



Effects of heterogeneous reactions on global tropospheric chemistry

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Abstract. This study uses a chemistry-climate model CHASER (MIROC) to explore the roles of heterogeneous reactions (HRs) in global tropospheric chemistry. Three distinct HRs of N₂O₅, HO₂, and RO₂ are considered for surfaces of aerosols and cloud particles. The model simulation is verified with EANET and EMEP stationary observations, R/V MIRAI ship-based data, ATOM1 aircraft measurements, satellite observations by OMI, ISCCP, and CALIPSO-GOCCP, and reanalysis data JRA55. The heterogeneous chemistry facilitates improvement of model performance with respect to observations for NO₂, OH, CO, and O₃, especially in the lower troposphere. The calculated effects of heterogeneous reactions cause marked changes in global abundances of O₃ (-3%), NO_x (-2.2%), CO (+3.3%), and global mean CH₄ lifetime (+5.9%). These global effects were contributed mostly by N₂O₅ uptake onto aerosols in the middle troposphere. At the surface, HO₂ uptake gives the largest contributions, with a particularly significant effect in the North Pacific region (-24% O₃, +68% NO_x, +8% CO, and -70% OH), mainly attributable to its uptake onto clouds. The RO₂ reaction has a small contribution, but its global-mean negative effect on O₃ is not negligible. In general, the uptakes onto ice crystals and cloud droplets that occur mainly by HO₂ and RO₂ radicals cause smaller global effects than the aerosol-uptake effects by N₂O₅ radicals (+1.34% CH₄ lifetime, +1.71% NO_x, -0.56% O₃, +0.63% CO abundances). Nonlinear responses of tropospheric O₃, NO_x, and OH to the N₂O₅ and HO₂ uptakes are found in the same modelling framework of this study ($R > 0.93$). Although all HRs showed negative tendencies for OH and O₃ levels, the effects of HR(HO₂) on the tropospheric abundance of O₃ showed a small increment with an increasing loss rate. However, this positive tendency turns to reduction at higher rates (>5 times). Our results demonstrate that the HRs affect not only polluted areas but also remote areas such as the mid-latitude sea boundary layer and upper troposphere. Furthermore, HR(HO₂) can bring challenges to pollution reduction efforts because it causes opposite effects between NO_x (increase) and surface O₃ (decrease).

1 Introduction

Heterogeneous reactions (HRs) on the surfaces of atmospheric aerosols and cloud droplets are regarded as playing crucial roles in atmospheric chemistry. They affect ozone (O₃) concentrations in various pathways via the cycle of odd hydrogens (HO_x) and nitrogen oxides (NO_x) (Jacob, 2000). Tropospheric ozone, an important greenhouse gas, causes damage to human health,



30 crop, and ecosystem productivity (Monks et al., 2015). Although tropospheric O₃ was recognized as a critical oxidant species; its global distribution has not been adequately captured to date because of the limited number of observations. Whereas many sites in the heavily polluted regions of eastern Asia show ozone increases since 2000 (Liu and Wang, 2020), many sites in other regions show decreases (Gaudel et al., 2018). Moreover, O₃ responds to changes of multiple pollutants such as NO_x and VOCs in different ways, which challenge the local pollutant control policy. For instance, since the Chinese government
35 released the Air Pollution Prevention and Control Action Plan in 2010 (Zheng et al., 2018), the targets of SO₂, NO_x, and particulate matter (PM) decreased drastically, but urban ozone pollution has been worsening (Liu and Wang, 2020). Indeed, the O₃ responses are controlled by several mechanisms including heterogeneous effects of HO₂ and N₂O₅ onto aerosols (Kanaya et al., 2009; Taketani et al., 2012; Li et al., 2019; Liu and Wang, 2020).

Stationary observations and laboratory experiments are important for enhancing the understanding of the tropospheric
40 chemistry of O₃ and other essential components (NO_x, HO_x). However, direct observation of vertical O₃ distribution including upper tropospheric O₃ was not available before 1970. It has been deployed only at limited sites of the globe. Global atmospheric modelling is a useful method to reanalyze or to forecast the past and future changes in O₃ and their effects on human health and climate. To serve this task, atmospheric models use both laboratory and observational data to help achieve accurate simulations of O₃ and its precursors (HO_x, NO_x, hydrocarbons). To date, many modelling studies have suggested that
45 heterogeneous chemistry be included in a standard model for tropospheric chemistry (Jacob, 2000; MacIntyre and Evans, 2010, 2011; de Reus et al., 2005).

One fundamentally important HR in the troposphere is the uptake of N₂O₅ onto aqueous aerosols, known as a removal pathway for NO_x at night (Platt et al., 1984). Actually, NO_x plays crucially important roles in the troposphere because it controls the cycle of HO_x and the production rate of tropospheric O₃ (Logan et al., 1981; Riemer et al., 2003). The morning
50 photochemistry can be affected by NO₃ and N₂O₅, which are important nocturnal oxidants. Since the early 1980s, the role of urban NO_x chemistry in Los Angeles pollution (National Research Council, 1991) has been acknowledged, but the proclamation of nighttime radicals remained sparse. It was only recognized in the past decade that N₂O₅ radical chemistry could have a much more perceptible effect stemming from reasons counting a refined understanding of heterogeneous processes occurring at night (Brown and Stutz, 2012). The HR of N₂O₅ was revealed under different meteorological conditions
55 in the US, Europe, and China (photosmog, high relative humidity (RH), or seasonal variation) for particles of various types: ice, aqueous aerosols with organic-coating, urban aerosols, dust, and soot (Apodaca et al., 2008; Lowe et al., 2015; Qu et al., 2019; Riemer et al., 2003, 2009; Wang et al., 2018; Wang et al., 2017; Xia et al., 2019). The uptake of N₂O₅ can markedly enhance nitrate concentration in nocturnal chemistry or PM_{2.5} explosive growth events in summer, decrease NO_x, and either increase or decrease O₃ concentrations in different NO_x conditions (Dentener and Crutzen, 1993; Qu et al., 2019; Riemer et al., 2003; Wang et al., 2017). Even during daytime, N₂O₅ in the marine boundary layers can enhance the NO_x to HNO₃ conversion, and chemical destruction of O₃ (Osthoff et al., 2006). The 10–20 ppbv reduction of O₃ because of N₂O₅ uptake in
60 the polluted regions of China has also been reported (Li et al., 2018). At mid- to high latitudes, N₂O₅ uptakes on sulfate aerosols



could engender 80% and 10% NO_x reduction, respectively, in winter and summer, leading to approximate 10% reduction of O₃ in both seasons (Li et al., 2018).

65 Another vital process taking place on particles is the HRs of peroxy radicals (HO₂ and RO₂). Peroxy radicals are the primary chain carriers driving O₃ production in the troposphere. Moreover, it can drive the hydrocarbons and NO_x concentration which are important for nocturnal radical chemistry (Geyer et al., 2003; Richard, 2000; Salisbury et al., 2001). In the past, the HR(HO₂) effects have been well considered in the laboratory (Macintyre and Evans, 2011) and field observations (Kanaya et al., 2001, 2002a, 2002b, 2003, 2007; Taketani et al., 2012), but many technical problems (e.g.,
70 detecting HO₂) have created difficulties that challenge its reported importance in the troposphere, as asserted from recent studies (Liao and Seinfeld, 2005; Martin et al., 2003; Tie et al., 2001). More recently, global modelling reports have described that the inclusion of HO₂ uptake can affect atmospheric constituents strongly by the increment in tropospheric abundances for carbon monoxide (CO) and other trace gases because of reduced oxidation capacity (Lin et al., 2012; Macintyre and Evans, 2011). The HO_x loss on aerosols can reduce O₃ concentrations by up to 33% in remote areas and up to 10% in a smog episode
75 (Saathoff et al., 2001; Taketani et al., 2012). The HO_x loss on sea-salt, sulfate, and organic carbon in various environments can decrease respectively HO₂ levels by 6–13%, 10–40%, and 40–70% (Martin et al., 2003; Taketani et al., 2008, 2009; Tie et al., 2001). For RO₂ with a typical representative of CH₃CO.O₂ (peroxyacetyl radical, PA), it plays a big role in the long-range transport of pollution (VOC, NO_x) (Richard, 2000; Villalta et al., 1996). It can bring NO_x from polluted domains as PAN to remote regions in the ocean and higher altitudes (Qin et al., 2018; Richard, 2000). The concentrations of HO₂ and RO₂ at
80 nighttime in the marine boundary layer were measured and confirmed (Geyer et al., 2003; Salisbury et al., 2001). Moreover, some evidence suggests uptake of HO₂ and PA on clouds, aqueous aerosols, and other surfaces in high humidity conditions, although the mechanism is uncertain (Geyer et al., 2003; Jacob, 2000; Kanaya et al., 2002b; Liao and Seinfeld, 2005; Lin et al., 2012; Richard, 2000; Salisbury et al., 2001). The predominance of peroxy uptake to clouds results from the ubiquitous existence and larger SAD maxima of cloud droplets in the atmosphere. Indeed, aqueous-phase chemistry might represent an
85 important sink for O₃ (Lelieveld and Crutzen, 1990). Also, PA loss on aqueous particles can mediate the loss of PAN (CH₃CO.O₂NO) in fog (Villalta et al., 1996). Some modelling studies indicate that HO_x loss (including HO₂ loss) on aqueous aerosols causes about 2% reduction, 7% and 0.5% increments, respectively, in the annual mean global burden of OH, CO, and O₃ (Huijnen et al., 2014). However, in a coastal environment in the Northern Hemisphere it increases 15% OH and reduces 30% HO₂ (Sommariva et al., 2006; Thornton et al., 2008).

90 Although the contributions of each uptake category to tropospheric chemistry differ and must be considered both separately and as a whole, few studies have provided a global overview of heterogeneous chemistry the comprehensively examines the uptakes of N₂O₅, HO₂, and RO₂ on widely various particles. For instance, both uptakes of N₂O₅ and HO₂ tend to reduce O₃ in particular environments (Li et al., 2018; Saathoff et al., 2001; Taketani et al., 2012), but the HO₂ loss on clouds can increase the tropospheric O₃ burden (Huijnen et al., 2014). The latter trend is not widely suggested yet because the cloud
95 chemistry is still neglected in many O₃ models (Stadtler et al., 2018; Thornton et al., 2008). The predominant effects of HO₂ uptake on aerosols compared to the effect by N₂O₅ were reported during the summer smog condition (Saathoff et al., 2001),



but with lack of confirmation on a global scale. Moreover, the heterogeneous effects of RO_2 have been investigated only insufficiently (Jacob, 2000). In this study, we examine these uncertainties using the global model CHASER to perceive the respective and total effects of the HRs of N_2O_5 , HO_2 , and RO_2 on the tropospheric chemistry. For the interface of HRs in the atmosphere, we tentatively consider surfaces of cloud particles and those of aerosols and discuss details of its effects in this study. In the following text, the research method, including model description and configuration, is described in section 2. In section 3.1, our model is verified with available observations including ground stations, ship/aircraft and satellite measurements, particularly addressing the roles of the HRs. The global effects of N_2O_5 , HO_2 , and RO_2 uptake are discussed in section 3.2 to elucidate cloud-particles and aerosol effects. Section 3.3 will discuss sensitivities of tropospheric chemistry to the magnitudes of HRs. Section 4 presents a summary and concluding remarks.

2 Method

2.1 Global chemistry model

The global chemistry model used for this study is CHASER (MIROC-ESM) (Sudo et al., 2002, 2007; Watanabe et al., 2011), which considers detailed photochemistry in the troposphere and stratosphere. The chemistry component of the model, based on CHASER-V4.0, calculates the concentrations of 92 chemical species and 262 chemical reactions (58 photolytic, 183 kinetic, and 21 heterogeneous reactions including reactions on PSCs); more details on CHASER can be found in an earlier report of the literature (Morgenstern et al., 2017). Its tropospheric chemistry considers the fundamental chemical cycle of O_x - NO_x - HO_x - CH_4 - CO along with oxidation of non-methane volatile organic compounds (NMVOCs). Its stratospheric chemistry simulates chlorine and bromine-containing compounds, CFCs, HFCs, OCS, NO_2 , and the formation of polar stratospheric clouds (PSCs) and heterogeneous reactions on PSC surfaces. In the framework of MIROC-Chem, CHASER is coupled with the MIROC-AGCM atmospheric general circulation model (ver. 4; Watanabe et al., 2011). The meteorological fields simulated by MIROC-AGCM were nudged toward the six-hourly NCEP FNL data. For this study, the spatial resolution of the model was set as T42 (about $2.8^\circ \times 2.8^\circ$ grid spacing) in horizontal and L36 (surface to approx. 50 km) in vertical. Anthropogenic emissions for O_3 and aerosol precursors like NO_x , CO, VOCs, and SO_2 are specified using the HTAP-II inventory for 2008 (http://edgar.jrc.ec.europa.eu/htap_v2/), with biomass burning emissions derived from the MAC reanalysis system.

In the model, the aerosol concentrations for BC/OC, sea-salt, and soil dust are handled by the SPRINTAR module, which is also based on the CCSR/NIES AGCM (Takemura et al., 2000). The bulk thermodynamics for aerosols are applied, including SO_4^{2-} chemistry (SO_2 oxidation with OH, $\text{O}_3/\text{H}_2\text{O}_2$, cloud-pH dependent) SO_4^{2-} - NO_3^- - NH_4^+ and SO_4^{2-} -dust interaction.

2.2 Heterogeneous reactions in the chemistry–climate model (CHASER)

The CHASER-V4 model considers HRs in both the troposphere and stratosphere. In this work, we particularly examine HRs in the troposphere. In the current version of CHASER, tropospheric HRs are considered for N_2O_5 , HO_2 , and RO_2 , using uptake coefficients for the distinct surfaces of aerosols (sulfate, sea-salt, dust, and organic carbons) and cloud particles (liquid/ice) as



130 listed in Table 2. Although some other views incorporate the catalysis of transition metal ions (TMI) Cu(I)/Cu(II) and Fe(II)/Fe(III) for the HO₂ conversion on aqueous aerosols (Li et al., 2018; Mao et al., 2013; Taketani et al., 2012), this mechanism remains uncertainties (Jacob, 2000). The TMI mechanism might lead to either H₂O₂ (Jacob, 2000) or H₂O product (Mao et al., 2018). However, this may not cause any significant difference since recycling HO₂ from H₂O₂ is ineffective (Li et al., 2018). For this study, the uptake of HO₂ is affirmed with H₂O₂ as the product (Loukhovitskaya et al., 2009; Taketani et al., 2009), generally used in many atmospheric models such that this is not counted as a terminal sink for HO₂ (Jacob, 2000; Lelieveld and Crutzen, 1990; Morita et al., 2004; Thornton et al., 2008). The RO₂ uptakes are assumed with inert products, as
135 suggested by Jacob (2000). The heterogeneous pseudo-first-order loss rate β for the species i is given using the theory of Schwartz (Dentener and Crutzen, 1993; Jacob, 2000; Schwartz, 1986), in which it is simply treated with the mass transfer limitations operating two conductances represented free molecular and continuum regimes for tropospheric clouds and aerosols, in addition to using reactive uptake coefficient (γ) instead of the mass accommodation coefficient as

$$\beta_i = \sum_j \left(\frac{4}{v_i \gamma_{ij}} + \frac{R_j}{D_{ij}} \right)^{-1} \cdot A_j \quad (1)$$

140 Therein, v_i stands for the mean molecular speed (cm s⁻¹) of species i , D_{ij} is the gaseous mass transfer (diffusion) coefficient (cm² s⁻¹) of species i for particle type j , and A_j expresses the surface area density (cm² cm⁻³) for particle type j . In the model, the particle size and effective radius R_j for aerosols are calculated as a function of RH (Takemura et al., 2000). The aerosol concentrations are based on SPRINTAR for BC/OC, sea-salt, and dust (Takemura et al., 2000). The surface area density (SAD) for aerosols (A_j) is estimated using lognormal distributions of particle size (SF_j) with mode radii variable with the RH (Sudo
145 et al., 2002) as

$$A_{j,ae} = C_N * 4\pi R_j^2 * SF_j, \quad (2)$$

where C_N represents number density (cm⁻³), R_j signifies the effective radii (cm) of particle type j . To calculate SAD for cloud particles, the liquid water content (LWC) and ice water content (IWC) in the AGCM are converted using the cloud droplet distribution of Battan and Reitan (1957) and the relation between IWC and the surface area density for ice clouds (Lawrence
150 and Crutzen, 1998; McFarquhar and Heymsfield, 1996).

$$A_c = 10^{-4} * IWC^{0.9}$$

$$A_{j,ice} = 3 * A_c, \quad (3)$$

In those equations, A_c represents the cross-section area for ice crystals (cm² cm⁻³). For liquid clouds, the following holds.

$$A_{j,liq} = LWC * 10^{-6} * \frac{3}{R_j} \quad (4)$$

155 The uptake coefficient parameter (γ) is defined as the net probability that a molecule X undergoing a gas-kinetic collision with a surface is actually taken up onto the surface. Although several recent model studies that consider dependency of γ on RH and/or T, majority of the earlier studies uses constant γ values which only vary with aerosol particle compositions (Chen et al., 2018; Evans and Jacob, 2005; Macintyre and Evans, 2010, 2011). For one study, γ_{HO_2} for the uptake onto aqueous aerosols is



considered with pH dependence (Thornton et al., 2008). However, another study demonstrated that the uptake is large,
160 irrespective of the solubility in cloud water or pH (Morita et al., 2004). Therefore, we instead choose γ_{HO_2} as fix values
depending on the type of particle. Indeed, from Eq. (1) it is apparent that uptake coefficients should be unimportant for uptake
onto large particles such as cloud droplets. In this study, γ for cloud particles of liquid and ice phases are given based on
suggestions from earlier reports (Dentener and Crutzen, 1993; Jacob, 2000). One study (Dentener and Crutzen, 1993) used a
constant $\gamma_{N_2O_5}$ of 0.1 for uptake on seasalt, sulfate, and cloud particles. They also revealed that smaller $\gamma_{N_2O_5}$ of 0.01, which
165 had been reported as laboratory measurements, has insensitivity to effects on tropospheric oxidant components. Results of
another study (Jacob, 2000) indicated constants $\gamma_{N_2O_5} = 0.1$ and $\gamma_{HO_2} = 0.2$ for uptakes on both liquid clouds and aerosols, the
later aims to involve the HO_2 scavenging by clouds without accounting for details of aqueous-phase chemistry. For ice crystals,
Jacob suggested $\gamma_{HO_2} = 0.025$ based on a report by Cooper and Abbatt (1996). Jacob recommended using $\gamma_{RO_2} = 0.1$ for
hydroxy- RO_2 group produced by oxidation of unsaturated hydrocarbons and $\gamma_{RO_2} = 4 \times 10^{-3}$ for PA. The γ values for aerosols
170 are assumed to be fundamentally the same as those for liquid cloud particles in this study. It is noteworthy that the γ values
for cloud particles are given tentatively in this study and are adjusted based on evaluation of the resulting species concentrations
of O_3 , NO_y , and OH with the observations.

2.3 Experiment setup

In this study, simulations of two types were conducted to isolate the distinct effects of each HR for the surface types considered
175 in the model (Table 3 and Table S 1). Whereas a control simulation STD considers all HRs, noHR cases intentionally ignore
one or all of the HRs to calculate effects of individual HRs. The sensitivity runs that turned off the separate HRs onto clouds
(liquid and ice) and aerosols were also added to exploit the separate aerosol-heterogeneous and cloud-heterogeneous effects,
as suggested in many earlier studies (Apodaca et al., 2008; Jacob, 2000; Lelieveld and Crutzen, 1990, 1991; Morita et al.,
2004). The HR effects are determined as the differences between noHR cases and STD simulation as Eq. (5).

$$180 \quad Impact(i)_j = \frac{(STD_i - noHR(j)_i)}{noHR(j)_i} * 100 (\%) \quad (5)$$

Therein, STD_i stands for the concentration of investigated atmospheric component i in the STD run; and $noHR(j)_i$ denotes the
concentration of component i in the sensitivity run in which the HRs of/onto j was ignored (j could be N_2O_5 , HO_2 , RO_2 , clouds,
aerosols).

An additional sensitivity test was run to examine the sensitivity of the troposphere's responses with the amplified HRs
185 magnitudes (Table S 1). These simulations only apply for HR(N_2O_5) and HR(HO_2) to verify some uncertainties that have been
argued among earlier studies (Chen et al., 2018; Evans and Jacob, 2005; Macintyre and Evans, 2010, 2011).



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

Base model	MIROC4.5 AGCM
Spatial resolution	Horizontal, T42 ($2.8^\circ \times 2.8^\circ$); 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 MAC reanalysis
Aerosol	BC/OC, sea-salt, and dust BC aging with SO_x /SOA production
Chemical process	94 chemical species, 263 chemical reaction (gas phase, liquid phase, non-uniform O_x - NO_x - HO_x - CH_4 -CO chemistry with VOCs SO_2 , DMS oxidation (sulfate aerosol simulation) SO_4 - NO_3 - NH_4 system and nitrate formation Formation of SOA BC aging (+) Heterogeneous reactions: 8 reactions of N_2O_5 , HO_2 , RO_2 ; constant uptake coefficients (γ) on types of aerosols (Ice, Liquid, Sulfate, Sea salt, Dust, OC)

190 **Table 2: Heterogeneous reactions in CHASER**

No	Reactions	γ_{ice}	γ_{liq}	γ_{sulf}	γ_{salt}	γ_{dust}	γ_{oc}
1	$\text{HO}_2 \rightarrow 0.5\text{H}_2\text{O}_2 + 0.5\text{O}_2$	0.02	0.1	0.1	0.1	0.1	0.1
2	$\text{N}_2\text{O}_5 \rightarrow 2\text{HNO}_3$	0.01	0.08	0.1	0.1	0.1	0.1
	$\text{RO}_2 \rightarrow \text{products}$:						
3	$\text{HOC}_2\text{H}_4\text{O}_2 \rightarrow \text{product}^*$	0.02	0.2	0.2	0.2	0.2	0.2
4	$\text{HOC}_3\text{H}_6\text{O}_2 \rightarrow \text{product}^*$	0.02	0.2	0.2	0.2	0.2	0.2
5	$\text{ISO}_2 \rightarrow \text{product}^*$	0.01	0.1	0.1	0.1	0.1	0.1
6	$\text{MACRO}_2 \rightarrow \text{product}^*$	0.01	0.1	0.1	0.1	0.1	0.1
7	$\text{CH}_3\text{COO}_2 \rightarrow \text{product}^*$	0	0.001	0.004	0.004	0.004	0.004

References and the mention of adjustments are given in the main text. The RO_2 uptakes are assumed with inert products as suggested by Jacob (2000).

Table 3: Main sensitivity simulations for HRs in this work

No.	Simulation ID	HR: N_2O_5	HR: HO_2	HR: RO_2	HRs on clouds	HRs on aerosols
1	STD	x	x	x		
2	noHR					
3	noHR.n2o5		x	x		
4	noHR.ho2	x		x		
5	noHR.ro2	x	x			
6	noHR.Cld					x
7	noHR.Ae				x	



2.4 Observation data for model evaluation

195 Model simulations with and without HRs are evaluated distinctively with stationary, ship-based, aircraft-based, and satellite-based measurements. The observational information and locations of the surface site and ship/aircraft tracks for the observations used for this study are summarized in Table 4 and Fig. 1.

200 EANET is well known as the Acid Deposition Monitoring Network in eastern Asia. The monthly data from 45 stations over 13 countries during 2010–2016 were used to verify surface concentrations of aerosols (sulfate, nitrate) and trace gases (HNO₃, NO_x, O₃) in eastern Asia. We also used data of the European Monitoring and Evaluation Programme (EMEP), which compile observations over 245 European stations.

205 Additionally, we exploited ship-based observational data from R/V MIRAI cruise (<http://www.godac.jamstec.go.jp/darwin/e>) undertaken by the Japan Agency for Marine–Earth Science and Technology (JAMSTEC). This study used data for surface CO and O₃ concentrations in summer 2015–2017 along the Japan–Alaska, Japan–Indonesia–Australia routes (Kanaya et al., 2019). The model data were compiled in hourly time-steps and were interpolated corresponding with the MIRAI time step and coordinates. For verification of the vertical tropospheric profiles, we used Atmospheric Tomography (ATom1) aircraft measurements (<https://espo.nasa.gov/atom/content/ATom>) for NO₂, OH, CO, and O₃.

210 The simulated tropospheric ozone was also evaluated using the tropospheric column O₃ (TCO) derived from the OMI satellite data (<https://daac.gsfc.nasa.gov/>). For distribution of the cloud fraction, satellite data from International Satellite Cloud Climatology Project (ISCCP, <https://isccp.giss.nasa.gov/>), GCM-Oriented CALIPSO Cloud Products (CALIPSO-GOCCP, https://eosweb.larc.nasa.gov/project/calipso/calipso_table), and Japanese 55-year reanalysis (JRA-55 - <https://doi.org/10.5065/D6HH6H41>) were used.

Model bias and normalized root mean squared error (NRMSE) for each species were calculated as shown below, where n is the number of available data (number of stations \times time-step).

$$215 \quad \text{bias} = \frac{\sum_1^n \text{Model} - \text{Observation}}{n} \quad (6)$$

$$\text{NRMSE} = \frac{\sqrt{\frac{\sum_1^n (\text{Model} - \text{Observation})^2}{n}}}{\text{Observation}} \quad (7)$$

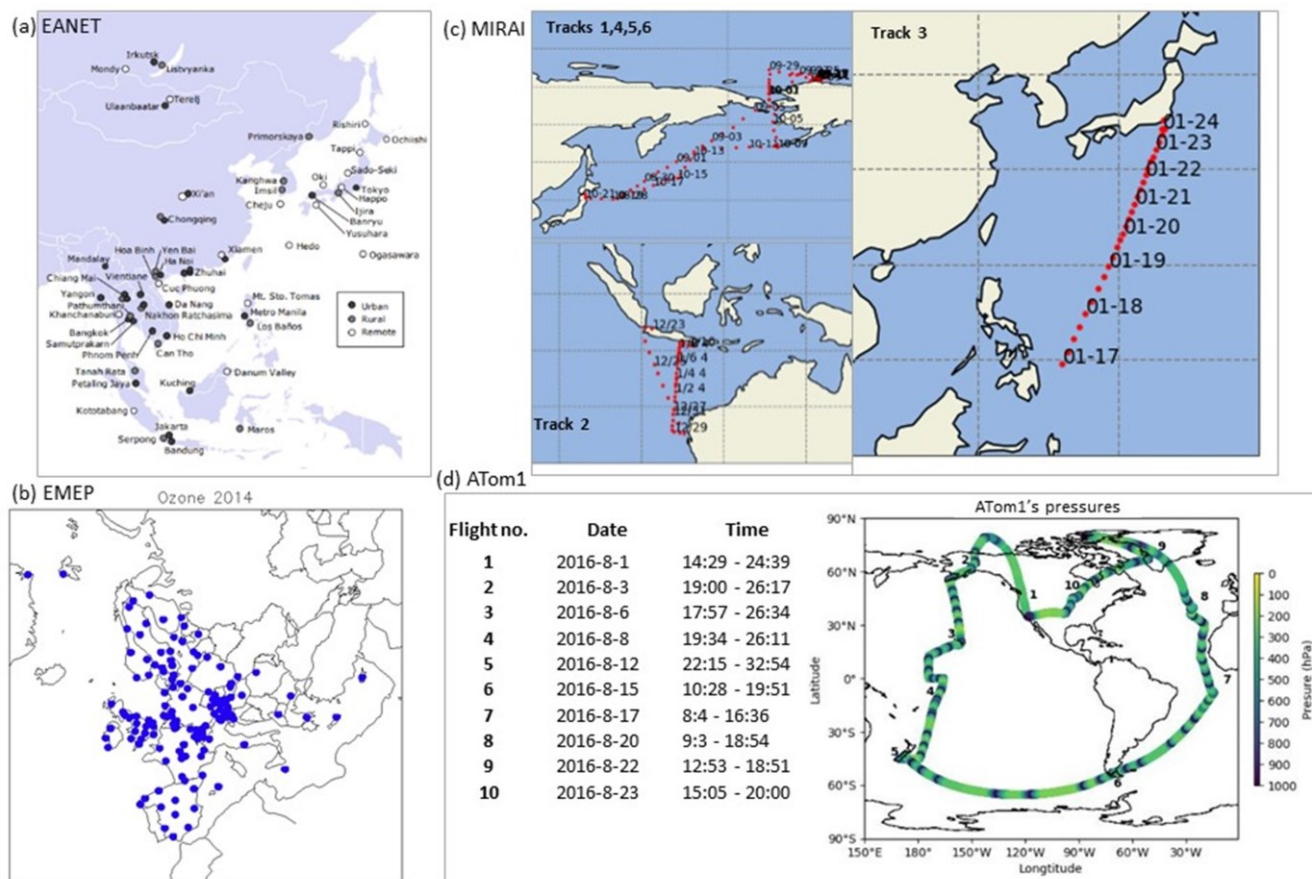


Figure 1: Locations of EANET stations (a), EMEP stations (b), MIRAI cruises (c), and ATom1 flights (d).

220 Source: (a) <https://monitoring.eanet.asia/document/overview.pdf>; (b) <https://projects.nilu.no/CCC/>

Table 4: Datasets used for verification in this study

Verified species	Regions	Data	Time series	Time-step
Sulfate, nitrate, NO _x , O ₃ , HNO ₃	Eastern Asia	EANET	2010–2016	Daily to 2-weekly
Sulfate, nitrate, NO _x , O ₃ , CO	Europe	EMEP	2010–2016	Hourly
CO, O ₃	Surface of the Pacific Ocean (Australia – Indonesia – Japan – Alaska)	MIRAI	8,9/2015 1,8,9/2016 7,8,9/2017	30 min
NO ₂ , OH, CO, O ₃	Various altitudes above the Pacific and Atlantic Ocean	ATOM1	8/2016	30 min
TCO	60S–60N (Satellite)	OMI	2010–2016	Daily
Cloud fraction	Global (Satellite)	ISCCP	2000–2009	Monthly
	Global (Satellite)	CALIPSO-GOCCP	2007–2017	Monthly
	Global (Reanalysis)	JRA55	2000–2015	6-hourly

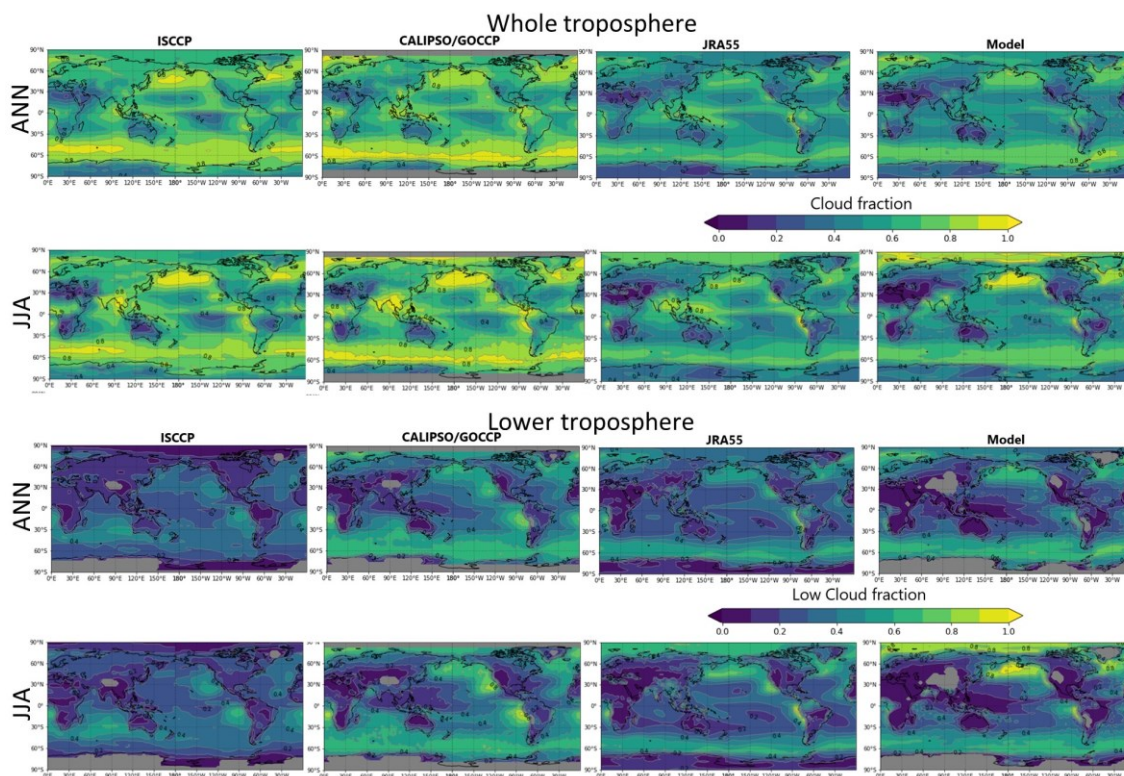
3 Results and Discussion

3.1 Model verifications

Cloud verification

225 For this study, we tentatively consider HRs on the cloud particle surface. Given the great uncertainties related to the reaction coefficient (γ) (Macintyre and Evans, 2010, 2011), the cloud distributions must be examined adequately in the model to the greatest extent possible. The model-calculated cloud distributions were verified using satellite observation data ISCCP D2, CALIPSO-GOCCP, and reanalysis data JRA55.

For the entire troposphere, the calculated cloud fraction was generally underestimated against the satellite observations and reanalysis data (Fig. 2, the first row). At the North Pacific region in JJA (Fig. 2, the second row), when the cloud fraction peaked in the region, the model was able to reproduce the satellite observations (ISCCP and CALIPSO). However, for the lower troposphere over the region, the cloud fraction calculated using CHASER in JJA appears to be overestimated (Fig. 2, the fourth row), suggesting that the resulting HR effects would also be exaggerated to some extent.



235 **Figure 2: Comparisons for cloud fraction in the whole troposphere (first and second rows) and lower troposphere (third and fourth rows). ANN denotes annual mean; JJA denotes June + July + August mean. First column for ISCCP (2000–2009), second column for CALIPSO/GOCCP (2007–2017), and third and fourth columns for JRA55 and CHASER (2000–2015). Color-bars are the same for all panels. In ISCCP and CALIPSO data, the pressure boundary layer of the low troposphere is > 680 hPa. In JRA55, the low troposphere was defined as 850–1100 hPa of pressure.**

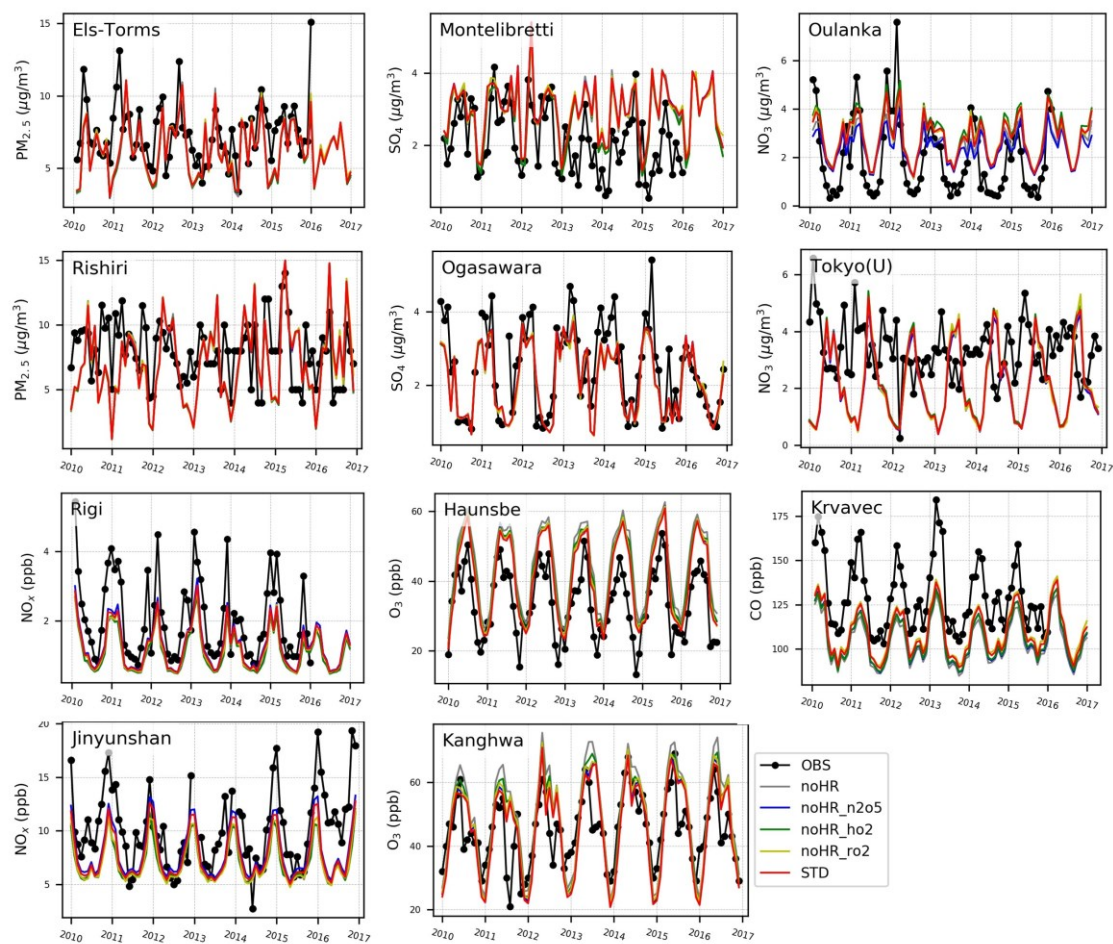


240 Verification with stationary observations

Verifications with EANET and EMEP stationary observations were conducted to assess the model performance on land domains of eastern Asia and Europe, particularly addressing the roles of the heterogeneous reactions considered for this study. The mass concentrations of particulate matter ($PM_{2.5}$), sulfate (SO_4^{2-}), nitrate (NO_3^-), aerosols and gaseous HNO_3 , NO_x , O_3 , and CO (CO only for EMEP) of 2010–2016 were evaluated (see Fig. S3 to S10 for monthly concentrations and Fig. S12: for correlations). In general, the model can moderately reproduce the $PM_{2.5}$, SO_4^{2-} , and NO_3^- aerosol concentrations at these locations ($R = 0.3$ – 0.7 , Table 5), although $PM_{2.5}$ was underestimated, sulfate was overestimated slightly. Nitrate was underestimated for EANET and overestimated for EMEP. It is noteworthy that the model performance for EMEP stations was better than that for EANET. The $PM_{2.5}$ concentration was better estimated with the inclusion of N_2O_5 and HO_2 uptakes (bias reduction in Table 5). The high negative biases for NO_3^- are significant at urban sites, e.g. at Tokyo (Fig. 3), which can be associated with undervaluation for NO_x and which can thereby lessen the effects of N_2O_5 uptake.

Nitric acid in both regions was overestimated. The correlations, biases, and normalized root mean square error (NRMSE) of the model for SO_4 , NO_3 , and HNO_3 are in the ranges as reported in a multi-model study by Bian et al. (2017) (Table 6).

The NO_x concentration for eastern Asia and Europe was underestimated, with significant bias for Asian polluted locations. The increasing effects of NO_x attributable to heterogeneous reactions, although minor, mitigated these underestimations. In Fig. 3, although NO_x was partly reduced via uptake of N_2O_5 , the NO_x level was mostly increased because of HO_2 and RO_2 uptake. CO for EMEP was underestimated by the model. This undervalue was mitigated by increasing effects because of HRs of N_2O_5 and HO_2 . The uptakes of RO_2 , in contrast, minorly reduced CO levels so that the model bias was worsened slightly. For O_3 , whereas the model tends to overestimate this tracer for both regions, O_3 reduction effects of all HRs also alleviated the model overestimates, especially in June, July, and August (JJA). In December, January, and February (DJF), the model tended to underestimate O_3 levels at some stations. The reduction effects on O_3 extended this undervalue. In general, STD simulation with coupled HRs partly improved the agreement related to the particulate and gaseous species, showing less bias than that of simulations without HRs (Table 5).



265 **Figure 3: Observations and sensitivity simulations at represented EMEP and EANET stations: first row – PM_{2.5}, SO₄²⁻, and NO₃⁻ for EMEP; second row – same as first row but for EANET; third row – NO_x, O₃, CO for EMEP; fourth row – NO_x and O₃ for EANET.**

Table 5: Model correlations and biases with EANET/EMEP observations: three-sigma-rule outlier detection is applied for each station before calculating all data. For NO_x, all data were filtered once more using the two-sigma-rule. Bias of the sensitivity run is shown as bold if it is higher than the bias of the STD run.

	EANET						EMEP						
	PM _{2.5}	SO ₄ ²⁻	NO ₃ ⁻	HNO ₃	NO _x	O ₃	PM _{2.5}	SO ₄ ²⁻	NO ₃ ⁻	HNO ₃	NO _x	O ₃	CO
R(STD)	0.37	0.56	0.379	0.177	0.233	0.6	0.475	0.633	0.715	0.116	0.698	0.651	0.534
bias (STD)	-7.526	1.048	-0.395	0.311	-3.929	3.927	-2.966	0.784	0.273	0.081	-0.773	4.071	-3.439
bias (noHR)	-7.442	0.971	-0.452	0.292	-4.011	6.808	-3.262	0.603	0.106	0.067	-0.895	7.189	-9.062
bias (noHR_n2o5)	-7.575	1.05	-0.46	0.295	-3.869	4.93	-3.223	0.774	0.042	0.07	-0.707	5.013	-6.822
bias (noHR_ho2)	-7.607	0.925	-0.37	0.312	-4.02	5.126	-3.136	0.55	0.335	0.078	-0.895	5.489	-6.896
bias (noHRs_ro2)	-7.38	1.021	-0.427	0.305	-4.008	4.931	-2.858	0.839	0.275	0.079	-0.833	4.893	-2.276

270



Table 6: Comparisons between EANET and EMEP observations with atmospheric models. Outlier detection follows in Table 5. The model result is shown as bold if it is better than or agreed with Bian’s report.

EANET	SO ₄ [$\mu\text{g m}^{-3}$]	NO ₃ [$\mu\text{g m}^{-3}$]	HNO ₃ [ppb]
This study	$r = \mathbf{0.56}$ bias = 1.048 nrmse = 0.954	$r = \mathbf{0.379}$ bias = -0.395 nrmse = 1.58	$r = \mathbf{0.177}$ bias = 0.311 nrmse = 2.491
Bian et al., 2017	$r = 0.449\text{--}0.640$ bias = 0.358–1.353 nrmse = 0.840–0.968	$r = 0.226\text{--}0.448$ bias = 0.338–1.920 nrmse = 1.494–2.080	$r = 0.098\text{--}0.370$ bias = 0.347–3.596 nrmse = 0.980–2.880
EMEP	SO ₄ [$\mu\text{g m}^{-3}$]	NO ₃ [$\mu\text{g m}^{-3}$]	HNO ₃ [$\mu\text{g m}^{-3}$]
This study	$r = \mathbf{0.633}$ bias = 0.784 nrmse = 0.961	$r = \mathbf{0.715}$ bias = 0.273 nrmse = 0.91	$r = 0.116$ bias = 0.886 nrmse = 3.33
Bian et al., 2017	$r = 0.230\text{--}0.463$ bias = 0.452–1.699 nrmse = 0.514–0.818	$r = 0.393\text{--}0.585$ bias = 0.539–1.421 nrmse = 0.745–1.031	$r = 0.157\text{--}0.502$ bias = 0.570–3.836 nrmse = 0.908–2.542

Verification with ship-based measurements

275 The model simulations were also verified with O₃ and CO observations from the Research Vessel (R/V) MIRAI for the Pacific Ocean region. This study specifically examines data from the four cruises of R/V MIRAI for the Japan–Alaska region (40° N–75° N, 140° E–150° W) in summer, designated as Track 1 (2015/8/28–9/29), Track 4 (2016/8/22–9/14), Track 5 (2017/7/11–7/29), and Track 6 (2017/8/24–9/8), and cruises during DJF for the Indonesia–Australia region (5°–25° S, 105–115° E) designated as Track 2 (2015/12/23–2016/1/10) and for the Indonesia–Japan region (10–35° N, 129°–140° E) designated as
 280 Track 3 (2016/1/17–1/24). Data for the North Pacific region (40°–60° N) are addressed for analysis in Sect. 3.2.

Table 7 shows correlation coefficients (plotted in Fig. S13), indicating that the CHASER simulations for CO and O₃ are in good agreement with MIRAI observations ($R = \text{approx. } 0.6$). However, the model still shows some discrepancies for both CO and O₃ concentrations. In general, the estimated CO and O₃ are both reduced for T1, T4–6 as compared to observations whereas superior for the data located in 20° S–20° N during T2–3. Overestimations for CO and O₃ occurring in the region with
 285 considerably low levels of these species might be attributed to the lack of halogen chemistry in the model, as also discussed for the nearby region in a past report (Kanaya et al., 2019). Undervalues for CO and O₃ levels in the higher latitudes (T1, T4–6) are ascribable to the insufficient downward mixing process of stratosphere O₃ in the model (Kanaya et al., 2019).

The negative biases in the noHR simulations for CO are lower in the STD run for all cruises, as they are for the North Pacific region (second versus third/fourth/fifth data rows for CO, Table 7). The CO-increasing effects by N₂O₅ and HO₂ uptakes
 290 are consistent with the comparison for EMEP. So are CO-reduction effects because of HRs(RO₂). Whereas the effects by N₂O₅ and HO₂ reduce the model bias, the CO-reducing effects by HRs(RO₂) exaggerated the CO bias (second versus sixth data rows for CO in Table 7), which is already apparent for comparison with EMEP (last column, Table 5).

For O₃ level, the model undervalues (Table 7) are in the opposite direction to the O₃ overestimates for EANET and EMEP stations (Table 5). The lower panels presented in Fig. 4 show marked O₃ reduction with all HRs, mostly contributed from the
 295 HO₂ uptake onto cloud particles (gaps between red and green lines). This marked reduction of the O₃ level is evident at some



points during the cruises, especially in the North Pacific region (the shaded areas), especially for T4. Unlike comparisons for land-domain data (Table 5), O₃ reduction because of HRs extends the model underestimates during the MIRAI cruises. It is noteworthy that one cannot necessarily confirm whether the STD run better simulates these species than the noHR does because tropospheric CO and O₃ levels are controlled by a complicated chemical mechanism and an interplay of emission, transport, deposition, and local mixing in the boundary layers. As discussed later in Sect. 3.2, the surface aerosols concentration in the West Pacific Ocean mostly dominated by liquid clouds (exceed 50,000 μm² cm⁻³ during JJA) and sulfate aerosols (approximately 75 μm² cm⁻³ in JJA). The model improvements in reproducing CO by adding N₂O₅ and HO₂ uptake indicate that the appropriate mechanisms of these processes onto cloud droplets and sulfate aerosols are well-established in the model. For HRs(RO₂), which induce the smallest and opposite effects on CO compared with the effects of N₂O₅ and HO₂ uptakes, it can be stated in general for the total HR effects that including all three HRs partially improves the model during MIRAI cruises.

Table 7: Model correlations and biases for MIRAI. No outlier filtration is applied. The bias of the sensitivity run is shown as bold if it is higher than the bias of STD run. The unit for the biases is ppb.

	CO	O ₃	CO (40–60° N)	O ₃ (40–60° N)
R(STD)	0.689	0.617	0.58	0.665
bias (STD)	-4.988	-4.996	-11.668	-3.493
bias (noHR)	-10.324	-2.388	-17.625	1.211
bias (noHR_n2o5)	-8.127	-4.362	-14.804	-2.738
bias (noHR_ho2)	-9.036	-3.358	-16.358	-0.226
bias (noHR_ro2)	-3.433	-4.431	-10.035	-2.526
bias (noHR_cld)	-6.821	-3.199	-14.005	0.025

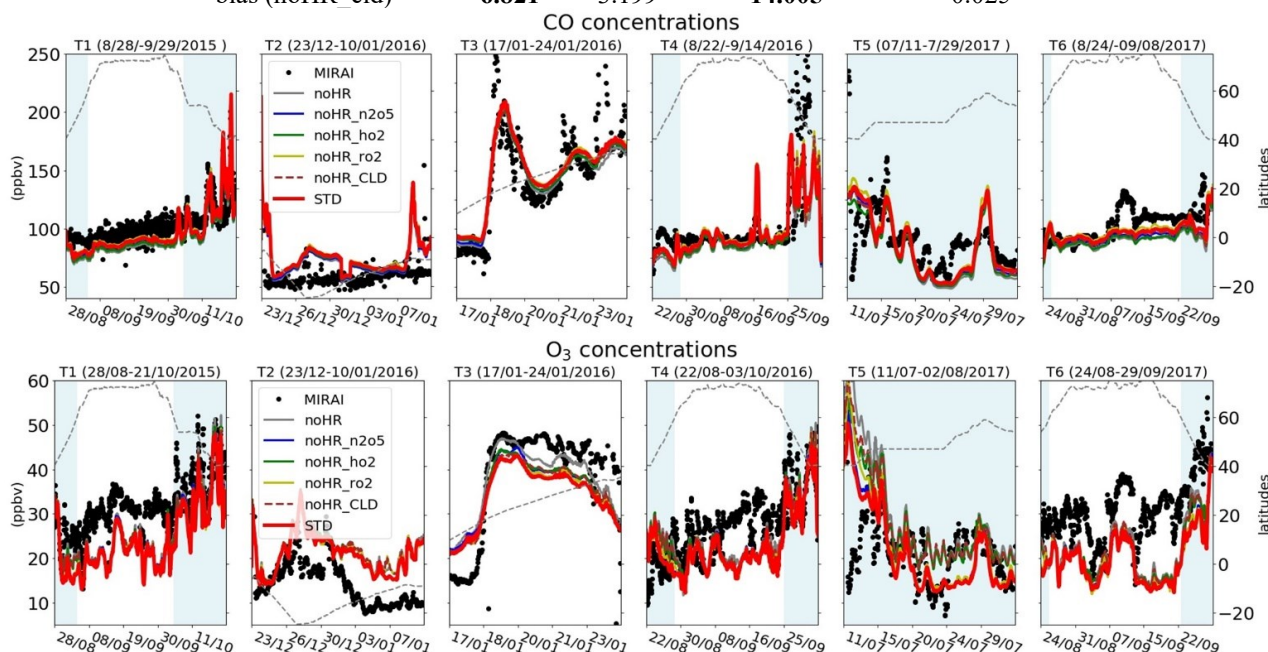


Figure 4: Sensitivity simulations for CO (upper panels) and O₃ (lower panels) during MIRAI cruises. The left axis shows concentrations. Dashed lines show latitudes of cruises scaled with the right axis. The horizontal axis shows cruise travel times. Shaded areas show data in the North Pacific region (140–240° E, 40–60° N). Brown dashed lines representing the noHR_CLD run are discussed in Sect. 3.2.



Verification using aircraft measurements

To verify the model performance in the free troposphere, we used ATom1 aircraft measurements in August of 2016 (for NO₂, OH, CO, and O₃). The spatial and temporal concentrations are available in Fig. S11. Correlations are shown in Fig. S14.

In general, the model simulations for NO₂, OH, CO, and O₃ adequately agree with aircraft measurements with $R > 0.5$ (Fig. S14). However, NO₂ and CO still tend to be underestimated by the model, which is consistent with comparisons for EANET/EMEP and MIRAI observations. In Fig. 5, the CO-increasing effects, mostly by the uptake of N₂O₅ and HO₂, mitigated the negative bias of the model. This CO bias reduction was visible for all flight altitudes, the lower troposphere, and North Pacific region (Table 8). Both N₂O₅ and HO₂ uptakes show improvements for CO reproduction of the model. However, RO₂ uptake seems to worsen the model's CO bias, which is consistent with the MIRAI comparison.

For the O₃ level, the model generally overestimates O₃ when calculating for all altitudes or lower troposphere, which is similar to the EANET/EMEP observations. In the North Pacific region with $P > 600$ hPa (40–60° N, 198–210° W), the model bias for O₃ in STD run turns to underestimate (second data row – second column from the right, Table 8), which might be similar with MIRAI data verification for the western North Pacific (143° E–193° W). However, for the underlayers (>700 hPa) show overestimation again (second data row – last column, Table 8). As MIRAI and Atom1 data show, the underestimates for O₃ exist at the marine boundary layer in the western North Pacific and extend to the upper troposphere (<700 hPa) of the east side, might be ascribed to the insufficient downward mixing process of stratosphere O₃ in the model as discussed previously.

The HR effects on O₃ are generally negative effects (all-flight mean concentration is 78.17 ppb by STD and 80.178 ppb by noHR runs), although they are small and barely recognizable in Fig. 5, which mitigates the model bias in the noHR run. This model improvement is consistent for all flight altitudes, the low troposphere, and the North Pacific region (second versus third data rows in Table 8). Both HR(N₂O₅) and HR(RO₂) typically contribute to this improvement (second versus fourth, fifth data rows in Table 8). In contrast, HR(HO₂) seems only to reduce the model bias in the ground layer, which is > 800 hPa for all flights and > 700 hPa for the North Pacific region (second versus sixth rows in Table 8). At the bottommost layers in this region, the model's overestimates for O₃ are reduced by the negative effects of HO₂ uptake. The extension of model bias because of HO₂ uptake above 800 hPa is attributable to its increasing effect on O₃ level: the all-flight mean concentration is 78.17 ppb by STD and 77.96 ppb by noHR_ho2 runs. We recognize that this O₃ increase effect is opposite to the effects for EANET/EMEP and MIRAI comparisons, which is discussed in Sect. 3.2 for HO₂ uptake effects.

The vertical means of model biases for all four species (NO₂, OH, CO, O₃) are presented in Fig. 6. In general, the STD run reduces model biases for all four species, with better performance for broader regions (all flight-pressures and Northern Hemisphere) than for the smaller region (North Pacific). In the North Pacific region, the negative bias for O₃ is observed only for the 500–900 hPa layers (right-bottom panel of Fig. 6). The model bias is apparently extended in this region. However, the inclusion of HR(HO₂) reduces O₃ bias in this region (red line versus green line in the same panel), which might indicate that the O₃ increase effect by HR(HO₂) is verified particularly in 500–900 hPa layers during ATom1.

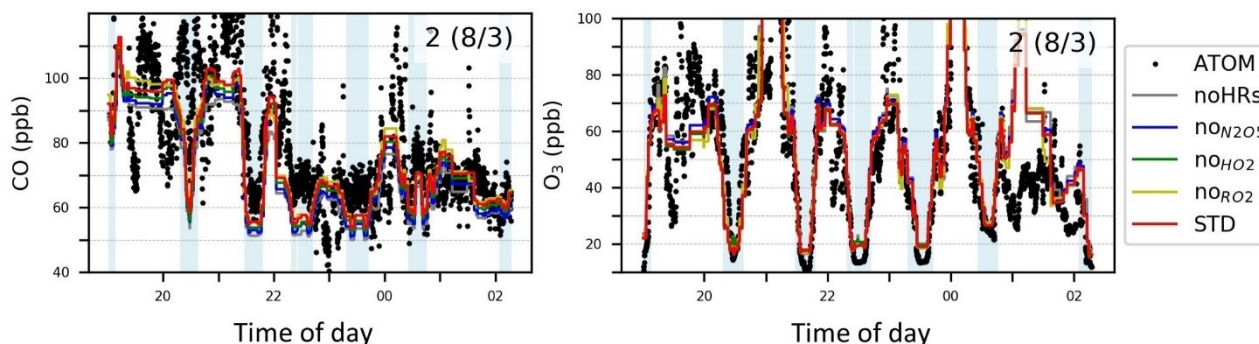


345 We also verify the total uptake of N_2O_5 , HO_2 , and RO_2 onto ice and liquid clouds using data obtained from ATom1 flights within the free troposphere. As Table 8 and Fig. 6 show, the inclusion of HRs onto clouds reduces the model biases for CO and O_3 in all calculations. The vertical-mean biases for NO_2 , OH, CO, and O_3 species are all reduced by the inclusion of HRs onto clouds. However, Fig. 6 shows model worsening at 500–900 hPa, which coincides with the area in which O_3 is underestimated as described above. This result might prove that cloud overestimation for the North Pacific, as revealed at the beginning of this section, affects the model bias in this region.

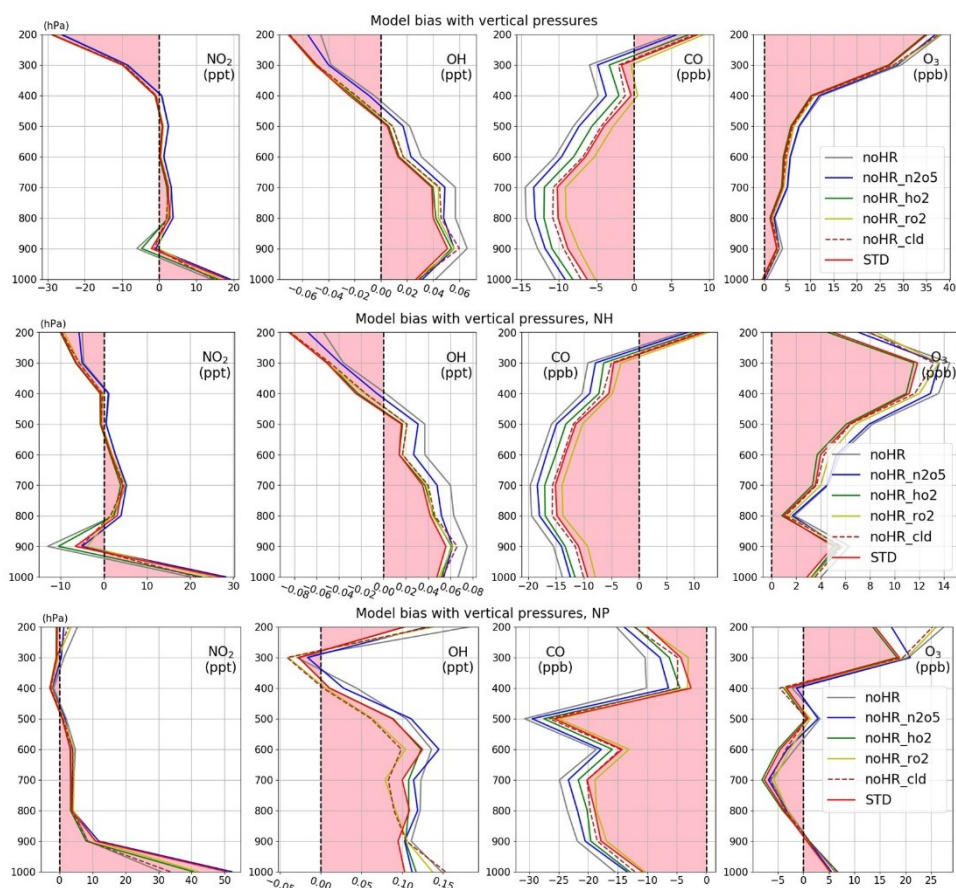
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Table 8: Model correlations and biases with ATom1: three-sigma-rule was applied for CO and O_3 . NP denotes North Pacific region (140–240° E, 40–60° N). The bias of sensitivity run, which is higher than the bias of STD run, is presented as bold.

	CO	O_3	CO (>600 hPa)	O_3 (>600 hPa)	O_3 (>800 hPa)	CO (NP, >600 hPa)	O_3 (NP, >600 hPa)	O_3 (NP, >700 hPa)
R(STD)	0.642	0.742	0.805	0.679	0.659	0.918	0.755	0.844
Bias (STD)	-4.462	15.337	-9.42	2.162	1.257	-16.548	-0.239	2.022
Bias (noHR)	-8.581	17.345	-13.589	3.266	2.365	-21.025	0.902	2.884
Bias (noHR_n2o5)	-7.583	16.697	-12.477	2.925	1.829	-19.44	0.32	2.44
Bias (noHR_ho2)	-6.101	15.127	-11.278	2.095	1.312	-18.247	0.035	2.526
Bias (noHR_ro2)	-3.359	16.412	-8.241	2.55	1.537	-15.741	0.574	2.163
Bias (noHR_cld)	-4.978	16.141	-10.023	2.403	1.596	-17.199	0.725	2.904



355 **Figure 5: Sensitivity simulations for CO and O_3 during Atom1 flight 2 (198–210° E, 20–62° N). Blue shaded areas show data for $P > 600$ hPa.**



360 **Figure 6: Vertical bias against ATOM1. Data for each pressure level P are calculated within the range of $P \pm 50$ hPa, with the applied three-sigma-rule for outlier detection. First, second, and third rows respectively show calculations for all flight domains, Northern Hemisphere, and North Pacific region. The horizontal axis shows model bias with units written in each panel. The vertical axis shows pressure (hPa). Brown dashed lines representing the noHR_cld run.**

Verification with OMI satellite observation for TCO

We also tested STD and noHR simulations using the tropospheric column ozone (TCO) derived from the OMI satellite instrument (Fig. S1 and Fig. 7). In a large area of the Northern Hemisphere, the inclusion of HRs (STD run) generally improved the consistency with the OMI TCO (Fig. 7), particularly enhancing the winter minima (first and second panels in Fig. S1). This improvement in DJF is attributed mostly to the reductive effects of HR(N_2O_5) and HR(RO_2) in the lower (800 hPa) and middle troposphere (500 hPa), respectively (see Fig. 10 for vertical profiles of HR(N_2O_5) on O_3 and Fig. 14 for vertical profiles of HR(RO_2)). In the North Pacific, HRs appeared to extend O_3 underestimates, especially for latitudes higher than 40° N (Fig. 7) during the first half of the year (third panel, Fig. S1). However, such a discrepancy, which was also observed from comparison for R/V MIRAI observations (Fig. 4), might result from other factors such as deposition or vertical mixing rather than by HRs.

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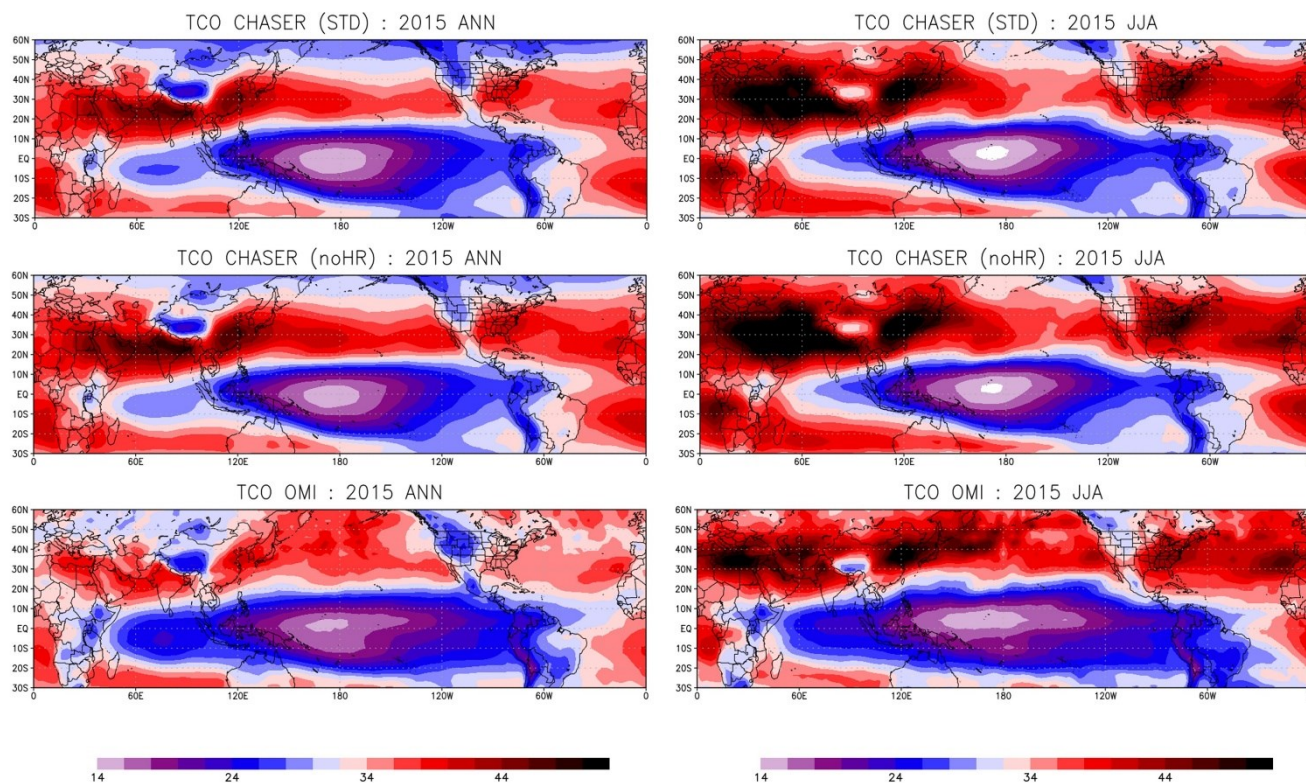


Figure 7: Tropospheric column ozone (TCO) by CHASER (first and second rows) and OMI (third row): ANN is annual; JJA is June, July, and August.

375 3.2 HR effects

This section presents a discussion of the global effects of HRs calculated using CHASER with their spatial distributions in the troposphere using standard (STD) and sensitivity simulations (noHR_n2o5, noHR_ho2, noHRs_ro2, noHR) for the meteorological year of 2011. Aside from the main simulations described in Table 3, additional runs that separately turned off the uptakes onto clouds or aerosols for each HR are also conducted to exploit the contributions of effects to the troposphere.

380 Distribution of clouds and aerosols surface aerosol density (SAD)

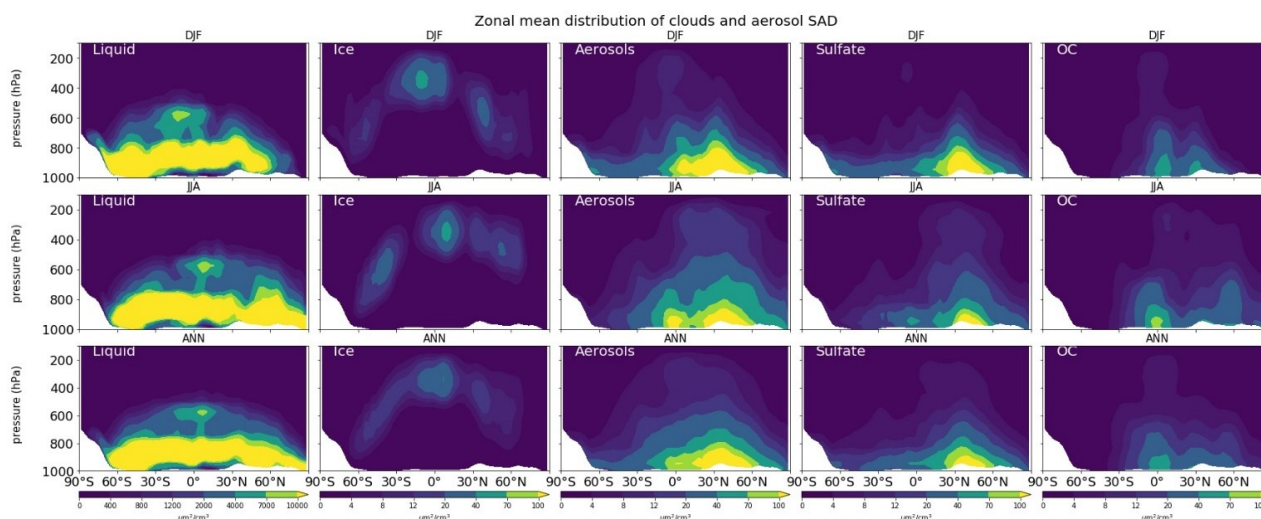
To obtain the parameters for uptake to clouds and aerosols, SAD estimations are used together with cloud fraction and aerosols concentration. Hereinafter, we discuss SAD distributions for total aerosol, ice clouds, and cloud droplets, which are estimated for the model using Eqs. (2), (3), and (4), respectively.

In Fig. 8, total surface area concentrations of liquid clouds and aerosols are both much lower aloft than at the surface (as
385 counted on the dry and wet depositions). The liquid cloud SAD results are two orders of magnitude larger than ice cloud SAD and total aerosol SAD. The ice cloud SAD, distributed at the middle and upper troposphere, is enhanced for N/S middle latitudes in wintertime. Liquid cloud SAD concentrates mainly at the surface with distributions extending to 500 hPa, and



maximized at approx. 800 hPa over the mid-latitude storm tracks and in tropical convective systems, especially at 60° N in JJA. Total aerosol SAD was derived mainly from pollution sources at 40° N during both seasons with higher concentrations
 390 apparent for DJF, with a greater spatial spread observed for JJA. Sulfate aerosols are becoming the dominant source of aerosol surface area in the model above 600 hPa (approx. 20 $\mu\text{m}^2 \text{cm}^{-3}$) in addition with organic carbons and soil dust (both are approx. 10 $\mu\text{m}^2 \text{cm}^{-3}$ in JJA) for the Northern Hemisphere.

In Fig. S2, showing the SAD distribution at the surface, the SAD for liquid clouds is dominant in JJA reaching approx. 50,000 $\mu\text{m}^2 \text{cm}^{-3}$ for middle-latitude and high-latitude ocean regions. Liquid clouds are the most contribution to the SAD at
 395 the surface. Our model performance for aerosols SAD shows agreement with that presented in an earlier report (Thornton et al., 2008). Sulfate aerosols are prevalent in the northern mid-latitudes near industrial bases, maximize at the surface in DJF for the Chinese region (exceeding 1,000 $\mu\text{m}^2 \text{cm}^{-3}$), NE U.S. (approx. 500 $\mu\text{m}^2 \text{cm}^{-3}$), western Europe, and transport to the North Pacific region in JJA (approx. 250 $\mu\text{m}^2 \text{cm}^{-3}$). Soil dust aerosol SAD dominate in the regions of the Sahara and Gobi deserts, reaching annual average values exceeding 100 $\mu\text{m}^2 \text{cm}^{-3}$. Organic carbon (OC) is a dominant source of aerosol SAD over
 400 biomass burning regions in China (up to 1,000 $\mu\text{m}^2 \text{cm}^{-3}$ in DJF), South Africa (up to 800 $\mu\text{m}^2 \text{cm}^{-3}$ in JJA), West Europe, and South America. The black carbon (BC) surface area can reach values exceeding 600 $\mu\text{m}^2 \text{cm}^{-3}$ in DJF for the region of China or other significant industrial areas (India reaches 75 $\mu\text{m}^2 \text{cm}^{-3}$, NE U.S., Europe) or over tropical forests, primarily in Africa. Sea salt aerosols are most important in high-latitude oceans during winter. However, the maximum contributions only reach 2 $\mu\text{m}^2 \text{cm}^{-3}$ in our model, which is much underestimated compared to Thornton's work (75 $\mu\text{m}^2 \text{cm}^{-3}$) (Thornton et al., 2008). In
 405 brief, SAD for aerosols of all types contributes the most during DJF, whereas during JJA, the SAD for liquid clouds and sulfate aerosols are dominant, particularly for the northern high-latitude and mid-latitude oceans. The total aerosols SAD in this region are approx. 75 $\mu\text{m}^2 \text{cm}^{-3}$, which is consistent with estimation by Thornton (2008).



410 **Figure 8: Zonal, seasonal mean (upper and middle), and annual mean (lower) distribution of cloud droplet surface aerosol density (SAD), cloud ice SAD, total aerosol SAD, sulfate aerosol SAD, and organic carbon SAD (from left to right).**



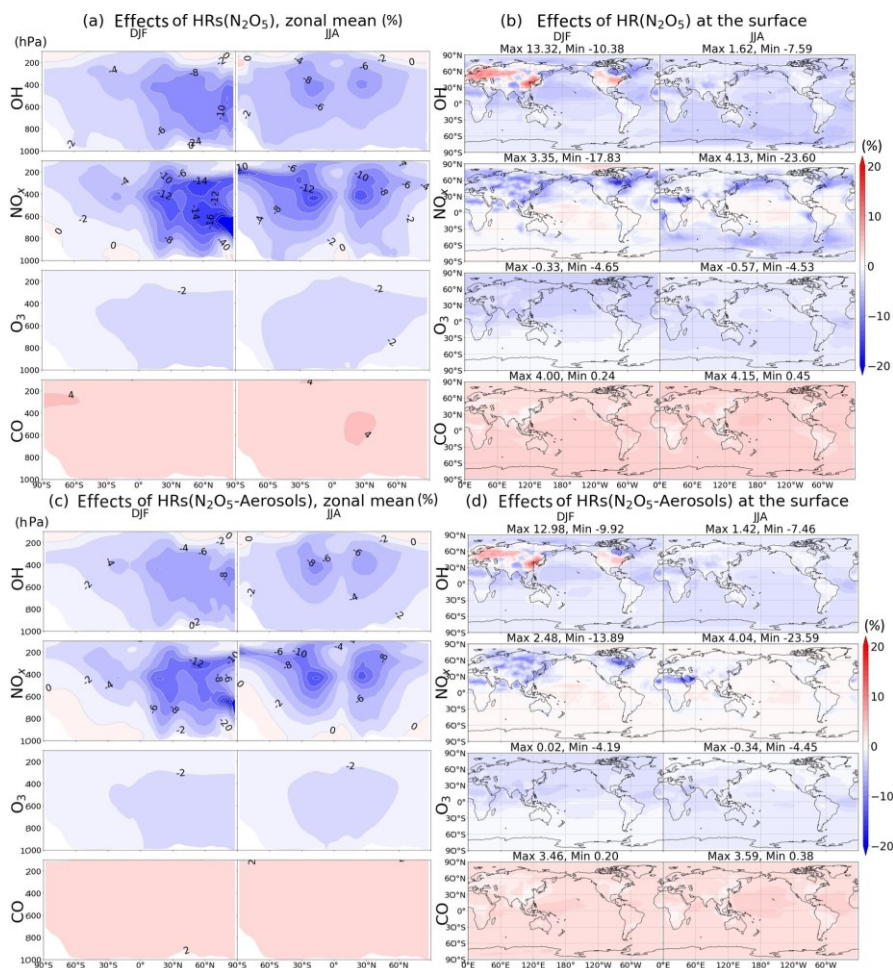
Effects of N₂O₅ heterogeneous reaction (HR(N₂O₅))

The inclusion of HR(N₂O₅) in the model increases global methane lifetime by +4.48% and changes NO_x, O₃ and CO abundances respectively by -5.51%, -2.12%, and +3.42% (Table 9).

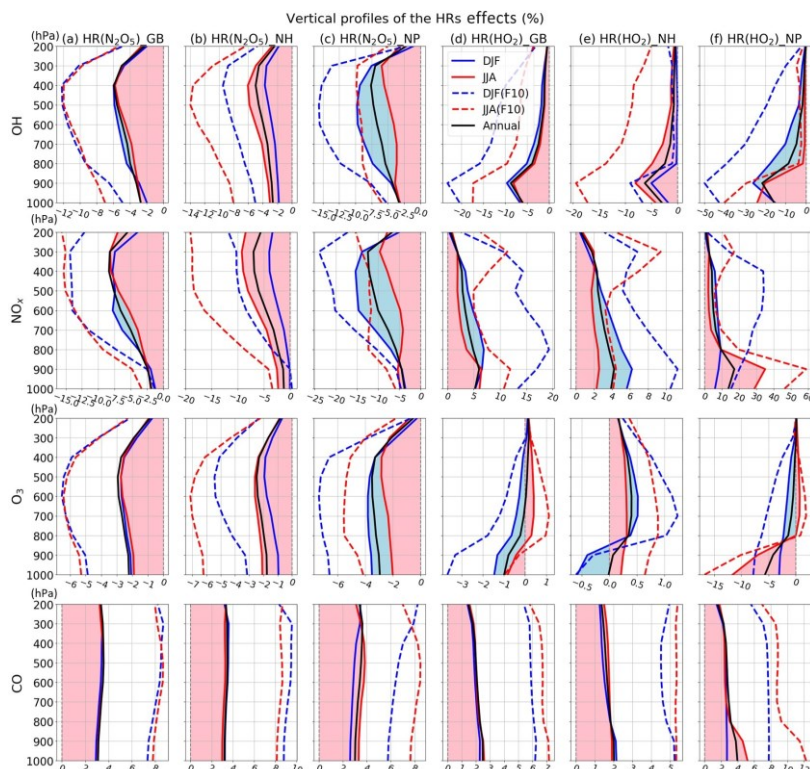
In Fig. 9, the changes in OH, NO_x, O₃, and CO are most significant in the middle troposphere (400–600 hPa). These changes are attributed mostly to uptakes of N₂O₅ onto aerosols, preferably onto clouds (apparent through correlation among effects by all HR(N₂O₅) and that by the HR(N₂O₅) onto total aerosols, Fig. 9). Marked negative effects on NO_x concentration are apparent for DJF in the middle troposphere (600–700 hPa) of the 60° N and the Arctic region (>-20% at 700 hPa). The effects are probably associated with high concentrations of sulfate aerosols, organic carbons or soil dusts in the middle troposphere (see the paragraph above) and are also related to a long chemical lifetime of NO_y in the middle-upper troposphere in winter. When it comes to JJA, these negative effects become significant at higher altitudes around the 30°N/S (>-10% at 400 hPa). At the surface, HR(N₂O₅) causes negative effects on NO_x, O₃, OH concentrations (up to -23%, -4.5% and -7.5% respectively) and positive effects on CO concentration (up to +4.1%), also mainly attributable to the N₂O₅ uptake on aerosols.

In Fig. 10, the latitude–longitude means of HR(N₂O₅) effects are calculated for each pressure range (pressure ranges are defined as in Fig. 6). The global NO_x decrease is up to -8.5% at 300–400 hPa. This decrease causes correspondent reductions in O₃ and OH, which are calculated as about -3% and -7% at 400–600 hPa, respectively, for global mean O₃ and OH. About 3.5–4% global mean CO increment throughout the entire troposphere responds to decreased OH.

The small effects of HR(N₂O₅) on O₃ in the lower troposphere are consistent with findings from an earlier study (Riemer et al., 2003). Reductions in O₃ and NO_x concentrations also well agree with the collective knowledge summarized in work reported by Brown and Stutz (2012). Despite a considerable HR(N₂O₅) effect calculated in the middle troposphere, its effect in the whole troposphere is apparently not as great as reported to date. Another study assessed HR(N₂O₅) effects on annual burdens of NO_x, O₃, and OH, respectively as -11%, -5%, and -7% when using a similar $\gamma_{N_2O_5}$ value (0.1) (Macintyre and Evans, 2010). Although the effects of magnitude estimated in our work (Table 9) are almost half less than this earlier study (probably because of differences in NO_x emissions, estimation of SAD, and chemical mechanism), the effect tendencies are similar. A strong increase of ozone attributed to N₂O₅ uptake under high-NO_x conditions calculated using box models was reported from an earlier study (Riemer et al., 2003), but this is only slightly apparent in our global model. Our results revealed that the HR(N₂O₅) effect might help clean up NO_x pollutant. However, it increases the concentration of other pollutants (such as CO) because of the effects of reducing oxidizing agents in the atmosphere.



440 **Figure 9: Effects of HR(N₂O₅) in zonal-mean and at surface.**
 a–b: Effects by N₂O₅ uptake onto both clouds and aerosols. c–d: Effects by N₂O₅ uptake onto aerosols.
 Positive effects are presented in shades of red. Negative effects are in shades of blue. The contour interval is 2% in the plots for zonal mean.



445 **Figure 10: Effects of N_2O_5 (a-c) and HO_2 uptakes (d-f) for each air pressure ranges. Calculations are for global (a,d), Northern Hemisphere (b,e), and North Pacific region (c,f). Additional dashed lines show effects by FCTHR_10 run (Sect. 3.3).**

Effects of HO_2 heterogeneous reaction ($HR(HO_2)$)

Regarding the effects of $HR(HO_2)$, the tropospheric methane lifetime increases by approx. 1.5%. Abundances in NO_x , O_3 , and CO change, respectively, by +3.3%, +0.05%, and +1.9% (Table 9). In the entire troposphere, the influences of $HR(HO_2)$ are not as large as that of $HR(N_2O_5)$.

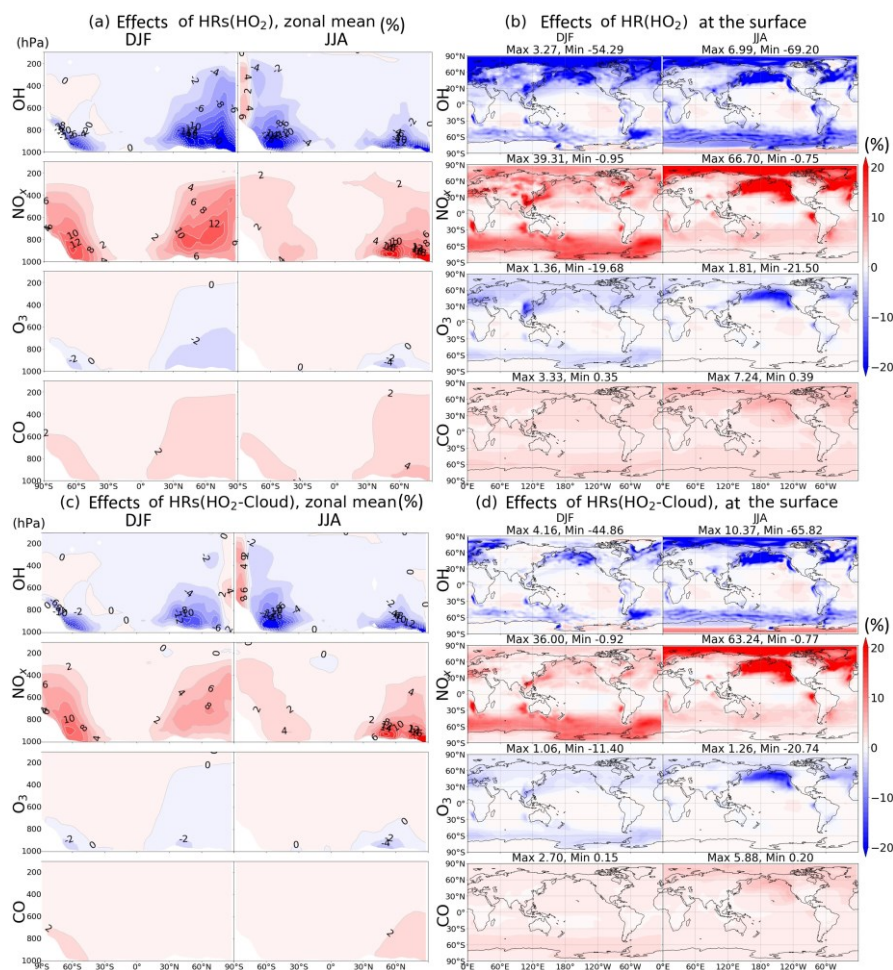
450 As Fig. 11 shows, the zonal-mean effects of $HR(HO_2)$ on NO_x , OH, and O_3 are more widespread in DJF, but are more concentrated at the surface in JJA because of the high level of HO_2 . The most substantial effects by $HR(HO_2)$ are calculated in JJA at the surface of North Pacific (140–240° E, 40–60° N) by as much as +68.7% (NO_x), +7.29% (CO), -70% (OH), and -21% (O_3), which are more significant than those of $HR(N_2O_5)$ at the surface. These effects are primarily attributable to $HR(HO_2)$ in clouds rather than to aerosols (which is opposite to N_2O_5 uptake). These OH and O_3 reduction effects go along
 455 with past studies in which approx. 50% OH and approx. 10% O_3 reductions are calculated for the low troposphere of northern mid-latitude region ascribed to aqueous-phase HO_x sink in clouds (Lelieveld and Crutzen, 1990, 1991). The efficient scavenge of HO_2 radical by cloud droplets might associate with acid–base dissociation HO_2/O_2^- and electron transfer of O_2^- to HO_2 to produce H_2O_2 (Jacob, 2000). Furthermore, cloud droplets SAD in our model are two orders of magnitude higher than total aerosol SAD (Fig. 8), which also contributes to the preference of the aqueous-phase HO_2 sink. Our large calculated effects for



460 the North Pacific region are new findings from other models, which have considered only aqueous aerosols (Stadtler et al.,
2018; Thornton et al., 2008), because cloud particles are dominant at remote marine areas in addition to sulfate and aqueous
sea salt particles (discussed at the beginning of Sect. 3.2). The HO₂ uptake onto aerosols is minor; it is observed only in DJF
at the Arctic region and polluted areas (China and US), with apparent changes of up to +17% NO_x, -40% OH, and -14% O₃ at
the local surface (panel b, Fig. 11). The aerosol negative-effect of HR(HO₂) on surface O₃ concentration is significant at the
465 Chinese area, which might be in line with other studies of the Chinese O₃ trend (Kanaya et al., 2009; Li et al., 2019; Liu and
Wang, 2020; Taketani et al., 2012), which suggests that the observed recent O₃ increases can be attributed to reduced HO₂
uptake under aerosol (PM) decreases brought about by the new Chinese Air Pollution policy.

In Fig. 10, vertical profiles show that the latitude–longitude (lat-long) averaged effect of HR(HO₂) on OH is -9% in the
lower troposphere. As a result, the lat-long mean CO level increases +2.5% at the surface. Additionally, the daytime NO_x
470 oxidation by OH is suppressed. Also, NO_x might be preserved in clouds (Dentener, 1993), which increases the lat-long
averaged NO_x level by +6% at 900 hPa. The lat-long mean O₃ is reduced by -1% at the surface, but it is increased at higher
altitudes (about +0.2% at 300 hPa). The reduction of O₃ associates with HO₂ depletion in clouds and aqueous aerosols as
described above, coupled with the NO_x preservation in clouds, which enhance the NO/NO_x ratio. The preserved NO_x in clouds
might remain available for O₃ production after the cloud evaporates (Dentener, 1993), along with the low SAD for both liquid
475 clouds and aerosols at higher altitudes (Fig. 8), thereby increasing O₃ in places other than aqueous phase. The O₃ increment
might be trivial in DJF, but enhanced in JJA. As a result, the Northern Hemisphere-mean O₃ in JJA exhibits only positive
effects. In contrast, for the North Pacific region in JJA, because of its large cloud fraction, an O₃ reduction effect is apparent
in this region. The effects in JJA for this region show changes of -25% OH, +35% NO_x, -12% O₃, and +5% CO at 900–100
hPa as the most remarkable HR(HO₂) effects as described above. In general, the regional mean effects of HR(HO₂) in the
480 North Pacific region are enhanced in JJA, but the mean global effects of HR(HO₂) are slightly favored in DJF because of the
additional effects of aerosols during this season.

Macintyre and Evans (2011) also found a similar contrast between the behaviors of HR(N₂O₅) and HR(HO₂): the uptake
of N₂O₅ produces both regional and global effects on O₃, whereas the uptake of HO₂ affects O₃ at regional scales more strongly
than on a global scale (Macintyre and Evans, 2011). Such features are generally consistent with our results.



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Figure 11: Effects of HR(HO₂) in zonal mean and at the surface layer. a-b: Effects of HR(HO₂) onto both clouds and aerosols. c-d: Effects of HR(HO₂) onto clouds. The contour interval is 2% in the plots for zonal mean.

Effects of RO₂ heterogeneous reactions (HRs(RO₂))

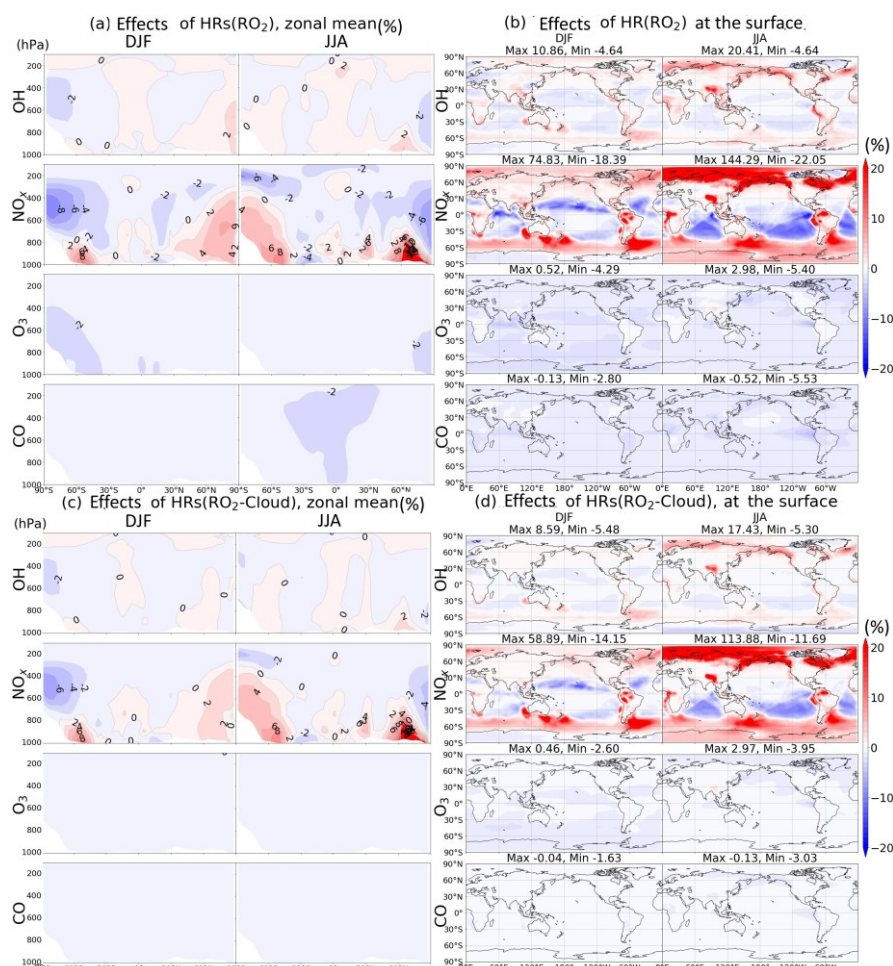
Effects of HR(RO₂) increase the global mean methane lifetime by +0.15% and change tropospheric abundances of NO_x (+0.52%), O₃ (-0.93%), and CO (-1.78%) (Table 9). In Fig. 12, significant latitudinal contrasts exist in the NO_x changes: large NO_x increases at high latitudes with decreases at lower latitudes. These NO_x changes probably reflect the reduced formation of PANs which decreases NO_x transport from source regions to remote areas and from the surface to the upper troposphere (Villalta et al., 1996). The model calculated especially large NO_x increases (>50%) for high latitudes around the Arctic sea in JJA, indicating reduction in the formation of PANs (NO₂ + RO₂ → PANs), which is linked tightly to the enhanced biogenic emissions of VOCs such as isoprene and terpenes in summer. The corresponding changes in OH concentration (because of the reduced NO_x levels) at the surface are in the range of -4.6% to +20.4%. The effects of HR(RO₂) are primarily attributed to the heterogeneous reaction on clouds rather than on aerosols, although this cloud-effect is far smaller than the cloud-effect to the HO₂ uptake. Although it is proper to expect the high solubility of RO₂ (e.g. CH₃O₂) from its peroxy substituent (Betterton,

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1992; Shepson et al., 1996), it is much less soluble than HO₂ because of its lower polarity, therefore the lower Henry law constant (Jacob, 2000). Consequently, the possible accumulation of CH₃O₂ in the cloud is rather attributable to suppression of its gas-phase sink with HO₂ (Jacob, 1996).

Fig. 14 a–c show latitude–longitude means of HR(RO₂) effects calculated for the respective pressure ranges: the latitude–longitude are constrained for the entire globe, the Northern Hemisphere, and North Pacific region. For the entire globe, the contrast effects of HR(RO₂) between the lower and higher troposphere on NO_x and OH are shown clearly (+3.5% NO_x and +0.55% OH at 900 hPa, but -2.5% NO_x and -0.75% OH at 400–500 hPa annually). As a result, the annual mean O₃ and CO levels decreased throughout the troposphere, reaching their lowest at -1.6% O₃ and -1.5% CO at the surface. In JJA, the global effects by HR(RO₂) are more concentrated in the lower troposphere, especially in the North Pacific (+3% OH, +10% NO_x, -3% O₃, -2% CO at 900–1000 hPa). In DJF, the HR(RO₂) effects are observed mostly in the middle and higher troposphere, especially when considering the Northern Hemisphere (-1.25% OH, -4% NO_x, -2% O₃ at 500–800 hPa).



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Figure 12: Effects of HR(RO₂) in the zonal mean and at the surface layer. a-b show effects of the uptake onto both clouds and aerosols. c-d show separate effects of the uptake onto clouds. The contour interval is 2% in the plots for zonal mean.



Total effects of all HRs

As discussed above, different heterogeneous reactions affect tropospheric chemistry differently. However, their effects can either augment or negate others in performing for the atmospheric chemistry. HR(N_2O_5) is the greatest contributor to reduction of tropospheric OH, O_3 , and NO_x abundances, which is more active in the middle troposphere. HR(HO_2) reduces OH, but increases the abundances of O_3 and NO_x globally, whereas it exposes a negative effect on O_3 level at the surface of the North Pacific region. HR(RO_2), similarly, has a smaller distribution to the total heterogeneous effects but its global-mean negative effects for O_3 are not negligible. The uptake of N_2O_5 mainly takes place to aerosols, whereas the uptakes of HO_2 and RO_2 occur more to liquid and ice clouds. Overall, the total effects of all HRs for the whole troposphere are +5.9% for global mean CH_4 lifetime, -2.2% for NO_x (tropospheric abundance), -2.96% for O_3 , and +3.3% for CO (Table 9). At the surface, the annual effects ranged from -52.7 to +2.3% for OH, -13.1 to +51.1% for NO_x , -13.1 to -1.5 for O_3 , and -0.3 to +5.8% for CO (Fig. 13).

As Fig. 14 d–f show for the vertical profiles of HR effects, the change of OH largely concentrated in the lower troposphere (-10% OH at 900 hPa, calculated for the entire globe) is associated with the HO_2 uptake. By contrast, the NO_x change is more intensive at higher altitudes (-9% NO_x at 400 hPa, calculated for the entire globe), associated with N_2O_5 and RO_2 uptakes. The global-mean HR effects on O_3 and CO are vertically even, with the highest effects reaching -4.5% O_3 and +3.8% CO at the surface. Globally, HR effects on atmospheric oxidants (OH and O_3) are enhanced in DJF because of the higher pollution in the Northern Hemisphere. However, the largest HR effects are apparent for JJA at the surface of the North Pacific (-25% OH, +38% NO_x , -14% O_3 , +6% CO as calculated for the 950–1000 hPa layer). These effects are mostly ascribed to HO_2 uptake onto clouds. This finding is also apparent from Fig. S15-c: these effects reach -66% for OH, +120% for NO_x , -23% for O_3 , and +4.4% for CO at the surface. They were able to extend up to 400 hPa in the atmosphere. These substantial effects are readily apparent for the large reduction of O_3 level during MIRAI observation (red line versus green line in T5 bottom panel, Fig. 4). However, the major contribution of HR(HO_2) to these effects is only partially verified by the ATom1 measurements in this study (red versus green lines in the bottom-right panel, Fig. 6). Because of model overestimates of cloud fraction in JJA for the North Pacific region, these effects of HR(HO_2) should have existed at some smaller magnitude. For HR effects in the middle to upper troposphere, the N_2O_5 uptake on aerosols are mostly ascribed, which is intensive in both DJF and JJA.

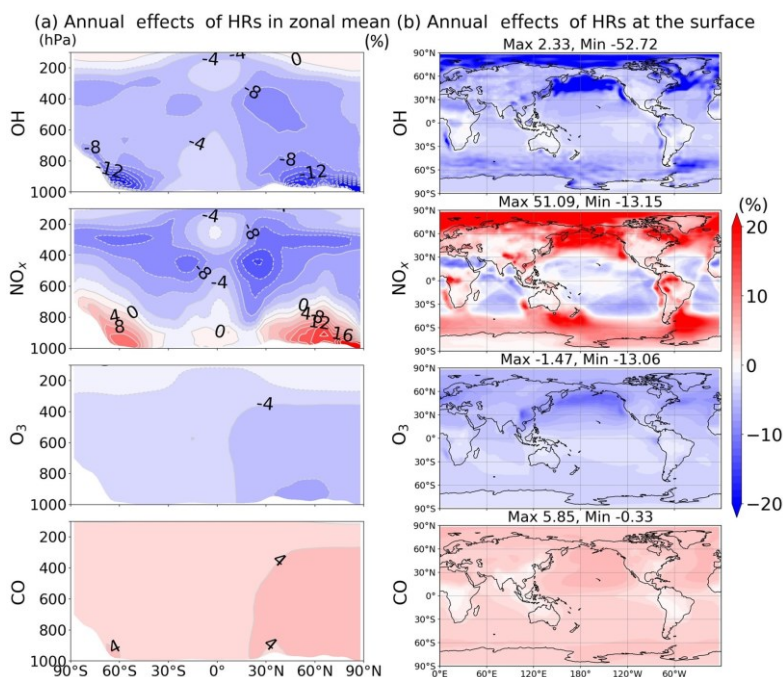


Figure 13: Annual zonal-mean and surface total-HR effects.

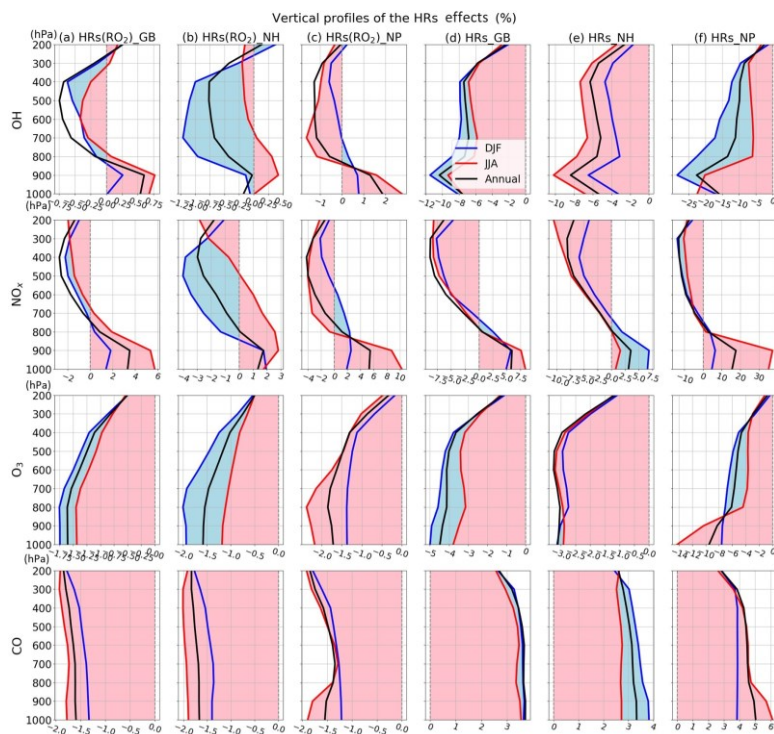


Figure 14: Effects of RO₂ uptakes (a-c) and all HRs (d-f) averaged for each air pressure range. Calculations are for global (a,d), Northern hemisphere (b,e), and North Pacific region (c,f).



Table 9: Tropospheric abundances changes by HR(N₂O₅), HR(HO₂), HR(RO₂), and all HRs onto clouds and aerosols

	CH ₄ (year)	lifetime	Tropospheric abundances		
			NO _x (TgN)	O ₃ (TgO ₃)	CO (TgCO)
STD	9.44		0.115	402.29	337.12
noHR.n2o5	9.04		0.122	410.99	325.98
noHR.n2o5-Cld	9.41		0.116	402.81	336.43
noHR.n2o5-Ae	9.09		0.121	409.81	327.46
noHR.ho2	9.30		0.111	402.09	330.67
noHR.ho2-Cld	9.35		0.113	402.25	332.97
noHR.ho2-Ae	9.40		0.114	402.17	335.29
noHRs.ro2	9.43		0.114	406.06	343.23
noHR.ro2-Cld	9.42		0.115	403.96	339.06
noHR.ro2-Ae	9.45		0.115	404.03	340.76
noHR	8.91		0.118	414.55	326.43
noHR.Cld	9.32		0.113	404.55	335.03
noHR.Ae	9.06		0.119	411.38	329.20
STD – noHR.n2o5	+4.48%		-5.51%	-2.12%	+3.42%
STD – noHR.n2o5-Cld	+0.30%		-0.43%	-0.13%	+0.21%
STD – noHR.n2o5-Ae	+3.87%		-4.56%	-1.83%	+2.95%
STD – noHR.ho2	+1.51%		+3.26%	+0.05%	+1.95%
STD – noHR.ho2-Ae	+0.41%		+1.11%	+0.03%	+0.55%
STD – noHR.ho2-Cld	+1.00%		+1.87%	+0.01%	+1.25%
STD – noHRs.ro2	+0.15%		+0.52%	-0.93%	-1.78%
STD – noHRs.ro2-Cld	+0.23%		+0.39%	-0.41%	-0.57%
STD – noHRs.ro2-Ae	-0.12%		+0.09%	-0.43%	-1.07%
STD – noHR	+5.91%		-2.19%	-2.96%	+3.28%
STD – noHR.Cld	+1.34%		+1.71%	-0.56%	+0.63%
STD – noHR.Ae	+4.15%		-3.44%	-2.21%	+2.41%



3.3 Sensitivities of tropospheric chemistry respond to heterogeneous reactions

From the discussion presented above, marked effects of HRs on global tropospheric chemistry are apparent. Here we examine how the tropospheric chemistry responds to the magnitude of HRs. To do this, we introduced a factor F for application to the first-order loss rate shown in Eq. (1) for artificially manipulating the HR magnitude.

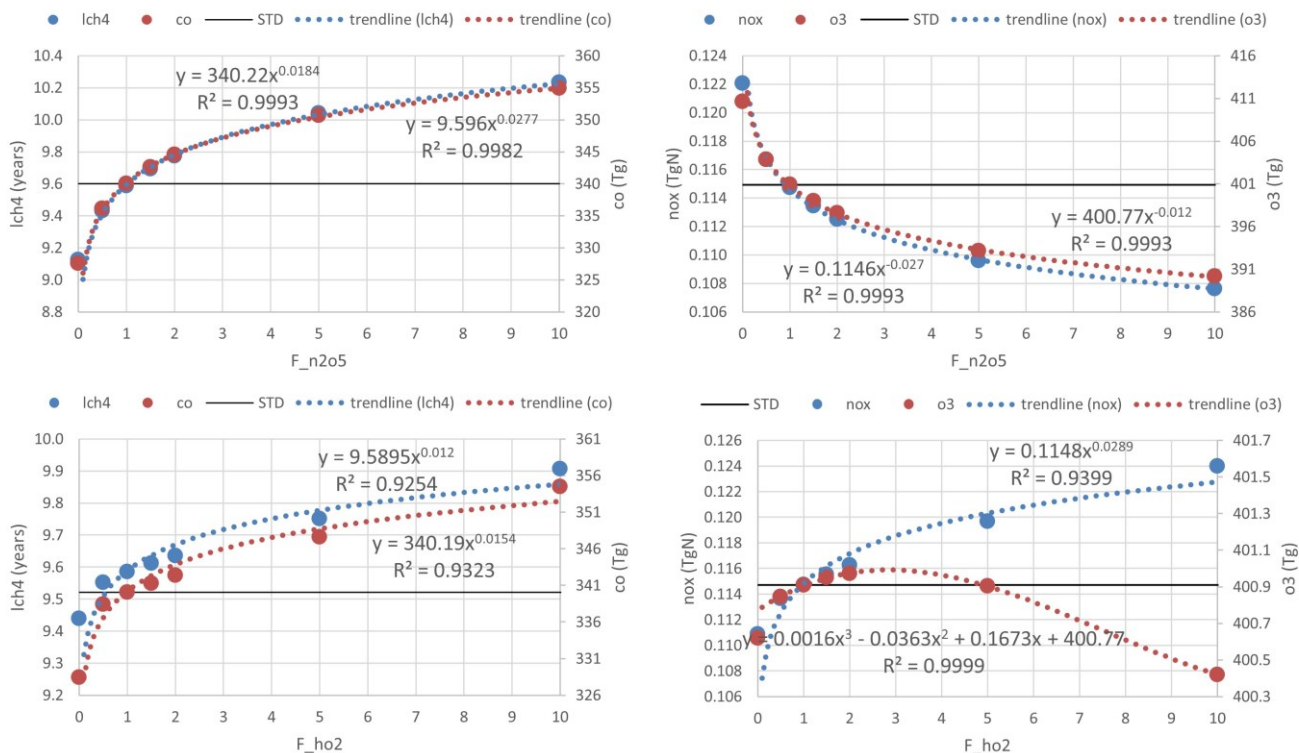
$$550 \quad \beta_i = \sum_j \left(\frac{4}{v_{ij} \gamma_{ij}} + \frac{R_j}{D_{ij}} \right)^{-1} \cdot A_j \times F \quad (8)$$

For this sensitivity test, we only specifically examine HR(HO₂) and HR(N₂O₅) and consider factors of 0–10 to the STD (Table S 1). This test might help to show the effective-oxidation sensitivity of the troposphere because future pollution and climate change might enhance the activities of these HRs.

For both effects, we performed nonlinear function fitting with their uptake loss rates, which yielded correlation coefficients
555 higher than 0.93 (Fig. 15). Although both HRs showed negative tendencies for OH and O₃ levels, the effect of HR(HO₂) on the tropospheric abundance of O₃ showed only a small increment with an increasing loss rate (maxima at around $F = 3$), and turned to reduction at higher rates ($F > 5$). As discussed along with HR(HO₂) effects, the O₃ level is expected to be reduced primarily only in JJA at the surface of the North Pacific region. At the same time, O₃ will be increased gradually elsewhere because of the persistent NO_x increment. This behavior produces a positive global mean effect. Fig. 10 (dashed lines) shows
560 that manipulation of the HR(HO₂) loss rate ten factors higher will effectively increase the negative HR(HO₂) effects on O₃ in DJF (blue dashed versus solid blue lines, third row – fourth column panel), which results in a higher tendency of negative values for global-mean effects. This sensitivity in DJF might be attributable to the HO₂ uptake to aerosols rather than to clouds during this polluted period, which is apparent through comparison of Fig. 11 and Fig. S16 for notable events. In DJF, as amplifying a factor of 10 to HO₂ uptake loss rate, the effects for the polluted Chinese area (because of HO₂ uptake onto
565 aerosols) significantly magnify from -18% (third row – first column in panel b, Fig. 11) to -47% (third row – first column in panel b, Fig. S16). In contrast, effects at the surface O₃ level in JJA for the North Pacific region (because of HO₂ uptake onto clouds) only enhance from -21% (third row-second column in panel b, Fig. 11) to -29% (third row – second column in panel b, Fig. S16).

As amplifying a factor of 10 to HR(N₂O₅), the sensitivities of global effects show no seasonal variation. The HR(N₂O₅)
570 effects are more sensitive in DJF for the North Pacific region, which link to the higher concentration of aerosol in this season. Otherwise, the HR(N₂O₅) effects for the generic Northern Hemisphere tend to be more sensitive in JJA as a result of pollutant transportation to the higher troposphere.

Consequently, we suggest that the sensitivity of tropospheric chemistry to HR(N₂O₅) and HR(HO₂) might be attributable to loss activities to aerosols rather than to clouds. The sharp-curved effect on O₃ because of amplification of HR(HO₂) makes
575 sense in plans for ozone pollution control when increased pollution or climate change factors cause the rate of HRs in the future to increase by 3–5 times or more.



580 **Figure 15: Trendlines for the sensitivity of HR(N₂O₅) (upper panel) and HR(HO₂) effects (lower panel) with uptake rates. The left panels show the CH₄ lifetime (blue) and tropospheric abundance of CO (red). The right panels show tropospheric abundances of NO_x (blue) and O₃ (red).**

4 Conclusion

The “CHASER” chemistry–climate model was used to investigate global effects of N₂O₅, HO₂, and RO₂ uptake. Verification of the model with observations from inland and ocean domains showed adequate agreement for PM_{2.5}, SO₄²⁻, NO₃⁻ particles, gaseous HNO₃, NO_x, OH, CO, and O₃ concentrations. *R*, bias, and NRMSE values for SO₄²⁻, NO₃⁻, and HNO₃ at EANET and
 585 EMEP stations are comparable with other models. Inclusion of HR reduced model bias for OH, NO₂, CO, and O₃, especially in the low troposphere. However, verification with satellite and reanalysis data showed deterioration by HRs for TCO, and an overestimate for cloud fraction in the North Pacific region.

The total effects of HRs are important for the tropospheric chemistry that might change +5.9% CH₄ lifetime, -2.19% NO_x, -2.96% O₃, and +3.3% CO abundances. Global effects are -9% NO_x at 400 hPa, -10% OH at 900 hPa, -4.5% O₃ and +3.8%
 590 CO at the surface. Global HR effects tend to be enhanced in DJF because of greater amounts of pollution in the Northern Hemisphere.

Total HR effects are contributed mainly by HR(N₂O₅) onto aerosols in the middle troposphere. At the surface, HR(HO₂) is more active and leaves a remarkable disturbance in JJA at the North Pacific region with changes of -70% for OH, -24% for O₃, +68% for NO_x, and +8% for CO. These effects were attributed to the uptake of HO₂ on cloud particles, which were partially



595 verified with ATOM1 observations. However, the effect magnitude requires further investigation because of model overestimates for cloud fractions in this region.

The sensitivity of tropospheric chemistry with the HR magnitude was determined as nonlinear functions. The increasing effect for the global O₃ abundance by HR(HO₂) will sharply change to a decreasing effect when the uptake rate is amplified by more than three times. This turning is ascribed to the uptake onto aerosols in DJF. In general, uptake to aerosols is more
600 responsive to the heterogeneous loss rate than uptake to clouds.

Overall, the N₂O₅ and HO₂ uptakes will sweep away atmospheric oxidants, thereby enhancing concentrations of pollutants. Our results reveal that although HRs are reported to be associated with polluted regions, the global effects of HRs reach further remote regions such as the marine boundary layer at the middle latitude and the upper troposphere. For ground-based studies of polluted regions such as China, it should be considered that HR(HO₂) and HR(RO₂) were able to contribute respectively to
605 the NO_x increment in DJF and JJA. Moreover, the HR(HO₂) effect might hinder efforts at reducing environmental pollution in urban areas because it increases NO_x but decreases O₃ at the surface. Therefore, if this reaction is minimized because of a decrease in particulate matter, then the surface ozone level might increase.

Code availability

The source code for CHASER V4.0 and input data to reproduce results in this work can be obtained from the repository at
610 <http://doi.org/10.5281/zenodo.4153452> (Ha et al., 2020).

Author contribution

Ha T.M.P. performed all simulations (except simulations for the cloud-fraction validation), interpreted the results and wrote the manuscript. Sudo K. developed the model code, conceived of the presented idea, supervised the findings of this work and the manuscript preparation. Matsuda R. carried out the simulations and plots for the validation of cloud fraction. Kanaya Y.
615 and Taketani F. provided the R / V MIRAI ship data as well as contributed to the discussion of the work's findings.

Competing interests

The authors declare that they have no conflict of interest.

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using the supercomputer (NEC SX-Ace and SX-Aurora TSUBASA) at NIES, Japan. The surface observational data for the model validation were taken from the monitoring networks EANET (<https://www.eanet.asia/>) and EMEP (<https://www.emep.int/>).

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