# **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  $NO_x$  and  $HO_x$ , but its role in global atmospheric photochemistry is not fully understood. This study 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

- 15 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
- 20 for PM<sub>2.5</sub>, NO<sub>3</sub><sup>-</sup>/HNO<sub>3</sub>, NO<sub>2</sub>, OH, O<sub>3</sub>, 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 NO<sub>2</sub> near surface and in the middle troposphere, cloud uptake, and direct HONO emission are all potential yet-unknown HONO sources. The most promising daytime source for HONO found in this study is the combination of enhanced aerosol uptake of NO<sub>2</sub> and surface-catalyzed HNO<sub>3</sub> photolysis, which can also remedy the model bias for NO<sub>2</sub> and O<sub>3</sub> during EMeRGe. We also found that the simulated HONO abundance and its impact on NO<sub>x</sub>-O<sub>3</sub> chemistry are sensitive to the yield of the heterogeneous and conversion of NO<sub>2</sub> to HONO (vs. HNO<sub>2</sub>)
- 30 conversion of NO<sub>2</sub> to HONO (vs. HNO<sub>3</sub>).

Inclusion of HONO reduces global tropospheric  $NO_x$  (NO + NO<sub>2</sub>) levels by 20.4%, thereby weakening the tropospheric oxidizing capacity (OH, O<sub>3</sub>) occurring for NO<sub>x</sub>-deficit environments (remote regions and upper altitudes), which in turn,

increases CH<sub>4</sub> lifetime (13%) and tropospheric 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 O<sub>3</sub> (30–45%) in the NP region during summer, given the significant reduction of NO<sub>x</sub> level (50–95%). In contrast, HRs on aerosol surfaces in China (Beijing) enhance OH and O<sub>3</sub> winter mean levels by 600–1700% and 10–33%, respectively, with regards to their minima in winter. Furthermore, sensitivity simulations reveal that the heterogeneous formation of HONO from NO<sub>2</sub> and heterogenous photolysis of HNO<sub>3</sub> coincides in the real atmosphere. Nevertheless, the global effects calculated in the combined case, which most captured the measured daytime
- 40 HONO level, still reduce tropospheric oxidizing capacity. Overall, our findings suggest that a global model that does not consider HONO heterogeneous mechanisms (especially photochemical heterogeneous formations) 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 (NO<sub>x</sub> = NO + NO<sub>2</sub>)
and radical chemistry (OH, HO<sub>2</sub>, and RO<sub>2</sub>) (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

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:

attention of researchers (Kleffmann et al., 2003; Li et al., 2014; VandenBoer et al., 2013; Xue et al., 2021a,b; Ye et al., 2018).

(R1) HONO +  $h\nu \rightarrow$  OH + NO (300 nm <  $\lambda$ < 405 nm)

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(R2) NO + OH + M  $\rightarrow$  HONO + M (R3) HONO + OH  $\rightarrow$  NO<sub>2</sub> + H<sub>2</sub>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 O<sub>3</sub> 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).

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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 NO<sub>2</sub> for grassland in eastern England (Harrison and Kitto, 1994). Two reactions have been widely suggested to

- 65 produce HONO on aerosol surfaces:  $2NO_2 + H_2O \rightarrow HONO + HNO_3$  and  $NO + NO_2 + H_2O \rightarrow 2HONO$ . The first process has been proven to be first-order with NO<sub>2</sub> and H<sub>2</sub>O 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 O<sub>3</sub> and when NO<sub>2</sub> was the dominant form of NO<sub>x</sub> (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;
- 70 Gerecke et al., 1998). In the past two decades, researchers have investigated the heterogeneous NO<sub>2</sub> 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<sub>2</sub> → 0.5 HONO + 0.5 HNO<sub>3</sub> (R4) and NO<sub>2</sub> → 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 Wahner, 1995), and deliquescent aerosol surfaces (Harrison and Collins, 1998). The loss process occurs via the reaction HONO +  $H_2O \rightarrow NO^- + H_3O^+$ , simplified in our model as HONO  $\rightarrow$  NO (R6) for surfaces of liquid and aqueous sulfate aerosols.
- 80 The natural sources of HONO include plant-foliar 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<sup>-1</sup> 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<sub>x</sub> 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 field observational studies reported unknown HONO sources during the day, and various mechanisms have been proposed as efficient daytime HONO formation mechanisms. The photolysis of particle-phase  $NO_3^-$  ( $aNO_3^-$ ) < 300 nm has been previously suggested as a supplemental  $NO_x$  source (Romer et al., 2018) and 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; Scharko et al., 2014; Ye et al., 2018). Another study addressed the altitudes below 300 m, where
- 95 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). Such a parameter for ground surfaces in a global model is somewhat uncertain. Moreover, the HONO source from ground surfaces may only affect the lower boundary layer while insignificantly contributing to the tropospheric HONO budget (Ye et al., 2018; Zhang et al., 2009). Furthermore, the particle-phase NO<sub>3</sub><sup>-</sup> photolysis can occur

on both ground and aerosol surfaces (HNO<sub>3</sub> + h $\nu \rightarrow$  HONO) with a 2-orders-of-magnitude faster rate than its rate in the gas

phase (Lee et al., 2016; Lu et al., 2018). Photolysis of ortho-nitrophenols, photoexcited NO<sub>2</sub> gas reaction (HO<sub>2</sub>×H<sub>2</sub>O + NO<sub>2</sub>
 → HONO), photosensitized heterogeneous conversion of NO<sub>2</sub> on grounds are all potential daytime HONO sources (Jorba et al., 2012; Lee et al., 2016; Li et al., 2014), yet the mechanisms are complicated, and their efficiency are merely evaluated for ground-based observation.

Many scholars have scrupulously addressed the effects of HONO in polluted regions as well. For instance, HONO-induced

- 105 enhancements in winter daytime HO<sub>x</sub> (up to >200% for OH) and O<sub>3</sub> (6–12%) over urban sites in China have been reported (Li et al., 2011; Lu et al., 2018; Zhang et al., 2016). A box modelling study analysed the detailed budget of HONO in London and found that HONO chemistry increased OH by 20% during the day (Lee et al., 2016). A global modelling study found increments for OH and O<sub>3</sub> across the globe and throughout the troposphere, with a maximum of 30 ppb O<sub>3</sub> in Eastern Asia and slight NO<sub>2</sub> increment, although the results were evaluated with only ground-based data (Jorba et al., 2012). However, enhanced
- 110 O<sub>3</sub> levels in response to additional OH production from the HONO photolysis only occur in high-NO<sub>x</sub> regions, although they can be decreased in some areas under low NO<sub>x</sub> 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<sub>x</sub> and reported similar patterns for O<sub>3</sub> changes regarding HONO chemistry (Elshorbany et al., 2012). The NO<sub>x</sub> reduction effects that follow the NO<sub>2</sub> conversion are suggested to be more critical over the oceans than over continental regions, with up to 20% NO<sub>x</sub> reduction and 5%–20% HNO<sub>3</sub> enhancement over ocean 115 regions of the lower troposphere (Martin et al., 2003).

As H<sub>2</sub>O is required for the uptake of NO<sub>2</sub> on surfaces, wet surfaces have been broadly recommended as favoured surfaces for NO<sub>2</sub> uptake. Therefore, cloud droplets can be an important surface for heterogeneous reactions of NO<sub>2</sub> because they are ubiquitous in the troposphere. Heterogeneous reactions by clouds can have a similar impact as aerosol particles on tropospheric O<sub>3</sub> and OH levels (Christopher et al., 2019). However, this aspect has been overlooked many times in previous studies, leading to potential underestimating (or even dismissing) the potential effects over remote environments.

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- This study introduces HONO chemistry into the global atmospheric chemistry model CHASER-V4.0 for the first time. The standard model configuration uses basic mechanisms of HONO chemistry, while various sensitivity cases implement other potential HONO sources are also conducted to force simulation into an agreement with the observed HONO values. The main idea for the HONO inclusion is to elaborate the model simulation for tropospheric oxidative substances while focusing on
- 125 aerosol and cloud processes. The model includes the detailed online calculation of O<sub>3</sub>-HO<sub>x</sub>-NO<sub>x</sub>-CH<sub>4</sub>-CO coupling and oxidation of non-methane hydrocarbons (NMHCs) (Sudo et al., 2002) and heterogeneous processes for N<sub>2</sub>O<sub>5</sub>, HO<sub>2</sub>, and RO<sub>2</sub> 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 aircraft/ship, ground stations, particularly addressing the
- 130 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, verification for global effects to TCO with OMI satellite, global

HONO impacts including different effects from each pathway and a discussion on the uncertainty of the calculated effects. Finally, Section 4 effectively represents the summary and concluding remarks.

# 2. Method and configurations

### 135 **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 94 total species and 258 chemical reactions (57 photolytic, 180 kinetic, and 21 heterogeneous reactions on tropospheric aerosol and cloud surfaces and polar stratospheric clouds) (Table 1),
excluding 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: 16<sup>th</sup>, Nov 2021) for O<sub>3</sub> and aerosol precursors (NO<sub>x</sub>, CO, VOCs, SO<sub>2</sub>), 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 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<sub>x</sub> emissions (hereafter denoted as EM); and (3) the HONO conversion from NO<sub>2</sub> (R4, R5) and its loss on liquid/ice surfaces and aqueous aerosols (R6), which is hereafter denoted as HRs.
- 150 The heterogeneous photolysis of HNO<sub>3</sub> (HNO<sub>3</sub> +  $h\nu \rightarrow$  HONO), which was suggested as an efficient HONO source at daytime (Lee et al., 2016; Zhou et al., 2011), is investigated in Chapter 3 as sensitivity cases in the effort of making simulation for daytime HONO compatible with measurement. This photolysis is simplified using a factor multiply with HNO<sub>3</sub> photolysis in the gas phase (HNO<sub>3</sub> +  $h\nu \rightarrow$  OH + NO<sub>2</sub>) (see Sect. 3.1.2). The light-dependent gas-phase HONO source (HO<sub>2</sub>×H<sub>2</sub>O + NO<sub>2</sub>  $\rightarrow$  HONO) (Li et al., 2014) is not investigated in this study. However, a simple gas-phase reaction, HO<sub>2</sub> + NO<sub>2</sub>  $\rightarrow$  HONO +
- 155  $O_2$  (Burkholder et al., 2015), was introduced, but it did not successfully preserve the total reactive nitrogen chemistry (NO<sub>y</sub>); hence, it was omitted in this study.

#### 2.2. Experimental setup

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The Global Emissions Initiative (GEIA) inventory (http://www.geiacenter.org/) is applied to quantify the soil NO<sub>x</sub> emissions (6 TgN yr<sup>-1</sup>) and anthropogenic NO<sub>x</sub> emissions (45 Tg N yr<sup>-1</sup>). Since this broadly applied inventory is not currently available for HONO, this study tentatively imposes the HONO direct emissions based on the above NO<sub>x</sub> emission inventory through a

constant factor of 0.1 (10% of NO<sub>x</sub> emissions). This assumption (soils + combustion) leads to a global HONO soil-emission estimate of about 0.6 TgN yr<sup>-1</sup>, which is equivalent to the estimate from Porada et al. (2019), and it suggests that the anthropogenic emission for HONO is 4.5 TgN yr<sup>-1</sup>. 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"

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Base model	MIROC4.5 AGCM
Spatial resolution	Horizontal, T42 (2.8° × 2.8°); vertical, 36 layers (surfaces approx. 50 km)
Meteorology (u, v, T)	Nudged to the NCEP2 FNL reanalysis
Emission (anthropogenic, natural)	Industry traffic, Vegetation Ocean Biomass burning specified by MACC reanalysis
Aerosol	BC/OC, sea-salt, and dust BC ageing with SO <sub>x</sub> /SOA production
Chemical process	<ul> <li>94 chemical species, 263 chemical reactions (gas phase, liquid phase, non-uniform O<sub>x</sub>-NO<sub>x</sub>-HO<sub>x</sub>-CH<sub>4</sub>-CO chemistry with VOCs SO<sub>2</sub>, DMS oxidation (sulfate aerosol simulation) SO<sub>4</sub>-NO<sub>3</sub>-NH<sub>4</sub> system and nitrate formation Formation of SOA BC ageing</li> <li>(+) Heterogeneous reactions: 8 reactions of N<sub>2</sub>O<sub>5</sub>, HO<sub>2</sub>, RO<sub>2</sub>; constant uptake coefficients (γ) on types of aerosols (Ice, Liquid, Sulfate, Sea salt, Dust, OC)</li> </ul>

The photolysis reaction HONO +  $h\nu \rightarrow$  OH + NO (300 nm <  $\lambda$ < 405 nm) (R1) is employed with the wavelength-dependent 170 cross-sections following the recent study of Burkholder et al. (2015).

The kinetic of homogeneous reactions NO + OH + M  $\rightarrow$  HONO + M (R2) and HONO + OH  $\rightarrow$  NO<sub>2</sub> + H<sub>2</sub>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 only surface reactions are considered

in CHASER, 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

- 180 with a surface is taken up onto the surface. An average uptake coefficient for NO<sub>2</sub> (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., 2018). The NO<sub>2</sub> 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  $3 \times 10^{-3}$  (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<sub>2</sub> 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 <  $4\times10^{-8}$  for 5-day aged surfaces (Saathoff et al., 2001). In organic soot,  $\gamma$  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<sub>2</sub> conversion on organic carbon and soot (R5) was tentatively applied with uptake coefficients of  $10^{-4}$  and  $3\times10^{-4}$ , respectively, which also falls within the 190 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,  $3.7 \times 10^{-3}$  at 178 K to  $1.3 \times 10^{-5}$  at 200 K for the ice surface (Fenter and Rossi, 1996; Chu et al., 2000) and  $4 \times 10^{-3}$ - $4 \times 10^{-2}$  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
- 195 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 the atmosphere (Table 2: last row).

		Yice	Yliq.	Ysulf.	Ysalt	Ydust	Yoc	Yec
R4	NO <sub>2</sub> → 0.5HONO + 0.5HNO <sub>3</sub>	0.0	0.0001	0.0001	0.0001	0.0001	0.0001	0.003
R5	$NO_2 \rightarrow HONO$	0.0	0.0	0.0	0.0	0.0	0.0001	0.0003
R6	HONO → NO	0.002	0.03	0.003	0.0	0.0	0.0	0.0

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

#### 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, with a heterogeneous scheme containing eight reactions on N<sub>2</sub>O<sub>5</sub> (N<sub>2</sub>O<sub>5</sub>  $\rightarrow$  2HNO<sub>3</sub>), HO<sub>2</sub> (HO<sub>2</sub>  $\rightarrow$  0.5 H<sub>2</sub>O<sub>2</sub> + 0.5 O<sub>2</sub>), and RO<sub>2</sub> (RO<sub>2</sub>  $\rightarrow$  inert products) (Ha et al., 2021). The control case (STD) considers all three types of HONO sources: direct emissions (EM), gasphase reactions (GRs), and heterogeneous reactions (HRs). To quantify the effects of each mechanism using Eq. (1), two

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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 = OH, O<sub>3</sub>, NO<sub>x</sub>, CO) by concentration differences of i in two relevant cases being compared to that in the OLD case

$$E_i = \frac{(Case1_i - Case2_i)}{OLD_i} * 100 \,(\%),\tag{1}$$

where  $Case1_i$  and  $Case2_i$  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

215 ice and cloud particles.

Table 3: Sensitivity simulations in this work.

No	Simulation ID	Н	IRs	GRs	EM
INO.	Simulation ID	(HC	DNO)	(HONO)	(HONO)
		clouds	aerosols		
1	OLD				
2	GR			×	
3	GR+HR(cld)	×		×	
4	GR+HR	×	×	×	
5	STD	×	×	×	×

#### 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 6, and Figure S6.

Simulated tropospheric column ozone was also evaluated by using tropospheric column O<sub>3</sub> (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<sub>3</sub>, NO<sub>x</sub>, O<sub>3</sub>) in the Acid Deposition Monitoring Network in eastern Asia (EANET: https://www.eanet.asia/). We also used the European

- 225 Monitoring and Evaluation Programme (EMEP: https://www.emep.int/) data, which compiles observations over 245 European stations. We also utilized ship-based observational data from the R/V Mirai cruise the (http://www.jamstec.go.jp/e/about/equipment/ships/mirai.html) undertaken by Japan Agency for Marine-Earth Science and Technology (JAMSTEC). This study uses the surface CO and O<sub>3</sub> concentration data from summers 2015–2017 along the Japan-Alaska routes. The model data were compiled in the hourly timestep and interpolated, corresponding to the Mirai time 230 step and coordinates. То verify the vertical tropospheric profiles, ATom1 aircraft measurements
- (https://espo.nasa.gov/atom/content/ATom) for NO<sub>2</sub>, OH, CO, and O<sub>3</sub> 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 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.



Figure 1: Location of measurements. (a) EANET stations for NO<sub>x</sub> and O<sub>3</sub> and (b) for PM<sub>2.5</sub>, SO<sub>4</sub><sup>2</sup>, NO<sub>3</sub><sup>-</sup>, and HNO<sub>3</sub>, (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.

Verified species	Regions	Dataset	Time	Measuring	Model step	Interpolating
		name		step		step
$PM_{2.5}, SO_4^{2-}, NO_3^{-},$	East Asia	EANET	2010-2016	Daily to 2-	Daily	Monthly
NO <sub>x</sub> , O <sub>3</sub> , HNO <sub>3</sub>		(station)		weekly		
$PM_{2.5}, SO_4^{2-}, NO_3^{-},$	Europe	EMEP	2010-2016	Hourly	Daily	Monthly
$NO_x, O_3, CO$		(station)				
CO, O <sub>3</sub>	Australia –	Mirai	8,9/2015	30 min	1 h	30 min
	Indonesia – Japan –	(vessel)	1,8,9/2016			
	Alaska		7,8,9/2017			
$NO_2$ , OH, CO, $O_3$	Pacific, Atlantic	ATom1	8/2016	30 min	1 h	30 min
	ocean, Greenland,	(aircraft)				
	North America					
Tropospheric column	60°S - 60°N	OMI	2010-2016	Daily	Daily	Monthly
ozone (TCO)		(Satellite)		-	-	-
HONO	Jeju-Korea, Taiwan,	EMeRGe	17/3/2018-	15–30 s	Hourly	14–30 s
	and Philippine	(aircraft)	4/4/2018			

#### 3. Results and Discussion

# 3.1. Verification and validation of model simulations for cloud fraction, surface area density, atmospheric species, and effects on HONO mechanisms

#### 3.1.1. Cloud fraction and surface area density for cloud and aerosols

In this study, besides NO<sub>2</sub> conversion onto clouds and aqueous particles (R4), the losses of HONO onto the ice and liquid clouds (R6) are also included. 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%) underestimated 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).

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The heterogeneous processes by clouds and aerosol particles are parameterized by using surface area 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 a peculiarly

265 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<sup>-3</sup>) compared to their work (up to 75  $\mu m^2$  cm<sup>-3</sup>). This disagreement may be ascribed to the two models' different size distributions for sea salt. The calculated SAD for the liquid cloud is two orders of magnitude higher than SAD for ice cloud and total aerosols. Liquid cloud SAD maximized at ~ 800 hPa in the tropical convective systems and over the midlatitude

- storm tracks, reaching ~ 50,000  $\mu$ m<sup>2</sup> cm<sup>-3</sup> at the surface of the North Pacific region in JJA. Sulfate aerosols dominate above 600 hPa for the Northern Hemisphere (~ 20  $\mu$ m<sup>2</sup> cm<sup>-3</sup>) among the total aerosol surface area, followed by organic carbons and soil dust (~ 10  $\mu$ m<sup>2</sup> cm<sup>-3</sup> in JJA). At the surface layer, sulfate aerosols are prevalent in DJF for the Chinese region (> 1,000  $\mu$ m<sup>2</sup> cm<sup>-3</sup>), north-eastern U.S. (~ 500  $\mu$ m<sup>2</sup> cm<sup>-3</sup>), and North Pacific region in JJA (~ 250  $\mu$ m<sup>2</sup> cm<sup>-3</sup>). SAD for soil dust dominates in desert regions, with annual average values > 100  $\mu$ m<sup>2</sup> cm<sup>-3</sup>. Organic carbon (OC) is dominant in winter over
- 275 biomass burning regions such as China (up to 1,000  $\mu$ m<sup>2</sup> cm<sup>-3</sup>) and South Africa (up to 800  $\mu$ m<sup>2</sup> cm<sup>-3</sup>). For the Chinese region, SAD for black carbon (BC) can reach 600  $\mu$ m<sup>2</sup> cm<sup>-3</sup> in DJF and 75  $\mu$ m<sup>2</sup> cm<sup>-3</sup> in India. The total-aerosol SAD for the northern high-latitude and mid-latitude oceans is ~ 75  $\mu$ m<sup>2</sup> cm<sup>-3</sup>, consistent with the estimation by Thornton et al. (2008). The distribution of SAD is discussed in more detail in an earlier report (Ha et al., 2021).

#### 3.1.2. Daytime concentrations of HONO and other atmospheric species

- 280 This section evaluated CHASER-based HONO estimates using the HONO measurements collected during the EMeRGe campaign off-coast eastern Asia in spring 2018 (Andrés Hernández et al., 2021). This is the first global HONO modelling work using EMeRGe as the validation source. 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
- 285 measurements using the HALO mini-DOAS (differential optical absorption spectroscopy) instrument, in which the absorbed UV light (310–440 nm) 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
- 290 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 5). The ratR4+CLD case is run in an attempt to produce more HONO from heterogeneous sources by altering the HONO: HNO<sub>3</sub> yield ratio in (R4) to 0.9: 0.1, and  $\gamma_{iq}$  increased a hundred-fold ( $10^{-4} \rightarrow 10^{-2}$ ). The main idea here is to evaluate whether the missing

295 HONO source was sensitive to cloud uptake in this region or not. The maxST case maximized the uptake coefficients ( $\gamma$ -values) of NO<sub>2</sub> on organic and black carbons to 0.1 (R4, R5), to estimate 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  $\gamma$ -value

of  $10^{-1}$  (Ammann et al., 1998; Kalberer et al. 1999). In three other runs (JANO3-A, JANO3-B, JANO3-C), the photolysis of aerosol nitrate / adsorbed HNO<sub>3</sub> on the ground and other surfaces (NO<sub>3</sub><sup>-</sup>/HNO<sub>3</sub>) were examined, simply as HNO<sub>3</sub> + hv  $\rightarrow$ 

- 300 HONO (R7)). These heterogeneous photolyses of HNO<sub>3</sub> were previously proposed as potential HONO sources at day (Lee et al., 2016; Scharko et al., 2014; Zhou et al., 2011). Because aerosol nitrate and aqueous surfaces are ubiquitous in the atmosphere, the photolysis (R7) is simply set for the gaseous HNO<sub>3</sub> species to occur in particular model spatial grids exposing ground surfaces and sufficient surface area density for aerosols and clouds. The photolysis (R7) is taken at a faster rate by two orders of magnitude than the gas-phase photolysis rate of HNO<sub>3</sub> (HNO<sub>3</sub> + hv  $\rightarrow$  OH + NO<sub>2</sub>) (Zhou et al., 2011) and presumably
- 305 yield 100% HONO to access the maximum effects by this photolysis (Lee et al., 2016). This setting allows (R7) not only to occur at the surfaces of particles but also in the gas and bulk phases. However, in this test, (R7) generally refers to surface-catalyzed photolysis or heterogeneous photolysis of HNO<sub>3</sub>. The JANO3-A case investigated the photolysis of adsorbed HNO<sub>3</sub> on ground surfaces by implementing (R7) for the first vertical layer (z=1). The JANO3-B explored photolysis of nitrate particles and adsorbed HNO<sub>3</sub> gas on both grounds and aerosol surfaces, applying (R7) for model grid cells with the SAD of
- 310  $10^{-6} \sim 10^{-4} \text{ cm}^2 \text{ cm}^{-3}$  (100 to 10,000 µm<sup>2</sup> cm<sup>-3</sup>) to use  $10^{-4} \text{ cm}^2 \text{ cm}^{-3}$  threshold to exclude cloud surfaces (Sect. 3.1.1). The JANO3-C case examines (R7) for regions present of all particles with SAD  $\geq 10^{-7} \text{ cm}^2 \text{ cm}^{-3}$  (10 µm<sup>2</sup>/cm<sup>3</sup>). The SAD of  $10^{-6}$  and  $10^{-7} \text{ cm}^2 \text{ cm}^{-3}$  is supposed to be the threshold for continental aerosols. The maxST and JANO3-B / JANO3-C cases are also combined in two additional cases (maxST+JANO3-B and maxST+JANO3-C, respectively), given the contrary effects on NO<sub>2</sub>-O<sub>3</sub>-CO chemistry of these cases might be neutralized, is discussed next. Other tests examined the possible HONO sources
- 315 from aviation crafts (AIRC), amplified emissions (EMx8), amplified homogeneous HONO formation (R2) (GRx8), which descriptions were listed in the supplement Table S3.

The correlation coefficient (*R*) and model biases against EMeRGe for HONO are shown in Table S4. As seen for the STD run, general underestimations of HONO simulations are identified, in which better correlations are found at 1000–2000 m (*R*=0.31–0.49). Vertical profiles for HONO and other species (NO<sub>2</sub>, O<sub>3</sub>, CO), retrieved from the EMeRGe flights, were applied for the measurement-based model evaluation (Figure 2). The model discrepancies for the measurement for HONO ( $\Delta_{\text{HONO}}$ ) and NO<sub>2</sub> ( $\Delta_{\text{NO2}}$ ) in each flight trajectory, i.e., from Taiwan to South Korea, Japan, and the Philippines, are separated

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into bins of altitude ranges 0-1,000-3,000-5,000-6,000 m (Figure 3). The frequency distributions of  $\Delta_{\text{HONO}}$ ,  $\Delta_{\text{NO2}}$ ,  $\Delta_{\text{O3}}$ , and  $\Delta_{\text{CO}}$  are shown in Figures S7 and S8.

- Figure 2(a) shows the vertical average score (cruising altitudes  $\pm$  500 m) for the measured (blacks) and simulated HONO 325 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 ( $\pm$  500 m), with mean values dropping from 70 ppt (2,000 m  $\pm$  500 m) to < 20 ppt (5,000 m  $\pm$  500 m) and < 10 ppt above. These measured HONO values for this Asian coastal region are surprisingly high, which range from 10-115 ppt for 2,000 m  $\pm$  500 m altitudes, compared to Wang's report of < 100 ppt (maximum) and < 30
- ppt (4 daytime hours means) for 1,500-2,000 m altitudes measured by a MAX-DOAS at a station nearby the HONO source
   (Wang et al., 2019). This indicates that the source of HONO during EMeRGe might relate to other mechanisms than emission

sources. In this study, the simulated HONO concentration in the STD case significantly underestimated the observations. They reached only 30–70 ppt at 1,000 m and nearly zero from 2,000 m upward (Figure 2(a): red versus black triangles for the simulation and the observations, respectively). These discrepancies indicate a significant unknown HONO source during the daytime, although the proposed heterogeneous HONO formation mechanisms were incorporated in our model. This finding

335 daytime, although 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).

Table 5: Additional sensitivity simulations in this work.

No.	Simulation ID	Description	Note
1	maxST	$\gamma_{oc}$ and $\gamma_{ec}(R4, R5) = 0.1$	See Table 2 for $\gamma$ -values in STD
2	ratR4	NO <sub>2</sub> $\rightarrow$ 0.9HONO + 0.1HNO <sub>3</sub> (R4)	Product ratio is 0.5:0.5 in STD
3	ratR4+CLD	ratR4 and $\gamma_{liq}(R4) = 0.01$	= 0.0001 in STD
4	JANO3-A	Add HNO <sub>3</sub> + hv $\rightarrow$ HONO (R7) (z=1, rate = 100 × rate of HNO <sub>3</sub> + hv $\rightarrow$ OH + NO <sub>2</sub> )	HONO from HNO <sub>3</sub> photolysis (adsorbed on ground surfaces) (Lee et al., 2016)
5	JANO3-B	Add (R7) (100 < SAD < 10,000 $\mu$ m <sup>2</sup> cm <sup>-3</sup> )	HONO from HNO3 photolysis (adsorbed on ground and aerosol surfaces for continental regions excluding cloud surface)
6	JANO3-C	Add (R7) (SAD ≥ 10 μm <sup>2</sup> cm <sup>-3</sup> )	Similar to JANO3-B but using a larger SAD threshold
7	<mark>maxST+</mark> JANO3-B	$\gamma_{oc}$ and $\gamma_{ec}(R4, R5) = 0.1$ Add (R7) (100 < SAD < 10,000 µm <sup>2</sup> cm <sup>-3</sup> )	Combination of maxST and JANO3-B cases
8	maxST+ JANO3-C	$\gamma_{oc}$ and $\gamma_{ec}(R4, R5) = 0.1$ Add (R7) (SAD $\geq 10 \ \mu m^2 cm^{-3}$ )	Combination of maxST and JANO3-C cases

- 340 In Figure 3, which shows model discrepancies, the measured NO<sub>2</sub> below 3,000 m (±500 m) close to land is captured well in the model (Figure 3(a,e,i): magentas and greens), with 34% of the data being quite close for NO<sub>2</sub> (±70 ppt) (Figure S7(d)). However, the modelling still underestimated the simulated HONO mixing ratio by up to 250 ppt (Figure 3(a): green). Over the off-coast of Taiwan bound to Japan, NO<sub>2</sub> is overestimated by up to 600 ppt in the model, corresponding to 20–70 ppt missing HONO (Figure 3(a,e): small oranges left of vertical line). The missing HONO can be driven by low HONO emission from land and low uptake of NO<sub>2</sub> on organic carbon and soot, as the amplified EMx8 and maxST cases could alleviate the model
- 345 land and low uptake of NO<sub>2</sub> on organic carbon and soot, as the amplified EMx8 and maxST cases could alleviate the model underestimates for HONO (Figure 3(a vs b): oranges, (a vs c and e vs f): greens and magentas). The model also underestimated O<sub>3</sub> and CO, usually by 25 ppb O<sub>3</sub> (freq. 79%) and 100 ppb CO (freq. 60%) (Figures S10, S11), which are larger than the model biases against ATom1 observations (Sect. 3.1.3; Figure 5) because of possible inland influence. More accurate and detailed emission inventory for substances such as HONO, NO<sub>x</sub> and CO is thus sensible as this region is the outflow of the Pearl River
- 350 Delta and Yangtze River Delta regions. Besides the uptake on organic and black carbon, identified in the maxST simulations, we identified the NO<sub>2</sub> uptake on sulfate nearly as important through a parallel test (not shown). Especially, the heterogeneous photolysis of HNO<sub>3</sub> can provide a large HONO amount near Taiwan, South-Korea, Japan (in JANO3-B and JANO3-C cases) and a small HONO amount for the route bound to the Philippines (in JANO3-C case) for the altitudes below 2,500 m (Figure 3(d,h): greens, oranges, blues).

- For the middle troposphere (5,000–6,000 ± 500 m) over the Taiwan Island, too abundant NO<sub>2</sub> is predicted by the model during the cruises bounding to South Korea (up to 40 ppt) and the Philippines (up to 20 ppt) (Figure 3(m,p): 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 NO<sub>2</sub> and the corresponding missing HONO are also sensitive to the AIRC and GRx8 cases (Figure 3(n,q)), indicating that aircraft-exhaust of HONO could adjust the HONO/NO<sub>2</sub> ratio and more homogeneous HONO production might contribute more, given the high abundances of oxidizing substances at these altitudes. The possibility of emission of aviation-induced particles on which NO<sub>2</sub>.
- abundances of oxidizing substances at these altitudes. The possibility of emission of aviation-induced particles on which NO<sub>x</sub> to HONO conversion could reach 45% (Meilinger et al., 2005) can support the need for NO<sub>2</sub> reduction and HONO formation for this height across EMeRGe's near-land domains. Moreover, the surface-catalyzed photolysis of HNO<sub>3</sub> in the JANO3-C runs can serve as an efficient source and greatly reduce the model negative bias for HONO at 6,000 m, although the NO2
  reproduction is too strong (because less NO<sub>x</sub> is removed via deposition of HNO<sub>3</sub>), which turns the model bias for NO<sub>2</sub> become overestimates (Figure 3(s)).

The model underestimation for HONO is also associated with the concurrent underestimation of NO<sub>2</sub>, which was observed more often at the altitudes of > 1000 m. The likely erroneous NO<sub>2</sub> concentrations of ~1.8 ppb (1,000 m) and ~220 ppt (3,000 m) across Taiwan, linked with HONO of as high as 290 ppt (1,000 m) and 140 ppt (3,000 m), were not reproduced

- 370 (Figure 3(e,i)). These likely inadequate NO<sub>2</sub> abundances can be partially alleviated through the enhanced HONO/NO<sub>x</sub> emission ratio and more efficient NO<sub>x</sub> recycling process in the ratR4+CLD cases, respectively (Figure 3(g,j)). Here, the missing HONO is largely supplemented only at ~1,000 m over the marine environment, namely, during the Taiwan-Japan cruise, when we identified more products for HONO on cloud in the ratR4+CLD case. (Figure 3(e,g): red-orange diamonds). At ~6,000 m, small deficits of 60 ppt NO<sub>2</sub> corresponding to ~10 ppt HONO (Figure 3(p): oranges and magentas) might correspond to
- 375 lightning NO<sub>x</sub> emissions (Sudo et al., 2002) and stratospheric sources. Some homogeneous mechanisms at ~6,000 m as in the GRx8 could be effective (Figure 3(n,o)). Moreover, the heterogeneous photolysis of HNO<sub>3</sub> in the JANO3-C case can be an effective HONO supplement above 5,500 m (Figure 3(s)), while this photolysis can act as a NO<sub>2</sub> production mechanism at any altitudes.

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In general, the upper limit for the aerosol uptake coefficients (maxST case) may be applicable for the lowest cruising altitudes, which induced the increase of modelled HONO levels during both daytime and nighttime (Figure S10). The

- photolysis of adsorbed HNO<sub>3</sub> on ground surfaces implemented in the JANO3-A case is impractical to be a source for HONO during EMeRGe, as this case only provided a mild HONO amount at a thin surface layer (<500 m; not shown). Fortunately, the surface-catalyzed photolysis of HNO<sub>3</sub> in JANO3-B and JANO3-C cases can remedy the model-measurement discrepancies, i.e. *R*<sub>HONO</sub>>0.6 and model bias for HONO was reduced from -112 ppt (STD) to -22 ppt (JANO3-B) and -18 ppt (JANO3-C)
  for 0-500 m (Table S4). The HONO source from this photolysis of HNO<sub>3</sub> is sufficient for continental and near-land regions. In particular, the photolysis of HNO<sub>3</sub> adsorbed on particles with smaller SAD (JANO3-C case) can be responsible for the 500 3,000 m atmosphere around Philipines and South Korea and at higher altitudes where robust solar radiance can enhance the
  - HNO<sub>3</sub> photolysis. In the combined cases (maxST+B and maxST+C), HONO production was boosted, and the estimated

NO<sub>2</sub>/O<sub>3</sub> concentrations were best captured for 2,000 – 5,000 m (±500 m) (Figure 2(a,b,d): black diamonds vs orange circles).

390 Furthermore, as discussed in Sect. 3.2.3, the sensitivity cases including combined cases can change the global tropospheric effects differently.

These discussions demand further exploitation of this model towards efficient HONO formation mechanisms, especially elaborating the combined HONO production mechanisms from enhanced NO<sub>2</sub> aerosol-uptakes and HNO<sub>3</sub> photolysis. Moreover, it requires (1) better emission inventories for South-East Asia and East Asia, the lightning source for NO<sub>x</sub> and HO<sub>x</sub>,

395 and aviation-induced aerosols, (2) improvements in the model's vertical mixing and stratospheric air mass transport.

The remaining drawbacks in reproducing HONO and other atmospheric species (NO<sub>2</sub>, O<sub>3</sub>, 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 NO<sub>x</sub> and HO<sub>x</sub>, and aviationinduced aerosols, (2) to improve the vertical mixing and air mass transport from the stratosphere, (3) to apply other potential HONO formation mechanisms and NO<sub>x</sub> recycling processes alongside the selection and algorithm development among the

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sensitivity tests provided here, especially for the maxST and JANO3-B runs; and (4) to simulate the lower and upper limits for the uptake coefficients of NO2 on aerosols and clouds. (a) (b) 12000 12000 OBS STD OLD OBS \* STD maxST 11000 11000 10000 10000 maxST JANO3-B IANO3-B 9000 9000 IANO3-C 8000 8000 maxST+JANO3-B maxST+JANO3-C JANO3-C maxST+JANO3-B (m) Ē 7000 7000 Altitudes Altitudes maxST+IANO3-C 6000 6000 5000 5000 4000 4000 3000 3000 2000 2000 1000 1000 1200 400 500 200 600 80 1000 200 300 HONO (ppt) NO<sub>2</sub> (ppt) (d) (c 12000 12000 11000 11000 10000 10000 9000 9000 8000 8000 ĵ, (m 7000 7000 6000 OBS STD Altitudes 6000 Altitudes OBS STD 5000 • 5000 OLD ٠ OLD 4000 4000 maxST JANO3-B maxST 3000 3000 IANO3-B 2000 2000 IANO3-C JANO3-C maxST+JANO3-E 1000 maxST+IANO3-E

405

1000

0

50

100

150

200

CO (ppb)

250

С

80

100

O₃ (ppb)

maxST+IANO3-C

350

300

maxST+JANO3-C

140



Figure 2: Vertical profiles of (a) HONO, (b) NO<sub>2</sub>, (c) CO, and (d) O<sub>3</sub> measured in EMeRGe campaign and calculated in the sensitivity runs. Diamonds (for OBS, STD, OLD), batches (for maxST, JANO3-B, JANO3-C cases), and filled circles (for maxST+JANO3-B, maxST+JANO3-C cases) show mean vertical concentrations, and the corresponding boxes indicate 25th - 75th value ranges. 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 all plots, black is for observation (OBS), colours are for simulations: STD (red), OLD (grey), maxST (magenta), JANO3-B (cyan), JANO3-C (orange), maxST+JANO3-B (filled cyan), and maxST+JANO3-C (filled orange).



**Figure 3:** Model's discrepancies from measurements for HONO ( $\Delta_{HONO}$ ) versus that for NO<sub>2</sub> ( $\Delta_{NO2}$ ). Only results from STD (first column) and helpful sensitivity cases (second, third, and fourth columns) are plotted. The scale is shared for each row. The altitude range (0, 1000, 3000, 5000, 6000 m ± 500 m) and the sensitivity case names are shown at the top of each panel. Small points represent discrepancies distribution (observation – model). Diamonds mark the median point of each cruise distribution. Edge and fill colours indicate flight cruises (see legend). Vertical, horizontal, diagonal lines show  $\Delta_{NO2} = 0$ ,  $\Delta_{HONO} = 0$ ,  $\Delta_{NO2} = \Delta_{HONO}$ , respectively.

#### 3.1.3. NO<sub>2</sub>, OH, O<sub>3</sub>, and CO concentrations within the oceanic free troposphere

The model performance of the free troposphere was evaluated through the atmospheric tomography (ATom1) aviation in August 2016 for NO<sub>2</sub>, OH, CO, and O<sub>3</sub>. The STD run reconstructed the chemical field observed in ATom1 with moderate or strong positive correlations for NO<sub>2</sub>, OH, CO, and O<sub>3</sub> ( $R_{NO2}$ =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 specific means distribute laws ( $R_{NO2}$ =0.751,  $R_{OH}$ =0.600,  $R_{NO2}$ =0.407,  $R_{NO2}$ =0.506, Table

420 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<sub>2</sub> and CO were consistently higher in the STD run than those in the OLD run, while for OH and O<sub>3</sub>, the *R* values are only improved for the NP region (Table S2).

Figure 4 shows measured (grey) and simulated (red and black) NO<sub>2</sub>, O<sub>3</sub>, OH, CO concentrations and the effects of including HONO in the simulation for the NP region (flight #2 on August  $3^{rd}$ ). Figure 5 displays vertical profiles of the model

- 425 biases in STD vs OLD cases and photochemical effects by each HONO formation mechanism. Here, the data in all flights or in the NP region are classified based on the air pressure from 1000–200 hPa (±50 hPa) and separated into nine bins. In the NP region, the OLD run (black lines) tends to overestimate NO<sub>2</sub>, O<sub>3</sub>, OH, but it underestimates CO at the lower troposphere, whereas the unsteady discrepancies at the upper layer are visible (Figure 4(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 5(e-h). The
- 430 HONO inclusion in STD run (red lines) has reduced NO<sub>2</sub>, OH, O<sub>3</sub> and has increased CO levels, thereby, dwindling the model biases for NO<sub>2</sub>, OH, and CO in the NP region except near the tropopause (Figure 5(e,g,h)).

In the NP region, the surface NO<sub>2</sub> level is reduced under the effects of HONO uptake on clouds (Figure 4(c): orange bars in vertical pink shades and Figure 5(p)). Hence, O<sub>3</sub> and OH are correspondingly reduced as their formations are limited in the absence of sufficient NO<sub>x</sub>, that is, OH formation via HO<sub>2</sub> + NO  $\rightarrow$  OH + NO<sub>2</sub> (Figure 4(d,g): orange bars in pink columns and

- Figure 5(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<sub>3</sub>, and CO concentrations (Figure 4(c,d,g,h) and Figure 5(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<sub>3</sub>, and CO, whereas the effects manifest in the upper troposphere rather than in the lower troposphere. This is likely the most influential factor that increases OH and O<sub>3</sub> levels at these high altitudes (Figure 4(d,g) and Figure 5:
- 440 blue bars). The additional HONO from direct emissions had minor effects on NO<sub>2</sub> and OH but contributed to the reductions of O<sub>3</sub> and CO at high altitudes (Figure 4(c,d,g) and Figure 5(q,s): red bars). At 900 hPa, the HONO emissions significantly reduced NO<sub>2</sub> near the continental areas (Figure 5(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<sub>2</sub>, O<sub>3</sub>, OH, and CO (Figure 5(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
- 445 NP region (51.7% for NO<sub>2</sub> 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<sub>2</sub> and OH levels are still required (Figure 5(a,c)). At these altitudes, NO<sub>x</sub> and HO<sub>x</sub> 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 have a stronger impact on atmospheric chemistry at higher altitudes than the near-surface layer. Also, their effects should be enhanced through the additional NO<sub>x</sub> and HONO sources to reconcile the model simulations with the observations.

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Figure 4: Concentrations and variations by HONO chemistry for NO<sub>2</sub>, O<sub>3</sub>, 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.



Figure 5: Vertical profile of model bias against aerial ATom1 data (a-h) and changes by HONO chemistry (l-s) for NO<sub>2</sub>, O<sub>3</sub>, OH, and CO (from left to right columns). Biases in OLD (black lines) and STD (red lines) runs are calculated for all flights (a-d) and NP region (e-h). The red numerical texts are the relative reductions (%) of the bias in the STD run compared to that in the OLD run. Changes by GRs (blue), HRs on clouds (orange), HRs on aerosols (green), and EM (red) are calculated for all flights (i-o) and NP region (p-s).

#### 3.1.4. Surface O<sub>3</sub> and CO in the marine environment

- The simulations also compared with the *research vessel (R/V) Mirai*'s observation in the western Pacific Ocean for O<sub>3</sub> and CO. The interpolation of model results for six cruises across Japan–Alaska region (40° N– 75° N, 140° E–150° W) in 7-8-9/2015–2017 (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*
- 470 *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  $O_3$  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  $O_3$  is

- 475 increased. The model biases exhibit negative trend for both CO and  $O_3$  in the OLD case. This simulation pattern for  $O_3$  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  $O_3$  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 6(a,c), overestimations of CO and  $O_3$  are visible along Japan-Indonesia-Australia (Track-2) during the low
- 480 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 6 shows the model's percentage discrepancies for O<sub>3</sub> from *Mirai*'s data, except those from HONO concentrations interpolated for these regions. The underestimated simulations of O<sub>3</sub> are enlarged, especially in the Japan – Alaska region, being driven by the reduction effects in the STD case. In another way, these effects weaken the O<sub>3</sub> overestimates across the land areas, namely, over the region near Japan and Indonesia-Australia. Moreover, the higher
- 485 HONO levels are identified for these off-shore data with up to 1.4 ppb abundances (Figure 6(c): red numbers). This high HONO level might underestimate an accurate level as a stronger reduction for O<sub>3</sub> is required for the STD run (Figure 6(a): red marks).

The effects of the HONO chemistry along *the R/V Mirai* tracks exhibit various trends for each mechanism. Figure 7(b,d) illustrates O<sub>3</sub> and CO changes triggered by the HONO gas reactions (GRs), uptakes (HRs), and emission (EM). The gaseous reactions (blue bars) have mostly increased CO levels due to the reduced OH and O<sub>3</sub> levels (Figure S14). The gaseous mechanisms cause some reductions at the peak CO level because higher OH level from HONO photolysis near land domain or extra OH flux from stratosphere near 60 °N latitude could dilute CO. Furthermore, O<sub>3</sub> level is slightly increased due to GRs north of 60° N, as GRs is a source for NO<sub>2</sub> thus enhance O<sub>3</sub> formation at these high latitudes (Figure S14). O<sub>3</sub> level is often decreased in the NP region since minor NO<sub>2</sub> increase and stronger OH reduction are seen for this region (Figure S14). The
change tendencies in O<sub>3</sub> near land areas are varied (T2, T3) because the vertical effects to NO<sub>x</sub> and OH are stronger during

DJF for this region (Figure S14). HRs, largely consuming NO<sub>2</sub>, reduced O<sub>3</sub> (as large as 8 ppb), and increased CO (~10 ppb)



levels (Figure 7(b,d): orange+green). HRs, (particularly HRs on cloud surfaces, shown by orange bars), exerted the strongest contribution to the calculated changes in  $O_3$  and CO among the three HONO pathways. This predominant cloud effect was also prominent in the previous comparisons, especially EMEP (Figure 8(ii,jj): blue), thereby, indicating substantial effects of

- 500 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<sub>3</sub> concentrations off-coast Japan (track #3). It should be noted that this is not enough to explain the simulation bias with regard to the measurements. The additional HONO from direct emission (red bars) has mainly increased O<sub>3</sub> and has reduced CO concentrations, especially near land (latitude < 50° N). This finding resonates with the comparison for continental stations (Figure 8(cc,ff,ii,jj): oranges). The overall effects of the HONO
- 505 chemistry along *Mirai* cruises tend to reduce O<sub>3</sub> and 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 5(g,h)). Thus, the strengthened underestimation of O<sub>3</sub> 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 510 comparison turns neutral or positive for the aircraft measurements in the same region (Figure 5(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.



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Figure 6: Percentage discrepancies of STD (a) and OLD (b) simulations from *Mirai* for O<sub>3</sub> and HONO concentration in STD (c). The red numbers in (c) indicate maximum HONO concentrations for each cruise.



Figure 7: Validation with ship-based data. Observed and simulated concentrations (a, c) and daily mean effects by HONO chemistry (b, d) for O<sub>3</sub> 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).

#### 3.1.5. NO<sub>x</sub>, O<sub>3</sub>, and other atmospheric species at ground-based stations

- 525 The effects of HONO chemistry in the continental near-surface layer of East Asia and Europe were also investigated. To this end, we conducted model comparisons versus EANET and EMEP stationary observations for mass and gaseous concentrations of  $PM_{2.5}$ ,  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $HNO_3$ ,  $NO_x$ ,  $O_3$ , and CO (CO for EMEP only). Table 7 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) = 0.71), and HNO\_3
- 530 (R(EANET) = 0.18, R(EMEP) = 0.12), 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).

Figure 8 compares the measured versus simulated HNO<sub>3</sub>, NO<sub>x</sub>, HONO, O<sub>3</sub>, and CO concentrations for the EANET and EMEP stations. The stations were divided into three groups: (1) high-NO<sub>x</sub> 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<sub>3</sub>, 22 for O<sub>3</sub>, and 15 for NO<sub>x</sub>); and (3) all EMEP stations. The ground-based observations in the period 2010–2016 revealed the slightly decreasing NO<sub>x</sub> for moderate NO<sub>x</sub> concentrations, as well as PM<sub>2.5</sub>, and aerosols (Figure 8(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<sub>x</sub> and PM<sub>2.5</sub> concentrations are generally underestimated in the model (OLD), especially in high-NO<sub>x</sub> regions (Figure 8(b,e,h) and Figure
- 540 S4(a,d,g)) with model's averaged biases of -0.8 ppb NO<sub>x</sub> for EMEP and -4 ppb NO<sub>x</sub> for EANET (Table 7). These underestimations were stronger during winter, particularly for the high-NO<sub>x</sub> 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  $1.1^{\circ}$ , 0.56° or even higher, could remedy such effects (Sekiya et al., 2018).
- HONO chemistry in the STD case increases HNO<sub>3</sub>, NO<sub>3</sub>-, SO<sub>4</sub><sup>2-</sup>, and PM<sub>2,5</sub> for EANET and EMEP stations compared to 545 the OLD case (Figure 8 and Figure S4: red vs blue lines). HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> are increased as products of NO<sub>2</sub> conversion (R4); thus, the model underprediction for NO<sub>3</sub><sup>-</sup> in EANET stations is mitigated (bias OLD→STD: -0.439→-0.223  $\mu$ m m<sup>-3</sup>). As a result of the increased OH level at the surface of these ground-based stations, SO<sub>4</sub><sup>2-</sup> is also increased (Li et al., 2015; Lu et al., 2018) (Figure S4(j,k,I)), although this effect enlarges the model overestimation for SO<sub>4</sub><sup>2-</sup> species at EANET and EMEP stations (Table 7). The consequent increase in PM<sub>2.5</sub>, though minor, remedy the model underestimate for PM<sub>2.5</sub>, e.g., model bias in
- 550 OLD  $\rightarrow$  STD: -3.044  $\rightarrow$  -2.494 µm m<sup>-3</sup> (EMEP). Unfortunately, the model overestimates for HNO<sub>3</sub> in the OLD case is enlarged with the inclusion of HONO.

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In the STD case, including HONO photochemistry, the negative biases of NO<sub>x</sub> in the model have adversely enhanced due to the NO<sub>2</sub> loss processes (bias OLD $\rightarrow$ STD: -3.997 $\rightarrow$ -4.358 ppb for EANET (Table 7)). These processes also suppressed the NO<sub>x</sub> seasonality observed at most sites (Figure 8(b,h), red lines). The lack of seasonality was driven by the substantial loss of NO<sub>2</sub> on the surfaces of atmospheric particles during winter. For EANET's low NO<sub>x</sub> and EMEP stations, this huge NO<sub>2</sub> loss is attributed to cloud surfaces (Figure 8(ee,hh): blue bars). However, NO<sub>2</sub> uptake by aerosols has a comparable contribution

effect to the cloud effect in high-NO<sub>x</sub> environments such as Jinyunshan (Figure 8(bb), grey bars). Namely, nearly half of the NO<sub>2</sub> was converted to HNO<sub>3</sub> in R4 (Figure 8(aa,dd,gg)) without an efficient recycling process, leading to an overall removal of NO<sub>x</sub>. This lack of NO<sub>x</sub> could be the main driver for the seasonal NO<sub>x</sub> deterioration and the exacerbated overestimations of

560 HNO<sub>3</sub> by simulations.

The STD O<sub>3</sub> simulation exhibited moderate and strong positive correlations with EANET and EMEP observations, 0.595 and 0.707, respectively (Table 7). The model improvements for  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $PM_{2.5}$ , and  $HNO_3$  were minor. However, the model improvement for O<sub>3</sub> was considerable, 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<sub>3</sub> chemical destruction (because lacking oxygen atom

- 565 from NO<sub>2</sub> photolysis), which in turn, reduces the model overestimates for O<sub>3</sub> in the OLD case (Table 7; Figure 8(c,f,i), red versus blue lines). However, further improvements in the chemical scheme are necessary to reproduce the O<sub>3</sub> measurements better; namely, a larger O<sub>3</sub> reduction for the summer and a reduced effect in simulated O<sub>3</sub> 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<sub>3</sub> was prominent for the low-NO<sub>x</sub> EANET stations (Figure 8(f)). The effects of HONO chemistry on
- 570 the mean OH levels were small, although it showed slight increases for OH's minima (Figure S4(j,k,l)). Thus, due to the apparent O<sub>3</sub> reduction for EMEP stations, CO was increased. Despite the reductions in NO<sub>x</sub> and O<sub>3</sub> levels being exaggerated during winter, the increment in CO reconciles the model's underestimation of CO high peaks in spring (Figure 8(j)), thereby strongly dwindling the bias for CO by ~59% (Table 4). However, the CO concentrations during summer should be reduced in the STD case to capture the measurement. This finding might indicate inadequate HONO emissions for the EMEP stations 575 (Figure 8(jj): oranges), which otherwise have reducing effects to NO<sub>x</sub>, O<sub>3</sub>, and CO levels during summertime.
  - The break-down scrutinies for aerosols and clouds effects for the ground-based stations (EANET/EMEP) also reveal the vast role of cloud-uptakes in the HONO impacts on  $NO_3^-$  aerosols,  $NO_x$ ,  $O_3$ , and CO (Figure 8 and Figure S16: blue bars), while the HONO impacts on  $HNO_3$ ,  $PM_{2.5}$ , and  $SO_4^{2-}$  aerosols were governed by aerosol-uptakes and HONO emission (grey and yellow bars).
- The existing ill-reproduction in NO<sub>x</sub>'s seasonality and overestimations for HNO<sub>3</sub> might be amended by an explicit inventory for direct NO<sub>x</sub> emissions and an efficient NO<sub>x</sub>-recycle process. Such mechanism via HNO<sub>3</sub> uptakes on soot surfaces (HNO<sub>3</sub> $\rightarrow$ NO<sub>2</sub>) was also tested in this study using the uptake coefficients range from  $3\times10^{-5}$  -  $4.6\times10^{-3}$  (Lary et al., 1997; Akimoto et al., 2019). Unfortunately, this heterogeneous HNO<sub>3</sub> conversion could not solely serve as a productive NO<sub>x</sub> recycling process in the EANET/EMEP stations (not shown). Among the sensitivity cases discussed in the EMeRGe comparison, the alternated HONO : HNO<sub>3</sub> (0.9 : 0.1) product ratio of (R4) (ratR4 case) showed a good remedy for NO<sub>x</sub> at EMEP stations (Figure S11(g): brown vs black). For the EANET sites, the photolysis of adsorbed HNO<sub>3</sub> on ground surfaces (JANO3-A case) avoiding NO<sub>x</sub> removal via HNO<sub>3</sub> can remedy the NO<sub>x</sub> seasonality issue for these ground-based stations (Figure S11(a,d): greens vs blacks). However, the photolysis of adsorbed HNO<sub>3</sub> on grounds and aerosol/cloud surfaces
- 590 differences in surface NO<sub>x</sub> levels compared to STD case (Figure S11(a,d,g): cyans and oranges vs reds). However, the
  - 24

(JANO3-B and JANO3-C cases) is not an effective NO<sub>x</sub> recycling for EANET/EMEP measurements, leaving only slight

heterogeneous photolysis of HNO<sub>3</sub> increased O<sub>3</sub> and OH at the high NO<sub>x</sub> regions instead of O<sub>3</sub> reduction in the STD case (Figure S11(b,c): cyans and oranges vs blues), which brought reconciliation to the underestimates for O<sub>3</sub> peak in springs (Figure S11(e): dotted cyan vs dotted blacks), although the runs with HNO<sub>3</sub> photolysis still not capture the O<sub>3</sub> minimum in summer. Only the ratR4 case can capture the O<sub>3</sub> minimum in summer among the sensitivity cases, which indicate the need for

595 stronger NO<sub>x</sub> recycle processes for these ground-based stations.

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Table 7: 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<sub>x</sub> 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<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>: µm m<sup>-3</sup>; HNO<sub>3</sub>, NO<sub>x</sub>, O<sub>3</sub>, CO: ppb.

		ЕМЕР								EAN	IET		
	PM <sub>2.5</sub>	$SO_4^{2-}$	NO <sub>3</sub> -	HNO <sub>3</sub>	NO <sub>x</sub>	O <sub>3</sub>	CO	PM <sub>2.5</sub>	$SO_4^{2-}$	NO <sub>3</sub> -	HNO <sub>3</sub>	NO <sub>x</sub>	O <sub>3</sub>
R(STD)	0.528	0.655	0.755	0.115	0.637	0.707	0.526	0.344	0.560	0.359	0.228	0.202	0.595
R(OLD)	0.469	0.631	0.713	0.115	0.698	0.650	0.535	0.357	0.559	0.364	0.181	0.235	0.613
bias (STD)	-2.494	0.889	0.632	0.073	-1.680	-1.708	2.943	-7.231	1.161	-0.223	0.396	-4.358	1.410
bias (OLD)	-3.044	0.752	0.247	0.077	-0.818	5.154	-7.138	-7.583	0.981	-0.439	0.302	-3.997	5.494



Figure 8: 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-NO<sub>x</sub> EANET (first and fourth rows), low-NO<sub>x</sub> EANET (second and fifth rows), and all EMEP stations (third and sixth rows). First column: HNO<sub>3</sub>; second column: NO<sub>x</sub>, third column: O<sub>3</sub>, fourth column: CO.

#### 610 **3.2.1. Global HONO distribution and burden**

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This section sheds 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 9(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:

- 615 Northeast America (seasonal mean up to 0.5–1 ppbv), India (up to 1–3 ppbv), forest regions, especially the extra-tropic 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
- 620 (10–30 pptv) in the free troposphere (at 2500 m) were simulated over Africa's biomass burning region during wet months (JJA) (Figure 9(c,d)), which could arise due to the NO<sub>2</sub> 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 10) 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

- 625 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 10(a,b)). Besides cloud particles, HRs on aqueous aerosols also produce HONO in a continental atmosphere rich in sulfate, dust, and soot particles (Figure 10(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,
- 630 based on spaceborne observations for HONO in wildfire plumes (Theys et al., 2020) and along ship tracks in the marine boundary layer (Figure 10(e,f)).

Table 8 summarizes the global sources and sinks of tropospheric HONO quantified by CHASER. The simulations indicate that GRs contribute only 11% of the HONO net production. HRs and EM produce more significant HONO (63% and 26% HONO net production, respectively). The pyrogenic HONO emission estimated in this study might be underestimated as HONO/NO<sub>x</sub> 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 a 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)

640 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.

HONO production calculated in sensitivity cases (Sect. 3.1.2) are recorded in Table S5 (last column), and the spatial distributions are plotted in Figure S12. The small supplement by the photolysis of adsorbed HNO<sub>3</sub> on ground surfaces (JANO3-A case) to surface HONO concentration and tropospheric HONO burden ( $1.40 \rightarrow 1.45$  TgN) is consistent with the discussion

- for EmeRGe campaign. In the JANO3-B and JANO3-C cases, tropospheric HONO burden is increased to 2.02 TgN and 2.93
  TgN, respectively, mainly remaining for the lower troposphere (~600 hPa) (Figure S12(g,h)). Compared to HNO<sub>3</sub> photolysis, the enhanced aerosol-uptake (maxST case) produces HONO more extensively over the source region and in the winter hemisphere where there is no photolysis (Figure S12(a-d)). Therefore, the maxST case does not produce enough HONO during EMeRGe (worse than JANO3 cases). However, the global HONO burden in maxST case is added to 7.79 TgN, which might be because we set the enhanced aerosol uptake of NO<sub>2</sub> for all environments. The combined cases (maxST+JANO3-B or
- maxST+JANO3-C), although appropriately approaching daytime HONO production as well as NO<sub>2</sub> and O<sub>3</sub> levels during EMeRGe, incredibly escalate the global HONO burden to 12.64 and 17.13 TgN, respectively (Table S5), more via the enhanced aerosol-uptake setting that could reach the upper troposphere (Figure S12(k,l)). However, it might be more realistic if HONO production stayed at the lower troposphere (Eshorbany et al., 2012). Further work for the combined cases to be standard cases,
- the amplified NO<sub>2</sub> conversion on aerosols should be confined in high SAD regions (Kalberer et al., 1999; Stadler et al., 2000),
   or at daytime only (Notholt et al., 1992; Stemmler, 2007).

Table 8: Global sources and sinks of tropospheric HONO calculated by CHASER (2011).

Sources (TgN/yr)	35.17	Sinks (TgN/yr)	33.77	Net productions (TgN/yr)	1.40
P <sub>GR</sub>	13.24	L <sub>GR</sub>	13.09	GRs	0.15(11%)
P <sub>HR</sub>	15.31	L <sub>HR</sub>	14.43	HRs	0.88 (63%)
P <sub>HR(cld)</sub>	9.57	L <sub>HR(cld)</sub>	9.40	HRs(cld)	0.17 (11.8%)
P <sub>HR(ae)</sub>	5.74	L <sub>HR(ae)</sub>	5.03	HRs(ae)	0.72 (51.2%)
$S_{EM}$	6.62	L <sub>EM</sub>	6.25	EM	0.37 (26%)

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. Bold lines show the most significant

660 contributing mechanisms to the HONO burden.



Figure 9: Distribution of HONO levels at the surface (a-b) and meridional mean (c-d).



Figure 10: 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.

# 3.2.2. Global effects on tropospheric column ozone

- Comparison between simulation and satellite OMI observation for tropospheric column ozone (TCO) can be examined as a global effect for ozone. In Figure 11, the STD run with HONO inclusion improves the overall tropospheric column ozone 670 (TCO) distribution observed by the OMI, especially at the mid-latitudes. Figure S3 indicates a TCO reduction when HONO chemistry is included in the STD case (red lines vs green lines). Although HONO photolysis (R1) is a source of OH, supposedly increasing the tropospheric oxidizing capacity, the calculation in STD case shows the OH and  $O_3$  increases only occur at the surface of polluted sites (Figure 12(a,e)). The NO<sub>2</sub> conversion to HONO and HNO<sub>3</sub> (R4) becomes a NO<sub>x</sub>'s removal pathway
- 675 at remote regions, thus restricting the formation of  $O_3$  and OH for the larger part of the troposphere (lacking oxygen atom from  $NO_2$  photolysis), Figure 11 shows that the O<sub>3</sub>-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 O<sub>3</sub> underestimates in the NP
- 680 region are also visible for the modelled surface air versus the measurements during the *Mirai* cruises (Figure 6(a,b)). Notably, these underestimates for  $O_3$  could hold up to 400 hPa, as seen in comparison with the ATom1 flights (Figure 5(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 9), the O<sub>3</sub> reducing effects exacerbate the model discrepancy. The HONO
- 685 photochemistry is unlikely to be the primary driver of this phenomenon as the ozone simulation is improved over the continents when the HONO photochemistry is included.

In the combined sensitivity case maxST+JANO3-B (Sect. 3.1.2), O<sub>3</sub> was further reduced than the STD case. The reduction in TCO might be due to the enhanced NO<sub>2</sub> uptake on aerosols leading to more substantial O<sub>3</sub> formation restriction. The maxST+JANO3-B case showed better harmony with OMI for the regions of TCO overestimations (Figure 11(g,h,k)),

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especially the annual mean (g panel). However, the underscores of TCO, including the NP region, were worsened. These results indicated that the reduction for  $O_3$  by HONO chemistry is reasonable, and the combined cases such as maxST+JANO3-B can be plausible, although the estimated reduction degree should be reduced by elaborating the maxST's reactive conditions.



Figure 11: 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.

#### 3.2.3. 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 CH<sub>4</sub>, and the budgets of NO<sub>x</sub>, O<sub>3</sub>, and CO. The gaseous reactions of HONO tend to increase the abundance of NO<sub>x</sub>, O<sub>3</sub>, and CO (+1.01%, +0.15%, +0.44%, respectively) and CH<sub>4</sub> 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 NO<sub>x</sub>, O<sub>3</sub>, 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 CH<sub>4</sub> lifetime by 15% and CO abundance by 10%. HRs also reduces NO<sub>x</sub> level by 23% and O<sub>3</sub> 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 NO<sub>x</sub> levels, with consequences for OH and O<sub>3</sub> 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 NO<sub>x</sub> level at the surface (-60% in O4 and -40% in O3) (Figure 12(a-f): blue areas). These reductions in NO<sub>x</sub>, OH, and O3 levels extend up to 400 hPa at high
- N/S latitudes (Figure 12(k, l)). All these reduction effects for NO<sub>x</sub>, OH, and O<sub>3</sub> levels are due to the removal of HONO on ice and cloud particles (R6) (Figure 10(a, b): blue fields). On the one hand, it accelerates the conversion of NO<sub>2</sub> to HONO and ultimately strengthen its deposition by particulate nitrate (R4) (Figure S13(a)). On the other hand, HRs occurring on aerosol surfaces lead to increments in OH and O<sub>3</sub> 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 NO<sub>x</sub>, +1500% OH, +48% in O<sub>3</sub>, Figure 12(a,c,e)). However, these OH and O<sup>3</sup> levels increase 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 NO<sub>x</sub> level (-15% versus -8%) and cause threefold effects on the tropospheric oxidation capacity (+11.5% in CH<sub>4</sub> lifetime, -4.6% in O<sub>3</sub>, +7% in CO), compared with HRs on aerosol (+3.5% CH<sub>4</sub> lifetime, -1.5% O<sub>3</sub>, +2.6%
- 720 CO) (Table 9).

Given the direct emissions of HONO (~10% of NO<sub>x</sub> emission inventory), the surface NO<sub>x</sub>, O<sub>3</sub>, and OH concentrations are generally enhanced in the STD case compared to the GR+HR case. They induce the concentration modification for NO<sub>x</sub> (+1.77%), O<sub>3</sub> (+0.97%), CO (-1.63%), and a significant reduction (-2.3%) in the CH<sub>4</sub> lifetime (Table 9). Remarkable enhancements for NO<sub>x</sub> (up to +198%), OH (+243%), and O<sub>3</sub> (+24%) (Figure 12(b,d,f): red fields) were identified for the

725 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). NO<sub>x</sub> and OH were elevated in these mid-latitude regions because of the enhanced HONO photolysis (R1) by the additional HONO source. However, OH, NO<sub>x</sub>, and O<sub>3</sub> levels were reduced near the surface of the Northern Hemisphere's land during summer (up to -47% OH, -82% NO<sub>x</sub>, and -15% O<sub>3</sub>) (Figure 12(b,d,f)). The latter phenomenon is similar to the 730 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 NO<sub>x</sub>, -5% in O<sub>3</sub>, +8% in CO, and a significant increase of +13% CH<sub>4</sub> lifetime in the troposphere (Table 9). Figure 13 highlights the consequences of HO<sub>x</sub>, NO<sub>x</sub>, and O<sub>3</sub> for the Chinese and NP regions. NO<sub>x</sub> level reduction accumulates in the Arctic and Antarctic during summer, especially over the NP ocean (reducing NO<sub>x</sub> level by 60–90%, Figure 13(i)). These

- reductions in NO<sub>2</sub> 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 O<sub>3</sub> levels for a larger part of the troposphere. As NO<sub>x</sub> is essential in regulating O<sub>3</sub> and OH in the troposphere, a reduction of NO<sub>x</sub> level increases the HO<sub>2</sub>/OH ratio (due to the HO<sub>2</sub> + NO  $\rightarrow$  OH + NO<sub>2</sub> reaction), which restrains the formation of OH and ultimately of O<sub>3</sub>. Moreover, a NO<sub>2</sub>-deficit environment directly affects the O<sub>3</sub> level as NO<sub>2</sub> is a primary source of an oxygen atom that engages in the formation of O<sub>3</sub>. Thus, in summer, both
- 740 OH and O<sub>3</sub> levels are drastically reduced over the NP region (35–67% for OH, 30–43% for O<sub>3</sub>, Figure 13(g,k)), and 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  $NO_x$  level by 48–78% (Figure 12(c)) due to the uptake of  $NO_2$  onto aqueous aerosols. At the surface, OH level is enormously increased as a result of HONO photolysis (R1), heterogeneous  $NO_2$  conversions (R4, R5), and additional direct emissions

745 (Figure 13(a,b)). The corresponding increase in O<sub>3</sub> 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<sub>x</sub> emissions, VOC-limited O<sub>3</sub> chemistry is likely the driving mechanism (Liu et al., 2010). The vast increases in OH and O<sub>3</sub> 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<sup>6</sup> molecules cm<sup>-3</sup>) and O<sub>3</sub> (0.3–0.5 ppbv) concentrations over polluted regions in China during winter.

- 750 Compared with Elshorbany's work, the increases in OH and O<sub>3</sub> concentrations in our model are higher due to the different HONO mechanisms applied in the two models, simply an averaged HONO/NO<sub>x</sub> ratio (0.02) in their model. In particular, our newly added heterogeneous reactions on cloud particles (R4) caused significant reductions in OH, NO<sub>x</sub>, and O<sub>3</sub> 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.,
- 755 2003) and agree with those previously reported for other HRs (HO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, and RO<sub>2</sub>) 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<sub>3</sub> concentrations in remote areas and, thus, will underestimate the potential effects in polluted regions.

The estimated global effects of HONO chemistry in the STD case is the abatement of global tropospheric oxidizing power, despite surface OH and O<sub>3</sub> levels being increased at polluted sites. The reduction tendency in global OH and O<sub>3</sub> contrasts with

- other modelling studies (e.g. Elshorbany et al., 2012; Jorba et al., 2012; Lee et al., 2016; Zhang et al., 2021). Some discussions on the tendency of HONO's global effects are addressed here. The amplified aerosol uptake of NO<sub>2</sub> (maxST case) further reduces an unrealistic degree of global NO<sub>x</sub> abundance (-55.4%) and tropospheric oxidizing capacity, leading to 14.5 years for a global CH<sub>4</sub> lifetime. The ratR4+CLD case introducing an approach to recycle NO<sub>x</sub> led to lowered global effects of HONO (only 8.57% NO<sub>x</sub> is reduced globally, CH<sub>4</sub> lifetime = 9.6 years). The photolysis of adsorbed HNO<sub>3</sub> on ground surfaces (JANO3-
- 765 A case) still reduces global abundances of OH and O<sub>3</sub> (Table S5). The ground-surface HNO<sub>3</sub> photolysis in the JANO3-A case causes only minor changes for a thin surface layer which is in line with other studies (Ye et al., 2018; Zhang et al., 2009). In JANO3-B and JANO3-C cases, a recycling process for NO<sub>x</sub> via HNO<sub>3</sub> photolysis is expected. However, only the JANO3-C case shows an increment in global NO<sub>x</sub> and O<sub>3</sub> (+29% and +16.1%, respectively), leading to only 5.4 years for the global CH<sub>4</sub> lifetime, which is impractical. This is because that simplified approach and maximum thresholds for the phase HNO<sub>3</sub> photolysis
- 770 are used. The combined cases maxST+JANO3-B lead to more convincing effects (CH<sub>4</sub> lifetime was 10.2 years; Table S5), which held the same tendencies as those calculated in the STD case. However, validating this combined case is only conducted for the daytime environment during EMeRGe (Sect. 3.1.2) and for TCO at northern mid-latitudes with OMI (Figure 11). In conclusion, we suggest the global effects tendency is towards tropospheric oxidizing capacity reduction, although further elaboration for enhanced aerosol-uptakes of NO<sub>2</sub> and surface-catalyzed photolysis of HNO<sub>3</sub> can change the effect magnitude.
- 775 The implication of HONO chemistry in a bottom-up approached global model such as CHASER securely needs intense examination on possible HONO sources and profound evaluations with observed HONO in the troposphere.

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<b>Fable 9: CH4 lifetime and</b>	l tropospheric abundances i	for NO <sub>x</sub> , O <sub>3</sub>	, CO and the	changes by H	ONO chemistry
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Simulation ID	CH <sub>4</sub> lifetime	Ab	undances of tropo	ospheric
	(yr)	NO <sub>x</sub>	O <sub>3</sub>	СО
		(TgN)	(TgO <sub>3</sub> )	(TgCO)
OLD	9.09	0.119	408.79	327.20
GR	9.12	0.120	409.38	328.65
GR+HR	10.49	0.092	384.25	359.90
GR+HR(cld)	10.17	0.102	390.46	351.53
STD	10.28	0.094	388.21	354.57
Effects		Cha	nges (%)	
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 <sub>2</sub> O <sub>5</sub> ,HO <sub>2</sub> ,RO <sub>2</sub> )	157	2 97	2.01	+2.42
(Ha et al., 2021)	+3.7	-3.07	-2.91	+3.43



Figure 12: Effects of the HONO photochemistry on the tropospheric oxidants OH (first row of panels), NO<sub>x</sub> (second row of panels), 785 O<sub>3</sub> (third row of panels) and (CO last row of panels). Effects at 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), NO<sub>x</sub> (middle panels), and O<sub>3</sub> (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 (1<sup>st</sup> column heterogeneous reactions ice and clouds (3<sup>rd</sup> column) and direct HONO emission (2<sup>nd</sup> and 4<sup>th</sup> columns).

#### 4. Conclusion

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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<sub>2.5</sub>, NO<sub>3</sub> components, O<sub>3</sub>, and CO concentrations when the HONO photochemistry is included. The HONO inclusion mostly reduces the overestimations of OMI-based TCO by simulations given its reducing effects for O<sub>3</sub>, which notably includes the geographical region that embraces China. Although the simulation underestimations of surface O<sub>3</sub> in the NP region is associated with the inconsistent surface deposition or vertical fluxes (c.f. from the stratosphere) becoming strong, the model still stands out with NO<sub>2</sub>, 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 coastal region of East Asia and discerned good agreement between the measured and calculated NO<sub>2</sub>, O<sub>3</sub>, and CO profiles. However, the model does not reflect the influence of the Chinese river delta regions, 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 eastern China during winter. Only 5–10 ppt of HONO can be transported up to ~2000 m, indicating that its impacts remain mainly in the planetary boundary layer. We argue that these simulated HONOs 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

- 810 are not reproduced by the STD simulation but moderately captured by the combined simulation, which enhanced aerosoluptakes of NO<sub>2</sub> and heterogeneous photolysis of HNO<sub>3</sub> (maxST+JANO3-B). However, the enhancement for NO<sub>2</sub> uptakes on aerosols should be confined to particular environments to eliminate the effect exaggeration. Moreover, 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<sub>x</sub> and CO from South-Eastern and Eastern Asia, (2) the lighting-related NO<sub>x</sub> module is upgraded, and (3) the 815 vertical mixing and downward fluxes from the stratosphere to be elaborated.
- One or more renoxification mechanisms converting HNO<sub>3</sub> into NO<sub>x</sub> should be added to the model to overcome the observed and simulated NO<sub>x</sub> seasonality mismatches. Shifting the product ratio towards more HONO and less HNO<sub>3</sub> in reaction R4 can also provide more HONO and mitigate the deteriorated representation of NO<sub>x</sub> seasonality. The sensitivity tests also suggest that more robust aerosol processing in polluted areas and less HNO<sub>3</sub> product in R4 can further reduce O<sub>3</sub> level in summer, reducing the bias against measurements. The photolysis of adsorbed HNO<sub>3</sub> on ground surfaces (JANO3-A case) can
  - also serve as a recycling process for NO<sub>x</sub> at Asian ground-based sites (EANET).

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<sub>4</sub> 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  $NO_2$ 

- 825 conversions on soot induce significant photochemical effects over eastern Chinese with changes of -60% in NO<sub>x</sub>, +1700% in OH, +33% in O<sub>3</sub>. During summer, HRs on ice and cloud particles could cause significant changes of -67% in OH, -45% in O<sub>3</sub>, -75% in NO<sub>x</sub>, and +17% in CO in the NP region. Albeit the more significant contribution of aerosols' heterogeneous reactions to the net HONO production, the heterogeneous processes involving ice and cloud particles are more significant globally. We found that the HONO chemistry, including the heterogeneous processes on cloud particles, can reduce the troposphere's
- 830 oxidizing capacity on a global scale. It should be underlined that this finding is rather unexpected and contrasts 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. However, the tendencies and magnitudes of HONO's global effects are still debated along with the effort regarding daytime HONO formation mechanisms. In capturing HONO measurement during EMeRGe campaign, the combined case enhancing NO<sub>2</sub> aerosol uptake and implementing heterogeneous
- 835 photolysis of HNO<sub>3</sub> (maxST+JANO3-B) still results in the reduction for global tropospheric oxidizing capacity. In this case, the effect magnitude is smaller for CH<sub>4</sub> lifetime, but those for the NO<sub>x</sub>-O<sub>3</sub>-CO chemistry are stronger compared with the calculation in the STD case. Overall, our results prove that a global model without heterogeneous HONO formation, especially photochemical heterogeneous HONO formations, 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.

#### 840 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. 845 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 an 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

850 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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