LETTER

Is oxidation of atmospheric mercury controlled by different mechanisms in the polluted continental boundary layer vs. remote marine boundary layer?

Maor Gabay¹, Shira Raveh-Rubin ², Mordechai Peleg ³, Erick Fredj ⁴ and Eran Tas ¹ ²

¹ The Department of Soil and Water Sciences, The Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot, Israel
² Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel
³ Institute of Earth Sciences, Edmond J. Safra Campus, Givat Ram, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
⁴ Department of Computer Science, Jerusalem College of Technology, Jerusalem 91160, Israel

E-mail: eran.tas@mail.huji.ac.il

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Abstract
Deposition of atmospheric mercury is of global concern, primarily due to health effects associated with efficient bioaccumulation of mercury in marine food webs. Although oxidation of gaseous elemental mercury (GEM), the major fraction of atmospheric mercury, is a critical stage in regulating atmospheric mercury deposition efficiency, this oxidation is currently not well-characterized, limiting modeling-based assessments of mercury in the environment. Based on a previous study, we hypothesized that the oxidation of GEM is predominantly controlled by multistep bromine- and chlorine-induced oxidation (MBCO) in the remote marine boundary layer (RMBL), and by photochemical smog oxidants, primarily ozone (O₃) and hydroxyl radical (OH), in the polluted continental boundary layer (PCBL). To test this hypothesis, we used the following analyses: (i) application of a newly developed criterion to evaluate the gaseous oxidized mercury (GOM)–O₃ association based on previous studies in the RMBL and PCBL; (ii) measurement-based box simulations of GEM oxidation in the RMBL and at a PCBL site; and (iii) measurement-based analysis of photochemical oxidation vs. other processes which potentially influence GOM. Our model simulations indicated that the MBCO mechanism can reproduce GOM levels in the RMBL, but not in the PCBL. Our data analysis suggested the important role of photochemical smog oxidants in GEM oxidation in the PCBL, potentially masked by the effect of relative humidity and entrainment of free tropospheric air.

1. Introduction
Atmospheric mercury consists mostly (>90%) of the relatively inert gaseous elemental mercury (GEM), associated with a lifetime of 6–24 months (Schroeder and Munthe 1998, Cole et al 2013). The environmental impact of atmospheric mercury stems from its deposition from the atmosphere as a major source of mercury, even in remote aquatic systems (Mason et al 1994, Fitzgerald et al 1998). Methyl mercury (CH₃Hg) in both terrestrial and aquatic ecosystems is of global concern, and has been widely reviewed for its effects on both human health and the ecosystem (Clarkson and Magos 2006, Grandjean et al 2010, Driscoll et al 2013). Due to its bioaccumulation, consumption of seafood is the predominant pathway for most human exposure to CH₃Hg (Mergler et al 2007, Driscoll et al 2013, Kim et al 2016).

Oxidation of GEM to Hg²⁺ is a critical stage in the transport of atmospheric mercury into the bio-aquatic and terrestrial ecosystem, because Hg²⁺ is associated with much more reactive and soluble species than GEM, both in the gaseous phase (gaseous oxidized mercury [GOM]) and as particulate matter (particulate-bound mercury [PBM]). Due to their shorter lifetimes compared to GEM, GOM and PBM are associated with a much higher deposition velocity than GEM (Munthe et al 2009). Therefore, accurate
characterization of chemical GEM-oxidation pathways and their kinetics is highly important in assessing the transfer of atmospheric mercury to biogeochemical systems. Although numerous studies in recent decades have focused on investigating the kinetics of GEM oxidation, our understanding of the related mechanisms is still far from complete (Subir et al 2011), resulting in large uncertainty in mercury modeling (see Ariya et al 2009, 2015 for review).

These large uncertainties in atmospheric mercury oxidation are related not only to the rate constants of related reactions, but also to the chemical pathways themselves (Si and Ariya 2018). While early modeling of GEM oxidation in the troposphere accounted for a high impact of photochemical smog by considering ozone (O$_3$) and hydroxyl radical (OH) as major GEM oxidants (Seigneur et al 1994, Lin and Pongprueksa 2007), more recent modeling studies indicate a major role for the bromine atom (Br) in GEM oxidation on a global scale, and particularly in the marine boundary layer and free troposphere (Lin et al 2004, 2006, Holmes et al 2006, 2010). Recent thermodynamics-based studies have suggested that the resulting intermediate products are too thermally unstable to enable oxidation by OH and O$_3$ under atmospheric conditions (Goodsite et al 2004, Dibble et al 2012). Similarly, Dibble et al (2012) indicated that nitrate (NO$_3$) cannot initiate GEM oxidation in the atmosphere, which seems to contradict previous evidence supporting the important role of NO$_3$ in nighttime GEM oxidation (Mao et al 2008, 2012). Instead, theoretical and experimental studies (Dibble et al 2012, Sun et al 2016) suggested multistep oxidation of GEM according to

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Hg^0 + X + M \rightarrow Hg^1X + M \quad (1)
\]

\[
Hg^1X + M + Y \rightarrow Hg^{1+}XY + M \quad (2)
\]

where $X$ is either Br or a chlorine atom (Cl), $Y$ is a second-stage $Hg^1$ oxidant and $M$ is an air molecule. Dibble et al (2012) suggested that radicals such as nitrogen dioxide (NO$_2$), hydroperoxyl (HO$_2$), bromine oxide (BrO) and chlorine oxide (ClO) can act as $Hg^1X$ oxidants. The rate of reaction 2 is expected to be predominantly controlled by NO$_2$ in more polluted regions, and possibly HO$_2$ in more remote regions, considering the apparently relatively small influence of the nature of $Y$, compared to that of its concentration, on the reaction rate (Dibble et al 2012, Jiao and Dibble 2017). Regional modeling over the northeastern United States by Ye et al (2018) indicated relatively good seasonal and diurnal agreement for GEM oxidation and produced GOM and PBM when applied with the updated multistep bromine-induced mechanism (Ye et al 2016), excluding GEM oxidation by OH and O$_3$.

Nevertheless, as discussed in Si and Ariya (2018), there are indications that in the lower troposphere, particularly in the boundary layer, GEM oxidation is more complex and its initiation may predominantly occur by OH, O$_3$ and other oxidants, as suggested by earlier studies, instead, or in addition to oxidation by halogen radicals. For instance, an investigation of the composition of measured oxidized mercury by Gustin et al (2015) pointed to GEM oxidants other than Br and BrO, particularly for polluted continental air masses. Measurement-based simulations using an updated state-of-the-art chemical mechanism by Ye et al (2016) demonstrated that while GEM oxidation is controlled by Br and BrO in the marine boundary layer, at coastal and inland sites, GEM oxidation is dominated by O$_3$ and OH, and predominantly initiated by hydrogen peroxide during the night. Global and regional measurement-based state-of-the-art simulations by Travnikov et al (2017) also pointed to OH playing an important role in GEM oxidation in the continental boundary layer. Moreover, field measurements performed at a continental semiarid site, where exceptionally high NO$_3$ concentrations were frequently observed during the night (Peleg et al 2015), indicated nighttime involvement of NO$_3$ in GEM oxidation. Model simulations of these data further indicated the involvement of OH and O$_3$ in daytime GEM oxidation (Gabay et al 2017).

Here we hypothesize that different mechanisms dominate GEM oxidation in the polluted continental boundary layer (PCBL) compared to other parts of the atmosphere which are richer in Br and are less polluted, such as the free troposphere and remote marine boundary layer (RMBL). This hypothesis is supported by the apparent enhancement of GEM oxidation by OH and O$_3$ in the presence of aerosols, as discussed by Ariya et al (2009), Rutter et al (2012) and Subir et al (2012), considering that available aerosol surface area tends to be higher under anthropogenic air pollution than in the remote atmosphere (Finlayson-Pitts and Pitts 2000). The notion that aerosols play a significant role in GEM oxidation by OH and O$_3$ is supported by experimental studies in a chamber indicating higher-than-expected efficiency of this oxidation, where the chamber walls apparently increased the available surface area for the reaction (Hall 1995, Pal and Ariya 2004, Hedgecock et al 2005, Seigneur et al 2006).

We test our hypothesis by analyzing (i) reported field-observation data in both the RMBL and the PCBL to evaluate GEM oxidation by photochemical smog oxidants, using a newly developed criterion based on the GOM–O$_3$ correlation vs. O$_3$ concentration and (ii) field measurements at a PCBL site, under elevated photochemical pollution and aerosol loading, as a case study, using box model simulation and correlation analysis. Special focus was given to identifying the effects of processes that potentially occur concurrently with oxidation-induced GOM formation at this site, including horizontal GOM advection and GOM transport from the free troposphere via intrusion and boundary layer expansion.
2. Methods

For our analyses, we used measured data that has been reported in the literature for the RMBL, PCBL or polluted marine boundary layer (PMBL), as well as model simulations and reanalysis, as described in the following.

2.1. Model simulations

The CAABA/MECCA chemical box model (Sander et al 2005, 2011) was used for the numerical simulations. 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, subject to kinetic limitations (Sander and Crutzen 1996). The chemical mechanism accounts for the O – H – C – N – S – Cl – Br – I – Hg chemical mechanism, with a total of 952 equations (330 gas phase, 366 aqueous phase, 162 heterogeneous, 94 photolysis). The default chemical mechanism of MECCA is available at: www.mecca.messy-interface.org/. MECCA has been used to study the oxidation of GEM in the troposphere (Xie et al 2008, Obrist et al 2011, Tas et al 2012), and we updated the chemical mechanism according to the multistep chemical mechanism for GEM oxidation proposed by Horowitz et al (2017) (HMS; see tables S2(stacks.iop.org/ERL/15/064026/mmedia), S3). All simulations applied a temperature of 293 K and boundary layer height of 1000 m, with specific conditions as described below and in table 1.

2.1.1. Remote marine boundary layer simulation

The RMBL simulation was performed to represent GEM oxidation in the RMBL. The RMBL simulation used coarse soluble and accumulation soluble aerosol modes with the MECCA default aerosol composition and liquid water content (IWC) for the RMBL. The used initial and boundary conditions ensured relatively low photochemical activity (average and maximum daytime peak O$_3$ was 14.2 ppbv and 16.4 ppbv, respectively), as is typical for the RMBL (see section S1; Laurier 2003, Laurier and Mason 2007), and agreement of the reactive bromine and chlorine species mixing ratios with the corresponding typical mixing ratios, based on observations in the marine boundary layer (Sander et al 2003, Saiz-Lopez and Von Glasow 2012).

2.1.2. Polluted continental boundary layer simulations

The PCBL simulation was based on field measurements carried out in Jerusalem, Israel (JRSLM; 31°47’N 35°13’E, 760 m above sea level) from 24 Jun to 2 Aug 2012. The measurements and their results are described in detail by Peleg et al (2015). Briefly, they included quantification of GEM, GOM and PBM (using Tekran Instrument analyzers, models 2537B, 1130 and 1135, Toronto, Canada; the reported 5 min limit of detection [LOD] for model 2537B is <0.02 ng m$^{-3}$). Strict quality-assurance and quality-control procedures were applied to all measured mercury data based on the standards discussed in Steffen et al (2012) and by the Atmospheric Mercury Network (AMNet) (NADP 2011), as described in more detail in Peleg et al (2015). Recently, reservations have been raised regarding the efficiency of denuder and filter trapping of Hg(II) species, particularly in correlation with relative humidity (RH) (Huang and Gustin 2015). We expect that such an effect of RH on our measurements will be relatively small considering the relatively low RH at the JRSLM site in the summer. Complementary measurements were carried out for carbon monoxide, sulfur dioxide, nitrogen oxides (NO$_x$ = [NO] + [NO$_2$]) and O$_3$ (using models 48i, 43i, 42i and 49 C, respectively; all from Thermo Environmental Instruments Inc. Waltham, MA, USA; LODs of 4.0 ppm, 2.0 ppb, 0.4 ppb and 1.0 ppb, respectively), wind speed, wind direction, temperature, pressure, RH and global solar radiation (GSR) (using Met One Instruments, Grant Pass OR, USA; LODs of 0.5 m s$^{-1}$, 5°, 0.4 K, 0.2 torr, 3%, and 50 W m$^{-2}$, respectively).

The measurement area can be characterized as a suburban area under semiarid conditions, with the major source of local air pollution from transportation emissions. The area is exposed to relatively elevated regional photochemical pollution (daytime average and hourly average O$_3$ peaks were 79 ppbv and 85 ppbv, respectively) and high loading of sulfate aerosols, typically ~8 µg m$^{-3}$ (Wagner et al 2000, Formenti et al 2001, Andreason et al 2002). Possible mercury pollution sources are two major power plants located about 80 km to the NW and 65 km to the SW. Average GEM levels at the measurement site were 1.75 ng m$^{-3}$, in agreement with typical rural and remote sites in the northern hemisphere (Valente et al 2007).

Initial and boundary conditions in MECCA were set to adequately represent photochemical conditions, based on onsite field measurements (Gabay et al 2017). The PCBL-BASE simulation used coarse soluble and accumulation soluble aerosols, while Br and Cl aerosol composition, as well as IWC, were based on field measurements by Andreason et al (2002) in Sde Boker, the Negev desert, Israel. Sulfate aerosol number density was set to represent the high concentration in the area (Wagner et al 2000, Formenti et al 2001, Andreason et al 2002). Considering that these data provided no more than a realistic representation of the aerosol composition and concentrations, additional simulations were performed to investigate potential inaccuracies in the aerosol setup, which may affect GEM oxidation. Specifically, as presented in table 1, three simulations were performed to individually test the effects of lower total IWC as well as enrichment in gaseous BrO$_x$ (Br + BrO) and ClO$_x$ (Cl + ClO) potentially resulting from
underestimation of aerosol Br and Cl concentrations in PCBL-BASE. Simulations PCBL-H-Br and PCBL-H-Cl applied higher Br$_2$ and Cl$_2$ fluxes, respectively, to reach the maximum of the mean daily JRSLM GOM profile. Simulation PCBL-L-LWC applied aerosol LWC that was lower by a factor of 10 compared to PCBL-BASE, keeping the aerosol number concentration unchanged.

2.2. Processing of field-measured data using atmospheric reanalysis

Measured GOM can be influenced by air intrusions from the middle and upper troposphere (Lyman and Jaffe 2012, Shah et al 2016), or other forms of large-scale advection (UNECO 2010, Wu et al 2010). Therefore, dates with such influences had to be filtered out for both correlation- and modeling-based analysis of the field measurements in JRSLM. This analysis was carried out in two steps. First, dates with intrusions from the free troposphere were determined by a systematic backward trajectory analysis based on the European Centre for Medium-range Weather Forecasts (ECMWF) ERA5 reanalyzed wind field data (Hersbach and Dee 2016), using the Lagrangian Analysis Tool LAGRANTO 2.0 (Sprenger and Wernli 2015). ERA5 data are available at an hourly temporal resolution for 137 vertical levels, and are interpolated to a horizontal grid of 0.5° by 0.5°. For every hour of the study period, we computed 72-h backward air-particle trajectories from 35.13°E, 31.47°N from all available models’ vertical levels, with pressure within the range of 1050–850 hPa. Based on the trajectory data, we considered dates with free-tropospheric intrusion to be the ones for which at least one air-particle trajectory originated from a pressure lower than 600 hPa, 72 h prior to its arrival at JRSLM. Furthermore, we excluded measured data 12 h prior to and following each intrusion event, to account for unresolved mixing processes. Note that this 12-h interval was found to be the minimal interval that ensures no effect on GOM by intrusion, based on correlation analysis between GEM and GOM (see section S3).

In the second step, we filtered out days with hourly-based coefficients of determination ($r^2$) $\geq 0.1$ for the regression of GEM vs. GOM, because we found these data to be potentially influenced by advection of GOM (section S3). Application of these two screening criteria resulted in an hourly-based daily $r^2 < 0.07$ for GEM vs. GOM, for all remaining measurement days. Overall, 26 out of 35 measurement days were excluded (section S3). In the following, the resulting GOM dataset and the unfiltered data are termed filtered-GOM and unfiltered-GOM, respectively.

Boundary layer height (BLH) data were obtained from ERA5, where BLH is determined as the lowest height at which the bulk Richardson number reaches a critical value of 0.25 (ECMWF 2016). Data were available at 1-h time resolution during the measurements at JRSLM, and were used for correlation analysis (section 3.3).

3. Results and discussion

3.1. GOM–O$_3$ correlation in polluted vs. remote boundary layer

To address our main hypothesis that different chemical pathways play a dominant role in GEM oxidation in the RMBL vs. PCBL (see section 1), we evaluated the correlation of GOM–O$_3$ with O$_3$ mixing ratios, based on a literature review (see table S1), for various sites which can be classified as either polluted or remote, as presented in figure 1. Note that we considered a site as remote only if its mean daily O$_3$ maximum was lower than 30 ppbv. Due to nonuniformity of the used datasets, and depending on the data availability from each source, the GOM–O$_3$ correlation was evaluated based on either hourly mean or daily maximum reported values of O$_3$ and GOM. In both cases, the correlation is presented vs. the daily maximum O$_3$ mixing ratios, which were used to represent the photochemical pollution level at each specific site (figure 1; see section S1 for more information).

Figure 1 demonstrates that the Pearson correlation coefficient ($r$) obtained for the GOM–O$_3$ correlation can be divided into two different sections: RMBL, with a strong GOM–O$_3$ anti-correlation, and either marine or continental photochemically polluted sites with a more variable (~0–0.8), neutral to substantially positive GOM–O$_3$ correlation (see also table S1). A positive GOM–O$_3$ correlation indicates

| Simulation   | Br  [pptv] | Cl  [pptv] | O$_3$ [ppbv] | BrO [pptv] | ClO [pptv] | GOM [pg m$^{-3}$] | LWC (CS) [µg m$^{-3}$] | LWC (AS) [µg m$^{-3}$] |
|--------------|------------|------------|--------------|------------|------------|-------------------|-------------------------|-------------------------|
| PCBL-BASE    | 4.5E-3     | 2.5E-6     | 90           | 0.11       | 1.1E-3     | 1.8               | 9.9                     | 27                      |
| PCBL-H-Br    | 5.3E-2     | 5.7E-5     | 70           | 1.3        | 2.2E-2     | 30                | 9.9                     | 27                      |
| PCBL-H-Cl    | 5.1E-3     | 2.4E-3     | 71           | 0.12       | 7.6E-1     | 30                | 9.9                     | 27                      |
| PCBL-L-LWC   | 6.1E-3     | 7.0E-6     | 75           | 0.10       | 3.6E-3     | 3.4               | 0.99                    | 2.7                     |
| RMBL         | 7.0E-2     | 2.7E-4     | 16           | 0.94       | 9.8E-2     | 37                | 1.1                     | 31                      |

Table 1. Key to the model simulations. Presented are daily maximum mixing ratios of key species and LWC, individually for coarse soluble (CS) and accumulation soluble (AS) aerosols for the different model simulations (see sections 2.1 and S2 for additional information on the model simulations).
dominant GEM oxidation by photochemical smog oxidants, potentially facilitated by particles’ surface area in the more polluted areas (PaI and Ariya 2004, Seigneur et al 2006, Ariya et al 2015, Horowitz et al 2017). The anti-correlation between GOM and O3 in the RMBL suggests that GEM oxidation under these conditions is predominantly controlled by Br, which simultaneously leads to a reduction in O3 (Laurier 2003, Laurier and Mason 2007). The larger variations in the GOM–O3 correlation for PMBL than for PCBL, as inferred from figure 1(a), may result from the higher relative impact of Br in the PMBL.

Note that the fundamental differences in the GOM–O3 correlation for the different location types can be affected by several factors that are not directly accounted for by our analysis. Such factors include technical limitations due to lack of data availability, including OH concentrations, intrusion of O3 and GOM from above the boundary layer (Selin et al 2008, Lyman and Jaffe 2012), and varying efficiency of GEM oxidation by OH and O3 across the different sites. The latter can result, for instance, from varying aerosol surface area across the different sites, considering the role that aerosols have been proposed to play in GEM oxidation by OH and O3 based on theoretical and experimental studies (Hall 1995, PaI and Ariya 2004, Seigneur et al 2006, Ariya et al 2015, Horowitz et al 2017), as well as field measurements (Hedgecock et al 2005). Note that the relatively strong correlation between the GOM–O3 correlation and O3 mixing ratios obtained for the hourly-based analysis \((r = 0.70, P = 0.017; \text{figure 1(b)})\) reinforces the notion that the GOM–O3 correlation results primarily from photochemical smog-induced oxidation, rather than GOM transport.

3.2. Model simulations: remote marine boundary layer vs. a polluted continental boundary layer measurement site

Our model simulations further aimed to shed light on variations in GEM oxidation between the RMBL and PCBL, as presented in figure 2. Figure 2 indicates that while the HMS mechanism can reproduce the reported measured RMBL GOM, it cannot reproduce the measured JRSLM filtered-GOM, consistent with previous measurement-based modeling (Gabay et al 2017). Although PCBL-BASE is based on gas-phase and aerosol-composition observations (section 2.1), we investigated the impact of a potentially inaccurate representation of LWC, as well as gaseous Br and Cl loadings in our model, using simulations PCBL-H-Br and PCBL-H-Cl to reach the mean maximum JRSLM GOM and simulation PCBL-L-LWC, respectively. LWC can significantly affect GOM levels via gas–aerosol transfer (Ye et al 2016, Gabay et al 2017).

PCBL-H-Br and PCBL-H-Cl simulated enrichment of the atmosphere by Br and Cl, respectively, above the level that is expected by equilibrium of the aerosols with the surrounding air. Such enrichment could result, for instance, through GOM transport from the free troposphere via intrusion and boundary layer expansion. These processes may result in Br and Cl enrichment in case that their concentrations are higher in the free troposphere than in the boundary layer, as supported for reactive bromine species (Wang et al 2015, Schmidt et al 2016, Badia et al 2019) and more speculatively for reactive chlorine species (Wilmouth et al 2018, Wang et al 2019).

Br was higher by a factor of ~11 in PCBL-H-Br than in PCBL-BASE. The maximum BrO mixing ratio that was used for PCBL-BASE was higher by a factor...
of 13 than 0.1 pptv (see table 1), which has been proposed to be the maximum mixing ratio over the continental boundary layer (Yang et al. 2005). Hence, it is not likely that the underestimation of GOM by PCBL-BASE predominantly results from inaccurate representation of Br for this simulation. Note further, for instance, that Br\textsubscript{2} in PCBL-H-Br was higher by a factor of ~5.5 than the maximal continental Br\textsubscript{2} measured under strong anthropogenic pollution at a coastal site (Finley and Saltzman 2008).

Similarly, considering that the observed JRSLM GOM was reproduced using Cl or ClO for PCBL-H-Cl that was higher by factors of ~1000 and ~800, respectively, than in PCBL-BASE, it is suggested that underestimation of GOM by PCBL-BASE does not predominantly result from inaccurate representation of gaseous reactive chlorine species in this simulation. Note further, for instance, that Cl\textsubscript{2} for PCBL-H-Cl was ~400 times larger than that measured in southeast Texas, with a daytime Cl\textsubscript{2} source of up to 35 ppt h\textsuperscript{−1} (Faxon et al. 2015).

PCBL-L-LWC applied a constant LWC value, lower by a factor of ten than that used by PCBL-BASE. Thus, PCBL-L-LWC does not provide insight into the effect of changing LWC during the daytime, which could result from a daytime decrease in RH and subsequent enhanced transition of reactive mercury from the aerosol to the gas phase. The fact, however, that maximum GOM was higher for PCBL-L-LWC compared to PCBL-BASE by only a factor of ~1.9 suggests that the underestimation of GOM by PCBL-BASE does not result from overestimation of LWC. Furthermore, while [GOM]/[PBM] for PCBL-BASE was smaller by a factor of 9.9 compared to PCBL-L-LWC, it was still higher than [GOM]/[PBM] observed in JRSLM, by a factor of 7.3. The relatively low simulated [PBM] compared to the observations might result from processes that took place during our measurements, but were not well-represented in our model. Such processes might include rapid uptake of HgO by aerosols due to its low vapor pressure (Schroeder and Munthe 1998, Lu and Schroeder 2004, Hedgecock et al. 2005), following HgO formation via heterogeneous-induced oxidation processes (e.g. see Stephens et al. 2012). The role of RH in affecting GOM is further discussed in section 3.3.3.

3.3. GEM oxidation by photochemical smog oxidants vs. other processes affecting GOM in a polluted continental boundary layer site

While the underestimation of JRSLM GOM by our model simulation suggests the involvement of photochemical smog oxidants (section 3.2) in GEM oxidation, probably induced primarily by O\textsubscript{3} and OH during the daytime (see section 1), it is currently not possible to adequately simulate GEM oxidation by O\textsubscript{3}, OH and NO\textsubscript{3} considering the large uncertainties surrounding the related mechanisms and rate constants. Alternatively, in this section, we used the field measurements to investigate the association of filtered-GOM with other factors that potentially affect GOM concentration. Such factors might include: advection from anthropogenic sources (UNECE 2010, Wu et al. 2010), intrusion from the upper atmosphere (Lyman and Jaffe 2012, Shah et al. 2016), entrainment of GOM from above the boundary layer following its expansion, and reduction in RH, which would result in enhanced release of oxidized mercury from the aerosol to the gas phase, according to Henry’s law. To exclude advection and intrusion from our analyses, we used the filtered-GOM (see section 2.2), and explored its association with BLH, RH, O\textsubscript{3} and global solar radiation, GSR. Note that GSR was used as a proxy for OH concentrations,

Figure 2. Simulated GOM using the HMS mechanism for RMBL vs. PCBL. (a) Simulated O\textsubscript{3} and GOM curves are presented vs. whisker plots for the RMBL. Circles and triangles represent reported mean maximal GOM and O\textsubscript{3} mixing ratios, respectively, in the RMBL, while corresponding field measurement sites are indicated (see table S1 for additional information). (b) Diurnal profile of JRSLM filtered-GOM (see section 2.2) vs. PCBL-BASE and PCBL-L-LWC (see table 1 for simulation abbreviations). Error bars represent the standard deviation of the mean. Dark shading represents nighttime hours.
assuming a correlation between OH concentration and UV intensity. Although OH has been generally reported to strongly correlate with GSR in both the marine and continental boundary layers (Platt et al. 1988, von Glasow et al. 2002, Smith et al. 2006, Acker et al. 2006, Ren et al. 2006a, 2006b), in the latter, a weaker correlation may occur due to interaction with nitrogen oxides as well as volatile organic compounds (e.g. Creasey et al. 2001, Ren et al. 2003). Our detailed model simulations (Gabay et al. 2017) revealed a strong correlation between simulated OH and measured GSR ($r^2 = 0.99$), with a temporal shift of about 33 min between their peaks (see section S4). Hence, we strongly believe that GSR can be used as a reliable proxy for OH mixing ratios during the measurements at the JRSLM site. While HO$_2$ also tends to strongly correlate with GSR, it is not expected to significantly affect GEM-oxidation rate in polluted regions (section 1, Dibble et al. 2012, Jiao and Dibble 2017).

Figure 3 presents the average diurnal profiles of filtered-GOM and unfiltered-GOM together with the corresponding average diurnal profiles of BLH, RH, O$_3$ and GSR (figure 3(a)) and a principal component analysis (Wold et al. 1987) of filtered-GOM with BLH, RH, O$_3$ and GSR, as well as wind direction and GEM (figure 3(b); see section S5). Table 2 complements figure 3 by presenting the hourly daytime correlations and P-values for filtered-GOM and unfiltered-GOM with all of the parameters presented in figure 3(b). Large differences were seen between the unfiltered-GOM and filtered-GOM (figure 3(a)). Higher levels for the former during the day, except when filtered-GOM peaked, emphasize that the peak of filtered-GOM is not significantly influenced by either intrusion or advection. The relatively small difference between filtered-GOM and unfiltered-GOM during the night further supports the notion that the strong correlation between NO$_3$ and GOM, as presented by Peleg et al. (2015) for the same measured data, is not significantly affected by intrusion from the upper atmosphere, reinforcing the role of NO$_3$ in GEM oxidation.

Figure 3(a) shows that the daytime increase in both filtered-GOM and unfiltered-GOM is accompanied by a daytime increase in GSR, BLH and O$_3$ and a decrease in RH, which makes it difficult to identify mechanistic associations between each of these four parameters and filtered-GOM. The timing of the O$_3$ and GSR peaks may indicate that filtered-GOM is controlled by both OH and O$_3$, with varying contributions of each of the oxidants with time, and a maximum combined contribution between ~1100 and 1400 h (figure 3(a)). If the HMS mechanism dominantly affected GEM oxidation in JRSLM, NO$_2$ would be a much more effective oxidant of Hg$^0$ than HO$_2$ due to the relatively polluted conditions studied here (section 1; Dibble et al. 2012, Jiao and Dibble 2017). However, facilitated by a strong photolytic rate, NO$_2$ tends to be at a minimum around noontime, suggesting that GEM-oxidation rate is not limited by its mixing ratios.

Figure 3(b) and table S4 suggest that the investigated variables are predominantly controlled by two main components, seemingly oxidation-related processes (component 1, 62.1%) and to a lesser extent, horizontal advection-related processes (component 2, 29%). Figure 3(b) indicates a small association between filtered-GOM and advection-related processes, as reinforced by the weak correlations between filtered-GOM and wind direction, as well as filtered-GOM and GEM (table 2). The principal component analysis further suggests that GOM oxidation is indirectly controlled by BLH and RH (figure 3(b), table S4). The BLH diurnal profile peaked later than that of the filtered-GOM (indicated by the blue rectangle in figure 3(a)), suggesting that even if simultaneous entrainment of GOM and O$_3$ from above the planetary boundary layer occurred, the GOM–O$_3$ correlation is not predominantly affected by entrainment. Hence, while the strong association between BLH and O$_3$ (figure 3(b)) suggests entrainment of O$_3$ from above the boundary layer, this process probably did not play a major role in the GOM–O$_3$ correlation. This suggests that the apparently underestimated oxidation rate of GEM by the HMS mechanism for JRSLM (section 3.2) cannot be explained by changes in BLH which were not accounted for by the simulations, supporting the notion that the GOM–O$_3$ correlation is predominantly caused by O$_3$ and/or OH oxidation.

Yet, figure 3(b) and table 2 further suggest a stronger association of filtered-GOM with RH and/or GSR ($r^2 = 0.84; P < 0.0001$), than with BLH ($r^2 = 0.47; P < 0.01$) or O$_3$ ($r^2 = 0.50; P < 0.005$). The

| Filter         | Hourly mean correlation | $r^2$ | P     |
|----------------|-------------------------|-------|-------|
| Unfiltered-GOM | O$_3$                   | 0.095 | 0.28  |
|                | RH                      | 0.73  | 0.0001*|
|                | GSR                     | 0.72  | 0.0001*|
|                | BLH                     | 0.10  | 0.26  |
|                | WDD                     | 0.33  | 0.031*|
|                | GEM                     | 0.39  | 0.016*|
| Filtered-GOM   | O$_3$                   | 0.50  | 0.0048*|
|                | RH                      | 0.84  | <0.0001*|
|                | GSR                     | 0.84  | <0.0001*|
|                | BLH                     | 0.47  | 0.0071*|
|                | WDD                     | 0.011 | 0.72  |
|                | GEM                     | 0.066 | 0.37  |

*Statistically significant at $P < 0.005$. Statistically significant values are in bold.
Figure 3. Association of GOM with photochemical smog oxidants and other factors. (a) Average diurnal profile of filtered-GOM (black; filtered for intrusion and advection, see section 2.2) and corresponding \( \text{O}_3 \), GSR (used as a proxy for \( \text{OH} \)), RH and BLH, during JRSLM measurements. Unfiltered-GOM (gray) is also presented. Error bars represent the standard deviation of the mean. Gray and blue rectangles indicate the duration of the maximum daytime filtered-GOM mixing ratios and BLH, respectively. (b) Principal component analysis for filtered-GOM (see more information in section S5). Values in brackets are the daytime hourly-based coefficients of determination (\( r^2 \)) with filtered-GOM. *Statistically significant (\( P < 0.005 \)) values. Note that the BLH and \( \text{O}_3 \) arrows overlap.

relatively strong daytime anti-correlation between RH and GSR (e.g. figure 3(a)) makes it difficult to separate their effects on GOM levels. Nevertheless, the fact that daytime measured PBM levels in JRSLM were lower, on average, by about a factor of 7 than the corresponding GOM (Peleg et al 2015) points to a relatively minor impact of gas-particle partitioning on GOM concentration, supporting a significant role for \( \text{OH} \), indirectly represented here by GSR, in GEM oxidation in JRSLM. Furthermore, the limited contribution of the gas-particle partitioning of reactive mercury to the GOM levels in JRSLM is also supported by our model simulations.

4. Summary and conclusions

The main objective of this study was to investigate whether, in contrast to the RMBL, GEM oxidation in the PCBL is predominantly controlled by photochemical smog oxidants. Our literature review-based analysis indicated an opposite trend in the correlation of \( \text{O}_3 \) with GOM for the RMBL compared to both PCBL and PMBL, with a significant association between \( \text{O}_3 \) and GOM for the latter two. This implies a dominant role for photochemical smog oxidants in GEM oxidation under photochemical pollution in both the marine and continental boundary layers. Model simulations further supported the notion that while the HMS mechanism can account for observed GOM in the RMBL, it is not likely to account for GOM levels in JRSLM. Aerosol–gas GOM transfer induced by daytime reduction in RH until around noontime is also not a probable reason for the underestimated simulated GOM for JRSLM, considering the relatively small measured [PBM]/[GOM] ratio. In addition, the PCBL-L-LWC simulation showed that the underestimation of GOM in the PCBL-BASE simulation cannot be explained by inaccurate LWC representation in the model. The strong increase in filtered-GOM around noon therefore points to the role of \( \text{OH} \) in GEM oxidation. While planetary boundary layer expansion affected the GOM–\( \text{O}_3 \) correlation, our analysis indicates that the association between \( \text{O}_3 \) and GOM is primarily controlled by direct oxidation, rather than by boundary layer expansion. Overall, these findings support a dominant role of \( \text{O}_3 \) and \( \text{OH} \) in GEM oxidation in the polluted boundary layer. The analyses further reinforce the involvement of nighttime NO\(_3\) in GEM oxidation. Considering that according to quantum mechanics calculations, direct oxidation of GEM by \( \text{OH} \), \( \text{O}_3 \) or NO\(_3\) is not likely, further study on indirect oxidation of GEM by these species, possibly involving surface reactions, is warranted.

The study further indicates that processes other than direct GEM oxidation can potentially largely affect GOM level and its correlations with \( \text{O}_3 \) and \( \text{OH} \). Such processes include GOM intrusion from the upper atmosphere, GOM advection, gas-particle partitioning of reactive mercury, and GOM as well as GEM oxidants entrainment to the boundary layer, via its expansion. Hence, future field measurement-based analyses of GEM oxidation should take these processes into account.
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Data availability

The data that support the findings of this study are available upon request from the authors.

ORCID iDs

Shira Raveh-Rubin https://orcid.org/0000-0001-6244-8693
Eran Tas https://orcid.org/0000-0002-1570-4241

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