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

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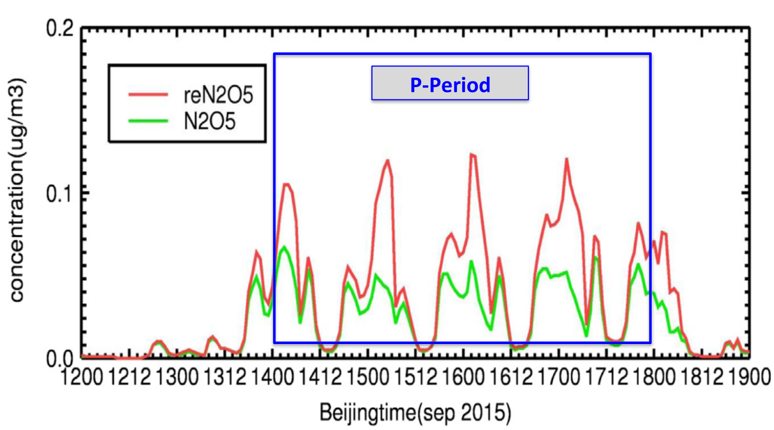
HIGHLIGHTS

- Effect of heterogeneous hydrolysis of N_2O_5 on aerosol pollution in Beijing, China is studied.
- The hydrolysis has important effect on the formation of nitrate (NO_3^-) and ammonium (NH_4^+) during pollution days.
- During low-pollution periods, the effect of hydrolysis of N_2O_5 is insignificant.
- A regional dynamical/chemical model WRF-Chem is applied.

GRAPHICAL ABSTRACT



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ABSTRACT

Beijing, the capital of China, is a mega city with a population of >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 $PM_{2.5}$ concentration over 100 μg/m^3), the concentrations of NO_2 and O_3 were high, with maxima of 90 and 240 μg/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 μg/m^3 and 23 μg/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 ($PM_{2.5}$ concentration over 100 μg/m^3). During low-pollution

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periods ($PM_{2.5}$ concentration <100 μg/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.

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 >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. (2003a) 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 NOx ($NO_x = NO_2 + NO$) 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 website 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, 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 (online) 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, 1989), gas-phase chemistry, radiation and photolysis rates (Madronich and Flocke, 1999; Tie et al., 2003a,b), 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).

2.2. Model configuration

This study uses a single domain, with 6×6 km^2 resolution in the horizontal direction centered on Beijing, covering an area of 906×906 km^2. Fig. 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., 2003a,b), in which the impacts of aerosols and clouds on the photochemistry are considered (Li et al., 2011b).

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