and VOCs as boundary conditions for the model during the simulations. Note that the maximum daytime simulated BASE O$_3$ reached about 83 ppb, in agreement with the average over the corresponding measured values.
BASE was used with the rate constant for the oxidation of GEM by \( \text{O}_3 \) \( (k[\text{O}_3+\text{Hg}^0]) \) suggested by Hall (1995). The PAL-ARIYA simulation used the \( k[\text{O}_3+\text{Hg}^0] \) suggested by Pal and Ariya (2004b). A set of simulations, HI-PHOT-CHM, used a daily maximal \( \text{O}_3 \) concentration of \( \sim 120 \) ppb, instead of \( \sim 83 \) ppb. The set of simulations FIT used different combinations of rate constants for GEM oxidation, based on the literature and measured RGM (Sect. S3 of the Supplement). The set of simulations DRYDEP used dry deposition rates ranging from 0.1–5 \( \text{cm s}^{-1} \) (Sect. S4 of the Supplement).

Preliminary simulations indicated that while the GEM oxidation rates used in the model lead to reasonable agreement of simulated HgO with the measured RGM for a single simulation day, the day-to-day accumulation of RGM is overestimated by the model. We attribute this to underestimation of nighttime HgO-removal processes, possibly due to lack of processes in the model accounting for the uptake of RGM and/or FPM by wet surfaces other than aerosols. Instead of parameterizing these removal processes into the model, we accounted for their effect on the daytime analyses by using a \( k[\text{NO}_3+\text{Hg}^0] \) value of 5.00E-17 \( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \), which is lower than the value suggested by us (2.0E-15–3.0E-15 \( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \); see Sect. 3.3). Exceptional were the simulations PAL-ARIYA* and BASE*, which were run with \( k[\text{NO}_3+\text{Hg}^0] \) of 2.00E-15 and 3.00E-15, respectively (see Table 1), and used to explore nighttime GEM oxidation.
3 Results and discussion

3.1 Model evaluation

In this section, we evaluate the model's ability to reproduce the observations, and test the sensitivity of the model configuration to removal processes by aerosols, using the BASE and PAL-ARIYA simulations. Analysis of the sensitivity to dry deposition is presented in Sect. S4 of the Supplement.

3.1.1 GEM oxidation and reactive mercury partitioning

In the marine boundary layer and the upper troposphere, GEM oxidation by reactive halogen species, and in particular Br (Holmes et al., 2010; Lin et al., 2004), is considered a major sink for GEM on a global scale. We do not expect to have substantial concentrations of halogens at the measurement site due to its remoteness from the sea (see Sect. 2.2). Therefore, we did not include oxidation reactions of GEM by reactive halogen species in the model. Previous studies have indicated that HgO can be considered the main product of GEM reactions with OH, O₃, NO₃ and H₂O₂ (Pal and Ariya, 2004a, 2004b; Sommar et al., 2001). However, several studies have suggested that some of the produced HgO might be considered Hg(s) due to its low vapor pressure and its fast uptake by aerosols (Hedgecock et al., 2005; Lu and Schroeder, 2004; Schroeder and Munthe, 1998), or due to rapid heterogeneous-induced oxidation mechanisms (e.g., see Stephens et al., 2012), which we address in Sect. 3.1.2. Note that while our model includes GEM oxidation by H₂O₂, its role is not discussed in
the paper, considering its low average and maximum contribution to GEM oxidation: 0.64% and
6.58%, and 2.43% and 4.62%, during the day and at night, respectively.

Figure 1 shows high nighttime variability in the average measured diurnal profile of RGM,
with no clear pattern, reflecting the fact that nighttime oxidants NO$_3$ and O$_3$ do not show any clear
temporal pattern (Peleg et al., 2015). During the day, however, three distinct time periods, associated
with three local maxima in RGM concentrations, can be observed (see Fig. 1). The local maximum
in RGM level in the morning (~0700 h) could be due to vaporization of deposited mercury from wet
surfaces and/or from aerosols (green color in Fig. 1). The rapid increase in RGM between ~0800 and
1100 h is probably due to the corresponding increase in OH and/or O$_3$. However, the subsequent
decrease in RGM between ~1200 and 1400 h followed by a later increase in RGM between ~1400
and 1600 h suggests that the higher peak at ~1100 h occurs predominantly due to oxidation of OH
(yellow color in Fig. 1), while the smaller peak at ~1600 h is predominantly due to oxidation by O$_3$
(red color in Fig. 1).

Figure 2 presents the diurnal concentrations of both RGM and the major GEM oxidants O$_3$,
OH, and NO$_3$, for the BASE and PAL-ARIYA simulations, separated into daytime and nighttime
periods. The BASE and PAL-ARIYA simulations showed a daytime HgO peak, which can be related
mainly to oxidation of GEM by O$_3$ and OH. The nighttime HgO concentrations are dictated by the
prescribed $k[NO_3+Hg^0]$ used in the model to reproduce the average measured nighttime RGM
concentrations (see Sect. 3.3). Note that PAL-ARIYA and BASE were performed with a significantly
lower $k[NO_3+Hg^0]$ than the value evaluated in this study, to compensate for underestimation of
nighttime HgO-removal processes in our model, and avoid day-to-day accumulation of HgO (see
Sect. 2.2). These simulations are used to study only daytime GEM oxidation, and we used different simulations to explore nighttime GEM oxidation (Sect. 3.3). The much lower HgO and FPM daytime peaks obtained by the BASE and PAL-ARIYA simulations, compared to the measurements, suggests that the daytime oxidation rates used by these simulations were significantly underestimated relative to the actual rates. For PAL-ARIYA, O₃ was higher than BASE by a factor of ~3.6, leading to a RGM peak at around ~1500 h, about 4 h later than the measured daytime RGM peak.

Figure 3 shows peak values of RGM and FPM to compare the measured and simulated RGM and FPM daytime and nighttime partitioning for the BASE and PAL-ARIYA (daytime) and BASE* and PAL-ARIYA* (nighttime) simulations. The measured daytime and nighttime RGM and FPM peaks refer to the average, over their highest daytime and nighttime concentrations, for days on which clear peaks in RGM concentrations were observed, with no association with changes in RH during the day (27 days) or night (19 days).

According to Fig. 3, daytime partitioning between RGM and FPM was 62% and 38% for BASE and 71% and 29% for PAL-ARIYA, as compared with the measurements: 86% and 14%, respectively. The corresponding nighttime partitioning, using k[NO₃ + Hg⁰]] of 2.00E-15 and 3.00E-15 cm³ molecule⁻¹ s⁻¹ for PAL-ARIYA and BASE, respectively (see Sect. 3.3), was similar for PAL-ARIYA (84% and 16%), BASE (87% and 13%) and the measurements (89% and 11%). Overall, Fig. 3 indicates relatively good agreement between simulated and measured gas-particle partitioning of reactive mercury for both nighttime (<6%) and daytime (<25%). However, considering additional removal processes for reactive mercury which are not taken into account by the model (Sect. 3.1.2) and the potential underestimation of the measured FPM (e.g. Feddersen et al., 2012), Fig. 3 may only
provide a rough understanding of the gas-particle partitioning of reactive mercury. Hence, the combined effect of GEM oxidation rates and RGM removal by aerosols is studied in Sect. 3.2 and 3.3, on the basis of magnitude and time of appearance of the measured RGM peak.

Figure 3 shows that prescribing the nighttime RGM using $k[\text{NO}_3+\text{Hg}_0] = 2.00\text{E}-15$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for PAL-ARIYA and $k[\text{NO}_3+\text{Hg}_0] = 3.00\text{E}-15$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for BASE led to relatively good agreement with the measured RGM of 114% and 112%, respectively. The simulated daytime RGM level remained low for PAL-ARIYA (42%) and BASE (12%) relative to the average measured value. This suggests that the daytime oxidation in the model was underestimated, as will be further discussed in Sect. 3.1.2 and 3.2, together with heterogeneous cycling and removal processes.

3.1.2 Aqueous-phase processes

Aqueous-phase chemistry plays a significant role in the removal and recycling of atmospheric mercury species (Amos et al., 2012; Ariya et al., 2015). HgO is highly soluble in water (Henry's Law constant of $2.7 \times 10^{12}$ M atm$^{-1}$), and thus readily dissolves in aqueous aerosols and clouds (Selin et al., 2007). While Fig. 3 demonstrates that inclusion of gas-aerosol exchange in the model can reasonably explain the measured partitioning into RGM and FPM, there are other processes that may have occurred during the measurements that are not well represented by the model, such as RGM uptake by wet surfaces and nucleation. Removal by wet surfaces is expected to be more efficient during the night when RH increases, and may explain the apparent underestimation of RGM removal in the model (see Sect. 2.2). These removal processes are not taken into account by the model and...
therefore, RGM removal may be underestimated, which may result in underestimation of the modeled GEM oxidation rate, as discussed in Sect. 3.2 and 3.3. Considering the dry conditions at the measurement site, and the relatively reasonable agreement of the partitioned reactive mercury into gas and particulate phases (Fig. 3), we do not expect the absence of such processes in our model to lead to a significant underestimation of GEM oxidation rate. In this study, we explore the role of aerosols in RGM removal and recycling on the basis of RGM formation rate and timing of appearance. First, we explore the overall potential impact of aerosols on oxidation product concentration.

Simulation NOARSL was used to investigate the influence of aerosols on GEM oxidation (see Table 1). NOARSL is similar to the BASE simulation, but lacks aerosol chemistry. The NOARSL RGM concentrations were higher by about 50 ppq than the measured RGM, which required an increase in the dry deposition rate of RGM to 5 cm s\(^{-1}\), as compared with 0.5 cm s\(^{-1}\) (Mason and Sheu, 2002) in the BASE scenario, to obtain the measured RGM concentrations. This suggests that when aerosol activity is not included in the model, either the simulated removal processes in the gas phase are too slow or the GEM oxidation rates are too high, or both, to account for RGM removal.

Overall, Sect. 3.1 demonstrates potentially high sensitivity of the evaluated GEM oxidation rate to heterogeneous processes, including aerosol loading during the day, and apparently, additional removal processes at night. Therefore, in the following we compare the simulated HgO with the measured RGM under various combinations of aerosol loadings and GEM oxidation rates. The evaluation of the rate constants is based on both magnitude and timing of appearance of HgO.
Ultimately, the evaluated simulated GEM oxidation rate is compared with the rate constants that were calculated directly from the measurements.

### 3.2 Daytime oxidation

To investigate the efficiency of O$_3$ and OH in GEM oxidation, we used different combinations of their rate constant with GEM, as well as different realistic photochemical activities and liquid water contents (LWCs). Note that the different LWC values represent different integrated available volumes for gas–aerosol partitioning and aerosol aqueous-phase reactions, which were indicated as potentially having a large effect on our results (see Sect. 3.1.2).

Figure 4 shows the impact of using different combinations of $k[\text{OH+Hg}^0]$ and $k[\text{O}_3+\text{Hg}^0]$ (panels a and b) and LWCs (panels c and d) on daytime HgO concentrations. The measured average diurnal RGM profile and the simulated concentrations of O$_3$ and OH obtained by PAL-ARIYA and BASE are also presented in panels a and b, respectively. Note that the dashed line inside the box in the upper panels indicates the average measured daytime RGM maximum (5.88 ppq; see Fig. 3) and the time period during which it occurred (~0900–1300 h; see Fig. 1). The vertical dimension of the box in the upper panels marks the corresponding standard deviation of the mean of the daytime measured RGM maxima (0.53 ppq). Figures 4a and 4b indicate poor agreement of simulated HgO with measured RGM for both PAL-ARIYA and BASE in terms of concentrations. In two simulations with higher photochemical activity (HI-PHOT-CHM; see in Table 1), employing significantly higher O$_3$ and OH, the simulated HgO values are significantly lower than the measured RGM (Figs. 4a and
4b). In all of these simulations, the maximum simulated HgO occurs at around 1500 h, significantly later than the peak of the measured RGM, and well timed with the afternoon RGM peak which we attribute to oxidation by ozone. Figures 4a and 4b show that the simulated OH peak is much closer in time to the measured noontime RGM peak than both the simulated and measured ozone peaks. This implies that $k[OH + Hg^0]$ is underestimated in our model relative to $k[O_3 + Hg^0]$. Indeed, increasing $k[OH + Hg^0]$ to 6.5 E-13 and 9.0 E-13 cm$^3$ molecule$^{-1}$ s$^{-1}$ for PAL-ARIYA and BASE, respectively, resulted in better agreement between measured and simulated RGM in terms of both magnitude and timing of maximum occurrence (Figs. 4a and 4b).

Figures 4c and 4d investigate the impact of aerosol LWC on simulated HgO concentrations. It is shown that a higher LWC is associated with lower HgO concentrations and earlier peaks. These two effects are caused by more efficient uptake of HgO by aerosols when applying a higher LWC. Applying a LWC value of 5 μg m$^{-3}$ combined with $k[OH+Hg^0]$ of 1.5E-12 cm$^3$ molecule$^{-1}$ s$^{-1}$ (Fig. 4a) and 1.8E-12 cm$^3$ molecule$^{-1}$ s$^{-1}$ (Fig. 4b) for PAL-ARIYA and BASE scenarios, respectively, the simulated HgO shows relatively good agreement with the simulated RGM in terms of both magnitude (5.88 ppb) and timing of peak occurrence (~0900–1300 h). This suggests that if a higher aerosol LWC occurs at the measurement site than the default value used in the present study (1.08 μg m$^{-3}$), the $k[OH + Hg^0]$ may be much higher than the values suggested above of 9E-13 and 6.5E-13 cm$^3$ molecule$^{-1}$ s$^{-1}$ for $k[OH + Hg^0]$. LWC lower than 1.08 μg m$^{-3}$ is associated with late appearance of the simulated HgO daytime peak (see Figs. 4c and 4d), making it unrealistic. Hence, we conclude that based on our analyses, a value of 6.5E-13 cm$^3$ molecule$^{-1}$ s$^{-1}$ can be considered a lower-limit rate constant for $k[OH + Hg^0]$, even if the default LWC of 1.08 μg m$^{-3}$ is incorrect. We suggest that this
value can be considered a lower limit because the derived daytime HgO peak only marginally fits with the average daytime peak in terms of timing (Fig. 4a). In addition, we expect that the used OH concentrations are either equal to or higher than the actual OH at the measurement site (see Sect. 2.1). Note that this suggested lower-limit rate constant \( k[OH + Hg^0] = 6.5E-13 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) is larger by a factor of ~7 than the conventional value suggested by Sommar et al. (2001).

The \( k[OH + Hg^0] \) 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 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, using the Hall (1995) and Pal and Ariya (2004b) \( k[O_3 + Hg^0] \) 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 \( k[OH + Hg^0] \). Note, however, that these calculated \( k[OH + Hg^0] \) 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 \( k[OH + Hg^0] \) by the kinetic calculations.

Figure 5 presents an additional set of simulations like those shown in Fig. 4, but with constant \( k[OH+Hg] \), and different aerosol LWCs, \( O_3 \) concentrations and \( k[O_3 + Hg0] \) values according to PAL–ARIYA and BASE simulations. The daytime HgO concentrations are presented for PAL–ARIYA and BASE using different aerosol LWCs (Fig. 5a) and the same \( k[OH + Hg^0] \) (9.52E-14 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; Sommar et al., 2001) combined with average and higher \( O_3 \) concentrations (see HI-PHOT-CHM in Table 1) and varying values for \( k[O_3 + Hg^0] \) (Fig. 5b). Note that the dashed line inside the box in the two panels of Fig. 5 indicate the average of the measured daytime RGM maximum levels (5.88 ppq; see Fig. 3) and the time during which they occurred (~0900 h–1300 h; see Fig. 1). The vertical
dimension of the box in the upper panels marks the corresponding standard deviation of the mean of the measured daytime RGM maxima (0.53 ppq).

Using $k[O_3+Hg^0]$ according to Hall (1995) yields HgO concentrations similar to those obtained when $k[O_3+Hg^0] = 0$. PAL-ARIYA provides significantly higher HgO, but it is still much lower than the compatible RGM concentrations (Fig. 5b). The simulated daytime HgO peak is similar to the compatible measured RGM concentrations only for simulations using the highest $k[O_3+Hg^0]$ value of 1.8E-18 cm$^3$ molecule$^{-1}$ s$^{-1}$, about 1.5 orders of magnitude larger than Pal and Ariya's (2004b) rate constant. Moreover, the timing of the daytime peak, in this case, occurs later than actually observed. We checked whether a combination of higher $k[O_3+Hg^0]$ (5E-18 cm$^3$ molecule$^{-1}$ s$^{-1}$) and relatively high LWC (5 μg m$^{-3}$) would result in a more realistic HgO profile. The resulting maximum HgO concentrations were similar to the compatible measured RGM maximum concentration, but still peaked several hours later than the measured HgO (Fig. 5a).

Overall, lowering LWC resulted in a large delay in the simulated HgO peak compared with the compatible measured RGM, while increasing LWC resulted in an HgO value that is too low. Figure 5 therefore indicates that the observed RGM concentrations cannot be reproduced by the model when using a combination of different higher $k[O_3+Hg^0]$ values and LWCs, and that the underestimation of the daytime HgO formation is predominantly due to using too low a value for $k[OH+Hg^0]$, rather than to inaccuracies in $k[O_3+Hg^0]$. Overall, Figs. 4 and 5 suggest that reasonable reproduction of the measured RGM can only be achieved by significantly reducing the commonly used $k[O_3+Hg^0]$ with respect to $k[OH+Hg^0]$ (see also Sect. S3 of the Supplement).
3.3 Nighttime oxidation

There is no published information available regarding the oxidation rate of GEM by NO$_3$ except for the upper limit of 4E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ suggested by Sommar et al. (1997). To investigate GEM oxidation by NO$_3$, simulations were performed using a k[OH+Hg$^0$] of 9.52E-14 cm$^3$ molecule$^{-1}$ s$^{-1}$ as proposed by Sommar et al. (2001), both k[O$_3$+Hg$^0$] values from Hall (1995) and Pal and Ariya (2004b), and varying LWC values. The simulation day used the BASE* conditions, representing a day with average O$_3$ concentrations (peaking at ~83 ppb) and a nighttime peak NO$_3$ of ~78 ppt. The NO$_3$ peak value represents the average over measured NO$_3$ peaks at night, with relatively high peak NO$_3$ 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. The vertical dimension of the shaded rectangle marks the corresponding standard deviation of the mean of these RGM peaks (0.95 ppq).

Best agreement with the measured RGM concentrations was obtained when a value of 2.00E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ and 3.00E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ was used with the k[O$_3$+Hg$^0$] values from Pal and Ariya (2004b) and Hall (1995), respectively. This suggests that k[NO$_3$+Hg$^0$] = 2E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ can be considered the lower limit for the oxidation rate of Hg$^0$ involving NO$_3$. The calculated k[NO$_3$+Hg$^0$] was 2.8 (±0.5) E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ using Hall's k[O$_3$+Hg$^0$], and 1.9 (±0.5) E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ using Pal and Ariya's k[O$_3$+Hg$^0$], with errors representing the standard deviations of the mean.
Figure 6 further indicates that nighttime HgO concentrations span an order of magnitude for LWCs ranging from 0.5–5 µg m\(^{-3}\), implying that changes in RH and aerosol concentration could significantly impact this estimated lower rate limit for k[NO\(_3\)+Hg\(^0\)]. Nevertheless, considering that our analyses indicate underestimation of RGM-removal processes during the night in our model, we do not expect the nighttime LWC at the site to be lower than that used by the default PAL-ARIYA simulation (i.e., 1.08 µg m\(^{-3}\)). Therefore, we suggest that because heterogeneous processes can significantly impact RGM removal, 2E-15 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) may be considered the lower limit for the oxidation rate of Hg\(^0\) involving NO\(_3\).

4 Summary and conclusions

4.1 Daytime oxidation

The oxidation rates proposed for GEM by ozone span 22 orders of magnitude, ranging from E-40 to E-18 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (Subir et al., 2011). In the present study, we chose two rate constants at the high end of the scale: 3.11E-20 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) as proposed by Hall (1995), and 7.5E-19 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) from Pal and Ariya (2004b), which are the most commonly used values in GEM oxidation modeling (Subir et al., 2011). Our measurement-based modeling showed that neither of these rate constants can reproduce the measured daytime and nighttime GEM oxidation rates. Best agreement with measured results, in terms of both magnitude and timing, were obtained using a k[OH+Hg\(^0\)] of at least 6.5-9E-13 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Based on our analyses, we suggest that this
value, which is higher by a factor of at least 7 than the rate constant suggested by Sommar et al. (2001), should be considered the lower limit rate for the oxidation of Hg\(^0\) by OH. Our analyses further suggest that the actual rate for this process is probably higher, considering the timing of the appearance of the simulated HgO peak compared with the measured RGM. The two k[O\(_3\)+Hg\(^0\)] values tested, 3.11E-20 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) and 7.5E-19 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), seem to overestimate the actual k[O\(_3\)+Hg\(^0\)], in agreement with Calvert and Lindberg (2005). It is possible, however, that O\(_3\) plays a significant role in GEM oxidation via heterogeneous processes, as suggested by previous studies (e.g., Stephens et al., 2012), such that the overall oxidation rate of GEM by O\(_3\) was underestimated in our study. Nevertheless, our simulations demonstrate the unlikelihood of the strong noontime RGM peak being explained by a higher GEM oxidation rate by O\(_3\). Based on our analyses, the only explanation for this peak is a higher oxidation rate by OH than is commonly used.

The calculated k[OH+Hg\(^0\)] based on the measurement results was found to be 2.8(±0.5)E-13 and 1.1(±0.5)E-13 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) using the k[O\(_3\)+Hg\(^0\)] values from Hall (1995) and Pal and Ariya (2004b), respectively. These values, which agree with the theoretical 3.2 E-13 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (Goodsite et al., 2004), represent lower limits, because they do not take into account any RGM-removal processes (see Sect. 3.2). The calculated value agrees with the theoretical rate constant of 3.2 E-13 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (Goodsite et al., 2004), rather than the rate constant of 9–12E-14 cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) or lower, which was suggested based on previous experimental studies (Bauer et al., 2003; Pal and Ariya, 2004a; Sommar et al., 2001) and is commonly used in models (Subir et al., 2011).
4.2 Nighttime oxidation

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 4E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ (Sommar et al., 1997).

Peleg et al. (2015) used measured data to show the correlation between NO$_3$ and RGM, suggesting that NO$_3$ plays an important role in nighttime GEM oxidation. As far as we know, this is the first paper to provide an estimation for nighttime NO$_3$-induced GEM oxidation based on field measurements. Using these measurements, our modeling analyses indicated a lower-limit rate constant of about 2.0E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ for NO$_3$, and 3.0E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ for GEM oxidation by NO$_3$ together with the k[O$_3$+Hg$^0$] values of 3.11E-20 and 7.5E-19 cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively.

The calculated k[NO$_3$+Hg$^0$] based directly on the measurement results was found to be 2.8(±0.5)E-15 and 1.9(±0.5)E-15 cm$^3$ molecule$^{-1}$ s$^{-1}$ using the k[O$_3$+Hg$^0$] values from Hall (1995) and from Pal and Ariya (2004b), respectively.

The present study indicates that nighttime oxidation of GEM by NO$_3$ must be taken into account in GEM oxidation calculations, and that the importance of OH as a GEM oxidant is probably higher than previously assumed. However, the impact of the relatively rapid oxidation of GEM by NO$_3$ and OH indicated in the present study may vary in regions with different conditions, indicating the need for future studies of GEM oxidation. In particular, the present study was performed under relatively dry conditions. Under the influence of high RH levels (>50%), lower concentrations of NO$_3$ and OH are expected, together with higher recycling and scavenging of oxidized mercury products.
due to the increase in aerosol activity. Therefore, this study emphasizes the need for future study of GEM-oxidation pathways using detailed heterogeneous models.

5. Data availability

The data of this paper are available upon request. Please contact the corresponding author Eran Tas (eran.tas@mail.huji.ac.il).

Acknowledgements: We wish to thank deeply Menachem Luria for motivating us to publish this research. We thank Menachem Luria, Valeri Matveev, Daniel Obrist and Chris Moore for their contribution to obtaining the measurement results which were used for the present study. E.T. holds the Joseph H. and Belle R. Braun Senior Lectureship in Agriculture.

References


Ten-year trends of atmospheric mercury in the high Arctic compared to Canadian sub-Arctic and mid-latitude sites, Atmos. Chem. Phys., 13, 1535-1545, 2013.


Table 1. Key to different simulation types.

<table>
<thead>
<tr>
<th>Simulation/ name</th>
<th>$K [O_3+Hg^0]$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$K [OH+Hg^0]$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>$K [NO_3+Hg^0]$ [cm$^3$ molecule$^{-1}$ s$^{-1}$]</th>
<th>Sulfate aerosol LWC [µg m$^{-3}$]</th>
<th>Dry deposition [cm s$^{-1}$]</th>
<th>$O_3$ daily maximum [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE</td>
<td>3.11E-20$^a$</td>
<td>9.52E-14$^b$</td>
<td>5.00E-17</td>
<td>1.08</td>
<td>0.5$^c$</td>
<td>83</td>
</tr>
<tr>
<td>BASE*$^*$</td>
<td>3.11E-20</td>
<td>9.52E-14</td>
<td>3.00E-15</td>
<td>1.08</td>
<td>0.5</td>
<td>83</td>
</tr>
<tr>
<td>NOARSL</td>
<td>3.11E-20</td>
<td>9.52E-14</td>
<td>5.00E-17</td>
<td>Non</td>
<td>0.5</td>
<td>83</td>
</tr>
<tr>
<td>PAL-ARIYA</td>
<td>7.50E-19$^d$</td>
<td>9.52E-14</td>
<td>5.00E-17</td>
<td>1.08</td>
<td>0.5</td>
<td>83</td>
</tr>
<tr>
<td>PAL-ARIYA*$^*$</td>
<td>7.50E-19</td>
<td>9.52E-14</td>
<td>2.00E-15</td>
<td>1.08</td>
<td>0.5</td>
<td>83</td>
</tr>
<tr>
<td>Liquid water content (LWC)</td>
<td>3.11E-20 – 5E-18</td>
<td>9.52E-14 – 1.8E-12</td>
<td>5.00E-17 ,2.00E-15</td>
<td>LWC= 0.5-5</td>
<td>LWC</td>
<td>3.11E-20 – 5E-18</td>
</tr>
<tr>
<td>DRYDEP</td>
<td>3.11E-20</td>
<td>9.52E-14</td>
<td>-</td>
<td>1.08</td>
<td>0.1-5</td>
<td>83</td>
</tr>
<tr>
<td>HI-PHOT-CHM</td>
<td>3.11E-20, 7.5E-19</td>
<td>9.52E-14</td>
<td>5.00E-17 (day), 2.00E-15 (night)</td>
<td>1.08</td>
<td>0.5</td>
<td>120</td>
</tr>
<tr>
<td>FIT</td>
<td>3.11E-20, 7.50E-19, 1.80E-18</td>
<td>9.52E-14, 9.00E-13, 6.50E-13</td>
<td>1.60E-15, 2.30E-15,1.50E-16</td>
<td>1.08</td>
<td>0.5</td>
<td>83</td>
</tr>
</tbody>
</table>

$^b$Sommar et al. (2001)
$^c$Mason and Sheu (2002).
Figure 1. Ozone and RGM hourly average measured concentrations and OH constructed concentration. The vertical lines represent the standard deviation of the mean for the measured $O_3$ and RGM concentrations. The shaded areas indicate nighttime. The highest average measured daytime RGM levels coincide with the constructed OH peak, rather than with the $O_3$ peak. The average hourly daytime RGM concentrations are marked by three different colors, indicating three distinct time periods, 0600–0800 h (green), 0800–1400 h (yellow), 1400–2000 h (red), which were apparently controlled by different processes (see Sect. 3.1.1).
Figure 2. Simulated diurnal profile of major GEM oxidants and oxidation products used in the model. Presented are the diurnal profiles of the GEM oxidants O₃, OH and NO₃ used in the model, multiplied by a factor of 1E+8, 5E+13 and 1E+11, respectively, together with the diurnal profiles of the oxidation products RGM and FPM, multiplied by a factor of 1E+15 and 1E+16, respectively. The concentrations are presented for both the BASE simulation (upper panel) and PAL-ARIYA simulation (lower panel). GEM was kept constant at 210 ppq (not shown here).
Figure 3. Concentration and partitioning of the oxidized Hg. Average measured (M) maximum daytime and nighttime levels of FPM and RGM are presented versus the compatible simulated concentrations, which were obtained by BASE (B)/BASE* (B*) and PAL-ARIYA (P&A)/PAL-ARIYA* (P&A*).
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 15 February 2017
© Author(s) 2017. CC-BY 3.0 License.
Figure 4. HgO concentration as a function of GEM oxidation by OH and aerosol LWC. (a) HgO concentrations obtained using different $k[OH+Hg^0]$ values with Pal and Ariya's (2004b) $k[O_3+Hg^0]$, LWC = 5 μg m$^{-3}$, and $[O_3] = 120$ ppb (HI-PHOT-CHM), when indicated. Black squares represent PAL-ARIYA scenario (see Table 1). (b) HgO concentrations obtained using different $k[OH+Hg^0]$ values with Hall's (1995) $k[O_3+Hg^0]$, LWC = 5 μg m$^{-3}$ and $[O_3] = 120$ ppb (HI-PHOT-CHM), when indicated. The filled boxes represent the BASE scenario (see Table 1). The dashed line inside the box in the upper panels indicates the average measured daytime RGM maximum and the time during which it occurred (~0900–1300 h; see Fig. 1). The vertical dimension of the box in the upper panels marks the corresponding standard deviation of the mean of the daytime measured RGM maximum. The lower panels present daytime HgO concentrations obtained using different LWC values (0.50–5.00 μg m$^{-3}$) and $k[O_3+Hg^0]$ based on Pal and Ariya (2004b) (c) and on Hall (1995) $k[O_3+Hg^0]$ (d). The shaded areas represent the timing of the maximal daylight RGM levels observed from the average diurnal profile of RGM (~0900–1300 h; see Fig. 1).
Figure 5. Dependence of HgO diurnal profile on oxidation by OH, O₃ and LWC. The figure shows the HgO concentration obtained using $k_{[OH+Hg^0]} = 9.52E-14$ cm³ molecule⁻¹ s⁻¹ and different $k_{[O_3+Hg^0]}$ values and O₃ concentrations (a) and different $k_{[O_3+Hg^0]}$ values and aerosol LWCs (b). The dashed line inside the box indicates the average measured daytime RGM maximum level (5.88 ppq; see Fig. 3) and the time during which it occurred (~0900–1300 h; see Fig. 1). The vertical dimension of the box marks the corresponding standard deviation of the mean (0.53 ppq) of the measured daytime RGM maximum.
Figure 6. Simulated HgO concentration as a function of GEM oxidation rate by NO₃, O₃ concentration and aerosol LWC. The width of the rectangles represents the time span of the maximal nighttime RGM (all night; see Fig. 1), while the dashed line inside the rectangles denotes the average measured nighttime RGM maxima (6.17 ppq) for selected nights (see text). The vertical dimension of the rectangles represents the corresponding standard deviation of the mean over the measured RGM peaks (0.95 ppq). The black squares represent BASE* and PAL–ARIYA* simulations, respectively (see Table 1).