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1 **Quantifying nitrous acid formation mechanisms using**
2 **measured vertical profiles during the CalNex 2010**
3 **campaign and 1D column modeling**

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26 **Key Points:**

- 27 • Measured vertical profiles of HONO near Los Angeles in May 2010 suggest a het-
28 erogeneous HONO source at the ground.

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- 29 • A new 1D chemistry and transport model that includes HONO formation on the
30 ground reproduces the HONO concentration profiles.
- 31 • The main daytime HONO source is adsorbed nitric acid/ nitrate photolysis, fol-
32 lowed by photo-enhanced NO₂ conversion.

33 **Abstract**

34 Nitrous acid (HONO) is an important radical precursor that can impact secondary
 35 pollutant levels, especially in urban environments. Due to uncertainties in its heteroge-
 36 neous formation mechanisms, models often under predict HONO concentrations. A num-
 37 ber of heterogeneous sources at the ground have been proposed but there is no consen-
 38 sus about which play a significant role in the urban boundary layer. We present a new
 39 one-dimensional chemistry and transport model which performs surface chemistry based
 40 on molecular collisions and chemical conversion, allowing us to add detailed HONO for-
 41 mation chemistry at the ground. We conducted model runs for the 2010 CalNex cam-
 42 paign, finding good agreement with observations for key species such as O₃, NO_x, and
 43 HO_x. With the ground sources implemented, the model captures the diurnal and ver-
 44 tical profile of the HONO observations. Primary HO_x production from HONO photol-
 45 ysis is 2-3 times more important than O₃ or HCHO photolysis at mid-day, below 10 m.
 46 The HONO concentration, and its contribution to HO_x, decreases quickly with altitude.
 47 Heterogeneous chemistry at the ground provided a HONO source of 2.5x10¹¹ molecules
 48 cm⁻² s⁻¹ during the day and 5x10¹⁰ molecules cm⁻² s⁻¹ at night. The night time source
 49 was dominated by NO₂ hydrolysis. During the day, photolysis of surface HNO₃/nitrate
 50 contributed 45-60% and photo-enhanced conversion of NO₂ contributed 20-45%. Sen-
 51 sitivity studies addressing the uncertainties in both photolytic mechanisms show that,
 52 while the relative contribution of either source can vary, HNO₃/nitrate is required to pro-
 53 duce a surface HONO source that is strong enough to explain observations.

54 **1 Introduction**

55 Nitrous acid (HONO) chemistry in the polluted boundary layer has been an area
 56 of research for nearly five decades. It is well established that HONO photolysis (R1) is
 57 an important source of hydroxyl radicals (OH) throughout the day, contributing up to
 58 55% of the primary OH formation (Alicke et al., 2002, 2003; Kleffmann et al., 2005; Kl-
 59 effmann, 2007; Ren et al., 2003; Volkamer et al., 2010; Young et al., 2012; Elshorbany
 60 et al., 2009; Mao et al., 2010; Dusanter et al., 2009).



62 Although it has a large impact on the oxidative capacity of the atmosphere, HONO
 63 chemistry is often excluded from or simplified in 3D air quality models due to uncertain-
 64 ties in its formation mechanisms. This leads to an underestimation of HONO, which con-
 65 sequently impacts predicted concentrations of radicals and secondary pollutants like ozone
 66 (Czader et al., 2012; Elshorbany et al., 2012). Developing accurate HONO source rep-
 67 resentation is necessary to improve air quality modeling, which is increasingly important
 68 as air quality standards become more strict (Sarwar et al., 2008).

69 HONO chemistry includes homogeneous and heterogeneous reactions, biological pro-
 70 cesses in soil, and direct emission from combustion sources (Figure 1). The main gas phase
 71 reactions include loss via photolysis (R1) and reaction with OH (R2), and production
 72 through the NO + OH reaction (R3).

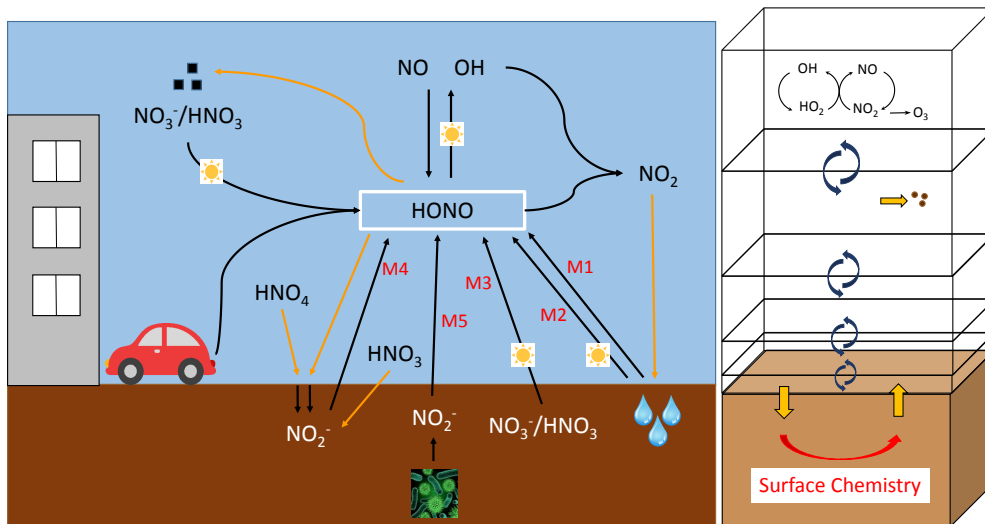


Figure 1. The cartoon on the left shows common HONO sources and sinks, with heteroge-
 neous processes labeled M1-M5 in red. On the right is an example model grid schematic showing
 the interaction between gas phase chemistry, surface chemistry, vertical mixing, and aerosol
 uptake.

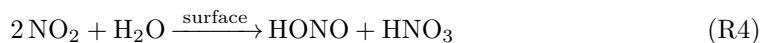


75 Measured diurnal profiles show that HONO concentrations accumulate through-
 76 out the night and drop off in the early morning once photolysis becomes active. Noc-
 77 turnal surface levels can reach up to several ppb in urban regions (Kleffmann et al., 2006;
 78 Stutz et al., 2010; Wong et al., 2011), while daytime levels have been reported up to a
 79 few hundred ppt (Kleffmann et al., 2005; Acker et al., 2006; Zhou et al., 2007; Wong et
 80 al., 2012). A strong HONO source is required to maintain these levels, particularly dur-
 81 ing the day when the HONO lifetime is only 10-20 minutes.

82 Pseudo-steady state (PSS) calculations and models show that HONO levels are greatly
 83 underestimated when only homogeneous chemistry (R1 - R3) is considered (Zhou et al.,
 84 2002; Kleffmann et al., 2005; Kleffmann, 2007; Tsai et al., 2018; Sarwar et al., 2008; Li
 85 et al., 2011; Czader et al., 2012). HONO is directly emitted by anthropogenic combus-
 86 tion processes, but this is less than 1% of NO_x emissions (Kirchstetter et al., 1996; Kurten-
 87 bach et al., 2001; Neuman et al., 2016; Kramer et al., 2019) and cannot explain atmo-
 88 spheric levels by itself. Measured vertical profiles show HONO concentrations are great-
 89 est near the ground (Kleffmann et al., 2003; Villena et al., 2011; Wong et al., 2011, 2012;
 90 VandenBoer et al., 2013), indicating that a surface source is likely. Multiple heteroge-
 91 neous formation mechanisms have therefore been proposed to explain this missing HONO
 92 source.

93 1.1 Heterogeneous HONO chemistry

94 Laboratory studies have found that HONO is produced from NO₂ conversion on
 95 humid surfaces (mechanism M1 in Figure 1), following a reaction mechanism (R4) which
 96 is first order with respect to both NO₂ and water vapor (Sakamaki et al., 1983; Svens-
 97 son et al., 1987; Pitts et al., 1984; Jenkin et al., 1988; Lammel & Cape, 1996).



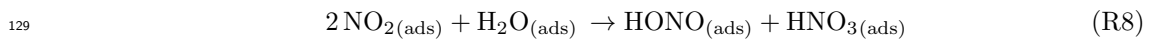
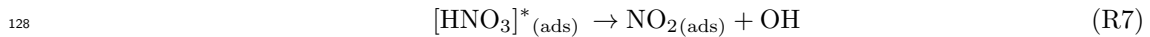
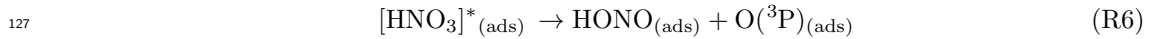
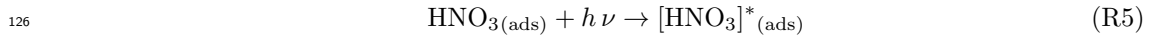
99 There is significant evidence that this reaction is the main source of nocturnal HONO
 100 and allows for an accurate description of HONO and HONO/NO₂ ratios at night (Alicke
 101 et al., 2003; Kleffmann et al., 2003; Wong et al., 2011; VandenBoer et al., 2013). While
 102 R4 occurs during the day as well, it does not produce HONO at the rate needed to sus-
 103 tain daytime levels and many studies have shown evidence that a photolytic source is
 104 required (Alicke et al., 2002; Kleffmann et al., 2005; Acker et al., 2006; Wong et al., 2012).

105 Photo-enhanced heterogeneous conversion of NO_2 to HONO (M2 in Figure 1) has
 106 been found to occur on a variety of surfaces, including soot (Ammann et al., 1998; Aubin
 107 & Abbatt, 2007; Khalizov et al., 2010; Monge et al., 2010), humic acid (Stemmler et al.,
 108 2006, 2007; Bartels-Rausch et al., 2010), and organic films (Gutzwiller et al., 2002; George
 109 et al., 2005; Brigante et al., 2008). A mechanism proposed by Stemmler et al. (2006) sug-
 110 gests HONO formation from NO_2 conversion on humic acid surfaces is first order in NO_2
 111 and linearly dependent on irradiance and surface area (SA).

$$112 \quad P_{\text{HONO}} \propto SA \times [\text{NO}_2] \times \text{irradiance} \quad (1)$$

113 Wong et al. (2013) included a sunlight dependent NO_2 to HONO reactive uptake
 114 coefficient (γ) in their 1D model study and found good agreement between modeled and
 115 observed HONO levels during the 2009 SHARP field campaign in Texas. Without this
 116 parameterization, daytime HONO levels were underestimated by at least 50%. Other stud-
 117 ies also suggest this conversion provides a major daytime source, showing that HONO
 118 correlates with NO_2 levels and/or NO_2 photolysis rates (Vogel et al., 2003; Laufs et al.,
 119 2017; Tsai et al., 2018).

120 Another daytime HONO source is the photolysis of surface adsorbed HNO_3 /nitrate
 121 (M3 in Figure 1), which proceeds at a rate 1-4 orders of magnitude faster than gas phase
 122 or aqueous HNO_3 photolysis (Zhou et al., 2002, 2003; Ramazan et al., 2004; Baergen &
 123 Donaldson, 2013, 2016; Ye et al., 2016, 2019). R5 - R8 describes the mechanism proposed
 124 by Zhou et al. (2002). NO_2 in R7 is the dominant product over R6 in the actinic region
 125 of solar radiation.

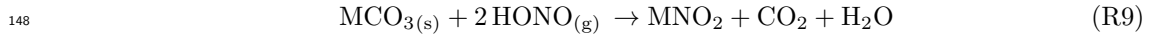


130 The HONO produced in R6 and R8 can desorb from the surface into the gas phase.
 131 This mechanism has been shown to be important in low NO_x forested environments (Zhou
 132 et al., 2011; Zhang et al., 2012). Although photo-enhanced conversion of NO_2 is often

133 thought to be the dominant HONO formation pathway in high NO_x areas, HNO_3 photo-
 134 lysis has also been confirmed as a significant source in the urban regions near Philadel-
 135 phia (Sarwar et al., 2008) and Houston (Karamchandani et al., 2014). Enhanced photo-
 136 lysis has been shown to occur on glass (Zhou et al., 2002; Ye et al., 2019), building ma-
 137 terials (Ye et al., 2016), and urban grime (Baergen & Donaldson, 2013, 2016), indicat-
 138 ing that this mechanism likely plays a role in urban HONO production.

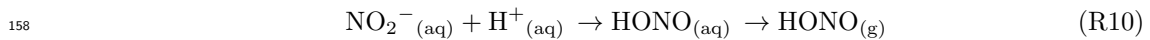
139 Both of these proposed photolytic mechanisms can occur on aerosols in addition
 140 to the ground. Due to the much smaller surface area available on aerosols and deacti-
 141 vation of reactive sites during aging, the aerosol source is thought to be minor in com-
 142 parison in typical settings (Kalberer et al., 1999; Kleffmann et al., 2003; Vogel et al., 2003;
 143 Stemmler et al., 2007).

144 A recent HONO source proposed by VandenBoer et al. (2015) is the displacement
 145 of surface nitrite by strong atmospheric acids like HCl and HNO_3 (M4 in Figure 1). Through-
 146 out the night, the primary HONO sink is deposition to the surface, where it can react
 147 with carbonate material to form nitrite.



149 VandenBoer et al. (2013) suggests that this nocturnally deposited HONO may form a
 150 surface reservoir that can be released the following day. Laboratory studies find that HCl
 151 and HNO_3 can displace surface nitrite with an efficiency of 1-20%. Using the mean value
 152 of 9%, VandenBoer et al. (2015) showed that this mechanism contributed up to 23% of
 153 the total noontime HONO flux in Bakersfield, California during the CalNex campaign.

154 Biological processes in soil provide another potential atmospheric HONO source
 155 (M5 in Figure 1) (Su et al., 2011; Oswald et al., 2013; Maljanen et al., 2013; Scharko et
 156 al., 2015; Meusel et al., 2018). Nitrification and denitrification produce nitrite, which un-
 157 dergoes acid-base reactions and partitioning between air and the aqueous phase in soil.



159 R10 depends on the pH and NO_2^- concentration of the soil. Oswald et al. (2013) per-
 160 formed laboratory studies to compare emissions of HONO and NO from soils from a va-
 161 riety of ecosystems. They found that HONO can account for up to 50% of the total re-

162 active nitrogen released from soil, especially in arid and arable soils with water content
163 below 20% water holding capacity.

164 **1.2 Linking surface chemistry to atmospheric measurements**

165 A challenge in studying the link between chemical transformations on the ground
166 and the chemistry in the overlying atmosphere is the role of vertical transport to and
167 from the surface. This was illustrated by 1D modeling studies by Geyer and Stutz (2004a,
168 2004b), who showed that concentrations change on the scale of one meter or less near
169 the surface. Similar conclusions were derived by nighttime and daytime HONO model-
170 ing studies (Wong et al., 2011, 2013; Tsai et al., 2018), which all showed a strong con-
171 centration gradient near the surface. Another challenge for modeling studies of atmo-
172 spheric HONO is the poorly known surface (ground) formation chemistry. To address
173 this issue, flexibility in the model setup and the ability to perform sensitivity studies are
174 essential.

175 One-dimensional chemistry and transport models are an ideal tool to study poorly
176 constrained surface chemistry. A number of 1D models have provided valuable insight
177 into similar atmospheric systems, such as the interaction of snow with the atmosphere
178 (Cao et al., 2014, 2016; Thomas et al., 2011, 2012; Toyota et al., 2014; Wang et al., 2020),
179 forest canopies (Boy et al., 2011), and the marine boundary layer (von Glasow et al., 2002a,
180 2002b). However, only few studies have addressed the surface chemistry of HONO (Wong
181 et al., 2011, 2013; Karamchandani et al., 2014; Tsai et al., 2018). To investigate this spe-
182 cific surface-atmosphere chemical system, we present a newly developed 1D model, the
183 Platform for Atmospheric Chemistry and vertical Transport in one dimension (PACT-
184 1D). PACT-1D is based on the success of our previous modeling (Wong et al., 2011, 2013;
185 Tsai et al., 2018), and includes improved capability to perform mechanistic and sensi-
186 tivity studies of these systems.

187 In this paper we analyze observed vertical concentration profiles of HONO, NO₂,
188 and other compounds during the 2010 CalNex field experiment (Section 2) using PACT-
189 1D (Section 3). We use PACT-1D to test if HONO surface formation can reproduce the
190 observations, and explore the contribution of the mechanisms (Section 4).

2 Measurements

The 2010 CalNex experiment took place in Pasadena, CA from mid-May to mid-June, 2010 (Ryerson et al., 2013). The ground-site was located on the California Institute of Technology (Caltech) campus with in-situ measurements collected near the surface at altitudes between 3 and 10 m and remote sensing observations on top of Caltech’s library at ~35 m agl. All CalNex observations are publicly available at www.esrl.noaa.gov/csd/projects/calnex/.

In this study we focus on observations relevant for understanding the formation of HONO and its impact on atmospheric chemistry. We use HONO data from two instruments: UCLA’s long-path Differential Optical Absorption Spectroscopy instrument (LP-DOAS) and NOAA’s Chemical Mass Spectrometer (CIMS). NOAA’s CIMS sampled air at 3 m agl, while the LP-DOAS probed air between 33-556 m agl in four different altitude intervals. All other in-situ measurements used here were sampled at 10 m agl on top of a scaffolding tower.

We concentrate on a four day period, May 26 - May 30, 2010, during which a variety of conditions were encountered, including cloudy days and the highest ozone levels of the experiment. This period also has the best coverage of all instruments, in particular the LP-DOAS instrument.

2.1 LP-DOAS

The setup of the LP-DOAS during CalNex, as well as the data retrieval techniques, have been described previously (Wong et al., 2011, 2012; Tsai et al., 2014), therefore we will only briefly describe them here. Figure 2 shows a schematic of the site setup. The LP-DOAS consists of a main telescope/spectrometer unit, which was located on top of Millikan Library on the Caltech campus at 33 m altitude. Four arrays of retroreflectors were mounted on a nearby mountain at different distances and altitudes. We refer to these retroreflectors and the associated air samples by their relative altitudes: lower (78 m), middle (121 m), high (255 m), highest (556 m). The instrument was aimed at the four reflectors using a cycle of measurements with a repeat interval of 15 - 30 min, depending on visibility. The light received back was measured in the 300-380 nm range with a spectral resolution of 0.6 nm. Trace gas path-averaged concentrations were retrieved using established DOAS techniques as described in Platt and Stutz (2008). Average de-

222 tection limits for NO_2 and HONO on a single absorption path were 0.16 ppb and 0.06
 223 ppb, respectively. It should also be pointed out that the LP-DOAS, which was located
 224 around 550 m southeast of the other instruments, averaged over $\sim 5\text{--}7$ km absorption light
 225 paths.

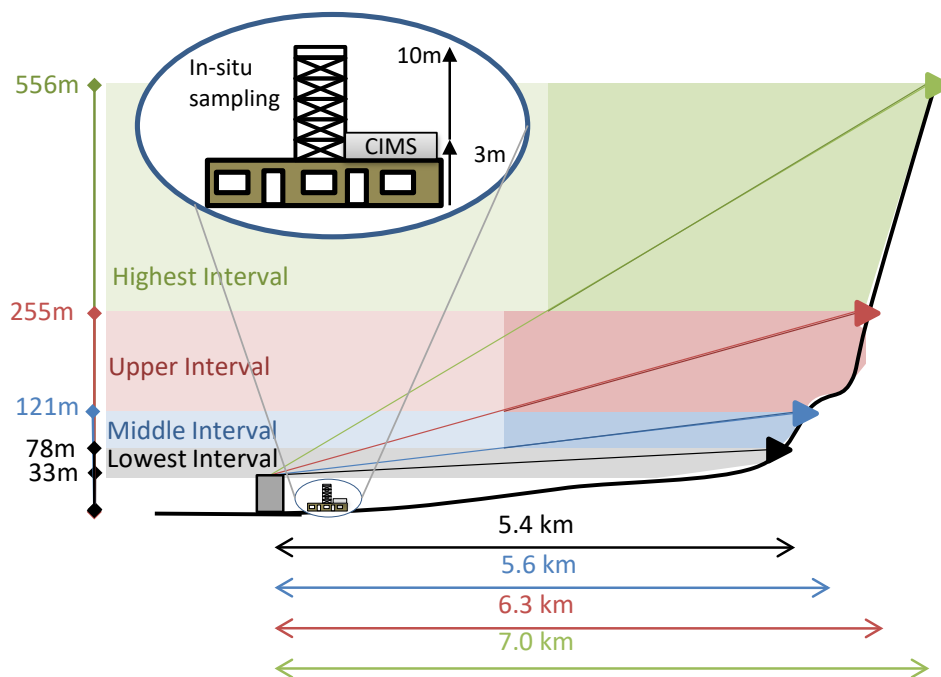


Figure 2. Sketch of the LP-DOAS field setup during the CalNex 2010 experiment

226 The LP-DOAS measured continuously throughout CalNex, however, low visibil-
 227 ity and low clouds blocked the light beams at some times. Low clouds were especially
 228 common during the night and often only the lowest light path data was available. The
 229 dates chosen for this modeling study had good coverage along all light paths. Vertical
 230 profiles from LP-DOAS measurements were constructed following the method described
 231 in Tsai et al. (2014). Briefly, the path-averaged mixing ratios were first linearly inter-
 232 polated onto the time grid of the lowest light path and then converted to height interval-
 233 average mixing ratios. These averages are reported at the midpoint of each height in-
 234 terval (55.5, 99.5, 188, and 405.5 m).

2.2 NI-PT-CIMS

A negative-ion proton-transfer chemical ionization mass spectrometer (NI-PT-CIMS) using acetate ions provided HONO and HNO₃ observations at 1-minute resolution during CalNex and has been described previously (Roberts et al., 2010; Veres et al., 2011). Briefly, ambient air was sampled through a 1.5 m PTFE inlet heated from a point approximately 3 m agl. Acidic molecules are ionized via proton abstraction reactions with acetate ions (CH₃COO⁻) and detected, as the conjugate anion, using a quadrupole mass spectrometer. Instrument backgrounds using a sodium carbonate denuder were performed every 190 min for 30 min.

HONO calibrations were performed in-field approximately every two days using using a portable source described elsewhere (Roberts et al., 2010). Measurement of HONO by the NI-PT-CIMS required correction for NO₂. Correction factors were determined through laboratory additions of NO₂ as a function of relative humidity with NO₂ quantified by CRDS. Detection limits for HONO were 10 ppt, with an uncertainty of 30% + 20 ppt for 1-min measurements. Nitric acid calibrations were performed during post-field laboratory work using a permeation source calibrated using UV optical absorption (Neuman et al., 2003). HNO₃ was measured with a detection limit of 15 ppt, with a stated uncertainty of 30% + 30ppt for 1-min measurements.

2.3 Other measurements

We use a number of other observations from CalNex in our analysis and model evaluation. Table 1 lists these parameters, the respective instruments, and literature references of the CalNex results.

3 The Platform for Atmospheric Chemistry and vertical Transport in one dimension (PACT-1D)

3.1 Model description

In this study we describe and use a new vertical column model, the Platform for Atmospheric Chemistry and vertical Transport in one dimension (PACT-1D). The new model is similar to past vertical column models used to study the interactions between chemical processing and vertical transport processes, where chemistry is calculated on-line and dynamics and physics are provided as input (Geyer & Stutz, 2004a). PACT-

Table 1. Overview of CalNex measurements used in this study

Species / Parameter	Instrument	Operator	Reference
O ₃	UV-absorption	Univ. Houston (UH)	
NO / NO ₂	Chemiluminescence with photolytic converter	Univ. Houston (UH)	(Pollack et al., 2010)
NO ₂	Cavity Ring-Down Spectroscopy (CRDS)	NOAA	(Washenfelder et al., 2011)
OH / HO ₂	Laser Induced Fluorescence (LIF-FAGE)	Indiana Univ.	(Dusanter et al., 2009; Griffith et al., 2016)
VOC	GC-MS	NOAA	(Gilman et al., 2010; Borbon et al., 2013)
Actinic Flux	Spectroradiometer	Univ. Houston (UH)	(Shetter & Müller, 1999)
Aerosol Number Distribution	TSI SMPS	CU Boulder	(Hayes et al., 2013)
HONO, HNO ₃	CIMS	NOAA	(Veres et al., 2008)

265 1D solves both 1D transport and chemical kinetics resulting in the time evolution (t) of
266 a chemical species (i) at altitude (z). The continuity equation for the change in concen-
267 tration C for the 1D chemical system is given by Eqn 2.

$$268 \quad \frac{dC_{(i,t,z)}}{dt} = P_{(i,t,z)} - L_{(i,t,z)} + F_{(i,t,z)} + E_{(i,t,z)} \quad (2)$$

269 P and L represent chemical production and loss, F refers to the flux in/out of the box
270 due to vertical mixing, including loss to the ground (deposition), and E is the rate of

emissions. We treat each process including chemistry, vertical mixing, and emissions as separable using operator splitting.

Emissions are provided as input and are time and height dependent. Chemical production and loss are described using the Regional Atmospheric Chemistry Mechanism version 2 (RACM2) (Goliff et al., 2013), implemented with the Kinetics Pre-Processor (Sandu & Sander, 2006). Photolysis rates are provided as input. In addition to the RACM2 gas phase chemistry, we include non-reactive uptake of gases to aerosols and heterogeneous surface reactions on aerosols. For heterogeneous chemistry, the aerosol surface area (S) is prescribed in each model level (z) at a given time (t) according to

$$S_{(z,t)} = 4\pi r_{(z,t)}^2 N_{(z,t)} \quad (3)$$

where r and N represent the radius and number concentration of a mono-disperse aerosol that best represents the surface area available for reactions. Aerosol physical properties (N and r) are given as model input. Therefore, no aerosol physics is calculated online within the model. Irreversible uptake to and heterogeneous reactions on aerosols are treated with the rate constant (k_T) given by

$$k_T = \frac{1}{4} \nu S \gamma J \quad (4)$$

where ν is the mean molecular speed, S is the aerosol surface area, and γ represents the probability of irreversible uptake or interfacial reaction. The flux of molecules to the aerosol surface in the transition regime, J , is calculated according to Fuchs and Sutugin (1971). This corrects the rate of diffusion for gas molecules towards an aerosol surface when the particle size is similar to the mean free path in air, the so called *transition regime*.

Vertical mixing and loss to the the ground are solved together in the vertical mixing term, given as $F_{(i,t,z)}$ in Eqn. 2. We treat vertical mixing and surface loss (i.e. deposition) for each species according to

$$\frac{\partial}{\partial t} \phi_{(i,t,z)} = \frac{1}{\rho_{(i,t,z)}} \frac{\partial}{\partial z} \left(\rho_{(i,t,z)} K_{D(i,t,z)} \frac{\partial}{\partial z} \phi_{(i,t,z)} \right) + R_{(1,t)} \quad (5)$$

where ϕ_i is the species concentration in mixing ratio units, ρ is the air density, and R represents loss to the ground in the lowest model level. $K_{D(i,t,z)}$ is the sum of eddy diffusivity ($K_{(t,z)}$) plus molecular diffusion ($D_{(i,t,z)}$). To treat vertical mixing and loss to

299 the ground, we discretize the model levels below 1 meter using a log scale grid such that
 300 the lowest model level is appropriate for treatment of a laminar molecular diffusive layer
 301 in direct contact with the Earth’s surface. $K_{(t,z)}$ decreases in a log profile towards the
 302 surface to a molecular diffusion coefficient in the lowest model level.

303 A unique feature of the model is that uptake and chemistry on the ground (R) are
 304 calculated using molecular collisions on the ground and applying an uptake probability
 305 (α) or reactive uptake coefficient (γ). We then solve Eqn. 5 numerically using the Crank-
 306 Nicolson method (Brasseur & Jacob, 2017), which is numerically stable for a variety of
 307 non-uniform grids and time steps.

308 Upon solving Eqn. 5, we calculate the deposition rate for each time step. This method
 309 allows for molecular level interaction with the surface, resulting in deposition without
 310 the need to prescribe a deposition velocity. We include interactive surface chemistry, which
 311 can lead to release of species from the ground into the gas phase. More details are pro-
 312 vided in the Section 3.3.

313 **3.2 Model setup for CalNex campaign**

314 PACT-1D was initialized using both model data (from WRF-Chem, MOZART, MEGAN,
 315 and CAMS) and observational data from the CalNex 2010 campaign (Table 1). The 24-
 316 hour period from May 26, 2010 18:00 through May 27, 2010 17:00 was used as model spin
 317 up. The model subdivides the lowest 5000 m of the atmosphere into 26 grid cells, with
 318 model grid box upper boundaries at: 1×10^{-3} , 0.01, 0.1, 1, 3, 6, 10, 20, 33, 50, 78, 90, 110,
 319 121, 150, 175, 255, 300, 556, 750, 1000, 1500, 2000, 3000, 4000, and 5000 m. A 20 sec-
 320 ond chemical time step was used for each model run.

321 Time varying profiles of temperature, relative humidity, and pressure were extracted
 322 from a WRF-Chem model run for CalNex (Kim et al., 2016), which provided values above
 323 ~ 180 m. These were interpolated onto the 1D vertical grid and measured meteorolog-
 324 ical data was used to create a profile to the surface. Below 180 m, temperature was cal-
 325 culated based on 10 m measurements of wind speed and temperature, the measured bound-
 326 ary layer height, and atmospheric stability parameters. Relative humidity was given a
 327 constant value equal to the measurements at 10 m and pressure was calculated using the
 328 surface pressure and scale height. We take eddy diffusion coefficients (K_z) from WRF-
 329 Chem as well (Kim et al., 2016). These values start at ~ 50 m and a log interpolation was

330 implemented to parameterize Kz values to the ground. The vertical mixing considered
331 boundary layer height variation over the three day period, which is explicitly calculated
332 via the planetary boundary layer (PBL) parameterization used within WRF-Chem.

333 Aerosol number concentration profiles were initialized using data from the TSI Scan-
334 ning Mobility Particle Sizer (SMPS) instrument. Within the boundary layer, the num-
335 ber concentration was set equal to the measurements at 10 m and then decreased expo-
336 nentially to one fifth of this value in the top layer of the model. The aerosol radius was
337 assumed to be constant at 150 nm, following the study by Tsai et al. (2014). Photoly-
338 sis rates were initialized using the Tropospheric Ultraviolet-Visible (TUV) radiation model
339 (v5.0) which was run for our test date and location. To account for clouds, measured NO₂
340 photolysis rates were used to scale the TUV values for all species.

341 Input anthropogenic emissions are based on the U.S. Environmental Protection Agency
342 (EPA) National Emission Inventory (NEI) and the Fuel-based Inventory for motor Ve-
343 hicle Emission (FIVE), which have been processed for use in WRF-Chem (Kim et al.,
344 2016). Biogenic emissions are from the MEGAN model for May 2010. Anthropogenic
345 NO_x emissions were emitted between 0.1-1 m and VOC emissions were emitted between
346 0.1-10 m. The emissions were scaled so that model concentrations matched those observed
347 by the LP-DOAS and in-situ observations, using realistic emission injection altitudes for
348 different emission source types. In some cases, the emissions are scaled by up to 50% in
349 order to reproduce realistic VOC and NO_x concentrations, as well as NO₂ concentration
350 profiles. Emissions scaling is needed to reproduce observations due to the fine model ver-
351 tical resolution, which employs a much higher resolution grid vertically than typical 3D
352 chemical transport models. 3D models quickly dilute these emissions into larger volumes
353 of air resulting in lower concentrations of species that are directly emitted which impacts
354 ozone chemistry and other non-linear atmospheric chemical cycling. In addition, the WRF-
355 Chem emissions are general values for either weekday or weekend and have large uncer-
356 tainties when modeling specific dates and events at high time resolution. This period in-
357 cludes the weekend (Saturday 5/29 and Sunday 5/30) before a major holiday (Memo-
358 rial day).

359 Soil NO emissions are taken from the Copernicus Atmospheric Monitoring Service
360 (CAMS) global and regional emissions dataset, which considers surface type, for May
361 2012 near Pasadena, CA (Simpson et al., 2014; Granier et al., 2019). Anthropogenic

362 HONO emissions were included using an emission ratio of $\text{HONO}/\text{NO}_x = 0.003$ (Kurtenbach
 363 et al., 2001). A range of 0.003-0.008 is reported in literature (Kirchstetter et al., 1996;
 364 Kurtenbach et al., 2001; Neuman et al., 2016; Kramer et al., 2019) and due to the lower
 365 number of diesel engine vehicles in the United States compared to Europe where many
 366 of these studies were conducted, we chose a value at the lower end of this range.

367 To better simulate the urban atmosphere, chlorine chemistry and parameterized
 368 nitrate aerosol chemistry were added to the RACM2 mechanism. Aerosol nitrate is formed
 369 through uptake of HNO_3 and N_2O_5 , with aerosol uptake coefficients of 0.1 and 0.02, re-
 370 spectively. Partitioning between gas phase HNO_3 and aerosol nitrate is based on the study
 371 by Guo et al. (2017), who found a campaign average partitioning ratio, $\epsilon(\text{NO}_3^-)$, of 39%
 372 for PM1 during CalNex.

$$373 \quad \epsilon(\text{NO}_3^-) = \frac{\text{NO}_3^-}{\text{HNO}_3 + \text{NO}_3^-} \quad (6)$$

374 Similar to photolysis of HNO_3 on the ground, nitrate in aerosol can also photolyze to
 375 give HONO. This is added to the mechanism with a rate 45 times that of gas phase ni-
 376 tric acid (Zhou et al., 2003; Karamchandani et al., 2014).

377 **3.3 Interactive treatment of surface chemistry**

378 The proposed HONO formation mechanisms occur at the ground, therefore we im-
 379 plemented detailed surface heterogeneous chemistry within PACT-1D. Deposition is cal-
 380 culated from the number of molecular collisions with the ground and an uptake coeffi-
 381 cient, allowing for molecular level chemical conversions and surface emissions. The quan-
 382 tity of species available for reactions on the ground was initialized using a model spin-
 383 up of four days to achieve near steady state conditions. The HONO formation mecha-
 384 nisms described in Section 1.1 were added to PACT-1D with model implementation de-
 385 scribed below.

386 **3.3.1 NO_2 hydrolysis**

387 Conversion of NO_2 to HONO on the ground is implemented into the model using
 388 reaction R4. NO_2 deposition is tracked and for every two molecules deposited, one HONO
 389 molecule is released from the surface and one HNO_3 molecule is added to the surface stor-
 390 age term. The ground NO_2 uptake coefficient ($\gamma_{\text{NO}_2, \text{dark}}$) is set at 1×10^{-5} (Trick, 2004).

391 **3.3.2 Photo-enhanced NO₂ conversion**

392 The photo-enhanced conversion of NO₂ to HONO is included using the parame-
 393 terization by Wong et al. (2013). In Wong et al. (2012) and Wong et al. (2013), daytime
 394 HONO concentrations in Houston, Texas correlated with solar irradiance and they de-
 395 termined that the reactive uptake coefficient for NO₂ could be parameterized with a cu-
 396 bic dependence on the NO₂ photolysis rate (Eqn. 7).

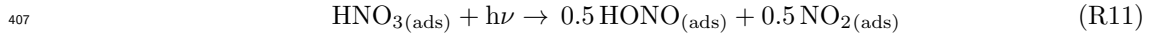
$$397 \quad \gamma_{\text{NO}_2, \text{photo}} = 6 \times 10^{-5} \frac{J_{\text{NO}_2}^3}{J_{\text{NO}_2, \text{noon}}^3} \quad (7)$$

398 6×10^{-5} is the maximum reactive uptake coefficient. The average noontime photolysis
 399 rate for NO₂ ($J_{\text{NO}_2, \text{noon}}$) during the four days that we focused on (May 26-30 2010) is
 400 $7 \times 10^{-3} \text{ s}^{-1}$. This photo-enhanced NO₂ uptake occurs in addition to dark uptake, giv-
 401 ing an effective NO₂ deposition rate (ν_{d, NO_2}) according to the following equation, where
 402 ν is the mean molecular speed. ν_{d, NO_2} drives NO₂ deposition in the model.

$$403 \quad \nu_{d, \text{NO}_2} = \frac{1}{4} \nu \gamma_{\text{NO}_2, \text{dark}} + \frac{1}{4} \nu \gamma_{\text{NO}_2, \text{photo}} \quad (8)$$

404 **3.3.3 Surface nitric acid/nitrate photolysis**

405 Following the modeling study of Sarwar et al. (2008), we parameterize photolysis
 406 of surface adsorbed HNO₃ using the following reaction.



408 Surface HNO₃ is initialized in the model and it's concentration is updated considering
 409 deposition and surface chemistry. HONO and NO₂ produced in R11 are released into
 410 the lowest model layer via desorption. HNO₃ deposition to the ground is calculated us-
 411 ing an uptake coefficient of 0.1. The photolysis rate constant of this reaction ($J_{\text{HNO}_3, \text{surf}}$)
 412 is set to 45 times that of gas-phase HNO₃ (Zhou et al., 2003; Karamchandani et al., 2014),
 413 giving noon time values of $2.0 \times 10^{-5} \text{ s}^{-1}$ on May 27 and $2.5 \times 10^{-5} \text{ s}^{-1}$ on May 28 and
 414 29. These rate constants are in accordance with the value of $2.5 \times 10^{-5} \text{ s}^{-1}$ reported by
 415 Zhou et al. (2003), and are also used for aerosol nitrate photolysis. The scaling factor
 416 of 45 is also consistent with that used by Fu et al. (2019) and Liu et al. (2021), who cal-
 417 culate $J_{\text{HNO}_3, \text{surf}}$ with the following equation.

$$J_{\text{HNO}_3, \text{surf}} = \frac{3.4 \times 10^{-5}}{7 \times 10^{-7}} J_{\text{HNO}_3} \quad (9)$$

3.4x10⁻⁵ is the median $J_{\text{HNO}_3, \text{surf}}$ reported by Ye et al. (2016) and 7x10⁻⁷ is the average noontime $J_{\text{HNO}_3, \text{gas}}$.

3.3.4 HONO uptake, nocturnal storage, acid displacement

Uptake to the ground is an important loss for atmospheric HONO, especially at night. Once deposited, it forms surface nitrite through R9 and a similar reaction occurs with HNO₄. According to VandenBoer et al. (2015), this nitrite can be recycled back to gaseous HONO when displaced by a strong acid. In the model we assume that all HONO and HNO₄ deposited to the ground is converted to nitrite. Every HNO₃ molecule deposited then results in a HONO molecule emitted to the lowest model layer. The uptake coefficients for HONO, HNO₄, and HNO₃ are 1x10⁻⁴, 0.01, and 0.1, respectively. To ensure there is a sufficient amount of nitrite present to be displaced, it's concentration is tracked and if it falls below a monolayer (~1x10¹³ molec cm⁻²), the HONO source is scaled by $\frac{[\text{NO}_2^-]}{1 \times 10^{13}}$.

3.3.5 Biogenic emissions

Oswald et al. (2013) determined that HONO can contribute up to 50% of reactive nitrogen released from soil, comparable to soil NO emissions. Soil NO emissions are included in the model as input. We assume that NO and HONO make up the majority of reactive nitrogen and therefore set HONO emissions equal to NO as an upper limit.

4 Results and discussion

We use PACT-1D to simulate HONO levels during the CalNex campaign and analyze the importance of ground sources. An overview of each model run is provided in Table 2 and each is discussed below.

4.1 Model run without HONO surface chemistry (NoSurf run)

A model run (NoSurf) was first performed to investigate HONO concentrations without ground surface chemistry. In this run, HONO was impacted by gas phase chemistry,

Table 2. Overview of PACT-1D model runs

Model Run	Description
NoSurf	HONO chemistry on the ground not included
Base	HONO chemistry on the ground included
Sens1	$\gamma_{\text{NO}_2, \text{max}}$ decreased by 50%, $J_{\text{HNO}_3, \text{surf}}$ increased by 25%
Sens2	$\gamma_{\text{NO}_2, \text{max}}$ increased by 2x, $J_{\text{HNO}_3, \text{surf}}$ decreased by 20%
Sens3	$\gamma_{\text{NO}_2, \text{max}}$ decreased by 90%, $J_{\text{HNO}_3, \text{surf}}$ increased by 60%
Sens4	$\gamma_{\text{NO}_2, \text{max}}$ increased by 5x, $J_{\text{HNO}_3, \text{surf}}$ decreased to gas phase J_{HNO_3}

444 direct emissions, deposition to the ground with an uptake coefficient of 1×10^{-4} , uptake
 445 on aerosol surfaces with an uptake coefficient of 1×10^{-3} , and formation from aerosol ni-
 446 trate photolysis. HONO levels at 3 m were compared to the CIMS measurements (Fig-
 447 ure 3, bottom right). Modeled HONO, shown in orange, remained around 0.1 ppb or lower
 448 during daytime periods. May 28 and 29 showed an early morning peak between 0.15-
 449 0.3 ppb. Daytime and nighttime concentrations for all three days were significantly lower
 450 than observations, indicating that gas phase formation, direct emissions, and aerosol ni-
 451 trate photolysis cannot completely explain HONO levels and that an additional source
 452 is required.

453 4.2 Model results with interactive surface chemistry (Base run)

454 When heterogeneous HONO formation sources at the ground were implemented
 455 in PACT-1D (Base run), the model matched observations much better (Figure 3). The
 456 model captures the general trend and values of major species including NO_x , HO_x , and
 457 O_3 . Due to lack of horizontal advection in PACT-1D, however, there are some discrep-
 458 ancies related to changes in air mass, for example near midnight on May 30. The model
 459 also misses some of the afternoon NO_x peaks, which are due to advection of polluted air
 460 from downtown Los Angeles. These dates correspond to the start of the Memorial Day
 461 holiday weekend as well, making traffic emissions more difficult to estimate.

462 The overprediction of OH and underprediction of HO_2 in PACT-1D is consistent
 463 with results from Griffith et al. (2016) and is likely due to missing radical processes in
 464 the RACM2 mechanism. Griffith et al. (2016) suggests that reactivity between OH and

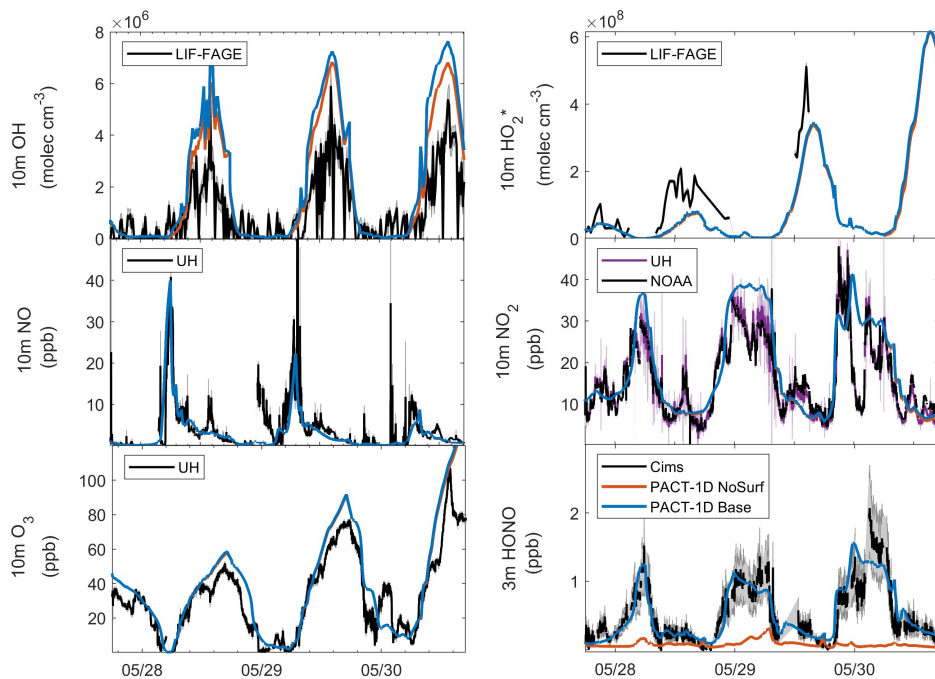


Figure 3. Overview plot showing NoSurf (orange) and Base (blue) model results compared to observations from May 27, 2010 18:00 through May 30, 2010 18:00. Measurement details are included in Table 1. HO_2^* is $\text{HO}_2 + 0.3\text{RO}_2$, following Griffith et al. (2016).

465 saturated hydrocarbons and OH and aldehydes is under predicted in the mechanism which
 466 leads to an over prediction of OH and under prediction of HO_2 . Similar results were re-
 467 ported by Wolfe et al. (2016), who found that production of HO_2 from reactions of OH
 468 with HCHO, CO and other hydrocarbons was too slow in the RACM2 mechanism to ac-
 469 curately capture OH and HO_2 observations.

470 The diurnal HONO trend is captured in the Base run, showing mixing ratios in-
 471 creasing over night, followed by a sharp decrease in the early morning. Concentrations
 472 are substantially higher compared to the NoSurf run, with daytime values ranging be-
 473 tween 0.1-0.5 ppb and night time values increasing to 1.2-1.6 ppb. Modeled HONO does
 474 not capture the early morning peaks around 6:00-7:00 on May 29 and 30. This and the
 475 delayed decrease in HONO during the morning of May 30 indicate that the morning mix-
 476 ing may not be completely accurate in the model. A delay in morning boundary layer
 477 growth can prevent HONO formed overnight from mixing away from the surface. The

478 quick changes in observed O_3 , NO_2 , and NO also indicate that there are air mass changes
479 that the model cannot capture. Overall, these results show very good agreement between
480 model and observations and show that a heterogeneous HONO surface source is neces-
481 sary to simulate realistic atmospheric HONO levels. The mechanisms implemented here
482 appropriately describe this heterogeneous source during CalNex.

483 **4.3 HONO vertical profiles**

484 Since HONO photolyzes quickly during transport away from the ground where it
485 is formed, vertical profiles must be considered to understand HONO's sources and its
486 total impact to air quality in the boundary layer. Observed profiles were constructed by
487 vertically interpolating between the NOAA CIMS measurements at 3 m and the LP-
488 DOAS measurements at 55.5 m, 99.5 m, 188 m, and 405.5 m. The CIMS and LP-DOAS
489 instruments showed excellent agreement in another field experiment (UBWOS 2012). We
490 are therefore confident that the two datasets can be combined to construct vertical con-
491 centration profiles of HONO. Figure 4 shows the observed profile compared to PACT-
492 1D for the entire 3 day period and Figure 5 shows select hours between May 27 18:00
493 and May 28 17:00.

494 In the observed profile, the highest HONO concentrations are typically at the sur-
495 face, which is consistent with vertical profiles measured in other field campaigns (Kleffmann
496 et al., 2003; Villena et al., 2011; Wong et al., 2011, 2012; Young et al., 2012; Vanden-
497 Boer et al., 2013; Tsai et al., 2018). The quick decay in HONO with altitude in the low-
498 est 100 m, especially during the day, emphasizes the importance of vertical profile mea-
499 surements and modeling. HONO's role in boundary layer chemistry can easily be over
500 or under estimated if measurements at a single altitude are used. In particular, this can
501 have a significant impact on OH production rates, which will be discussed in the follow-
502 ing section. Similar to other studies, we conclude that these profiles provide evidence for
503 a ground source of HONO. The underestimation of HONO in the NoSurf run (Figure
504 5, right), shows that direct emissions cannot be the primary ground source. Accurately
505 implementing the heterogeneous HONO surface sources allowed us to better model HONO
506 both near the surface and at higher altitudes.

507 The underestimation of HONO in the NoSurf run (Figure 5, right), which includes
508 heterogeneous HONO formation from aerosol nitrate only, also shows that aerosol sources

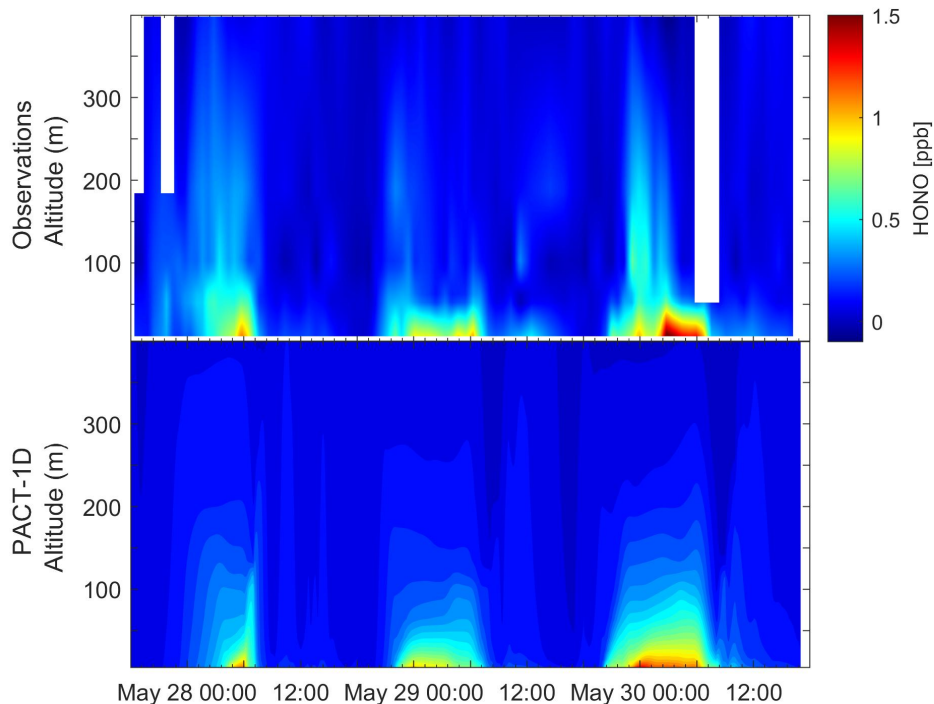


Figure 4. Comparison of HONO vertical concentration profiles between observations (top) and model (bottom), from May 27 18:00 to May 30 17:00. The observed profile is constructed from LP-DOAS data and NOAA CIMS data.

509 of HONO are less significant than ground sources. The aerosol source shows a diurnal
 510 trend, peaking in the early afternoon and decreasing to zero at night. In the Base run,
 511 the source peaks near 7×10^5 molec $\text{cm}^{-3} \text{s}^{-1}$ on May 28, 9×10^5 on May 29, and 8×10^5
 512 on May 30, within the LP-DOAS altitude range (50-400 m). Lower values on May 28
 513 are due to smaller photolysis rates and lower aerosol number concentrations that day.
 514 Aerosol nitrate concentrations are under predicted compared to observations on this day
 515 as well so the values reported by our model are likely too low. On May 29, modeled aerosol
 516 nitrate concentrations are slightly higher than observed, indicating that the HONO aerosol
 517 source may be slightly over predicted as well. The values we report are generally con-
 518 sistent with other studies in urban areas, including Wong et al. (2013) who reports noon-
 519 time values of $1.0\text{-}1.7 \times 10^6$ molec $\text{cm}^{-3} \text{s}^{-1}$ in Houston, Texas. Our values are lower than
 520 those reported in more polluted cities with larger available aerosol surface area. Liu et
 521 al. (2021), for example, found approximately 1 ppb hr^{-1} (6.9×10^6 molec $\text{cm}^{-3} \text{s}^{-1}$) of

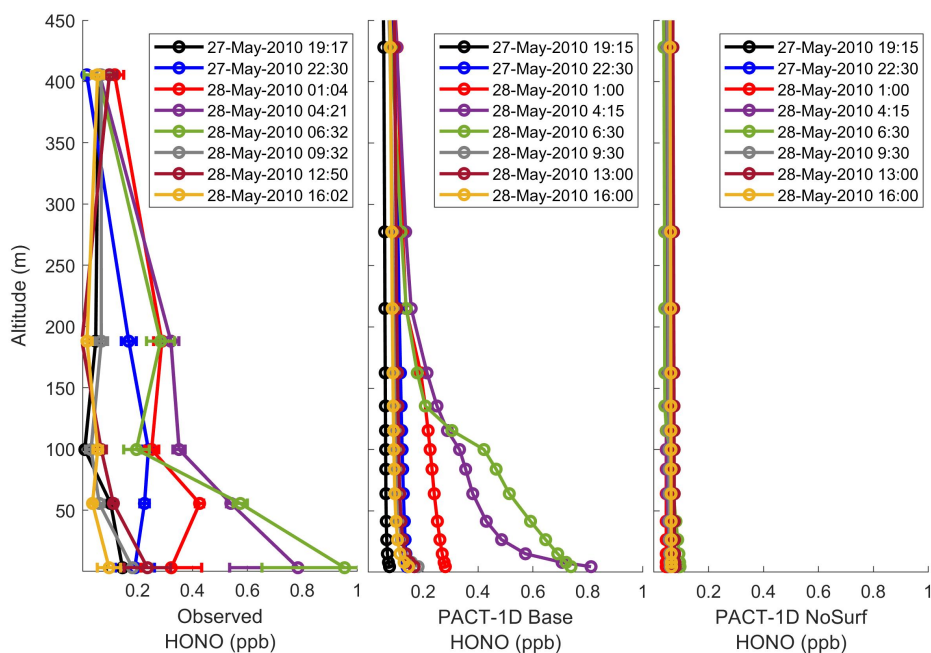


Figure 5. Comparison of HONO vertical concentration profiles between observations and model from May 27 to 28. The left panel is the observed profile, the middle is the PACT-1D Base run including surface chemistry, and the right panel is the PACT-1D NoSurf run excluding surface chemistry. The observed profile is constructed from LP-DOAS data (top four data points) and NOAA CIMS data (lowest data point).

522 HONO could be formed from aerosol sources at noon in Beijing in summer. The higher
 523 rates in Beijing are likely due to the higher aerosol loading in that study.

524 Net vertical transport rates of HONO from below are more variable from day to
 525 day but, in general, are greater than or about equal to HONO production from aerosol
 526 nitrate. For most of the three day period, the primary source of HONO below 500 m
 527 is upward transport from the surface (Figure 6). The large difference in surface area be-
 528 tween aerosols and the ground can explain the greater importance of ground sources and
 529 is in agreement with other studies (Kalberer et al., 1999; Kleffmann et al., 2003; Vogel
 530 et al., 2003; Stemmler et al., 2007). Compared to observations, daytime HONO levels
 531 between 50-400 m in the Base run tend to be over predicted. This may indicate that
 532 the sources aloft (formation on aerosols and transport from below) are too high. There
 533 is uncertainty in the photolysis rate for the aerosol source in the model, and the verti-

534 cal transport from the ground. Consequently, it is currently unclear which process is re-
 535 sponsible for the disagreement.

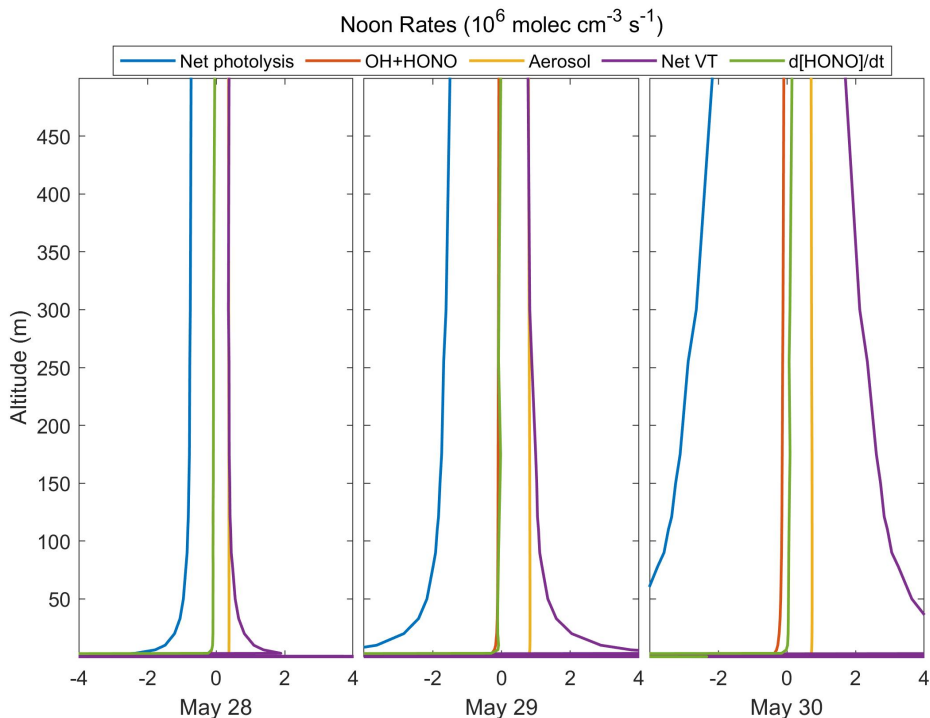


Figure 6. Noon time HONO budget for May 28 (left), 29 (middle), and 30 (right) from the Base run. Rates are reported in $\text{molec cm}^{-3} \text{s}^{-1}$ and include net photolysis (HONO photolysis minus formation from the OH+NO reaction), loss via the HONO+OH reaction, formation from aerosol nitrate photolysis, net vertical transport, and the HONO concentration change with time.

536 4.4 Primary HO_x production

537 To determine the importance of HONO to the radical budget, primary HO_x pro-
 538 duction (P_{HO_x}) was calculated for the Base run and measurements. We considered three
 539 major primary HO_x production pathways, HONO photolysis, HCHO photolysis, and O₃
 540 photolysis followed by reaction of O(¹D) with H₂O. Since HONO levels change quickly
 541 with altitude, as seen in the previous section, we again used vertical profiles to calcu-
 542 late P_{HO_x} . In addition to HONO measurements, the LP-DOAS observed vertical pro-
 543 files of HCHO and O₃. These were combined with the 3 m CIMS measurements of HONO,
 544 and the University of Houston’s (UH) 10 m O₃ measurements to construct concentra-
 545 tion profiles. 10m measurements of photolysis rates, temperature, and relative humid-

546 ity (Table 1) were used to calculate P_{HO_x} , assuming the values are constant over the al-
 547 titude range considered here (0-450 m). Figure 7 shows vertical profiles of P_{HO_x} from
 548 observations (solid lines) and model (dashed lines). These values are averages from 10:00
 549 am - 12:00 pm on May 28, 2010.

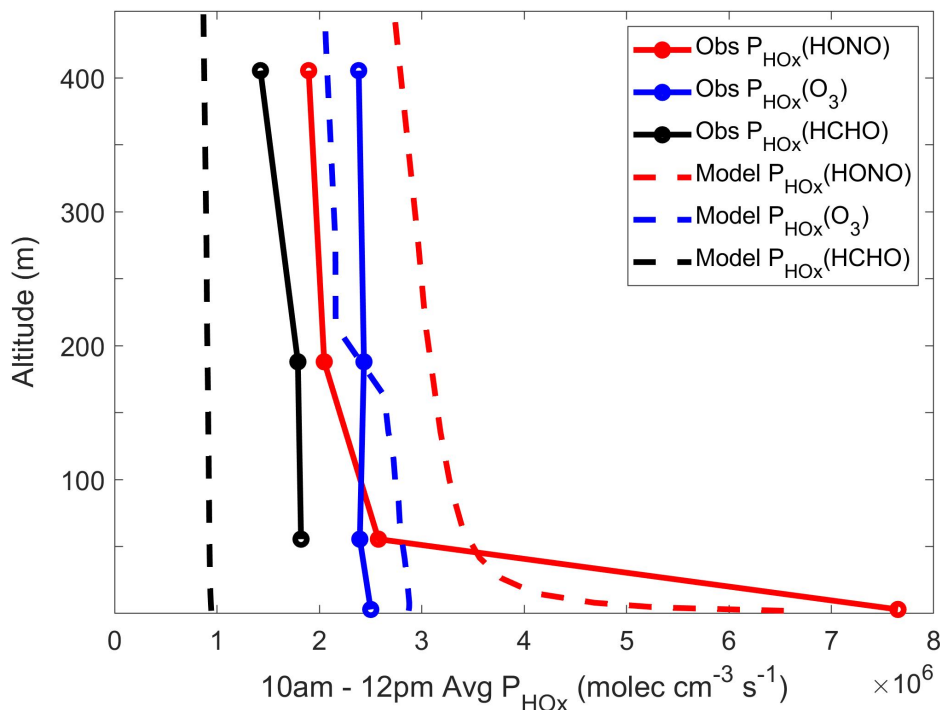


Figure 7. Primary HO_x production due to HONO (red), O_3 (blue), and HCHO (black). Observations are shown as dotted lines and model data from the Base run is shown as solid lines. Values are averaged between 10am-12pm on May 28, 2010.

550 In both PACT-1D and observations, the contribution to P_{HO_x} from HCHO and O_3
 551 remains relatively constant with height, with higher values for O_3 . PACT-1D underes-
 552 timates P_{HO_x} from HCHO compared to the observations, but captures the O_3 contri-
 553 bution well. Comparing HCHO LP-DOAS measurements to the model shows that PACT-
 554 1D under predicts HCHO levels at these altitudes, which leads to the under prediction
 555 of $P_{\text{HO}_x}(\text{HCHO})$.

556 Both observations and PACT-1D show that HONO photolysis is dominant near the
 557 surface, contributing 2-3 times more than O_3 below 10 m. $P_{\text{HO}_x}(\text{HONO})$ decreases quickly
 558 moving away from the surface, following the trend seen in the HONO concentration pro-

559 file. PACT-1D underestimates $P_{\text{HOx}}(\text{HONO})$ compared to the observations at the sur-
 560 face by about 15% compared to observations, and over predicts at higher altitudes by
 561 25-35%. The model also underestimates HONO concentrations at the surface and over
 562 predicts them aloft during this time period (Figure 5) which can explain this difference
 563 in $P_{\text{HOx}}(\text{HONO})$. The discrepancy between model and observations, for both the con-
 564 centration and $P_{\text{HOx}}(\text{HONO})$, is likely due to the high sensitivity of HONO to the ver-
 565 tical mixing or an over prediction of the HONO aerosol source, as discussed above.

566 A study by Griffith et al. (2016) found that during the CalNex campaign, HONO
 567 photolysis contributed 26% to the total radical production rate on weekends and hol-
 568 idays and 29% on weekdays. Using these average values, their $P_{\text{HOx}}(\text{HONO})$ between
 569 10:00 am and 12:00 pm ranged from about 5×10^6 and 8×10^6 molec $\text{cm}^{-3} \text{s}^{-1}$. They note
 570 that these values are most appropriate for 10 m altitude where measurements were recorded,
 571 and are consistent with the values we report here at low altitudes. HCHO photolysis con-
 572 tributed 9-10% to the total radical production, giving rates between 1.5×10^6 and 3×10^6
 573 molec $\text{cm}^{-3} \text{s}^{-1}$. The observations reported here are in agreement with these values, but
 574 again PACT-1D under predicts $P_{\text{HOx}}(\text{HCHO})$ due to the HCHO concentration being too
 575 low. O_3 photolysis contributed 11-14%, with rates of 2×10^6 - 4.5×10^6 molec $\text{cm}^{-3} \text{s}^{-1}$, match-
 576 ing our values well.

577 4.5 HONO source mechanisms

578 The HONO surface formation mechanisms added to PACT-1D in the Base run pro-
 579 vided an additional source of up to 2.5×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$ during the day and up
 580 to 5×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$ during the night. Figure 8 shows the source rate for our
 581 three day period, including the contributions from individual mechanisms. Values remained
 582 relatively constant throughout each of the nights around 1×10^{10} to 5×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$
 583 and then increased quickly in the early morning as photolytic formation mechanisms be-
 584 come effective. Our values are higher than source rates reported by other field studies,
 585 which include a forest canopy (Zhang et al., 2009; Zheng et al., 2011), an agricultural
 586 site (Ren et al., 2011), and polluted rural site (Tsai et al., 2018). These studies report
 587 average noontime fluxes between 1×10^{10} to 3×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$, measured at 10-
 588 20 m altitudes. Our surface flux is provided directly at the ground which likely explains
 589 the higher values. Loss of HONO through photolysis or deposition back to the ground
 590 decreases the amount that is transported to higher altitudes. We calculated the flux of

591 HONO across 10 m in the model and found noontime values of 5×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$
 592 for May 28 and 29 and 1.1×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$ for May 30. These are in better agree-
 593 ment with previous studies. Our urban site likely has a higher HONO source due to higher
 594 NO_2 concentrations and deposition, and higher surface HNO_3 concentrations.

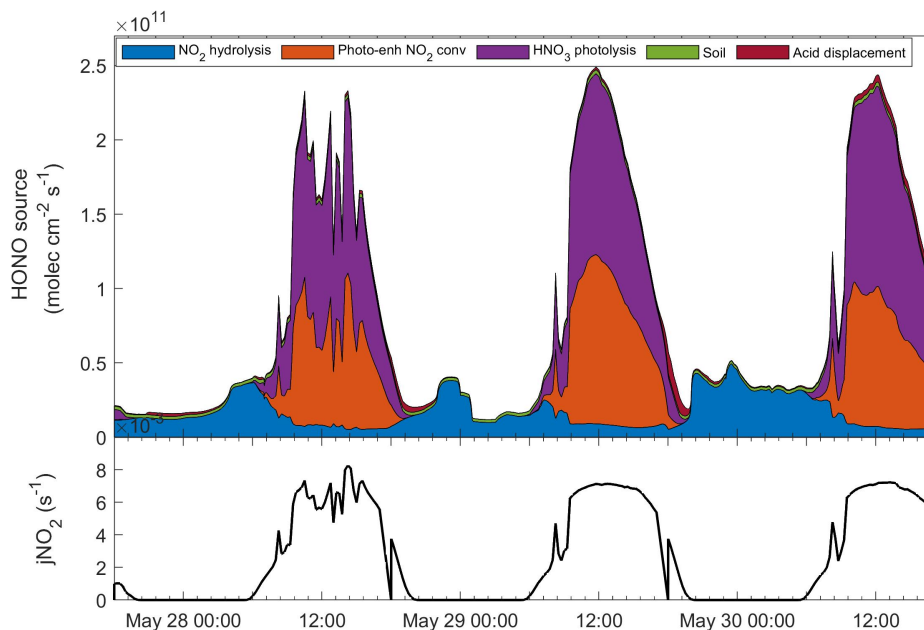


Figure 8. Contribution of individual mechanisms to the total HONO surface source in the Base run, from May 27, 2010 18:00 through May 30, 2010 17:00. The 10 m NO_2 photolysis rate for the 3 day period is shown in the lower panel.

595 The night time source was dominated by hydrolysis of NO_2 , which is consistent with
 596 previous studies (Kleffmann et al., 2003; Wong et al., 2011; VandenBoer et al., 2013).
 597 Photolysis of surface HNO_3 dominated throughout the day, contributing 45-60% of the
 598 total source during mid-day. Photo-enhanced conversion of NO_2 was also significant, con-
 599 tributing 20-45% of the daytime source (Figure 8).

600 Previous studies have suggested that the photo-enhanced conversion of NO_2 is the
 601 dominant heterogeneous mechanism under high- NO_x urban conditions while the pho-
 602 tolysis of surface HNO_3 is more important under low- NO_x conditions (Zhou et al., 2003;
 603 Elshorbany et al., 2012). We find the opposite during CalNex. Pusede et al. (2015) ex-
 604 amined how HONO levels during the CalNex campaign changed compared to NO_x and

605 found daytime HONO production did not vary with weekday/weekend changes in NO₂.
 606 They suggested therefore that NO₂ conversion is not the dominant HONO formation path-
 607 way. Although HNO₃ can also show a dependence on NO_x levels, its deposition and sub-
 608 sequent photolysis occur on a longer time scale which would not necessarily correlate with
 609 atmospheric NO₂ levels. Baergen and Donaldson (2016) suggests that HNO₃ photoly-
 610 sis on urban grime and its dependence on relative humidity would also cause a discrep-
 611 ancy between NO₂ and HONO production. Our results therefore support the findings
 612 by Pusede et al. (2015).

613 It is currently unclear however, why these differ from the study performed by Wong
 614 et al. (2013) in Houston, Texas. They found that photo-enhanced NO₂ conversion was
 615 the dominant HONO source based on a clear correlation between HONO and NO₂ lev-
 616 els. It is possible that surface HNO₃/NO₃⁻ concentrations are higher in Los Angeles,
 617 giving more importance to its photolytic source. The scarcity of significant rain events
 618 in Southern California may cause a buildup of HNO₃ on surfaces, whereas the much more
 619 frequent precipitation in Houston can lead to surface adsorbed species being washed away.
 620 Guo et al. (2017) did find that particle nitrate and HNO₃ concentrations during CalNex
 621 were higher than measurements from summertime campaigns in the southeast United
 622 States. They suggest this is due to the higher NO_x versus SO₂ sources in southern Cal-
 623 ifornia. This leads to a higher NO₃⁻ to SO₄⁻² ratio in particles, which raises the pH.
 624 The higher pH then creates a positive feedback which forms more NO₃⁻. Although Guo
 625 et al. (2017) focused on particles, it is possible that similar chemistry is occurring at the
 626 ground as well. Our results show that HNO₃ photolysis should be considered as an im-
 627 portant HONO source in certain urban areas and may be especially important in regions
 628 with low precipitation and high NO_x emissions.

629 **4.6 Source sensitivity to uptake coefficient and photolysis rate**

630 We performed sensitivity tests to better understand how the daytime HONO sur-
 631 face source is impacted by uncertainties in the mechanisms. The goal for these tests was
 632 to determine if the balance between the two major daytime mechanisms, the photo-enhanced
 633 conversion of NO₂ and the photolysis of surface HNO₃, could be adjusted and still pro-
 634 vide a sufficient HONO source to match observations. We focused on uncertainties in
 635 the maximum reactive uptake coefficient ($\gamma_{\text{NO}_2, \text{max}}$) and the photolysis rate enhance-
 636 ment of surface HNO₃ ($J_{\text{HNO}_3, \text{surf}}$) compared to the gas phase. Results from the sen-

637 sensitivity tests (Figure 9) are compared to the Base model run and a description of the changes
 638 made for each test are included in Table 2.

- 639 • Sens1 - To address the impact of uncertainties in $\gamma_{\text{NO}_2, \text{max}}$, its value was reduced
 640 by 50% in Sens1. A corresponding increase in $J_{\text{HNO}_3, \text{surf}}$ by 25% was then needed
 641 to maintain a surface source similar to the Base run. The noontime surface source
 642 increased from 1.6×10^{11} in the Base run to 1.9×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$ in Sens1.
 643 The contribution of photo-enhanced NO_2 conversion at noon decreased from 32%
 644 of the total source in the Base run to 26%. The contribution from surface HNO_3
 645 photolysis increased from 60% in the Base to 65%.
- 646 • Sens2 - Doubling $\gamma_{\text{NO}_2, \text{max}}$ required reducing $J_{\text{HNO}_3, \text{surf}}$ by 20% to maintain a
 647 surface source consistent with the Base run. This run again led to good agreement
 648 with the Base run, with the total source decreasing slightly to 1.5×10^{11} molecules
 649 $\text{cm}^{-2} \text{s}^{-1}$. The contribution of photo-enhanced NO_2 conversion at noon increased
 650 to 39% and the contribution from surface HNO_3 photolysis decreased slightly to
 651 58%.
- 652 • Sens3 - Reducing $\gamma_{\text{NO}_2, \text{max}}$ by 90% and increasing $J_{\text{HNO}_3, \text{surf}}$ by 60% caused the
 653 3 m HONO concentration and the total HONO source to become slightly higher.
 654 The concentration is still within the margin of error of the HONO CIMS measure-
 655 ments.
- 656 • Sens4 - To test if the photo-enhanced NO_2 conversion could contribute the ma-
 657 jority of the ground HONO source, $\gamma_{\text{NO}_2, \text{max}}$ was increased by a factor of 5 and
 658 $J_{\text{HNO}_3, \text{surf}}$ was set equal to $J_{\text{HNO}_3, \text{g}}$. This test clearly failed to produce a strong
 659 enough source to describe HONO concentrations at 3 m. It is evident therefore
 660 that surface HNO_3 photolysis is an essential contributor to the HONO source and
 661 that it needs to proceed at a faster rate than gas phase HNO_3 photolysis. It is also
 662 interesting that the photo-enhanced NO_2 source is lower here than in Sens2 at most
 663 times throughout the day. Increasing $\gamma_{\text{NO}_2, \text{max}}$ between the Base run and Sens2
 664 caused an increase in the source due to greater NO_2 uptake and conversion but
 665 this trend obviously does not continue as $\gamma_{\text{NO}_2, \text{max}}$ is increased more. The NO_2
 666 concentration in the lowest model layer in Sens4 is less than half the concentra-
 667 tion in Sens2, indicating that the mechanism becomes transport limited. Although
 668 NO_2 is converted at a greater rate, this is depleting NO_2 near the surface that can-

669 not be replenished quickly enough from aloft, leading to an overall decrease in HONO
 670 production.

671 Since both photolytic mechanisms have similar dependencies, including irradiance
 672 and NO_x concentrations, it can be difficult to determine which is more important for HONO
 673 production. These sensitivity tests show that the contributions from each mechanism
 674 are uncertain due to poorly constrained $\gamma_{\text{NO}_2, \text{max}}$ and $J_{\text{HNO}_3, \text{surf}}$. While it is possible
 675 for surface HNO_3 photolysis to explain most of the HONO source, NO_2 conversion alone
 676 cannot produce enough HONO in our case. Without additional laboratory studies that
 677 demonstrate the specific importance of each of these two mechanisms, it is clear that both
 678 can be considered important HONO sources in urban regions.

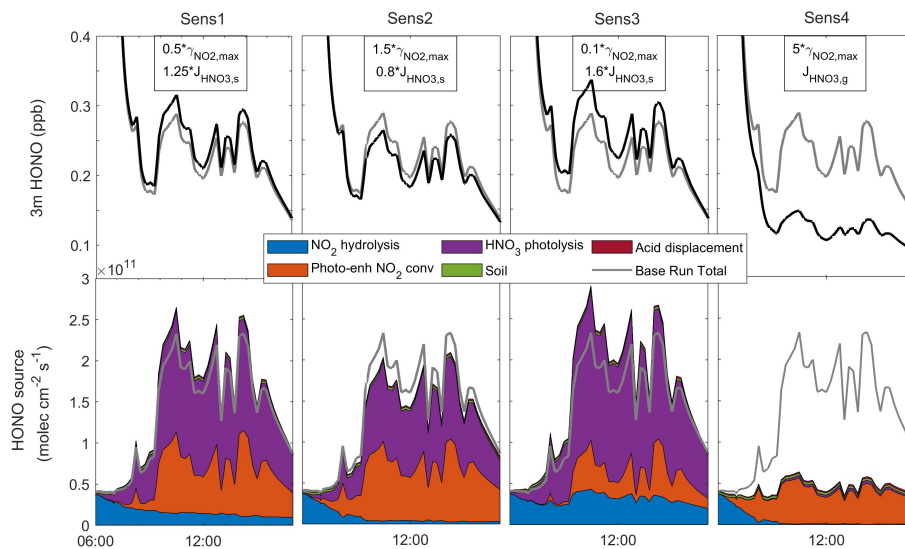


Figure 9. Results from sensitivity studies, showing 3 m HONO (top, black line) and the HONO ground source (bottom) for the afternoon of May 28. The Base run is shown in gray.

679 5 Conclusion

680 HONO's impact on secondary pollutant formation makes it an important species
 681 in urban environments. Since it's heterogeneous formation mechanisms are poorly un-
 682 derstood, we have developed a new one-dimensional chemistry and transport model, PACT-

683 1D, to perform mechanistic studies that can help constrain the HONO budget. In par-
684 ticular, PACT-1D has the ability to do molecular level surface chemistry and emissions.
685 The model has been tested against observations from the CalNex field campaign, which
686 was performed in the urban region of Los Angeles. Multiple heterogeneous source mech-
687 anisms at the ground were added to the model which helped better simulate atmospheric
688 HONO levels, both at the ground and throughout the boundary layer. We determined
689 that the daytime HONO source was dominated by HNO_3 /nitrate photolysis at the ground,
690 followed by photo-enhanced conversion of NO_2 . At night, the major HONO source was
691 conversion of NO_2 on the ground. With these sources implemented we determined that
692 HONO photolysis is the dominant contributor to primary OH production near the sur-
693 face. This contribution decreases quickly with altitude, showing a similar vertical pro-
694 file to HONO concentrations. These results emphasize the importance of atmospheric
695 mixing when considering HONO's total impact to the boundary layer and help better
696 understand the HONO sources in urban environments. Tests were also performed to de-
697 termine the sensitivity of the two major daytime HONO sources to uncertainties in their
698 mechanisms. While their relative contributions vary with the uncertainties, it's clear that
699 both HNO_3 /nitrate photolysis and photo-enhanced conversion of NO_2 should be con-
700 sidered to simulate HONO in urban atmospheres.

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707 The PACT-1D model code used in this study is available at <http://doi.org/10.5281/zenodo.4776419>.
708 Output files for the base run used in this study are available at: <https://doi.org/10.5281/zenodo.4776977>.
709 The CALNEX data set is available at <https://www.esrl.noaa.gov/csd/projects/calnex/>.

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