Implementation of HONO into the chemistry-climate model CHASER (V4.0): roles in tropospheric chemistry

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Abstract. Nitrous acid (HONO) is an important atmospheric gas given its contribution to the cycles of NOₓ and HOₓ, but its role in global atmospheric photochemistry is not fully understood. This study, for the first time, implemented three pathways of HONO formation in the chemistry-climate model CHASER (MIROC-ESM) to explore three physical phenomena: gas-phase kinetic reactions (GRs), direct emission (EM), and heterogeneous reactions on cloud/aerosol particles (HRs). We evaluated the simulations by the atmospheric measurements from the OMI (Ozone Monitoring Instrument), EANET (Acid Deposition Monitoring Network in eastern Asia) / EMEP (European Monitoring and Evaluation Programme) ground-based stationary observations, observations from the ship R/V Mirai, and aircraft-based measurements by ATom1 (atmospheric tomography) and EMeRGe-Asia-2018 (Effect of Megacities on the Transport and Transformation of Pollutants on the Regional to Global scales). We showed that the inclusion of the HONO chemistry in the modeling process reduces the model bias against the measurements for PM₂·₅, NOₓ/HNO₃, NO₂, OH, O₃, and CO, especially in the lower troposphere and the North Pacific (NP) region.

We found that the retrieved global abundance of tropospheric HONO was 1.4 TgN. Of the three source pathways, HRs and EM contributed 63% and 26% to the net HONO production, respectively. We also observed that, reactions on the aerosol surfaces contributed larger amounts of HONO (51%) than those on the cloud surfaces (12%). The model exhibited significant negative biases for daytime HONO in the Asian off-coast region, compared with the airborne measurements by EMeRGe-Asia-2018, indicating the existence of unknown daytime HONO sources. Strengthening of aerosol uptake of NO₂ near surface and in the middle troposphere, cloud uptake, and direct HONO emission are all potential yet-unknown HONO sources. We also found that the simulated HONO abundance and its impact on NOₓ-O₃ chemistry are sensitive to the yield of the heterogeneous conversion of NO₂ to HONO (vs. HNO₃).

Inclusion of HONO reduces global tropospheric NOₓ (NO + NO₂) levels by 20.4%, thereby weakening the tropospheric oxidizing capacity, which in turn, increases CH₄ lifetime (13%) and CO abundance (8%). HRs on the surfaces of cloud particles, which have been neglected in previous modeling studies, are the main drivers of these impacts. This effect is
particularly salient for the substantial reductions of levels of OH (40–67%) and O₃ (30–45%) in the NP region during summer given the significant reduction of NOₓ level (50–95%). In contrast, HRs on aerosol surfaces in China (Beijing) enhances OH and O₃ winter mean levels by 600–1700% and 10–33%, respectively, with regards to their minima in winter. Overall, our findings suggest that a global model that does not consider HONO heterogeneous mechanisms (especially HRs on cloud particle surfaces) may erroneously predict the effect of HONO in remote areas and polluted regions.

1 Introduction

Nitrous acid (HONO) is an important atmospheric gas as it participates in the cycles of nitrogen oxides (NOₓ = NO + NO₂) and radical chemistry (OH, HO₂, and RO₂) (Kanaya et al., 2007; Ren et al., 2013; Whalley et al., 2018). Researchers have suggested to include the HONO chemistry in atmospheric chemistry models for more accurate simulations of oxidative substances (Jacob, 2000; Li et al., 2011). Despite the empirical evidences have indicated that the HONO concentrations in urban environments can reach 14 ppbv at night and can reach several hundred pptv throughout the day (Appel et al., 1990; Febo et al., 1996; Kanaya et al., 2007; Lee et al., 2016; Tan et al., 2017; Whalley et al., 2018), the HONO formation mechanism remains unclear. More specifically, the mechanisms of the HONO daytime sources have recently attracted considerable attention of researchers (Kleffmann et al., 2003; Li et al., 2014; VandenBoer et al., 2013; Xue et al., 2021a,b; Ye et al., 2018).

The only homogeneous reaction known to produce HONO in the troposphere is the direct combination of OH and NO (R2). Note that the major loss of HONO occurs via photolysis (R1) in the atmosphere at 300–405 nm:

\[(R1) \text{HONO} + \text{hv} \rightarrow \text{OH} + \text{NO} (300 \text{ nm} < \lambda < 405 \text{ nm}).\]

\[(R2) \text{NO} + \text{OH} + \text{M} \rightarrow \text{HONO} + \text{M}\]

\[(R3) \text{HONO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}\]

Moreover, the photolysis of HONO (R1) has attracted considerable attention in the literature as a critical source of OH radicals in the polluted urban atmosphere (e.g., Calvert et al., 1994; Harris et al., 1982; Jenkin et al., 1988; Platt and Perner, 1980). The OH level at sunrise can be increased by a factor of 5 due to the photolysis of HONO, with the regional daily maximum O₃ level increasing by 8% (Jenkin et al., 1988). Besides the direct loss via photolysis, the reaction of HONO with OH (R3) may also contribute to the daytime loss of HONO (Burkholder et al., 1992).

Notably, some night-time measurements hinted on the heterogeneous sources of HONO from aerosol surfaces. For instance, Harrison and Kitto (1994) have provided evidence about the HONO source from high concentration episodes of > 10 ppbv NO₂ for grassland in eastern England (Harrison and Kitto, 1994). Two reactions have been widely suggested to produce HONO on aerosol surfaces: 2NO₂ + H₂O → HONO + HNO₃ and NO + NO₂ + H₂O → 2HONO. The first process has been proven to be first-order with NO₂ and H₂O in reaction chamber studies (Sakamaki et al., 1983; Jenkin et al., 1988). The second process was evaluated by using laboratory surfaces (Sakamaki et al., 1983, Jenkin et al., 1988) and by using field observations in the presence of high O₃ and when NO₂ was the dominant form of NOₓ (Kessler and Platt, 1984). As a result, the second process was proposed as a peculiarly important source of HONO in the urban atmosphere (Ammann et al., 1998;
Gerecke et al., 1998). In the past two decades, researchers have investigated the heterogeneous NO$_2$ reactivity on vegetated, aqueous, sea salt, carbonaceous, and soot surfaces (Acker et al., 2001, 2006; Arens et al., 2001; Kleffmann and Wiesen, 2005; Kleffmann et al., 1998; Lammel and Cape, 1996; Lee et al., 2016; Notholt et al., 1992; Reisinger, 2000; Rubio et al., 2002; Stutz et al., 2002). In our model, these two processes are simplified as NO$_2$ → 0.5 HONO + 0.5 HNO$_3$ (R4) and NO$_2$ → HONO (R5).

Also, some modeling studies have reported overestimations of HONO over remote areas, indicating the HONO release from or deposition in snow (Chu et al., 2000; Fenter and Rossi, 1996; Kerbrat et al., 2010), partitioning to cloud water (Bongartz et al. 1994; Cape et al., 1992; Harrison and Collins, 1998; Mertes and Wahrner, 1995), and deliquescent aerosol surfaces (Harrison and Collins, 1998). The loss process occurs via the reaction HONO + H$_2$O → NO$^+$ + H$_3$O$^+$, simplified in our model as HONO → NO (R6) for surfaces of liquid and aqueous sulfate aerosols.

The natural sources of HONO include plant-leaf cuticles or soil biological crust (Hayashi and Noguchi, 2006; Oswald et al., 2013; Porada et al., 2019; Su et al., 2011), with estimated global total emission of 0.69 Tg yr$^{-1}$ HONO–N (Porada et al., 2019). Given the widespread occurrence of nitrite-fertilized soil in natural environment, highly acidic soils are arguably the strong sources of HONO and OH (Su et al., 2011). This potentially important source has been likely overseen by many previous modeling studies at both global and regional scales. Soil emissions could sustain the daytime HONO budget at relatively low aerosol concentrations (Lu et al., 2018). Anthropogenic activities can also directly emit HONO through incomplete combustion, as vehicles, for instance, can yield as high concentrations as 7 ppb (Kirchstetter et al., 1996; Kurtenbach et al., 2001). In regional air quality models, HONO sources from vehicles and vessels are often given at 0.8–2.3% of NO$_x$ emissions level, given the differences between gasoline and diesel vehicle types (e.g., Aumont et al., 2003; Kurtenbach et al., 2001; Li et al., 2011; Zhang et al., 2016). Many scholars have scrupulously addressed the effects of HONO in polluted regions as well.

For instance, HONO-induced enhancements in winter daytime HO$_x$ (up to >200% for OH) and O$_3$ (6–12%) over urban sites in China have been reported (Li et al., 2011; Lu et al., 2018; Zhang et al., 2016). However, another global modeling study suggested that O$_3$ levels are enhanced in response to additional OH production from the HONO photolysis only in high-NO$_x$ regions, despite they can be decreased in some areas under low NOx conditions (Jorba et al., 2012). At the same time, another 3D modeling study used a constant occurrence ratio for HONO as 0.02 of NO$_x$ and reported similar patterns for O$_3$ changes regarding HONO chemistry (Elshorbany et al., 2012). The NO$_x$ reduction effects that follow the NO$_2$ conversion are suggested to be more critical over the oceans than over continental regions, with up to 20% NO$_x$ reduction and 5%–20% HNO$_3$ enhancement over ocean regions of the lower troposphere (Martin et al., 2003).

As H$_2$O is required for the uptake of NO$_2$ on surfaces, wet surfaces have been broadly recommended as favored surfaces for NO$_2$ uptake. Therefore, cloud droplets can be an important surface for heterogeneous reactions of NO$_2$ because they are ubiquitous in the troposphere. Heterogeneous reactions by clouds can have a similar impact as aerosol particles on tropospheric O$_3$ and OH levels (Christopher et al., 2019). However, this aspect has been overlooked many times in previous studies, thereby, leading to potential underestimation (or even dismissing) of the potential effects over remote environments.
In this study, we introduce the HONO chemistry into the global atmospheric chemistry model CHASER-V4.0 for the first time. The main idea for the HONO inclusion is to elaborate the model simulation for tropospheric oxidative substances, while focusing on aerosol and cloud processes. The model includes the detailed online calculation of O$_3$-HO$_x$-NO$_x$-CH$_4$-CO coupling and oxidation of non-methane hydrocarbons (NMHCs) (Sudo et al., 2002) and heterogeneous processes for N$_2$O$_5$, HO$_2$, and RO$_2$ radicals (Ha et al., 2021; Sekiya and Sudo, 2014; Sekiya et al., 2018; Sudo and Akimoto, 2007). In Section 2, we describe the approach, including the model description and configuration. In Section 3.1, our model is evaluated by the available observations for atmospheric species, including observations from satellites, ground stations, and ship/aircraft, particularly addressing the roles of the HRs. In addition, simulated daytime HONO was verified with aircraft measurements for an Asian off-coast region. Section 3.2 presents the model results for HONO distributions and global HONO impacts, including separate effects from each pathway. Finally, Section 4 effectively represents the summary and concluding remarks.

2 Method and configurations

2.1 Global chemistry model

This study applied the global chemistry model CHASER (MIROC-ESM) (Sudo et al., 2002, 2007; Watanabe et al., 2011), which considers the detailed photochemistry in the troposphere and stratosphere. The chemistry component of the model, based on CHASER-V4.0, retrieves the concentrations of 95 chemical species and 262 chemical reactions (58 photolytic, 183 kinetic, and 21 heterogeneous reactions on polar stratospheric clouds), including the new HONO chemistry implemented in this study. We used the HTAP-II (Hemispheric Transport of Air Pollution) emission inventory for 2008 (https://edgar.jrc.ec.europa.eu/dataset_htap_v2, last access: 16th, Nov 2021) for O$_3$ and aerosol precursors (NO$_x$, CO, VOCs, SO$_2$), with biomass burning emissions derived from the MACC (Monitoring Atmospheric Composition and Climate) reanalysis system (https://gmao.gsfc.nasa.gov/reanalysis/MERRA/ceop.php). The details about the CHASER can be found in the earlier studies (Ha et al., 2021; Morgenstern et al., 2017; Sekiya et al., 2018). In this study, the newly added HONO system includes three pathways of HONO formation and interactions: (1) gas phase formation via the NO + OH reaction (R2), the photolysis of HONO (R1), and the reaction of HONO with OH (R3), hereafter denoted as GRs; (2) HONO direct emissions estimated from anthropogenic- and soil-NO$_x$ emissions (hereafter denoted as EM); and (3) the HONO conversion from NO$_2$ (R4, R5) and its loss on liquid/ice surfaces and aqueous aerosols (R6), which is hereafter denoted as HRs.

2.2 Experimental setup

The Global Emissions Initiative (GEIA) inventory (http://www.geiacenter.org/) is applied to quantify the soil NOx emissions (6 Tg N yr$^{-1}$) and anthropogenic NO$_x$ emissions (45 Tg N yr$^{-1}$). Since this broadly applied inventory is not currently available for HONO, this study tentatively imposes the HONO direct emissions based on the above NO$_x$ emission inventory through a constant factor of 0.1 (10% of NO$_x$ emissions). This assumption (soils + combustion) leads to a global HONO soil-emission estimate of about 0.6 TgN yr$^{-1}$, which is equivalent to the estimate from Porada et al. (2019), and it suggests that the...
anthropogenic emissions for HONO is 4.5 TgN yr\(^{-1}\). For HONO from exhaust sources, this factor (10%) is considerably higher than the previously reported estimate of 0.7%, derived for combustion (Xue et al., 2021b) or 0.8–2.3% for on-road vehicles (Aumont et al., 2003; Kurtenbach et al., 2001; Li et al., 2011) and 3%–6% for commercial aircraft (Lee et al., 2011). This factor intends to show the apparent potential impacts of direct HONO sources on the troposphere.

Table 1: Computation packages in the chemistry-climate model "CHASER"

<table>
<thead>
<tr>
<th>Base model</th>
<th>MIROC4.5 AGCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spatial resolution</td>
<td>Horizontal, T42 (2.8° × 2.8°); vertical, 36 layers (surfaces approx. 50 km)</td>
</tr>
<tr>
<td>Meteorology (u, v, T)</td>
<td>Nudged to the NCEP2 FNL reanalysis</td>
</tr>
</tbody>
</table>
| Emission (anthropogenic, natural) | Industry traffic, Vegetation Ocean  
Biomass burning specified by MACC reanalysis                                                                 |
| Aerosol             | BC/OC, sea-salt, and dust  
BC ageing with SO\(_4\)/SOA production                                                                                       |
| Chemical process    | 94 chemical species, 263 chemical reactions (gas phase, liquid phase, non-uniform  
O\(_{2}\)-NO\(_x\)-HO\(_x\)-CH\(_x\)-CO chemistry with VOCs  
SO\(_2\), DMS oxidation (sulfate aerosol simulation)  
SO\(_x\)-NO\(_x\)-NH\(_x\) system and nitrate formation  
Formation of SOA  
BC ageing  
(+) Heterogeneous reactions: 8 reactions of N\(_2\)O\(_5\), HO\(_2\), RO\(_2\); constant uptake coefficients (\(\gamma\)) on types of aerosols (Ice, Liquid, Sulfate, Sea salt, Dust, OC) |

The photolysis reaction of HONO (R1) is employed with the wavelength-dependent cross-sections following the recent study of Burkholder et al. (2015).

The kinetic of homogeneous reactions \(\text{NO} + \text{OH} + \text{M} \rightarrow \text{HONO} + \text{M} \) (R2) and \(\text{HONO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O} \) (R3) is applied with the low and high-pressure-limit rate constants, which are temperature dependent, as suggested in the aforementioned study.

In CHASER, the heterogeneous chemistry of interest is simplified as a first-order chemical loss in the aerosol phase for a species transferred from the gas phase. The rate of this pseudo loss is combined, and the first-order-loss rate for heterogeneous processes is calculated by using the Schwartz theory (Jacob, 2000; Schwartz, 1986), being simply treated with the mass transfer limitations in addition to the reactive uptake coefficient (\(\gamma\)) (Ha et al., 2021). Note that in CHASER, only surface reactions are considered, and there is no bulk particle reaction for the HR scheme.

The uptake coefficient parameter (\(\gamma\)) is defined as the net probability that a molecule X undergoing a gas-kinetic collision with a surface is taken up onto the surface. An average uptake coefficient for NO\(_2\) (R4) of \(10^{-4} \) (\(10^{-6}–10^{-3}\)) for the conversion of aqueous aerosols and clouds has been previously suggested (Jacob, 2000; Kleffmann et al., 1998; Li et al., 2018; Lu et al.,...
The NO$_2$ uptake by organic carbon aerosols has been reported to have similar coefficient values (Salgado-Muñoz and Rossi, 2002). The uptake coefficient for fresh black carbon is highly efficient and equals 3×10$^{-3}$ (Ammann et al., 1998; Li et al., 2018). The parameters for the uptake coefficients of R4 applied in the CHASER model are shown in Table 2.

As previous studies have noted, the fast initial uptake of NO$_2$ is observed on soot with an uptake coefficient in the range of 10$^{-1}$–10$^{-4}$ (Ammann et al., 1996, 1998). However, it rapidly decreased to ~10$^{-7}$ over 5 min (Kleffmann et al., 1999) to < 4×10$^{-8}$ for 5-day aged surfaces (Saathoff et al., 2001). In organic soot, γ is in the range of 10$^{-4}$–10$^{-6}$ (Al-Abadleh et al., 2000; Ammann et al., 1996; Arens et al., 2001; Salgado-Muñoz et al., 2002). In CHASER, the NO$_2$ conversion on organic carbon and soot (R5) was tentatively applied with uptake coefficients of 10$^{-4}$ and 3×10$^{-4}$, respectively, which also falls within the previously suggested range (10$^{-6}$–10$^{-3}$) considering the higher efficiency for soot (Table 2).

Also, previous laboratory experiments have introduced a wide range for the uptake coefficient of HONO by (R6), that is, 3.7×10$^{-3}$ at 178 K to 1.3×10$^{-5}$ at 200 K for the ice surface (Fenter and Rossi, 1996; Chu et al., 2000) and 4×10$^{-3}$–4×10$^{-2}$ at 278 K (Mertes and Wahner, 1995) or 0.03 × 0.15 at 297 K (Bongartz et al. 1994) for liquid water surfaces. In the aerosol flow reactor experiment on deliquescent sodium chloride and ammonium sulfate droplets at 279 K, the HONO reactive uptake coefficient of 0.0028 for 85% relative humidity has been previously obtained (Harrison and Collins, 1998). In CHASER, the aforementioned reference values for HONO uptake on ice, liquid clouds, and aqueous sulfate are simply averaged to be used as a heterogeneous loss of HONO (R6) in atmosphere (Table 2: last row).

**Table 2: Uptake coefficients for heterogeneous formation and loss of HONO**

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Ice</th>
<th>Liq</th>
<th>Sulf</th>
<th>Salt</th>
<th>Dust</th>
<th>Oc</th>
<th>Ec</th>
</tr>
</thead>
<tbody>
<tr>
<td>R4</td>
<td>NO$_2$ → 0.5HONO + 0.5HNO$_3$</td>
<td>0.0</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.003</td>
</tr>
<tr>
<td>R5</td>
<td>NO$_2$ → HONO</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0001</td>
<td>0.0003</td>
</tr>
<tr>
<td>R6</td>
<td>HONO → NO</td>
<td>0.002</td>
<td>0.03</td>
<td>0.003</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

### 2.3 Simulations

In this study, two main simulations, OLD and STD, and three sensitivity simulations (Table 3, no. 2–4) were conducted to isolate the distinct impacts of each pathway of the HONO chemistry for different surface types considered in the model (Table 3). The OLD simulation is run with the base model configuration without any HONO chemistry (see more details about the OLD case in Ha et al., 2021), whereas the control case (STD) considers all three types of HONO sources: direct emissions (EM), gas-phase reactions (GRs), and heterogeneous reactions (HRs). To quantify the effects of each mechanism using Eq. (1), two sensitivity cases (GR, GR+HR) intentionally implement GRs (R1, R2, R3) into the OLD case and HRs (R1, R2, R3, R4, R5, R6) into the GR case, respectively. GR+HR (cld) is another sensitive case like GR+HR, with HRs on aerosols excluded to investigate the different effects of clouds and aerosols. Eq. (1) determines the effects of each mechanism on atmospheric...
species \( i (i = \text{OH, O}_3, \text{NO}_x, \text{CO}) \) by concentration differences of \( i \) in two relevant cases being compared to that in the OLD case.

\[
E_i = \frac{(\text{Case1}_i - \text{Case2}_i)}{\text{OLD}_i} \times 100 \% ,
\]

where \( \text{Case1}_i \) and \( \text{Case2}_i \) are the concentrations of \( i \) in two separate cases: GR and OLD cases for the pure effects by the gaseous mechanism; GR+HR and GR cases for the effects of heterogeneous mechanisms; STD and GR+HR cases for the HONO emissions effects; and GR+HR(cld) and GR cases for the effects of heterogeneous reactions that exclusively occur on ice and cloud particles.

### Table 3: Sensitivity simulations in this work.

<table>
<thead>
<tr>
<th>No.</th>
<th>Simulation ID</th>
<th>HRs (HONO)</th>
<th>GRs (HONO)</th>
<th>EM (HONO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OLD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>GR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>GR+HR(cld)</td>
<td>×</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>GR+HR</td>
<td>×</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>STD</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
</tbody>
</table>

#### 2.4 Observation data for model evaluation

We evaluated the OLD, STD, and sensitivity simulations with ground-based, ship-based, aircraft, and satellite measurements. The observational information and locations of the surface site and ship/aircraft tracks for the observations used in this study are summarized in Table 4, Figure 1, Figure 4, and Figure S5.

Simulated tropospheric column ozone was also evaluated by using tropospheric column \( \text{O}_3 \) (TCO) derived from the OMI (Ozone Monitoring Instrument) spaceborne observations (https://daac.gsfc.nasa.gov/). To this end, the monthly data from 45 stations during 2010–2016 were used to verify aerosol surface concentrations (sulfate, nitrate) and trace gases (HNO\(_3\), NO\(_x\), \( \text{O}_3 \)) in the Acid Deposition Monitoring Network in eastern Asia (EANET: https://www.eanet.asia/). We also used the European Monitoring and Evaluation Programme (EMEP: https://www.emep.int/) data, which compiles observations over 245 European stations. We also utilized the ship-based observational data from the R/V Mirai cruise (http://www.jamstec.go.jp/e/about/equipment/ships/mirai.html) undertaken by the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). This study uses the surface CO and \( \text{O}_3 \) concentration data from the summers of 2015–2017 along the Japan-Alaska routes. The model data were compiled in the hourly timestep and interpolated, corresponding to the \( \text{Mirai} \) time step and coordinates. To verify the vertical tropospheric profiles, ATom1 aircraft measurements (https://espo.nasa.gov/atom/content/ATom) for \( \text{NO}_2\), OH, CO, and \( \text{O}_3 \) were employed.

Daytime HONO concentrations were also analyzed by using the DLR-HALO aircraft (Operator Deutsches Zentrum für Luft- und Raumfahrt - High-Altitude and Long-Range research aircraft) measurements made during the EMeRGe-Asia (Effect of Megacities on the Transport and Transformation of Pollutants on the Regional to Global scales) campaign in March and
April 2018, over an off-coast region between Korea (including the Jeju Island as the part of the domain), Taiwan, and the Philippines (http://www.iup.uni-bremen.de/emerge/home/). The measuring time falls in the range of 0:00 UTC to 9:00 UTC, around 8:00 to 17:00 in local time (UTC+8). Verification with EMeRGe data helps to explore the daytime HONO chemistry mechanisms in the free troposphere.

A model bias for each species was calculated as the difference between the simulated and observed concentrations, as shown in Eq. (2), where N is the total number of data points used in the calculation.

\[
\text{bias} = \frac{\sum_{i=1}^{N} \text{Model} - \text{Observation}}{N}
\]  

Figure 1: Location of measurements. (a) EANET stations for NO\textsubscript{x} and O\textsubscript{3} and (b) for PM\textsubscript{2.5}, SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{2}, and HNO\textsubscript{3}, (c) EMEP stations, and (d) ATom1 cruising altitudes are plotted. In (a) and (b), each number described station name (see Table S1). In (d), numbers show flight tracks.

Table 4: Lists of the datasets used in this study for verification. Related simulations with their original model timestep are interpolated to the comparing timestep.

<table>
<thead>
<tr>
<th>Verified species</th>
<th>Regions</th>
<th>Dataset name</th>
<th>Time</th>
<th>Measuring step</th>
<th>Model step</th>
<th>Interpolating step</th>
</tr>
</thead>
</table>

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3 Results and Discussion

3.1 Model verifications for cloud fraction, surface aerosol density, atmospheric species, and effects on HONO mechanisms

3.1.1 Verification for cloud fraction, surface aerosol density, and tropospheric column ozone

In this study, besides the conversion of NO$_2$ onto clouds and aqueous particles (R4), the losses of HONO onto ice and liquid clouds were also included (R6). Therefore, for accurate simulations of HRs, we need to examine the cloud distribution. The CHASER model applies the common cloud maximum-random overlap assumptions (MRAN) in the radiation and cloud microphysics schemes as other general circulation models to estimate the distribution of the cloud fraction. The verification by using the satellite observation data ISCCP D2, CALIPSO-GOCCP, and reanalysis data JRA55 generally revealed good correlation, whereas notable (10–20%) underestimation for the entire troposphere was yet salient. During June – July – August (JJA), CHASER’s cloud fraction is likely overestimated for the lower troposphere of the North Pacific (NP) region (10–20% compared to JRA55 reanalysis data). This finding indicates that thorough scrutiny of any impacts in this region is highly required (see the discussion in Section 3.2). Note that more detailed information for cloud verification for CHASER has been provided by Ha et al. (2021).

The heterogeneous processes by clouds and aerosol particles are parameterized by using surface aerosol density (SAD) estimations alongside the cloud fraction and aerosol concentration. During DJF, the simulated total SAD is attributed to all types of aerosols. However, for JJA, liquid clouds and sulfate aerosols are the principal SAD sources. This is peculiarly visible pattern for the northern polar and mid-latitude maritime regions. The performance for aerosol SAD in our model is in line with the earlier report by Thornton et al., (2008), except for sea salt density, which was very low in our model (up to 2 $\mu$m$^2$ cm$^{-3}$) compared to their work (up to 75 $\mu$m$^2$ cm$^{-3}$). This disagreement may be ascribed to the different size distributions for sea salt in the two models. The distribution of SAD is discussed in more detail in an earlier report (Ha et al., 2021).
The STD run with HONO improves the overall tropospheric column ozone (TCO) distribution observed by the OMI, especially at the mid-latitudes. Figure 2 shows that the O₃-reducing effects of HONO chemistry greatly reduced the model overestimates in the OLD simulation for the general Northern Hemisphere and polluted regions such as China. However, in the NP region, the inclusion of HONO only reduces the model overestimates during the insignificant episodes of TCO (autumn to early winter) while extending the underestimates for TCO for the rest of the year (Figure S3(b)). These O₃ underestimates in the NP region are also visible for the modeled surface air versus the measurements during the Mirai cruises (Figure 4(a,b)). Notably, these underestimates for O₃ could hold up to 400 hPa, as seen in comparison with the ATom1 flights (Figure 7(f): 400–900 hPa). This phenomenon can be related to the stratospheric downward transport and insufficient vertical mixing, as discussed in Sections 3.1.3 and 3.1.4, for comparisons in the NP region’s surface air and free troposphere. Although the HONO level in STD remains < 10 ppt for this area (Figure 10), the O₃ reducing effects exacerbate the model discrepancy. The HONO photochemistry is unlikely to be the main driver of this phenomenon as the ozone simulation is improved over the continents when the HONO photochemistry is included.

Figure 2: TCO percentage differences between model and OMI. Left panels show STD versus OMI; right panels show OLD versus OMI for annual (a,b), December – January – February (c,d), June – July – August (e,f). Black boxes indicate the NP region; dash boxes indicate the Chinese region.

3.1.2 Effects of HONO chemistry in the continental near-surface layer

The effects of HONO chemistry in the continental near-surface layer of East Asia and Europe were investigated as well. To this end, we conducted model comparisons versus EANET and EMEP stationary observations for mass and gaseous
concentrations of PM$_{2.5}$, SO$_4^{2-}$, NO$_x$, HNO$_3$, NO$_x$ O$_3$, and CO (CO for EMEP only). Table 5 shows the correlation coefficients ($R$) and model biases for each species in the OLD and STD cases. The OLD simulation has its fair correlations and RMSEs with observation for SO$_4^{2-}$ ($R$(EANET) = 0.56, $R$(EMEP) = 0.63), NO$_3^-$ ($R$(EANET) = 0.36, $R$(EMEP) = 0.713), and HNO$_3$ ($R$(EANET) = 0.181, $R$(EMEP) = 0.115), which are in line with other atmospheric chemistry models’ $R$ and RMSE values against EANET and EMEP (Brian et al., 2017), as also discussed in Ha et al. (2021).

Overall, the inclusion of HONO improved the $R$ for PM$_{2.5}$, SO$_4^{2-}$, NO$_3^-$, O$_3$ (EMEP), and HNO$_3$ (EANET). The $R$ estimates for HNO$_3$/NO$_3^-$ are slightly improved because of the inclusion of HONO photochemistry (OLD $\rightarrow$ STD: 0.713 $\rightarrow$ 0.755 for NO$_3^-$ in EMEP, 0.181 $\rightarrow$ 0.228 for HNO$_3$ in EANET, Table 4). However, its effects are not pivotal for modifying (increasing/decreasing) levels of NO$_x$, which is additionally underestimated in the STD run due to the NO$_2$ loss by heterogeneous processes (bias OLD $\rightarrow$ STD: -3.997 $\rightarrow$ -4.358 for EANET). Figure 3 compares the measured versus simulated HNO$_3$, NO$_x$ HONO, O$_3$, and CO concentrations for the EANET and EMEP stations. The stations were divided into three groups: (1) high-NO$_x$ EANET stations, including Jinyushan (China), Kanghwa, Imsil, Jeju (South Korea), Bangkok, Nai Muaeng, Samutprakarn, Si Phum (Thailand), Metro Manila (Philippines), and Ulaanbaatar (Mongolia); (2) other EANET stations (39 for HNO$_3$, 22 for O$_3$, and 15 for NO$_x$); and (3) all EMEP stations. The ground-based observations in the period 2010–2016 revealed the slightly decreasing NO$_x$ for moderate NO$_x$ concentrations, as well as PM$_{2.5}$, and aerosols (Figure 3(e,h) and Figure S4(e,g,h,i)). These decreasing trends were not captured by our simulations that used the high emission scenario for the EDGAR/HTAP-2008 inventory. Note that NO$_x$ and PM$_{2.5}$ concentrations are generally underestimated in the model (OLD), especially in high-NO$_x$ regions (Figure 3(b,e,h) and Figure S4(a,d,g)) with model’s averaged biases of -0.8 ppb NO$_x$ for EMEP and -4 ppb NO$_x$ for EANET (Table 5). These underestimations were stronger during winter, particularly for the high-NO$_x$ regions. It is possible that complex domestic sources could lead to diluted emissions for the simulations' moderate horizontal resolution (∼2.8°). Higher model resolutions such as 1.1°, 0.56° or even higher, could remedy such effects (Sekiya et al., 2018). In the STD case, including HONO photochemistry, the negative biases of NO$_x$ in the model have adversely increased due to the NO$_2$ loss processes. These processes also suppressed the observed NO$_x$ seasonality observed at most sites (Figure 3(b,h), red lines). The lack of seasonality was driven by the substantial loss of NO$_2$ on the surfaces of atmospheric particles during winter. For EANET’s low NO$_x$ and EMEP stations, this huge NO$_2$ loss is attributed to cloud surfaces (Figure 3(ee,hh), blue bars). However, NO$_2$ uptake by aerosols has a comparable contribution effect to the cloud effect in high-NO$_x$ environments such as Jinyunshan (Figure 3(bb), grey bars). Namely, nearly half of the NO$_2$ was converted to HNO$_3$ in R4 (Figure 3(aa,dd,gg)) without an efficient recycling process, leading to an overall removal of NO$_x$. This lack of NO$_x$ could be the main driver for the seasonal NOx deterioration and for the exacerbated overestimations of HNO$_3$ by simulations.

The STD O$_3$ simulation exhibited moderate and strong positive correlations with EANET and EMEP observations, 0.595 and 0.707, respectively (Table 5). The improvements in the concentrations of SO$_4^{2-}$, NO$_3^-$, PM$_{2.5}$, and HNO$_3$ were minor, but that for O$_3$ was large with a bias reduction of ∼67% for EMEP and ∼74% for EANET (Table 4). In the STD case, too little NO$_x$ is left from its heterogeneous loss, causing a net O$_3$ chemical destruction, which in turn, reduces the model overestimates for O$_3$ in the OLD case (Table 5; Figure 3(c,f,i), red versus blue lines). However, further improvements in the chemical scheme
are necessary to reproduce the O$_3$ measurements better; namely, a larger O$_3$ reduction for the summer and a reduced effect in simulated O$_3$ for the winter might alleviate the undesired effects. A delayed minimum from summer (as observed) to early winter (calculated in OLD and STD runs) causing opposite seasonality for O$_3$ is prominent for the low-NO$_x$ EANET stations (Figure 3(f)). Due to the O$_3$ reduction, the increment in CO for EMEP stations reconciles the model's underestimation of CO high peaks in spring (Figure 3(j)), thereby, strongly dwindling the bias for CO by ~59% (Table 4). However, the CO concentrations from May to the end of the year were overestimated in the STD run. This finding might indicate inadequate HONO emissions for the EMEP stations, which have a reducing effect and eliminate the model overestimates for CO (Figure 3(jj): oranges). In general, the verifications with EANET and EMEP showed that HONO impacts on NO$_x$, O$_3$, and CO were vastly dominated by cloud uptakes, except aerosol effects on NO$_x$ for high-NO$_x$ regions.

To solve the problem of underestimated NO$_x$ abundances and the ill-reproduced seasonality mentioned above, an explicit inventory for surface NO$_x$ emissions and/or a NO$_x$ recycling process is required. Figure 3(aa,dd,gg) shows that the improvements in the HNO$_3$ simulation could arise due to higher NO$_x$ emissions and strengthening aerosol uptake. Such a recycling mechanism via the reaction HNO$_3$ $\rightarrow$ NO$_2$ (R7) on soot particles (Lary et al., 1997; Akimoto et al., 2019) was also investigated by changing the HNO$_3$ uptake coefficient for HNO$_3$ from $3 \times 10^{-5}$ to $4.6 \times 10^{-3}$. Unfortunately, implementing R7 in CHASER could not successfully recycle NO$_x$ for the EANET and EMEP sites (the result is omitted). Furthermore, intensifying heterogeneous HONO formation in summer might further reduce O$_3$, as discussed in Section 3.1.5.

### Table 5: Model comparison of different species with observations at the EMEP and EANET stations.

Three-sigma-rule outlier detection is applied for each station before calculating correlation coefficients $R$. NO$_x$ data are filtered once more using the two-sigma-rule. $R$ and bias of the STD run are shown as bold if improved compared to the OLD run. Units for model biases for PM$_{2.5}$, SO$_2$, NO$_x$: µm m$^{-3}$; HNO$_3$, NO$_x$, O$_3$, CO: ppb.

<table>
<thead>
<tr>
<th></th>
<th>EMEP</th>
<th>EANET</th>
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<tr>
<td></td>
<td>PM$_{2.5}$</td>
<td>SO$_2$</td>
</tr>
<tr>
<td>R(STD)</td>
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<td>0.655</td>
</tr>
<tr>
<td>R(OLD)</td>
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<td>0.631</td>
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<tr>
<td>bias (STD)</td>
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<tr>
<td>bias (OLD)</td>
<td>-3.044</td>
<td>0.752</td>
</tr>
</tbody>
</table>
Figure 3: Concentrations and changes by HONO inclusion for EANET and EMEP stations. (a-j) Observed and simulated concentrations during 2010–2016. Black lines: observation; red: STD case; blue: OLD case. In (b), concentrations in STD and OLD are 10 times-folded for better visualization (red and blue lines). For each group of stations, dotted lines are all stations’ median from each station’s monthly-mean values. Thick solid lines represent two quarters averaged from dotted lines. (aa-jj) Calculated monthly-mean changes by HONO chemistry. Green bars: monthly changes by GRs; blue: by HRs on clouds; grey: by HRs on aerosols; orange: by EM. Stations are grouped as high-NOX EANET (first and fourth rows), low-NOX EANET (second and fifth rows), and all EMEP stations (third and sixth rows). First column: HNO3; second column: NOx, third column: O3, fourth column: CO.
3.1.3 Effects of HONO chemistry in coastal regions

The simulations also compared with the research vessel (R/V) Mirai’s observation in the western Pacific Ocean for O₃ and CO. The interpolation of model results for six cruises across Japan–Alaska region (40° N−75° N, 140° E−150° W) in 7-8/2015–2017 (summer), Indonesia–Australia region (5°−25° S, 105−115° E), and Indonesia–Japan region (10−35° N, 129°−140° E) are provided for the period of 12/2015 - 1/2016. All the measured and simulated data were provided, whereas the data for the NP region (40°−60° N) were analyzed separately, as discussed in Section 3.2. More detailed information about the R/V Mirai can be found in Kanaya et al. (2019). Furthermore, the model evaluation with Mirai for the OLD run can be found in Ha et al. (2021).

Table 6 shows correlation coefficients, which indicate that the STD simulation for CO and O₃ agree well with Mirai (R =−0.6). However, these correlation coefficients are slightly worsened, compared with the OLD case. Although the HONO inclusion mostly reduces the model bias for CO, especially in the NP region (-16.158 to -4.948 ppb), the model bias for O₃ is increased. The model biases exhibit negative trend for both CO and O₃ in the OLD case. This simulation pattern for O₃ in the NP region is in line with the OMI comparison (Sect. 3.1.1). This finding seemingly indicates an insufficient downward mixing process of O₃ in the free-troposphere or inconsistent surface deposition (Ha et al., 2021; Kanaya et al., 2019). However, the CO underestimations in the NP region might mark the inadequate CO emission in the HTAP inventory in CHASER (Ha et al., 2021). In Figure 4(a,c), overestimations of CO and O₃ are visible along Japan-Indonesia-Australia (Track-2) during the low episodes in December/January. Here, the larger model biases might account for the model's insufficient halogen chemistry (Kanaya et al., 2019; Ha et al., 2021). Figure 4 shows the model’s percentage discrepancies for O₃ from Mirai’s data, except those from HONO concentrations interpolated for these regions. The underestimated simulations of O₃ are enlarged, especially in the Japan – Alaska region, being driven by the reduction effects in the STD case. In other way, these effects weaken the O₃ overestimates across the land areas, namely, over the region near Japan and near Indonesia-Australia. Moreover, the higher HONO levels are identified for these off-shore data with up to 1.4 ppb abundances (Figure 4(c): red numbers). This high HONO level might be and underestimation of a true level as a stronger reduction for O₃ is required for the STD run (Figure 4(a): red marks).

The effects of the HONO chemistry along the R/V Mirai tracks exhibit various trends for each mechanism. Figure 5(b,d) illustrates O₃ and CO changes, triggered by the HONO gas reactions (GRs), uptakes (HRs), and emission (EM). The gaseous reactions (blue bars) have mostly increased CO level, except some reductions at the peak CO level for the NP region. Furthermore, O₃ level is slightly increased due to GRs north of 60° N, but is also often decreased in the NP region and varies near land areas. HRs, largely consuming NO₂, reduced O₃ (as large as 8 ppb), and increased CO (~10 ppb) levels (Figure 5(b,d): orange+green). HRs, (particularly HRs on cloud surfaces, shown by orange bars), exerted the strongest contribution to the calculated changes in O₃ and CO among the three HONO pathways. This predominant cloud effect was also prominent in the previous comparisons, especially EMEP (Figure 3(ii,ij): blue), thereby, indicating substantial effects of clouds at the mid-latitudes where the cloud SAD is higher (Figure S1). HRs on aerosols (green bars) have minor contributions during all cruises,
despite they caused a marked increase in the O$_3$ concentrations off-coast Japan (track #3). It should be noted that this is not enough to explain the simulation bias with regards to the measurements. The additional HONO from direct emission (red bars) has mainly increased O$_3$ and has reduced CO concentrations, especially near land (latitude < 50° N). This finding resonates with the comparison for continental stations (Figure 3(cc,ff,ii,jj): oranges). The overall effects of the HONO chemistry along Mirai cruises tend to reduce O$_3$ and to increase CO levels. For the NP region, CO level increase and OH revel reduction also can ameliorate the model performance. The improved model performance is evidenced from the comparison of the simulation with aircraft data as well (Figure 7(g,h)). Thus, the strengthened underestimation of O$_3$ concentration in the NP region is unlikely driven by HR on cloud particles (Sect 3.1.1 and Ha et al., 2021). It is rather related to the inconsistencies in the surface deposition of ozone. These inconsistencies are supported by empirical evidence as the negative bias in this comparison turns neutral or positive for the aircraft measurements in the same region (Figure 7(f): at 1000 hPa). The latter pattern is shown in the next section of this study as well.

### Table 6: Model comparison with Mirai cruises: no outlier filter is applied. N is the available data for each calculation. Correlation coefficient (R, no unit) and biases (ppbv) in STD run are shown as bold if better than those in OLD run.

<table>
<thead>
<tr>
<th></th>
<th>CO (N=4030)</th>
<th>CO (40–60° N) (N=1374)</th>
<th>O$_3$ (N=3893)</th>
<th>O$_3$ (40–60° N) (N=1418)</th>
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<tbody>
<tr>
<td>$R$(STD)</td>
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<td>0.586</td>
<td>0.568</td>
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<td>0.601</td>
<td>0.628</td>
<td>0.642</td>
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<tr>
<td>bias (STD)</td>
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<td>-8.823</td>
<td>-7.823</td>
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<tr>
<td>bias (OLD)</td>
<td>-8.136</td>
<td>-16.158</td>
<td>-3.625</td>
<td>-1.472</td>
</tr>
</tbody>
</table>

Figure 4: Percentage discrepancies of STD (a) and OLD (b) simulations from Mirai for O$_3$ and HONO concentration in STD (c). The red numbers in (c) indicate maximum HONO concentrations for each cruise.
Figure 5: Validation with ship-based data. Observed and simulated concentrations (a, c) and daily mean effects by HONO chemistry (b, d) for O₃ and CO during Mirai cruises. In (a, c), grey dots: observation, black lines: OLD case, red lines: STD case. In (b, d), blue bars: changes by GRs; orange: by HRs on clouds; green: by HRs on aerosols; red: by EM. The left axis exhibits the concentrations and changes (ppbv). The right axis shows cruising latitudes plotted as dashed lines. The horizontal axis is travel times (UTC). Vertical light-blue shaded areas are for data in the NP region (140–240° E, 40–60° N).
3.1.4 Effects of HONO chemistry in the free troposphere

The model performance of the free troposphere was evaluated through the atmospheric tomography (ATom1) aviation in August 2016 for NO$_2$, OH, CO, and O$_3$. The STD run reconstructed the chemical field observed in ATom1 with moderate or strong positive correlations for NO$_2$, OH, CO, and O$_3$ ($R_{NO2}=0.730$, $R_{O3}=0.751$, $R_{OH}=0.579$, $R_{CO}=0.659$; Table S2). For the NP region, the model correlations for these species were slightly lower ($R_{NO2}=0.621$, $R_{O3}=0.609$, $R_{OH}=0.407$, $R_{CO}=0.596$; Table S2). The $R$ values for NO$_2$ and CO were always higher in the STD run, compared with those in the OLD run, while for OH and O$_3$, the $R$ values are only improved for the NP region (Table S2).

Figure 6 shows measured (grey) and simulated (red and black) NO$_2$, O$_3$, OH, CO concentrations and the effects of including HONO in the simulation for the NP region (flight #2 on August 3rd). Figure 7 displays vertical profiles of the HONO chemistry's model biases and photochemical effects. Here, the data in all flights or in NP region are classified based on the air pressure from 1000–200 hPa (±50 hPa) and separated on nine bins. In the NP region, the OLD run (black lines) tends to overestimate NO$_2$, O$_3$, OH, but it underestimates CO at the lower troposphere, whereas the unsteady discrepancies at the upper layer are visible (Figure 6(a,b,e,f)). All four species tended to be underestimated near the tropopause (300–400 hPa) and to be overestimated in the lower stratosphere (Figure 7(e-h)). The HONO inclusion in STD run (red lines) has reduced NO$_2$, OH, O$_3$ and has increased CO levels, thereby, dwindling the model biases for NO$_2$, OH, and CO in the NP region except near the tropopause (Figure 7(e,g,h)).

In the NP region, the surface NO$_2$ level is reduced under the effects of HONO uptake on clouds (Figure 6(c): orange bars in vertical pink shades and Figure 7(p)). Hence, O$_3$ and OH are correspondingly reduced as their formations are limited in the absence of sufficient NO$_x$, that is, OH formation via HO$_2$ + NO → OH + NO$_2$ (Figure 6(d,g): orange bars in pink columns and Figure 7(q,r)). Near the surface, aerosol HRs only slightly affected atmospheric species, whereas at high altitudes, the aerosol uptake is more relevant to the OH, O$_3$, and CO concentrations (Figure 6(c,d,g,h) and Figure 7(q-s): green bars). The dominant cloud effects near the surface appear plausible for an ocean region with high cloud fractions at the lowest layer (Figure S2). GRs also affect OH, O$_3$, and CO, whereas the effects are rather manifested in the upper troposphere than in the lower troposphere. This is likely the most influential factor that increases OH and O$_3$ levels at these high altitudes (Figure 6(d,g) and Figure 7: blue bars). The additional HONO from direct emissions had minor effects on NO$_2$ and OH but contributed to the reductions of O$_3$ and CO at high altitudes (Figure 6(c,d,g) and Figure 7(q,s): red bars). At 900 hPa, the HONO emissions significantly reduced NO$_2$ near the continental areas (Figure 7(l): red bars) due to its uptake by particles. These effects of the HONO chemistry in the STD simulation somewhat reduce the model biases for NO$_2$, O$_3$, OH, and CO (Figure 7(a-h): red numerical texts are the percentage reduction in model bias). Note that these biases are very pronounced near-surface (~1000 hPa) in the NP region (51.7% for NO$_2$, and 77.3% for OH). To capture the patterns identified by observations in the upper troposphere, except the NP region, more robust increases for NO$_2$ and OH levels are still required (Figure 7(a,c)). At these altitudes, NO$_x$ and HO$_x$ sources from lightning (Brune et al., 2021) or aviation can be relevant, as discussed in Section 3.1.5.
Overall, the comparisons between the model and Mirai and ATom1 may indicate that the HRs on cloud surfaces are the main contributing factor to the marine boundary's photochemistry, whose effects emerged during the ATom1 flights in the marine atmosphere. GRs and aerosol HRs exert stronger impact on atmospheric chemistry at higher altitudes, compared with the near-surface layer. Also, their effects should be enhanced through the supplemental NOx and HONO sources to reconcile the model simulations with the observations.
Figure 6: Concentrations and variations by HONO chemistry for NO$_2$, O$_3$, OH and CO during ATom1 flight #2 (198–210° E, 20–62° N). In (a-b, e-f), concentrations by observation (grey dots), simulations in OLD case (black lines), and in STD case (red lines) are plotted. In (c-d, g-h), changes in concentrations by GRs (blue bars), EM (red), HRs on clouds (orange), and HRs on aerosols (green) are plotted. Vertical blue and grey columns reflect the data for the regions with air pressure P > 500 hPa.
3.1.5 Comparison of measured and simulated HONO concentrations at daytime

In this section, CHASER-based HONO estimates were evaluated by using the HONO measurements, collected during the EMeRGGe campaign off-coast eastern Asia in spring 2018 (Andrés Hernández et al., 2021). The HONO measurements in the free troposphere could provide essential information on the underlying gas-phase and heterogeneous HONO formation mechanisms as most current HONO measurements were conducted in the surface air. The daytime HONO concentration was retrieved from the aircraft-borne limb measurements using the HALO mini-DOAS (differential optical absorption spectroscopy) instrument, in which the UV light (310–440 nm) absorbed by HONO was detected (Hüneke et al., 2017). The mini-DOAS's measurement method relies on near-UV/VIS/IR skylight spectroscopy in nadir and limb geometry. Data evaluation consists of three steps: (1) retrieval of slant column densities (SCDs) of trace gases by the DOAS method (Platt and Stutz, 2008), (2) forward radiative transfer modeling for each measurement using McArtim (Deutschmann et al., 2011); and (3) retrieval of concentration through a new scaling method for UV/VIS data (Stutz et al., 2017; Hüneke et al., 2017; Werner et al., 2017; Kluge et al., 2020; Rotermund et al., 2021).

Additional sensitivity runs were conducted to explore potential HONO sources during the daytime (Table 7). The correlation coefficient (\( R \)) and model biases against EMeRGGe for HONO are shown in Table S3. As seen, general underestimations of HONO simulations are identified, in which better correlations are found at 1000–2000 m by the STD run (0.31–0.49). Vertical profiles for HONO and other species (NO\(_2\), O\(_3\), CO), retrieved from the EMeRGGe flights were applied for the measurement-based model evaluation (Figure 8). The model discrepancies for the measurement for HONO (\( \Delta \text{HONO} \)) and NO\(_2\) (\( \Delta \text{NO}_2 \)) in each flight trajectory, i.e., from Taiwan to South Korea, Japan, and the Philippines, are separated into bins of altitude ranges 0, 1000, 3000, 5000, and 6000 m (Figure 9). The frequency distributions of \( \Delta \text{HONO}, \Delta \text{NO}_2, \Delta \text{O}_3, \) and \( \Delta \text{CO} \) are shown in Figures S7 and S8. Plots similar to Figure 9 but for all cruising altitudes (0–8000 m) are shown in Figure S9, and those for O\(_3\) and CO are shown in Figures S10 and S11, respectively.

Figure 8(a) shows the vertical average score (cruising altitudes ± 500 m) for the measured (blacks) and simulated HONO concentrations in STD (reds) and those results of sensitivity cases. The measured daytime HONO concentration was close to the boundary layer (below 1,000 m) over Taiwan, averaged at 115 ppt, and was peaked at ~250 ppt. Also, the HONO concentration decreased up to 9,000 m, with mean values dropping from 70 ppt (2000 m) to < 20 ppt (5000 m) and < 10 ppt above. Unexpectedly, the simulated HONO concentration (STD) significantly underestimated the observations. They reached only 30–70 ppt at 1,000 m and nearly zero from 2,000 m upward (Figure 8(a): red versus black triangles for the simulation and the observations, respectively). These discrepancies indicate a significant unknown HONO source during the daytime, despite the proposed heterogeneous HONO formation mechanisms were incorporated in our model. This finding adds another
instance of evidence about missing HONO sources in the polluted boundary layer and free troposphere (e.g., Kleffmann et al., 2003; Li et al., 2014; VandenBoer et al., 2013; Xue et al., 2021a; Ye et al., 2018).

A previous study addressed the altitudes below 300 m, where HONO deposited onto the ground surface at night, and further proposed to be a significant reservoir for HONO during the day (VandenBoer et al., 2013). However, this source may only affect the lower boundary layer, while only insignificantly contributing to the tropospheric HONO budget (Ye et al., 2018; Zhang et al., 2009). Such a parameter for ground surfaces in a global model is somewhat uncertain, whereas the missing daytime HONO is still identified at 5000 m altitude. Thus, the amplified existing mechanisms and the additional sources for HONO in the free troposphere are examined in this study as well.

As the implemented HR HONO formation processes was likely insufficient, a series of additional sensitivity simulations was performed as well (Table 7). The AIRC case is aimed to evaluate another source of HONO emission, that is, aircraft emissions of HONO with a HONO/NO\textsubscript{x} emission by a factor of 0.4. In the EMx8 case, the HONO/NO\textsubscript{x} emission factor is amplified up to 0.8 (=0.1 in STD case), being focused to emphasize the sensitivity of HONO’s direct source from the ground layer, especially from soils as suggested by the previous study (Oswald et al., 2013). In the GRx8 case, the rate constant of (R2) is eightfold with the increase in homogeneous HONO production, given the fact that the daytime missing HONO could be relevant to other gas-phase formations (Romer et al., 2018; Li et al., 2014). Furthermore, the factor 8 applied in EMx8 and GRx8 cases were selected after testing with factors 2 and 4, aiming for simulations to agree with the measurements. In the maxST case, the uptake coefficients (γ-values) of NO\textsubscript{2} on organic and black carbons are maximized to 0.1 (R4, R5). Results from the maxST case can be used for estimation of the separate role of soot uptake under daytime conditions (George et al., 2005; Monge et al., 2010; Ndour et al., 2008), which could achieve an unrealistically high γ-value of 10\textsuperscript{-1} to 10\textsuperscript{-8} (Ammann et al., 1998; Kalberer et al. 1999). The ratR4 case is run in an attempt to produce more HONO from heterogeneous sources by altering the HONO: HNO\textsubscript{3} yield ratio in (R4) to 0.9: 0.1. The last case, ratR4+CLD, is the same as the ratR4 case, except for \( \gamma_{oc} \) increased a hundred-fold (1e\textsuperscript{-4} \rightarrow 1e\textsuperscript{-2}). The main idea here is to evaluate whether the missing HONO source was sensitive to cloud uptake in this region or not.

### Table 7: Additional sensitivity simulations in this work.

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<thead>
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<th>No.</th>
<th>Simulation ID</th>
<th>Description</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AIRC</td>
<td>aircraft HONO emission = 0.4% aircraft NO\textsubscript{x} emission</td>
<td>Not applied in STD</td>
</tr>
<tr>
<td>2</td>
<td>GRx8</td>
<td>Rate (R2) × 8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>EMx8</td>
<td>EM(HONO) = 0.8 NO\textsubscript{x} emission</td>
<td>= 0.1 in STD</td>
</tr>
<tr>
<td>4</td>
<td>maxST</td>
<td>( \gamma_{oc} ) and ( \gamma_{oc}(R4, R5) = 0.1 )</td>
<td>See Table 2 for γ-values in STD</td>
</tr>
<tr>
<td>5</td>
<td>ratR4</td>
<td>NO\textsubscript{2} \rightarrow 0.9HONO + 0.1HNO\textsubscript{3} (R4)</td>
<td>Product ratio is 0.5:0.5 in STD</td>
</tr>
<tr>
<td>6</td>
<td>ratR4+CLD</td>
<td>ratR4 and ( \gamma_{Hg}(R4) = 0.01 )</td>
<td>= 0.0001 in STD</td>
</tr>
</tbody>
</table>

In the model, the measured NO\textsubscript{2} below 3000 m (±500 m) close to land was captured well (Figure 9(a,d,h): magentas and greens), with 34% of the data being quite close for NO\textsubscript{2} (±70 ppt) (Figure S7(d)). However, the simulated HONO mixing ratio
is still underestimated by the modeling by up to 250 ppt (Figure 9(a): green). Over the off-coast of Taiwan bound to Japan, NO₂ was overestimated by up to 600 ppt in the model, corresponding to 20–70 ppt missing HONO (Figure 9(a,d): small oranges left of vertical line). The missing HONO can be driven by the low uptake of NO₂ on organic carbon and soot, as the amplified maxST cases could alleviate the model underestimates for HONO (Figure 9(a,d) versus (c,f)). The maxST run further reduces NO₂ level, thereby, implementing these cases in practice requires a more efficient recycling of NO₂. Besides the uptake on organic and black carbon, identified in the maxST simulations (they are the most efficient HONO producers), we identified the NO₂ uptake on sulfate nearly as important through a parallel test (not shown). For the middle troposphere (5000–6000 ± 500 m) over the Taiwan Island, too abundant NO₂ is predicted by the model during the cruises bounding to South Korea (up to 40 ppt) and the Philippines (up to 20 ppt) (Figure 9(k,n): small greens and blues left of the vertical line). These overabundances might hint on the deep stratospheric intrusion in springtime that caused imperfect downward mixing fluxes (Lin et al., 2012; Stohl et al., 2003; Trickl et al., 2014). This excessive NO₂ and the corresponding missing HONO are also sensitive to the AIRC and GRx8 cases (Figure 9(k,n) versus (l,m)), indicating that aircraft-exhaust of HONO could adjust the HONO/NO₂ ratio and more homogeneous HONO production might contribute more, given the high abundances of oxidizing substances at these altitudes.

The model underestimation for HONO is also associated with the concurrent underestimation of NO₂, which was observed more often at the altitudes of > 1000 m. The likely erroneous NO₂ concentrations of ~1.8 ppb (1000 m) and ~220 ppt (3000 m) across Taiwan, linked with HONO of as high as 290 ppt (1000 m) and 140 ppt (3000 m), were not reproduced (Figure 9(d,h)). These likely inadequate NO₂ abundances can be partially alleviated through the enhanced HONO/NO₂ emission ratio and more efficient NO₂ recycling process in the EMx8 and ratR4+CLD cases, respectively (Figure 9(e,g,i,j)). Here, the missing HONO is largely supplemented only at ~1000 m over the marine environment, namely, during the Taiwan-Japan cruise, when we identified more product for HONO on cloud in the ratR4+CLD case. (Figure 9(d,g): red-orange diamonds). At ~6000–8000 m, small deficits of 60 ppt NO₂ corresponding to ~10 ppt HONO (Figure 9(e-i): small oranges and magentas) might correspond to lightning NOₓ emissions (Sudo et al., 2002) and stratospheric sources. There were no heterogeneous or emission cases that succeeded in providing more HONO at this height, but some homogeneous mechanisms at ~6000 m as in the GRx8 case could be effective (Figure 9(n,o)).

However, these sensitivity cases only correspond to at most 35–45 ppt elevated HONO at ~1000 m (by maxST) for a total of 110–115 ppt HONO underpredicted (Figure 8(a)), requiring more efficient HONO formation mechanism. The model also underestimated O₃ and CO by less than 25 ppb (freq. 79%) and 100 ppb (freq. 60%), respectively (Figures S10, S11), which are larger than the model biases against ATom1 observations (Figure 7) because of possible inland influence. A further scrutiny of the higher proportion of HONO emissions and the increased uptake efficiencies for aerosols at 0–500 m and clouds at 1000 ± 500 m are recommended. For the boundary layer, the daytime HONO concentrations could be enhanced with a more accurate and detailed emission inventory for substances such as NOₓ and CO. This is sensible as this region is the outflow of the Pearl River Delta and Yangtze River Delta regions. To capture the measured patterns at the middle-to-high altitudes, NO₂ and O₃ levels should be adjusted through more sophisticated vertical mixing and downward fluxes of NOₓ and O₃ from the
stratosphere. The possibility of aircraft engine emissions should also be investigated further by elucidating the role emissions of aviation-induced particles on which NOx to HONO conversion could reach 45% (Meilinger et al., 2005).

The upper limit for the aerosol uptake coefficients (maxST case) may be applicable for the lowest cruising altitudes, which induced the increase of modeled HONO levels during both daytime and nighttime. For instance, the averaged summer mean of HONO in surface air reached the maximum at 0.8 ppb in the STD simulation, and it substantially increased up to 1.8 ppb in maxST (Figure S13(b): greens), thereby, alleviating the bias with regards to measurements (i.e., 2.0 ppb), reported in other studies (Li et al., 2012). This increase in the nighttime HONO level is also visible in the ratR4 simulation, but is twofold weaker, compared to that in maxST (Figure S12: blue). Moreover, the strong aerosol uptake parameters further reduced O3 concentrations down to the measured minima in summer (Figure S12(d,e,f): blues versus greys, as discussed for the continental data (Section 3.1.2)). The simulations with R4’s product-ratio HONO/HNO3 as large 9/1, enhancement for both NO2 and O3 compared to the STD case are expected given less NOx loss via HNO3 deposition. However, the enhanced uptake of clouds, applied in ratR4+CLD would reduce O3 concentration below 2500 m instead (Figure 8(b,d): browns < reds) as HNO3 can affect the O3 concentrations via renoxification mechanisms (Schneider et al., 1998). In fact, the HONO chemistry affects minor NO3 concentrations, compared to the product ratio 1:1 ratio in (R4) with the trial product ratio. In this way, the original NOx seasonality (Figure S12: cyan) is retained and the problem with NOx seasonality is mitigated (see details in Section 3.1.3). The trial ratio in R4 produced more HONO without disturbing the seasonal variability of NOx, thus leading to more OH. This effect on the OH concentration (ratR4) results in a slight increase in the CH4 lifetime, but less than in the STD case (+5.6% versus +13.1%). If (R4)’s product ratio towards more HONO formation is plausible, the impact of HONO on the tropospheric oxidizing power should be much smaller than that discussed in Section 3.2.2.

The photolysis of particle-phase NO3− (aNO3−) < 300 nm has been previously suggested as a supplemental NOx source (Romer et al., 2018) which might be another remedy for the inaccurate NOx seasonality in this study. Moreover, aNO3− photolysis can be the efficient HONO production mechanism during the daytime in an aqueous environment with low pH and the presence of OH scavengers (Benedict et al., 2017a; Benedict et al., 2017b; Ye et al., 2018). This mechanism is valid, despite the produced HONO may be destroyed by the liquid-phase OH (Scharko et al., 2014). To apply this particle-phase photolysis to a model as an efficient HONO source, one needs to apply sophisticated computation of VOC and OH. Moreover, another light-dependent gas-phase HONO source might lead to a cycle with zero net production of HONO, NOx, and HOx, that is, HO2·H2O + NO2 → HONO followed by HONO photolysis (R1) (Li et al., 2014). In CHASER, only gas-phase NO3− photolysis was introduced with the only channel to regenerate NO2. The suggested reaction HO2 + NO2 → HONO + O2 (Burkholder et al., 2015) was introduced, but it did not successfully preserve the total reactive nitrogen chemistry (NOx); hence, it was omitted in this study. The remaining drawbacks in reproducing HONO and other atmospheric species (NO2, O3, CO) by model urges further elucidation of more efficient HONO formation mechanisms. To this end, one needs (1) to provide better emission inventories for anthropogenic sources of pollutants from Southeast Asia and East Asia, lightning-produced NOx and HOx, and aviation-induced aerosols, (2) to improve the vertical mixing and air mass transport from the stratosphere, (3) to apply other potential HONO formation mechanisms and NOx recycling processes alongside the selection and algorithm development.
among the sensitivity tests provided here; and (4) to simulate the lower and upper limits for the uptake coefficients of NO$_2$ on aerosols and clouds.

Figure 8: Vertical profiles of (a) HONO, (b) NO$_2$, (c) CO, and (d) O$_3$ measured in EMerGGe campaign and calculated in sensitivity runs. Diamonds (for OBS, STD, OLD) and dots (for other runs), boxes indicate mean, 25$^{th}$ and 75$^{th}$ values, respectively. In panel (a), whiskers with two caps show min and max HONO levels; all sensitivity runs are shown except OLD (the case without HONO chemistry). In (b), AIRC and GRx8 runs are omitted due to minor effects and obscured by STD run. In (c), (d), GRx8 run are omitted for the same reason and obscured by AIRC run. Colours are black for observation, red for STD run, orange for AIRC run, green for GRx8, blue for EMx8, magenta for maxST, cyan for ratR4, and brown for ratR4+CLD, grey for OLD.
3.2 HONO’s global distribution and effects

3.2.1 Global HONO distribution and budgets

This section sheds the light on the global HONO distribution computed for the STD case. The surface HONO concentration is peaked over the geographical region that embraces China, with seasonal mean levels up to 2.8 ppbv during summer and 7.8 ppbv during winter (Figure 10(a,b)). The winter peak agrees with observations for a large industrial region in the Yangtze River Delta of China (Zheng et al., 2020). The high concentrations of HONO are also identified in other industrial regional clusters: Northeast America (seasonal mean up to 0.5–1 ppbv), India (up to 1–3 ppbv), forest regions, especially the extratropic evergreen forest in Europe (up to 1–3 ppbv), and Africa (up to 0.5–1 ppbv). Over the ocean, HONO levels remain at 10–30 pptv in the coastal regions and below 10 pptv far off the coast. The simulated HONO distribution is in line with a previous study (Elshorbany et al., 2012) despite the peaks over polluted Chinese areas are markedly higher in our model (tenfold) The overestimation associated with the soot uptake in our model has been previously neglected. The highest HONO concentrations (10–30 pptv) in the free troposphere (at 2500 m) were simulated over Africa’s biomass burning region during wet months (JJA) (Figure 10(c,d)), which could arise due to the NO2 uptake on aerosols, originated from this wildfire source.

In the model, HRs and EM are the main contributors to HONO at the surface layer (Figure 11) by providing efficient HONO formation and promoting gas reaction (R2). Of the various surfaces, provided for HRs in our model, liquid/ice cloud particle surfaces are supposed to catalyze significant photochemical effects in remote regions. This phenomenon has not been previously addressed in detail. The uptake of liquid/ice cloud particles either increases HONO formation via (R4) for the tropical and southern oceans or reduce it via (R6) along 60 °S in DJF and Artic in JJA (Figure 11(a,b)). Besides cloud particles, HRs on aqueous aerosols also produce HONO in a continental atmosphere rich in sulfate, dust, and soot particles (Figure 11(c,d)). EM included in the model has sharply increased the HONO level over deserts (Sahara, Arabian), grasslands (South Africa, South America), boreal, and agricultural land (West Europe, Australia). This finding agrees well with another study, based on spaceborne observations for HONO in wildfire plumes (Theys et al., 2020), and along ship tracks in the marine boundary layer (Figure 11(e,f)).

Table 8 summarizes the global sources and sinks of tropospheric HONO quantified by CHASER. The simulations indicate that GRs contribute only for 11% of the HONO net production. More significant HONO is produced by HRs and EM (contribute to 63% and 26% HONO net production, respectively). The pyrogenic HONO emission estimated in this study might be underestimated as HONO/NOx emission ratio could be enhanced by up to 1 at extratropic evergreen forests (universally 0.1 in this study (STD)) (Theys et al., 2020). For large metropolitan areas such as those in China, HRs and EM
have also been reported as the two most significant contributors to HONO formation, at ~59% and 26–29%, respectively (Li et al., 2011; Zhang et al., 2016). Of the various surfaces provided for HRs, aerosols represent more effective HONO formation site (~51.2%), compared with ice and clouds as they are contributing only 11.8% to HONO production. Moreover, the HONO loss through photolysis (R1) and (R3) is equivalent to its uptake onto the particles (R6). In equilibrium, the tropospheric abundance of HONO averaged of the globe is estimated to be 1.4 TgN in our model.

Table 8: Global sources and sinks of tropospheric HONO calculated by CHASER. Data from 2011.

<table>
<thead>
<tr>
<th>Sources</th>
<th>35.17</th>
<th>Sinks (TgN/yr)</th>
<th>33.77</th>
<th>Net productions 1.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGR</td>
<td>13.24</td>
<td>LGR</td>
<td>13.09</td>
<td>GRs</td>
</tr>
<tr>
<td>PHR</td>
<td>15.31</td>
<td>LHR</td>
<td>14.43</td>
<td>HRs</td>
</tr>
<tr>
<td>PHR(cld)</td>
<td>9.57</td>
<td>LHR(cld)</td>
<td>9.40</td>
<td>HRs(cld)</td>
</tr>
<tr>
<td>PHR(ae)</td>
<td>5.74</td>
<td>LHR(ae)</td>
<td>5.03</td>
<td>HRs(ae)</td>
</tr>
<tr>
<td>SEM</td>
<td>6.62</td>
<td>LEM</td>
<td>6.25</td>
<td>EM</td>
</tr>
</tbody>
</table>

P denotes chemical production, S denotes source (emission + chemical production), and L denotes loss. The numbers in parentheses represent the portion of each pathway to the total HONO net production.

Figure 10: Distribution of HONO levels at the surface (a-b) and meridional mean (c-d).
3.2.2 Implication of HONO on the tropospheric photochemistry

In this section, the global impact of HONO photochemistry is elucidated. To this end, Table 8 summarizes the HONO budget and the contribution of each pathway to the HONO photochemical cycle. Table 9 describes its consequences for the lifetime of CH₄, and the budgets of NOₓ, O₃, and CO. The gaseous reactions of HONO tend to increase the abundance of NOₓ, O₃, and CO (+1.01%, +0.15%, +0.44%, respectively) and CH₄ lifetime (+0.36%) in the troposphere. Without heterogeneous and direct emissions, the relatively low HONO formation by gaseous reactions (11% of the total net HONO production; Table 8) did not cause any significant effects on NOₓ, O₃, and CO in the troposphere.

Heterogeneous reactions that produce HONO are the most salient contributing factors to tropospheric chemistry, thereby, decreasing the tropospheric oxidizing capacity and increasing the CH₄ lifetime by 15% and CO abundance by 10%. HRs also reduces NOₓ level by 23% and O₃ level by 6%, respectively (Table 9). The global HONO distribution from Figure 12 is mainly caused by the HR formation of HONO. Here, the reducing effects for NOₓ levels, with consequences for OH and O₃ level reductions by heterogeneous reactions, are significant at mid-to-high latitudes during summer. More specifically, in DJF along 60 °S and the Arctic and NP oceans during JJA, which amounted to about a -100% reduction in NOₓ level at the surface (-60%

Figure 11: Contribution of HRs and EM to surface HONO concentrations. Contributions of HRs onto ice and clouds (a,b), HRs onto aerosols (c,d), EM (e,f) in DJF (left) and JJA (right) are plotted. Each contribution is determined by the difference of HONO in two simulations: (a,b): GR+HR(cld) and GR, (c,d): GR+HR and GR+HR(cld), (e,f): STD and GR+HR, divide by HONO in STD case. The maximum and minimum values are out-scaled hence displayed at the tops of each panel.
in OH and -40% in O₃ (Figure 12(a-f): blue areas). These reductions in NOₓ, OH, and O₃ levels extend up to 400 hPa at high N/S latitudes (Figure 12(k, l)). All these reduction effects for NOₓ, OH, and O₃ levels are due to the removal of HONO on ice and cloud particles (R6) (Figure 11(a, b)). On one hand, it accelerates the conversion of NO₂ to HONO and ultimately strengthens its deposition by particulate nitrate (R4). On the other hand, HRs occurring on aerosol surfaces lead to increments in OH and O₃ near the surface of polluted regions during winter. These are the main contributors to the regional photochemical effects over China, Western Europe, and East U.S. regions in winter (up to -74% in NOₓ, +1500% OH, +48% in O₃, Figure 12(a,c,e)). However, these increases of OH and O₃ levels are only accumulated in the surface layer (only small red areas at ~1000 hPa in Figure 12(i,m)). Compared to HRs on aerosol, HRs on clouds exhibit twofold effectiveness when reducing tropospheric NOₓ level (-15% versus -8%) and cause threefold effects on the tropospheric oxidation capacity (+11.5% in CH₄ lifetime, -4.6% in O₃, +7% in CO), compared with HRs on aerosol (+3.5% CH₄ lifetime, -1.5% O₃, +2.6% CO) (Table 9). Given the direct emissions of HONO (~10% of NOₓ emission inventory), the surface NOₓ, O₃, and OH concentrations are generally enhanced in the STD case compared to the GR+HR case. They induce the concentration modification for NOₓ (+1.77%), O₃ (+0.97%), CO (-1.63%), and a significant reduction (-2.3%) in the CH₄ lifetime (Table 9). Remarkable enhancements for NOₓ (up to +198%), OH (+243%), and O₃ (+24%) (Figure 12(b,d,f): red fields) were identified for the cropland and shrubland/forest regions in Australia, South America, and South Africa during JJA, and the boreal vegetation prevailing at mid-high latitudes in Europe, North America, and the polluted Chinese region in DJF (up to +748% OH) (Figure 12(a): red fields). NOₓ and OH were elevated in these mid-latitude regions because of the enhanced HONO photolysis (R1) by the additional HONO source. However, OH, NOₓ, and O₃ levels were reduced near the surface of the Northern Hemisphere’s land during summer (up to -47% OH, -82% NOₓ, and -15% O₃) (Figure 12(b,d,f)). The latter phenomenon is similar to the heterogeneous cloud effects for the high latitudes discussed above.

Overall, the inclusion of the three HONO processes (gas phase, aerosol and cloud uptakes, direct emission) causes -20% in NOₓ, -5% in O₃, +8% in CO, and a significant increase of +13% CH₄ lifetime in the troposphere (Table 9). Figure 13 highlights the consequences of HOₓ, NOₓ, and O₃ for the Chinese and NP regions. NOₓ level reduction accumulates in the Arctic and Antarctic during summer, especially over the NP ocean (reducing NOₓ level by 60–90%, Figure 13(i)). These reductions in NO₂ and HONO concentrations are due to their uptake onto ice and clouds in these regions. However, these reducing effects cause further reductions in OH and O₃ levels for a larger part of the troposphere. As NOₓ is essential in regulating O₃ and OH in the troposphere, a reduction of NOₓ level increases the HO₂/OH ratio (due to the HO₂ + NO → OH + NO₂ reaction), which restrains the formation of OH and ultimately of O₃. Thus, in summer, both OH and O₃ levels are drastically reduced over the NP region (35–67% for OH, 30–43% for O₃, Figure 13(g,k)), but CO level is increased by 18% in this region (Figure 12(h)).

The significant impacts of HONO photochemistry are especially relevant over Eastern China in winter, which may reduce NOₓ level by 48–78% (Figure 12(c)) due to the uptake of NO₂ onto aqueous aerosols. At the surface, OH level is enormously increased as a result of HONO photolysis (R1), heterogeneous NO₂ conversions (R4, R5), and additional direct emissions (Figure 13(a,b)). The corresponding increase in O₃ level was only identified at the surface of the Beijing region during winter,
with +28.8% caused by HRs on aerosols (Figure 13(e)). For Beijing with high NO\textsubscript{x} emissions, VOC-limited O\textsubscript{3} chemistry is likely the driving mechanism (Liu et al., 2010). The vast increases in OH and O\textsubscript{3} levels over Beijing in winter are basically in line with the present knowledge of HONO photochemistry (e.g., Lu et al., 2018). Elshorbany et al. (2012) also reported an increase in OH (2–5×10\textsuperscript{6} molecules cm\textsuperscript{-3}) and O\textsubscript{3} (0.3–0.5 ppbv) concentrations over polluted regions in China during winter. Compared with Elshorbany’s work, the increases in OH and O\textsubscript{3} concentrations in our model are higher due to the different HONO mechanisms applied in the two models, simply an averaged HONO/NO\textsubscript{x} ratio (0.02) in their model. In particular, our newly added heterogeneous reactions on cloud particles (R4) caused significant reductions in OH, NO\textsubscript{x}, and O\textsubscript{3} levels in the NP region during summer, which their model does not cover. The overall reductions in tropospheric oxidizing capacity due to HONO photochemistry are in line with the expected response to heterogeneous processes (Liao et al., 2003; Martin et al., 2003) and agree with those previously reported for other HRs (HO\textsubscript{2}, N\textsubscript{2}O\textsubscript{5}, and RO\textsubscript{2}) previously reported (Ha et al., 2021) (Table 9). Our findings indicate that a global model without heterogeneous processes for HONO would neglect the significant changes in OH and O\textsubscript{3} concentrations in remote areas and, thus, will underestimate the potential effects in polluted regions.

Table 9: CH\textsubscript{4} lifetime and tropospheric abundances for NO\textsubscript{x}, O\textsubscript{3}, CO and the changes by HONO chemistry

<table>
<thead>
<tr>
<th>Simulation ID</th>
<th>CH\textsubscript{4} lifetime (yr)</th>
<th>NO\textsubscript{x} (TgN)</th>
<th>O\textsubscript{3} (TgO\textsubscript{3})</th>
<th>CO (TgCO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLD</td>
<td>9.09</td>
<td>0.119</td>
<td>408.79</td>
<td>327.20</td>
</tr>
<tr>
<td>GR</td>
<td>9.12</td>
<td>0.120</td>
<td>409.38</td>
<td>328.65</td>
</tr>
<tr>
<td>GR+HR</td>
<td>10.49</td>
<td>0.092</td>
<td>384.25</td>
<td>359.90</td>
</tr>
<tr>
<td>GR+HR(cld)</td>
<td>10.17</td>
<td>0.102</td>
<td>390.46</td>
<td>351.53</td>
</tr>
<tr>
<td>STD</td>
<td>10.28</td>
<td>0.094</td>
<td>388.21</td>
<td>354.57</td>
</tr>
</tbody>
</table>

Effects | Changes (%) |
by GRs: | +0.36 +1.01 +0.15 +0.44 |
by HRs: | +14.99 -23.19 -6.15 +9.55 |
by HR(cld): | +11.52 -15.28 -4.63 +6.99 |
by HR(ae): | +3.47 -7.91 -1.52 +2.56 |
by EM: | -2.30 +1.77 +0.97 -1.63 |
Total: | +13.05 -20.40 -5.03 +8.36 |
by HRs(N\textsubscript{2}O\textsubscript{5},HO\textsubscript{2},RO\textsubscript{2}) (Ha et al., 2021) | +5.7 -3.87 -2.91 +3.43 |
32

Figure 12: Effects of the HONO photochemistry on the tropospheric oxidants OH (first row of panels), NOx (second row of panels), O3 (third row of panels) and (CO last row of panels). Effects at near the surface (a-h) and zonal means (i-p) are shown.

Figure 13: Effects of HONO photochemistry for the surface layer, for OH (upper panels), NOx (middle panels), and O3 (lower panels) over northeastern China region in DJF (a-f) and NP region in JJA (g-l) from dominant pathways of HONO by heterogeneous reactions of aerosols (1st column heterogeneous reactions ice and clouds (3rd column) and direct HONO emission (2nd and 4th columns).

4 Conclusion

The HONO photochemical processes, including (a) the gas-phase reaction involving HONO, (b) direct HONO emission from combustion and soil crust, as well as (c) heterogeneous processes involving HONO; all were added to the chemistry-climate
model (CHASER) for the first time by this study. We found that the model biases are reduced against the EANET/EMEP stationary observations for PM$_{2.5}$, NO$_3$ components, O$_3$, and CO concentrations when the HONO photochemistry is included. The overestimations of OMI-based TCO by simulations are mostly reduced by the HONO inclusion given its reducing effects for O$_3$, which notably includes the geographical region that embraces China. Although the simulation underestimations of surface O$_3$ in the NP region is associated with the inconsistent surface deposition or vertical fluxes (c.f. from the stratosphere) becoming stronger, the model still stands out with NO$_2$, OH, and CO improvements in this region, compared with the observations made during Mirai and ATom1. We also compared the measurements during the EMeRGe flights off the coast region of East Asia and discerned good agreement between the measured and calculated NO$_2$, O$_3$, and CO profiles. However, the influence of the Chinese river delta regions is not reflected in the model, as the large reductions in air masses affected by land emissions were identified.

In the model, the tropospheric abundance for HONO is 1.4 TgN and is made by 26% from the direct emission and 63% by HRs, in which HRs on clouds cause 11.8% and HRs on aerosols cause 51.2%. The HONO concentrations over the continents range from 30 ppt to 7 ppb and are maximized due to HRs over the eastern China during winter. Only 5–10 ppt of HONO can be transported up to an altitude of ~2000 m, thereby, indicating that its impacts remain mainly in the planetary boundary layer. We argue that these simulated HONO$_3$s may underestimate the actual concentrations off-coast of eastern Asia in spring 2018. The unknown daytime HONO concentrations of up to 200 ppt measured in the boundary layer and free troposphere during the EMeRGe campaign are not reproduced well by the model, possibly due to the small concentrations of NO$_2$, O$_3$, and CO in the model. Therefore, a further improvement of the model performance for the HONO photochemistry requires (1) the revised model’s emission inventory with the emission sources of NO$_x$ and CO from South-Eastern and Eastern Asia, (2) the lightning-related NO$_x$ module is upgraded, and (3) the vertical mixing and downward fluxes from the stratosphere to be elaborated. Higher uptake coefficients for aerosols near the surface and in the middle troposphere and on cloud droplets at ~1000 m could also produce more HONO and, therefore, alleviate the model discrepancies. The direct emissions of HONO from aircraft traffic may be an efficient local HONO source during the daytime. Moreover, the potential presence of aviation-originated aerosols in the middle troposphere for NO$_2$ conversion should be further investigated. One or more renoxification mechanisms converting HNO$_3$ into NO$_3$ should be added to the model to overcome the observed and simulated NO$_x$ seasonality mismatches. Shifting the product ratio towards more HONO and less HNO$_3$ in reaction R4 can also provide more HONO and can mitigate the deteriorated representation of NO$_x$ seasonality. The sensitivity tests also suggest that more robust aerosol processing in polluted areas and less HNO$_3$ product in R4 can further reduce O$_3$ level in summer, therefore, reducing the bias with regards to measurements. Besides that, both the diurnal and nocturnal HONO concentrations can be enhanced.

Of the three HONO sources, HRs produced the most prominent effects on the tropospheric photochemistry: reducing OH, NO$_x$, O$_3$, and increasing CO levels in the troposphere, leading to a +13.05% longer CH$_4$ lifetime, and -20.4% less NO$_x$, -5.03% less O$_3$, and an increased CO (+8.36%) abundance. In winter near the surface, gas-phase reactions involving HONO and NO$_2$ conversions on soot induce significant photochemical effects over eastern Chinese with changes of -60% in NO$_x$, +1700% in OH, +33% in O$_3$. During summer, HRs on ice and cloud particles could cause significant changes of -67% in OH, -45% in O$_3$,
-75% in NO\textsubscript{x}, and +17% in CO in the NP region. Albeit the more significant contribution of heterogeneous reactions to aerosols, the net HONO production, heterogeneous processes involving ice and cloud particles are more significant on a global scale. We found that the HONO chemistry, including the heterogeneous processes on cloud particles, can reduce the troposphere's oxidizing capacity on a global scale. It should be underlined that this finding is rather unexpected and is in contrast with the increasing oxidation capacity, previously reported for polluted areas. This new finding may also affect climate change mechanisms and, as a result, may influence its mitigation policies. Overall, our results prove that a global model without heterogeneous HONO formation, especially HRs on cloud particles, can bias the overall impacts of HONO on tropospheric photochemistry as it neglects the photochemical effects of HONO in remote areas and underestimates them in polluted regions. Notably, these photochemical effects of the HONO photochemistry on the tropospheric oxidizing power can be dwindled in the case of shifting of (R4)'s product ratio toward more HONO and less HNO\textsubscript{3} production, thereby, causing a reduction in the CH\textsubscript{4} lifetime from +13.1% to +5.6%.

**Code availability**

The CHASER V4.0 source code and input data to recreate this work’s results can be acquired from the repository at https://doi.org/10.5281/zenodo.4153452 (Ha et al., 2020).

**Data availability**

The primary data from *R/V Mirai* cruises for the period 2015–2017 are available from http://www.godac.jamstec.go.jp/darwin/e (last access: 30 September 2021). Due to a recent data security incident, the data owner (JAMSTEC) is suspending public access to this dataset. For any inquiries, please send email to yugo@jamstec.go.jp. The data collected by HALO aircraft during the EMerGe campaign are listed on https://www.iup.uni-bremen.de/emerge/home/halo_payload.html and can be acquired via email to Klaus.Pfeilsticker@iup.uni-heidelberg.de.

**Author contribution**

HP composed all simulations and text. SK has the model code and supervised the findings of this study. KY and TF provided *R/V Mirai* ship data. HM, BS, and KP provided EMerGe-Asia data. All authors have equally contributed to the discussion provided within the manuscript, and post-writing formatting and revisions.

**Competing interests**

The authors declare that they have no conflicts of interest.
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