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Understanding mercury oxidation and air–snow exchange on the East Antarctic Plateau: a modeling study

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Abstract. Distinct diurnal and seasonal variations of mercury (Hg) have been observed in near-surface air at Concordia Station on the East Antarctic Plateau, but the processes controlling these characteristics are not well understood. Here, we use a box model to interpret the Hg$^0$ (gaseous elemental mercury) measurements in this year 2013. The model includes atmospheric Hg$^0$ oxidation (by OH, O$_3$, or bromine), surface snow Hg$^{II}$ (oxidized mercury) reduction, and air–snow exchange, and is driven by meteorological fields from a regional climate model. The simulations suggest that a photochemically driven mercury diurnal cycle occurs at the air–snow interface in austral summer. The fast oxidation of Hg$^0$ in summer may be provided by a two-step bromine-initiated scheme, which is favored by low temperature and high nitrogen oxides at Concordia. The summertime diurnal variations of Hg$^0$ (peaking during daytime) may be confined within several tens of meters above the snow surface and affected by changing mixed layer depths. Snow resublimation of Hg$^0$ is mainly driven by photoreduction of snow Hg$^{II}$ in summer. Intermittent warming events and a hypothesized reduction of Hg$^{II}$ occurring in snow in the dark may be important processes controlling the mercury variations in the non-summer period, although their relative importance is uncertain. The Br-initiated oxidation of Hg$^0$ is expected to be slower at Summit Station in Greenland than at Concordia (due to their difference in temperature and levels of nitrogen oxides and ozone), which may contribute to the observed differences in the summertime diurnal variations of Hg$^0$ between these two polar inland stations.

1 Introduction

Mercury (Hg) is an environmental concern due to its health effects on humans and wildlife (Mergler et al., 2007). This trace element undergoes long-range transport in the atmosphere and is readily cycled at the Earth’s surfaces (Selin, 2009), and thus even the remote Antarctic Plateau, a vast (about $5 \times 10^6$ km$^2$) and elevated (about 3 km above sea level) region of snow-covered ice, receives significant mercury inputs (Dommergue et al., 2010).

Over the past decade, field studies have investigated mercury in air and/or snow at a few inland Antarctic stations, i.e., Concordia Station (Dome C, 75$^\circ$ S, 123$^\circ$ E), Dome Argus (80$^\circ$ S, 77$^\circ$ E), Dome Fuji (77$^\circ$ S, 40$^\circ$ E), and the South Pole (90$^\circ$ S), as well as along several transects on the plateau (Brooks et al., 2008; Dommergue et al., 2012; Han et al., 2014; Li et al., 2014; Angot et al., 2016b, c; Wang et al.,...
2 Methods

We have built a multiple-layer box model to account for mercury chemistry and transport in the lower troposphere and surface snow, and the exchange between them. Details on the model setup are given in this section. The modeling results are mainly compared with the measurement data of $\text{Hg}^0$ in the year 2013. Briefly, $\text{Hg}^0$ concentrations were measured at three inlets (25, 210, and 1070 cm above the surface) of a meteorological tower located in the “clean area” of Dome C (where snow is kept undisturbed). $\text{Hg}^0$ concentrations were also measured in the near-surface air and snow interstitial air with multi-inlet snow sampling manifolds (the so-called “snow towers”). The mercury measurements were performed using a Tekran 2537A automated analyzer (Tekran Inc., Toronto, Canada). The experimental details have been described in Angot et al. (2016c).

2.1 Model overview

The model accounts for vertical transport using outputs from a regional climate model (Sect. 2.2). As shown in Fig. 1, $\text{Hg}^0$ can be oxidized to $\text{Hg}^{\text{II}}$ by different gas-phase chemical schemes (Sect. 2.3). The photoreduction of $\text{Hg}^{\text{II}}$ in aqueous clouds and aerosols is not considered in the model because its mechanism is poorly understood, and also because the air above the plateau is cold and dry. The vertical resolution is $\sim 2$ m near the surface and gradually decreases with height above the surface, and there are 33 atmospheric layers in total below 500 m. In the free troposphere, $\text{Hg}^0$ and $\text{Hg}^{\text{II}}$ concentrations are prescribed (Sect. 2.4). $\text{Hg}^0$ and $\text{Hg}^{\text{II}}$ are transferred from air to snow through dry deposition (Sect. 2.5). Wet deposition is not considered due to low snow accumulation rates and large uncertainty in parameterizing this process (France et al., 2011; Palerme et al., 2017). Note that Spolaor et al. (2018) have recently suggested that frequent snowfall and diamond dust (tiny ice crystals) events in summer may lead to quick mercury deposition. However, a quantitative parameterization for this process has not been available, and it is thus not included in this model. The model tracks $\text{Hg}^0$ and $\text{Hg}^{\text{II}}$ in a surface snow reservoir, in which $\text{Hg}^{\text{II}}$ may be reduced to $\text{Hg}^0$ photolytically or in the dark (Sect. 2.5). The depth of the surface snow layer is set to 20 cm, equivalent to one to two $e$-folding light penetration depths at Dome C (France et al., 2011). The exchange of mercury between the surface snowpack and the deeper snowpack is not considered in the model because the photochemistry in the deeper snowpack is less active, and also because the diffusive transfer of $\text{Hg}^0$ between these two snow layers should be slower. Our model calculations are not expected to capture day-to-day variations, since horizontal transport is ignored, and are thus compared with the average monthly and diurnal observations at Dome C as reported in Angot et al. (2016c). Major assumptions and simplifications made in the model are summarized in Table 1.

2.2 Meteorology

A surface-based temperature inversion layer exists at Dome C for most of the year, mainly due to radiation imbalance, while a convective mixed layer up to several hundred meters
The depth of the inversion/mixed layers (~500 m) in our model, and the air above is regarded as the free troposphere. The vertical atmospheric transport is represented with turbulent diffusion coefficients ($K_z$) from the polar-oriented regional climate model MAR (Modèle Atmosphérique Régional) (Sect. S1). The MAR data have been used to simulate several other atmospheric processes (e.g., NO$_x$ and HONO) in the 2011–2012 summer Oxidant Production in Antarctic Lands and Export (OPALE) campaign at Dome C (Legrand et al., 2014; Frey et al., 2015; Preunkert et al., 2015). In general, MAR simulations agree well with meteorological observations at Dome C (Gallée and Gorodetskaya, 2010; Gallée et al., 2015), whereas the intermittent warming events occurring primarily during the non-summer period, which decrease temperature inversion strength and strongly enhance vertical turbulence (leading to large $K_z$ values), may not be well represented. The vertical temperature gradients measured at a meteorological tower at Dome C indicate that the actual intensities of warming events should be weaker than results from MAR (Genthon et al., 2010). This is likely related to the cloud microphysical scheme in MAR, which is responsible for estimating the cloud cover and thus affects the estimation of surface temperature and buoyant forcing of turbulence. For example, in the wintertime, when the cloudiness is overestimated by the model, the downward infrared radiation is also overestimated. This overestimation limits surface cooling and subsequently the inhibition of turbulence, which is essentially generated by the wind shear. An accurate estimate of the warming events is challenging, and here we tentatively adjust MAR-modeled $K_z$ values during warming events using a rough empirical relationship between the temperature gradients and $K_z$, resulting in weaker exchange between the surface layers and free troposphere. It is important to note that such an adjustment is subject to large uncertainties and tends to underestimate the strength of vertical turbulence (Sect. S1). Thus, due to uncertainties in estimating warming events and their effects on the vertical transport of mercury in the non-summer period, both original and adjusted $K_z$ values are used to drive the mercury model in this study.
The gas-phase oxidations of Hg by NO\_2, O\_3, and OH (R1–R10) are all uncertain. As shown in Table 2, the rate constants of these reactions are expressed in Eq. (1), as-refer to concentrations, and k\_r and k\_I are the rate constants of the forward and reverse reactions, respectively. The uncertainty ranges of reaction rate constants of R4–R10 are unknown as only computational kinetic data are available for these reactions (Jiao and Dibble, 2017).

The recombination of Hg\_II is oxidized readily by R6–R10, where terms in brackets refer to concentrations, and k\_3–k\_10 are reaction rates of R3–R10. The gas-phase oxidations of Hg\_II by other species and the aequous and heterogeneous processes are not considered here (Sect. S2) (Lin and Pekhonen, 1999; Subir et al., 2011; Ariya et al., 2015).

\[ k_{\text{eff}} = \frac{k_3[\text{Br}] + k_4[\text{NO}_2] + k_7[\text{OH}] + k_8[\text{HO}_2]}{k_4[\text{Br}] + k_5[\text{NO}_2] + k_6[\text{OH}] + k_9[\text{HO}_2]} \]  

Concentrations of chemical species, including O\_3, HO\_3 (OH, HO\_2), BrO\_3 (Br, BrO), and NO\_3 (NO, NO\_2), are prescribed based on the available measurements and global chemical transport model (CTM) simulations (details in Sect. S3). Monthly and diurnal averages are computed. The temporal variations of O\_3 and NO\_2 are specified based on in situ measurements in near-surface air (Angot et al., 2016c; Legrand et al., 2016a; Helmig et al., 2018), and a uniform O\_3 vertical profile within the inversion/mixed layers is assumed, consistent with aircraft observations on the plateau (Slusher et al., 2010; Legrand et al., 2016a). The NO\_3 vertical profile has not been measured and is estimated assuming an exponential decay with height starting at the surface (Slusher et al., 2010). The previously reported potential bias in the measurement ratios of [NO]/[NO\_2] (Frey et al., 2015) does not significantly affect our model results, as suggested by a sensitivity test. The HO\_3 concentrations in summer are set based on measurements from the OPALE campaign, and their values in other seasons are estimated using relationships with J(NO\_2) and NO (Kukui et al., 2014). The uncertainties in O\_3 and OH concentrations are assumed to be 2% and 50%, respectively, as inferred from in situ measurements at Dome C (Kukui et al., 2014).

For BrO concentrations, due to lack of measurements, we rely on two global CTMs, GEOS-Chem and p-TOMCAT (Yang et al., 2005; Sherwen et al., 2016). We assume no diurnal and vertical variations of BrO (Stutz et al., 2011; Legrand et al., 2016b). The modeled BrO mixing ratios from these two CTMs are similar: less than 0.1 pptv in winter and ~0.4 pptv in other seasons (Fig. S8 in the Supplement). The modeled BrO is likely at the lower limits of its uncertainty range, as suggested by the comparison of the modeled tropospheric BrO columns and their values retrieved from the Global Ozone Monitoring Experiment-2 (GOME-
2) satellite (Sherwen et al., 2016). Legrand et al. (2016b) measured total inorganic gaseous bromine concentrations at Dome C and suggested that the upper limit of BrO is $\sim 1$ pptv. Based on the above information, the uncertainty of BrO concentrations is set as a factor of 2.5. It is important to note that the seasonal patterns of the modeled BrO by the CTMs may have biases, as indicated by the total inorganic bromine measurements at Dome C (Legrand et al., 2016b). The modeled BrO is likely biased high in fall and spring, which affects Hg$^0$ concentrations simulated by the mercury model (Sect. 3.4). The concentrations of Br are estimated assuming a photochemical steady state: $[\text{Br}] / [\text{BrO}] = (J_{\text{BrO}} + k_{\text{BrO+NO}}[\text{NO}]) / (k_{\text{Br+O}_3}[\text{O}_3])$ (Holmes et al., 2010), where $J_{\text{BrO}}$ is the BrO photolysis frequency, and $k_{\text{BrO+NO}}$ and $k_{\text{Br+O}_3}$ are rate constants for BrO + NO $\rightarrow$ Br + NO$_2$ and Br + O$_3$ $\rightarrow$ BrO + O$_2$, respectively (Sander et al., 2011).

### 2.4 Mercury concentrations in the free troposphere

Due to lack of measurements, we rely on two global CTMs, GEOS-Chem (version 9-02) and the Global European Monitoring and Evaluation Programme (EMEP) Multimedia Modelling System (GLEMOS), to specify the free tropospheric mercury concentrations (Angot et al., 2016a; Travnikov et al., 2017). The former uses a Br oxidation scheme, whereas the latter assumes OH and O$_3$ to be the oxidants of Hg$^0$. Monthly Hg$^0$ and Hg$^{\tt II}$ concentrations at 500 m above ground level in the Dome C grid box are extracted from these two CTMs. Studies have identified that the CTMs show significant seasonal biases in modeled mercury concentrations when compared to mercury observations at two southern hemispheric background stations, Amsterdam Island (38° S, 78° E) and Cape Point (34° S, 18° E) (Angot et al., 2014; Song et al., 2015; Horowitz et al., 2017; Martin et al., 2017), implying potential biases in modeled mercury budgets for the Southern Hemisphere. Hence, we adjust the modeled free tropospheric mercury concentrations using the scaling factors estimated by model–observation comparisons for these two background stations: $R_{i,j} = \frac{X_{\text{obs},i,j}}{X_{\text{mod},i,j}}$, where $X$ represents the average mercury concentrations, and $i$ and $j$ indicate each month and model, respectively. The two CTMs predict similar total gaseous mercury (Hg$^{\tt I}$ = Hg$^0$ + Hg$^{\tt II}$) concentrations with annual means of $\sim 1.0$ ng m$^{-3}$, whereas the modeled Hg$^{\tt II}$ concentrations during the sunlit period are much higher in GEOS-Chem than in GLEMOS due to their different chemical mechanisms (Fig. S9).

In our simulations, the free tropospheric mercury data are chosen from either GEOS-Chem or GLEMOS according to the chemical oxidation scheme (O$_3$, OH, or Br) used in each model scenario, for consistency. For example, the GEOS-Chem free tropospheric mercury data are used when the Br scheme is assumed in the box model simulation. Both CTMs use reaction rate constants at the lower limits. When the upper-limit reaction rates are assumed in the model scenarios, we expect more mercury should exist in its oxidized form, Hg$^{\tt II}$, in the free troposphere, and thus we adjust free tropospheric concentrations of Hg$^0$ and Hg$^{\tt II}$ according to this equation: $Hg^{\tt II}_{\text{upper}} / Hg^0_{\text{upper}} = R \times (Hg^{\tt II}_{\text{lower}} / Hg^0_{\text{lower}})$, where $R$ is the ratio between the upper- and lower-limit reaction rate constants, whereas the total Hg$^0$ concentrations remain unchanged.

### 2.5 Air–snow mercury exchange and snow mercury transformation

Dry deposition fluxes of Hg$^0$ and Hg$^{\tt II}$ are determined by their concentrations at the atmospheric ground level and prescribed deposition velocities ($V_d$). The effects of wind speeds and snow properties on $V_d$ are not included here. As indicated by previous studies (Lindberg et al., 2002; Brooks et al., 2006; Skov et al., 2006), the values of $V_d$ for Hg$^0$ and Hg$^{\tt II}$ are set to $1 \times 10^{-4}$ and 1 cm s$^{-1}$, respectively (Zhang et al., 2009). These $V_d$ parameters are not well constrained, but we find that varying the values of $V_d$ by a factor of 2 does not change the main findings of this study. For Hg$^{\tt II}$, the bidirectional fluxes between surface snow and air are considered and estimated by Hg$^0$ concentration differences and the turbulent and molecular diffusion coefficients in the snow interstitial air. Following Durnford et al. (2012), the molecular diffusion coefficient ($D_m$) in our model is set to $6 \times 10^{-5}$ m$^2$ s$^{-1}$. The turbulent diffusion coefficients ($D_t$) can be estimated by an explicit representation of the vertical wind pumping within the snowpack, which include several uncertain parameters, such as the height and wavelength of sastrugi (snow-eroded grooves or ridges) and the permeability of surface snowpack (Cunningham and Waddington, 1993; Thomas et al., 2011; Zatko et al., 2013; Toyota et al., 2014b). The estimated values of $D_t$ using this approach and the air and snow properties at Dome C may vary from the order of $10^{-6}$ to $10^{-4}$ m$^2$ s$^{-1}$ for the surface snowpack with a depth of 20 cm. Here, a more simple approach is adopted following Durnford et al. (2012), in which $D_t$ is set proportional to the atmospheric ground-level turbulent kinetic energy (TKE) obtained from the MAR model: $D_t = \text{TKE} \times 3 \times 10^{-3}$ s. $D_t$ varies by season and by time of day and has an annual median value of $3 \times 10^{-4}$ m$^2$ s$^{-1}$. The choice of the scaling factors ($3 \times 10^{-3}$ s by default in the model) is found to affect the modeled Hg$^0$ concentrations in the snow interstitial air (Sect. 3.2). A more explicit consideration of the influence of air and snow properties on air–snow exchange is recommended for future mercury modeling studies.

Previous studies have suggested that Hg$^{\tt II}$ can be reduced both photolytically and in the dark, and the photolytic and dark oxidation of Hg$^0$ may also occur, but the reaction rates and reductants/oxidants of individual pathways are largely unknown (for a review, see Durnford and Dastoor, 2011). Sunlight, in particular UV-B (280–320 nm) radiation, greatly enhances the formation of Hg$^0$ (Poulin et al., 2004; Dommergues et al., 2007; Johnson et al., 2008). Similar to previous models (Durnford et al., 2012; Toyota et al., 2014a),
we include a first-order photoreduction of Hg\(^{II}\) in the surface snowpack and scale its rate by \(J(\text{O}^1\text{D})\), the photolysis frequency of O\(_3\). In doing so, we assume that the supply of reductants is ample and that all Hg\(^{II}\) is reducible (Durnford and Dastoor, 2011). The photoreduction rate is poorly constrained, with a corresponding lifetime (denoted as \(\tau_{PR}\)) from a few days to several weeks (Toyota et al., 2014a). We also include dark reduction of snow Hg\(^{II}\) (the corresponding lifetime denoted as \(\tau_{DR}\)) in our model simulations for the non-summer period (Sect. 3.4).

3 Results and discussion

3.1 Atmospheric Hg\(^0\) oxidation rates

We have computed ranges of atmospheric Hg\(^0\) oxidation rates for different schemes (O\(_3\), OH, and two-step Br), using the low (i.e., lower-limit) and high (i.e., upper-limit) rate constants listed in Table 2 and uncertainties of oxidant concentrations (Sect. 2.3). As shown in Fig. 2, the Hg\(^0\) oxidation rates for these schemes in the inversion/mixed layers have large uncertainty ranges. Since the OH and Br concentrations are largely determined by the amount of solar radiation, the oxidation rates of Hg under these schemes exhibit strong seasonal and diurnal variations, while the O\(_3\) scheme does not. In austral summer (November–February), the two-step Br oxidation scheme (corresponding Hg\(^0\) oxidation lifetimes denoted as \(\tau_{OX}\) ~ 1.7–22 days) is more efficient than the O\(_3\) (\(\tau_{OX}\) ~ 19–1300 days) and OH (\(\tau_{OX}\) ~ 17–350 days) oxidation schemes. We find that the fast two-step Br oxidation is favored by low ambient temperature, high concentrations of NO\(_3\), and low concentrations of O\(_3\) at Dome C. This is because the thermal dissociation rates of the intermediate Hg\(^4\)Br decrease rapidly at a lower temperature, and because the concentrations of Br are influenced by the concentrations of NO\(_3\) and O\(_3\) (Sect. 2.3). In austral winter (May–August), by contrast, the O\(_3\) oxidation scheme (\(\tau_{OX}\) ~ 13–900 days) is usually more efficient than the others. A series of combinations of oxidation schemes, oxidant concentrations, and chemical kinetics are tested in our model simulations.

3.2 Strong photochemistry in summer

During the summer months, the observed Hg\(^0\) concentrations in near-surface Dome C air show a pronounced diurnal pattern, which usually peaks in the daytime and is minimized at night, as shown in Figs. 3 and S10. The amplitudes of diurnal variations of observed Hg\(^0\) reach ~0.4 ng m\(^{-3}\) in January and ~0.3 ng m\(^{-3}\) in February and November, respectively, which are higher than those during other seasons. This characteristic has been attributed to enhanced re-emissions of Hg\(^0\) in the daytime (Angot et al., 2016c; Wang et al., 2016), highlighting a dynamic Antarctic surface snowpack. The solar zenith angle has a diurnal cycle during summer, and a convective layer develops in the daytime as a response to surface heating, enhancing strengths of vertical mixing and snow ventilation. Previous studies have suggested rapid recurring cycles of oxidation and re-emission of Hg\(^0\) in summer, but chemical mechanisms have not been well defined (Angot et al., 2016c; Wang et al., 2016). As photochemical processes in the air and surface snow are of obvious importance for summer, we have conducted a series of mercury model sensitivity simulations by varying atmospheric oxidants (O\(_3\), OH, or Br), their concentrations (high or low) and chemical reaction rate constants (upper or lower), and surface snow Hg\(^{II}\) photoreduction rates (\(\tau_{PR}\) from 3 days to 3 weeks). In total, we ran 24 model sensitivity scenarios (Table S1 in the Supplement). Through comparing modeling results to observations, key atmospheric Hg\(^0\) oxidants may be identified, and surface snow Hg\(^{II}\) photoreduction rates may be constrained. Some of these scenarios have large biases compared to observations for the non-summer months, which is likely due to several factors in these simulations that will be discussed in detail in Sect. 3.4: (1) the adjusted \(K_z\) values during the warming events are used, which tends to underestimate the mercury vertical transport from the free troposphere, (2) the Br concentrations used in the model calculations are likely overestimated in the non-summer period, and/or (3) the dark reduction of snow Hg\(^{II}\), which may be important in the non-summer period, is not included.

The modeled Hg\(^0\) concentrations in near-surface air from various scenarios are compared to observations in Fig. 3 and in Sect. S4 (only the data collected at 25 cm above the surface are shown, and the model–observation comparison results for the data at 210 and 1070 cm are similar). We find, during summer, that model scenarios using either OH or O\(_3\)
oxidation schemes do not reproduce the diurnal variations of Hg0, and tend to overestimate atmospheric Hg0 concentrations, even when high oxidant concentrations and upper-limit reaction rates are assumed (resulting in τOX ≈ 20 days). Among the scenarios with the bromine oxidation scheme, BR_HH_14d (using high Br concentrations and upper-limit reaction rate constants; τOX ≈ 2 days and τPR of 2 weeks in summer) best reproduces the concentrations of atmospheric Hg0 and its diurnal patterns during the summer months (calculated normalized root mean square errors of < 20 %; Sect. S4). This scenario shows larger Hg0 diurnal variations in January–December than February–November, consistent with observations (Angot et al., 2016c; Spolaor et al., 2018). The differences in solar radiation in these summer months are expected to influence the strength of photochemical activities (such as Br concentration and photoreduction rates of snow HgII). Therefore, these sensitivity simulations suggest that a fast oxidation for atmospheric Hg0 occurs in the surface layers at Dome C in summer, and that the fast oxidation of Hg0 may be provided by a two-step Br scheme with its upper-limit reaction rates.

The summertime average Hg0 concentrations modeled by the BR_HH_14d scenario are also compared with those measured at different sampling heights, as shown in Fig. 4. The snow tower measurements indicate that Hg0 concentrations in the surface snow interstitial air (10 cm below the surface) are about 0.2 ng m⁻³ higher than those in the air (50 cm above the surface). The model predicts a similar Hg0 difference of about 0.3 ng m⁻³. These results suggest the snow-to-air transport of Hg0 and the production of Hg0 in the surface snowpack. It is noted that the modeled difference in Hg0 concentrations depends on the assumed turbulent diffusion
Figure 4. Summertime average Hg\(^0\) concentrations at different heights from observations and model. The observations include the meteorological tower (25, 210, and 1070 cm above the snow surface) and snow tower (50 cm above the snow surface and 10, 30, 50, and 70 cm below the snow surface). Model results from the BR_HH_14d scenario are shown. Measurement data are from the snow tower no. 1 as reported in Angot et al. (2016c). Error bars indicate 25 % and 75 % percentiles.

coefficients (\(D_l\)). Larger \(D_l\) implies faster vertical mixing of Hg\(^0\) and thus corresponds to smaller differences between the surface snowpack and atmosphere (Fig. S12). The measured Hg\(^0\) concentrations in the interstitial air of the deeper snowpack are lower than those in the surface snowpack, suggesting that the production of Hg\(^0\) may mainly occur in the snow near the surface. In the model, the production of Hg\(^0\) in surface snow arises from the photoreduction of Hg\(^{II}\) during summer. The photoreduction rates of surface snow (top 20 cm) Hg\(^{II}\) in BR_HH_14d (\(t_{PR}\) of 2 weeks) agree well with observations at the South Pole in Brooks et al. (2008), who estimated a lifetime of surface snow mercury (assumed to be the top 15 cm) of \(\sim 16\) days. The surface snow mercury concentrations modeled by BR_HH_14d are \(\sim 20\) ng L\(^{-1}\) (Fig. S13). The available measurements suggest that surface snow mercury concentrations were highly variable, ranging from \(\sim 3\) to 50 ng L\(^{-1}\) (Angot et al., 2016c; Spolaor et al., 2018).

The summertime vertical and diurnal profiles of modeled Hg\(^0\) concentrations in near-surface air are shown in Fig. 5a. Model results are from the BR_HH_14d scenario (using high Br concentrations and upper-limit reaction rates; \(t_{OX}\) \(\sim 2\) days and \(t_{PR}\) of 2 weeks), which best reproduces the observed Hg\(^0\) in summer. We find that the diurnal variation ranges of Hg\(^0\) are greater than 0.2 ng m\(^{-3}\) only for near-surface levels from snow to about 50 m above. As shown in Fig. 5b, the summertime Hg\(^0\) cycles in the inversion/mixed layers are primarily driven by diffusion from snow and oxidation loss. The dry deposition and transport from the free troposphere are insignificant. The amplitude of Hg\(^0\) oxidation loss increases during the daytime due to enhanced photochemical activities. Diffusion of Hg\(^0\) from surface snow is controlled by the rate of snow Hg\(^{II}\) photoreduction, which also peaks in the daytime. The diurnal profiles of the modeled Hg\(^0\) fluxes from simulations using the O\(_3\) and OH oxidation schemes are given in Fig. S14. As expected, the amplitudes of their fluxes are much smaller than this bromine oxidation model scenario. In order to elucidate the drivers of strong diurnal variations of Hg\(^0\) in near-surface vertical levels in summer, we calculated the diurnal cycles of Hg\(^0\) concentrations and all related fluxes for 0–50 m above the snow (Fig. 5c and d). The net diffusion of Hg\(^0\) refers to difference in its diffusion from snow and to upper levels. The latter is controlled by the changing mixed layer heights, which are low at night (<50 m) and strongly increased during the daytime (Angot et al., 2016c). Thus, at night, all Hg\(^0\) diffused from snow remains inside the shallow mixed layer, while in the daytime a large fraction is transferred to the air above 50 m. The net Hg\(^0\) flux, the derivative of its diurnal variation, is determined by the net diffusion and oxidation loss of Hg\(^0\). As shown in Fig. 5d, the net flux is positive in the morning but becomes negative in the afternoon, thus leading to the Hg\(^0\) maximum around noon. Overall, the diurnal variations of Hg\(^0\) in near-surface levels in summer are determined by the changes in the Hg\(^0\) oxidation loss, snow Hg\(^{II}\) photoreduction, and mixed layer depth, all of which are in turn controlled by the strong photochemical activity during this time period at Dome C.

Furthermore, our model results suggest that the air above Dome C is enriched in Hg\(^{II}\) during summer, consistent with its strong photochemical activity. As shown in Fig. 6, the predicted Hg\(^{II}\) by the BR_HH_14d scenario increases with height, from \(\sim 0.1\) near the surface to \(\sim 0.5\) ng m\(^{-3}\) at 500 m. Such Hg\(^{II}\) concentrations are comparable to the levels identified in the upper free troposphere for the midlatitudes (Bieser et al., 2017). A diurnal pattern of Hg\(^{II}\) with higher concentrations in the afternoon is predicted in near-surface air by the model. These characteristics should be verified by future measurement studies. Preliminary field sampling using polyethersulfone cation-exchange membranes in a 2014–2015 summer campaign obtained Hg\(^{II}\) of about 0.4 ng m\(^{-3}\) (average concentration from three filter samples) (Angot, 2016).

3.3 Comparison with summertime data at Summit Station, Greenland

Dome C (75° S, 123° E; 3 km above sea level) and Summit Station, Greenland (73° N, 38° W; 3.2 km above sea level), are both located in high altitude and far from the ocean (hundreds of kilometers). As a result, their meteorological and chemical conditions have similarities. In summer, both stations have shallow boundary layers that are stable at night.
but convective during the day (Helmig et al., 2002; Cohen et al., 2007; Van Dam et al., 2013). Active bromine chemistry was found to occur at Summit Station in summer (Thomas et al., 2011), and the average BrO mixing ratios in near-surface air were 0.9–1.5 pptv (Liao et al., 2011; Stutz et al., 2011), comparable to the 1 pptv upper limit at Dome C (Legrand et al., 2016b). Thus, it is expected that these two stations may have similar mercury variabilities in near-surface air. Brooks et al. (2011) measured atmospheric mercury concentrations in the summer of 2007–2008 at Summit Station but did not observe a significant diurnal cycle of Hg\(^0\) peaking at noon as was seen at Dome C. Based on our model analysis, we can identify several potential factors that can contribute to differences in the diurnal cycles of Hg\(^0\) between these two inland polar locations.

First, although BrO concentrations at Summit Station are comparable or higher than at Dome C, the concentrations of Br at Summit Station, the primary oxidant of Hg\(^0\), may be much lower. As described in Sect. 2.3, the \([\text{Br}]/[\text{BrO}]\) ratios are positively related to the concentrations of NO and negatively related to the concentrations of O\(_3\). Reported summertime NO\(_x\) concentrations at Summit Station (~20 pptv) are lower than at Dome C (~300 pptv), whereas O\(_3\) at Summit Station (~50 ppbv) is approximately 2 times that at Dome C (~25 ppbv) (Helmig et al., 2008a; Frey et al., 2015; Kramer et al., 2015; Van Dam et al., 2015; Huang et al., 2017). The larger NO\(_x\) concentrations at Dome C have been suggested to arise in part from larger NO\(_x\) emissions from surface snow, which are in turn driven by the photolysis of nitrate in the surface snowpack (Frey et al., 2015). A back-of-the-envelope calculation shows, assuming the same BrO concentrations, that Br concentrations at Dome C would be on average a factor of 6 higher than at Summit Station. Second, the thermal dissociation rate of the intermediate Hg\(^{\cdot}\)Br at Summit Station should be 1 order of magnitude greater than that at Dome C. This is because this rate strongly depends on temperature (Table 2), and the ambient temperature at Summit Station is about 15 K higher than at Dome C. Third, the oxidation of Hg\(^{\cdot}\)Br by NO\(_2\) (the dominant second step oxidant) is significantly slower at Summit Station than at Dome C, due to their different concentrations of NO\(_2\). In fact, the rates of oxidation by NO\(_2\) and dissociation of Hg\(^{\cdot}\)Br are comparable at Summit Station. This is in contrast with Dome C, where the oxidation by NO\(_2\) can easily outcompete the thermal dissociation of Hg\(^{\cdot}\)Br. All in all, we expect that the Br-initiated oxidation of Hg\(^0\) should be slower at Summit Station than at
Dome C, leading to weaker oxidation/re-emission cycling of Hg$^0$ during summer. It is also noted that atmospheric circulation on Greenland may be influenced by stronger synoptic-scale events than over the Antarctic Plateau, because the air is thicker over the Greenland ice sheet (leading to a weaker decrease of relative vorticity when a large-scale eddy propagates from the ice sheet margin towards the center). However, the impact of this circulation pattern on the diurnal cycle of Hg$^0$ is unclear.

3.4 Non-summer period

We showed above that the model simulations including the photoreduction of snow Hg$^{II}$ and a fast bromine oxidation of atmospheric Hg$^0$ could reasonably explain the observed atmospheric mercury variations during summer. However, these simulations strongly underestimate Hg$^0$ concentrations in the non-summer months (Fig. 3), when solar radiation is weakened or completely absent. Based on our understanding of air and snow mercury cycling (Fig. 1), such model–observation discrepancies may imply, for the non-summer period, that in the model the vertical transport of mercury from the free troposphere is underestimated. As modeled by BR_HH_14d and BR_S1, such enhanced air and snow mercury cycling (Fig. 1), such model–observation discrepancies may imply, for the non-summer period, that in the model the vertical transport of mercury from the free troposphere is underestimated. As modeled by BR_HH_14d and BR_S1, the reduction of snow Hg$^{II}$ is underestimated, and/or the oxidation of atmospheric Hg$^0$ is overestimated. All these processes are poorly constrained in the non-summer period in part because previous studies have mainly focused on the summer season. The model performance can be improved by modifying the representation of these processes.

First of all, it is important to note in the above simulations that the adjusted $K_v$ values in the warming events are used to drive the mercury model, which tends to underestimate the transport of mercury from the free troposphere. We therefore conducted a sensitivity simulation (BR_S1) to examine the possible effects of warming events on modeling results. The difference between BR_S1 and BR_HH_14d (using high Br concentrations and upper-limit reaction rates; $\tau_{OX} \sim 2$ days and $\tau_{PR}$ of 2 weeks in summer) is that the original MAR-modeled $K_v$ values are used in BR_S1, which may overestimate the transport of mercury from the free troposphere. As shown in Fig. 7a, in the non-summer months, near-surface air Hg$^0$ concentrations by BR_S1 are close to the prescribed Hg$^0$ concentrations in the free troposphere and are significantly higher than those from BR_HH_14d. However, the BR_S1 scenario cannot reproduce the high atmospheric Hg$^0$ concentrations of $\sim 1.2$ ng m$^{-3}$ in fall (exceeding its levels at the Antarctic coastal regions and the southern hemispheric midlatitude sites) and the diurnal cycles of Hg$^0$ in fall peaking in the night. This result indicates that Hg$^0$ may be produced below the atmospheric mixed layers at Dome C. In addition, surface snow Hg concentrations by BR_S1 exhibit an increase during the non-summer period (Fig. 7b), as a result of Hg$^{II}$ transport in warming events from the free troposphere (Fig. 7c). The deposited Hg$^{II}$ is accumulated in surface snow (photoreduction of Hg$^{II}$ is weak in the non-summer period). Such an enhancement of snow mercury was not measured at Dome C (Angot et al., 2016c). Therefore, we postulate that the existence of warming events during the non-summer period can significantly enhance Hg$^0$ concentrations in near-surface air but is unlikely to be the only reason for the observed mercury variations.

Second, the reduction of snow Hg$^{II}$ might occur in the dark, which would produce Hg$^0$ and sustain atmospheric
concentrations of Hg\(^0\) through snow-to-air diffusion and convective transport. The possibility of the presence of dark reduction has been reported in previous laboratory and field studies (Lalonde et al., 2003; Ferrari et al., 2004; Dommergue et al., 2007; Faïn et al., 2007), although actual mechanisms remain unclear. The reduction might be a continuation of photolytically initiated reactions or through reactions requiring no insolation at all (Durnford and Dastoor, 2011). The HO\(_2\) radical produced in the dark surface snowpack may serve as a potential Hg\(^{II}\) reductant (Dommergue et al., 2003; Ferrari et al., 2004). The dark reduction rates estimated in these studies are much lower than the photoreduction rates of Hg\(^{II}\). Some observational evidence at Dome C supports the hypothesis of snow Hg\(^{II}\) dark reduction. Near-surface air Hg\(^0\) concentrations peaked in the night in fall, and Hg\(^0\) concentrations in snow interstitial air were higher than air Hg\(^0\) in fall and winter (Angot et al., 2016c). Thus, we have conducted a sensitivity simulation, BR_S2, which added a first-order dark reduction of snow Hg\(^{II}\) based on BR_HH_14d, in order to examine the possible effects of dark reduction on model results. The reaction rate corresponds to an average \(\tau_{DR}\) of \(\sim 1\) year for the non-summer period and is scaled by NO\(_x\) concentrations since this process is likely related to nitrogen chemistry. As shown in Fig. 8, the hypothesized snow Hg\(^{II}\) dark reduction process leads to a small increase in the snow-to-air diffusive fluxes of Hg\(^0\) (<0.5 ng m\(^{-2}\) h\(^{-1}\)), which can increase the concentrations of atmospheric Hg\(^0\) in the non-summer period, especially in winter. This scenario also better reproduces the diurnal variation of Hg\(^0\) in the fall months.

Third, oxidation of atmospheric Hg\(^0\) may be overestimated in our model in the non-summer period. As described in Sect. 2.3, the modeled BrO concentrations by the CTMs may have seasonal biases. Total inorganic bromine measurements at Dome C (Legrand et al., 2016b) have suggested that the modeled BrO is likely biased high by up to a factor of 3 in fall and spring. The reasons remain unknown but are probably related to several factors, including depositions of Br-containing species, snow re-emission or long-distance transport of Br\(_2\)/BrCl, and photochemical Br reactions (Xin Yang, British Antarctic Survey, personal communication, 2017). In order to qualitatively evaluate this potential bias in BrO (and Br) concentrations, we have conducted a sensitivity simulation that reduces BrO (and thus Br) concentrations in fall by a factor of 3. We find that reducing BrO in fall could increase the modeled air Hg\(^0\) concentrations during the fall and winter months (Fig. S15).

Based on the above sensitivity analysis, we find that the all these three processes (intermittent warming events, dark reduction of snow mercury, and overestimation of bromine oxidation) can help explain the observed high mercury concentrations in the non-summer period. Their relative contributions, however, are difficult to constrain since the understanding of these processes is limited.

Figure 8. Possible impacts of snow mercury dark reduction on Hg\(^0\) concentrations and fluxes in the non-summer period. Panel (a) shows Hg\(^0\) observations at 25 cm above the snow surface at Dome C, and the shaded regions indicate 25 % and 75 % percentiles. The modeled Hg\(^0\) concentrations from BR_HH_14d and BR_S2 are also shown. Panel (b) shows the modeled Hg\(^0\) snow-to-air diffusion fluxes from BR_HH_14d (left axis) and the difference of snow-to-air diffusive fluxes between BR_S2 and BR_HH_14d (right axis).

4 Summary and future research needs

We have conducted box model calculations to explore important chemical and physical processes controlling the diurnal and seasonal variations of mercury at Dome C. The atmospheric Hg\(^0\) oxidation rates of the OH, O\(_3\), and the two-step Br-initiated schemes all have large uncertainty ranges due to uncertain chemical kinetics and oxidants concentrations. In austral summer, the Br oxidation scheme, favored by low ambient temperature and high concentrations of NO\(_x\), is more efficient than the OH and O\(_3\) schemes. The model simulations support the hypothesis that rapid recurring cycles of oxidation and re-emission of Hg\(^0\) occur in summer. Among the model scenarios tested, the simulations using the Br oxidation scheme (with upper-limit reaction rates) can best match mercury observations in summer. The modeling results indicate that strong diurnal variations of Hg\(^0\) in summer may be confined within several tens of meters above the snow surface and are primarily determined by changes in Hg\(^0\) oxidation loss, snow Hg\(^{II}\) photoreduction, and mixed layer depths. For the non-summer period, the model–observation comparisons at Dome C suggest the intermittent warming events and a hypothesized dark reduction of snow Hg\(^{II}\) may be important processes controlling the mercury variations, but their relative importance is uncertain. The Br-initiated oxidation of Hg\(^0\) is expected to be slower at Summit Station, Greenland,
because of high temperatures, high O$_3$, and low NO$_x$ conditions, which might contribute to the observed differences in the summertime diurnal variations of Hg$^{0}$ between these two polar inland locations.

In order to obtain a better understanding of mercury cycling over the East Antarctic Plateau, we suggest several areas for future research. (1) It is essential to better constrain the concentration levels of bromine species, especially BrO$_3^{-}$, through more field experiments and modeling studies. (2) It is important to reduce uncertainties in existing chemical kinetic parameters of bromine oxidation mechanisms. The rate constant of Hg$^{0}$ reaction with Br from existing theoretical and experimental studies varies by a factor of 4. (3) Our modeling indicates relatively high atmospheric Hg$^{II}$ concentrations in summer, which remains to be verified by additional field measurements. (4) A better characterization of atmospheric vertical transport during the non-summer period is needed, in particular the role of intermittent warming events. (5) The chemical mechanisms and reaction rates for snow mercury processes, including photoreduction and dark reduction, should be further investigated. Future modeling work should also improve the representation of those processes (e.g., diamond dust) shown in Table 2.

Given the rapid exchange of mercury between the surface snowpack and the above atmosphere (especially during summer), regional modeling studies should be conducted in the future in order to understand the total and speciated mercury budgets over the entire Antarctic Plateau and the influence of the plateau on the coastal environments.

Data availability. The mercury box model is available at http://github.com/shaojiesong/Hg_DomeConcordia (last access: 30 October 2018). The mercury measurement data at Dome C are available upon request at http://sdi.iia.cnr.it/geoint/publicpage/GMOS/gmos_historical.zul (GMOS, 2018). The ozone and NO$_x$ measurement data at Dome C are available upon request to the authors.

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Author contributions. SS, NES, and AD initialized and designed the study. SS, HA, and NES developed the model. HG provided MAR data. HA, FS, NP, OM, and AD conducted Hg observations, and DH and JS conducted NO$_x$ observations used in the model. SS wrote the paper with input from all the authors.

Competing interests. The authors declare that they have no conflict of interest.

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