

Review of Comprehensive Measurements of Speciated NO_y and its Chemistry: Need for Quantifying the Role of Heterogeneous Processes of HNO_3 and HONO

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ABSTRACT

To improve the credibility of chemistry schemes employed in chemical transport models (CTMs) aiming at predicting ozone mixing ratios in urban, rural, and regional scales, validation of models not only by observational data of O_3 and NO_x but also by individual species of reactive nitrogen NO_y is necessary because the formation and dissipation of O_3 in the atmosphere occur via reactions accompanying the transformation of NO_x and NO_y . The disagreement of the simulated results of CTM with observational data of HNO_3 and HONO have often been reported, and this paper reviews previous studies on the heterogeneous “renoxification” reaction of gaseous HNO_3 to form NO , NO_2 , and/or HONO; the formation of HONO from the heterogeneous dark reaction of NO_2 and H_2O , and the photolysis of adsorbed HNO_3 and NO_3^- on surfaces. For the further validation of CTMs with individual species of NO_y , previous field studies of comprehensive observation of NO_y speciation in ground-based and aircraft campaigns have also been reviewed. Studies combining observations of speciated NO_y and model simulations need to be performed to improve chemistry models used in CTMs.

Keywords: Reactive nitrogen, Nitric acid, Nitrous acid, Ozone, Chemical transport model

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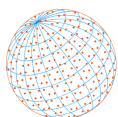
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1 INTRODUCTION

In the field of atmospheric environmental sciences, chemical transport models (CTMs) are widely employed to tackle social issues as well as scientific challenges. For example, CTMs have been employed to elucidate tropospheric chemistry mechanisms (e.g., Lelieveld *et al.*, 2016; Hu *et al.*, 2018) to establish ozone and $\text{PM}_{2.5}$ control strategies (e.g., U.S. EPA, 2018) and to infer the intensity and distributions of surface nitrogen oxides (NO_x) emissions from the satellite observations of tropospheric NO_2 columns (e.g., Han *et al.*, 2009; Schaap *et al.*, 2013; Streets *et al.*, 2013). In particular, regional-scale CTMs have long been used since the late 1970s (e.g., De Wispelaer, 1981), and the scientific bases of gas-phase chemistry in the troposphere have been well established (Finlayson-Pitts, 2000; Akimoto *et al.*, 2016). Therefore, they may be thought that they can be reliably used to predict photochemical ozone production where the gas-phase chemistry plays a central role.

Recently, an international model intercomparison project, MICS-Asia III (Model Intercomparison Study for Asia Phase III), was conducted with a particular emphasis on the East Asian region. This project revealed that, despite using common precursor emissions, meteorological field, and boundary conditions, the simulated surface O_3 and NO_x concentrations among various models and between models and observations disagree seriously (Li *et al.*, 2019). This prompted us to elucidate the causes of disagreements to improve the credibility of CTMs (Akimoto *et al.*, 2019).

The uncertainty of simulated results of CTMs is known to arise mainly from physical factors related to the vertical transport of chemical species, as well as chemical factors such as atmospheric lifetime of organic nitrates and heterogeneous reactions of NO_x (Canty *et al.*, 2015;



Akimoto *et al.*, 2019). In this paper, in order to reduce the uncertainty of chemical schemes in CTMs, we discuss the importance of atmospheric heterogeneous chemistry of nitrogenous species, and review previous field studies of comprehensive observation of reactive nitrogen (hereafter NO_y) species, aiming at a future proposal of a new observational campaign for comprehensive NO_y measurements to validate the chemistry schemes of CTMs.

2 RESULTS AND DISCUSSION

2.1 Necessity of Model Validation for NO_y Species and Evaluation for Heterogeneous Reactions Related to HNO_3 and HONO

Nitrogen oxides, NO_x ($\text{NO} + \text{NO}_2$), emitted into the atmosphere transform into various oxidized nitrogen compounds in the atmosphere, which are collectively referred to NO_y (total reactive oxidized nitrogen species). Thus, $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{HONO} + \text{HNO}_3 + \text{HO}_2\text{NO}_2 + \text{N}_2\text{O}_5 + \text{NO}_3 + \text{pNO}_3^- + \text{PANs} + \text{OrgN}$, where PANs are peroxyacetyl nitrates including peroxyacetyl nitrate (PAN), and orgN and pNO_3^- are gaseous organic nitrates and particulate inorganic nitrate, respectively. Fig. 1 depicts a scheme of formation processes of specified NO_y , in which black solid and block arrows show homogeneous gas-phase reactions, and heterogeneous processes, respectively, and red block arrows show the heterogeneous HONO formation and HNO_3 renoxification process discussed in this paper.

Among the species consisting NO_y , NO_x (NO and NO_2) are the major components followed by PAN, HNO_3 and HONO in typical polluted urban air. For example, in Beijing and Mexico City where the mixing ratios of NO_y reaches 20–40 ppbv, PAN up to a few ppbv, HNO_3 at 2–5 ppbv and HONO up to 1–3 ppbv have been reported (Zheng *et al.*, 2008; Shao *et al.*, 2009; Li *et al.*, 2015a; Li *et al.*, 2015b). In rural and remote air, the relative importance of HNO_3 increases with HNO_3 becoming a major component of total NO_y (Buhr *et al.*, 1990; Atlas *et al.*, 1992). It should be noted that the atmospheric lifetime of HNO_3 is relatively long, an order of a week (Hanke *et al.*, 2003), while that of HONO is rather short, ~20 min (Li *et al.*, 2012). Among OrgN, alkyl nitrate such as methyl nitrate is usually minor (less than 1 ppbv) (Buhr *et al.*, 1990), but there is still large uncertainty for the importance of unidentified OrgN such as formed from biogenic hydrocarbons. The atmospheric lifetime of methyl nitrate is estimated to be 13 days assuming the 1×10^6 particle cm^{-3} of OH radicals, and those for other alkyl nitrates may be one order of magnitude shorter considering the rate constants with OH (Finlayson-Pitts and Pitts, 2000). Thermal decomposition process determines the atmospheric lifetime of PAN, which is estimated as

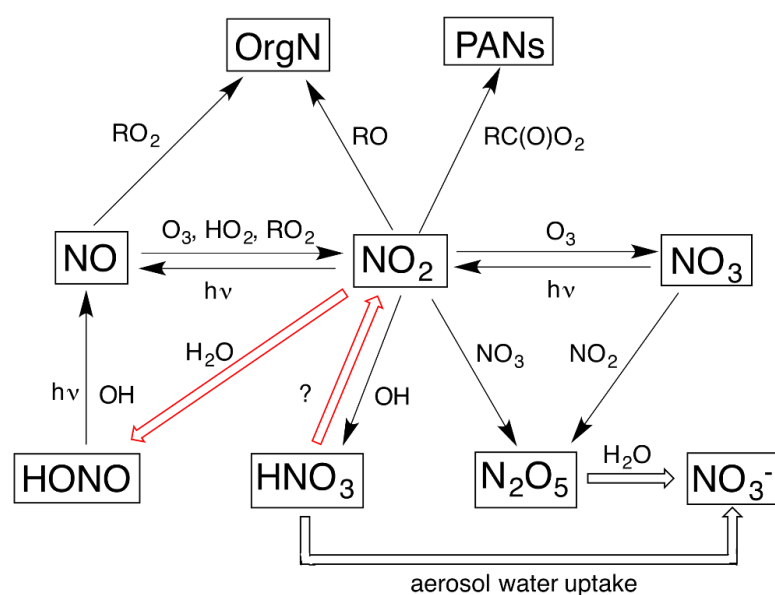
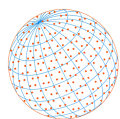


Fig. 1. Scheme of the formation processes of specified NO_y . Single-line arrows are for the gas-phase reactions, and block arrows are for the heterogeneous processes.



50 min at 298 K (Finlayson-Pitts and Pitts, in Beijing up to ≤ 490 pptv and ≤ 30 pptv, respectively (Li *et al.*, 2018). The concentration and 2000). The peak values of mixing ratios of N_2O_5 and NO_3 radical have been measured relative importance of pNO_3^- vary extensively depending on the atmospheric conditions. Detail data of measurements of individual NO_y species and their ratios are described later in the following section.

In most of previous studies on simulation of boundary layer O_3 , observation-based evaluation of CTMs has been performed only for O_3 , validation for NO_x and volatile organic carbons (VOCs) are scarce, and validation by various species of NO_y (other than NO_x) are very limited (e.g., Zhang *et al.*, 2006). It has been customary known that in the simulation of O_3 by regional CTMs, reproduction of observed O_3 mixing ratio can be achieved more easily than those of NO_x and NMVOC since the observational values of O_3 has much wider spatial representativeness as compared to those of NO_x and NMVOC, whose spatial heterogeneity is much higher. However, achieving of good reproduction of present observational data of O_3 alone by the suitable tuning of model parameters without validation of its precursor species (i.e., NO_x and NMVOC) does not guarantee the accuracy of future prediction of O_3 when the precursor emissions will be changed. In order to obtain further credibility of CTMs, validation not only of NO_x and NMVOC, but also of several key species of NO_y (i.e., HNO_3 , PAN, HONO, etc.) is recommended from scientific point of view.

In the recent MICS-Asia III project, overestimation of O_3 associated with the underestimation of NO_x in the urban areas of Beijing and Tokyo in July has been noted for the selected models of CMAQ (Community Multiscale Air Quality Modeling System) v.4.7.1 and v.5.0.2, whereas better agreement between the modeling results and observational data was seen for the NAQPMS (Nested Air Quality Prediction Modeling System) (Akimoto *et al.*, 2019). The latter model included the heterogeneous renoxification and HONO formation reactions of



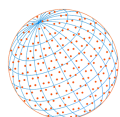
with $\gamma_{\text{HNO}_3} = 3.0 \times 10^{-3}$ for Reaction (1) and $\gamma_{\text{HONO}} = 1.0 \times 10^{-4}$ for Reaction (2). For example, the CMAQs and NAQPMS gave ca. 80 and ca. 50 ppbv of monthly averaged daily maximum of O_3 as compared to the observed value of ca. 60 ppbv in Tokyo in July, respectively. The simulated monthly averaged daily maximum of NO by the CMAQs and NAQPMS was ca. 1–2 and ca. 5 ppbv, respectively, compared to the observed value of ca. 5 ppbv. The observed values of HNO_3 and HONO was not available and no sensitivity analysis of the above heterogeneous processes for O_3 and NO has been made in the MICS-Asa III study though.

Since early 1980s high concentrations of HONO, which cannot be explained by the well-known gas-phase reaction of $\text{OH} + \text{NO} (+\text{M}) \rightarrow \text{HONO}$, are known to exist during nighttime in urban air (Platt *et al.*, 1980; Harris *et al.*, 1982). Because HONO is photolyzed easily by sunlight in the atmosphere to yield OH, which directly affects the O_3 formation rate, it is extremely important to identify the unknown HONO sources to validate CTMs simulating air quality including O_3 . Assuming only the HONO formation reaction in the gas phase ($\text{NO} + \text{OH} + \text{M} \rightarrow \text{HONO} + \text{M}$) alone, the mean simulated HONO mixing ratio by a regional model (WRF-Chem) is 0.04 ppbv, ~25 times lower than the corresponding observed value of up to ~3 ppbv in Beijing in August, and inclusion of heterogeneous reaction,



can considerably improve HONO simulation (Li *et al.*, 2011, 2015b). Qin *et al.* (2009) revealed strong linear correlation between PM_{10} and HONO mixing ratios and the HONO-to- NO_2 ratio, which is consistent with the supposition that aerosol surface was involved in the conversion of NO_2 to HONO. In addition to aerosols, buildings and ground would also provide the active surface for the heterogeneous formation of HONO.

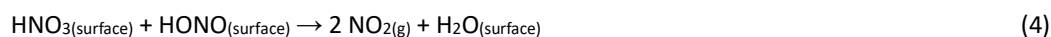
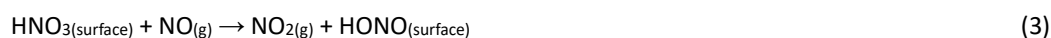
It should be noted that that the HONO and HNO_3 are not independent but their mixing ratios depend each other as revealed by Li *et al.* (2011b). Thus, simultaneous measurement of HNO_3 and HONO together with other NO_y species are highly recommended for the validation of CTMs.



2.2 Previous Studies on Heterogeneous Renoxification Reaction of HNO₃ and Heterogeneous Formation Reactions of HONO

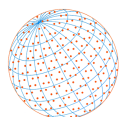
On comparing observational data of NO₂ and HNO₃ obtained via aircraft campaigns in the early 1990s in the upper troposphere with a CTM model, overprediction of HNO₃ and underprediction of NO₂ by the model were noted. The heterogeneous reaction of HNO₃ at the aerosol surface to form NO₂ was proposed and referred to as a “renoxification” reaction (Chatfield *et al.*, 1994; Hauglustaine *et al.*, 1996; Lary *et al.*, 1997). Later studies have reported the overprediction of HNO₃ and underprediction of NO₂ also in urban air, and better agreement between observation and model simulation has been obtained by assuming the presence of the renoxification reaction (Knipping *et al.*, 2002; Li *et al.*, 2015a).

Many laboratory studies have been conducted to investigate the heterogeneous reaction of HNO₃ to form NO/NO₂/HONO. These laboratory studies have been performed on silica glass (Mochida and Finlayson-Pitts, 2000; Saliba *et al.*, 2001; Rivera-Figueroa *et al.*, 2003), soot (Rogaski *et al.*, 1997; Salgado Muñoz and Rossi, 2002), and mineral dust (Underwood *et al.*, 2001). For example, Saliba *et al.* (2001) reported that HNO₃ is adsorbed physically with -Si-OH group by hydrogen bonding, and gaseous NO reacts with the adsorbed HNO₃ to form HONO + NO₂. This reaction is thought to be exothermic because of the hydration of the reactant and product species. HONO stays on the surface and further reacts with the adsorbed HNO₃ to release NO₂ into the gas phase.



However, the heterogeneous reactions involving HNO₃ are extremely complex and depend on HNO₃ concentration. Although the release of NO₂ and HONO into the gas phase has been reported by experiments using relatively high concentrations of HNO₃ (Rogaski *et al.*, 1997; Disselkamp *et al.*, 2000; Rivera-Figueroa *et al.*, 2003), the experimental value of uptake coefficient (γ) of HNO₃ in the atmospheric concentration range is much smaller than 10⁻⁴, while it needs to be greater than 10⁻⁴ for atmospheric importance. Hence, the renoxification from HNO₃ may not be important in the atmosphere based on several laboratory experiments (e.g., Saathohoff *et al.*, 2001; Underwood *et al.*, 2001; Kleffmann and Wiesen, 2005). On the other hand, photolysis of HNO₃ or NO₃⁻ adsorbed on the solid surface of aerosol particles effectively produces HONO and NO_x in the gas phase. This reaction is important not only as a source of daytime HONO, which will be discussed later, but also as a possible contributor to renoxification during daytime (Zhou *et al.*, 2003; Ramazan *et al.*, 2006; Ye *et al.*, 2016b).

Regarding the formation mechanism of HONO other than the gas-phase reaction, a heterogeneous dark reaction of NO₂ and H₂O, Eq. (3), has been known since the 1980s (Sakamaki *et al.*, 1983; Pitts *et al.*, 1984; Svensson *et al.*, 1987; Jenkin *et al.*, 1988). For the formation of HONO in the ambient air during nighttime, the heterogeneous dark reaction and direct emissions from combustion sources are the main sources in urban air (Winer *et al.*, 1994; Vogel *et al.*, 2003; Kotamarthi *et al.*, 2001; Tang *et al.*, 2014). To explain the nighttime concentrations of HONO in the ambient air, the reactive uptake coefficient of NO₂ of ~10⁻⁴ is appropriate, < ~10⁻⁵ is non-effective, and > ~10⁻³ overestimates (Tang *et al.*, 2014). Relatively high daytime concentrations of HONO have also been observed even though the concentrations should be lower due to the photolysis by sunlight (Vogel *et al.*, 2003; Kleffmann and Wiesen, 2005), which strongly suggests additional source of HONO would be present in the daytime. Laboratory experiments have shown that the photolysis of the HNO₃·H₂O complex and NO₃⁻ formed by the adsorption of HNO₃ on aerosol surfaces is an important source of HONO (Zhou *et al.*, 2003; Kleffmann, 2007). In general, the absorption cross-sections of HNO₃ adsorbed on metal or ice surfaces are much larger than that in the gas phase, with a high quantum yield to give NO₂ + OH (e.g., Zhu *et al.*, 2010). In fact, the photoirradiation of aerosol surface sampled in urban air and leaf surface of plants produces HONO in high yield (Zhou *et al.*, 2011; Baergen and Donaldson, 2013; Ye *et al.*, 2016a, b, 2017). For example, the photoirradiation ($\lambda < 400$ nm) of PM_{2.5} sampled in Beijing yielded HONO at an increased rate under acidic conditions, and the production rate was one order of magnitude



larger than that on other solid surfaces, such as Al_2O_3 , TiO_2 , and glass (Bao *et al.*, 2018). By incorporating the heterogeneous photochemical reaction of nitrate adsorbed on solid particles and ground surfaces, reproduction of high concentrations of daytime HONO has been well demonstrated (Couzo *et al.*, 2015; Ye *et al.*, 2016b; Wang *et al.*, 2017).

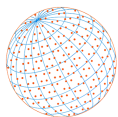
The atmospheric concentrations of HNO_3 and HONO affect the concentrations of NO and NO_2 , e.g., by the photolysis of HONO, which in turn affect the formation of O_3 and pNO_3^- directly and indirectly. Therefore, the simultaneous measurements of at least HNO_3 , HONO, pNO_3^- , and NO_x are necessary for the validation of CTM models which are employed to predict photochemical O_3 and $\text{PM}_{2.5}$ formation, as well as to estimate the emission source strength from the NO_2 column density derived from satellite observations.

2.3 Comprehensive Observation of NO_y Speciation and Chemistry

Table 1 summarizes the previous comprehensive field observations of specified NO_y conducted on the ground and using aircrafts. Comprehensive observation of NO_y species started in the mid-1980s mainly in the United States to understand tropospheric chemistry. Simultaneous observations of NO, NO_2 , PAN, HNO_3 , NO_3^- , NO_y , and O_3 were conducted at a mountainous ground-based station at Niwot Ridge in Colorado in the summer-autumn of 1984 (Fahey *et al.*, 1986). In this study, total- NO_y was measured using a conventional NO_x analyzer employing a gold catalytic converter with a small amount of CO as a reducing agent, replacing conventional molybdenum oxide catalyst, to achieve efficient conversion of all reactive NO_y including pNO_3^- comprehensively to NO. Simultaneously, pNO_3^- and gaseous HNO_3 were measured separately by trapping pNO_3^- with a Teflon filter in the first stage and HNO_3 with a Nylon filter in the second

Table 1. Summary of comprehensive field observations of specified NO_y .

Place	Dates	Species	Ref.
Niwot Ridge, Colorado	Summer–Autumn, 1984	NO, NO_2 , HNO_3 , NO_3^- , PAN, NO_y , O_3	Fahey <i>et al.</i> , 1986
Alert, Canada	March, 1985	NO_2 , $\text{HNO}_3 + \text{NO}_3^-$, PAN, O_3	Bottenheim and Gallant, 1986
Boulder and Niwot Ridge, Colorado	Aug.–Sep., 1987 (BLD) June–July, 1987 (NR)	NO, NO_2 , HNO_3 , NO_3^- , NO_y , PAN, OrgN, O_3	Ridley <i>et al.</i> , 1990
Scotia, Pennsylvania	July–August, 1988	NO, NO_2 , PAN, HNO_3 , NO_3^- , NO_y , OrgN, O_3	Buhr <i>et al.</i> , 1990
Mauna Loa, Hawaii (MLOPEX)	May–June, 1988	NO, NO_2 , PAN, HNO_3 , NO_3^- , NO_y , OrgN, O_3	Atlas <i>et al.</i> , 1992
northeastern North America (US and Canada)	Summer–Autumn, 1988	NO, NO_2 , PAN, HNO_3 , NO_3^- , NO_y , O_3	Parrish <i>et al.</i> , 1993
Aircraft: Alaska (ABLE 3A), Canada (ABLE 3B)	Summer, 1988 (3A) Summer, 1990 (3B)	NO, NO_2 , HNO_3 , PAN, OrgN, NO_3^- , NO_y , O_3 , CO, NMHC	Sandholm <i>et al.</i> , 1994
Aircraft: western Pacific (PEM-West A)	September–October, 1991	NO, NO_2 , HNO_3 , PAN, OrgN, NO_3^- , NO_y , CO, O_3 , CH_4 , NMHC	Singh <i>et al.</i> , 1996
Aircraft: western Pacific (PEM-West B)	February–March, 1994	NO, NO_2 , HNO_3 , PAN, OrgN, NO_3^- , NO_y , CO, O_3 , CH_4 , NMHC	Kondo <i>et al.</i> , 1997
Aircraft: western Pacific (TRACE-P)	February–March, 2001	NO, NO_2 , HNO_3 , PAN, OrgN, NO_3^- , NO_y , O_3 , CO	Talbot <i>et al.</i> , 2003
Blodgett Forest region, near Sacramento, California	February, 2002	NO, NO_2 , total peroxy nitrates, total alkyl nitrates, HNO_3 , O_3 , CO	Day <i>et al.</i> , 2009
Mexico City (MILAGRO/MCMA-2006)	March, 2006	HNO_3 , N_2O_5	Zheng <i>et al.</i> , 2008
Aircraft: Huston, Texas (TexAQS 2006).	August–October, 2006	NH_3 , HNO_3 , NO_3^-	Nowak <i>et al.</i> , 2010
Beijing, Tianjin, and Hebei (CAREBeijing-2007)	August, 2007	NO, NO_2 , HONO, NO_3^- , PAN, O_3 , CO, NMHC	Li <i>et al.</i> , 2015b
Kaiping, Guangdong	October–November, 2008	NO, NO_2 , HONO, HNO_3 , O_3 , CO, NMHC	Li <i>et al.</i> , 2015a
Beijing	September 2015–July 2016	NO, NO_2 , HONO, HNO_3 , NO_3^- , O_3 , CO	Wang <i>et al.</i> , 2017b
Beijing	September–October 2016	NH_3 , NO, NO_2 , HNO_3 , N_2O_5 , O_3	Wang <i>et al.</i> , 2017a



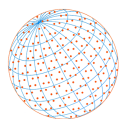
stage, respectively, using a high-volume sampler. The samples were analyzed using ion chromatography after extraction with a buffer solution at an interval of 2 hours. In this observation, NO_x ratio was the highest, 20–30% of NO_y , followed by PAN (15–20%), gaseous HNO_3 (10%), and pNO_3^- (~5%). The mixing ratio of NO_y was always larger than the sum of each component, and the missing NO_y was suggested to be unidentified organic nitrates. In a later observation in rural Pennsylvania in 1988, alkyl nitrates were measured, and under the condition of $[\text{NO}_y] = 1\text{--}30$ ppbv, $[\text{NO}_x]/[\text{NO}_y] = 15\text{--}25\%$, $[\text{HNO}_3]/[\text{NO}_y] = 30\text{--}45\%$, and $[\text{pNO}_3^-]/[\text{NO}_y] = 5\%$ were reported (Buhr *et al.*, 1990). In this study, the contribution of alkyl nitrates was only 1.5%, and 15% of missing NO_y still existed. Because the behavior of the missing NO_y was similar to that of PAN and alkyl nitrates, the contribution of other organic nitrates was suggested (Buhr *et al.*, 1990). In a later ground-based comprehensive NO_y observation conducted at Mauna Loa in Hawaii (MLOPEX) in the early 1990s (Atlas *et al.*, 1992) and in the northeastern part of North America (United States and Canada) (Parrish *et al.*, 1993), $[\text{HNO}_3]/[\text{NO}_y]$ ratio was found to be 43% and 20–30%, respectively, which was in good agreement with previous studies, and HNO_3 was reported to be a major constituent of NO_y . Only in Canadian arctic located at 82°N latitude, PAN was reported to be dominant NO_y , ca. 70% of all observed NO_y species [$\text{NO}_2 + \text{t-NO}_3$ (gaseous $\text{HNO}_3 + \text{pNO}_3^-$) + PAN] (Bottenheim and Gallant, 1986).

Meanwhile, comprehensive measurement of NO_y species in the troposphere using aircrafts were conducted extensively in the Global Tropospheric Experiment (GTE) of NASA in the late 1980s and 1990s. For example, ABLE 3B (1988 and 1990) over Alaska and Canada in the western Pacific (Sandholm *et al.*, 1994), PEM-West A (September–October, 1991) (Singh *et al.*, 1996) and PEM-West B (February–March, 1994) (Kondo *et al.*, 1997) over western Pacific, and TRACE-P (February–March, 2001) over western Pacific (Talbot *et al.*, 2003) measured $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{PAN} + \text{C}_1\text{--C}_3$ alkyl nitrate, O_3 , and CO. In these observations, the disagreement between the total NO_y and the sum of each component was termed as “ NO_y deficit,” and the discussion regarding NO_y closure continued as an important research subject. The uncertainty of measurement of gaseous HNO_3 , a major component of NO_y , was speculated to play a role in NO_y deficit. Therefore, the filter-pack method was replaced by the mist chamber (MC)-IC method which was thought to be more accurate. Kondo *et al.* (1997) reported that $90 \pm 10\%$ of NO_y could be explained by $\text{NO}_x + \text{PAN} + \text{HNO}_3$ in all air masses from the boundary layer to an altitude of 7 km based on the data of PEM-West B.

Since the 2000s, comprehensive measurements of NO_y have mostly focused on the measurement of HONO and its production sources. The observational regions have been expanded from North America to other areas, such as Mexico and China, and regional CTMs, such as CMAQ, have been used for evaluations. Further, real-time direct measurement methods, such as chemical ionization mass spectrometry (CIMS) for HNO_3 (Huey, 2007) and incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) for HONO (Zheng *et al.*, 2018), have been developed and used in campaigns. The direct measurement for N_2O_5 and NO_3 , another species of NO_y , using cavity ringdown spectroscopy (Brown *et al.*, 2001), CIMS (Slusher, 2004), and LIF (Wood *et al.*, 2003; Matsumoto *et al.*, 2005; Wood *et al.*, 2005) have also been performed. Direct continuous measurement of pNO_3^- has been made possible with the use of time-of-flight aerosol chemical speciation monitor (ToF-ACSM) (Fröhlich, 2013).

As an example of comprehensive NO_y measurements after 2000, the simultaneous measurements of NO, NO_2 , total peroxy nitrates (ΣONs), total alkyl nitrates (ΣANs), HNO_3 , CO, and O_3 were conducted in the forest area near Sacramento, California in February, 2002 (Day *et al.*, 2009). NO_x and HNO_3 were found to be persistent in the residual layer in early morning, implying that they have a nighttime sink in the nocturnal boundary layer. In Mexico City in March 2006, HNO_3 and N_2O_5 were simultaneously measured with the use of ion-drift chemical ionization mass spectrometry (ID-CIMS) (Zheng *et al.*, 2008). In addition, diurnal variation of HNO_3 and NO_2 was observed, and it was reported that the concentration of HNO_3 was lower than 200 pptv during nighttime and increased to 0.5–3 ppbv during daytime.

In China, comprehensive measurements of NO_y including NO, NO_2 , HONO, HNO_3 , pNO_3^- , and PAN together with O_3 and VOCs were conducted in Beijing and Tianjin as part of the CAREBeijing-2007 campaign (August, 2007) (Li *et al.*, 2015b). Elucidation of additional sources of HONO was one of the research objectives of the campaign. WRF-Chem simulations have shown that additional HONO increases the concentrations of HNO_3 , pNO_3^- , and PAN and decreases those of



NO and NO₂, which significantly affects the NO_y budget. In modeling the observation data from Kaiping in Guangdong Province (October–November, 2008), the observed data of HNO₃, HONO, pNO₃⁻, and NO_x were reproduced using a box model and a regional CTM model, NAQPMS (Li *et al.*, 2015a). Overestimation of HNO₃ and underestimation of HONO were greatly improved assuming the heterogeneous reactions of Eq. (1) HNO₃ + soot → NO + NO₂ ($\gamma = 3.0 \times 10^{-3}$) and Eq. (2) NO₂ + soot → 0.5 HONO + 0.5 HNO₃ ($\gamma = 1 \times 10^{-4}$) as noted before. The introduction of additional HONO formation was shown to increase HNO₃ and pNO₃⁻, which could be compensated by the introduction of the heterogeneous reaction of HNO₃, resulting in good agreement with the observed data. During September 2015 and July 2016, continuous measurement of HONO, HNO₃, and pNO₃⁻ using ambient ion monitor-ion chromatography (AIM-IC) was performed in Beijing (Wang *et al.*, 2017a). The concentration of HONO was the maximum in autumn and minimum in winter. The source of nighttime HONO was shown to be the heterogeneous reaction of NO₂ on wet surfaces, and that of daytime HONO to be the photolysis of adsorbed HNO₃/NO₃⁻. The direct measurements of N₂O₅ by the cavity-enhanced absorption spectrometer (CEAS); HNO₃, HCl, and NH₃ by the gas and aerosol collector combined with ion chromatography (GAC-IC); and aerosol components by ToF-ACSM have been conducted at the campus of Peking University (September–October 2016) (Wang *et al.*, 2017b). The maximum concentration and uptake coefficient of N₂O₅ have been reported to be 1.3 ppbv and 0.025–0.072, respectively.

As for the aircraft observation, NH₃ and HNO₃ were simultaneously measured using CIMS in a campaign over Houston, Texas (2006), and the chemical equilibrium of NH₃–HNO₃–NH₄NO₃ has been discussed (Nowak *et al.*, 2010). A regional CMAQ (MM5-CMAQ v4.4) was evaluated for the first time using aircraft data of O₃, NO, and NO_y over Seattle in August 2001 (Xie *et al.*, 2011).

3 CONCLUSIONS

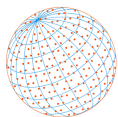
A substantial number of comprehensive field measurements of NO_y species have been conducted over the past decades. However, studies combining the quantification of heterogeneous processes related to NO_x and NO_y with a strong emphasis on overall evaluation/validation of CTMs have not been conducted. Real-time direct measurements of comprehensive NO_y species in urban areas where NO_x and NO_y concentrations are relatively high and NO_x emission inventories are relatively accurate would be the most useful to evaluate and quantify the heterogeneous processes relating to these species with the use of CTMs. It is recommended that such a campaign combining observation and model simulation be performed in the near future to further improve CTMs.

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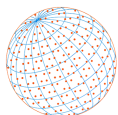
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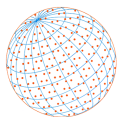
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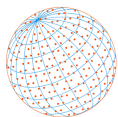
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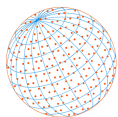
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