Review of Comprehensive Measurements of Speciated NOy and its Chemistry: Need for Quantifying the Role of Heterogeneous Processes of HNO3 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 O3 and NOx but also by individual species of reactive nitrogen NOy is necessary because the formation and dissipation of O3 in the atmosphere occur via reactions accompanying the transformation of NOx and NOy. The disagreement of the simulated results of CTM with observational data of HNO3 and HONO have often been reported, and this paper reviews previous studies on the heterogeneous “renoxification” reaction of gaseous HNO3 to form NO, NO2, and/or HONO; the formation of HONO from the heterogeneous dark reaction of NO2 and H2O, and the photolysis of adsorbed HNO3 and NO3– on surfaces. For the further validation of CTMs with individual species of NOy, previous field studies of comprehensive observation of NOy speciation in ground-based and aircraft campaigns have also been reviewed. Studies combining observations of speciated NOy 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

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 PM2.5 control strategies (e.g., U.S. EPA, 2018) and to infer the intensity and distributions of surface nitrogen oxides (NOx) emissions from the satellite observations of tropospheric NO2 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 O3 and NOx 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 NOx (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 NOy) species, aiming at a future proposal of a new observational campaign for comprehensive NOy measurements to validate the chemistry schemes of CTMs.

2 RESULTS AND DISCUSSION

2.1 Necessity of Model Validation for NOy Species and Evaluation for Heterogeneous Reactions Related to HNO3 and HONO

Nitrogen oxides, NOx (NO + NO2), emitted into the atmosphere transform into various oxidized nitrogen compounds in the atmosphere, which are collectively referred to NOy (total reactive oxidized nitrogen species). Thus, NOy = NO + NO2 + HONO + HNO3 + N2O5 + NO3 + pNO3– + PANs + OrgN, where PANs are peroxyacyl nitrates including peroxyacetyl nitrate (PAN), and orgN and pNO3– are gaseous organic nitrates and particulate inorganic nitrate, respectively. Fig. 1 depicts a scheme of formation processes of specified NOy, 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 HNO3 renoxification process discussed in this paper.

Among the species consisting NOy, NOx (NO and NO2) are the major components followed by PAN, HNO3 and HONO in typical polluted urban air. For example, in Beijing and Mexico City where the mixing ratios of NOy reaches 20–40 ppbv, PAN up to a few ppbv, HNO3 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 HNO3 increases with HNO3 becoming a major component of total NOy (Buhr et al., 1990; Atlas et al., 1992). It should be noted that the atmospheric lifetime of NOy 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...
50 min at 298 K (Finlayson-Pitts and Pitts, in Beijing up to ≤ 490 pptv and ≤ 30 pptv, respectively (Li et al., 2018). The peak values of mixing ratios of N2O5 and NO3 radical have been measured relative importance of pNO3 vary extensively depending on the atmospheric conditions. Detail data of measurements of individual NOy species and their ratios are described later in the following section.

In most of previous studies on simulation of boundary layer O3, observation-based evaluation of CTMs has been performed only for O3, validation for NOx and volatile organic carbons (VOCs) are scarce, and validation by various species of NOy (other than NOx) are very limited (e.g., Zhang et al., 2006). It has been customary known that in the simulation of O3 by regional CTMs, reproduction of observed O3 mixing ratio can be achieved more easily than those of NOx and NMVOC since the observational values of O3 has much wider spatial representativeness as compared to those of NOx and NMVOC, whose spatial heterogeneity is much higher. However, achieving of good reproduction of present observational data of O3 alone by the suitable tuning of model parameters without validation of its precursor species (i.e., NOx and NMVOC) does not guarantee the accuracy of future prediction of O3 when the precursor emissions will be changed. In order to obtain further credibility of CTMs, validation not only of NOx and NMVOC, but also of several key species of NOy (i.e., HNO3, PAN, HONO, etc.) is recommended from scientific point of view.

In the recent MICS-Asia III project, overestimation of O3 associated with the underestimation of NOx 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 renoxidation and HONO formation reactions of

\[
\begin{align*}
\text{HNO}_3 + \text{soot} & \rightarrow \text{NO} + \text{NO}_2 \\
\text{NO}_2 + \text{soot} & \rightarrow 0.5 \text{HONO} + 0.5 \text{HNO}_3
\end{align*}
\]

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 O3 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 HNO3 and HONO was not available and no sensitivity analysis of the above heterogeneous processes for O3 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 OH + NO (+M) \( \rightarrow \) 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 O3 formation rate, it is extremely important to identify the unknown HONO sources to validate CTMs simulating air quality including O3. Assuming only the HONO formation reaction in the gas phase (NO + OH + M \( \rightarrow \) HONO + 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,

\[
2\text{NO}_2 + \text{H}_2\text{O} \text{(on surface)} \rightarrow \text{HONO} + \text{HNO}_3
\]

can considerably improve HONO simulation (Li et al., 2011, 2015b). Qin et al. (2009) revealed strong linear correlation between PM10 and HONO mixing ratios and the HONO-to-NO2 ratio, which is consistent with the supposition that aerosol surface was involved in the conversion of NO2 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 HNO3 are not independent but their mixing ratios depend each other as revealed by Li et al. (2011b). Thus, simultaneous measurement of HNO3 and HONO together with other NOy 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.

\[
\text{HNO}_3(\text{surface}) + \text{NO}(g) \rightarrow \text{NO}_2(g) + \text{HONO}(\text{surface}) \quad (3)
\]

\[
\text{HNO}_3(\text{surface}) + \text{HONO}(\text{surface}) \rightarrow 2 \text{NO}_2(g) + \text{H}_2\text{O}(\text{surface}) \quad (4)
\]

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 (\(\gamma\)) 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 NO₂ 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 \(\sim 10^{-8}\) is appropriate, \(< 10^{-5}\) is ineffective, and \(> 10^{-5}\) 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 PM₂.₅ 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 Al₂O₃, TiO₂, 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 HNO₂ and HONO affect the concentrations of NO and NO₂, e.g., by the photolysis of HONO, which in turn affect the formation of O₃ and pNO₃⁻ directly and indirectly. Therefore, the simultaneous measurements of at least HNO₃, HONO, pNO₃⁻, and NOₓ are necessary for the validation of CTM models which are employed to predict photochemical O₃ and PM₂.₅ formation, as well as to estimate the emission source strength form the NO₂ column density derived from satellite observations.

### 2.3 Comprehensive Observation of NOₓ Speciation and Chemistry

Table 1 summarizes the previous comprehensive field observations of specified NOₓ conducted on the ground and using aircrafts. Comprehensive observation of NOₓ species started in the mid-1980s mainly in the United States to understand tropospheric chemistry. Simultaneous observations of NO, NO₂, PAN, HNO₃, NO₃⁻, NO₉, and O₃ 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-NOₓ was measured using a conventional NOx 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 NO₉ including pNO₃⁻ comprehensively to NO. Simultaneously, pNO₃⁻ and gaseous HNO₃ were measured separately by trapping pNO₃⁻ with a Teflon filter in the first stage and HNO₃ with a Nylon filter in the second

<table>
<thead>
<tr>
<th>Place</th>
<th>Dates</th>
<th>Species</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>Niwot Ridge, Colorado</td>
<td>Summer–Autumn, 1984 March, 1985</td>
<td>NO, NO₂, HNO₃, NO₃⁻, PAN, NOₓ, O₃ NO₂, HNO₃ + NO₃⁻, PAN, O₃</td>
<td>Fahey et al., 1986</td>
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<tr>
<td>Alert, Canada</td>
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<td>Bottenheim and Gallant, 1986</td>
</tr>
<tr>
<td>Scotia, Pennsylvania</td>
<td>July–August, 1988</td>
<td>NO, NO₂, PAN, HNO₃, NO₃⁻, NO₉, OrgN, O₃</td>
<td>Buhr et al., 1990</td>
</tr>
<tr>
<td>Mauna Loa, Hawaii (MLOPEX)</td>
<td>May–June, 1988</td>
<td>NO, NO₂, PAN, HNO₃, NO₃⁻, NO₉, OrgN, O₃</td>
<td>Atlas et al., 1992</td>
</tr>
<tr>
<td>northeastern North America (US and Canada)</td>
<td>Summer–Autumn, 1988</td>
<td>NO, NO₂, PAN, HNO₃, NO₃⁻, NO₉, O₃</td>
<td>Parrish et al., 1993</td>
</tr>
<tr>
<td>Aircraft: Alaska (ABLE 3A), Canada (ABLE 3B)</td>
<td>Summer, 1988 (3A) Summer, 1990 (3B)</td>
<td>NO, NO₂, HNO₃, PAN, OrgN, NO₄⁻, NO₉, O₅, CO, NMHC</td>
<td>Sandholm et al., 1994</td>
</tr>
<tr>
<td>Aircraft: western Pacific (PEM-West A)</td>
<td>September–October, 1991</td>
<td>NO, NO₂, HNO₃, PAN, OrgN, NO₄⁻, NO₉, CO, O₅, CH₄, NMHC</td>
<td>Singh et al., 1996</td>
</tr>
<tr>
<td>Aircraft: western Pacific (PEM-West B)</td>
<td>February–March, 1994</td>
<td>NO, NO₂, HNO₃, PAN, OrgN, NO₄⁻, NO₉, CO, O₅, CH₄, NMHC</td>
<td>Kondo et al., 1997</td>
</tr>
<tr>
<td>Aircraft: western Pacific (TRACE-P)</td>
<td>February–March, 2001</td>
<td>NO, NO₂, HNO₃, PAN, OrgN, NO₄⁻, NO₉, CO</td>
<td>Talbot et al., 2003</td>
</tr>
<tr>
<td>Blodgett Forest region, near Sacramento, California</td>
<td>February, 2002</td>
<td>NO, NO₂, total peroxy nitrates, total alkyl nitrates, HNO₃, O₅, CO</td>
<td>Day et al., 2009</td>
</tr>
<tr>
<td>Mexico City (MILAGRO/MCMA-2006)</td>
<td>March, 2006</td>
<td>HNO₃, N₂O₅</td>
<td>Zheng et al., 2008</td>
</tr>
<tr>
<td>Aircraft: Huston, Texas (TexAQS 2006)</td>
<td>August–October, 2006</td>
<td>NH₃, HNO₃, NO₃⁻</td>
<td>Nowak et al., 2010</td>
</tr>
<tr>
<td>Beijing, Tianjin, and Hebei (CAREBeijing-2007)</td>
<td>August, 2007</td>
<td>NO, NO₂, HONO, NO₅⁻, PAN, O₅, CO, NMHC</td>
<td>Li et al., 2015b</td>
</tr>
<tr>
<td>Kaiping, Guangdong</td>
<td>October–November, 2008</td>
<td>NO, NO₂, HONO, HNO₃, O₅, CO, NMHC</td>
<td>Li et al., 2015a</td>
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<tr>
<td>Beijing</td>
<td>September 2015–July 2016</td>
<td>NO, NO₂, HONO, HNO₃, NO₃⁻, O₅, CO</td>
<td>Wang et al., 2017b</td>
</tr>
<tr>
<td>Beijing</td>
<td>September–October 2016</td>
<td>NH₃, NO, NO₂, HNO₃, N₂O₅, O₅</td>
<td>Wang et al., 2017a</td>
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mass spectrometry (ID-CIMS) (Zheng et al., 2003). NO2 and O3 were conducted in the forest area near Sacramento, California in February, 2002 (Day et al., 2005). The direct measurement for N2O5 and NO3, another major component of NOy, was speculated to play a role in NOy deficit. Kondo et al. (1997) reported that 90% of the missing NOy was attributed to NOy closure continued as an important research subject. The uncertainty of measurement of gaseous HNO3, a major component of NOy, was speculated to play a role in NOy 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 ± 10% of NOy could be explained by NOx + PAN + HNO3 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 NOy species 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 HNO3 (Huey, 2007) and incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) for HONO (Fröhlich, 2013), have been developed and used in campaigns. The direct measurement for NO2, NOy, and NOy species in the troposphere using aircrafts have been 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 NOy = NO + NO2 + HNO3 + PAN + C1-C3 alkyl nitrates, O3, and CO. In these observations, the disagreement between the total NOy and the sum of each component was termed as “NOy deficit,” and the discussion regarding NOy closure continued as an important research subject. The uncertainty of measurement of gaseous HNO3, a major component of NOy, was speculated to play a role in NOy 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 ± 10% of NOy could be explained by NOx + PAN + HNO3 in all air masses from the boundary layer to an altitude of 7 km based on the data of PEM-West B.

As an example of comprehensive NOy measurements after 2000, the simultaneous measurements of NO, NO2, total peroxy nitrates (ΣONs), total alkyl nitrates (ΣANs), HNO3, CO, and O3 were conducted in the forest area near Sacramento, California in February, 2002 (Day et al., 2009). NO and HNO3 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, HNO3 and N2O5 were simultaneously measured with the use of ion-drift chemical ionization mass spectrometry (ID-CIMS) (Zheng et al., 2008). In addition, diurnal variation of HNO3 and NO2 was observed, and it was reported that the concentration of HNO3 was lower than 200 pptv during nighttime and increased to 0.5–3 ppbv during daytime.

In China, comprehensive measurements of NOy including NO, NO2, HONO, HNO3, pNO3-, and PAN together with O3 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 HNO3, pNO3-, and PAN and decreases those of...
NO and NO$_2$, which significantly affects the NO$_x$ budget. In modeling the observation data from Kaiping in Guangdong Province (October–November, 2008), the observed data of HNO$_3$, HONO, pNO$_3^-$, and NO$_x$ were reproduced using a box model and a regional CTM model, NAQPMS (Li et al., 2015a). Overestimation of HNO$_3$ and underestimation of HONO were greatly improved assuming the heterogeneous reactions of Eq. (1) HNO$_3$ + soot → NO + NO$_2$ ($\gamma = 3.0 \times 10^{-3}$) and Eq. (2) NO$_2$ + soot → 0.5 HONO + 0.5 HNO$_3$ ($\gamma = 1 \times 10^{-4}$) as noted before. The introduction of additional HONO formation was shown to increase HNO$_3$ and pNO$_3^-$, which could be compensated by the introduction of the heterogeneous reaction of HNO$_3$, resulting in good agreement with the observed data. During September 2015 and July 2016, continuous measurement of HONO, HNO$_3$, and pNO$_3^-$ 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 NO$_2$ on wet surfaces, and that of daytime HONO to be the photolysis of adsorbed HNO$_3$/NO$_3^-$.

As for the aircraft observation, NH$_3$ and HNO$_3$ were simultaneously measured using CIMS in a campaign over Houston, Texas (2006), and the chemical equilibrium of NH$_3$–HNO$_3$–NH$_4$NO$_3$ has been discussed (Nowak et al., 2010). A regional CMAQ (MM5-CMAQ v4.4) was evaluated for the first time using aircraft data of O$_3$, NO, and NO$_x$ over Seattle in August 2001 (Xie et al., 2011).

### 3 CONCLUSIONS

A substantial number of comprehensive field measurements of NO$_x$ 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$_x$ 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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