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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<sup>0</sup> (gaseous elemental mercury) measurements in the year 2013. The model includes atmospheric Hg<sup>0</sup> oxidation (by OH, O<sub>3</sub>, or bromine), surface snow Hg<sup>II</sup> (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<sup>0</sup> 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<sup>0</sup> (peaking during daytime) may be confined within several tens of meters above the snow surface and affected by changing mixed layer depths. Snow re-emission of Hg<sup>0</sup> is mainly driven by photoreduction of snow Hg<sup>II</sup> in summer. Intermittent warming events and a hypothesized reduction of Hg<sup>II</sup> 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<sup>0</sup> 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<sup>0</sup> 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<sup>2</sup>) 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° S, 123° E), Dome Argus (80° S, 77° E), Dome Fuji (77° S, 40° E), and the South Pole (90° 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.,

2016; Han et al., 2017; Spolaor et al., 2018). Most of these studies only measured atmospheric mercury in austral summer, whereas Angot et al. (2016c) reported a year-round observational record at Dome C. All these measurements suggest that in summer (November–February), a photochemical mercury cycle occurs between the atmospheric boundary layer and surface snowpack, including the oxidation of gaseous elemental mercury ( $\text{Hg}^0$ ) in air, the deposition of oxidized mercury ( $\text{Hg}^{\text{II}}$ ) onto snow, the photoreduction of snow  $\text{Hg}^{\text{II}}$ , and the re-emission of  $\text{Hg}^0$  from the snowpack surface. A clear diurnal cycle of  $\text{Hg}^0$  (peaking at midday and decreasing to a minimum around midnight) was observed in near-surface air and has been attributed to enhanced  $\text{Hg}^0$  re-emission in the daytime as a result of increasing solar radiation (Dommergue et al., 2012; Angot et al., 2016c; Wang et al., 2016). The summertime photochemical mechanism of  $\text{Hg}^0$  oxidation in air is unknown but has been related to the high oxidizing capacity of the plateau, which is characterized by high concentrations of  $\text{NO}_x$ , OH, and other oxidants within the Antarctic mixed layers (Eisele et al., 2008; Helmig et al., 2008a, b; Neff et al., 2008; Kukui et al., 2014; Frey et al., 2015). Interestingly, such summertime diurnal variations of  $\text{Hg}^0$  have not been seen at the polar inland Summit Station atop the Greenland ice sheet (Brooks et al., 2011). As for other seasons, observations at Dome C showed high atmospheric  $\text{Hg}^0$  in fall (March–April), exceeding those measured at the Antarctic coast and southern hemispheric midlatitude sites. Such seasonal cycles were repeatedly measured in 2012–2015 at Dome C (Angot et al., 2016a). Moreover, in fall, the concentrations of  $\text{Hg}^0$  peaked during the night. In winter (May–August), as expected, the diurnal cycle of  $\text{Hg}^0$  disappeared, and a gradual decline of  $\text{Hg}^0$  was seen in near-surface air.

Overall, these observed seasonal and diurnal features of atmospheric mercury on the plateau are not well understood and not reproduced by global chemical transport models, likely due to their imperfect representations of boundary layer dynamics and chemical reaction pathways (Angot et al., 2016a) and to the singularity of their longitude–latitude grid at the poles. Here, we present detailed box model calculations to interpret observational data collected at Dome C in 2013, and to explore important chemical and physical processes controlling diurnal and seasonal variations of atmospheric mercury. A better knowledge of these characteristics is helpful for evaluating the potential influence of the Antarctic Plateau on the coastal environment (Bargagli, 2016) and for understanding processes occurring in other polar regions.

## 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 re-

sults 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

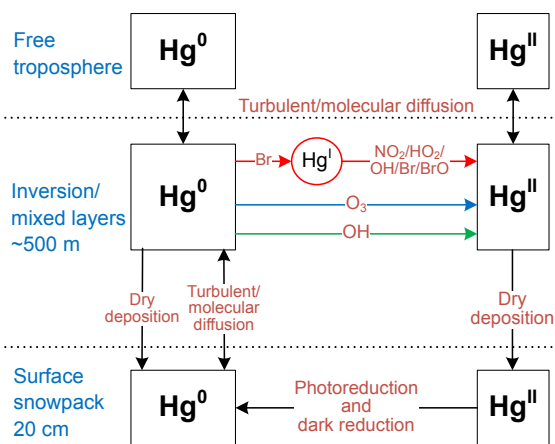
The model accounts for vertical transport using outputs from a regional climate model (Sect. 2.2). As shown in Fig. 1,  $\text{Hg}^0$  can be oxidized to  $\text{Hg}^{\text{II}}$  by different gas-phase chemical schemes (Sect. 2.3). The photoreduction of  $\text{Hg}^{\text{II}}$  in aqueous clouds and 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

**Table 1.** Major assumptions and simplifications made in the mercury model.

Description	Note
Physical or chemical processes not considered	
Horizontal transport	The model is not expected to capture day-to-day variability
Photoreduction of Hg <sup>II</sup> in aqueous cloud/aerosol	The air is cold and dry
Wet deposition of Hg <sup>II</sup> (snowfall and diamond dust)	Large uncertainty in its parameterization
Exchange with deep snowpack Hg	The diffusive transfer is expected to be slower
Simplifications for specific species or parameters	
Free tropospheric Hg concentration	Specified based on CTMs
HO <sub>x</sub> concentration	Estimated based on OPALE measurements, NO, and $J(\text{NO}_2)$
BrO <sub>x</sub> concentration	Specified based on CTMs
Air turbulent diffusion coefficient ( $K_z$ )	Modeled by MAR (with an optional adjustment for warming events)
Dry deposition velocities ( $V_d$ )	Typical values from the literature
Depth of surface snow layer	Specified based on $e$ -folding light penetration depth
Air–snow molecular diffusion coefficient ( $D_m$ )	Typical value from the literature
Air–snow turbulent diffusion coefficient ( $D_t$ )	Parameterized based on surface level turbulent kinetic energy (TKE)



**Figure 1.** Chemical and physical processes represented in the mercury box model. Hg<sup>0</sup> can be oxidized to Hg<sup>II</sup> by three different gas-phase chemical schemes (OH, O<sub>3</sub>, or a two-step Br-initiated scheme). Note that the concentrations of the intermediate Hg<sup>I</sup> in the two-step Br-initiated oxidation mechanism are not tracked since its lifetime is short, and thus effective reaction rates are used to describe the oxidation of Hg<sup>0</sup> to Hg<sup>II</sup> for this mechanism (Sect. 2.3). The dark reduction of surface snow Hg<sup>II</sup> may be only important for the non-summer period (Sect. 2.5).

in depth develops during the daytime in summer in response to surface heating (see the Supplement, Sect. S1) (Pietroni et al., 2014). Here, the depth of the inversion/mixed layers is specified as  $\sim 500$  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

species (e.g., NO<sub>x</sub> 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.

**Table 2.** Gas-phase mercury reactions used in the mercury model.

No.	Reaction	Rate constant <sup>a</sup>	Reference
R1	$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{\text{II}}$	$k_1 = 1.7 \times 10^{-18}$ (upper) $k_1 = 3 \times 10^{-20}$ (lower)	Schroeder et al. (1991) Hall (1995)
R2	$\text{Hg}^0 + \text{OH} \rightarrow \text{Hg}^{\text{II}}$	$k_2 = 3.2 \times 10^{-13} \times (T/298)^{-3.06}$ (upper) $k_2 = 8.7 \times 10^{-14}$ (lower)	Goodsite et al. (2004) Sommar et al. (2001)
R3	$\text{Hg}^0 + \text{Br} \rightarrow \text{Hg}^{\text{I}}\text{Br}$	$k_3 = 3.2 \times 10^{-12}$ (upper) $k_3 = 1.46 \times 10^{-32} \times (T/298)^{-1.86} \times [M]$ (lower)	Ariya et al. (2002) Donohoue et al. (2006)
R4 <sup>b</sup>	$\text{Hg}^{\text{I}}\text{Br} \rightarrow \text{Hg}^0 + \text{Br}$	$k_4 [\text{s}^{-1}] = k_3 / K_{\text{eq}}$	Dibble et al. (2012)
R5	$\text{Hg}^{\text{I}}\text{Br} + \text{Br} \rightarrow \text{Hg}^0 + \text{Br}_2$	$k_5 = 3.9 \times 10^{-11}$	Balabanov et al. (2005)
R6	$\text{Hg}^{\text{I}}\text{Br} + \text{NO}_2 \rightarrow \text{Hg}^{\text{II}}$	$k_6 = 8.6 \times 10^{-11}$	Dibble et al. (2012); Wang et al. (2014)
R7	$\text{Hg}^{\text{I}}\text{Br} + \text{OH} \rightarrow \text{Hg}^{\text{II}}$	$k_7 = 6.3 \times 10^{-11}$	Dibble et al. (2012); Wang et al. (2014)
R8	$\text{Hg}^{\text{I}}\text{Br} + \text{HO}_2 \rightarrow \text{Hg}^{\text{II}}$	$k_8 = 8.2 \times 10^{-11}$	Dibble et al. (2012); Wang et al. (2014)
R9	$\text{Hg}^{\text{I}}\text{Br} + \text{Br} \rightarrow \text{Hg}^{\text{II}}$	$k_9 = 6.3 \times 10^{-11}$	Dibble et al. (2012); Wang et al. (2014)
R10	$\text{Hg}^{\text{I}}\text{Br} + \text{BrO} \rightarrow \text{Hg}^{\text{II}}$	$k_{10} = 1.1 \times 10^{-10}$	Dibble et al. (2012); Wang et al. (2014)

<sup>a</sup> Rate constants are in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  unless otherwise stated.  $T$  represents temperature in K.  $[M]$  is the number density of air in  $\text{molecule cm}^{-3}$ . The “upper” and “lower” indicate the highest and lowest reaction rate constants determined by different kinetic studies (for a review, see Ariya et al., 2015), 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). <sup>b</sup> R3 and R4 are a pair of reversible reactions.  $K_{\text{eq}} (= 9.14 \times 10^{-24} e^{7801/T} \text{ cm}^3 \text{ molecule}^{-1})$  is the equilibrium constant estimated by Dibble et al. (2012), which is very close to the value of  $9.25 \times 10^{-23} \times (T/298)^{-2.76} e^{7292/T} \text{ cm}^3 \text{ molecule}^{-1}$  calculated by Goodsite et al. (2012).

### 2.3 Atmospheric mercury chemistry

In the model,  $\text{Hg}^0$  is oxidized in the atmosphere to  $\text{Hg}^{\text{II}}$ , while the oxidants, chemical kinetics, and oxidant concentrations are all uncertain. As shown in Table 2, the rate constants of  $\text{Hg}^0$  reactions with  $\text{O}_3$  (R1),  $\text{OH}$  (R2), and  $\text{Br}$  (R3) from existing theoretical and experimental studies may vary by factors of about 60, 8, and 4, respectively. While used in several chemical transport models,  $\text{O}_3$ - and  $\text{OH}$ -based chemical mechanisms are unlikely as pure gas-phase reactions since the formation of  $\text{HgO}$  is endothermic (Subir et al., 2011). The two-step  $\text{Br}$ -initiated scheme (R3–R10) can explain polar atmospheric mercury depletion events (Sprovieri et al., 2005; Steffen et al., 2008) and is likely the dominant  $\text{Hg}^0$  oxidation pathway globally (Holmes et al., 2006; Horowitz et al., 2017; Ye et al., 2018). The recombination of  $\text{Hg}^0$  and  $\text{Br}$  forms unstable  $\text{Hg}^{\text{I}}\text{Br}$ , which either dissociates or is oxidized to  $\text{Hg}^{\text{II}}$  by  $\text{NO}_2$ ,  $\text{HO}_2$ ,  $\text{OH}$ ,  $\text{Br}$ , or  $\text{BrO}$ . The effective oxidation rate constant of this two-step scheme is expressed in Eq. (1), assuming a steady state of  $\text{Hg}^{\text{I}}\text{Br}$ , as it forms slowly by R3, and 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  $\text{Hg}^0$  by other species and the aqueous and heterogeneous processes are not considered here (Sect. S2) (Lin and Pehkonen, 1999; Subir et al., 2011; Ariya et al., 2015).

$$k_{\text{eff}} = \frac{k_3[\text{Br}] \cdot (k_6[\text{NO}_2] + k_7[\text{OH}] + k_8[\text{HO}_2] + k_9[\text{Br}] + k_{10}[\text{BrO}])}{k_4 + k_5[\text{Br}] + k_6[\text{NO}_2] + k_7[\text{OH}] + k_8[\text{HO}_2] + k_9[\text{Br}] + k_{10}[\text{BrO}]} \quad (1)$$

Concentrations of chemical species, including  $\text{O}_3$ ,  $\text{HO}_x$  ( $\text{OH}$ ,  $\text{HO}_2$ ),  $\text{BrO}_x$  ( $\text{Br}$ ,  $\text{BrO}$ ), and  $\text{NO}_x$  ( $\text{NO}$ ,  $\text{NO}_2$ ), 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  $\text{O}_3$  and  $\text{NO}_x$  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  $\text{O}_3$  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  $\text{NO}_x$  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  $[\text{NO}]/[\text{NO}_2]$  (Frey et al., 2015) does not significantly affect our model results, as suggested by a sensitivity test. The  $\text{HO}_x$  concentrations in summer are set based on measurements from the OPALE campaign, and their values in other seasons are estimated using relationships with  $J(\text{NO}_2)$  and  $\text{NO}$  (Kukui et al., 2014). The uncertainties in  $\text{O}_3$  and  $\text{OH}$  concentrations are assumed to be 2 % and 50 %, respectively, as inferred from in situ measurements at Dome C (Kukui et al., 2014).

For  $\text{BrO}$  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  $\text{BrO}$  (Stutz et al., 2011; Legrand et al., 2016b). The modeled  $\text{BrO}$  mixing ratios from these two CTMs are similar: less than 0.1 pptv in winter and  $\sim 0.4$  pptv in other seasons (Fig. S8 in the Supplement). The modeled  $\text{BrO}$  is likely at the lower limits of its uncertainty range, as suggested by the comparison of the modeled tropospheric  $\text{BrO}$  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<sup>0</sup> concentrations simulated by the mercury model (Sect. 3.4). The concentrations of Br are estimated assuming a photochemical steady state:  $[\text{Br}]/[\text{BrO}] = (J_{\text{BrO}} + k_{\text{BrO}+\text{NO}}[\text{NO}]) / (k_{\text{Br}+\text{O}_3}[\text{O}_3])$  (Holmes et al., 2010), where  $J_{\text{BrO}}$  is the BrO photolysis frequency, and  $k_{\text{BrO}+\text{NO}}$  and  $k_{\text{Br}+\text{O}_3}$  are rate constants for  $\text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2$  and  $\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$ , 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<sub>3</sub> to be the oxidants of Hg<sup>0</sup>. Monthly Hg<sup>0</sup> and Hg<sup>II</sup> 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:  $R_{i,j} = \overline{X}_{\text{obs},i,j} / \overline{X}_{\text{mod},i,j}$ , where  $\overline{X}$  represents the average mercury concentrations, and  $i$  and  $j$  indicate each month and model, respectively. The two CTMs predict similar total gaseous mercury (Hg<sup>T</sup> = Hg<sup>0</sup> + Hg<sup>II</sup>) concentrations with annual means of  $\sim 1.0 \text{ ng m}^{-3}$ , whereas the modeled Hg<sup>II</sup> 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<sub>3</sub>, 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 ox-

idized form, Hg<sup>II</sup>, in the free troposphere, and thus we adjust free tropospheric concentrations of Hg<sup>0</sup> and Hg<sup>II</sup> according to this equation:  $\text{Hg}_{\text{upper}}^{\text{II}} / \text{Hg}_{\text{upper}}^{\text{0}} = R \times (\text{Hg}_{\text{lower}}^{\text{II}} / \text{Hg}_{\text{lower}}^{\text{0}})$ , where  $R$  is the ratio between the upper- and lower-limit reaction rate constants, whereas the total Hg<sup>T</sup> concentrations remain unchanged.

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

Dry deposition fluxes of Hg<sup>0</sup> and Hg<sup>II</sup> 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<sup>0</sup> and Hg<sup>II</sup> are set to  $1 \times 10^{-4}$  and  $1 \text{ cm s}^{-1}$ , 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<sup>0</sup>, the bidirectional fluxes between surface snow and air are considered and estimated by Hg<sup>0</sup> 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  $6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ . 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  $10^{-4} \text{ m}^2 \text{ s}^{-1}$  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:  $D_t = \text{TKE} (\text{m}^2 \text{ s}^{-2}) \times 3 \times 10^{-3} \text{ s}$ .  $D_t$  varies by season and by time of day and has an annual median value of  $3 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ . The choice of the scaling factors ( $3 \times 10^{-3} \text{ s}$  by default in the model) is found to affect the modeled Hg<sup>0</sup> 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<sup>II</sup> can be reduced both photolytically and in the dark, and the photolytic and dark oxidation of Hg<sup>0</sup> 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<sup>0</sup> (Poulain et al., 2004; Domergue 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  $\text{Hg}^{\text{II}}$  in the surface snowpack and scale its rate by  $J(\text{O}^{\text{I}}\text{D})$ , the photolysis frequency of  $\text{O}_3$ . In doing so, we assume that the supply of reductants is ample and that all  $\text{Hg}^{\text{II}}$  is reducible (Durnford and Dastoor, 2011). The photoreduction rate is poorly constrained, with a corresponding lifetime (denoted as  $\tau_{\text{PR}}$ ) from a few days to several weeks (Toyota et al., 2014a). We also include dark reduction of snow  $\text{Hg}^{\text{II}}$  (the corresponding lifetime denoted as  $\tau_{\text{DR}}$ ) in our model simulations for the non-summer period (Sect. 3.4).

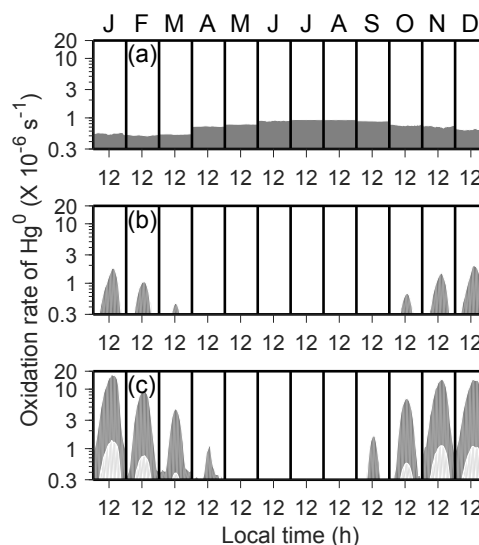
### 3 Results and discussion

#### 3.1 Atmospheric $\text{Hg}^0$ oxidation rates

We have computed ranges of atmospheric  $\text{Hg}^0$  oxidation rates for different schemes ( $\text{O}_3$ , 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  $\text{Hg}^0$  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  $\text{O}_3$  scheme does not. In austral summer (November–February), the two-step Br oxidation scheme (corresponding  $\text{Hg}^0$  oxidation lifetimes denoted as  $\tau_{\text{OX}} \sim 1.7\text{--}22$  days) is more efficient than the  $\text{O}_3$  ( $\tau_{\text{OX}} \sim 19\text{--}1300$  days) and OH ( $\tau_{\text{OX}} \sim 17\text{--}350$  days) oxidation schemes. We find that the fast two-step Br oxidation is favored by low ambient temperature, high concentrations of  $\text{NO}_x$ , and low concentrations of  $\text{O}_3$  at Dome C. This is because the thermal dissociation rates of the intermediate  $\text{Hg}^{\text{I}}\text{Br}$  decrease rapidly at a lower temperature, and because the concentrations of Br are influenced by the concentrations of  $\text{NO}_x$  and  $\text{O}_3$  (Sect. 2.3). In austral winter (May–August), by contrast, the  $\text{O}_3$  oxidation scheme ( $\tau_{\text{OX}} \sim 13\text{--}900$  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

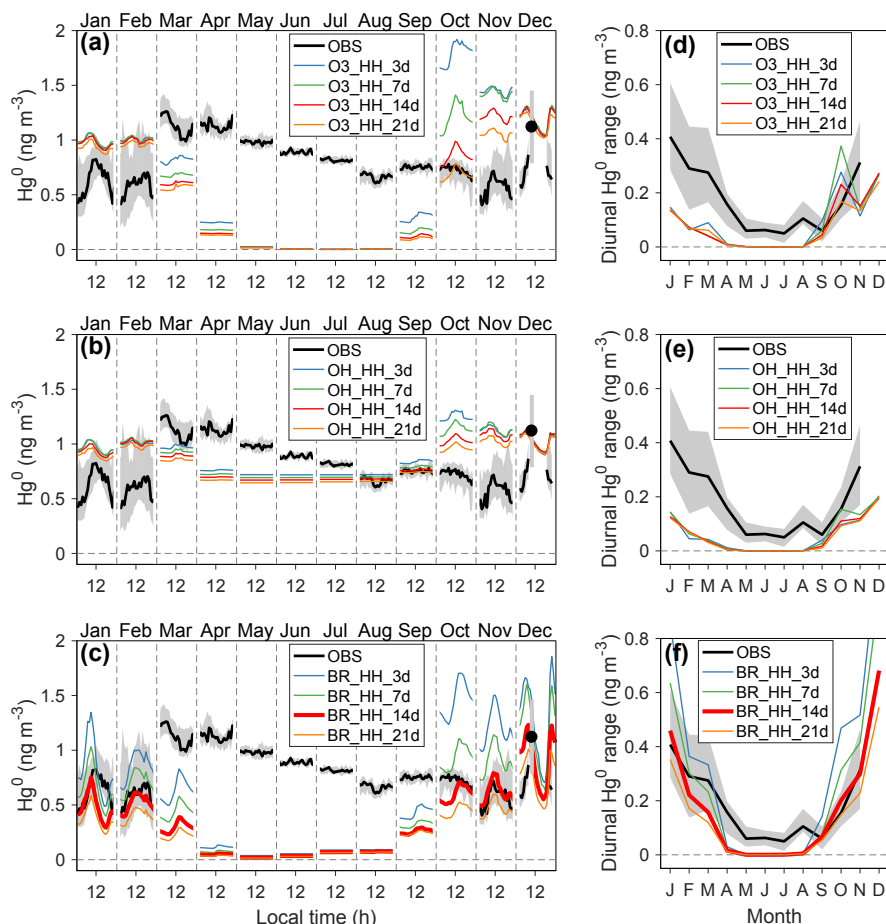
During the summer months, the observed  $\text{Hg}^0$  concentrations in near-surface Dome C air show a pronounced diurnal pattern, which usually peaks in the daytime and is minimized at night, as shown in Figs. 3 and S10. The amplitudes of diurnal variations of observed  $\text{Hg}^0$  reach  $\sim 0.4 \text{ ng m}^{-3}$  in January and  $\sim 0.3 \text{ ng m}^{-3}$  in February and November, respectively, which are higher than those during other seasons. This characteristic has been attributed to enhanced re-emissions of  $\text{Hg}^0$  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



**Figure 2.** Uncertainty ranges of atmospheric  $\text{Hg}^0$  oxidation rates within the inversion/mixed layers: (a)  $\text{O}_3$ , (b) OH, and (c) Br. Monthly and diurnal variations in the year 2013 are shown in the shaded regions. Note that the y axis is in log scale.

heating, enhancing strengths of vertical mixing and snow ventilation. Previous studies have suggested rapid recurring cycles of oxidation and re-emission of  $\text{Hg}^0$  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 ( $\text{O}_3$ , OH, or Br), their concentrations (high or low) and chemical reaction rate constants (upper or lower), and surface snow  $\text{Hg}^{\text{II}}$  photoreduction rates ( $\tau_{\text{PR}}$  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  $\text{Hg}^0$  oxidants may be identified, and surface snow  $\text{Hg}^{\text{II}}$  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  $\text{Hg}^{\text{II}}$ , which may be important in the non-summer period, is not included.

The modeled  $\text{Hg}^0$  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  $\text{O}_3$



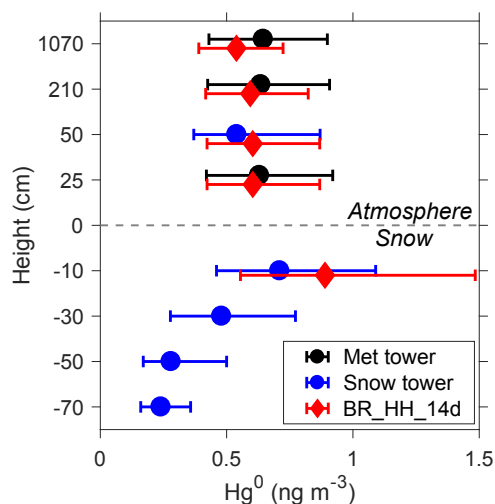
**Figure 3.** Comparison of seasonal and diurnal variations of near-surface atmospheric  $\text{Hg}^0$  concentrations between observations and model. Panels (a)–(c) show monthly and diurnal  $\text{Hg}^0$  observations in the year 2013 and modeling results from different scenarios. Panels (d)–(f) show diurnal  $\text{Hg}^0$  ranges calculated from the maximum and minimum hourly concentrations in each month. The shaded regions indicate 25 % and 75 % percentiles in observations. Observations were conducted at 25 cm above the snow surface at Dome C. The name of each scenario reflects the atmospheric oxidant, its concentration levels, chemical reaction rates (H indicates “high” or “upper”; L indicates “low” or “lower”), and the photoreduction rates of snow mercury (in days). For example, the scenario with name “O<sub>3</sub>HH\_3d” assumes O<sub>3</sub> as the oxidant, and high oxidant concentrations and high reaction rates are applied, and  $\tau_{\text{PR}}$  is set to 3 days.

oxidation schemes do not reproduce the diurnal variations of  $\text{Hg}^0$ , and tend to overestimate atmospheric  $\text{Hg}^0$  concentrations, even when high oxidant concentrations and upper-limit reaction rates are assumed (resulting in  $\tau_{\text{OX}} \sim 20$  days). Among the scenarios with the bromine oxidation scheme, BR\_HH\_14d (using high Br concentrations and upper-limit reaction rate constants;  $\tau_{\text{OX}} \sim 2$  days and  $\tau_{\text{PR}}$  of 2 weeks in summer) best reproduces the concentrations of atmospheric  $\text{Hg}^0$  and its diurnal patterns during the summer months (calculated normalized root mean square errors of  $< 20\%$ ; Sect. S4). This scenario shows larger  $\text{Hg}^0$  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  $\text{Hg}^{\text{II}}$ ). Therefore, these sensitivity simulations suggest that a fast oxidation for atmospheric  $\text{Hg}^0$  occurs in the surface layers at Dome C in summer, and that the fast oxidation of  $\text{Hg}^0$  may be provided by a two-step Br scheme with its upper-limit reaction rates.

The summertime average  $\text{Hg}^0$  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  $\text{Hg}^0$  concentrations in the surface snow interstitial air (10 cm below the surface) are about  $0.2 \text{ ng m}^{-3}$  higher than those in the air (50 cm above the surface). The model predicts a similar  $\text{Hg}^0$  difference of about  $0.3 \text{ ng m}^{-3}$ . These results suggest the snow-to-air transport of  $\text{Hg}^0$  and the production of  $\text{Hg}^0$  in the surface snowpack. It is noted that the modeled difference in  $\text{Hg}^0$  concentrations depends on the assumed turbulent diffusion





**Figure 4.** Summertime average  $\text{Hg}^0$  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 ( $D_t$ ). Larger  $D_t$  implies faster vertical mixing of  $\text{Hg}^0$  and thus corresponds to smaller differences between the surface snowpack and atmosphere (Fig. S12). The measured  $\text{Hg}^0$  concentrations in the interstitial air of the deeper snowpack are lower than those in the surface snowpack, suggesting that the production of  $\text{Hg}^0$  may mainly occur in the snow near the surface. In the model, the production of  $\text{Hg}^0$  in surface snow arises from the photoreduction of  $\text{Hg}^{\text{II}}$  during summer. The photoreduction rates of surface snow (top 20 cm)  $\text{Hg}^{\text{II}}$  in BR\_HH\_14d ( $\tau_{\text{PR}}$  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  $\sim 20 \text{ ng L}^{-1}$  (Fig. S13). The available measurements suggest that surface snow mercury concentrations were highly variable, ranging from  $\sim 3$  to  $50 \text{ ng L}^{-1}$  (Angot et al., 2016c; Spolaor et al., 2018).

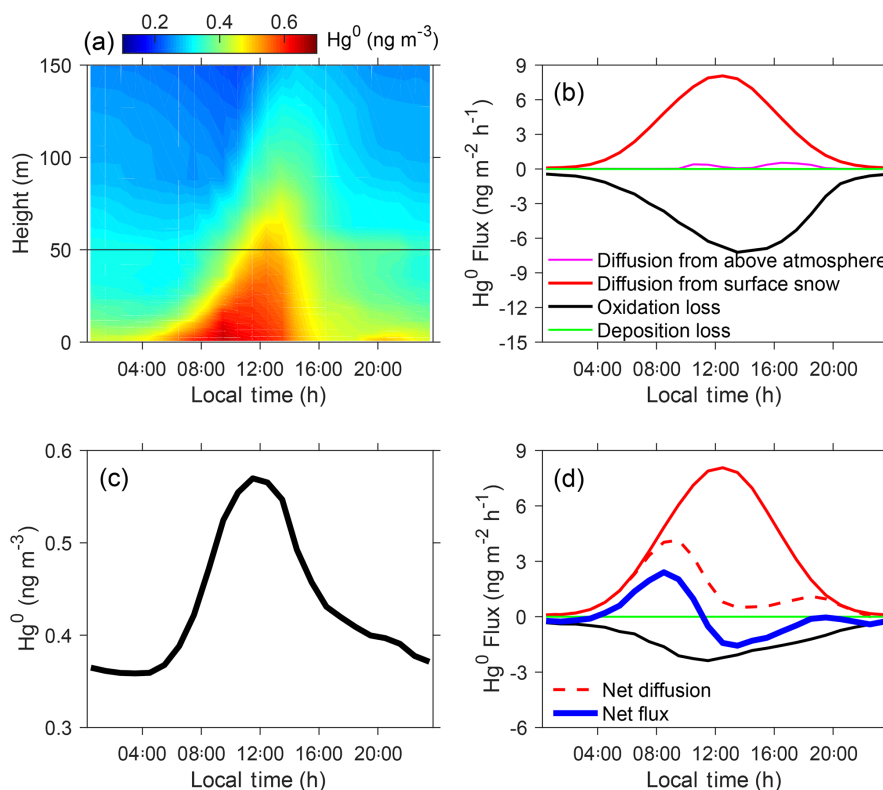
The summertime vertical and diurnal profiles of modeled  $\text{Hg}^0$  concentrations in near-surface air are shown in Fig. 5a. Model results are from the BR\_HH\_14d scenario (using high Br concentrations and upper-limit reaction rates;  $\tau_{\text{OX}} \sim 2$  days and  $\tau_{\text{PR}}$  of 2 weeks), which best reproduces the observed  $\text{Hg}^0$  in summer. We find that the diurnal variation ranges of  $\text{Hg}^0$  are greater than  $0.2 \text{ ng m}^{-3}$  only for near-surface levels from snow to about 50 m above. As shown in Fig. 5b, the summertime  $\text{Hg}^0$  cycles in the inversion/mixed layers are primarily driven by diffusion from snow and ox-

idation loss. The dry deposition and transport from the free troposphere are insignificant. The amplitude of  $\text{Hg}^0$  oxidation loss increases during the daytime due to enhanced photochemical activities. Diffusion of  $\text{Hg}^0$  from surface snow is controlled by the rate of snow  $\text{Hg}^{\text{II}}$  photoreduction, which also peaks in the daytime. The diurnal profiles of the modeled  $\text{Hg}^0$  fluxes from simulations using the  $\text{O}_3$  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  $\text{Hg}^0$  in near-surface vertical levels in summer, we calculated the diurnal cycles of  $\text{Hg}^0$  concentrations and all related fluxes for 0–50 m above the snow (Fig. 5c and d). The net diffusion of  $\text{Hg}^0$  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  $\text{Hg}^0$  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  $\text{Hg}^0$  flux, the derivative of its diurnal variation, is determined by the net diffusion and oxidation loss of  $\text{Hg}^0$ . As shown in Fig. 5d, the net flux is positive in the morning but becomes negative in the afternoon, thus leading to the  $\text{Hg}^0$  maximum around noon. Overall, the diurnal variations of  $\text{Hg}^0$  in near-surface levels in summer are determined by the changes in the  $\text{Hg}^0$  oxidation loss, snow  $\text{Hg}^{\text{II}}$  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  $\text{Hg}^{\text{II}}$  during summer, consistent with its strong photochemical activity. As shown in Fig. 6, the predicted  $\text{Hg}^{\text{II}}$  by the BR\_HH\_14d scenario increases with height, from  $\sim 0.1$  near the surface to  $\sim 0.5 \text{ ng m}^{-3}$  at 500 m. Such  $\text{Hg}^{\text{II}}$  concentrations are comparable to the levels identified in the upper free troposphere for the midlatitudes (Bieser et al., 2017). A diurnal pattern of  $\text{Hg}^{\text{II}}$  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  $\text{Hg}^{\text{II}}$  of about  $0.4 \text{ ng m}^{-3}$  (average concentration from three filter samples) (Angot, 2016).

### 3.3 Comparison with summertime data at Summit Station, Greenland

Dome C ( $75^\circ \text{ S}$ ,  $123^\circ \text{ E}$ ; 3 km above sea level) and Summit Station, Greenland ( $73^\circ \text{ N}$ ,  $38^\circ \text{ W}$ ; 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

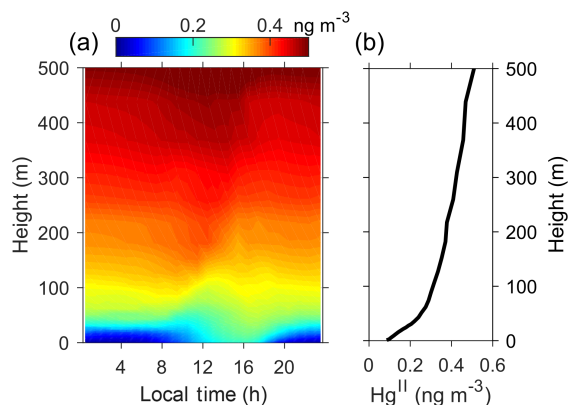


**Figure 5.** Summertime diurnal cycles of  $\text{Hg}^0$  concentrations and fluxes. Panel (a) shows the modeled vertical distributions of  $\text{Hg}^0$  concentrations in near-surface air, (b) the modeled  $\text{Hg}^0$  fluxes in the inversion/mixed layers, (c) the modeled  $\text{Hg}^0$  concentration averaged for 0–50 m above the snow surface, and (d) the modeled  $\text{Hg}^0$  fluxes for the air in 0–50 m above the snow surface. Model results from the BR\_HH\_14d scenario are shown.

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  $\text{Hg}^0$  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  $\text{Hg}^0$  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  $\text{Hg}^0$ , 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  $\text{O}_3$ . Reported summertime  $\text{NO}_x$  concentrations at Summit Station ( $\sim 20$  pptv) are lower than at Dome C ( $\sim 300$  pptv), whereas  $\text{O}_3$  at Summit

Station ( $\sim 50$  ppbv) is approximately 2 times that at Dome C ( $\sim 25$  ppbv) (Helmig et al., 2008a; Frey et al., 2015; Kramer et al., 2015; Van Dam et al., 2015; Huang et al., 2017). The larger  $\text{NO}_x$  concentrations at Dome C have been suggested to arise in part from larger  $\text{NO}_x$  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  $\text{Hg}^1\text{Br}$  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  $\text{Hg}^1\text{Br}$  by  $\text{NO}_2$  (the dominant second step oxidant) is significantly slower at Summit Station than at Dome C, due to their different concentrations of  $\text{NO}_2$ . In fact, the rates of oxidation by  $\text{NO}_2$  and dissociation of  $\text{Hg}^1\text{Br}$  are comparable at Summit Station. This is in contrast with Dome C, where the oxidation by  $\text{NO}_2$  can easily outcompete the thermal dissociation of  $\text{Hg}^1\text{Br}$ . All in all, we expect that the Br-initiated oxidation of  $\text{Hg}^0$  should be slower at Summit Station than at



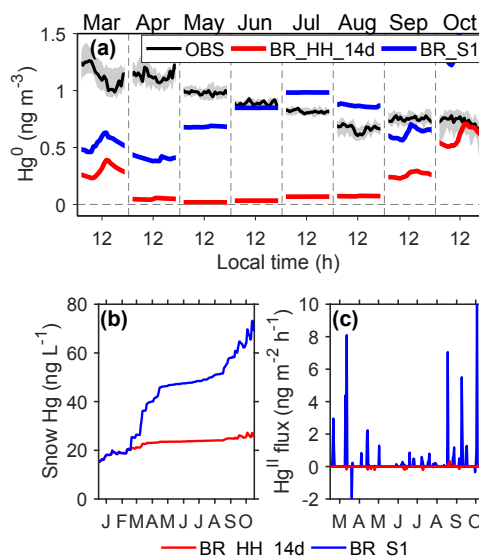
**Figure 6.** Summertime diurnal and vertical profiles of atmospheric  $\text{Hg}^{\text{II}}$  concentrations. Panel (a) shows both diurnal and vertical distributions, and (b) only shows the average vertical profile. Model results from the BR\_HH\_14d scenario are shown.

Dome C, leading to weaker oxidation/re-emission cycling of  $\text{Hg}^0$  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  $\text{Hg}^0$  is unclear.

### 3.4 Non-summer period

We showed above that the model simulations including the photoreduction of snow  $\text{Hg}^{\text{II}}$  and a fast bromine oxidation of atmospheric  $\text{Hg}^0$  could reasonably explain the observed atmospheric mercury variations during summer. However, these simulations strongly underestimate  $\text{Hg}^0$  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, the reduction of snow  $\text{Hg}^{\text{II}}$  is underestimated, and/or the oxidation of atmospheric  $\text{Hg}^0$  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  $K_z$  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



**Figure 7.** Possible impacts of warming events on mercury concentrations in the non-summer period. Panel (a) shows  $\text{Hg}^0$  observations at 25 cm above the snow at Dome C, and the shaded regions indicate 25 % and 75 % percentiles. The modeled  $\text{Hg}^0$  concentrations from BR\_HH\_14d and BR\_S1 are also shown. Panel (b) shows surface snow mercury concentrations from BR\_HH\_14d and BR\_S1. Panel (c) shows the exchange fluxes of  $\text{Hg}^{\text{II}}$  from the free troposphere modeled by BR\_HH\_14d and BR\_S1.

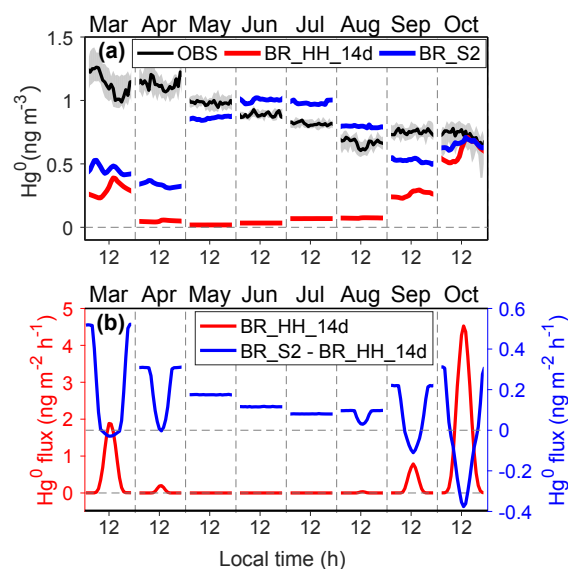
concentrations and upper-limit reaction rates;  $\tau_{\text{OX}} \sim 2$  days and  $\tau_{\text{PR}}$  of 2 weeks in summer) is that the original MAR-modeled  $K_z$  values are used in BR\_S1, which may overestimate the transport of mercury from the free troposphere. As shown in Fig. 7a, in the non-summer months, near-surface air  $\text{Hg}^0$  concentrations by BR\_S1 are close to the prescribed  $\text{Hg}^0$  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  $\text{Hg}^0$  concentrations of  $\sim 1.2 \text{ ng m}^{-3}$  in fall (exceeding its levels at the Antarctic coastal regions and the southern hemispheric midlatitude sites) and the diurnal cycles of  $\text{Hg}^0$  in fall peaking in the night. This result indicates that  $\text{Hg}^0$  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  $\text{Hg}^{\text{II}}$  transport in warming events from the free troposphere (Fig. 7c). The deposited  $\text{Hg}^{\text{II}}$  is accumulated in surface snow (photoreduction of  $\text{Hg}^{\text{II}}$  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  $\text{Hg}^0$  concentrations in near-surface air but is unlikely to be the only reason for the observed mercury variations.

Second, the reduction of snow  $\text{Hg}^{\text{II}}$  might occur in the dark, which would produce  $\text{Hg}^0$  and sustain atmospheric

concentrations of  $\text{Hg}^0$  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  $\text{HO}_2$  radical produced in the dark surface snowpack may serve as a potential  $\text{Hg}^{\text{II}}$  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  $\text{Hg}^{\text{II}}$ . Some observational evidence at Dome C supports the hypothesis of snow  $\text{Hg}^{\text{II}}$  dark reduction. Near-surface air  $\text{Hg}^0$  concentrations peaked in the night in fall, and  $\text{Hg}^0$  concentrations in snow interstitial air were higher than air  $\text{Hg}^0$  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  $\text{Hg}^{\text{II}}$  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  $\tau_{\text{DR}}$  of  $\sim 1$  year for the non-summer period and is scaled by  $\text{NO}_x$  concentrations since this process is likely related to nitrogen chemistry. As shown in Fig. 8, the hypothesized snow  $\text{Hg}^{\text{II}}$  dark reduction process leads to a small increase in the snow-to-air diffusive fluxes of  $\text{Hg}^0$  ( $< 0.5 \text{ ng m}^{-2} \text{ h}^{-1}$ ), which can increase the concentrations of atmospheric  $\text{Hg}^0$  in the non-summer period, especially in winter. This scenario also better reproduces the diurnal variation of  $\text{Hg}^0$  in the fall months.

Third, oxidation of atmospheric  $\text{Hg}^0$  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  $\text{Br}_2/\text{BrCl}$ , 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  $\text{Hg}^0$  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  $\text{Hg}^0$  concentrations and fluxes in the non-summer period. Panel (a) shows  $\text{Hg}^0$  observations at 25 cm above the snow surface at Dome C, and the shaded regions indicate 25 % and 75 % percentiles. The modeled  $\text{Hg}^0$  concentrations from BR\_HH\_14d and BR\_S2 are also shown. Panel (b) shows the modeled  $\text{Hg}^0$  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  $\text{Hg}^0$  oxidation rates of the OH,  $\text{O}_3$ , 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  $\text{NO}_x$ , is more efficient than the OH and  $\text{O}_3$  schemes. The model simulations support the hypothesis that rapid recurring cycles of oxidation and re-emission of  $\text{Hg}^0$  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  $\text{Hg}^0$  in summer may be confined within several tens of meters above the snow surface and are primarily determined by changes in  $\text{Hg}^0$  oxidation loss, snow  $\text{Hg}^{\text{II}}$  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  $\text{Hg}^{\text{II}}$  may be important processes controlling the mercury variations, but their relative importance is uncertain. The Br-initiated oxidation of  $\text{Hg}^0$  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  $BrO_x$ , 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](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.iaa.cnr.it/geoint/publicpage/GMOS/gmos\\_historical.zul](http://sdi.iaa.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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