Exploring Possible Missing Sinks of Nitrate and Its Precursors in Current Air Quality Models —A Case Simulation in the Pearl River Delta, China, Using an Observation-Based Box Model

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Abstract

Nitrate and its precursor (gaseous HNO_3) in China are generally overestimated by current chemical transport models in comparison to in-situ observations. In this study, we used an observation-based box model and in-situ measurements at a rural site in southern China to investigate possible missing sinks of nitrate. We found that a heterogeneous reaction of HNO_3 to NO_x on soot can better balance the NO_x/HNO_3 chemistry in models and improve model performance with regard to nitrate, particularly where an additional HONO source (the heterogeneous reaction of NO_2 on soot) is incorporated into current models. Through a series of sensitivity simulations, the uptake coefficients of heterogeneous reactions were suggested to be 3.0×10^{-3} and 1×10^{-4} for HNO_3 and HONO over southern China in fall, respectively. A 3-D simulation with the suggested uptake coefficients further confirmed that heterogeneous reactions significantly decreased the nitrate concentrations (PNO_3) in southern China, by up to $10 \mu\text{g m}^{-3}$ (50%–80% of simulated PNO_3) in polluted regions (e.g., the Yangtze River). In contrast to nitrate and HNO_3 , NO_x concentrations in China were enhanced, which partly explained the underestimation of NO_2 in current models compared to satellite observations.

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1. Introduction

There is growing concern over the role of nitrate aerosol in the increasingly common haze episodes in China (Jansen et al. 2014). However, recent simulations including the GEOS-Chem, CHASER and CMAQ models, have greatly overestimated nitrate levels in China, with predicted levels reaching four times of the observed annual concentration (Sudo et al. 2002; Kim et al. 2006; Wang et al. 2013). This suggests shortcomings in our current understanding of nitrogen oxides (NO_x) cycle and related processes. Recently, sporadic observations in China have suggested that the overestimation of gaseous nitric acid (HNO_3) in models might be the cause of the high nitrate levels in simulations. Li et al. (2015) simulated summer HNO_3 in Beijing using WRF-Chem and predicted levels in the range 2–5 parts per billion by volume (ppbv), which was much higher than observations (0–1 ppbv). Similar results were also found in the northwestern Pacific, where simulated HNO_3/NO_x and peroxy acetyl nitrate (PAN)/ NO_x were found to be 2–3 times higher than observations during the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign (Talbot et al. 2003). Tang et al. (2014) warned that if new additional sources of nitrous acid (HONO) were incorporated into current

models, simulated nitrate levels would increase by 80%–100% in China. Hence, a better understanding of the atmospheric chemistry of HNO_3 and its related reactive nitrogen-containing gases (e.g., nitrous acid) in current models is key to reproducing the evolution of nitrate on haze days.

Both dry/wet deposition and ammonia emissions could explain this overestimation of nitrate (Shimadera et al. 2014). However, neither process can completely explain why there has been such a large overestimation of the monthly mean gaseous HNO_3 and HNO_3/NO_x under the NO_x underestimation over China and northwestern Pacific. Recently, a heterogeneous reaction of HNO_3 on soot (R1) was proposed to explain the overestimation of HNO_3/NO_x in simulations (Rogasi et al. 1997). This mechanism has been successfully applied in some studies, although it has still to be confirmed in laboratory studies (Hauglustaine et al. 1996; Kleffmann and Wiesen 2005). Many uptake coefficients for R1 (γ_{HNO_3}), ranging from 10^{-7} to 10^{-2} , have been proposed based on laboratory and model experiments (Hauglustaine et al. 1996; Rogasi et al. 1997), and therefore studies of γ_{HNO_3} that are appropriate for the soot aerosol morphology in China are needed.

The heterogeneous reaction for HONO formation (R2) does greatly affect the nitrate concentration (Tang et al. 2014). Unfortunately, there have been few studies of the uptake coefficient of R2 (γ_{HONO}) in China (Li et al. 2012b). Tang et al. (2014) reported a suggested γ_{HONO} of 10^{-4} for the North China Plain, but this has not been tested in other regions in China.

In this study, we utilized an observation-based box model to estimate possible γ_{HNO_3} and γ_{HONO} that were appropriate for the soot morphology in southern China, which was expected to reduce the impacts of uncertainties resulting from the emission inventory. A 3-D chemical transport model was used to assess the regional-scale impact of heterogeneous reactions (R1 and R2) on atmospheric chemistry in southern China. The observations were taken from an integrated field campaign (Synthesized Prevention Techniques for Air Pollution Complex and Integrated Demonstration in Key City-Cluster Region: 3C-star) in the Pearl River Delta, China (Zhang 2009b).

2. Methodology

2.1 Sampling site and measurement technique

The measurements were made at a typical rural supersite (Kaiping, 22.32°N, 112.53°E; Fig. S1 in the supplement) about 120 km southwest of Guangzhou, a megacity in southern China. The 3C-star field campaign was conducted from 2008-10-15 to 2008-11-19, and involved more than 100 researchers from 12 research institutes. As one of two super sites, various gaseous (HNO_3 , HONO, sulfur dioxide/ SO_2 , NO_x and volatile organic compounds/VOCs) and aerosol pollutants were measured in Kaiping. A strict QA/QC procedure was performed, with details provided in Cheng et al. (2013). In this study, the period of 2008-10-28 to 2008-10-31 was selected because of the low wind velocity (mean value: 1.5 m s^{-1} and maximum: $< 3.5 \text{ m s}^{-1}$) and wet weather (mean rela-

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tive humidity: 80%; minimum: 60%) (Fig. S2 in the supplement). These meteorological conditions are favorable to the heterogeneous reactions on soot.

Hourly concentrations of gaseous HNO_3 , HONO, SO_2 , and inorganic aerosols (sulfate, nitrate, chloride, and ammonium) were measured by a Gas and Aerosol Collector with Ion-exchange Chromatography (GAC-IC) system developed by Dong et al. (Dong et al. 2012). An intercomparison of the GAC-IC and the TE 43c analyzer (for SO_2), LOPAP Path Absorption Photometer (LOPAP, for HONO), a filter-based method, and the Aerosol Mass Spectrometer (AMS, for inorganic aerosols) at Kaiping suggested a good consistency throughout the 3C-star campaign (Dong et al. 2012). Levels of CO , O_3 , and soot were measured by commercial instruments (Thermo Electron, Model 48C, 49C, and MAAP Model 5012, respectively). Levels of NO/NO_2 were measured with a photolytic chemiluminescence NO_x analyzer (Cheng et al. 2013). Aerosol extinction was measured by an integrating nephelometer. Two two online GC-FID/PID systems (Syntech Spectra GC-FID/PID GC955 series 611/811 VOC analyzer), one for the C3-C5 NMHCs, and the other for C6-C9 NMHCs were used to measure C3-C9 NMHCs concentrations with a time resolution of 30 min (Shao et al. 2009).

2.2 Box modeling calculations

a. Box model description

An integrated modular box model was used in this study, which had previously been successfully used to simulate atmospheric oxidation in Beijing during the 2008 Olympics (Li et al. 2011). In this box model, CBM-Z with 133 reactions, RADM, and ISORROPIAv1.7 were used to reproduce the gas, aqueous, and inorganic aerosol chemical processes in the atmosphere, respectively. An accurate radiative transfer model (TUV 4.5) was used to calculate on-line photolysis frequencies, considering the impact of clouds and aerosols. The heterogeneous chemistry module was updated to 28 reactions on four types of aerosols (soot, sulfate, dust, and sea salt) from eight reactions on two types of aerosol in Li et al. (2011) (Table S1 in the supplement). The dry deposition velocity of HNO_3 was set to 2 cm s^{-1} , in accordance with previous observations (Adon et al. 2013).

The observed hourly gaseous species (CO , O_3 , SO_2 , NO/NO_2 , NH_3 , and $\text{C}_2\text{-C}_{12}$ VOCs), aerosols (sulfate, nitrate, ammonium, chloride and soot), aerosol optical depth, boundary layer height, water vapor, ambient temperature, and pressure were averaged or interpolated with a time resolution of 5 min, and used as model constraints. Aerosol Surface Area (SA) was calculated from the observed aerosol mass concentrations. We assumed that aerosols were spherical, and the mean radius and mass density of sulfate and soot were taken from Tie et al. (2005) (sulfate: $0.24 \mu\text{m}$, 1.7 g cm^{-3} ; soot: $0.04 \mu\text{m}$, 1.0 g cm^{-3}), with a lognormal distribution. Dust and sea salts were divided into 4 bins (0–1 m; 1–2.5 m, 2.5–5 m, 5–10 m), with mass density of 2.2 g cm^{-3} and 2.65 g cm^{-3} , respectively. Observations of HNO_3 and HONO were only used to evaluate model performance in different scenarios, without inputting the box model.

b. Model setup

A series of sensitivity simulations were designed to obtain suitable uptake coefficients for southern China. In these simulations, the ranges of γ_{HNO_3} and γ_{HONO} were $0 \sim 1 \times 10^{-1}$ and $0 \sim 1 \times 10^{-2}$ with intervals of 1×10^{-5} , respectively. The values in which simulated HNO_3 and HONO were the closest (the smallest root mean square error) to observations were regarded as suitable uptake coefficients.

The model calculation was made for each day over the period of 2008-10-28 to 2008-10-31. The time of 00:00 LST was regarded as the initial time for each day. This integration was conducted three times to stabilize the concentrations of unconstrained species. The results calculated for the last 24 h were used as the output. The emission rates of several species were taken from Zhang et al. (2009a). Additional loss by deposition, with a corresponding lifetime of three days, was assumed to prevent the buildup of unrealistic amounts of secondary products.

3. Results and discussion

3.1 Observed levels of gaseous HONO, HNO_3 , and NO_x at Kaiping

Figure 1 shows the observed hourly gaseous HONO, HNO_3 , NO_x , HNO_3/NO_x , and black carbon (BC) at Kaiping during 2008-10-28 to 2008-10-31. Due to photolysis, the observed HONO reached its maximum ($\sim 1 \text{ ppbv}$) in the nighttime and fell back to the minimum ($\sim 0.2 \text{ ppbv}$) when the sun was overhead. Compared with HONO, gaseous HNO_3 displayed the reverse pattern, with a daytime maximum of 5–6 ppbv. The daytime HONO at Kaiping was similar to summertime observations at suburban sites in other megacities in China (e.g., Beijing and Shanghai), but was slightly higher than those in summer and winter at European and US suburban sites (Li et al. 2015; Michoud et al. 2014). Gaseous HNO_3 at Kaiping was almost 3–4 times higher than levels reported in California and Mexico City where the diurnal maximum in spring and summer was usually 1 ppbv (Day et al. 2009; Zheng et al. 2008). The hourly HNO_3/NO_x ratio was in the range 0.02–1.3, with a mean of 0.13, much less than observations in aged plumes over remote regions (average ~ 5) (Chatfield 1994). This indicated that levels in Kaiping were controlled by fresh plumes rather than aged plumes. BC concentrations ranged from $1\text{--}5 \mu\text{g m}^{-3}$, with a mean of $2.2 \mu\text{g m}^{-3}$, which provided an abundant surface area for heterogeneous reactions (R1 and R2).

3.2 The uptake coefficients for heterogeneous reactions (R1 and R2) suggested by the box model

Figure 2 shows the simulated gaseous HONO, HNO_3 , and HNO_3/NO_x in the box model sensitivity simulations. As expected, both simulated HONO and HNO_3 displayed a large discrepancy with the observations in current models without R1 and R2 (i.e., γ_{HONO} and γ_{HNO_3} were set to 0). The simulated mean HNO_3 was 2.1 ppbv in the whole period, 57% higher than observations (1.3 ppbv). This systematic overestimation was $\sim 2\text{--}3$ times higher than the observed values during the daytime. Consequently, an overestimation of HNO_3/NO_x is apparent in Fig. 2. During the daytime on 31st, the simulated HNO_3/NO_x ratio was four, while the observation was only ~ 1 . Levels of HONO were significantly underestimated without an additional source (R2), which was previously reported by Li et al (2015). We selected uptake coefficients for R1 and R2 in which simulated HNO_3 and HONO were closest to the observations. As shown in Fig. 2, a γ_{HNO_3} of 3.0×10^{-3} and γ_{HONO} of 1×10^{-4} were suggested for southern China in this study. The simulated mean HNO_3 and HONO for the suggested uptake coefficients were 1.29 ppbv and 0.36 ppbv, respectively, which were close to observations (HNO_3 : 1.30; HONO: 0.43 ppbv). The suggested γ_{HNO_3} was quite similar to that used in a labo-

Fig. 1. Observed hourly gaseous HONO, HNO_3 , and NO_x (ppbv), and black carbon ($\mu\text{g m}^{-3}$) at Kaiping during 2008-10-28 to 2008-10-31. The HNO_3/NO_x ratio is also shown.

Fig. 2. Comparison between observed and simulated HONO, HNO_3 , and HNO_3/NO_x in sensitivity simulations with different uptake coefficients for R1 and R2 in the box model at Kaiping during 2008-10-28 to 2008-10-31. The gray shaded area is the range of simulated HONO and HNO_3 .

ratory study by Muñoz et al. (2002), in which $4.6 \pm 1.6 \times 10^{-3}$ was obtained by experiments based on a Knudsen cell. Compared with other modeling study (3.0×10^{-7}) by Saathoff et al. (2001), our suggested γ_{HNO_3} was higher. This implied that previous simulations likely underestimated the impact of heterogeneous reactions on nitrate simulation on China.

Note that the observed daytime HONO was still underestimated using the suggested γ_{HONO} , which is likely to be because unknown additional sources depending on NO_2 photolysis rates was not included in this study (Li et al. 2015).

3.3 Regional impact of heterogeneous reactions (R1 and R2) on atmospheric chemistry in southern China

In this study, to assess the regional impact of heterogeneous reactions (R1 and R2) on nitrate chemistry in southern China, we used a 3-D chemical transport model (NAQPMS) developed by the Institute of Atmospheric Physics, Chinese Academy of Sciences, using the suggested γ_{HONO} and γ_{HNO_3} . NAQPMS has been widely used to simulate dust events, acid deposition, ozone, and aerosols in East Asia. A detailed description of the model is provided in Li et al. (2012a). Four simulations (S1: without R1 and R2; S2: with the suggested γ_{HONO} , but without γ_{HNO_3} ; S3: with the suggested γ_{HONO} , but without γ_{HNO_3} ; and S4: with the suggested γ_{HNO_3} and γ_{HONO}) were conducted based on the 2006 Multi-resolution Emission Inventory for China (INTEX-B) emissions prepared by Zhang et al. (2009a) at a 45 km resolution.

As shown in Fig. 3, heterogeneous reactions significantly improved the predicted accuracy of NAQPMS. The heterogeneous reaction R1 decreased the simulated average gaseous HNO_3 from 3.8 to 1.7 ppbv. The conversion from HNO_3 to NO_x by R1 increased the simulated NO_x from 7.4 to 12.7 ppbv, which was closer to the observed value (10.7 ppbv). The simulated PNO_3 also decreased from $\sim 9 \mu\text{g m}^{-3}$ to $\sim 6 \mu\text{g m}^{-3}$, close to observations ($4.8 \mu\text{g m}^{-3}$). An overestimation of NO_x was apparent around noontime (4:00–8:00 UTC), which was likely caused by the underestimation of vertical turbulence. The model in S4 with R2 also succeeded in capturing the magnitude of observed HONO peaks during the nighttime (~ 1 ppbv).

Figure 4 shows the spatial distribution of simulated gaseous HNO_3 , HONO, NO_x , and PNO_3 with R1 and R2 in southern China. The highest HNO_3 concentration appeared to the north of Guangzhou, with a magnitude of 4 ppbv. Kaiping station was located on the southern rim of the high concentration belt. Nitrate concentrations were more uniformly distributed over the land with a range of $6\text{--}9 \mu\text{g m}^{-3}$, while the maximum values were in areas along the Yangtze River ($15 \mu\text{g m}^{-3}$). The high nitrate along Yangtze River

Fig. 3. Comparison between observed and simulated diurnal averages of HONO, HNO_3 , NO_x , PNO_3 and BC in NAQPMS using the suggested uptake coefficients at Kaiping during 2008-10-28 to 2008-10-31.

Fig. 4. Spatial distribution of simulated surface HNO_3 , HONO, PNO_3 , and NO_x in southern China during 2008-10-28 to 2008-10-31. The locations of Guangzhou and Kaiping are also shown.

was likely caused by the lower temperature. Compared with HNO_3 and PNO_3 , high levels of NO_x and HONO were limited near to the locations of NO_x emissions.

Figure 5 shows the regional impact of R1 and R2 in southern China in the studying period. Clearly, nitrate concentrations significantly decreased in the modeling domain due to the heterogeneous reactions. The largest decrease occurred in the middle and lower reaches of the Yangtze River (25°N – 30°N , 110°E – 120°E), with a magnitude of $10 \mu\text{g m}^{-3}$ (50%–80% of simulated PNO_3 in S4) (Fig. 5g). At Kaiping, PNO_3 decreased by $1\text{--}3 \mu\text{g m}^{-3}$ (10%–30%). Note that the decrease was 30%–80% over coastal waters along the continent, which was likely a result of the low simulated PNO_3 concentrations. This overall decrease of PNO_3 was mostly caused by R1 instead of R2 (Fig. 5h). In R2, more NO_2 was converted to HONO, which yielded more OH. This increased the HNO_3 and PNO_3 concentrations through the reactions of $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$ and $\text{HNO}_3 + \text{NH}_3 \leftrightarrow \text{NH}_4\text{NO}_3$ (Fig. 5i). R1 and R2 had the opposite effect on PNO_3 , which suggested that R1 must be coupled into current models in cases where R2 is included (Li

Fig. 5. Regional impact of heterogeneous reactions (R1 and R2) on gaseous HNO_3 , HONO , PNO_3 , and NO_x in southern China during 2008-10-28 to 2008-10-31 (shaded: ppbv or $\mu\text{g m}^{-3}$; contour: %). The left, middle, and right columns represent the overall (Het_impact_all), R1 (Het_impact_R1), and R2 (Het_impact_R2) effects, respectively. The first, second, third and fourth line represent impacts on HNO_3 , HONO , PNO_3 and NO_x .

et al. 2015), to avoid a larger overestimation of nitrate.

Similar as PNO_3 , there was an overall negative effect of R1 and R2 on the HNO_3 concentration (Fig. 5a), although R2 alone slightly enhanced HNO_3 by 0.1–1 ppbv in the modeling domain (Fig. 5c). The overall decrease of HNO_3 when R1 and R2 were included reached 3–5 ppbv over most regions in southern China, which accounted for 70%–100% of the simulated HNO_3 . The regional impact of R1 and R2 on NO_2 showed the reverse pattern with HNO_3 and PNO_3 (Fig. 5j, k, l). The overall effect of R1 and R2 was to increase the NO_2 concentrations by 3–8 ppbv (30%–50%) in southern China, with levels reaching 8 ppbv at Kaiping (Fig. 5j). As shown in Fig. 5h, i, more HNO_3 was recycled back to NO_x by R1 than NO_x was lost on soot by R2 in southern China. This enhancement by R1 partly explains the underestimation of NO_2 in previous simulations without R1 (Han et al. 2015), and could have an important impact on the inverse modeling of NO_2 emissions in China. For HONO , the overall enhancement from two heterogeneous reactions reached 0.5–1 ppbv along the Yangtze River (Fig. 5d). In the Pearl River Delta, this enhancement was 0.2–0.5 ppbv. This enhancement of HONO accounted for more than 90%–95% of simulated HONO in S4, which indicates that heterogeneous chemistry was the dominant source of HONO , rather than the gas chemistry (Li et al. 2015). Among the heterogeneous reactions, R2 produced a more significant HONO enhancement than R1 (Fig. 5e, f).

4. Conclusion and recommendations

Nitrate aerosol and its precursor (gaseous HNO_3) are frequently overestimated over China by current 3-D chemical transport models. In this study, we used an observation-based box model in association with observations at a rural site in the Pearl River Delta of China during 28 to 31 October 2008 to examine the possible causes of this overestimation. We found that a heterogeneous reaction of HNO_3 to NO_x on soot tends to better balance the NO_x/HNO_3 chemistry in models and improve model performance with regard to nitrate. The previously reported heterogeneous reaction of NO_2 on soot (R2) effectively improved the model performance with regard to nighttime HONO , but tended to enhance HNO_3 and nitrate. Through a series of sensitivity simulations, a γ_{HNO_3} of 3.0×10^{-3} and γ_{HONO} of 1×10^{-4} were suggested for southern China in fall. A 3-D simulation using a chemical transport model with suggested uptake coefficients further confirmed that the two heterogeneous reactions had a noticeable effect on HNO_3 , nitrate, NO_x , and HONO in the whole of southern China. Studies investigating the seasonal cycles and interannual variability of the impacts of heterogeneous reactions on HNO_3 and nitrate are being conducted and will be the subject of a future paper.

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Supplement

The supplement describes the location of the Kaiping site and its meteorological parameters during the study period. Heterogeneous reactions in the study are also shown.

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