Effect of hydrolysis of N_2O_5 on nitrate and ammonium formation in Beijing China: WRF-Chem model simulation

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Abstract

Beijing, the capital of China, is a mega city with a population of more than 20 million. In recent years, the city has experienced heavy air pollution, with particulate matter (PM) being one of its top pollutants. In the last decade, extensive efforts have been made to characterize the sources, properties, and processes of PM in Beijing. Despite progress made by previous studies, there are still some important questions to be answered and addressed. The focus of this research is to study the impact of the heterogeneous hydrolysis of N_2O_5 on the formation of nitrate (NO_3^-) and ammonium (NH_4^+) in Beijing. The results show that during heavy pollution days (e.g., during 14-17 September, 2015, with $\text{PM}_{2.5}$ concentration over $100 \mu\text{g}/\text{m}^3$), the concentrations of NO_2 and O_3 were high, with maxima of 90 and $240 \mu\text{g}/\text{m}^3$, respectively, providing high precursors for the formation of N_2O_5 . In addition, the aerosol and sulfate concentrations were also high, with maxima of $201 \mu\text{g}/\text{m}^3$ and $23 \mu\text{g}/\text{m}^3$ respectively, providing reacting surface for the heterogeneous reaction. As a result, the hydrolysis of N_2O_5 led to 21.0% enhancement of nitrate (NO_3^-) and 7.5% enhancement of ammonium (NH_4^+). It is worth to note that this important effect only occurred in high pollution days ($\text{PM}_{2.5}$ concentration over $100 \mu\text{g}/\text{m}^3$). During low-pollution periods ($\text{PM}_{2.5}$ concentration less than $100 \mu\text{g}/\text{m}^3$), the effect of hydrolysis of N_2O_5 on the formation of nitrate and ammonium was insignificant (variation rate $< 5\%$). This study suggests that during heavy pollution periods, the hydrolysis of N_2O_5 enhances the level of aerosol pollution in Beijing, and needs to be further studied in order to perform efficient air pollution control and mitigation strategies.

Key words: Hydrolysis of N_2O_5 , Nitrate and Ammonium, Beijing, WRF-Chem

1. Introduction

Currently, China is undergoing a rapid economic development, which results in a higher demand for energy, greater use of fossil fuels, and inevitably lead to more emission of pollutants into the atmosphere (He et al., 2015). Satellite observations have revealed much higher aerosol pollution in eastern China than in eastern US (Tie et al., 2006). The high aerosol pollution causes a wide range of environmental consequences. According to a study by Tie et al. (2009), exposure to extremely high particle concentrations leads to a great increase of lung cancer cases. High PM concentrations also significantly reduce the range of visibility (Deng et al., 2008; Cao et al., 2012) and enhance atmospheric acidity (Cao et al., 2013) in China's large cities. According to a recent study, the high aerosol pollution causes important effects on the crop (rice and wheat) production in eastern China (Tie et al., 2016).

Beijing, the capital of China, is a mega city with a population of more than 20 million (Tie et al., 2015). In recent years, the city has experienced heavy air pollution, with particulate matter (PM) being one of its top pollutants (Chan and Yao, 2008). In the last decade, extensive efforts have been made to characterize the sources, properties, and processes of PM in Beijing (Quan et al., 2014). Recent studies indicate that a large mass fraction of ambient PM in Beijing is fine particles, of which carbonaceous, sulfate, nitrate, and ammonium particles are major components (Guinot et al., 2007; He et al., 2001; Yang et al., 2011). Despite progress made by previous studies, there are still some important questions to be answered and addressed. For example, Tie et al. (2003) suggest that the hydrolysis of N_2O_5 on sulfate aerosols has important effect on tropospheric NO_x and O_3 budgets. Their study shows that this heterogeneous reaction is only important in high latitudes of the Northern hemisphere, where these conditions are occurred, such as (1) the sunlight is weak, (2) the sulfate concentrations are high, and (3) the precursors of N_2O_5 (O_3 and NO_2) are high.

In this study, the effect of the hydrolysis of N_2O_5 on nitrate (NO_3^-) and ammonium (NH_4^+) in Beijing, China is studied. Although Beijing locates in the middle latitude

(39.9°N) of the Northern hemisphere, these above conditions, which are favorable for the hydrolysis of N_2O_5 , are often occurred during high aerosol pollution periods. During these periods, the sulfate concentrations are very high (Zhang et al., 2013); the solar radiation is strongly reduced (Bian et al., 2007); and the concentrations of NO_x ($\text{NO}_x = \text{NO}_2 + \text{NO}$) are significantly increased (Quan et al., 2014). Thus, it is important to investigate the effects of the hydrolysis of N_2O_5 on nitrate (NO_3^-) and ammonium (NH_4^+) in Beijing, China.

In order to analyze the effects of the hydrolysis of N_2O_5 , a high pollution episode, characterized by high O_3 and NO_2 concentrations (the precursors of N_2O_5) and high sulfate and aerosol concentrations needs to be defined for the study. A chemical/dynamical regional model (WRF-Chem) is applied to study the effect of the hydrolysis of N_2O_5 . The paper is organized by the following ways. First, the model calculation is evaluated by comparing the model results with the measured values. Second, a model-sensitive study is conducted by using two model simulations. The first model simulation includes the hydrolysis of N_2O_5 , while the second simulation excludes this reaction. Comparing to former works, the main difference of this work is to investigate the effect of N_2O_5 hydrolysis under a heavy pollution period in Beijing, China. The N_2O_5 hydrolysis under this condition is very different compared to previous studies, providing a new highlight for the effect of N_2O_5 hydrolysis on the nitrate formation.

2. Model and Method

2.1 WRF-Chem Model description

The Weather Research and Forecasting (WRF) Model is a next-generation mesoscale numerical weather prediction system designed for both atmospheric research and operational forecasting needs. It features two dynamical cores, a data assimilation system, and a software architecture facilitating parallel computation and system

extensibility. The model serves a wide range of meteorological applications across scales from to hundreds of kilometers to thousands of kilometers. The effort to develop WRF began in the latter part of the 1990's and was a collaborative partnership principally among the National Center for Atmospheric Research (NCAR), the National Oceanic and Atmospheric Administration (NOAA), the National Centers for Environmental Prediction (NCEP), the Forecast Systems Laboratory (FSL), the Air Force Weather Agency (AFWA), the Naval Research Laboratory, the University of Oklahoma, and the Federal Aviation Administration (FAA). A detailed description of the WRF model can be found on the WRF web-site <http://www.wrf-model.org/index.php>. The WRF model includes on-line calculation of dynamical inputs (winds, temperature, planetary boundary layer (PBL) etc.), transport (advection, convection and diffusion), dry deposition (Wesely et al., 1989) and wet deposition. The planetary boundary layer (PBL) calculation uses Yonsei University (YSU) PBL scheme.

In addition to dynamical calculation, a chemical model is fully (on-line) coupled with the WRF model (WRF-Chem). A detailed description of WRF-Chem is given by Grell et al. (2005). The version of the model, as used in the present study, includes simultaneous calculation of chemical tracer transport (advective, convective, and diffusive), dry deposition (Wesely et al., 1989), gas-phase chemistry, radiation and photolysis rates (Madronich and Flocke, 1999; Tie et al., 2003), and surface emissions (including on-line calculation of biogenic emission). The chemistry is represented in the model by a modified version 2 (RADM2) gas-phase chemical mechanism (Chang et al., 1989), which includes 66 species. The model has been used to evaluate the air pollution and aerosol budget in the Beijing region, and the model results provide the insights of the model validation (Tie et al., 2015).

2.1 model configuration

This study uses a single domain, with $6\times 6\text{ km}^2$ resolution in the horizontal direction centered on Beijing, covering an area of $906\times 906\text{ km}^2$. Figure 1 shows the model domain and the topography in the Beijing area. The model runs from September 11, 2015 to September 20, 2015, and the results from September 12, 2015 to September 19, 2015 are used for the analysis.

This version of WRF-Chem was developed by Li et al. (2010, 2011a, b, 2012) at the Molina Center for Energy and the Environment, with a new flexible gas-phase chemical module and the Community Multiscale Air Quality (CMAQ) (version 4.6) aerosol module developed by the US EPA (Binkowski and Roselle, 2003). The wet deposition follows the method used in the CMAQ module and the dry deposition of chemical species is parameterized following Wesely (1989). The photolysis rates are calculated using the Fast Tropospheric Ultraviolet and Visible Radiation Model (Tie et al., 2003; Li et al., 2005), in which the impacts of aerosols and clouds on the photochemistry are considered (Li et al., 2011b). The model system employs the Lin microphysics scheme (Noh et al., 2001).

The chemical boundary conditions are taken from the global Model for Ozone and Related Chemical Tracers (Mozart-4) (Emmons et al., 2010; Tie et al., 2005). The emission inventory (EI) used in the present study is based on the 2006 official EI for the MCMA and adjusted according to observations, as described in Song et al. (2010). The anthropogenic emission of SO_2 , CO , NO_x , NH_3 and 32 individual classes of VOC according to the RADM2 mechanism are pre-calculated with a spatial resolution of $1\times 1\text{ km}^2$, with a temporal resolution of one hour (Zhang et al., 2009). The biogenic emissions are calculated online using the Model of Emissions of Gases and Aerosols from Nature (MEGAN). The NCEP $1^\circ \times 1^\circ$ reanalysis data are used to obtain the meteorological initial and boundary conditions.

2.2 Simulation information

This study is focused on the effect of heterogeneous hydrolysis of N_2O_5 on the sulfate surface, which is expressed by

Where (g) represents gas-phase. The precursor of N_2O_5 is formed by a chain of reactions, and is expressed as:

According to the expression, the effect the hydrolysis can be important, only when the following conditions are satisfied. As suggested by Tie et al. (2003), the N_2O_5 and NO_3 are very short in chemical lifetime, and only can exist in less sunlight conditions. The first condition is the high concentrations of aerosols, which lead to less sunlight and the surface for the heterogeneous hydrolysis of N_2O_5 as shown in R1. The second condition is the high concentrations of NO_2 and O_3 , which are the precursors of N_2O_5 (Dentener et al., 1993; Goulette et al., 2016). Thus, the conditions require coexisting of high concentrations of PM, NO_2 and O_3 . In this study, a persistent air pollution episode from 12 to 19 September, 2015 in Beijing is simulated using the WRF-Chem model. During the episode, the observed mean daily $\text{PM}_{2.5}$ and NO_2 concentration were 73.8 and 40.0 $\mu\text{g}/\text{m}^3$, respectively. The averaged O_3 concentration in the afternoon reached to 237.0 $\mu\text{g}/\text{m}^3$ in Beijing. In this period, the conditions were favorable for the hydrolysis of N_2O_5 .

The real-time hourly measurements of O₃, NO₂, CO and PM_{2.5} used in this study are released by China MEP and can be accessed from the website <http://106.37.208.233:20035/>. The historical profile of the observed ambient pollutants can be accessed at <http://www.aqistudy.cn/>. The O₃, NO₂, CO and PM_{2.5} concentrations are measured, respectively, by using Model 49i Ozone Analyzer, Model 42i (NO-NO₂-NO_x) Analyzer, and Model 5030 SHARP Monitor from Thermo Fisher Scientific, USA. All the instruments are maintained and routinely calibrated by China MEP to ensure data quality.

In order to quantify the contributions of the heterogeneous hydrolysis of N₂O₅ to the formation of nitrate and ammonium, a sensitive study is carried out by conducting 2 model simulations. The first model simulation includes the hydrolysis, while the second model simulation excludes this reaction.

3 Results and discussion

3.1 Measured and calculated temporal variations

Figure 2 shows the temporal variations of observed and simulated near-surface O₃, NO₂, CO and PM_{2.5} concentrations from 12 to 19 September, 2015 in Beijing, China. In order to evaluate the model simulation, we calculated statistical differences between measurements and calculations, including MB (mean bias), RMSE (root mean square error), and IOA (index of agreement).

$$MB = \frac{1}{N} \sum_{i=1}^N (P_i - O_i)$$

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^N (P_i - O_i)^2 \right]^{\frac{1}{2}}$$

$$IOA = 1 - \frac{\sum_{i=1}^N (Pi - Oi)^2}{\sum_{i=1}^N (|Pi - \bar{O}| + |Oi - \bar{O}|)^2}$$

Where P_i and O_i are the simulated and observed variables, respectively. N is the total number of the predictions used for comparisons, and $\bar{o}$ denotes the average of the observation. IOA ranges from 0 to 1, with 1 indicating perfect agreement between model and observation.

Because O_3 and NO_2 are important precursor for the heterogeneous reaction of N_2O_5 , it is important to evaluate the model calculations. The CO variation is also investigated, because CO can be considered as a chemical inert tracer (Zhang et al., 2015), which can be used to evaluate the dynamical transport of the model.

The measured O_3 variation shows that there was a strong diurnal variation of O_3 , especially during a high pollution period (from 14 to 17, September; defined as P-Period). During the high pollution period (P-Period), there was a strong O_3 diurnal variation, with a maximum of O_3 ($240 \mu g/m^3$). The calculated O_3 variation was consistent with the measured result, with a strong diurnal variation. However, the calculated maximum of O_3 was lower than the measured value (about $180 \mu g/m^3$). The concentrations of NO_2 were also very high during the P-Period. The NO_2 diurnal variation was reversed compared with the diurnal variation of O_3 . For example, the measured NO_2 concentrations were high during night and were low during daytime. During the nighttime, the maximum of NO_2 reached to $120 \mu g/m^3$, while in daytime, the minimum of NO_2 was about $30 \mu g/m^3$ during noontime. The calculated NO_2 diurnal variation was consistent with the measurement, while the calculated values during night showed some estimates. The high values of O_3 and NO_2 provided high precursors for the N_2O_5 formation.

The CO simulation was used to evaluate the calculation of model transport. As indicated in Fig. 2, the calculated CO variation was consistent with the measured CO variability. There was a similar tendency for both measured and calculated CO concentrations, i.e., it started a low value, and increased during the P-Period. After the P-Period, both the calculated and measured CO concentrations rapidly decreased.

Figure 2d shows the comparison of calculated PM_{2.5} concentrations with the measured values. The results suggest that the PM_{2.5} concentrations were low on 12 September, and rapidly increased to 180 µg/m³ on 17 September. After the P-Period, both the calculated and measured PM_{2.5} concentrations rapidly decreased. The calculated tendency was generally similar to the measured result. However, it also showed some discrepancy between the calculation and measurement. For example, the calculated PM_{2.5} had a larger variability than the measured result. The high aerosol concentrations were favorable for the hydrolysis of N₂O₅ in two aspects, i.e., (1) it provided the higher sulfate surface for the heterogeneous reactions.

During the P-Period, the measured aerosol composition (including sulfate (SO₄), nitrate (NO₃), ammonium (NH₄), chloride (Cl), three primary organic (OA)) were in this study. The composition were measured by an Aerodyne high-resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). As shown in Figure 3, during the P-Period, there was about 25% of sulfate aerosol in total aerosol mass in Beijing. (2) The sunlight was reduced due to high aerosol, which increased the lifetime of NO₃ and N₂O₅ in the lower atmosphere.

3.2 Measured and calculated spatial distributions

Figure 4 shows the measured (squares) and calculated (contours) horizontal distribution of noontime O₃ from 13 to 18 September, 2015. Arrows indicate the wind fields. The result suggested that the O₃ distribution was a regional and large-scale pollution. Because the chemical lifetime of O₃ is about months (Seinfeld and Pandis, 1998), the

high O₃ plumes can be transported from large cities to rural areas, and distributed in a large region. Figure 4 shows that the O₃ pollution was significantly affected by meteorological conditions. For example, during north wind condition (18 September), the clean O₃ plumes were transport to Beijing, resulting in lower O₃ concentrations. During the P-Period (from 14 to 17 September), there were persistent south winds, producing higher regional O₃ concentrations, with about 200 µg/m³ in Beijing.

Figure 5 shows the measured (squares) and calculated (contours) horizontal distribution of noontime NO₂ from 13 to 18 September, 2015. Unlike O₃, the chemical lifetime of NO₂ is short (about hours) (Seinfeld and Pandis, 1998). As a result, the high NO₂ concentrations were centered in high emission regions, such as large cities (Emberson et al., 2001). Figure 5 shows that the NO₂ concentrations were often higher than 100 µg/m³ in Beijing, while the concentrations were less than 10 µg/m³ in rural areas. This result suggests that the hydrolysis of N₂O₅ plays more important roles in large cities than in rural areas, because the NO₂ (the precursor of N₂O₅) are higher in cities (Emberson et al., 2001). In this study, we select the mega city (Beijing) as an example to illustrate the importance of the hydrolysis of N₂O₅ for the formation of nitrate.

3.3 Impacts of N₂O₅ heterogeneous reaction on nitrate formation

The occurrence of the hydrolysis of N₂O₅ requires the formation of N₂O₅, and the precursors of N₂O₅ are NO₂ and O₃ (Brown and Stark, 2003; Dentener et al., 1993; Zaveri et al., 2010; Riemer et al., 2009). As shown in Fig. 5, the concentrations of NO₂ were centered in large cites. As a result, the hydrolysis of N₂O₅ plays more important roles in cities than in rural areas. Figure 6 shows the concentrations of N₂O₅ with and without the hydrolysis of N₂O₅. The results indicate that there was a strong diurnal variation of N₂O₅ (Riemer et al., 2003). The higher N₂O₅ occurred during night due to more stable them-dynamical equilibrium condition, while lower N₂O₅ occurred during daytime due to less stable them-dynamical equilibrium condition (Lowe et al., 2015; Li et al., 1993; Morgan et al., 2015). There was an indication that the N₂O₅ concentrations

were significantly higher during the P-Period than the un-polluted period, suggesting that the hydrolysis of N_2O_5 can only be important during the heavy pollution days in Beijing. In non-P-Period, the changes of N_2O_5 concentrations were small. By contrast, during the P-Period, including the hydrolysis of N_2O_5 caused the 50-60% reduction of N_2O_5 , leading to significant conversion from N_2O_5 to nitrate (NO_3^-).

Figure 7 shows the formation of nitrate (NO_3^-) due the hydrolysis of N_2O_5 . The result suggests that during the P-period, the heterogeneous reaction (R1) had a significant contribution to the formation of NO_3^- . For example, by including the hydrolysis of N_2O_5 (R1), the maximum of NO_3^- concentrations was $15 \mu\text{g}/\text{m}^3$, while by excluding the hydrolysis of N_2O_5 (R1), it was $10 \mu\text{g}/\text{m}^3$ on 15 September. It is worth to note that the hydrolysis of N_2O_5 played important roles during the nighttime (Lowe et al., 2015). During daytime, the hydrolysis of N_2O_5 had a minor impact on the formation of nitrate concentrations. (Lin and Wang, 2016) This strong diurnal variation was consistent with the diurnal variation of N_2O_5 concentrations. As shown in Fig. 6, the concentrations of N_2O_5 were very low during daytime, and the hydrolysis of N_2O_5 produced a small effect on the formation of NO_3^- .

3.4 Impacts on ammonium

According to Seinfeld and Pandis (1998), an important production of ammonium nitrate (NH_4NO_3) is resulted primarily from the reaction of gas-phase ammonia (NH_3) and nitric acid (HNO_3) through the reaction:

The reaction (R5) produces more ammonium (NH_4^+), when the HNO_3 increases due to the hydrolysis of N_2O_5 (R1).

Figure 8 shows the changes in NH_4^+ due to the hydrolysis of N_2O_5 (R1). The result shows that the concentrations of NH_4^+ increased in the P-Period. There was also an

indication that the increases in NH_4^+ occurred during the nighttime, with a maximum increase on 15 September, with and without the hydrolysis of N_2O_5 , the maximum concentrations of NH_4^+ were 7.0 and 5.5 $\mu\text{g}/\text{m}^3$, respectively. This shows that the hydrolysis of N_2O_5 had not only important effect on the formation of nitrate (NO_3^-), but also played important roles for the formation of ammonium (NH_4^+).

3. Summary

Beijing, the capital of China, is a mega city with a population of more than 20 million. Currently, Beijing is under going a rapid economic development, which results in a higher demand for energy, greater use of fossil fuels, and inevitably lead to more emission of pollutants into the atmosphere. In recent years, the city has experienced heavy air pollution, with particulate matter (PM) being one of its top pollutants. In the last decade, extensive efforts have been made to characterize the sources, properties, and processes of PM in Beijing. Despite progress made by previous studies, there are still some important questions to be answered and addressed. In this study, the effect of hydrolysis of N_2O_5 on the formation of nitrate (NO_3^-) and ammonium (NH_4^+) is studied. The results show the following highlights;

- (1) The effect of hydrolysis of N_2O_5 on the formation for nitrate and ammonium was significant during heavy pollution days. For example, during 14-17 September, 2015, the concentrations of NO_2 and O_3 were high, with maxima of 90 and 240 $\mu\text{g}/\text{m}^3$, respectively, providing high concentrations of precursors for the formation of N_2O_5 . During the pollution period, the aerosol and sulfate concentrations were also high, providing favorable conditions for the hydrolysis of N_2O_5 .
- (2) During the pollution period, the hydrolysis of N_2O_5 produced 21.0% of nitrate (NO_3^-) and 7.5% of ammonium (NH_4^+).
- (3) The effect of hydrolysis of N_2O_5 on the formation for nitrate and ammonium was insignificant during low pollution periods, due to the fact that there was lack of the precursors of N_2O_5 and the aerosol surfaces for occurring the heterogeneous

reaction.

This study suggests that during heavy pollution days, the hydrolysis of N_2O_5 enhanced the level of aerosol pollution in Beijing, and needs to be further studied to perform efficient air pollution control and mitigation strategies.

It is also worth noting that, although the WRF-Chem model well captures the spatial distributions and temporal variations of pollutants, the model biases still exist. The discrepancies between the simulations and observations are possibly caused by the uncertainties in the emission inventory and the meteorological fields simulations. Future studies need to be conducted to improve the WRF-Chem model simulations and emissions.

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Figure Caption

Figure 1. The model domain and topographic map of Beijing. The red dot represents the city of Beijing. The white squares indicate the measurement sites nearby Beijing.

Figure 2. The measured (black dots) and compared with the calculated (red lines) temporal variations of near-surface O_3 , NO_2 , CO and $PM_{2.5}$ concentrations from 12 to 19 September, 2015 in Beijing, China. The blue line represent a high pollution period with high concentrations of O_3 , NO_2 , and $PM_{2.5}$ (defined as P-Period).

Figure 3. The measured averaged percentage (%) of aerosol chemical composition during the P-Period (14 to 17 September, 2015) in Beijing, China.

Figure 4. The measured (squares) and calculated (contours) horizontal distribution of noontime O_3 from 13 to 18 September. Arrows indicate the wind fields.

Figure 5. The measured (squares) and calculated (contours) horizontal distribution of noontime NO_2 from 13 to 18 September. Arrows indicate the wind fields.

Figure 6. The calculated concentrations of N_2O_5 with and without the hydrolysis of N_2O_5 . Green and Red lines represent the calculations with and without the hydrolysis of N_2O_5 .

Figure 7. The calculated concentrations of nitrate (NO_3^-) with and without the hydrolysis of N_2O_5 . Green and red lines represent the calculations with and without the hydrolysis of N_2O_5 , respectively.

Figure 8. The calculated concentrations of ammonium (NH_4^+) with and without the hydrolysis of N_2O_5 . Green and red lines represent the calculations with and without the hydrolysis of N_2O_5 , respectively.

Table 1. Statistical comparison of simulated and measured O₃, NO₂, CO, PM_{2.5} from 12 to 19 September, 2015.

Species	MB	RMSE	IOA
O ₃	2.22	17.30	0.88
NO ₂	-2.66	10.60	0.80
CO	-0.22	0.11	0.90
PM _{2.5}	5.31	22.52	0.83

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