Short communication

Modeling the effect of relative humidity on nitrous acid formation in the Houston area

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HIGHLIGHTS

- Implementing relative humidity dependence of HONO heterogeneous reaction.
- Including relative humidity effect slightly reduces simulated NO_2 mean bias.
- Including relative humidity effect improves simulated HONO concentrations.

ARTICLE INFO

ABSTRACT

The field and laboratory based relative humidity (RH) impact on nitrous acid (HONO) heterogeneous reaction has not been considered in chemical transport models. This study parameterized this dependency into the Community Multiscale Air Quality (CMAQ) model. In view of the positive linear correlation between the reaction rate and RH, the HONO heterogeneous reaction rate constants were respectively scaled by the factors of RH/30 and RH/40. Two corresponding sensitivity tests were carried out in the period of September 2013 in Houston. Both tests significantly improved modeled HONO concentrations and reduced the bias for NO_2 in comparison with observations. However, the model is still not capable of reproducing the high HONO concentrations in the morning rush hours. Further work is needed to explore the underlying mechanisms for the early morning HONO formation.

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1. Introduction

The Houston-Galveston-Brazoria (HGB) area is classified as a marginal ozone nonattainment area under the 2008 8-h National Ambient Air Quality Standards (NAAQS) of 75 ppb by the United States Environmental Protection Agency (US EPA) (http://www.epa.gov/airquality/greenbook/hnc.html), thus sometimes experiencing elevated ozone levels. There were twenty-five ozone exceedance days in 2013 in this region with the highest daily maximum 8-h concentration of 124 ppb at La Porte on September 25 (http://www.tceq.texas.gov). Ozone production is driven by interactions between volatile organic compounds (VOCs) and nitrogen oxides (NO_x) in the presence of sunlight. The hydroxyl radical (OH) plays a crucial role in the oxidation of VOCs, particularly in urban areas

(e.g., Seinfeld and Pandis, 2006; Atkinson, 2000). A significant source of OH (especially in the morning) is nitrous acid (HONO) via photolysis as explained by Czader et al. (2012), Kleffmann et al. (2005), Alicke et al. (2003, 2002) and Lammel and Cape (1996).

However, current understanding of HONO formation in the atmosphere is limited as there are uncertainties related to its formation pathways and their importance in the total budget of HONO. Since the well-known homogeneous HONO formation from NO and OH (reaction (R1)) gets reversed in the atmosphere (Calvert et al., 1994), it is generally believed that the predominant atmospheric HONO source is the heterogeneous hydrolysis of nitrogen dioxide (NO_2) on humid surfaces outlined in reaction (R2) (e.g., Kleffmann, 2007; Stemmler et al., 2006; Jacob, 2000; Kleffmann et al., 1998; Svensson et al., 1987; Harris et al., 1982):

$$NO + OH \rightarrow HONO \tag{R1}$$

$$2\,NO_2 + H_2O \rightarrow HONO + HNO_3 \tag{R2}$$
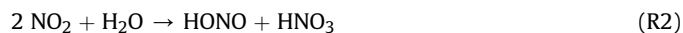
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Evidences supporting the conversion from NO_2 to HONO have been documented by several field campaigns in the recent past (e.g., Li et al., 2012; Su et al., 2008). Other chemical sources have also been proposed—for example the gas-phase formation from photo excited NO_2 (Wentzell et al., 2010; Li et al., 2008), and the heterogeneous conversion from nitric acid on aerosol surfaces (Ziemba et al., 2010). Additionally, HONO can be directly emitted from combustion sources such as mobile exhaust (Kurtenbach et al., 2001).

The heterogeneous HONO reaction (R2) has been implemented into 3-dimensional air quality models and substantially improved the simulation of HONO concentrations (Karamchandani et al., 2015; Czader et al., 2013, 2012; Foley et al., 2010; Sarwar et al., 2008). Laboratory studies have reported that the rate of HONO formation appears linear with water vapor content over a limited range of relative humidity (RH) (Finlayson-Pitts et al., 2003; Jenkin et al., 1988; Svensson et al., 1987; Pitts et al., 1984; Sakamaki et al., 1983). The water dependence of the HONO heterogeneous reaction in the real atmosphere is as yet unclear because of the lack of thorough studies. Based on data from different environments, Stutz et al. (2004) showed that the maximum [HONO]/[NO_2] ratio at the pseudo steady state (PSS) linearly increased with RH, and recommended parameterizing RH in chemical transport models to represent HONO formation correctly. Tong et al. (2015) and Hao et al. (2006) also observed that for urban and suburban regions in China, RH lineally promoted NO_2 to HONO conversion up to the RH value of 85%. Humidity in southeastern Texas is usually high, especially during summer and early fall when it can reach 80–90% during night times and early morning. Through this work, we will investigate the effect of relative humidity on HONO formation, and how the incorporation of the RH dependence affects model-measurement comparison.

2. Methodology

2.1. Measurements

The study period was September 2013 when the National Aeronautics and Space Administration (NASA)'s Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) field campaign was conducted in Houston. HONO was measured on several days by an in-situ instrument, long path absorption photometer (LOPAP) atop the University of Houston (UH)'s North Moody Tower (MT) (~70 m above ground level), 4 km southeast of downtown Houston. The accuracy of the measurements is within ±(10–15)%. A detailed description of the measuring system was given by Heland et al. (2001). In-situ measurements of NO_2 and RH in conjunction with HONO were also obtained.

2.2. Model setup

We used CMAQ model version 5.0.2 (Byun and Schere, 2006) using the Weather Research and Forecasting (WRF) model (Skamarock et al., 2008) to provide meteorological inputs. The model domain was built over 84 × 66 grid cells (4 km spatial resolution as depicted in Fig. 1) and 27 vertical layers. Another 12-km domain over the continental United States (US) provided initial and boundary conditions. The Carbon Bond 05 (CB05) chemistry mechanism (Yarwood et al., 2005) was chosen to represent gas-phase chemistry. Anthropogenic emission rates were taken from US EPA's National Emission Inventory 2011 (NEI 2011; http://www.epa.gov/ttn/chief/net/2011inventory.html), and model-ready emissions were prepared by the Sparse Matrix Operator Kernel Emissions (SMOKE) v3.6 model. Additional details of the modeling
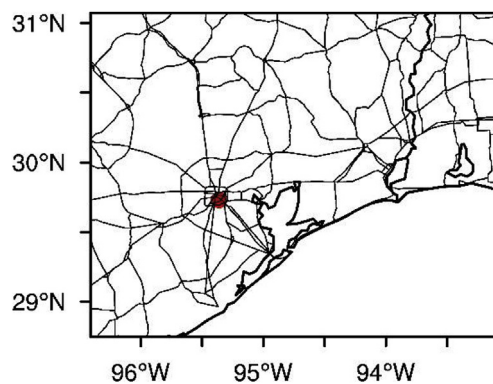

Fig. 1. The model domain with road map. The red dot represents Moody Tower measuring site. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

system are explained by Czader et al. (2015) and Pan et al. (2015). NEI 2011 was used for the current study as compared to NEI 2008 for them.

2.3. Parameterization of RH in the HONO heterogeneous reaction

In addition to the above mentioned reactions ((R1) and (R2)), another gas-phase reaction forming HONO in CMAQ is:

$$NO + NO_2 + H_2O \rightarrow 2\ HONO \tag{R3}$$
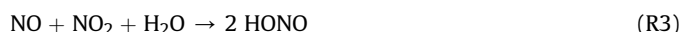
That pathway is insignificant for its slow reaction rate (Jacob, 2000). HONO is removed via photolysis (R4) and other gas-phase reactions ((R5) and (R6)):

$$HONO \rightarrow NO + OH \tag{R4}$$

$$OH + HONO \rightarrow NO_2 \tag{R5}$$

$$2\ HONO \rightarrow NO + NO_2 \tag{R6}$$

The HONO heterogeneous reaction (R2) is coded apart from gas-phase reactions in CMAQ and the product HNO_3 stays on the surface. The rate constant $k_{het} = 5.0 \times 10^{-5}(S/V)[s^{-1}]$ was derived by Kurtenbach et al. (2001) in a road traffic tunnel experiment, where S/V is the surface to volume ratio. The ratio takes account of both vegetation and urban structures, and varies over time and location. Refer to Zhang et al. (2011) for more detailed descriptions of the ratio. Aerosol surfaces are included in the model separately (Sarwar et al., 2008). The urban ground surface generally provides much bigger reactive areas than aerosol surfaces. During the study period, there were no highly polluted days with the monthly mean aerosol concentration of 9.65 μg/m³ (Supplementary Fig. S3). Two exceptional days were September 15th and 25th when the daily maximum aerosol concentrations exceeded 30 μg/m³ probably due to biomass burning.

Similar to the methodology of Gonçalves et al. (2012), we parameterized the RH dependence of the heterogeneous reaction through scaling the default rate constant of the reaction (R2) by factors of RH/30 and RH/40 respectively as in Eq. (1):

$$k_{het} = 5.0 \times 10^{-5} \cdot \frac{RH}{30\ (or\ 40)} \left(\frac{S}{V}\right) \tag{1}$$

with RH in %. This approach is based on the assumption that the unknown original RH value of the tunnel experiment was around