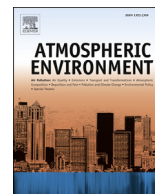




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# Implementation and refinement of a surface model for heterogeneous HONO formation in a 3-D chemical transport model

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## HIGHLIGHTS

- New module to represent surface heterogeneous HONO formation in grid model.
- Addresses under-predictions of HONO concentrations by grid models.
- Model performance for HONO strongly dependent on performance for NO<sub>2</sub> and HNO<sub>3</sub>.
- Modeled HONO:NO<sub>2</sub> and HONO:HNO<sub>3</sub> ratios compare well with observed ratios.
- Approach provides framework for future refinement based on scientific advances.

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## ABSTRACT

The photolysis of nitrous acid (HONO) is a potentially significant daytime source of the hydroxyl radical, OH, one of the main chemical species that controls the oxidizing capacity of the atmosphere and plays an important role in ozone and PM<sub>2.5</sub> formation. Research based on both field measurements and modeling has shown that HONO significantly affects the HO<sub>x</sub> budget in urban environments. Measurements during the Study of Houston Atmospheric Radical Precursors (SHARP) showed that radical production in the early morning in Houston was dominated by HONO photolysis. Field and laboratory studies suggest that nighttime heterogeneous conversion of NO<sub>2</sub> on ground or aerosol surfaces, as well as daytime photolysis of HNO<sub>3</sub> and NO<sub>2</sub> adsorbed onto ground surfaces, can be important sources of HONO. Air quality models that only simulate homogeneous formation of HONO have been shown to substantially under-estimate observed HONO concentrations. Direct emissions of HONO also cannot explain the high HONO:NO<sub>2</sub> ratios often measured in the boundary layer. These findings indicate that heterogeneous HONO formation plays an important role in the atmosphere. Previous approaches to include heterogeneous HONO formation in photochemical models have used surface to volume ratios to parameterize the chemistry on ground and aerosol surfaces. This paper describes the adaptation of a photochemical model to explicitly include a surface model that allows the treatment of the surface as a reservoir of deposited species that can be sorbed or penetrate into soils and vegetation, and undergo chemical degradation and transformation, and volatilization back into the air (re-emissions). The reactions in the surface model include HONO formation from thermal and photolytic reactions of deposited NO<sub>2</sub> and HNO<sub>3</sub>. The parameterizations for surface heterogeneous production of HONO are evaluated and refined using existing modeling databases for the Houston area during the SHARP study period. A companion paper describes the impacts of the new HONO formation pathways on radical sources and ozone chemistry in the Houston area.

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## 1. Introduction

Nitrous acid (HONO) plays an important role in atmospheric chemistry, since its photolysis leads to the rapid formation of the

hydroxyl radical, OH, during the early morning hours and even during the daytime in urban areas with high NO<sub>x</sub> levels (e.g., Elshorbany et al., 2012). The hydroxyl radical is extremely reactive and is the most important oxidizing species in the atmosphere. Its formation and reactions with volatile organic compounds (VOCs) in the presence of NO<sub>x</sub> initiates the radical chain oxidation cycle involving OH and the peroxy radical, HO<sub>2</sub>, collectively referred to as HO<sub>x</sub>, leading to the formation of ozone and other products, including inorganic and organic secondary particulate matter. The contribution of HONO photolysis to the total OH budget during the day can reach from 33 to 56% in urban, rural and forest environments (e.g., Alicke et al., 2002, 2003; Aumont et al., 2003; Kleffmann et al., 2005; Acker et al., 2006a, 2006b; Hofzumahaus et al., 2009; Liu et al., 2012; Tang et al., 2015).

Although the importance of HONO in influencing atmospheric chemistry is well recognized, the mechanisms leading to HONO formation are not as well understood. Potential sources of atmospheric HONO include production by homogeneous gas-phase reactions, direct emissions from combustion sources, e.g., in vehicle exhaust, or production by heterogeneous reactions on ground or aerosol surfaces. The dominant homogeneous HONO formation pathway in mechanisms commonly employed in photochemical models (e.g., Yarwood et al., 2005; Carter, 2010) is the gas-phase reaction of OH with NO (the reverse reaction to HONO photolysis). However, this pathway becomes insignificant at night because OH concentrations are negligible, and does not explain observed nocturnal and early morning HONO levels (e.g., Su et al., 2008; Wang et al., 2013).

Recent field observations have found unexpectedly high daytime HONO concentrations in both rural (e.g., Kleffmann et al., 2005; Acker et al., 2006b; Zhou et al., 2007; Li et al., 2012) and urban (e.g., Acker et al., 2006a; Elshorbany et al., 2009; Wong et al., 2012; Spataro et al., 2013) areas. These high daytime levels also cannot be explained by the homogeneous pathways for HONO formation currently included in photochemical models. Modeling studies with the U.S. EPA Community Multiscale Air Quality (CMAQ) model (e.g., Sarwar et al., 2008; Czader et al., 2012) and the Weather Research and Forecasting model with chemistry (WRF-Chem) (e.g., Li et al., 2010, 2011) have also shown consistently large (order of magnitude) under-predictions of observed HONO levels when only the gas-phase HONO formation pathway is included.

Other potential gas-phase formation pathways for HONO have been proposed, such as the daytime reaction of photoexcited NO<sub>2</sub> with water vapor (e.g., Li et al., 2008) to form HONO and OH, and the photolysis of ortho-nitrophenols (Bejan et al., 2006). Wennberg and Dabdub (2008) incorporated the reaction of Li et al. (2008) in a 3-D model simulation of a 1987 ozone episode in the South Coast Air Basin and found large impacts on ozone concentrations. They noted, however, that ozone concentrations were overestimated and that the rate of the reaction proposed by Li et al. (2008) was an order of magnitude higher than that found earlier by Crowley and Carl (1997). Other studies (e.g., Carr et al., 2009; Sarwar et al., 2009; Sörgel et al., 2011; Wong et al., 2013) indicate that the contribution of the photoexcited NO<sub>2</sub> reaction is small and Wong et al. (2012) argue that the photolysis of ortho-nitrophenols is also not a likely source of HONO in the polluted atmosphere of Houston.

More recently, Li et al. (2014) conducted observations of HONO onboard a Zeppelin airship and their findings suggest evidence for a strong gas-phase source of HONO consuming nitrogen oxides and potentially hydrogen oxide radicals. Rutter et al. (2014) have also proposed the reduction of HNO<sub>3</sub> on hydrocarbons as a possible source of HONO. These newly proposed formation pathways have not been independently analyzed in the field or the laboratory. Thus, their significance is highly uncertain, and more work,

especially in the laboratory, is required before these new mechanisms can be quantitatively included in models. In addition, many of these processes do not explain observed nighttime HONO levels. The analysis by Wong et al. (2012), who found a stronger correlation of the missing daytime HONO source with irradiance than with actinic flux, as well as the interpretation of vertical concentration profiles of HONO by Wong et al. (2013), favor a non-gas-phase source in an urban polluted atmosphere.

A number of field studies (e.g., Kleffmann et al., 2003; Wong et al., 2011, 2012, 2013; VandenBoer et al., 2013; Villena et al., 2011) and direct surface flux experiments (e.g., Ren et al., 2011; Zhang et al., 2012a) have measured large vertical gradients in HONO concentrations, with higher concentrations near the surface. This suggests the existence of surface sources of HONO, such as direct HONO emissions from combustion sources and heterogeneous reactions on ground surfaces. However, direct HONO emissions are believed to be less than 1% of NO<sub>x</sub> emissions, (Kirchstetter et al., 1996; Kurtenbach et al., 2001), although Rappenglück et al. (2013) suggest that the HONO to NO<sub>x</sub> ratio in vehicle emissions can be as high as 1.7% based on ambient air measurements taken at a highway junction in Houston.

Direct HONO emissions do not completely explain observed ambient HONO levels and HONO to NO<sub>2</sub> ratios. These ratios have been observed to range from 1 to 10% with an average value of about 4 to 6% in a number of studies in both urban and rural regions (e.g., Kleffmann et al., 2003; Acker et al., 2004, 2005, 2006a, 2006b; Stutz et al., 2004; Spataro et al., 2013). Hendrick et al. (2014) recently reported HONO to NO<sub>2</sub> ratios ranging from 1 to 8% based on four years of ground-based observations of HONO and NO<sub>2</sub> in the Beijing area. Wong et al. (2013) conducted 1D model simulations for Houston and attributed only 8–10% of the observed daytime HONO during the SHARP study period to traffic emissions in Houston. Sensitivity studies conducted with CMAQ, in which direct HONO emissions were included as 0.8% of NO<sub>x</sub> emissions in addition to the homogeneous gas-phase HONO formation pathway, showed large under-predictions of observed HONO levels (Sarwar et al., 2008; Gonçalves et al., 2012).

These findings indicate that there are heterogeneous pathways for both nocturnal and daytime HONO formation that need to be included in photochemical air quality models to explain observed HONO levels. The following section summarizes our current understanding of these heterogeneous pathways.

## 2. Heterogeneous pathways for atmospheric HONO formation

It is currently believed that a major source of nocturnal HONO is the heterogeneous hydrolysis of NO<sub>2</sub> on humid surfaces (e.g., Finlayson-Pitts et al., 2003; Ramazan et al., 2006; de Jesus Medeiros and Pimentel, 2011). Using a 1D chemistry and transport model, Wong et al. (2011) showed that this mechanism, together with an accurate description of vertical mixing, is able to successfully explain the nocturnal HONO observations in Houston. This mechanism also seems to depend on the amount of water adsorbed on the surface, i.e. the relative humidity, as pointed out by Stutz et al. (2004). Vertical nighttime profile measurements (e.g., Kleffmann et al., 2003; Wong et al., 2011; VandenBoer et al., 2013) suggest that NO<sub>2</sub> to HONO conversion on the ground is the dominant source of nocturnal HONO.

The nocturnal (or “dark”) heterogeneous HONO formation pathway is also operational during the day. However this mechanism is insufficient to explain observed daytime HONO levels (e.g., Wong et al., 2013). Observations in laboratory and field experiments over the past decade indicate the existence of other daytime heterogeneous HONO formation pathways. The two most likely daytime mechanisms occur on surfaces (e.g., ground, aerosols) and

are photolytically enhanced. Thus, HONO formation rates from these reactions are much faster in the presence of solar light than from the nocturnal HONO formation reaction described above. The first mechanism is the photolysis of surface adsorbed nitric acid (HNO<sub>3</sub>) (Zhou et al., 2002, 2011; Beine et al., 2002; Dibb et al., 2002; Zhou et al., 2003; Ramazan et al., 2004; Clemmshaw, 2006). This mechanism is believed to be important under low-NO<sub>x</sub> conditions (e.g., Zhou et al., 2003; Elshorbany et al., 2012). The second is the photo-enhanced conversion of gas-phase NO<sub>2</sub> on organic films or surfaces commonly found on the ground or aerosols (e.g., George et al., 2005; Stemmler et al., 2006, 2007). This mechanism dominates under high-NO<sub>x</sub> urban conditions (e.g., Elshorbany et al., 2012).

Reactions on aerosol surfaces have also been suggested as important sources of HONO under certain conditions (e.g., Stemmler et al., 2007; Ziemba et al., 2010; Li et al., 2011; Ma et al., 2013). However, most studies indicate that the photolysis of adsorbed NO<sub>2</sub> or HNO<sub>3</sub> on ground surfaces plays a more important role in daytime HONO production than the corresponding reactions on aerosol surfaces. In a 3-D modeling study, Gonçalves et al. (2012) included heterogeneous NO<sub>2</sub> hydrolysis on both ground and aerosol surfaces and found that the effects of NO<sub>2</sub> hydrolysis on aerosol surfaces were negligible.

Measurements taken during the 2006 Texas Air Quality Study (TexAQS) and the 2009 SHARP campaign showed strong vertical HONO concentration gradients during the day with higher values near the ground, which modeled homogeneous chemistry did not predict (e.g., Czader et al., 2012; Wong et al., 2012). Wong et al. (2012) hypothesized that the missing HONO formation pathways are photolytic and occur on or near the ground. Wong et al. (2013) used a one-dimensional chemistry and transport model to analyze daytime HONO and NO<sub>2</sub> vertical profiles, measured at three different height intervals in Houston, TX, during the 2009 SHARP field study. Using the SHARP data, they found that photolytic HONO formation at the ground was the major formation pathway in the lowest 20 m, while a combination of gas-phase, photolytic formation on aerosol, and vertical transport was responsible for daytime HONO between 200 and 300 m. High-resolution daytime vertical profiles of HONO measured during the winter 2011 Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) experiment also suggest that most of the daytime HONO production occurs on the ground surface (VandenBoer et al., 2013).

Based on these findings, we adopted a process-based approach to include a surface model for heterogeneous formation of HONO in the Comprehensive Air quality Model with extensions (CAMx; ENVIRON, 2014), a photochemical model that is used routinely for regulatory applications in Texas and other areas. Additional gas-phase formation processes, which have been recently proposed in the literature, were not considered in this study since these mechanisms and their significance are still highly uncertain as discussed previously. The new surface model provides a framework from which parameters can be further refined as our understanding of atmospheric HONO sources increases, leading to improvements in HONO predictions from the model. A companion paper (Couzo et al., submitted for publication) describes the use of process analysis to understand the impacts of these updates to the model on radical sources and ozone chemistry in the Houston area.

### 3. Surface model for HONO formation in CAMx

Several recent modeling studies with CMAQ (e.g., Sarwar et al., 2008; Czader et al., 2012; Gonçalves et al., 2012; Zhang et al., 2012b) and WRF-Chem (e.g., Li et al., 2010, 2011; Tang et al., 2015) have considered additional mechanisms for HONO formation, and have found improvement in model performance, although

the degree of improvement is variable depending upon the approach used. The Supplemental Section provides a brief review of the methods and results from some of these modeling studies. These previous studies considered multiple sources for HONO and followed a generally similar approach in characterizing the heterogeneous formation pathways, using parameterizations of surface to volume ratios and uptake coefficients. The surfaces could include aerosols, buildings, and/or the ground. This type of parameterization is a useful approximation for ground surfaces, but does not accurately represent the actual processes occurring on the ground. The approach in the study described here is based on a surface model that acts as a reservoir for deposited species and simulates surface processes such as deposition, sorption and penetration into soils and vegetation, chemistry, and volatilization back into the air. It should be noted that surface process modeling has previously been implemented in other air quality models, such as CMAQ, to simulate bidirectional fluxes of gases such as mercury (e.g., Bash et al., 2007; Bash, 2010) and ammonia (Pleim et al., 2013; Fu et al., 2015). Pleim and Ran, (2011) provide a comprehensive review of surface flux modeling for air quality applications.

The CAMx surface model tracks the accumulation of deposited mass on terrestrial surface media (soil and vegetation) for subsequent physical removal (leaching into soil and penetration into plant tissue), heterogeneous chemical transformations of adsorbed material including both photolytic and non-photolytic (thermal) reactions, and re-emission to the atmosphere by volatilization (Fig. 1). Deposition to water surfaces is assumed to be irreversible and thus is not tracked by the surface model. Table 1 lists the key model variables.

At every time-step in CAMx, the newly deposited mass is divided among soil and vegetation according to land-use dependent split factors, and added to total surface mass accumulated during the model run. The surface model uses partitioning (equilibrium) coefficients to calculate the amount of accumulated material sorbed to soil and vegetation. As shown in Fig. 1, the sorbed fraction is subject to chemical reactions and physical removal associated with leaching deep into the soil and penetration into plant tissue. Chemistry can decay deposited material as a removal process, or it can generate products that can be subsequently re-emitted. All surface removal processes are assumed to be irreversible and result in a permanent removal of mass. The fraction not sorbed to the surface media can be re-emitted based on chemical-specific soil–air and vegetation–air partitioning coefficients. These coefficients represent the equilibrium ratio of chemical on a surface to chemical in air at the air–surface interface.

Chemistry, soil leaching, and plant penetration are dependent on chemical properties of the adsorbed species and also on numerous site-specific factors such as soil and vegetation properties, highly transient meteorological conditions, etc. These factors are often unknown or fall within a range. The rates of these processes are defined as the process rate coefficient (*k*) times the mass on the surface area, or areic mass (*A*):

$$R_{\text{process}} = k_{\text{process}} \times A_{\text{surface}}$$

The approach for re-emission of volatilized (unsorbed) mass is consistent with the CAMx dry deposition algorithm that is based on Wesely (1989). Since water surfaces are not considered by the surface model, re-emission fluxes from water are precluded in this implementation. In CAMx, dry deposition of material from the lowest model layer to the surface is treated as an irreversible first-order flux through the use of a dry deposition velocity. Deposition velocity is calculated based on the electrical resistance analog:

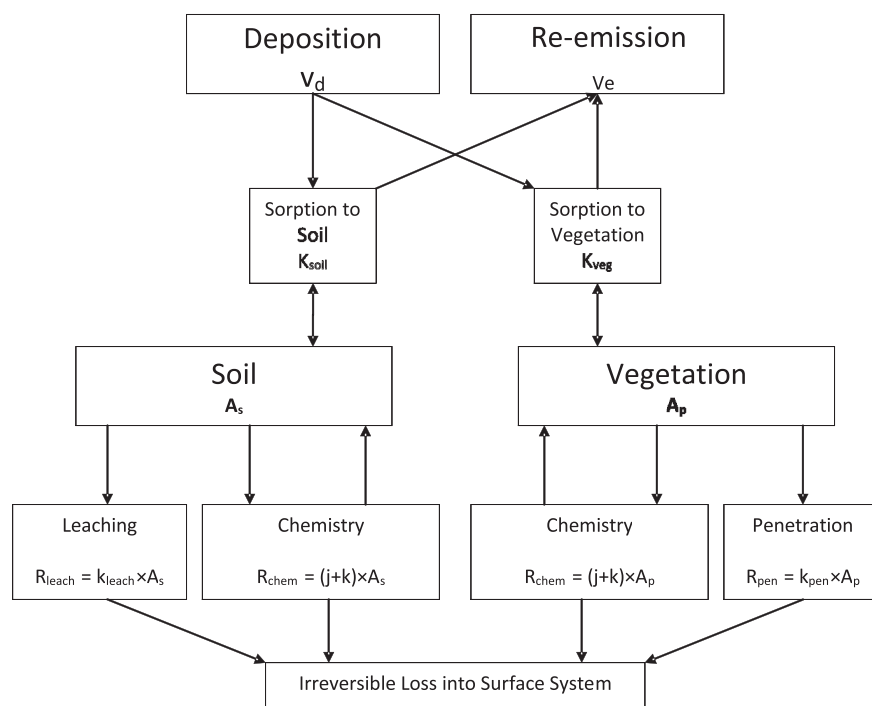


Fig. 1. Schematic of the CAMx surface model. See Table 1 for a description of the surface model parameters.

**Table 1**  
Description of CAMx surface model variables.

| Variable    | Definition                               | Units                                |
|-------------|------------------------------------------|--------------------------------------|
| $A_p$       | Areic mass of compound on vegetation     | $\text{mol ha}^{-1}$                 |
| $A_s$       | Areic mass of compound on the soil       | $\text{mol ha}^{-1}$                 |
| $K_{veg}$   | Vegetation-air partitioning coefficient  | unit-less                            |
| $K_{soil}$  | Soil-air partitioning coefficient        | unit-less                            |
| $k_{leach}$ | Leaching rate coefficient                | $\text{min}^{-1}$                    |
| $k_{pen}$   | Leaf penetration rate coefficient        | $\text{min}^{-1}$                    |
| $j$         | Photolysis chemistry rate coefficient    | $\text{min}^{-1}$                    |
| $k$         | Heterogeneous chemistry rate coefficient | $\text{min}^{-1}$                    |
| $R_{leach}$ | Leaching rate                            | $\text{mol ha}^{-1} \text{min}^{-1}$ |
| $R_{pen}$   | Leaf penetration rate                    | $\text{mol ha}^{-1} \text{min}^{-1}$ |
| $R_{chem}$  | Chemistry rate                           | $\text{mol ha}^{-1} \text{min}^{-1}$ |

$$v_d = \frac{1}{r_a + r_b + r_s}$$

Where the  $r$  values represent transfer “resistances” for various components of the circuit path: turbulent transfer through the surface layer and into the canopy ( $r_a$ ); diffusive transfer through the thin laminar layer in contact with the surface ( $r_b$ ); and an effective sorption resistance to a particular surface type ( $r_s$ ). The deposition velocity is thus dependent on atmospheric conditions, species characteristics (diffusivity, reactivity, solubility), and surface characteristics (e.g., landuse type). Dry deposition includes sorption to the surface, so it is considered a one-way irreversible process in CAMx.

The re-emission of volatilized mass is also treated as a first-order 1-way flux using an “effective” velocity that is similar in form to  $v_d$ :

$$v_e = \frac{1}{r_a + r_b}$$

The surface resistance term,  $r_s$ , is missing in the equation for  $v_e$

since only the pre-determined unsorbed fraction of surface mass is considered for surface-to-air transfer. The  $r_a$  and  $r_b$  terms are calculated by the surface model in exactly the same manner as the values used for dry deposition to ensure consistency.

Table 2 lists the key parameters that need to be specified for each chemical species for the surface model calculations. These are a subset of the full list of parameters shown previously in Table 1. Because there are considerable uncertainties associated with these parameters and their values, a semi-empirical approach was used in this study to refine the values of these parameters in an iterative manner. Initial values for these parameters were first assigned based on consideration of the physical and chemical attributes of the species participating in surface reactions believed to produce HONO. CAMx (with the surface model) was then applied for a period during the 2009 SHARP study, and model results were compared with measurements. A number of sensitivity studies were then conducted to determine the parameter set that best captured the observed features in the SHARP measurements for a majority of the modeling days. Additional details are provided in the following section.

#### 4. Model application and refinement of surface model parameters

The surface model parameters were refined by conducting a

**Table 2**  
User-specified surface model parameters.

| Parameter   | Definition                               | Units             |
|-------------|------------------------------------------|-------------------|
| $K_{veg}$   | Vegetation-air partitioning coefficient  | unit-less         |
| $K_{soil}$  | Soil-air partitioning coefficient        | unit-less         |
| $k_{leach}$ | Leaching rate coefficient                | $\text{min}^{-1}$ |
| $k_{pen}$   | Leaf penetration rate coefficient        | $\text{min}^{-1}$ |
| $j$         | Photolysis chemistry rate coefficient    | $\text{min}^{-1}$ |
| $k$         | Heterogeneous chemistry rate coefficient | $\text{min}^{-1}$ |



series of sensitivity studies for the April 15 to May 31, 2009 period corresponding to the SHARP campaign. A companion paper (Couzo et al., submitted for publication) describes the modeling databases used and the impacts of the additional HONO formation pathways on radical concentrations and ozone chemistry. The Supplemental Section provides some information on the model configuration used in the study. The modeling was conducted using a nested grid with 36/12/4 km resolution nests. Fig. 2 shows the nested grid modeling domain. The analysis of model results was focused on the innermost 4 km resolution grid around the Houston area where the SHARP measurements were conducted. Fig. 3 shows the subset of the 4 km resolution domain over downtown Houston, and also shows the location of the CAMx grid cell containing the Moody Tower (the black grid cell), where the SHARP measurements were made.

Several CAMx simulations were conducted for the study. The first simulation (Run A) represents the default or base case where the standard configuration of CAMx is used (no direct HONO emissions and no surface model). Thus, only the homogeneous gas-phase formation of HONO is considered in Run A. In the second simulation (Run B), direct HONO surface emissions are included in the model input files as 0.8% of surface NO<sub>x</sub> emissions, including on-road mobile emissions. Runs C through H are surface model sensitivity studies used to refine the surface model parameters based on the observed features from the SHARP campaign; these runs do not include direct HONO emissions.

Run C represents the case with the initial specification of surface model parameters, while runs D through G represent intermediate simulations that provided guidance on the key parameters and model response to these parameters and led to the final set of parameters in Run H. The final set of parameters provided the best overall model performance. This semi-empirical approach to refining model parameters was adopted because of gaps in our knowledge on the values of these parameters. Fig. 4 shows a simplified schematic of the three model species and key surface processes considered in the specification and refinement of the model parameters. Table 3 shows the parameter values for Run C and Run H. The rationales for the initial selection of the parameters for Run C and their subsequent adjustments are discussed below.

#### 4.1. Surface-air partitioning coefficients

Surface-air partitioning coefficients for vegetation ( $K_{veg}$ ) and

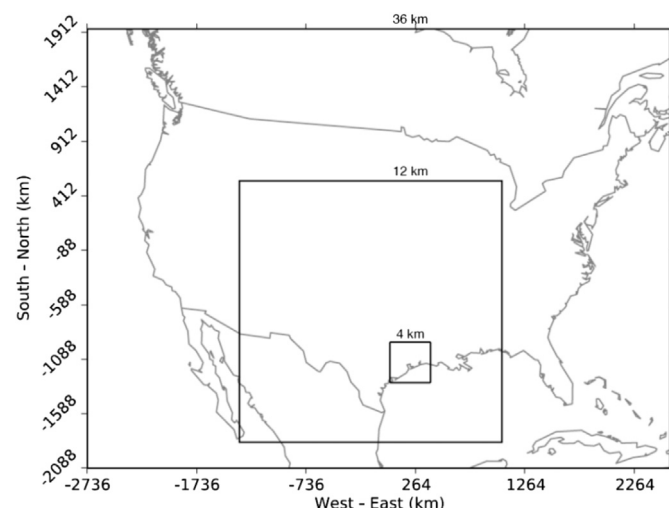


Fig. 2. Nested 36/12/4 km CAMx modeling domain.

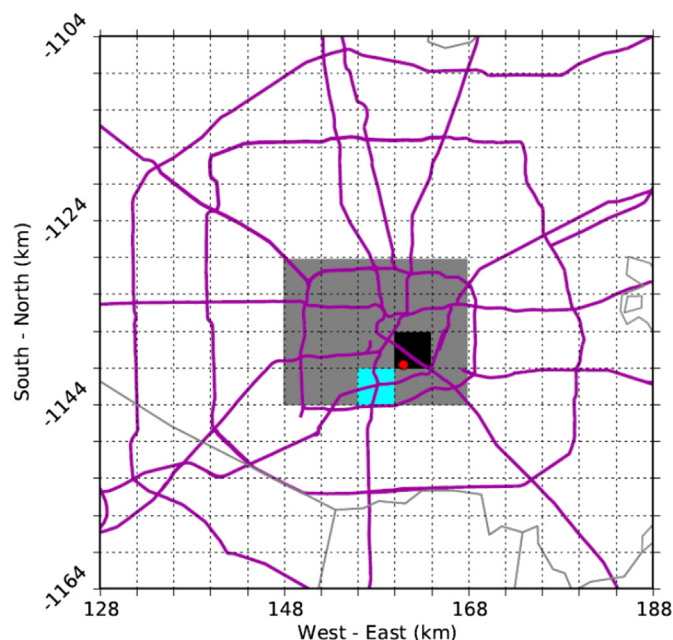


Fig. 3. A subset of the 4 km domain over downtown Houston. The purple lines represent the Houston highway network. Gray cells represent the Houston "Urban" region, the black grid cell contains the Moody Tower (indicated by the red symbol), and the light blue cell adjacent to and southwest of the Moody Tower grid cell is used for further model evaluation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

soil ( $K_{soil}$ ) are used in the surface model for each of the species of interest in Table 3a to determine the partitioning of deposited mass between the surface and air. These parameters define the affinity of the species for the surface after they are deposited. Higher values for these parameters will keep the species on vegetation or soil, while lower values will permit re-emission. Both NO<sub>2</sub> and HNO<sub>3</sub> are assumed to remain on the surface once they are deposited and were assigned very large values (1.E10) vegetation-air and soil-air partitioning coefficients. On the other hand, surface HONO is expected to volatilize and re-emit, and was assigned a moderate value of 1.0, i.e., the ratio of HONO on the surface to the HONO in air is 1. These partitioning coefficient values were maintained for all the sensitivity studies, and were the same for different vegetation types and soil moisture contents.

#### 4.2. Surface removal parameters

Removal from soil surfaces and vegetative surfaces occurs by leaching and by penetration into leaf tissues, respectively. Once removed, the material is no longer available at the surface for reaction or re-emissions. These removal terms are specified as first-order destruction rates and their values are not known. Initially, soil leaching rates ( $k_{leach}$ ) and vegetation penetration rates ( $k_{pen}$ ) for all three species were specified to be about 3% per hour. For HONO, these moderate rates allowed its re-emission after formation by surface reactions. For NO<sub>2</sub> and HNO<sub>3</sub>, the sensitivity studies showed that better agreement with SHARP measurements was obtained when NO<sub>2</sub> was leached at a higher rate (shorter lifetime) and HNO<sub>3</sub> was leached at a lower rate (longer lifetime). For both NO<sub>2</sub> and HNO<sub>3</sub>, higher values for the penetration rates (i.e., shorter lifetimes) provided results that were more consistent with the SHARP measurements. The shorter lifetime for NO<sub>2</sub> is consistent with our understanding that it is a volatile species. Furthermore, gas phase concentrations of HONO and NO<sub>2</sub> are well-correlated at

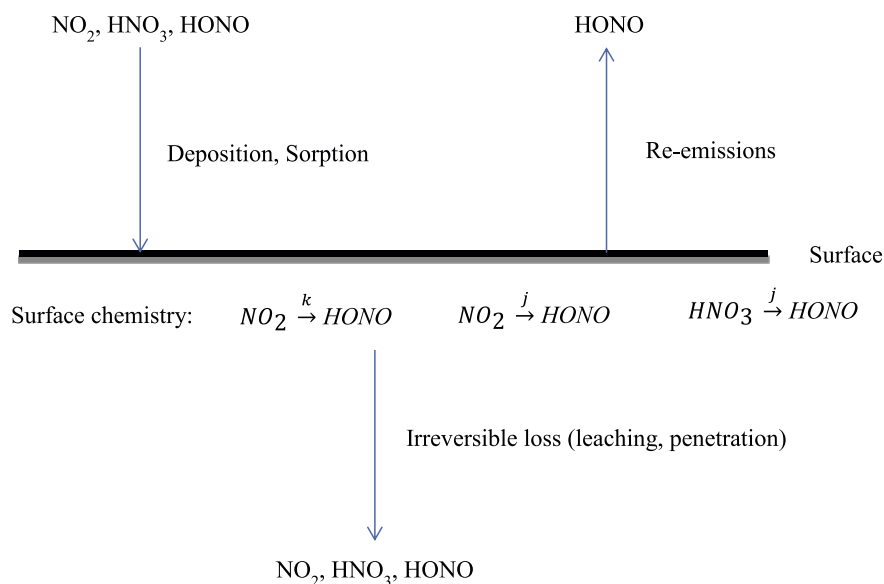


Fig. 4. Simplified schematic of key processes considered for heterogeneous HONO formation on ground surfaces.

Table 3a

Initial (Run C) and final (Run H) values for surface model soil and vegetation parameters.

| Parameter                              | Run C           |                  |         | Run H           |                  |         |
|----------------------------------------|-----------------|------------------|---------|-----------------|------------------|---------|
|                                        | NO <sub>2</sub> | HNO <sub>3</sub> | HONO    | NO <sub>2</sub> | HNO <sub>3</sub> | HONO    |
| K <sub>veg</sub> , unit-less           | 1.00E+10        | 1.00E+10         | 1.00    | 1.00E+10        | 1.00E+10         | 1.00    |
| K <sub>soil</sub> , unit-less          | 1.00E+10        | 1.00E+10         | 1.00    | 1.00E+10        | 1.00E+10         | 1.00    |
| k <sub>leach</sub> , min <sup>-1</sup> | 4.8E-04         | 4.8E-04          | 4.8E-04 | 0.01            | 2.4E-04          | 4.8E-04 |
| k <sub>pen</sub> , min <sup>-1</sup>   | 4.8E-04         | 4.8E-04          | 4.8E-04 | 0.01            | 0.01             | 4.8E-04 |

Table 3b

Initial (Run C) and final (Run H) values for surface model reaction rate constants.

| Rate coefficient (min <sup>-1</sup> ) | Run C                  |                         | Run H                  |                         |
|---------------------------------------|------------------------|-------------------------|------------------------|-------------------------|
|                                       | NO <sub>2</sub> → HONO | HNO <sub>3</sub> → HONO | NO <sub>2</sub> → HONO | HNO <sub>3</sub> → HONO |
| Photolysis (J)                        | 4.8E-04                | 4.8E-05                 | 0.01                   | 2.4E-03                 |
| Thermal (k)                           | 4.8E-04                | N/A                     | 0.002                  | N/A                     |

night, which suggests that surfaces are a short-lived reservoir for NO<sub>2</sub>. The longer leaching lifetime for HNO<sub>3</sub> is consistent with it being a semi-volatile species that has a high affinity for surfaces, while the higher value for the HNO<sub>3</sub> penetration rate can be attributed to the high solubility of HNO<sub>3</sub> and the water content of vegetation.

Note that rainfall events enhance both k<sub>leach</sub> and k<sub>pen</sub>. Thus, the surface model flushes soil and vegetation surfaces clean after a precipitation event, i.e., the accumulated mass on the surface is reset to zero in a grid cell with precipitation, shutting down the availability of HONO at the surface until the precipitation event is over.

#### 4.3. Surface reaction parameters

The surface reaction parameters determine the rates at which deposited NO<sub>2</sub> and HNO<sub>3</sub> are converted to HONO for subsequent re-emissions. The surface model considers two pathways for these reactions: a thermal pathway, active during both night and day, and a daytime photolytic pathway. Based on our understanding of the

reactions of these species, the thermal pathway was not considered for HNO<sub>3</sub> conversion to HONO. Thus, the only HONO formation pathway in the surface model at night is the thermal reaction of NO<sub>2</sub>. The NO<sub>2</sub> thermal reaction rate was initially set to a moderate value of about 3% per hour. However, model predictions of HONO:NO<sub>2</sub> ratios at night were in better agreement with observations when the reaction rate was increased by about a factor of 4.

The specified photolysis rates for the surface model are peak clear-sky values at zero zenith (solar noon) and are internally adjusted for solar angle, cloud attenuation, and shade fraction as a function of land-use type. Low values for the peak surface photolysis rates were used in the initial simulations, but these values resulted in insufficient daytime HONO formation and re-emissions. The final value for the peak surface NO<sub>2</sub> photolysis rate is a factor of 5 lower than the gas-phase value, while the final value for the surface HNO<sub>3</sub> photolysis reaction is about 50 times faster than in the gas-phase. The latter is consistent with the results of Zhou et al. (2003), who estimated that surface HNO<sub>3</sub> photolysis rates were 50–100 times faster than the homogeneous gas-phase rates.

#### 5. Model performance

The model results from the base (Run A), direct HONO emissions (Run B), and final surface model configuration (Run H) simulations were compared with measurements at the Moody Tower location in the downtown University of Houston campus during the April 15 to May 31, 2009 period corresponding to the SHARP campaign. The measurements include *in situ* measurements atop the Moody Tower at a height of 70 m above ground level (Lefer et al., 2010), as well as remote sensing measurements taken using long-path differential optical absorption spectroscopy (LP-DOAS) by the University of California, Los Angeles (Stutz et al., 2010). The LP-DOAS measurements provide vertically resolved concentrations at three different height intervals above ground level: 20–70 m, 70–130 m, and 130–300 m. These heights are referred to as “lower,” “middle,” and “upper” in the following discussion.

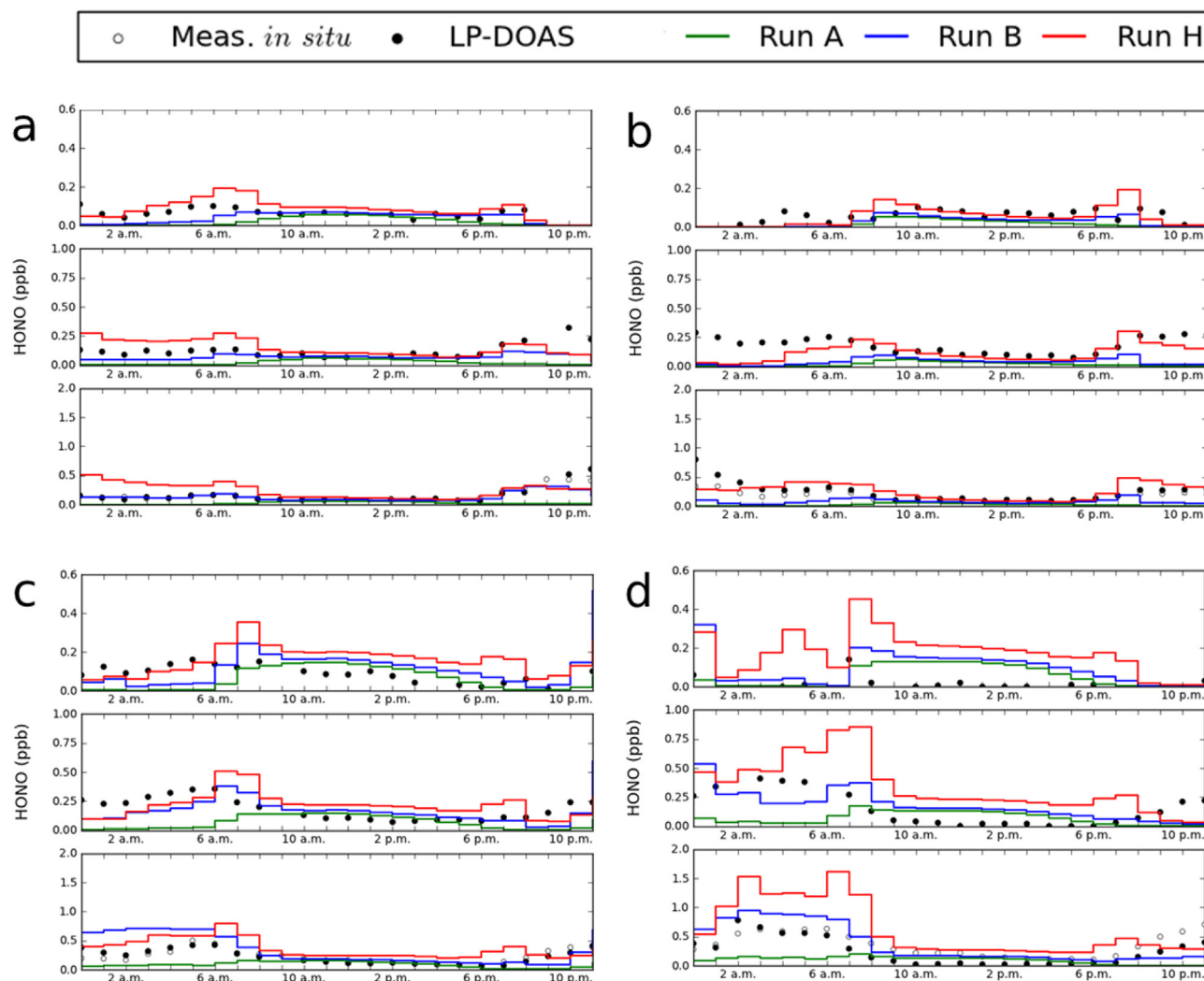
Simulated concentrations of NO<sub>2</sub> and HONO, and HONO:NO<sub>2</sub> ratios were compared with *in situ* and LP-DOAS measurements at the Moody Tower. Predicted and measured (*in situ* only) hourly ratios of HONO:HNO<sub>3</sub> were also compared. The ratios can be a

better measure of model performance for HONO than HONO concentrations because they are less dependent on uncertainties in NO<sub>x</sub> emissions and thus better suited to test the new HONO formation pathways implemented in CAMx. Four days from the SHARP campaign were selected for analysis and for conducting the refinement of the surface model parameters: April 20–21 and May 19–20. These were cloud-free week days with favorable conditions for ozone formation and some of the highest recorded HONO and ozone concentrations during the SHARP campaign.

Initially, model performance at the Moody Tower grid cell was used as the basis for refining the surface model parameters. It was found, however, that NO<sub>2</sub> concentrations at the Moody Tower grid cell were consistently and substantially over-predicted by the model (Couzo et al., submitted for publication). Fig. S1a, in the supplemental section, shows model performance for NO<sub>2</sub> in the Moody Tower grid cell for April 21, 2009. The large NO<sub>2</sub> over-predictions appear to be due to over-estimation of NO<sub>x</sub> emissions in the Moody Tower grid cell arising from possibly incorrect spatial allocation of emissions east of the Moody Tower. As discussed by Couzo et al. (submitted for publication), the largest NO<sub>x</sub> emissions in the region are in the Moody Tower grid cell and are the result of elevated NO<sub>x</sub> emissions coming from ship channel non-road activity (shipping, fork lifts, cranes, etc.) east of the Moody Tower

(Dennis McNally, personal communication, 2013). The over-estimates in NO<sub>2</sub> concentrations are accompanied by over-estimates in HONO concentrations in the direct HONO emissions simulation (Run B) and the simulation with the surface model (Run H) (Couzo et al., submitted for publication). Previous CAMx modeling using the same inputs showed that the best model performance for NO<sub>2</sub> was obtained when model predictions in the grid cell directly southwest of the Moody Tower grid cell were used for comparisons against observations (Dennis McNally, personal communication, 2013). This is also seen in the current modeling as described in the companion paper (Couzo et al., submitted for publication) and shown in Fig. S1b in the supplemental section. Note also that the Moody Tower is located near the southwest corner of the CAMx grid cell (see Fig. 3, black grid cell) in which it lies. Because the surface model performance for HONO and other NO<sub>x</sub> species, such as HNO<sub>3</sub>, is strongly dependent on CAMx performance for NO<sub>2</sub>, the refinement of the surface model parameters focused on using model predictions in the grid cell southwest of the Moody Tower (see Fig. 3, light blue cell).

Fig. 5 shows hourly simulated and measured HONO concentrations for the four days and runs A, B, and H. *In situ* measurements from the top of Moody Tower are compared to simulated concentrations in the grid cell directly southwest of the Moody Tower grid



**Fig. 5.** Time series of observed and predicted (Runs A, B and H) HONO at upper (130–300 m; top panel), middle (70–130 m) and lower (20–70 m; bottom panel) DOAS heights for four days: (a) April 20, (b) 21, (c) May 19, and (d) May 20.

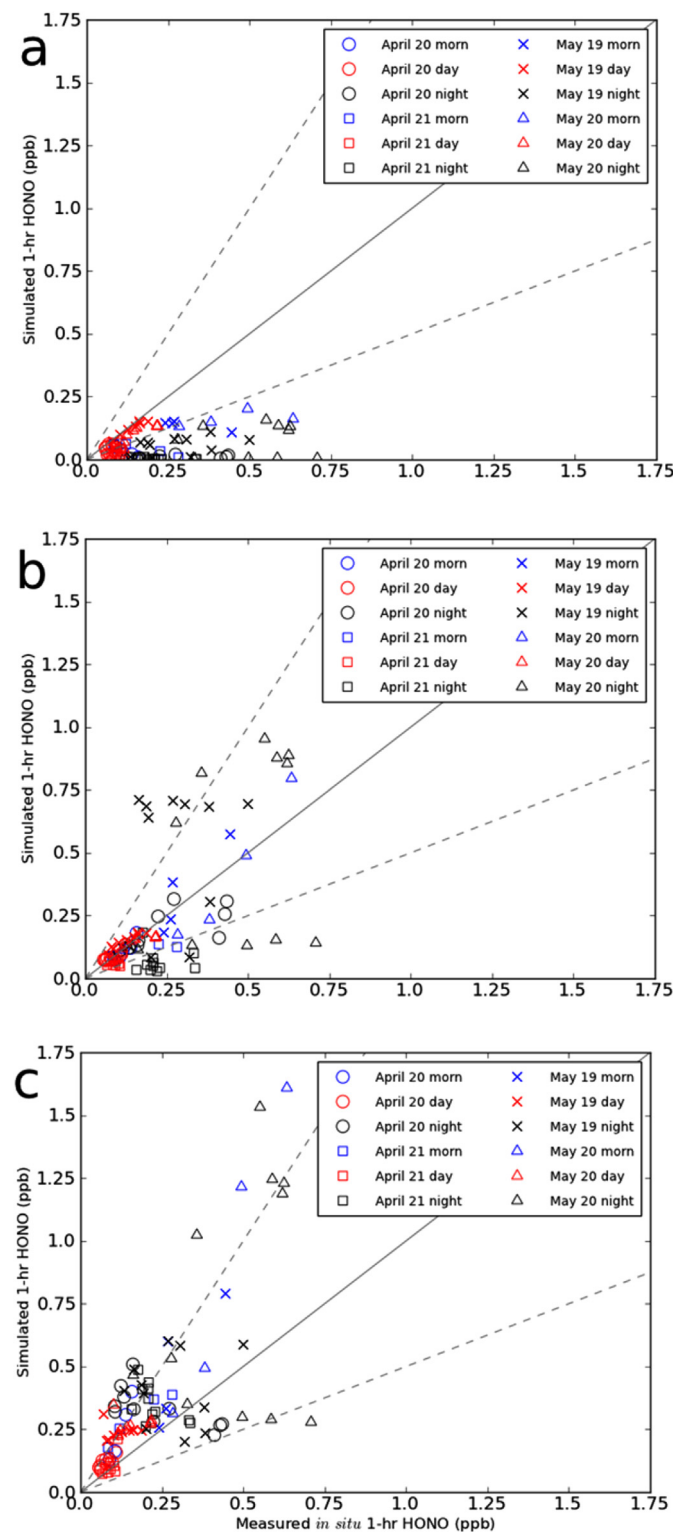
cell and the second vertical layer of the model. LP-DOAS measurements in the upper, middle and lower paths are compared to

simulated concentrations in the fourth, third, and second vertical layers in the model, respectively. The shaded circles represent the LP-DOAS measurements at the three different heights while the open circles represent the *in situ* measurements taken atop the Moody Tower. HONO values decrease with height as most HONO formation occurs near the ground where NO<sub>x</sub> concentrations are greatest.

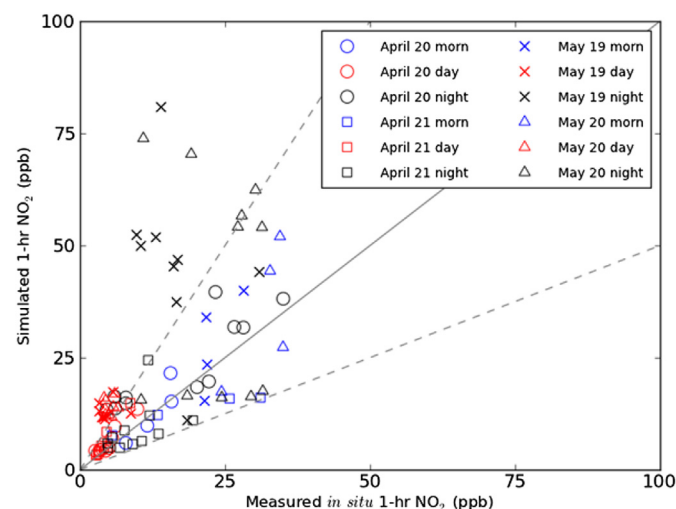
In the base run (Run A), HONO concentrations are under-predicted, especially in the early morning before sunrise and in the evening after sunset. The agreement is better during the middle of the day, particularly on April 20, indicating the importance of homogeneous HONO formation. On April 21, HONO concentrations in the middle of the day are still under-predicted, while during both days in May, the daytime values are over-predicted in the middle and upper heights.

Run B (homogeneous gas-phase HONO formation and direct HONO emissions) also under-predicts HONO levels before sunrise and at night on both days in April. In this run there are some noticeable increases in HONO coinciding with rush hour traffic during the morning and late afternoon to evening hours. During the middle of the day, the results from Run B and Run A are comparable, with Run B predicting slightly higher HONO concentrations than Run A. However, for the two days in May, Run B over-predicts *in situ* and lower height LP-DOAS HONO concentrations during the hours between midnight and sunrise, but under-predicts in the middle and upper LP-DOAS heights.

HONO levels from Run H (homogeneous gas-phase HONO formation and heterogeneous formation via the surface model) are always higher than those from Run A, as expected, and generally higher than those from Run B, except for a few nighttime hours during the two days in May. The introduction of the heterogeneous pathway for HONO formation in CAMx improves early morning HONO predictions near the surface (bottom plot) compared to Runs A and B on April 21 and May 19, but results in over-predictions on April 20 and May 20. During the night, after sunset, Run H is also able to more closely match observations than either Runs A or B. In the middle and upper LP-DOAS heights, Run H HONO levels are in good agreement with observed values in April, but HONO concentrations are over-predicted during the two days in May, especially on May 20.



**Fig. 6.** Simulated HONO versus measured *in situ* HONO for model runs (a) A, (b) B and (c) H and four days: April 20, April 21, May 19, and May 20. Blue symbols represent early morning concentrations, red symbols represent daytime concentrations and black symbols represent nighttime concentrations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 7.** Simulated NO<sub>2</sub> versus measured NO<sub>2</sub> for model run A and four days: April 20, April 21, May 19, and May 20. Blue symbols represent early morning concentrations, red symbols represent daytime concentrations and black symbols represent nighttime concentrations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 6 provides scatterplots comparing morning (6 am–10 am), daytime (10 am–7 pm) and nighttime (7 pm–6 am) time-paired HONO concentrations from Runs A, B, and H in the grid cell southwest of the Moody Tower with *in situ* measurements for all four days. Run A consistently under-predicts measured HONO concentrations during all time periods on all days. It is clear that homogeneous HONO formation alone is insufficient to match observations. Run B shows good agreement during the day, but there are large under-predictions during some nighttime hours. Run H tends to over-predict rather than under-predict. Daytime concentrations in May are over-predicted, but are often within a factor of two of the measurements. Run H nighttime predictions show improvement over Runs A and B, though performance on May 20 is markedly worse than the other three days.

Because nighttime surface production of HONO in Run H is solely dependent on NO<sub>2</sub>, model performance for HONO during the night. This appears to be the case for May 20 when the model over-predicts observed nighttime NO<sub>2</sub> levels substantially, as shown in Fig. 7, which compares time-paired *in situ* measured NO<sub>2</sub> concentrations with simulated values for model run A (all three model runs had almost identical performance for NO<sub>2</sub>). Nighttime model

performance for NO<sub>2</sub> is worse on May 19 and 20, explaining the over-predictions of HONO found on those days (particularly on May 20). The nighttime over-predictions of NO<sub>2</sub> (and HONO) could be due to over-estimation of NO<sub>x</sub> emissions or to insufficient vertical mixing. However, the HONO:NO<sub>2</sub> ratio and its vertical variation should be in better agreement with observations if the surface model is responding correctly to model inputs. This suggests that it is useful to consider the HONO:NO<sub>2</sub> ratio as an indicator of model performance.

Fig. 8 compares the time series of observed (*in situ* and LP-DOAS) and simulated HONO:NO<sub>2</sub> ratios from all three model runs for the 4 days. The predicted ratios for Run A are consistently lower than the corresponding ratios from the measurements. The low HONO:NO<sub>2</sub> ratios for Run A in the early morning and night are due to low HONO concentrations since NO<sub>2</sub> concentrations are essentially identical in the three model runs. The ratios from Run B show an improvement over those from Run A, especially at night, but are still often below the measurements. The ratios increase at nearly every hour in Run H, and the model is able to replicate both the observed diurnal pattern and the vertical variation on most days. It is important to note that, on April 21, predicted ratios in Run H are able to capture the sudden increase in observed ratios beginning at

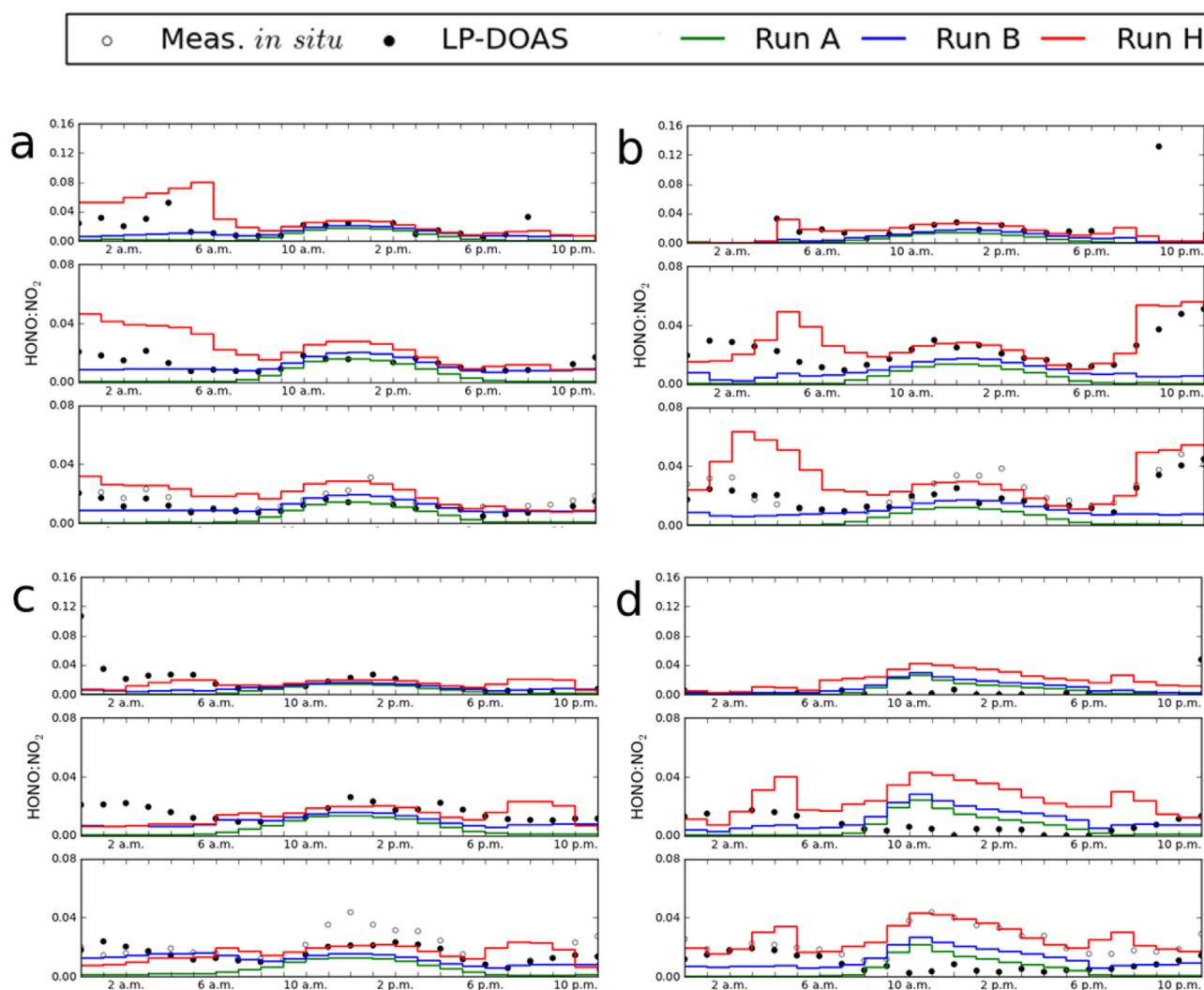


Fig. 8. Time series of observed and predicted (Runs A, B and H) hourly HONO:NO<sub>2</sub> ratios at upper (130–300 m; top panel), middle (70–130 m) and lower (20–70 m; bottom panel) DOAS heights for four days: (a) April 20, (b) April 21, (c) May 19, and (d) May 20.

7 p.m. Furthermore, there is very good agreement between nighttime observed HONO:NO<sub>2</sub> ratios and those simulated in Run H on May 20, confirming that the large over-predictions in nighttime HONO concentrations on May 20 are explained by the large over-predictions in NO<sub>2</sub> concentrations.

Fig. 9 compares the time series of *in situ* HONO:HNO<sub>3</sub> ratios with model predictions from Runs A, B, and H for the 4 days in April and May (the time series of HNO<sub>3</sub> concentrations for Runs A and H are shown in Fig. S2 in the supplemental section). For all 4 days, the base run under-predicts HONO:HNO<sub>3</sub> ratios consistently. The surface model ratios are in better agreement with the measured ratios for the two days in April, but the ratios are over-predicted in May in the morning hours, partly explaining the daytime HONO over-predictions in May.

Table 4 shows the normalized mean error (NME) and bias (NMB) for HONO, NO<sub>2</sub>, and HNO<sub>3</sub> concentrations for the entire simulation period from April 15 to May 31, 2009. Note that NO<sub>2</sub> performance is similar across all three model runs. Run H over-predicts HONO, but is an improvement over Run A, which significantly under-predicts HONO. Most of the over-predictions in HONO concentrations in Run H can be attributed to over-predictions in NO<sub>2</sub> and HNO<sub>3</sub> concentrations. In particular, the Run H nighttime HONO over-prediction bias of nearly 50% is consistent with the nighttime NO<sub>2</sub> over-prediction bias. Run B under-predicts HONO during the day by more than 20% and slightly under-predicts during the night. While the nighttime under-prediction bias for Run B is much lower than the nighttime over-prediction bias for Run H, the Run B under-prediction bias is not consistent with the large over-predictions in

**Table 4**

Normalized mean error and bias between measured and modeled HONO, NO<sub>2</sub>, and HNO<sub>3</sub> for Runs A, B and H for SHARP Campaign (April 15 to May 31, 2009) for daytime (9:00–20:00 LT) and nighttime (21:00–08:00 LT) periods.

| Model run/day-night | Normalized mean error (%) |                 |                  | Normalized mean bias (%) |                 |                  |
|---------------------|---------------------------|-----------------|------------------|--------------------------|-----------------|------------------|
|                     | HONO                      | NO <sub>2</sub> | HNO <sub>3</sub> | HONO                     | NO <sub>2</sub> | HNO <sub>3</sub> |
| Run A/day           | 60                        | 96              | 87               | –59                      | 70              | 58               |
| Run A/night         | 80                        | 105             | 121              | –83                      | 83              | 80               |
| Run B/day           | 42                        | 95              | 87               | –23                      | 69              | 59               |
| Run B/night         | 69                        | 105             | 122              | –2                       | 83              | 82               |
| Run H/day           | 48                        | 97              | 95               | 20                       | 71              | 72               |
| Run H/night         | 79                        | 107             | 130              | 50                       | 86              | 95               |

**Table 5**

Normalized mean error and bias between measured and modeled HONO:NO<sub>2</sub> and HONO:HNO<sub>3</sub> ratios for Runs A, B and H for SHARP Campaign (April 15 to May 31, 2009) for daytime (9:00–20:00 LT) and nighttime (21:00–08:00 LT) periods.

| Model run/day-night | Normalized mean error (%) |                       | Normalized mean bias (%) |                       |
|---------------------|---------------------------|-----------------------|--------------------------|-----------------------|
|                     | HONO:NO <sub>2</sub>      | HONO:HNO <sub>3</sub> | HONO:NO <sub>2</sub>     | HONO:HNO <sub>3</sub> |
| Run A/day           | 76                        | 89                    | –76                      | –89                   |
| Run A/night         | 95                        | 95                    | –95                      | –93                   |
| Run B/day           | 60                        | 81                    | –59                      | –68                   |
| Run B/night         | 64                        | 89                    | –63                      | –52                   |
| Run H/day           | 43                        | 70                    | –29                      | –63                   |
| Run H/night         | 48                        | 77                    | –29                      | –44                   |

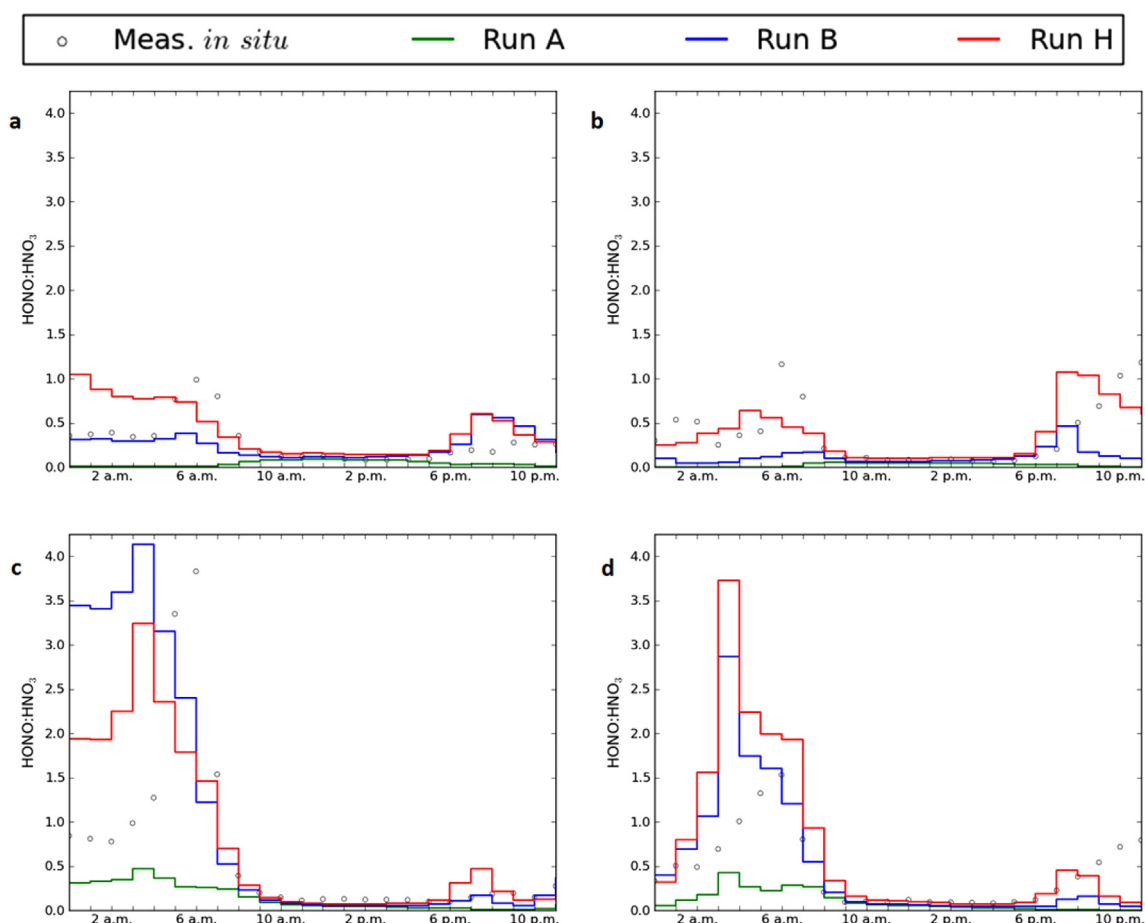


Fig. 9. Time series of observed (*in situ*) and predicted (Runs A, B and H) hourly HONO:HNO<sub>3</sub> ratios four days: (a) April 20, (b) April 21, (c) May 19, and (d) May 20.

NO<sub>2</sub> and HNO<sub>3</sub> concentrations. This inconsistency is seen in the NMB statistics for HONO:NO<sub>2</sub> and HONO:HNO<sub>3</sub> ratios shown in Table 5. When looking at the HONO:NO<sub>2</sub> and HONO:HNO<sub>3</sub> ratios, Run H shows the best performance among all three runs, with a lower bias (–30%) for HONO:NO<sub>2</sub> during both day and night, as compared to Run A and Run B biases ranging from –60 to –90%. The parameters used in Run H provide a balance between model performance for HONO concentration (biased high) and the HONO:NO<sub>2</sub> and HONO:HNO<sub>3</sub> ratios (biased low). These results also illustrate the strong dependence of the performance of the surface model for HONO on CAMx performance for NO<sub>2</sub> and HNO<sub>3</sub>.

Table 6 compares the daily HONO produced by surface reactions (Run H) in the grid cell southwest of the Moody Tower (light blue grid cell in Fig. 3) with direct surface emissions of HONO (Run B). The numbers are shown in both emission units (μmole/day) and mixing ratio production units (ppbv/day). As shown in Table 6, the amount of HONO produced in the surface model is more than a factor of two higher than direct HONO emissions for the two April days studied. For the two days in May in which NO<sub>2</sub> concentrations are over-predicted by factors of 3–4 (see Fig. 7), the production of HONO in the surface model is nearly a factor of 5–6 higher than direct HONO emissions.

## 6. Summary and conclusions

We have implemented an explicit process-based mechanism for heterogeneous HONO production in a photochemical air quality model (CAMx), using a surface module that acts as a reservoir for deposited species and simulates surface chemistry, re-emissions of deposited species and their secondary products, and irreversible loss to the surface. The implementation addresses a well-recognized inability of air quality models that include only the homogeneous gas-phase pathway for HONO production to predict measured HONO levels. Several recent modeling studies have included direct HONO emissions and incorporated parameterizations to simulate heterogeneous reactions on particle and ground surfaces to address this limitation, and have found some improvement in model performance for HONO, but there are uncertainties involved with the parameterizations and the models still tend to under-predict HONO concentrations. The surface model implementation described in this paper provides an alternative mechanistic approach that represents our best understanding of HONO formation at the surface. This understanding is consistent with the state of the science for the production of HONO on ground surfaces via photolysis of adsorbed HNO<sub>3</sub> and NO<sub>2</sub> and the thermal reaction of NO<sub>2</sub>. This implementation provides the flexibility of a mechanistic approach that can be made more robust by refining model parameters using HONO measurements in a variety of locations.

Measurements of HONO, NO<sub>2</sub> and HNO<sub>3</sub> during the 2009 SHARP campaign in Houston were used to evaluate CAMx predictions and

refine the surface model parameters. The results from the run with homogeneous gas-phase HONO formation only showed large under-predictions, consistent with numerous previous studies indicating that homogeneous gas-phase HONO formation alone cannot explain observed HONO levels.

Run B included direct HONO emissions as 0.8% of all low-level NO<sub>x</sub> emissions, which is one of the highest reported ratios. Few studies have reported observations of direct HONO emission rates, and the HONO/NO<sub>x</sub> emission ratio is thus uncertain. Deriving HONO/NO<sub>x</sub> emission ratios from ambient measurements is inconclusive because the HONO may have been formed secondarily. Although there was some improvement in model performance with direct HONO emissions, the model was unable to explain nocturnal HONO observations, often considerably underestimating HONO mixing ratios. During the day, the agreement between HONO observations and model was generally better. However, a comparison of simulated and HONO:NO<sub>2</sub> ratios showed that direct emissions alone could not adequately describe the observations. The HONO contribution from direct emissions was smaller than surface chemical formation of HONO by factors of 2–6 (Table 6). This interpretation is supported by the 1D model simulation of Wong et al. (2013), who attributed only 8–10% of the observed daytime HONO during SHARP to traffic emissions in Houston. This conclusion does not suggest that direct HONO emissions do not occur, but that more accurate and more direct measurements of HONO emission factors are needed to fully understand the importance of primary HONO emissions directly from combustion sources.

The comparisons of CAMx surface model results (Run H) with observations showed that the model performance for HONO was strongly dependent on model performance for NO<sub>2</sub>, particularly at night. Thus, the HONO:NO<sub>2</sub> ratios provide a better measure of model performance for HONO. For the most part, NO<sub>2</sub> concentrations were over-predicted, resulting in over-prediction of HONO concentrations with the surface model. However, predicted HONO:NO<sub>2</sub> and HONO:HNO<sub>3</sub> ratios were in much better agreement with observed ratios than the ratios from Run A or Run B.

The CAMx surface model described in this paper provides a process-based approach to model surface heterogeneous formation of HONO and improves model performance for HONO, including the tendency to under-predict HONO levels by large amounts. There are uncertainties associated with the surface model parameters, such as the surface reaction rates. Reducing uncertainty in these parameters should be the focus of future field studies in both urban and rural settings providing the data needed to refine the surface model.

## Acknowledgments

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.01.046>.

**Table 6**

24-h total surface HONO emissions (Run B) and surface HONO production (Run H) at 4 km grid cell southwest of Moody Tower.

| Date           | Run B (μmole/day) | Run B (ppbv/day) | Run H (μmole/day) | Run H (ppbv/day) |
|----------------|-------------------|------------------|-------------------|------------------|
| April 20, 2009 | 1.07              | 25.8             | 2.52              | 60.3             |
| April 21, 2009 | 1.06              | 25.8             | 2.87              | 69.9             |
| May 19, 2009   | 1.09              | 26.3             | 4.84              | 116.9            |
| May 20, 2009   | 1.08              | 26.4             | 6.45              | 156.9            |



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## 1 Supplemental Section

### 2 *Previous HONO Modeling Studies*

3 Sarwar et al. (2008) considered four different sources of nitrous HONO in a study using  
4 CMAQ for the northeastern U.S.: gas-phase reactions, direct emissions, the  
5 heterogeneous reaction for NO<sub>2</sub> hydrolysis on ground and aerosol surfaces, and a surface  
6 photolysis reaction for adsorbed HNO<sub>3</sub>. Following Kurtenbach et al. (2001), direct  
7 surface emissions of HONO from on-road and off-road vehicles were assumed to be  
8 0.8% of NO<sub>x</sub> emissions and the heterogeneous reaction on ground and aerosol surfaces  
9 was parameterized using surface to volume ratios. The photolysis rate of adsorbed nitric  
10 acid was assumed to be 24 times the photolysis rate of gaseous HNO<sub>3</sub> based on the work  
11 of Zhou et al. (2003). Sarwar et al. (2008) found that under-predictions of HONO  
12 decreased with these four pathways as compared to the case when only homogeneous  
13 gas-phase HONO formation was considered. The model still, however, under-predicted  
14 observed HONO levels by about 40%.

15  
16 Czader et al. (2012) applied CMAQ with several sources of HONO to model a month-  
17 long episode during the 2006 TEXAQS. The HONO sources considered were: gas-phase  
18 reactions, direct emissions, NO<sub>2</sub> hydrolysis on ground and aerosol surfaces, and photo-  
19 induced conversion of NO<sub>2</sub> into HONO on surfaces covered with organic materials. The  
20 gas-phase reactions included the standard reactions (R1 and R2) as well as the photo-  
21 induced formation from excited NO<sub>2</sub> (Li et al., 2008). They found a ten-fold increase in  
22 HONO mixing ratios with these additional formation pathways and a large improvement  
23 in HONO predictions, as compared to the standard gas-phase HONO mechanism.

Mismatches in observed and predicted HONO concentrations on some days were attributed largely to mismatches in NO<sub>2</sub> concentrations.

Gonçalves et al. (2012), studied the impacts of additional HONO sources on CMAQ performance in Spain. They found that the most effective scenario consisted of direct HONO emissions and heterogeneous NO<sub>2</sub> hydrolysis on ground surfaces. The effect of photo-enhanced reduction of NO<sub>2</sub> on surfaces was found to be negligible, as was the effect of NO<sub>2</sub> hydrolysis on aerosol surfaces. Although Gonçalves et al. (2012) found an improvement in model performance for HONO as compared to the base case (gas-phase production of HONO only), modeled HONO results were consistently below the observed levels. They noted that model results were sensitive to the parameterization of the available surface area for HONO production via heterogeneous reactions.

Zhang et al. (2012b) applied CMAQ with direct HONO emissions, two heterogeneous reactions and two surface photolysis reactions for the Pearl River Delta region in China. They found that HONO levels with these additional pathways were an order of magnitude higher than those obtained from gas-phase HONO production alone. Although this resulted in better performance, the modeled HONO concentrations were still lower than observations. Like Gonçalves et al. (2012), Zhang et al. (2012b) concluded that the parameterization of surface area for heterogeneous reactions was an important factor in their modeling. Direct HONO emissions had a smaller impact on modeled HONO levels than the heterogeneous pathways, and were more important in urban areas than in rural areas.

47

48 Li et al. (2010) used WRF-Chem to model air quality in Mexico City. Besides the  
49 homogeneous reaction of NO with OH, they considered four additional HONO sources:  
50 heterogeneous NO<sub>2</sub> reactions on 1) semi-volatile organics 2) freshly emitted soot, 3)  
51 aerosol surfaces and 4) ground surfaces. They used a relatively large uptake coefficient  
52 and obtained a substantial improvement in model performance for HONO during the  
53 night but noted some under-predictions in afternoon levels. They attributed the daytime  
54 under-predictions to not including other potential HONO sources, such as the photolysis  
55 of HNO<sub>3</sub> on surfaces.

56

57 In a WRF-Chem modeling application in China, Li et al. (2011) incorporated direct  
58 HONO emissions, the reaction of photoexcited NO<sub>2</sub> with water, and heterogeneous  
59 reactions on aerosol surfaces as additional HONO formation pathways. They found  
60 improvement in model performance for HONO, but found that HONO concentrations  
61 were still under-predicted on average by about 40%.

62

### 63 *Model Configuration for CAMx Simulations*

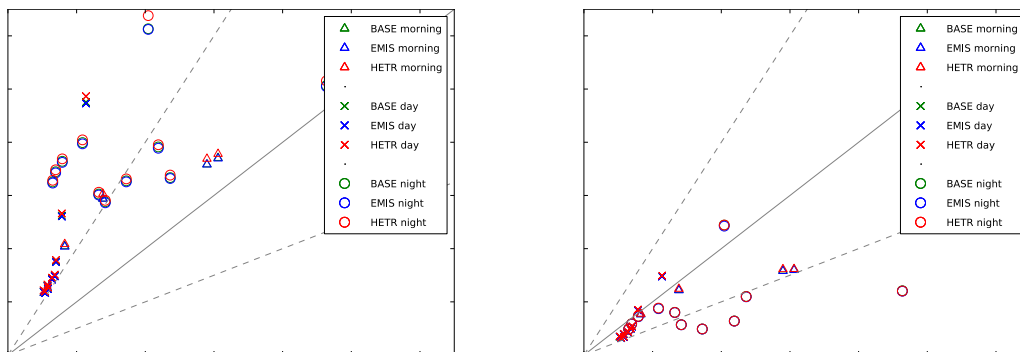
64 Alpine Geophysics LLC (AG) and Climate & Atmospheric Research Associates  
65 developed input databases for 2009, which focused primarily on the Houston O<sub>3</sub> non-  
66 attainment area. The model configuration used Advanced Research WRF (v3.2.1)  
67 dynamics, the Carbon Bond 6 chemical kinetic mechanism, Glo-BEIS (v3.1) for biogenic  
68 emissions over Texas, MEGAN (v2.04) for biogenics elsewhere in the domain,  
69 MOVES2010 for mobile sources, the TCEQ's 2009 point source inventory, and the U.S.



Environmental Protection Agency's 2008 National Emission Inventory. Lateral boundary conditions were developed from a 2009 MOZART-4 global simulation performed at the National Center for Atmospheric Research. Complete descriptions of the model algorithms, data base development procedures, simulation strategy, and performance evaluation methods are given in the modeling protocol (Tesche et al., 2010<sup>1</sup>). Performance evaluations for this ensemble member show O<sub>3</sub> mean normalized bias and mean normalized gross error were 9.5% and 20.6% on days when modeled daily maximum 8-hr O<sub>3</sub> was greater than 60 ppb. These statistics are within the tolerances commonly used for regulatory modeling.

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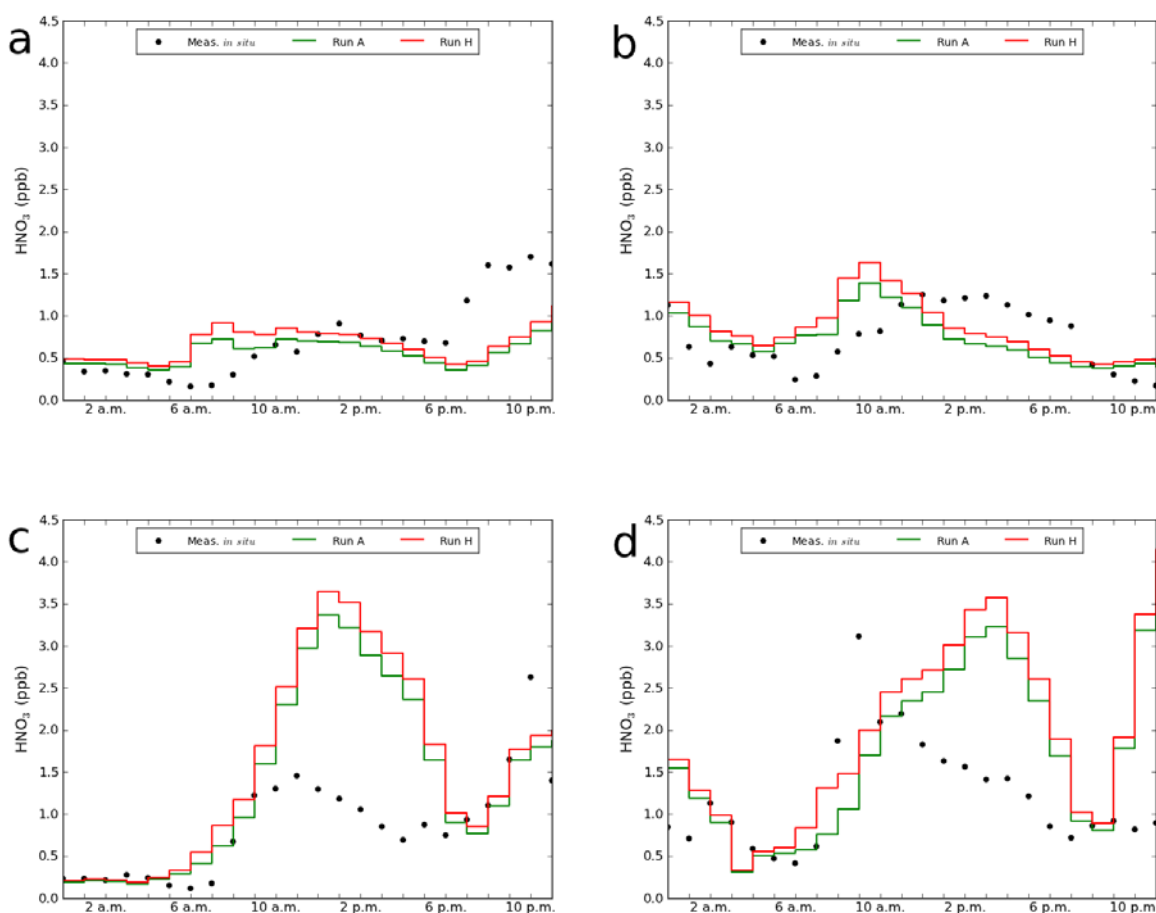
<sup>1</sup> T.W. Tesche, J.G. Wilkinson, G.M. Stella, D.E. McNally, and C.F. Loomis (2010). Modeling protocol for the 2013 Houston, TX, air quality model study: Ensemble modeling and probabilistic attainment demonstration for the new 8-hour ozone National Ambient Air Quality Standard. Prepared for the Houston 8-hr Ozone SIP Coalition by Climate & Atmospheric Research Associates (Boise, ID) and Alpine Geophysics, LLC (Arvada, CO).

81 *Model Performance for NO<sub>2</sub> in Moody Tower Grid Cell and Southwest Grid Cell*

Supplemental Figure S1. Simulated NO<sub>2</sub> versus LP-DOAS measured NO<sub>2</sub> on April 21, 2009. Measurements from Moody Tower are compared to (a) the Moody Tower grid cell and (b) the grid cell southwest of Moody Tower. Green markers show the BASE scenario (Run A), blue markers show EMIS predictions (Run B), and the red markers are from HETR (Run H). Predictions are from the second vertical layer, which corresponds to the height of the measurements.

## 82 Model Performance for $\text{HNO}_3$ for Runs A and H

83 Supplemental Figure S2 compares the time series of *in situ*  $\text{HNO}_3$  observations with  
 84 model predictions from Runs A and H for the 4 days in April and May. In the two days in  
 85 May, the model over-predicts  $\text{HNO}_3$  concentrations, likely leading to over-predictions in  
 86  $\text{HNO}_3$  surface loadings. This results in greater HONO daytime production from the  
 87 surface model and partly explains the daytime HONO over predictions in May.



Supplemental Figure S2. Time series of hourly simulated and measured  $\text{HNO}_3$  mixing ratios for runs A and H and four days: (a) April 20, (b) April 21, (c) May 19, and (d) May 20.