

論文題目 Roles of heterogeneous reactions of reactive nitrogen species and peroxy radicals in the tropospheric chemistry: a global modeling study

(対流圏化学における窒素酸化物・過酸化ラジカルの不均一反応の  
役割：全球モデルによる研究)

氏名 HA Thi Minh Phuc

This dissertation conveys an understanding of heterogeneous mechanisms of reactive nitrogen species ( $\text{N}_2\text{O}_5$ ,  $\text{NO}_2$ , HONO) and peroxy radicals ( $\text{HO}_2$ ,  $\text{RO}_2$ ) in the troposphere, employing the chemistry-climate CHASER (MIROC) model. The simulated results are verified with Asian and European stationary observations (EANET and EMEP), ship-based data along Indonesia-Japan-Alaska (*R/V Mirai*), atmospheric tomography aircraft measurements (ATom), satellite observations by OMI, ISCCP, and CALIPSO-GOCCP, and reanalysis data (JRA55).

The first part examines three distinct heterogeneous reactions (HRs) of  $\text{N}_2\text{O}_5$ ,  $\text{HO}_2$ , and  $\text{RO}_2$  on aerosols and cloud particles surfaces. The heterogeneous chemistry of these species improves model performance for  $\text{NO}_2$ , OH, CO, and  $\text{O}_3$  to observations, especially in the lower troposphere. The calculated effects of HRs cause pronounced changes in global abundances of  $\text{O}_3$  (-2.96%),  $\text{NO}_x$  (NO,  $\text{NO}_2$ ) (-2.19%), CO (+3.28%), and global mean  $\text{CH}_4$  lifetime (+5.91%). These global effects are mainly attributed to the  $\text{N}_2\text{O}_5$  conversion on aerosol particles in the middle troposphere.  $\text{HO}_2$  uptake is more important at the surface layer, causing a substantial effect in the North Pacific (NP) region (-24%  $\text{O}_3$ , -70% OH, +68%  $\text{NO}_x$ , and +8% CO); its uptake onto clouds contributes to a large extent. The  $\text{RO}_2$  reactions play a minor role in the global tropospheric chemistry, but they affect peroxyacetyl nitrate and  $\text{NO}_x$  substantially with +144%  $\text{NO}_x$  at the surface of NP and Atlantic regions in summer. Aerosol uptakes are more conducive than uptakes on ice crystals and cloud droplets regarding their effects on tropospheric chemistry (+1.34%  $\text{CH}_4$  lifetime, +1.71%  $\text{NO}_x$ , -0.56%  $\text{O}_3$ , +0.63% CO abundances). When amplifying  $\text{N}_2\text{O}_5$  and  $\text{HO}_2$  uptakes in the same modelling structure of this study, tropospheric abundances of  $\text{O}_3$ ,  $\text{NO}_x$ , and OH response nonlinearly with  $R > 0.93$ . Although all HRs show reduction tendencies for OH and  $\text{O}_3$  levels with an increased loss rate, HR  $\text{HO}_2$  shows a slight increase in the tropospheric abundance of  $\text{O}_3$  at loss rates  $< 3$  times.

The HONO chemistry is newly introduced into the CHASER model for the

second part of this work. HONO is an important intermediate in the atmosphere because it affects the cycles of  $\text{NO}_x$  and  $\text{HO}_x$  (OH,  $\text{HO}_2$ ). In this study, three principle mechanisms for HONO are established, namely (1) gas-phase reactions (GRs)  $\text{NO} + \text{OH} + \text{M} \rightarrow \text{HONO} + \text{M}$ ,  $\text{HONO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$ ,  $\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO}$ ; (2) heterogeneous reactions on aerosol and cloud surfaces (HRs)  $\text{NO}_2 \rightarrow 0.5\text{HONO} + 0.5\text{HNO}_3$ ,  $\text{NO}_2 \rightarrow \text{HONO}$ ,  $\text{HONO} \rightarrow \text{NO}$ ; (3) HONO direct emission (EM). The new model configuration is also evaluated with the observations mentioned above and HONO concentration measured from the EMeRGe-Asia-2018 project (Effect of Megacities on the Transport and Transformation of Pollutants on the Regional to Global Scales). The inclusion of HONO chemistry further reduces the model bias against observations for  $\text{PM}_{2.5}$ ,  $\text{NO}_3^-/\text{HNO}_3$ ,  $\text{NO}_2$ , OH,  $\text{O}_3$ , and CO. The model calculates 1.4 TgN for the global abundance of tropospheric HONO. HRs and EM, among the three mechanisms, respectively contribute 63% and 26% to the net HONO production. The reactions on aerosol surfaces generate more HONO (51%) than cloud surfaces' reactions (12%). Evaluation with airborne-measured data in the Asian off-coast region indicates the existence of unknown daytime HONO sources. Strengthening of aerosol and cloud uptakes of  $\text{NO}_2$  near-surface and in the middle troposphere and direct HONO emission are prospective yet-unknown HONO sources. The calculated HONO abundance and its effects on  $\text{NO}_x$ - $\text{O}_3$  chemistry are sensitive to the HONO yield (vs  $\text{HNO}_3$ ) from the heterogeneous conversion of  $\text{NO}_2$ . The HONO chemistry reduces the global tropospheric abundance of  $\text{NO}_x$  by 20.4%, thereby attenuating the tropospheric oxidizing capacity, increasing  $\text{CH}_4$  lifetime by 13% and CO abundance by 8%. The effect of  $\text{NO}_2$ 's cloud uptake is especially salient for the NP region during summer, with surface OH and  $\text{O}_3$  levels are reduced by 40–67% and 30–45%, respectively, given that 50–95% of surface  $\text{NO}_x$  level is reduced. In contrast, the aerosol uptake of  $\text{NO}_2$  enhances OH and  $\text{O}_3$  winter mean levels by 600–1,700% and 10–33%, respectively, in China (Beijing). HONO chemistry's reduction effect on tropospheric oxidant substances globally contradicts previous regional modeling studies, but the validation of these effects is supported via model verification for free marine troposphere (ATom).

This dissertation demonstrates that the HRs of reactive nitrogen species ( $\text{N}_2\text{O}_5$ ,  $\text{NO}_2$ , HONO) and peroxy radicals ( $\text{HO}_2$ ,  $\text{RO}_2$ ) affect polluted areas and remote areas. Such processes in distant regions, i.e.  $\text{N}_2\text{O}_5$  conversion on aerosol particles in the middle troposphere and cloud-uptakes of  $\text{HO}_2$ ,  $\text{RO}_2$ , and  $\text{NO}_2$  at the Northern mid-latitudes marine boundary layer, contribute dominantly to the global HRs effects.

Furthermore, HRs of HO<sub>2</sub>, RO<sub>2</sub>, NO<sub>2</sub>, and HONO are more active on cloud surfaces in terms of their effects on the tropospheric oxidizing power, affirming the need for cloud-surface reactions in a global atmospheric model. Moreover, understanding the mechanism of HRs, especially HR HO<sub>2</sub> which causes an increase in NO<sub>x</sub> and decrease in O<sub>3</sub>, shall contribute to the policy interventions seeking both NO<sub>x</sub> and O<sub>3</sub> reductions in polluted areas. For HONO chemistry, given that its global-scale studies are sparse at the moment, its enormous influence on the tropospheric chemistry simulated in CHASER model endures high uncertainty. Thus, further investigations of HONO formation mechanisms are crucial for calculating tropospheric oxidizing power, and it can affect the pollution policy strategies to mitigate this precursor emission.