IMPLEMENTATION AND EVALUATION
OF NEW HONO MECHANISMS IN A 3-D
CHEMICAL TRANSPORT MODEL FOR
SPRING 2009 IN HOUSTON

FINAL REPORT
(v. 12 February 2014)

AQRP PROJECT 12-028

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EXECUTIVE SUMMARY

The major chemical framework of ozone formation has been understood for decades but nevertheless new scientific discoveries continue to emerge and their impact on ozone formation must be properly evaluated. The roles of radical precursors such as nitrous acid (HONO), formaldehyde (HCHO), and highly reactive volatile organic compounds (HRVOCs) in Houston and other Texas cities continue to be the subject of research. Field measurements and modeling studies suggest that HONO can significantly affect the hydrogen oxide radical (HOx) budget in urban Houston. A robust analysis of how HONO formation influences local and regional photochemistry in Houston requires 3-D modeling with a realistic representation of the HONO sources.

In the Spring of 2009, scientists from many institutions collected extensive atmospheric measurements in urban Houston including nitric oxide (NO), nitrogen dioxide (NO2), reactive nitrogen compounds (NOy), HONO, nitric acid (HNO3), ozone (O3), carbon monoxide (CO), sulfur dioxide (SO2), HCHO, hydrogen peroxide (HOOH), hydroxyl radical (OH), hydroperoxy radical (HO2), oxygenated volatile organic compounds (OVOCs), volatile organic compounds (VOCs), actinic flux, planetary boundary layer (PBL) height, O3 production rates, and vertical profiles (from 40m to 300m) of NO2, HONO, O3, SO2, and HCHO, during the Study of Houston Atmospheric Radical Precursors (SHARP). The SHARP dataset provides a unique opportunity to examine and improve our understanding of atmospheric HONO formation processes and how they should be implemented in 3-D models such as the Comprehensive Air quality Model with extensions (CAMx). The objective of the study was to develop, implement, and evaluate new pathways for HONO formation in the CAMx model that is used to develop air quality management strategies for Houston and Texas.

Previous attempts to implement HONO into 3-D CTMs similar to CAMx have employed empirical parameterizations of HONO production. In contrast, this study explicitly modeled heterogeneous formation of HONO using a surface model available in CAMx. The process based approach developed in this study treats both dark (thermal) and light (photo-enhanced) heterogeneous HONO formation on ground level surfaces. This surface model allows the ground to act as a reservoir for deposited species rather than making the assumption that all processes on surfaces occur instantly. The surface model simulates deposition, photochemical degradation and transformation, and volatilization back into the air (re-emission).

Based on literature reviews and analysis of measurements, reactions of NO2 and HNO3 at the surface were implemented in the surface model. The study showed that the surface thermal reaction of NO2 was necessary to explain nighttime measurements during the SHARP study, while during the day, surface photolytic reactions of HNO3 and NO2 were necessary to achieve agreement with observations. Because uncertainties exist in our knowledge of the relevant surface parameters, initial estimates of these parameters were refined, using the SHARP observations, to obtain good agreement between observed and modeled HONO:NO2 ratios and HONO:HNO3 ratios.

The implementation of these new HONO formation pathways into CAMx shows that explicitly modeling reactions on surfaces (vegetation, soil) can do a good job of reconciling predicted with
observed HONO concentrations and HONO:NO₂ ratios. The best HONO agreement with the surface model was obtained for days when the model predicted the observed in-situ NO₂ mixing ratios well. Consequently, greater emphasis was placed on the overall model simulation of the HONO:NO₂ ratio than the absolute HONO agreement. Sensitivity simulations with direct emissions of HONO (as 0.8 % of NOₓ emissions) did not consistently reconcile predicted with observed HONO concentrations and HONO:NO₂ ratios. When using surface model parameters that are consistent with SHARP observations, the HONO produced was found to have a substantial impact on morning OH but only minor impacts on daytime OH and as much as 4 ppbv on maximum O₃.
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1. INTRODUCTION

1.1 BACKGROUND

Formation of ozone and particles, the most common compounds associated with air pollution, is driven by the hydroxyl radical, \( \cdot \text{OH} \) (Seinfeld and Pandis, 2006). The hydroxyl radical oxidizes volatile organic compounds (VOCs), leading to their degradation as well as the formation of lower vapor pressure compounds that add to particle mass. In addition, the formation of hydroperoxy radical (HO\(_2\)), followed by its reaction with nitric oxide (NO), leads to ozone formation. In the atmosphere, \( \cdot \text{OH} \) and HO\(_2\) are rapidly converted into each other and the two species together are thus often referred to as HOx. The significance of HOx for atmospheric chemistry dictates the need for an accurate understanding of their sources. While the photolysis of O\(_3\), followed by reaction with water, and the photolysis of HCHO are well known as HOx sources, we know much less about the role of the photolysis of nitrous acid, HONO.

Nitrous acid (HONO) is known to affect radical budgets in urban environments by serving as an \( \cdot \text{OH} \) source via the photolysis reaction:

\[
\text{HONO} + hv \rightarrow \text{NO} + \cdot \text{OH} \quad (\lambda < 400 \text{nm}).
\]  

It has long been established that Reaction 1 provides an early morning \( \cdot \text{OH} \) source before more dominant sources, such as formaldehyde (HCHO) and \( \text{O}_3 \), become significant, due to the nighttime accumulation of HONO (Harris et al., 1982; Harrison et al., 1996; Platt et al., 2002; Alicke et al., 2003). In recent years, it has also become clear that HONO is formed during the daytime and observations in Houston have shown that this daytime HONO compares to other daytime HOx sources.

While the sources of nocturnal HONO are somewhat understood, the sources of daytime HONO are currently under debate in the scientific community. This lack of understanding is, in part, responsible for the slow implementation of HONO chemistry in air quality models. It is thus the main goal of our project to develop a methodology that incorporates our current knowledge of HONO formation in the atmosphere in the CAMx model to improve the simulation of urban air chemistry in the Houston Area.

Below we review current implementations of HONO formation in urban airshed models and summarize the proposed mechanisms of HONO formation that could be implemented in these models.

Two chemical mechanisms commonly used in photochemical modeling – Carbon Bond (CB) and Statewide Air Pollution Research Center (SAPRC) - include only homogenous chemical HONO formation (Yarwood et al., 2005; Carter, 2010). The gas-phase reactions - Reactions 2 and 3 - are the most important homogeneous HONO formation pathways.

\[
\text{NO} + \cdot \text{OH} \rightarrow \text{HONO} \quad (R2)
\]

\[
\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HONO} \quad (R3)
\]
Several recent air quality modeling studies used the Community Multiscale Air Quality (CMAQ) model with the CB05 and SAPRC-99 chemical mechanisms, both of which include Reactions 2 and 3 (Sarwar et al., 2008; Czader et al., 2012; Concalves et al., 2012; Zhang et al., 2012), and examined the model performance compared to in-situ HONO observations. The models consistently showed HONO under-predictions compared to measurements. For example, Czader et al. (2012), reported biases of up to 2 ppb. Additional 3-D and 1-D modeling systems using only homogeneous HONO formation also under-predicted HONO substantially, oftentimes by a factor of ten (Li et al., 2010, 2011; Wong et al., 2011). It is clear from these efforts that homogeneous formation of HONO is not sufficient to match observed concentrations. The authors in the above modeling studies concluded that key sources of HONO exist in addition to Reactions 2 and 3.

Recent campaigns in Houston, Texas, have provided HONO observations that support the possibility of an additional source of HONO that is not included in current air quality models. Measurements taken during the 2006 Texas Air Quality Study and the 2009 Study of Houston Atmospheric Radical Precursors (SHARP) showed strong vertical HONO concentration gradients during the day with higher values near the ground - something modeled homogeneous chemistry did not predict (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.

It is commonly assumed that HONO is formed in the dark by the heterogeneous conversion of NO2 on humid surfaces. This reaction follows the following stoichiometry where $\text{ads}$ indicates adsorbed compounds:

$$\text{NO}_2 + \text{NO}_2 \rightarrow \text{ads} \rightarrow \text{HONO}_{\text{gas}} + \text{HNO}_3\text{ads}$$

(R4).

This mechanism appears to be first order in NO2 and the yield of HONO is 50% (Finlayson-Pitts et al., 2003; Kleffmann et al., 2005; Lammel and Cape, 1996). 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 explain nocturnal HONO observations in Houston well. 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).

Observations in laboratory and field experiments over the past decade have also uncovered a number of potential daytime HONO formation mechanisms. The two most likely mechanisms occur on surfaces (e.g., ground, aerosols) and are photolytically enhanced, i.e., they are much faster in the presence of solar light than the nocturnal HONO formation reaction described above.

The first mechanism is the photolysis of surface adsorbed nitric acid (HNO3) (Zhou et al., 2002; Beine et al., 2002; Dibb et al., 2002; Zhou et al., 2003; Ramazan et al., 2004; He et al., 2006; Zhou et al., 2007, 2011). Reactions 5 and 6 produce surface adsorbed HONO, which can volatilize into the gas-phase.
HNO\textsubscript{3}ads + hv \rightarrow NO\textsubscript{2}ads + ·OH \quad (R5)
2NO\textsubscript{2}ads + H\textsubscript{2}O\textsubscript{ads} \rightarrow HONO\textsubscript{ads} + HNO\textsubscript{3}ads \quad (R6)

The second HONO formation pathway is the photo-enhanced conversion of gas-phase NO\textsubscript{2} on organic films or surfaces commonly found on the ground or aerosols (George et al., 2005; Stemmler et al., 2006, 2007). Reactions 7-9 show the HONO formation described by Stemmler et al. (2006).

HA + hv \rightarrow A\textsubscript{red} + X \quad (R7)
A\textsubscript{red} + X \rightarrow A' \quad (R8)
A\textsubscript{red} + NO\textsubscript{2} \rightarrow A'' + HONO \quad (R9)

In the above reactions, HA is humic acid, A\textsubscript{red} and X are the reduced (as indicated by using \textcolor{red}{red}) and oxidized products of photolyzed HA, and A' and A'' are the derivatives of A\textsubscript{red}. In urban environments with abundant NO\textsubscript{x} concentrations, the rate-limiting step is Reaction 8 because both NO\textsubscript{2} and the oxidized HA product, X, compete for the reduced HA product, A\textsubscript{red}.

In addition to photo-enhanced heterogeneous chemical formation, HONO is directly emitted during combustion. The emitted HONO to emitted NO\textsubscript{x} ratio has been estimated to be about 0.8% for a variety of vehicle types (Pitts et al., 1984; Kurtenbach et al., 2001). Modeling efforts in recent years have attempted to include these new heterogeneous reactions and emission-based HONO sources. A number of studies have accomplished this using 3-D Eulerian grid models such as CMAQ (Sarwar et al., 2008; Czader et al., 2012; Concalves et al., 2012; Zhang et al., 2012), which is often used by state environmental agencies to demonstrate future attainment of the federal O\textsubscript{3} standard.

Li et al. (2010) and Li et al. (2011) used the Weather Research and Forecasting model coupled with Chemistry (WRF-CHEM) to model air quality in Mexico City and China and compared these model runs to measured HONO mixing ratios. In all cases, adding the photolytic and heterogeneous HONO formation pathways increased simulated HONO concentrations and improved agreement with HONO measurements. Sarwar et al. (2008) showed a normalized mean bias decrease from -98% to -42% when direct emissions and photo-enhanced heterogeneous HONO formation were included; Zhang et al. (2012) reported normalized mean bias improvement from -95% to 54%; for Li et al. (2011), mean normalized bias decreased from -97% to -39%; and Czader et al. (2012) found that the additional HONO sources increased morning HONO concentrations nearly ten-fold and improved correlation between simulated and measured values. These studies confirm that direct emissions and photo-enhanced heterogeneous formation are important contributors to atmospheric HONO concentrations. However, all but one (Zhang et al., 2012) of the modeling studies included direct emissions of HONO together with heterogeneous chemistry, thus making it difficult to assess the individual impacts of emissions and heterogeneous formation.

Czader et al. (2012) employed the process analysis (PA) utility that is useful in determining which physical processes and chemical reactions are dominant. PA can explain how the new HONO formation pathways have affected the simulated environment, not simply that it has been affected. The findings of Czader et al. (2012) provide insight into the origin and fate of ·OH and
how O₃ concentrations are impacted by additional HONO formation. From 6 p.m. to 9 p.m., the fractional contribution of HONO to ·OH production increased to 81% from 45% when direct emissions and photo-enhanced heterogeneous chemistry were included. Concentrations of ·OH in the morning were, on average, 35% greater when the additional HONO sources were included. Increases in O₃ concentrations of up to 11 ppb were also reported.

Much of the analysis in Czader et al. (2012) is limited to the model’s surface layer from which they found large vertical HONO fluxes. However, most of the HONO formed near the ground is transported vertically by convective transport, thus removing it from the analysis volume. Tracking changes to the oxidative chemical environment of the entire mixed planetary boundary layer (PBL) can elucidate more completely how new sources of HONO affect air quality. For example, chemical HONO loss pathways can be obtained. Restricting analysis to a sub-layer within the PBL can lead to the conclusion that such losses are due to physical processes like vertical transport. While that may be true for a particular model layer, it is not true for the entire volume of air below within PBL.

While each modeling study implemented the new HONO sources differently, the various approaches taken to represent HONO formation can be generalized as one that parameterizes heterogeneous rate coefficients as a function of surface area to volume. The surfaces could include aerosols, buildings, and/or the ground. This type of parameterization is a useful approximation, but it is not an accurate representation of the physical and chemical processes.

1.2 OBJECTIVES

The two primary objectives of this study were to use the SHARP 2009 dataset to (1) develop and implement new HONO formation mechanisms for the CAMx model, and (2) quantify the impacts of the new HONO sources on O₃ production in Houston.

Previous HONO modeling attempts in the literature overwhelmingly utilized empirical parameterizations of HONO production. Instead, we chose to employ a novel application of the CAMx surface model to provide a more accurate process based approach to both dark (thermal) and light (photo-enhanced) heterogeneous HONO formation on ground level surfaces. The CAMx surface model was reconfigured to allow fluxes of HNO₃ and NO₂ to accumulate a surface inventory via dry deposition. This revised surface model allows the ground to act as a reservoir for deposited species and simulates chemical deposition to the surface, sorption and penetration into soils and vegetation, photochemical degradation and transformation, and volatilization back into the air (re-emission). For the first time, dry deposition is not simply a removal process, but rather a dynamic process that makes deposited species available for further chemical processing.

The updated surface model is added to version (v6.1) of the Comprehensive Air quality Model with extensions (CAMx), which is a 3-D air quality model routinely used for regulatory purposes. This study implements missing HONO formation pathways into a previously unreleased version of CAMx. This is the first time the new HONO sources have been added to CAMx, and it is the first time that the surface model approach has been implemented to manage
thermal and photo-enhanced heterogeneous HONO formation. With the surface model and PA implemented, HONO re-emission is quantified, and the chemical effects of the additional HONO are analyzed throughout the PBL. Model performance is evaluated using the extensive set of measurements that were taken during the 2009 SHARP campaign in Houston.

1.3 TASKS

The following tasks were undertaken and completed in performing this study:

1. Task 1- Submit Work Plan with budget (including QAPP)
2. Task 2- Monthly Technical Reports and Financial Reports
3. Task 3- Interim Reports
4. Task 4a- HONO Parameterization Development
5. Task 4b- Implement and Test HONO Parameterization in CAMx Model
6. Task 4c- Apply Process Analysis Tools to CAMx Output
7. Task 5a- Draft Final Report
8. Task 5b- Final Report acceptable to TX AQRP
2. METHODS

2.1 SURFACE MODEL

In this study, we implemented a surface model in the core CAMx 6 code to enable modeling HONO formation by surface reactions and emission to the atmosphere. This surface model is based on an existing treatment that was originally implemented as an optional surface model for persistent organic pollutants (POPs) using the reactive tracer (RTRAC) probing tool. For this study, the surface model was extended to permit interactions with core model species, in this application NO₂, HNO₃ and HONO. The updated CAMx surface model will be released as part of the core CAMx code in version 6.1 of CAMx, with appropriate modifications to the User’s Guide.

Below, we describe the main features of the surface model and its extension to model surface HONO formation and subsequent re-emissions to the atmosphere. We also discuss some of the key parameters of the surface model. Because of the uncertainties in these parameters, a semi-empirical approach was adopted in which measurements during the SHARP study were used to refine initial guesses for these parameters.

2.1.1 Model Description

The CAMx surface model treats deposition of air concentrations to the surface, sorption and penetration into soils and vegetation, chemical degradation and transformation, and volatilization back into the air (re-emission). As mentioned above, the surface sub-model was originally developed as a component of the Reactive Tracer (RTRAC) module, and thus was a separate treatment from the core model’s algorithms. In this study, the model was expanded to treat any subset of species listed in the core model’s chemical mechanism.

The deposition of chemical species to the surface is treated in the core model algorithms. The 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), chemical transformation (both heterogeneous and photolysis), and re-emission to the atmosphere. Deposition to water surfaces is assumed to be irreversible and thus is not tracked by the surface model. The schematic of the surface model, shown in Figure 1, summarizes the various surface processes that are considered in the model. Table 1 provides the descriptions and units of the surface variables shown in Figure 1.

After deposition to each surface grid cell at each time step, the newly deposited mass increment is divided among soil and vegetation according to landuse-dependent split factors, and added to total surface mass accumulated during the model run. The fractional coverage of 11 landuse categories in each grid cell is an existing input to CAMx. For each grid cell, the net soil/vegetation split is determined by the combination of landuse-dependent split factors and the fractional coverage of each landuse type. The soil/vegetation splits for each of the 11 landuse
categories are assumed to be seasonally constant, and values were estimated based on simple conceptual considerations of the amount of annual-averaged vegetation (i.e., leaf area index) typical of each category (Table 2).

Figure 1. Schematic of the CAMx surface model.

Table 1. Description of CAMx surface model variables shown in Figure 1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_p$</td>
<td>Areic mass of compound on vegetation</td>
<td>mol ha$^{-1}$</td>
</tr>
<tr>
<td>$A_s$</td>
<td>Areic mass of compound on the soil</td>
<td>mol ha$^{-1}$</td>
</tr>
<tr>
<td>$K_{veg}$</td>
<td>Vegetation-air partitioning coefficient</td>
<td>unit-less</td>
</tr>
<tr>
<td>$K_{soil}$</td>
<td>Soil-air partitioning coefficient</td>
<td>unit-less</td>
</tr>
<tr>
<td>$K_{leach}$</td>
<td>Leaching rate coefficient</td>
<td>min$^{-1}$</td>
</tr>
<tr>
<td>$K_{pen}$</td>
<td>Leaf penetration rate coefficient</td>
<td>min$^{-1}$</td>
</tr>
<tr>
<td>$j$</td>
<td>Photolysis chemistry rate coefficient</td>
<td>min$^{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>Heterogeneous chemistry rate coefficient</td>
<td>min$^{-1}$</td>
</tr>
<tr>
<td>$R_{leach}$</td>
<td>Leaching rate</td>
<td>mol ha$^{-1}$ min$^{-1}$</td>
</tr>
<tr>
<td>$R_{pen}$</td>
<td>Leaf penetration rate</td>
<td>mol ha$^{-1}$ min$^{-1}$</td>
</tr>
<tr>
<td>$R_{chem}$</td>
<td>Chemistry rate</td>
<td>mol ha$^{-1}$ min$^{-1}$</td>
</tr>
</tbody>
</table>
Table 2. CAMx landuse categories and associated default annual-averaged soil/vegetation split factors and shade factors.

<table>
<thead>
<tr>
<th>Category Number</th>
<th>Land Cover Category</th>
<th>Soil Fraction Surface Parameter</th>
<th>Shade Fraction Surface Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Urban</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>Agricultural</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>Rangeland</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>Deciduous forest</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>Coniferous forest, wetland</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>Mixed forest</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>7</td>
<td>Water</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>8</td>
<td>Barren land</td>
<td>0.9</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>Non-forested wetlands</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>10</td>
<td>Mixed agricultural/range</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>11</td>
<td>Rocky (with low shrubs)</td>
<td>0.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The surface model uses partitioning (equilibrium) coefficients to calculate the amount of accumulated material sorbed to soil and vegetation. 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 simply 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 is subject to a volatilization flux (i.e., it is re-emitted). Separate chemical-specific soil-air and vegetation-air partitioning coefficients are set in the CAMx chemistry parameters file. They represent the equilibrium ratio of chemical on a surface to chemical in air at the air-surface interface. For example, a compound with a partitioning coefficient of 10,000 (unit-less) has an equilibrium concentration on the surface that is 10,000 times more than that in air, and will have negligible re-emissions.

Chemistry, soil leaching, and plant penetration are dependent on chemical properties of the compounds 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 ($A$):

$$R_{\text{process}} = k_{\text{process}} \times A_{\text{surface}}$$  \hspace{1cm} (R11)

When the actual rate coefficients (or inversely, the half-lives $t_{1/2}$) are unknown for the substance, they are generalized by 5 classes, as shown in Table 3 below.
Table 3. Generalized classes of substance half-lives and process rates used in the CAMx surface model.

<table>
<thead>
<tr>
<th>Class</th>
<th>Half-Life (days)</th>
<th>Process Rate day⁻¹</th>
<th>Process Rate min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very Fast</td>
<td>0.04</td>
<td>17</td>
<td>1.2×10⁻⁴</td>
</tr>
<tr>
<td>Fast</td>
<td>0.21</td>
<td>3.3</td>
<td>2.3×10⁻⁴</td>
</tr>
<tr>
<td>Moderate</td>
<td>1.00</td>
<td>0.69</td>
<td>4.8×10⁻⁴</td>
</tr>
<tr>
<td>Slow</td>
<td>5.00</td>
<td>0.14</td>
<td>9.7×10⁻⁵</td>
</tr>
<tr>
<td>Very Slow</td>
<td>25.0</td>
<td>0.03</td>
<td>2.1×10⁻⁵</td>
</tr>
</tbody>
</table>

A 6th class can be added by setting the k-value to zero or a de-minimis value to effectively remove the process from consideration. In this manner, chemicals can be modeled with an estimated half-life that is unique for each process.

Note that all the partitioning coefficients and reaction rates other than photolysis are fixed and ignore dependence on various environmental conditions (e.g., temperature, pressure, surface type, surface moisture, etc.). Photolysis rates are specified by the user to represent 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 landuse type (Table 2).

The approach for re-emission of volatilized (un-sorbed) mass is consistent with the CAMx dry deposition algorithm. Specifically, the surface model is tied to the Wesely (1989) option and is not available with the Zhang option (Zhang et al., 2001; 2003). 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 ($v_d$) is calculated based on the electrical resistance analog:

$$v_d = \frac{1}{r_a + r_b + r_s}$$  \hspace{1cm} (R12)

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 ($v_e$) that is similar in form to $v_d$:

$$v_e = \frac{1}{r_a + r_b}$$  \hspace{1cm} (R13)
where the $r_s$ term is missing 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.

### 2.1.2 Key Surface Model Parameters

Table 4 lists the parameters that need to be specified for each chemical for the surface model calculations. These are a subset of the full list of surface model variables shown previously in Table 1. There are considerable uncertainties associated with these parameters and a key component of this study was to leverage the HONO, NO$_2$ and HNO$_3$ measurements from the SHARP database to refine the values of these parameters in an iterative manner, as discussed in Section 3.

Initial values for these parameters were selected based on consideration of the physical and chemical attributes of the species participating in surface reactions believed to produce HONO. Sensitivity studies, described in Section 3.3, were conducted to determine the parameter set that best captured the observed features in the SHARP measurements for a majority of the modeling days. Tables 5a and 5b show the final values for these parameters derived from this iterative process.

**Table 4. User-specified surface model parameters.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{veg}$</td>
<td>Vegetation-air partitioning coefficient</td>
<td>unit-less</td>
</tr>
<tr>
<td>$K_{soil}$</td>
<td>Soil-air partitioning coefficient</td>
<td>unit-less</td>
</tr>
<tr>
<td>$k_{leach}$</td>
<td>Leaching rate coefficient</td>
<td>min$^{-1}$</td>
</tr>
<tr>
<td>$k_{pen}$</td>
<td>Leaf penetration rate coefficient</td>
<td>min$^{-1}$</td>
</tr>
<tr>
<td>$J$</td>
<td>Photolysis chemistry rate coefficient</td>
<td>min$^{-1}$</td>
</tr>
<tr>
<td>$k$</td>
<td>Heterogeneous chemistry rate coefficient</td>
<td>min$^{-1}$</td>
</tr>
</tbody>
</table>
Table 5a. Final values for surface model soil and vegetation parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NO$_2$</th>
<th>HNO$_3$</th>
<th>HONO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{veg}$, unit-less</td>
<td>1.00E+10</td>
<td>1.00E+10</td>
<td>1.00</td>
</tr>
<tr>
<td>$K_{soil}$, unit-less</td>
<td>1.00E+10</td>
<td>1.00E+10</td>
<td>1.00</td>
</tr>
<tr>
<td>$k_{leach}$, min$^{-1}$</td>
<td>0.01</td>
<td>2.4E-04</td>
<td>4.8E-04</td>
</tr>
<tr>
<td>$k_{pen}$, min$^{-1}$</td>
<td>0.01</td>
<td>0.01</td>
<td>4.8E-04</td>
</tr>
</tbody>
</table>

Table 5b. Final values for surface model reaction rates.

<table>
<thead>
<tr>
<th>Rate Coefficient</th>
<th>NO$_2$ --&gt; HONO</th>
<th>HNO$_3$ --&gt; HONO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis Rate Constant (J), min$^{-1}$</td>
<td>0.01</td>
<td>2.4E-03</td>
</tr>
<tr>
<td>Thermal Rate Constant (k), min$^{-1}$</td>
<td>0.002</td>
<td>0.00</td>
</tr>
</tbody>
</table>

2.2 CAMx SETUP

For the Houston 8-hr Ozone Coalition, Alpine Geophysics LLC (AG) and Climate & Atmospheric Research Associates (CARA) developed multi-model ensembles for 2008-2010 focusing primarily on the Houston O$_3$ non-attainment area (McNally et al., 2010). Four ensemble members were constructed with alternative science configurations of the MM5 (v3.7), WRF (v3.2.1), GloBEIS (v3.1), MEGAN (v2.04), and CAMx (v5.4.1) platforms. Thorough description of the model algorithms, data base development procedures, simulation strategy, and performance evaluation methods are given in the modeling protocol (Tesche et al., 2010).

This study used meteorology from WRF, GloBEIS for biogenic emissions over Texas, MEGAN for biogenics elsewhere in the domain, county-level MOVES for mobile sources, the Texas Commission on Environmental Quality’s (TCEQ) point source inventory and the U.S. Environmental Protection Agency’s (EPA) National Emission Inventory (NEI 2008). HONO emissions were not present in the emission inventories. Lateral boundary conditions were developed from a 2009 MOZART-4 global simulation performed at the National Center for Atmospheric Research.

Modeling in this study was performed with CAMx version 6.1 with CB6 (Yarwood et al., 2012). Based on CAMx version 6 (ENVIRON 2013), this new version of CAMx extends the surface model to allow for heterogeneous HONO formation as described in Section 2.

The modeling episode spans the 2009 SHARP campaign (April 15-May 31) and has an output time resolution of one hour. Figure 2 shows the nested 36/12/4 km domain and Figure 3, the
portion of the 4-km domain centered on Houston. SHARP measurements were taken at the Moody Tower site; the grid cell containing the Moody Tower is shaded black in Figure 3.

Figure 2: Nested 36/12/4 km CAMx modeling domain.
Figure 3. A subset of the 4 km domain over downtown Houston. Grey cells represent the Houston “Urban” region, black grid cell contains the Moody Tower, and the light blue cell is adjacent to and southwest of the Moody Tower.

### 2.3 PROCESS ANALYSIS

The CAMx simulations for this study include the Process Analysis (PA) option that is part of CAMx (ENVIRON, 2013). When the PA option is enabled, CAMx creates a set of files during runtime that contain rate information for all simulated chemical and physical processes. The analysis of PA outputs can be facilitated by using post-processing software to automate tasks, such as aggregating information over grid cells that are contained within a changing PBL height. The Python-based PA (pyPA) post-processing tool can aggregate multiple model layers, permitting an hour-by-hour tracking of model processes within the PBL (Henderson et al., 2011). The surface model implementation (Section 2) preserved the integrity of CAMx PA outputs: for example, the HONO emissions computed by the surface model are reported as surface emissions in PA output files. We also confirmed that pyPA is compatible with PA output generated by the modeling scenarios.
3. PROJECT RESULTS AND DISCUSSION

3.1 GENERAL MODEL PERFORMANCE

This study evaluated the impacts of new sources of HONO in a 3-D air quality model. Simulated concentrations of NO₂, HONO, HNO₃, and ozone were compared to measurements at Moody Tower. In addition to examining model performance for these chemical species, we also computed hourly ratios of HONO:NO₂. This ratio can be a better measure of model performance than looking solely at HONO concentrations because it is less dependent on the actual NO₂ levels and thus better suited to test any mechanism.

We chose four days to analyze: April 20-21 and May 19-20. These were clear week days with favorable conditions for ozone formation. Measured HONO and ozone concentrations were among the highest recorded during the SHARP campaign. Peak 1-hr HONO concentrations were 0.43 ppb (April 20), 0.34 ppb (April 21), 0.50 ppb (May 19), and 0.71 ppb (May 20). Peak 1-hr ozone concentrations were 63 ppb (April 20), 72 ppb (April 21), 74 ppb (May 19), and 81 ppb (May 20).

The modeling results showed poor performance for NO₂ concentrations at the Moody Tower grid cell (see Sections 0 through 0). The NOx emissions in this grid cell are over-estimated. This is a known issue with the 2009 ensemble modeling dataset, as pointed out by Alpine Geophysics, who provided the inputs for our study. The over-estimates are the result of the spatial allocation of NOx emissions coming from ship channel activity, likely from off-road equipment directly east of Moody Tower (personal communication, Dennis McNally). The high emissions are restricted to the row of grid cells in which the Moody Tower grid cell is located. A review of the spatial emission inventory plots by Alpine Geophysics indicated that off-road emissions were the most likely source of the locally high NOx emissions. Figure 4 shows total NO₂ surface layer emissions for April 20. The Moody Tower grid cell had far greater NO₂ emissions than surrounding grid cells.

Based on the poor NO₂ performance for the Moody Tower grid cell, the team chose to use simulation data from the grid cell directly southwest of Moody Tower for the development and refinement of the HONO mechanism. HONO formation is strongly coupled to NO₂ concentrations, and NO₂ performance is significantly better southwest of Moody Tower (see Sections 6.1 through 6.3). Shifting to the southwest grid cell removes unrealistic model behavior caused by artificially high NO₂ and allows for a clearer understanding of the impacts of direct HONO emissions and heterogeneous formation on surfaces.

When model data are compared against the in situ observations, predictions from the second model layer are used. This model layer approximately aligns with the 70m height of Moody Tower, where the measurements were made. LP-DOAS upper, middle, and lower levels are compared to the fourth, third, and second vertical layers (Figure 5).
Figure 4. Total NO\textsubscript{2} surface emissions for April 20\textsuperscript{th} for inner Houston domain. The black dot is the approximate location of the Moody Tower.
Figure 5. Schematic figure of the setup of UCLA’s LP-DOAS during SHARP 2009, showing the three LP-DOAS light paths and the height intervals for which concentrations were retrieved as well as the height intervals for first four CAMx model layer (ML-X) heights for layers 1-4.

### 3.2 REFINEMENT OF MODEL PERFORMANCE

As discussed in Section 2.1.2, initial values for the CAMx 6 surface model parameters were selected based on consideration of the physical and chemical attributes of the species (HNO₃, NO₂, and HONO) participating in surface reactions believed to produce HONO. These parameters were then adjusted within their range of plausible values by conducting a number of CAMx sensitivity simulations and comparing model results with SHARP measurements (see Section 3.3). The objective of the sensitivity studies was to arrive at a set of values for the surface model parameters that best captured the observed features in the SHARP measurements. In this section, we briefly describe the rationales for the initial values assigned to the model parameters, and subsequent refinements to these values to obtain the final parameter set shown previously in Table 5.
3.2.1 Surface-Air Partitioning Coefficients

Coefficients for two types of surfaces (vegetation and soil) are used in the surface model for each species 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 NO₂ and HNO₃ are assumed to remain on the surface once they are deposited and were assigned very high vegetation-air and soil-air partitioning coefficients (1E10), while surface HONO is expected to volatilize and re-emit, and was assigned a moderate value (1). These values were maintained for all the sensitivity studies conducted with CAMx.

3.2.2 Surface Removal Parameters

As in the case of the surface-air partitioning coefficients discussed above, the CAMx 6 surface model considers removal of deposited material to two types of surfaces, vegetation and soil. Once removed, the material is no longer available at the surface for reaction or re-emissions. Removal from soil surfaces occurs by leaching, while on vegetative surfaces removal is by penetration into leaf tissues. These removal terms are specified as first-order destruction rates. Table 3 shows the relationship between removal rates and surface lifetimes.

The leaching rate to soil is determined by the parameter \( k_{\text{leach}} \). A moderate value was assigned for the leaching rate of HONO to allow its re-emission after formation by surface reactions. The lifetimes of HNO₃ and NO₂ on soil surfaces are not known. Moderate values were also initially used for the leaching rates of NO₂ and HNO₃, but the modeling results showed that better agreement with SHARP measurements was obtained when NO₂ was leached at a higher rate (shorter lifetime) and HNO₃ was leached at a lower rate (longer lifetime). The shorter lifetime for NO₂ is consistent with our understanding that it is a volatile species. Furthermore, gas phase concentrations of HONO and NO₂ are well-correlated at night, which suggests that surfaces are a short-lived reservoir for NO₂. The longer lifetime for HNO₃ is consistent with it being a semi-volatile species that has a high affinity for surfaces.

Similarly, penetration into vegetation is determined by the parameter \( k_{\text{pen}} \). As in the case of soil leaching, moderate values were assigned initially for \( k_{\text{pen}} \) for all three species, but these values were later adjusted for NO₂ and HNO₃ based on the sensitivity study results. For both NO₂ and HNO₃, higher values for the penetration rates (i.e., shorter lifetimes) provided results that were more consistent with the SHARP measurements. The higher value for the NO₂ penetration rate can be justified using the same arguments as above for the NO₂ leaching rate, while the higher value for the HNO₃ penetration rate can be attributed to the high solubility of HNO₃ and the water content of vegetation.

Note that rainfall events enhance both \( k_{\text{leach}} \) and \( k_{\text{pen}} \). Thus, the surface model flushes soil and vegetation surfaces clean after a precipitation event.
3.2.3 Surface Reaction Parameters

The surface reaction parameters determine the rates at which deposited NO2 and HNO3 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 HNO3 conversion to HONO. Thus, the only HONO formation pathway in the surface model at night is the thermal reaction of NO2.

The NO2 thermal reaction rate was initially set to a moderate value. However, model predictions of HONO:NO2 ratios at night were in better agreement with observations when a higher reaction rate was used.

As discussed in Section 2.1.1, 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 NO2 photolysis rate is a factor of 5 lower than the gas-phase value, while the final value for the surface HNO3 photolysis reaction is about 50 times faster than in the gas-phase.

3.3 COMPARISON OF RUNS A (BASE) AND B (DIRECT EMISSIONS) TO FINAL RUN H (SURFACE MODEL)

Table 6 lists the various CAMx sensitivity simulations conducted for the SHARP period. Run A is the base run (i.e., without the surface model and without direct HONO emissions), Run B includes direct HONO emissions as 0.8% of surface NOx emissions (but no surface model), while Runs C through H represent iterations of CAMx applications with the surface model varying the model parameters. The final surface model run (Run H) provided results that were most consistent with observed HONO concentrations and HONO:NO2 ratios. The parameters for the surface model in Run H were shown previously in Tables 5a and 5b. The results presented in this section are based on Runs A, B, and H.

Figure 6 shows hourly simulated and measured HONO concentrations for the four days and the three different runs. One set of measurements was taken with UCLA’s LP-DOAS and are vertically resolved at three different heights (shaded circles); the other (in situ) was taken atop Moody Tower (open circles). Only simulation data from the grid cell southwest of Moody Tower is shown. HONO values decrease with height as most HONO formation occurs near the ground where NOx concentrations are greatest.
Table 6. List of CAMx Runs.

<table>
<thead>
<tr>
<th>Run</th>
<th>Description</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Base simulation: no surface model; no direct HONO emissions</td>
<td>Gas-phase HONO formation only</td>
</tr>
<tr>
<td>B</td>
<td>Sensitivity simulation; no surface model; direct HONO emissions = 0.8% of NOx emissions</td>
<td>Gas-phase HONO formation and direct emissions</td>
</tr>
<tr>
<td>C</td>
<td>Sensitivity simulation; surface model; no direct HONO emissions</td>
<td>Gas-phase and surface HONO formation; initial estimates of surface model parameters</td>
</tr>
<tr>
<td>D</td>
<td>Sensitivity simulation; surface model; no direct HONO emissions</td>
<td>Gas-phase and surface HONO formation; adjustment of surface model parameters</td>
</tr>
<tr>
<td>E</td>
<td>Sensitivity simulation; surface model; no direct HONO emissions</td>
<td>Gas-phase and surface HONO formation; adjustment of surface model parameters</td>
</tr>
<tr>
<td>F</td>
<td>Sensitivity simulation; surface model; no direct HONO emissions</td>
<td>Gas-phase and surface HONO formation; adjustment of surface model parameters</td>
</tr>
<tr>
<td>G</td>
<td>Sensitivity simulation; surface model; no direct HONO emissions</td>
<td>Gas-phase and surface HONO formation; adjustment of surface model parameters</td>
</tr>
<tr>
<td>H</td>
<td>Sensitivity simulation; surface model; no direct HONO emissions</td>
<td>Gas-phase and surface HONO formation; final set of surface model parameters, described in Table 5</td>
</tr>
</tbody>
</table>
Figure 6. HONO Timeseries Upper, Middle, Lower DOAS – Runs A, B and H (April 20, 21 & May 19, 20)

Run A (green line) under-predicts HONO, especially in the early morning before sunrise and in the evening after sunset. Accuracy improves during the middle of the day when ·OH concentrations reach maximum levels indicating the importance of homogeneous HONO formation. In May, the daytime predictions of HONO in Run A did show over-predictions in the middle and upper heights. Run B (blue line) under-predicts HONO during the morning and at night, though noticeable increases coincide with rush hour traffic. In Run H (Red) there were greater HONO predictions at every hour in all three layers except midnight. Early morning Run H second-layer (bottom plot) HONO predictions improved compared to Runs A and B on April 21 and May 19, but were over predicted on April 20 and May 20. During the night, Run H was able to more closely match observations. In the higher layers Run H continues to over-predict HONO, especially on May 20.

HONO performance for the three model runs varied substantially. Figure 7 compares time-paired HONO concentrations to in situ measurements for Runs A, B, and H for all four days. The solid line marks perfect agreement between measurements and predictions; the cone bounded by the dashed lines marks comparisons within a factor of two. Daytime is 9 a.m. to 6 p.m., and
nighttime is 7 p.m. to 8 a.m. HONO predictions from the grid cell to the southwest of Moody Tower were used to counteract the poor NO$_2$ performance in the Moody Tower grid cell, as discussed previously. Run A consistently shows under-predictions even during the day. It is clear that homogeneous HONO formation alone is insufficient to match observations. Run B shows good agreement during the day, but there are severe 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. Nighttime predictions show improvement over Runs A and B, though performance on May 20 was markedly worse than the other three days.
Figure 7. Simulated HONO versus LP-DOAS measured HONO (integrated between 40 and 300 m) for model runs A, B and H (day = red, night = black). Note different symbols for April 20, 21 & May 19, 20.
The nighttime production of HONO in Run H is solely dependent on NO₂ and thus is tied to the model’s ability to predict it. This is the case for May 20 where NO₂ model performance showed an over-prediction. Time-paired simulated and in situ measured NO₂ concentrations are shown in Figure 8 for model run A. NO₂ performance is similar across all three model runs (see Tables 8 and 9). Nighttime model performance is worse on May 19 and 20, which leads to the high concentrations of HONO found on those days (particularly May 20). As model performance improves for NO₂, so does HONO model performance.

Figure 8. Simulated NO₂ versus measured NO₂ for model run A (day = red, night = black). Note different symbols for April 20,21 & May 19,20.

Given the connection with NO₂ model performance and HONO predictions, an analysis was made using the ratio of the concentrations of these species. The time series of HONO:NO₂ ratios for Runs A, B, and H are shown in Figure 9 for all four days. During all hours the predicted ratio of concentrations for Run A is always less than observations (in situ). The low HONO:NO₂ ratios for Run A in the early morning and night are due to low HONO concentrations since NO₂ concentrations were consistent in the model runs. The ratios in Run B show an improvement over Run A especially at night, but are still often below the measurements. The ratio values increase at nearly every hour in Run H, and were able to replicate the observed diurnal pattern on most days. Daytime ratios more closely match observations. It is important to note that on April 21, predicted ratios in Run H were able to capture the sudden increase in observed ratios beginning at 7 p.m.
Figure 9. Timeseries of simulated and measured hourly HONO:NO\textsubscript{2} ratios for runs A, B and H (April 20,21 & May 19,20).

The time series of HNO\textsubscript{3} observations is shown in Figure 10, along with model predictions made during Runs A and H. In the May simulations, the model is predicting higher than observed HNO\textsubscript{3} concentrations likely leading to large surface loadings. This results in greater HONO daytime production from the surface model and is part of the cause of daytime HONO over predictions in May. The over prediction of HNO\textsubscript{3} seen in Figure 10 is consistent with the NO\textsubscript{2} over prediction (as shown in Figure 8).
Figure 10. Time series of hourly simulated and measured HNO₃ mixing ratios for runs A, B and H (April 20, 21 & May 19, 20).
Table 7 provides the total amount of HONO emitted for Runs B and H. It is important to note that in Run A there are zero emissions of HONO. It is clear from this table that the larger contribution of HONO from Run H more than doubles the HONO emitted from Run B.

Table 7. 24-hr total surface HONO emissions at 4km grid cell southwest of Moody Tower.

<table>
<thead>
<tr>
<th>Date</th>
<th>Run B (μmole/day)</th>
<th>Run B (ppbv/day)</th>
<th>Run H (μmole/day)</th>
<th>Run H (ppbv/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>April 20, 2009</td>
<td>1.07</td>
<td>25.8</td>
<td>2.52</td>
<td>60.3</td>
</tr>
<tr>
<td>April 21, 2009</td>
<td>1.06</td>
<td>25.8</td>
<td>2.87</td>
<td>69.9</td>
</tr>
<tr>
<td>May 19, 2009</td>
<td>1.09</td>
<td>26.3</td>
<td>4.84</td>
<td>116.9</td>
</tr>
<tr>
<td>May 20, 2009</td>
<td>1.08</td>
<td>26.4</td>
<td>6.45</td>
<td>156.9</td>
</tr>
</tbody>
</table>

Tables 8 and 9 show the normalized mean error (R14) and bias (R15), respectively, for the period from April 15 to May 31. As shown in the tables, Run H over-predicts HONO, but is an improvement over Run A. Much of this error can be attributed to the large over-predictions in NO2 and HNO3. When looking at the ratio of HONO to NO2, Run H shows the best performance. The parameters in the surface model scheme are uncertain and the final values from Run H balance model performance for HONO concentration (biased high) and HONO:NO2 ratio (biased low) as shown in Table 9.

\[ E_{NME} = \frac{\sum_{i=1}^{N} |M_i - O_i|}{\sum_{i=1}^{N} O_i} \times 100\% \]  
\[ \text{(R14)} \]

\[ B_{NMB} = \frac{\sum_{i=1}^{N} (M_i - O_i)}{\sum_{i=1}^{N} O_i} \times 100\% \]  
\[ \text{(R15)} \]

Table 8. Normalized Mean Error (NME) between measured and modeled HONO, NO2, and HNO3 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.

<table>
<thead>
<tr>
<th>Model Run/Day-Night</th>
<th>HONO NME</th>
<th>NO2 NME</th>
<th>HNO3 NME</th>
<th>HONO:NO2 NME</th>
<th>HONO:HNO3 NME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run A / Day</td>
<td>60.3</td>
<td>96.1</td>
<td>86.8</td>
<td>76.4</td>
<td>88.6</td>
</tr>
<tr>
<td>Run A / Night</td>
<td>80.3</td>
<td>105.2</td>
<td>120.8</td>
<td>95.1</td>
<td>94.5</td>
</tr>
<tr>
<td>Run B / Day</td>
<td>41.8</td>
<td>95.3</td>
<td>87.4</td>
<td>60.2</td>
<td>80.7</td>
</tr>
<tr>
<td>Run B / Night</td>
<td>69.4</td>
<td>104.7</td>
<td>121.9</td>
<td>63.5</td>
<td>88.9</td>
</tr>
<tr>
<td>Run H / Day</td>
<td>47.5</td>
<td>97.3</td>
<td>94.8</td>
<td>43.4</td>
<td>70.4</td>
</tr>
<tr>
<td>Run H / Night</td>
<td>79.0</td>
<td>107.4</td>
<td>130.3</td>
<td>47.6</td>
<td>77.2</td>
</tr>
</tbody>
</table>
Table 9. Normalized Mean Bias between measured and modeled HONO, NO₂, and HNO₃ 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.

<table>
<thead>
<tr>
<th>Model Run/Day-Night</th>
<th>HONO NME</th>
<th>NO₂ NME</th>
<th>HNO₃ NME</th>
<th>HONO:NO₂ NME</th>
<th>HONO:HNO₃ NME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run A / Day</td>
<td>-59.1</td>
<td>69.7</td>
<td>57.5</td>
<td>-76.2</td>
<td>-88.6</td>
</tr>
<tr>
<td>Run A / Night</td>
<td>-82.7</td>
<td>83.4</td>
<td>80.0</td>
<td>-95.1</td>
<td>-93.2</td>
</tr>
<tr>
<td>Run B / Day</td>
<td>-22.8</td>
<td>68.5</td>
<td>58.9</td>
<td>-58.9</td>
<td>-67.8</td>
</tr>
<tr>
<td>Run B / Night</td>
<td>-1.5</td>
<td>82.6</td>
<td>81.8</td>
<td>-63.4</td>
<td>-51.9</td>
</tr>
<tr>
<td>Run H / Day</td>
<td>19.7</td>
<td>71.3</td>
<td>71.9</td>
<td>-29.1</td>
<td>-63.3</td>
</tr>
<tr>
<td>Run H / Night</td>
<td>49.6</td>
<td>85.7</td>
<td>95.1</td>
<td>-28.5</td>
<td>-44.0</td>
</tr>
</tbody>
</table>

### 3.3.1 Evaluation of Direct HONO Emissions

Few studies have reported observations of direct HONO emission rates and the HONO/NOₓ emission ratio is thus uncertain. In model Run B we have adopted one of the highest reported ratios of HONO/NOₓ = 0.008. Nevertheless the model was unable to explain the nocturnal HONO observations, often considerably underestimating HONO mixing ratios (Figure 7). During the day the agreement between HONO observations and model was generally better. However, an analysis of the HONO:NO₂ ratio, which diminishes the dependence of the HONO simulations on NOₓ emissions and mixing ratios (Figure 9), shows that direct emissions alone are still too small to describe the observations.

Considering the disagreement at night, the lower than observed modeled HONO:NO₂ ratios, as well as the high uncertainty of the HONO emission ratios, we concluded that the contribution from direct emissions is likely small compared to the chemical formation on the surface. This interpretation is supported by the 1D model simulation by Wong et al. (2013), who attributed 8-10% of the observed daytime HONO during SHARP to traffic emissions in Houston. Careful consideration of our model results led to the exclusion of the direct emission pathway for Run H. We do not want to imply that HONO is not emitted directly from combustion processes, but think 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.

### 3.3.2 Evaluation of New HONO Surface Model Approach

The results from the CAMx simulations clearly show that the base model severely under-predicts HONO concentrations, and gas-phase HONO formation alone cannot explain HONO measurements during the SHARP period. Including direct HONO emissions results in an improvement in the HONO under-predictions but the improvement is inconsistent and the
observed diurnal variation is not captured. The surface model provides a mechanistic approach that represents our best understanding of HONO formation at the surface. CAMx performance for HONO with the surface model is strongly dependent on model performance for NO₂ concentrations and HONO concentrations and their diurnal variation are simulated well when predicted and observed NO₂ concentrations are in good agreement. Thus, the HONO:NO₂ ratios provide a better measure of model performance for HONO. For the most part, NO₂ concentrations are over-predicted, resulting in over-prediction of HONO concentrations with the surface model. However, predicted HONO:NO₂ ratios are in much better agreement with observed ratios.

Applications of CAMx with the surface model for other periods or regions where HONO measurements are available will provide further confidence in the use of the approach and will provide the opportunity to further refine and test the surface model parameters that worked well for the SHARP period.
3.4 PROCESS ANALYSIS

3.4.1 Impact on morning OH

Hourly OH initiation and VOC oxidation rates are shown in Figure 11 for April 21, 2009. The values in this figure are the hourly integrated reaction rates taken from the aggregation of all model layers below the PBL at the grid cell southwest of Moody Tower. The largest differences between the model runs occur at the start of the photochemical day. Beginning at 6 a.m., there is a four hour period during which OH initiation from HONO photolysis is significantly greater in Run H because there is more HONO available (Figure 11). During this four-hour period, 1.65 ppb OH is created from HONO photolysis, which is 55% of the daily total OH initiated from this reaction. In Runs A and B that percentage is only 35% and 45%. OH production from HONO photolysis in Run A are always below Runs B and H because Run A only has gas-phase HONO formation, and, thus, always has lower HONO concentrations.

Figure 11 also shows the amount of VOC oxidized by OH for the three model runs. As with HONO photolysis, the differences appear during the first few hours following sunrise. The extra OH created from HONO in Run H quickly begins to attack VOCs. At around 11 a.m., the reservoir of nighttime HONO in Run H is depleted, OH initiation approaches values found in Runs A and B, and VOC oxidation levels also align with those in Runs A and B.

![Figure 11. The rate of total OH initiation from HONO photolysis (ppbv/hr) in dashed lines for Runs A, B, and H (on left axis). Also shown is the rate of total VOC oxidized by OH (ppb VOC/hr) in solid lines for same three model runs.](image-url)
### 3.4.2 Impact of new HONO on NOx (and/or VOC) limitation

The ratio of hydrogen peroxide production to nitric acid production (commonly called the Sillman ratio) can be used to indicate whether the oxidative chemical environment is NOx-limited or NOx-inhibited. Higher ratios indicate that radical-radical reactions are occurring because NOx is scarce (NOx-limited); lower ratios indicate that nitric acid is being produced because NOx is in abundance, thus removing OH and NO2 from the system (NOx-inhibited). A cut-off of 0.35 was proposed by Sillman (1995) to mark the transition between the two regimes. Hourly Sillman ratios are provided from April 15 to May 31 for Runs A, B, and H in Figure 12. The figure shows very little difference between the three runs, indicating that NOx-sensitivity was not affected greatly by the additional HONO sources.

The ratio of nitric acid (HNO3) production to hydrogen peroxide (HOOH) production for the downtown Houston domain (grey area in Figure 3). This ratio is also known as the “Sillman Ratio”.

![Figure 12. Ratio of nitric acid (HNO3) production to hydrogen peroxide (HOOH) production for the downtown Houston domain (grey area in Figure 3). This ratio is also known as the “Sillman Ratio”](image-url)
### 3.4.3 Impact on ozone

Ozone mixing ratios for both sets of measurements (at Moody Tower) and all model scenarios (southwest of Moody Tower) are shown in Figure 13. The three model runs have similar O$_3$ concentrations, though Run H is 1-3 ppb higher at every hour in the second model layer (bottom plot). At 8 a.m. and 9 a.m., O$_3$ in the second-layer of Run B (primary HONO emissions) is 0.3 ppb greater than in the base case (Run A). These are the hours following rush hour traffic during which HONO is directly emitted in Run B. This additional HONO quickly photolyses as the sun rises, thus, creating the OH radical, which initiates O$_3$ production. The ozone mixing ratios in Run H are about 2.5 ppb greater than the base run (Run A) at 8 a.m. and 9 a.m. (and, therefore, about 2.2 ppb greater than Run B) because of the immediate photolysis of the heterogeneously formed ground-layer HONO.

![Simulated and Measured 1-hr O$_3$](image)

Figure 13. Comparison for simulated and observed 1-hr O$_3$ for April 21st. The top panel shows this comparison for the middle LP-DOAS (70-150 m above ground level), the middle panels shows comparison for the lower LP-DOAS measurement path (40-70 m above ground) and the bottom panel shows simulated and observed comparison for the in-situ measurements on the top of Moody Tower (70 m above ground).

All three scenarios under predict O$_3$ from 12 p.m. to 7 p.m., especially in the lower (second) model layer. Daytime under predictions for Run H range from 6 ppb to 21 ppb when compared to the in situ measurements during this window. Overall, however, O$_3$ performance is good for Run H. In this study, we chose to examine the Normalize Mean Error (NME) for 1-hr O$_3$ from 11 a.m. through 6 p.m., because this is the window during which the daily maximum 8-hr O$_3$ concentration is the greatest. For this mid-day to afternoon time window, the lower model layer
has a NME of 12% for Run H and 16% for Runs A and B relative to the Moody Tower in situ measurements. When compared to LP-DOAS lower path measurements (integrated measure of O₃ along 5 km path approximately 40-70 meters above ground level), NME improves to 4% and 7% for Run H and for both Run A/Run B scenarios, respectively.

Ozone PA time series difference plots are shown in Figure 14 for the 20-grid cell area covering downtown Houston (see Figure 3). In these difference plots, all model layers below the PBL have been aggregated using pyPA, which creates a column of grid cells with a textured top that rises and falls hourly with the PBL. Differences between the four net processes are shown, including: chemical production, horizontal transport (advection and diffusion), vertical transport (advection and diffusion), and the net effect of both vertical dilution (increased volume due to rising PBL) and entrainment (pollutant gain/loss due to height of column rising/falling). The black diamond symbols show modeled O₃ concentration differences at the beginning of each hour. The sum of all model processes within a given hour equals the concentration change from the beginning of the hour to the end. While not all model processes are shown in Figure 14 (e.g. wet and dry deposition are excluded), the four net processes shown are the ones that contributed most to changes in modeled O₃ values.

Figure 14 (top) shows why ozone in Run B was 0.3 ppb greater than in Run A (BASE) at 8 a.m. and 9 a.m. During a three-hour period beginning at 6 a.m., chemistry (red line) produced 0.8 ppb more ozone in Run B, while the combined effect of horizontal transport (blue line) and vertical dilution/entrainment (magenta line) removed 0.5 ppb more O₃. Thus, the net effect is a 0.3 ppb increase in O₃ over Run A. The differences in the removal processes become greater than chemical production differences beginning at 9 a.m., and the differences in concentrations between Run B and Run A become gradually smaller until the Run B values are approximately equal to the Run A values. Except for the morning activity, Run A generally produces 0.1 ppb/hr more O₃ than Run A, but that same amount is removed via horizontal transport resulting in no overall change in O₃ relative to Run A (BASE).

The ozone concentration and process rate differences between Run H and Run A are larger than those between Runs B and A (Figure 14 (bottom)). Before sunrise and after sunset, O₃ is 1-1.5 ppb greater. From 7 a.m. to 9 a.m., the difference increases to 2.5 ppb. During that two-hour period, chemistry and horizontal transport both contribute 1 ppb each more O₃ in Run H than in Run B, while vertical transport removes about 0.5 ppb more O₃. Thus, chemistry and horizontal transport increase O₃ by 1.5 ppb in Run H over Run A even after the increased vertical transport losses are considered. Note that the net effect of vertical dilution/entrainment is approximately zero over this two-hour period.
Figure 14. (top) Ozone Process Analysis (PA) time series difference plot (Run B – Run A) for the 20-grid cell area covering downtown Houston (see Figure 3) are shown for four net processes: chemistry, horizontal, vertical transport, and vertical dilution/entrainment. The black diamonds show modeled O3 concentration differences at the beginning of each hour. (bottom) Same as Figure 14a, except this Ozone PA time series difference plot is for Run H – Run A.

There are noticeable differences between this new heterogeneous HONO production scheme and primary HONO emissions, as shown by comparing the top and bottom panels of Figure 14. Run B increases chemical production of O3 over Run A during the entire 24-hour period, but that is only true of Run H during the daylight hours. Interestingly, before sunrise and after sunset there is greater chemical production in Run A compared to Run H. This is likely due to more O3 being removed by reactions with NOx in Run H. From midnight to 6 a.m., for example, approximately 0.3 ppb/hr more O3 is removed in Run H by reaction with NO and NO2. We also note that...
vertical transport removes more O₃ in Run H, while horizontal transport generally leads to O₃ increases when comparing Run H to Run A. This result suggests that while direct HONO emissions increase chemical production of O₃ locally where urban NOx emissions are high, the net effect is that O₃ is exported out of the downtown area.

Overall, it appears that heterogeneous HONO surface chemistry provides a regional increase of O₃ and leads to net import of O₃ into the downtown area. Concentration differences rise slowly throughout the day until 7 p.m. During this period, the O₃ difference decreases from 3.6 ppb to 2.0 ppb. Though horizontal transport adds 1.2 ppb more net O₃ in Run H, the differences in vertical transport (-1.4 ppb), chemistry (-1.0 ppb), and vertical dilution/entrainment (-0.1 ppb), decrease the “extra” O₃ present in Run H. Note that the net chemical loss in run H during this period is due to enhanced NOx “titration” of O₃.

The additional heterogeneous HONO increased ozone concentrations across the modeling domain on all four days at all grid cells. Figure 15 shows the effect on daily maximum 8-hr ozone concentrations at the surface. The values were obtained by calculating daily maximum 8-hr ozone for each grid cell in Runs A and H. Then, the two concentrations were subtracted. The resulting value is the increase in daily maximum 8-hr ozone that can be attributed to heterogeneous HONO formation. Note that the time at which the daily maximum 8-hr ozone concentration occurred need not be the same in both model runs. Maximum differences on each day were 2.5 ppb (April 20), 3.5 ppb (April 21), 3.0 ppb (May 19), and 3.5 ppb (May 20).
Figure 15: Modeled daily maximum 8-hr O₃ differences (in ppbv) for 4km domain (April 20, 21 & May 19, 20).
4. CONCLUSIONS AND RECOMMENDATIONS

1. We note that few studies have reported observations of direct HONO emission rates and that deriving HONO/NOx emission ratios from ambient measurements is inconclusive because the HONO may have been formed secondarily. Thus, we do not recommend including direct emissions of HONO in models, unless substantiated by direct source measurements, because available data suggest that HONO constitutes less than 1% of NOx for typical combustion sources, and including this small fraction of HONO in model emissions does not consistently reconcile predicted with observed HONO concentrations, nor does it match the observed HONO:NO2 ratios.

2. Explicitly modeling reactions on surfaces (vegetation, buildings, the ground) better reconciles predicted with observed HONO:NO2 and HONO:HNO3 ratios. At night, the thermal reaction of NO2 should be included. During the day, photolytic reactions of HNO3 and NO2 should be included.

3. Using surface model parameters that are consistent with SHARP measurements, the HONO produced has substantial impact on morning OH but only minor impacts on daytime OH. Due to the fact that HONO chemistry is happening throughout the region on both natural and urban surfaces, on some days the impact on daily maximum O3 in the Houston region could be as much as 4 ppbv.

4. The CAMx surface model developed in this study provides a process-based approach to model surface heterogeneous formation of HONO. However, there are uncertainties and limitations in the approach that should be addressed, as discussed below, since these will affect model predictions of ozone concentrations:

- The parameterizations developed in this study are based on one set of measurements. Furthermore, large over-predictions of NO2 and thus HONO in the Moody Tower grid cell, that appear to be related to over-estimates of NOx emissions, are a source of uncertainty in the parameterizations developed in this study. Basing the performance of the model on the HONO:NO2 ratios addresses this uncertainty to a certain extent but evaluating the parameterizations independently using other field studies, such as TRAMP, DISCOVER-AQ, PROPHET, etc., will provide more confidence in the surface model and an opportunity to refine the model. The model should be tested in both urban and rural settings.

- The CAMx surface model is currently implemented with the Wesely dry deposition scheme. It also should be implemented with the Zhang dry deposition scheme in CAMx. In this version of the surface model, deposition to water surfaces is assumed to be irreversible and thus is not tracked by the surface model. The surface model should be expanded to represent atmospheric interactions with surface waters.
5. REFERENCES


formation of HONO in a road traffic tunnel, Atmos. Environ., 35, 3385–3394.


Stutz, J., B. Alicke, R. Ackermann, A. Geyer, S. Wang, A. B. White, E. J. Williams, C. W. Spicer, and J. D. Fast (2004), Relative humidity dependence of HONO chemistry in...


6. APPENDICES

6.1 APPENDIX A-1.

NO\textsubscript{2} concentrations, Moody Tower southwest

[Graph showing daily NO\textsubscript{2} concentrations from April 15 to May 31, 2009, with data points for each day.]
APPENDIX A-2.

HONO concentrations, Moody Tower southwest

6.3 APPENDIX A-3.

Simulated and observed HONO:NO\textsubscript{2} ratio southwest the Moody Tower from April 15 to May 31, 2009.
6.4 APPENDIX B-1.

NO$_2$ concentrations, Moody Tower

6.5 APPENDIX B-2.

HONO concentrations, Moody Tower

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- Run A
- Run B
- Run H
- *in situ
APPENDIX B-3.

Simulated and observed HONO:NO$_2$ ratio at the Moody Tower from April 15 to May 31, 2009.