

VERTICAL STRUCTURE AND SURFACE INTERACTIONS OF
NITROUS ACID USING A 1D MODEL

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A THESIS SUBMITTED TO THE FACULTY OF GRADUATE
STUDIES IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTERS OF SCIENCE

GRADUATE PROGRAM IN CHEMISTRY
YORK UNIVERSITY
TORONTO, ONTARIO

April 2025

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Abstract

This study was undertaken in order to study the vertical distribution and surface interactions of gas-phase HONO under non-ideal mixing conditions during the 2011 NACHTT campaign using the Platform for Atmospheric Chemistry and vertical Transport in One Dimension (PACT-1D) model. This work builds on a previous 0D modelling study from the NACHTT campaign, where the greatest unknown source rate of HONO was found during the early morning when a morning burst of HONO were observed and a stable nocturnal boundary layer formed. The 48-hour model was initialized using observational constraints selected during periods where a morning burst of HONO were observed and a stable nocturnal boundary formed. The modelled HONO showed excellent agreement with observations when heterogeneous ground surface processes of HONO, surface water, and vertical mixing were accounted for without the need to apply additional daytime sources of HONO.

Acknowledgments:

First and foremost, I would like to acknowledge my supervisor, Dr. Trevor VandenBoer for accepting me as a graduate student several years ago. Your consistent support and guidance throughout my graduate career has not only allowed me to build up my confidence and skillset in becoming a more competent scientist, but also a more well-rounded human being. I would like to also acknowledge Dr. Cora Young who has been very supportive of my research during my graduate career and who I learned many important life lessons from, including the importance of networking and that striving for perfection can be the enemy of the just good-enough. I would like to acknowledge Dr. Mark Gordon for being a part of my committee and for providing me helpful insights in setting the vertical diffusion mixing term for the 1D model. I would also like to acknowledge a colleague and good friend of mine Noah Stanton for assisting me with initializing the WRF model in MATLAB and for discussing how variables from WRF can be coupled to PACT-1D. Without the assistance from Noah, we would not have been able to incorporate WRF and the predicted capability of the PACT-1D model would have decreased. I would like to acknowledge all the creators and developers of PACT-1D including Jotchen Stutz, Katie Tuite, Jennie Thomas, and Shaddy Ahmed for providing the base template codes for each component in the PACT-1D model. I want to also acknowledge the NSERC Canada Graduate scholarship Master's program in funding my research. I would also like to acknowledge all the group members and colleagues from the VandenBoer and Young group, especially Leyla Salehpour, Nasrin Dashti, Moxy Shah, Daniel Farahani., Na-Yung Seoh, Stephen Ye, Lisa Azzarello, Danial Persaud, Mayré Rodriguez, Dr. Igor Pereira de Silva, Andrea Angelucci, Alessia Colussi, and Dr. Kifle Aregahegn for all the support during time as a graduate student, from travelling to international conferences together, bouncing off new ideas to each other, and to being great friends. Outside of academia, I would also like to acknowledge my parents (Ali Ebrahimi-Iranpour and Nahid Anari), my sister (Solmaz Ebrahimi-Iranpour), and my dearest girlfriend, Kiana Ghafarizadeh, for their unwavering support during my time as a graduate student. I genuinely could not have finished writing this thesis without your emotional support and I would like to thank each and every one of you.

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LIST OF ACRONYMS AND ABBREVIATIONS

PACT-1D	Platform for Atmospheric Chemistry and vertical Transport in One Dimension
HONO	Nitrous Acid
NO ₂	Nitrogen Dioxide
NO ₂ ⁻	Nitrite ion
NO	Nitrogen monoxide
HNO ₃	Nitric Acid
HCl	Hydrochloric Acid
O ₃	Ozone
N ₂ O ₅	Dinitrogen Pentaoxide
OH•	Hydroxyl Radical
RO	Alkoxy Radical
NO ₃	Nitrate Radical
ppt	Parts Per Trillion
ppb	Parts Per Billion
n _x	number density in molecules cm ⁻³ s ⁻¹
PBL	Planetary Boundary Layer
IR	Infrared Radiation
NBL	Nocturnal Boundary Layer
RL	Residual Layer
ASL	Atmospheric Surface Layer
BLH	Boundary Layer Height
BL	Boundary Layer
VOC	Volatile Organic Compounds
PM	Particulate Matter
SATP	Standard Atmospheric Temperature and Pressure
k ₀	The rate coefficient in a lower pressure limit regime in cm ⁶ molecule ⁻² s ⁻¹
k _∞	the rate constant in a high pressure limit in cm ³ molecule ⁻¹ s ⁻¹
F _{dep}	Deposition flux in mol m ⁻² s ⁻¹
v _d	Deposition velocity in m s ⁻¹
[X] _{ground}	Concentration of gas-phase species near the ground surface in mol m ⁻³
$\bar{C}$	Mean molecular speed of the target gas-phase species in m s ⁻¹
R _a	The Aerodynamic Transport Resistance Term
R _b	The molecular diffusion resistance term
R _c	The surface reactive loss term
D	Molecular diffusivity of target gas in m ² s ⁻¹
μ	Wind speed in m/s.
k	The Von Karmon constant = 0.43
AGL	Above Ground Level
z	Altitude Above Ground Level
Z ₀	Surface Roughness Length
SOA	secondary organic aerosols
PAH	polycyclic aromatic hydrocarbons
K _H	Henry's law constant of HONO
K _a	Acid Dissociation constant

j_{HONO}	Photolysis rate coefficient of HONO
PSS	Photostationary state
NACHTT-11	Nitrogen, Aerosol Composition, and Halogens on a Tall Tower 2011 Campaign
BAO	Boulder Atmospheric Observatory
RH	Relative Humidity
WRF	Weather Research and Forecasting Model
MP	Model Period
MP1	Model Period I
MP2	Model Period II
OP	Observation Period
OP1	Observation Period I
OP2	Observation Period II
NO_GSS	PACT-1D model output with no ground surface source routines configured
BASE	PACT-1D model output with base surface source routines configured
BASE_WET	PACT-1D model output with RH-dependent surface parameter applied to the uptake of NO ₂ and HONO
S/V	Surface Area over volume ratio
CTMs	3D Chemical Transport Models
RACM2	Regional Atmospheric Chemistry Model V2
P	Chemical Production
L	Chemical Loss
E	Surface emissions
F	Flux
K_z	Vertical Diffusion Coefficient
$K_{z\text{ceil}}$	Preliminary K_z parametrization
$K_{z\text{final}}$	Final K_z parametrization included in the model
KPP	Kinetic PreProcessor
BOX_WALL	Defined height dimensions and levels of the box model
BOX_CH	Centre point height at each level of the box model
D01	Inner Grid of the WRF model
D02	Outer grid of the WRF model
XLAT	Latitude
XLONG	Longitude
HGT	Terrain Height
PHB	Base-state Geopotential
P	Perturbation Pressure
PB	Base-state Pressure
QVAPOR	Mixing ratio of water vapour in kg/kg
g	Earth's Gravitational constant = 9.81 m ² /s
N_a	Avogadro's number = 6.023x10 ²³ molecules
F_{HONO}	Fraction of HONO formed from the evaporation of nitrite
$C_{\text{NO}_2^-}$	Concentration of nitrite in mg/L
PISA	Portable Instrument Shelter with Amenities; vertical tower carriage
UHSAS	Ultra-High Sensitivity Aerosol Spectrometer
AMS	Aerosol Mass spectrometer
CRDS	Cavity-Ring down Spectrometer

IC	Ion-chromatography
GC	Gas Chromatography
CIMS	Chemical Ionization Mass Spectrometry
TOF-PTRMS	Time-of-flight Proton transfer reaction mass Spectrometry
WS	Wind Speed in m/s
WD	Wind Direction in °
HONO _{model}	hourly average HONO quantity that changes only due to the integrated photolytic loss of HONO in molecules cm ⁻³ s ⁻¹
$n_{(HONO,t=0)}$	the average number density of HONO between 06:45 – 07:00 MST of MP1 in molecule cm ⁻³ s ⁻¹ .
$P_{gas,net}$	net contribution from all gas phase mechanisms of HONO
P_E	Production from Hourly emission rates of HONO
P_{VT}	Loss of HONO by vertical transport above 50 m AGL
$\gamma_{NO_2,grd}$	Reactive Ground uptake coefficient of NO ₂ = 8.0x10 ⁻⁶
$\gamma_{HONO,grd}$	Reactive Ground uptake coefficient of HONO = 7.3x10 ⁻⁵

Chapter I: Current understanding of HONO chemistry and the importance of 1D Box modelling

1.1 Atmospheric Structure:

The Earth's atmosphere is comprised of five distinct layers, from the ground surface to the interfacial layer between the outer atmosphere and space. These layers include the troposphere (0–15 km), stratosphere (15 – 50 km), mesosphere (50 – 85 km), thermosphere (85–600 km), and exosphere (> 600 km), each defined by unique dimensions, thermal energy characteristics (i.e. radiative heat transfer from the ground, the stratospheric ozone (O₃) layer, and the absorption of high-energy photons by N₂ and O), chemical composition, density, and movement (**Figure 1.1**). Air parcels between these boundaries do not mix due to temperature inversions observed at the transition layers, where warm, buoyant air in the upper layer rises while cold, dense air in the lower layer descends—resulting in the alternating proportionality between air temperature and altitude in **Figure 1.1** (Finlayson-Pitts, 1999; Seinfeld and Pandis, 2006).

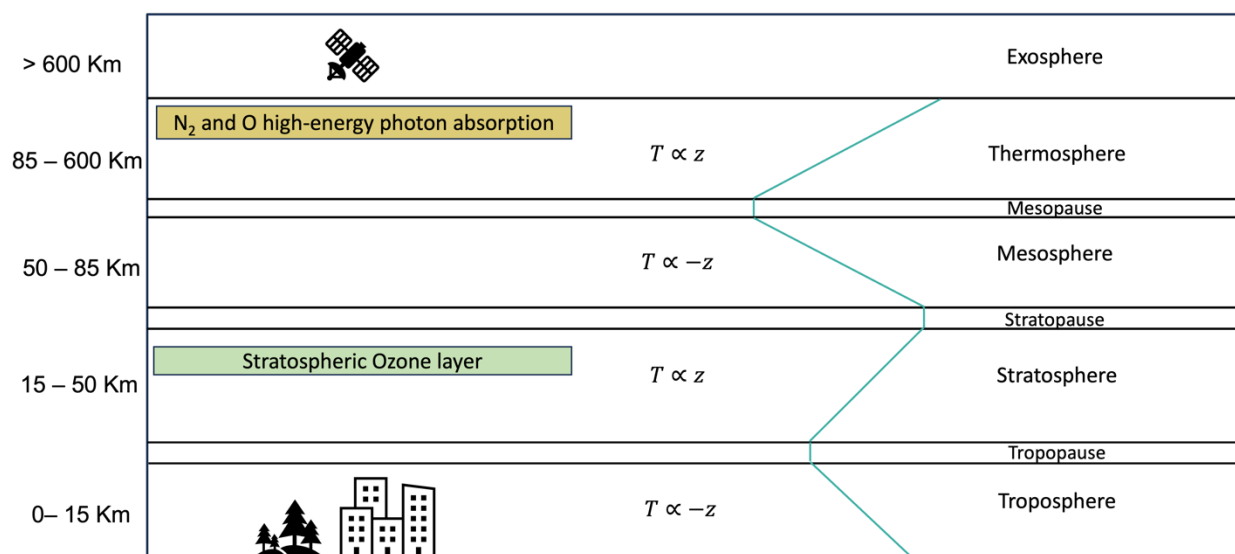


Figure 1.1. Schematic of five distinct layers in Earth's atmosphere: the troposphere, stratosphere, mesosphere, thermosphere, and exosphere. In each layer, the proportionality between ambient temperature and height has been defined in the center of the schematic layer. To the left of the layer, a depiction of the dominant radiation process is shown, including radiative heat transfer from the ground surface, the stratospheric ozone layer, and the absorption of high-energy photons by N₂ and O.

The lowest layer of the troposphere is the **Planetary Boundary Layer (PBL)**, which is the most important layer when it comes to studying air quality, as it is in direct contact with the ground surface (i.e. land or water) where people live and breathe. It also contains 2-30 % of the total mass of the Earth's atmosphere. During the day, the ground surface or that of a water body absorbs photons at a faster rate than air parcels in the atmosphere, emitting heat to the overlying air through radiative heat transfer. During the night, heat is dissipated from the black body surface of the earth to outer space in the form of Infrared (IR) radiation, a process known as the radiative cooling effect. The rate of heat transfer from the terrestrial ground surface is faster than from the surface of a water body due to the high heat capacity of water, resulting in a terrestrial ground surface heating faster during the day and cooling faster during the night. Where these two interfaces co-exist at the surface, well-known sea and lake breezes result from the differential diurnal heating and cooling. During the day, for a terrestrial-only system, heat is transferred from the ground surface to air parcels directly above when sunlight is present. The increase in energy in these air parcels raises their temperature, expands the gas volume lowering its density, and causes the parcel to rise. These processes create the PBL and the resulting mixing is termed turbulence as a result of the convective motion of the air parcels. The PBL reaches a maximum depth in the afternoon when radiative heat transfer from the ground surface is strongest (**Figure 1.2**). As the sun begins to set, turbulent mixing within the PBL ceases as the effect of radiative heating on the ground surface transitions to radiative cooling. This causes air parcels immediately above the ground surface to cool faster than the air further aloft, which results in a temperature inversion, and the cool air parcels near the ground surface are trapped in the **Nocturnal Boundary Layer (NBL)**, while the lofted air parcels from the previous day of mixing stay suspended in the **Residual Layer (RL)**. Above the PBL lies the stable free troposphere, which is dominated by strong wind shear and extends to the tropopause (**Figure 1.2**). At the next sunrise, the ground surface again heats up faster than the air parcels above it as a result of radiative heating, which then results in the predictable diurnal breakup of the NBL and another transition into the convective mixing layer. The formation of a stable NBL occurs only during the absence of turbulence, which can be broadly characterized as when horizontal wind speeds are ≤ 6 m/s (Van de Wiel et al., 2012). Within the NBL, the main source of mixing from synoptic scale pressure-gradient winds can be attributed to the turbulent drag induced at the earth's surface, which is controlled by the surface friction velocity (**Equation 1.1**).

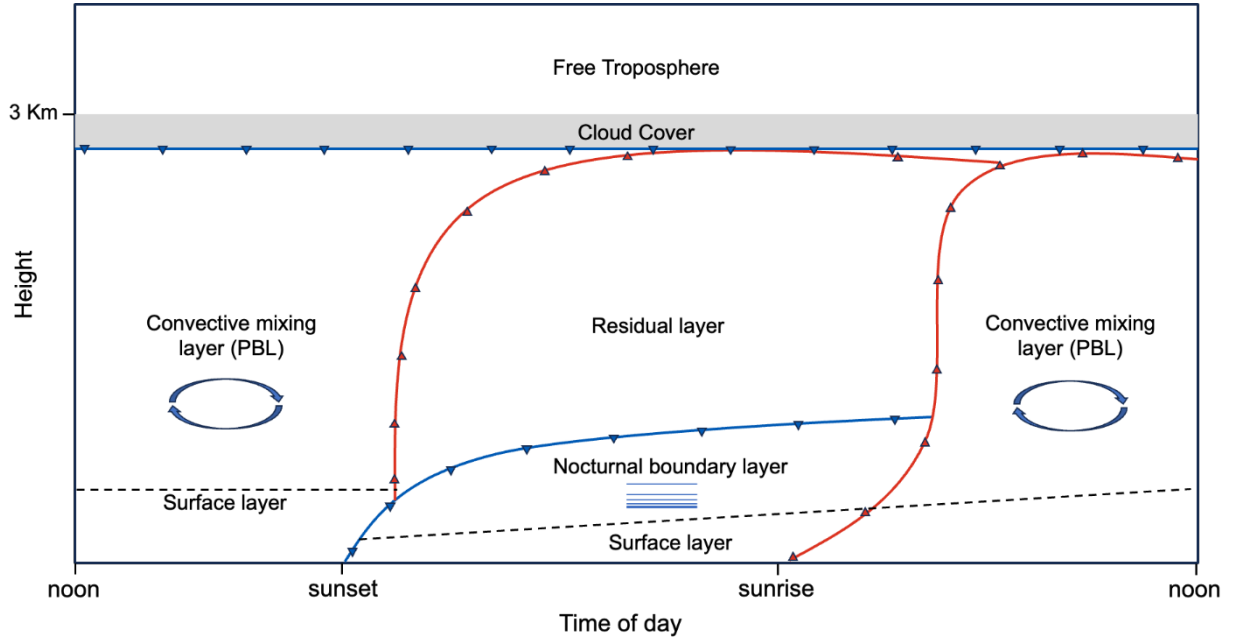


Figure 1.2. A schematic of the diurnal evolution of the PBL within the lowest layer of the troposphere, from the atmospheric surface layer to the free troposphere. The convective mixing layer forms during the day in the presence of radiative heat transfer from the ground surface and extends to the clouds, where a capping temperature occurs. At sunset, the development of a stable NBL begins to form due to a temperature inversion, where air parcels are vertically stratified. During the same timeframe, the formation of a residual layer occurs above the NBL. At sunrise, the effect of radiative heating causes a breakup of the NBL and a transition into a daytime PBL. Above the cloud cover lies the free troposphere, extending from the top of the PBL to the tropopause.

$$u_* = \sqrt{\frac{\tau}{\rho}} \quad (Eq. 1.1)$$

where μ_* is the surface friction velocity (m/s) of the wind at the surface, τ the surface shear stress (Pa), and ρ is the air density (kg/m^3).

At all times during the diurnal evolution of the PBL, an **Atmospheric Surface Layer (ASL)** exists, defined as 10 % of the PBL. This is the height at which surface friction and radiative heat transfer effects become significant and where wind profiles can be modelled using the logarithmic wind profile equation (**Equation 1.2**).

$$u(z) = \frac{u_*}{\kappa} \ln \left(\frac{z - d}{z_0} \right) \quad (\text{Eq. 1.2})$$

where u is the wind speed (m/s) expressed as a function of height, κ is the von Karman constant equivalent to 0.43, z is the height (m), d is the displacement height, z_0 is the surface roughness length (m).

The surface roughness is defined as the height at which the wind speed approaches zero, which varies based on terrain features, such as on the surface of smooth ice ($z_0 = 0.00001$ m; Saheb et al. 2014), the ocean surface ($z_0 = 0.001$ m; Tasneem et al., 2020), crops ($z_0 = 0.05$ m; Floors et al., 2022), forests ($z_0 = 0.5$ m; Floors et al., 2022), and urban structures found in cities ($z_0 = 3.0$ m; Bezrukovs et al., 2014). Generally, as the surface roughness increases, the friction velocity also increases as a result of greater turbulent drag, which increases mechanical mixing within the PBL. Another factor that affects surface dynamics and mixing of the ASL is the canopy height, which is defined by the average height of vegetation or urban obstacles on the surface, including forests and crops in rural areas and buildings in urban areas. The wind speed and turbulent mixing are reduced within the canopy, resulting in additional vertical stratification of air parcels. In contrast, turbulent mixing increases above the canopy surface due to shear wind speed. Given that wind speed is reduced at the top of the canopy, the displacement height is defined by the effective origin of the logarithmic wind profile equation. The ability to define physical properties such as wind speed and surface roughness that influence the depth of the surface layer is important in modelling tropospheric chemistry, given that the ground surface is where anthropogenic emissions are emitted and get diluted within the PBL, this raises the greatest concern for air quality closest to the ground. In this thesis, it will be shown that the ground surface production of gas-phase HONO, either through direct emissions or heterogeneous surface production can influence the PBL if the physical and chemical parametrizations of gas-phase HONO can be correctly captured.

1.2. Tropospheric Air Quality and its Drivers:

The production of hydroxyl radicals ($\text{OH}\cdot$) drives all the oxidative chemistry during the daytime by converting primary pollutants into secondary pollutants. In the troposphere, three mechanisms generally drive the production of OH radicals: photolysis of tropospheric O_3 ($\lambda \leq 310$ nm;), HONO ($\lambda \leq 405$ nm;), and formaldehyde ($\lambda \leq 310$ nm) – all of which are dependent on the intensity and the attenuation of photons entering the troposphere. The attenuation of high-energy photons arriving and leaving the boundary layer is dictated by factors that control the solar flux in the actinic region, including the solar zenith angle and the abundance of absorbing gases, surface albedo, cloud cover, and altitude. The probability of high-energy photons being absorbed in the troposphere increases with decreasing altitude, where photons reaching the ground surface have typical cutoff wavelength of approximately 300 nm.

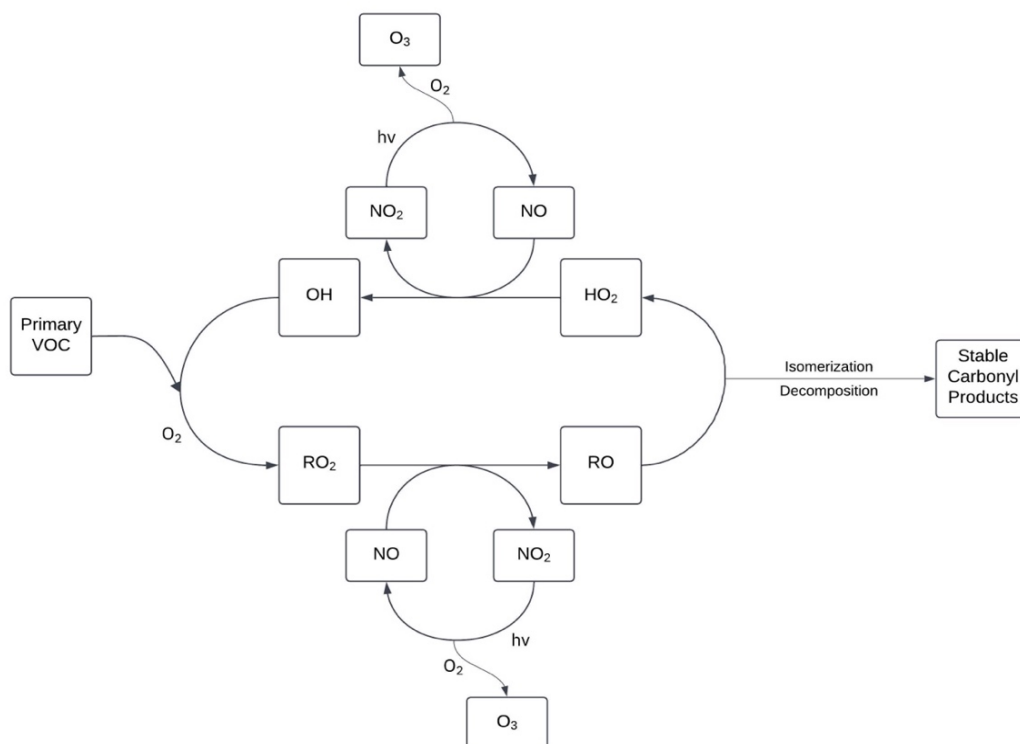


Figure 1.3. A schematic representing the VOC oxidation cycle in the troposphere and the influence of NO_x and HO_x chemistry in controlling the fate of VOCs in the troposphere, where they could lead to the formation of ozone and secondary organic aerosols, and stable carbonyl products.

The dominant mechanism for the production of OH• occurs in two steps, through the photolysis of O₃ forming an electronically excited oxygen atom (O(¹D)) and then reaction with water vapour to form OH•. Due to the higher background mixing ratios of O₃ and water vapour relative to HONO and HCHO in the troposphere, the photolysis of O₃ typically leads to the greatest contribution of OH• by midday. Given that the photolysis of NO₂ is the primary source of tropospheric ozone during the day, gas-phase NO₂ indirectly represents the most important precursor influencing the daytime production of OH•. Compared to other sources of OH•, the onset of HONO photolysis occurs earlier in the day when other processes, including the photolysis of O₃ and HCHO are limited (Young et al., 2012). The OH• that are formed during early morning processes (i.e. the photolysis of HONO) are responsible for initiating oxidative chemistry during the day and can contribute to radical propagation, effectively increasing the daytime production of secondary pollutants such as tropospheric O₃, Secondary Organic Aerosols (SOA), and stable carbonyl products via the oxidation of Volatile Organic Compounds (VOCs) (Young et al., 2012).

Atmospheric oxidation by OH• is fueled by VOCs that are emitted near the ground and can contribute to the formation of SOA and tropospheric O₃ via the VOC oxidation cycle, which is catalyzed by the chemistry of nitrogen oxides (NO_x = NO₂ + NO) on the cycling and fate of hydrogen oxide radicals (HO_x = OH + HO₂ + RO₂) (**Figure 1.3**). During the day, gas-phase VOCs can react with OH or undergo photolysis to form organic peroxy radicals (RO₂) in the presence of oxygen. When daytime levels of NO_x are elevated due to increased anthropogenic emissions, the RO₂ radical is quickly converted into the alkoxy radical (RO) through the conversion of NO to NO₂, subsequently leading to the production of O₃ via the photolysis of NO₂. The RO radical is then rapidly converted to the hydroperoxy radical (HO₂), where the reformation of the initial OH is reestablished through another conversion of NO to NO₂, leading to the photochemical production of tropospheric O₃ via the photolysis of NO₂. The accumulated O₃ can then proceed to generate additional OH•, and further formation of other harmful secondary pollutants like respirable particulate matter (PM). As the VOC oxidation cycle progresses throughout the day, secondary VOCs form via H-abstraction by OH•, while decomposition of RO₂ or RO species or their isomerization reactions could form particulate matter (PM.). Given its direct relation to the VOC oxidation cycle, the homogeneous gas-phase mechanisms of HONO have been studied extensively but alone, cannot explain the mixing ratios of gas-phase HONO observed in both urban

and rural environments. For this reason, surface sources of HONO on aerosols (Pawar et al., 2024; Li et al., 2024; Liu et al., 2014; Lu et al., 2018) and the ground surface (VandenBoer et al., 2013; Kleffmann et al., 2003; Tuite et al., 2021; Sörgel et al., 2011) have recently become recognized as a major source of HONO during the day and have gained an increased use in atmospheric chemistry models to ameliorate our understanding of air quality chemistry, given that HONO is both a source of NO and OH.

1.3. Chemical Kinetics in The Atmosphere

The ability to understand chemical kinetics in the atmosphere is fundamental for driving atmospheric chemistry models and being able to test known chemical processes against observations. In the troposphere, homogeneous gas-phase reactions can be postulated by bimolecular (R1) or three-body pressure-dependent kinetics (R6). In bimolecular reactions, two gas-phase species (i.e. A and B) collide to form a product or products without the formation of an intermediate, where its second-order rate law can be defined in **Equation 1.3**, and the rate coefficient can be represented by the Arrhenius equation, expressed as a function of temperature (**Equation 1.4**).



$$Rate = k[A][B] \quad (Eq. 1.3)$$

$$k\left(\frac{1}{T}\right) = A\left(-\frac{Ea}{R}\right) \quad (Eq. 1.4)$$

where k is the rate coefficient in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, A is the Arrhenius A factor, and Ea/R is the ratio of the activation energy for the reaction to proceed relative the gas constant, recommended temperature dependence in k (Section 1.3, Burkholder et al., 2019). Most homogeneous gas phase bimolecular reactions have a rate constant generally expressed for conditions of Standard Atmospheric Temperature and Pressure (SATP), where $T = 298 \text{ K}$ and $P = 1.01325 \times 10^5 \text{ Pa}$.

In a three-body pressure-dependent reaction, two gas-phase species collide in the presence of a third body ($M = O_2 + N_2$) to yield a single product species, where the elementary steps are defined in R2 – R5 and the overall reaction is defined in R6. The role of a third body is to stabilize the intermediate by removing excess energy present in the formation of the excited intermediate (i.e. AB^*) and then to dissipate it as heat to the surroundings.



If the rate-determining step is the formation of the excited product and the lifetime of AB^* is very short-lived, we can derive a steady-state approximation for the formation and loss of the excited product to obtain the overall rate law (**Equation 1.5**).

$$Rate = \frac{k_2 k_4 [A][B][M]}{k_3 + k_4 [M]} \quad (Eq. 1.5)$$

For the concentration of gas-phase O_2 and N_2 , which are the most abundant and relatively inert gases in the atmosphere, species M can be represented as their sum (M) in a pressure-dependent reaction. For such reactions two limits can arise depending on the concentration of M with respect to the dissociation of AB^* . In the case of a low-pressure limit ($[M] \ll k_4/k_3$), the overall rate law can be simplified to a first-order reaction that is linearly dependent on $[M]$ (**Equation 1.6**). In the case of a high-pressure limit ($[M] \gg k_4/k_3$), the overall rate law can be simplified to a second-order reaction that is dependent on the concentration of the reactants (**Equation 1.7**). Between the two limits, the rate must be determined by including the pressure dependent components of all reaction steps driving the mechanism.

$$Rate = k_0 [A][B][M] \quad (Eq. 1.6)$$

where k_0 is the rate constant in a lower pressure limit regime and can be expressed as $\frac{k_2 k_4}{k_3}$ with units of $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$.

$$Rate = k_\infty [A][B] \quad (Eq. 1.7)$$

where k_∞ is the rate constant in a high pressure limit and can be expressed as k_2 with units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Apart from homogeneous gas-phase kinetics, heterogeneous gas-phase mechanisms can also occur between the gas-phase and a surface of a condensed phase, including on the surface of aerosols and the ground. For the purpose of this thesis introduction, we will only focus on heterogeneous processes between the gas phase and the ground surface. Assuming an infinitesimal surface layer at the ground, a deposition flux of any gas-phase species due to a vertical concentration gradient can be defined using **Equation 1.8**.

$$F_{dep} = v_d [X]_{ground} \quad (Eq. 1.8)$$

where F_{dep} is the deposition flux in $\text{mol m}^{-2} \text{ s}^{-1}$, v_d is the deposition velocity in m s^{-1} , and $[X]_{ground}$ is the concentration of gas-phase species near the ground surface (mol m^{-3}).

The deposition velocity of any gas-phase species (Seinfeld and Pandis, 2006) can be estimated from observationally constrained measurements using an uptake coefficient that represents the probability of a gas-phase molecule being taken up by the ground surface (**Equation 1.9**).

$$v_d = \frac{1}{4} \gamma \bar{C} \quad (Eq. 1.9)$$

where v_d is the observed deposition velocity in m s^{-1} , γ is the unitless uptake coefficient of a target gas-phase species relative to a non-reactive (i.e. adsorption) or reactive surface, and $\bar{C}$ is the mean molecular speed of the target gas-phase species in m s^{-1} . The numerical probability of $\frac{1}{4}$ has been developed from a 2D physics perspective, where it states that if molecules can be transported vertically and horizontally, the contribution from dry deposition (i.e. downward

movement) would be a quarter of the total translation movement options of any gas-phase species.

Using an analogy of electrical systems (Seinfeld and Pandis, 2006), the observed deposition velocity of gas-phase species to the ground surface can be influenced by three resistance terms that are connected in series from the surface layer to the ground surface, including the aerodynamic transport resistance (R_a), the molecular diffusion resistance (R_b), and surface reactive loss (R_c) (**Equation 1.10**). The R_a term is dependent on atmospheric stability parameters, including wind speed and surface roughness, which become important in the surface layer as the influence of turbulent drag increases and transports gas-phase species to the surface, independent of their chemical or physical properties (**Equation 1.11**). Given its importance, the R_a term is commonly solved in 1D models in order to yield a dynamic deposition velocity term that changes with respect to meteorology. Between the surface layer and the ground surface, the R_b lies in a thin layer termed the quasi-laminar sublayer and is influenced by the molecular diffusivity of gas in the air and the surface roughness (**Equation 1.12**). The R_c is a more complicated resistance term that only becomes relevant in the presence of a canopy (e.g. trees or grass) and strictly depends on the nature of the surface (i.e. the canopy height), which can be defined with a reactive uptake coefficient and mean molecular speed (**Equation 1.13 and Equation 1.14**).

$$v_d = \frac{1}{R_a + R_b + R_c} \quad (Eq. 1.10)$$

$$R_a = \frac{1}{u \kappa^2} \left(\ln \left(\frac{z}{z_0} \right) \right)^2 \quad (Eq. 1.11)$$

$$R_b = \frac{z_0}{D} \quad (Eq. 1.12)$$

$$R_c = \frac{4}{\gamma \bar{C}} \quad (Eq. 1.13)$$

$$\bar{C} = \frac{\sqrt{8RT}}{\pi M} \quad (Eq. 1.14)$$

where the v_d is the deposition velocity of a target gas-phase species in m s^{-1} , the Ra is the aerodynamic transport term in s m^{-1} , u is the wind speed (m s^{-1}), k is the Von Karman constant, z is the altitude AGL in m, z_0 is the surface roughness length in m, R_b is the molecular diffusion resistance term in s cm^{-1} , D is the molecular diffusivity of a target gas in $\text{m}^2 \text{s}^{-1}$, γ is the unitless uptake coefficient, $\bar{C}$ is the average molecular speed of a target gas in m s^{-1} , R is the universal gas constant in $\text{J K}^{-1} \text{mol}^{-1}$, T is ambient temperature in K, π is a constant defined by the ratio of a circle's circumference to its diameter, and M is the molar mass of a target gas in mol g^{-1} .

In this study, both the vertical mixing and the chemistry are crucial parameters that must be accounted in order to properly model the chemistry of any gas-phase species that follows a negative gradient vertical profile and is driven by heterogeneous surface chemistry, like that for HONO.

1.4. Environmental Significance and Chemical Properties of HONO:

Nitrous acid (HONO) is well known to be a dominant reservoir of hydroxyl radicals ($\text{OH}\bullet$) and plays a vital role in initializing its production in the early morning when other processes, such as the photolysis of formaldehyde and ozone are limited (Young et al., 2012; Winer and Biermann., 1994; Harrison et al. 1996; Alicke et al., 2002). Given that $\text{OH}\bullet$ are the primary oxidants in the atmosphere, they can produce SOA and O_3 through VOC oxidation, can convert polycyclic aromatic hydrocarbons (PAH) into more toxic compounds, and yield photochemical pollutants (i.e. nitrates and sulphates) that are responsible for smog formation. In the early morning, it has been shown that HONO can contribute up to 64 % of the $\text{OH}\bullet$ radical budget in the summertime (Young et al., 2012) and up to 80.4 % of the $\text{OH}\bullet$ radical budget in the wintertime periods (Kim et al. 2014).

The general diurnal trend of gas-phase HONO is similar in all environments, but differs in magnitude between remote and urban sites, due to a greater availability of NO_x from anthropogenic emissions. During the night, HONO levels begin to accumulate as heterogeneous ground surface mechanisms, notably NO_2 hydrolysis dominate the production of HONO (Geyer and Stutz, 2004;

Stutz 2004). The accumulation of gas-phase HONO at night is further enhanced in the presence of a stable NBL, when vertical mixing and wind speeds are reduced (Alicke et al., 2003). During the day, the photolysis of gas-phase HONO results in a rapid loss of HONO, which decreases more rapidly with an increasing intensity of the solar flux, reaching a minimum generally by midday (**Figure 1.4**).

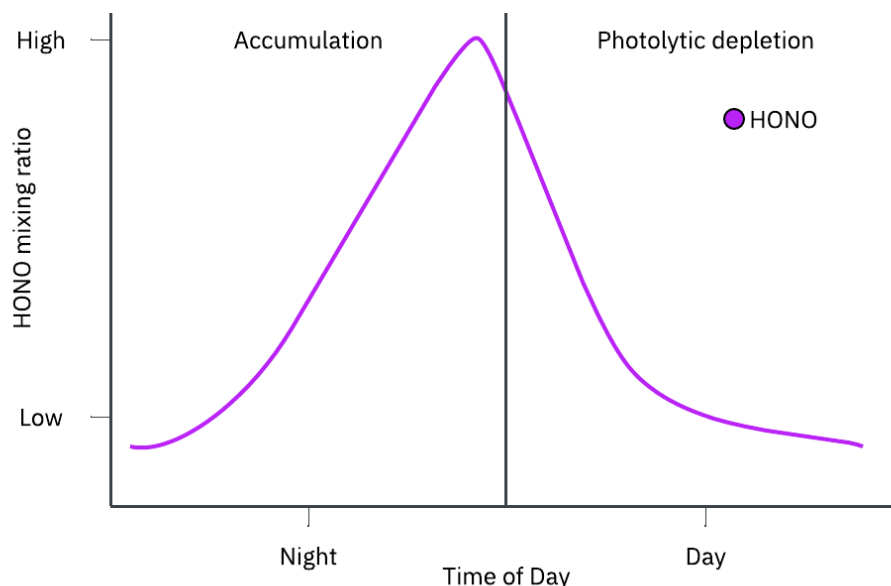


Figure 1.4. Schematic of the relative diurnal trend of gas-phase HONO (purple), where mixing ratios of HONO accumulates during the night and are depleted during the day due to photolysis. The black vertical line is placed to represent the contrast in HONO chemistry during the day and night.

Since HONO is a semi-volatile solute ($pK_a = 3.5$ at 298 K), it can dissociate to form nitrite (NO_2^-) and H^+ in the presence of condensed water (i.e. aerosols, fog droplet, or dew on the ground surface). The effective partitioning coefficient of HONO at the surface for release back to the gas phase is a product of its Henry's law constant ($K_H = 48.636 \text{ M atm}^{-1}$ at 298 K) the acid dissociation constant ($K_a = 5.62 \times 10^{-4}$ at 298 K), and the concentration of dissolved HONO, as a function of pH (**Equation 1.14**) (Sander, 1999; Wentworth et al., 2016). It has therefore been demonstrated that the pH of a bulk water solution governs the effective partitioning coefficient of HONO, such that

at higher pH there is a greater capacity for the water body to act as a reservoir (Sörgel et al., 2011; Ren et al., 2020; Su et al., 2011)

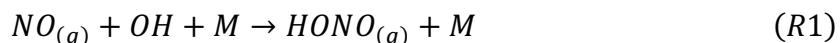
$$K_H^{Eff} = \frac{K_a \cdot K_H}{[H^+]} \quad (Eq. 1.14)$$

The daytime homogenous gas-phase mechanisms of HONO have been studied extensively and include the formation of HONO by OH and NO (R3; $k = 7.4 \times 10^{-12} \text{ s}^{-1}$; Anderson and Kauffman, 1972), the photolysis of HONO (R1; $j_{\text{HONO}} = 1.7 \times 10^{-3} \text{ s}^{-1}$; Leigh et al., 2016), and the loss of HONO by OH (R2; $k = 6.9 \times 10^{-12}$; Burkholder et al., 1992). Between these three mechanisms, a theoretical Photostationary state (PSS) is established during the daytime, with estimated HONO mixing ratios in the 10 pptv to 1000 pptv range in remote rural (Acker et al., 2006; Kleffmann et al., 2005; Ren et al., 2010; Su et al., 2008; Zhou et al., 2003) and polluted urban (Elshorbany et al., 2012; Wong et al., 2012; Tuite et al., 2021; Yu et al., 2009) environments, respectively. When compared to daytime field observations of HONO, mixing ratios have been routinely found much higher than the theoretical PSS, reaching up to 100 pptv/hr to over 1000 pptv/hr in rural and urban environments, respectively. This discrepancy between daytime observations of HONO and gas phase chemistry suggests a missing source of HONO in the atmosphere (Leigh et al., 2016). Numerous heterogeneous mechanisms have been proposed to explain the discrepancy between daytime observations of HONO and gas phase chemistry including the hydrolysis of NO_2 on surface adsorbed water (Finlayson-Pitts et al., 2003), uptake and release from fog water or dew (Ren et al., 2020; He et al., 2006), soil emissions (Su et al., 2011; Wu et al., 2019), displacement of surface nitrite by strong atmospheric acids (i.e. HCl and HNO_3) (VandenBoer et al., 2014; VandenBoer et al., 2015), and the photolysis of surface adsorbed HNO_3 on aerosol and ground surface (Zhou et al., 2002). After five decades of research, the parameterization of heterogeneous mechanisms of HONO under real atmospheric conditions is still not well understood, especially during winter periods (VandenBoer et al., 2013). To this date, the characterization of heterogeneous surface mechanisms of HONO under real atmospheric conditions is still an active area of research in the field of atmospheric chemistry.

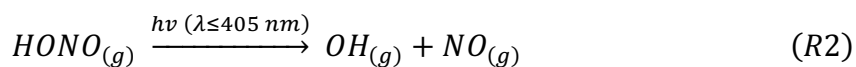
1.5. Known Sources and Sinks of HONO:

The direct emissions of HONO can arise from vehicle emissions, biomass burning, and biogenic sources. A tunnel study by Kurtenbach et al (2001) in Wuppertal, Germany, showed that the fraction of HONO/NO_x varied between 0.003 and 0.008, depending on the gasoline or diesel-based engine, and traffic density. From Kramer et al. (2020), another tunnel study situated in Birmingham, England was motivated by the use of newer technologies that reduced vehicle emissions, especially in diesel-based goods vehicles (i.e. delivery trucks), which have a greater overall impact on the vehicle emission of HONO. In this tunnel study, it was reported that the average emission ratio of HONO/NO_x over the course of the measurement period was found to be 0.0085, varying from 0.0072 to 0.101 between the morning and evening, respectively. The FIREX Fire Lab study in 2016 involved 75 controlled laboratory burns from biomass fuels (i.e. coniferous and chaparral) that are commonly found in the western North American wildfires. Roberts et al. (2020) reported total reactive nitrogen during the 2016 Fire Lab study and found that HONO emissions contributed on average 4.5 % to the total reactive nitrogen budget and was emitted by both flaming or smoldering combustion events. This suggests that biomass-burning plumes may play an important role as a direct emission of HONO. During the Western Wildfire Experiment for Cloud Chemistry, Aerosol Absorption, and Nitrogen (WE-CAN) campaign, aircraft measurements sampled smoke from 23 wildfires across the Western U.S during the summer of 2018. In a study by Lindaas et al. (2020) during the WE-CAN campaign, it was determined that reactive nitrogen species with the largest emission transect enhancements occurred for gas-phase HONO, NO₂, and NH₃, suggesting that biomass emissions are a direct source of gas-phase HONO in the atmosphere. Among biogenic sources of HONO, it has been shown in laboratory studies that soil nitrite can be formed through intermediary processes, including nitrite reduction and microbial ammonia oxidation, which can then be added to the pool of ground surface nitrite that can volatilize back into the atmosphere as gas-phase HONO (Su et al., 2011). Laboratory chamber studies have measured the emission fluxes of HONO in agricultural soil (Wu et al., 2019), biocrusts (Weber et al., 2015), and grasslands (Bhattarai et al., 2019) to estimate real-world fluxes of HONO and have found a dependency to soil water content (SWC), where the peak in HONO fluxes occurred when the water holding capacity of the soil $\leq 20\%$ (Oswald et al., 2013). In reality, the emission fluxes of HONO are different between real-world and laboratory conditions, given that deposition velocities of HONO are influenced by different factors.

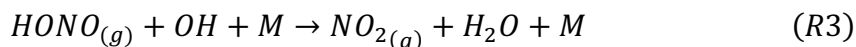
The chemical mechanisms governing the sources and sinks of HONO can be categorized into daytime and nighttime processes (**Figure 1.5**). During the day, the only known homogenous gas-phase source of HONO is the pressure-dependent third-body reaction of NO with OH (R1), with a rate constant of $7.4 \times 10^{-12} \text{ s}^{-1} \text{ s}$ at SATP. Another mechanism that has been proposed from laboratory studies is the reaction of photosensitive NO₂ with water vapour, which was found to be negligible in real atmospheric conditions because it is a two photon process (Wu and Chen, 2012).



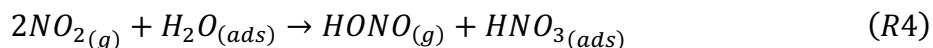
The dominant loss process during the day is the photolysis of HONO (R2) in the gas phase, which occurs at relatively long wavelengths, extending from 405 nm and lower. The photolysis of HONO is the most important early morning precursor of surface OH• in urban environments and also contributes to the NO_x cycle in the form of NO (**Figure 1.3**).



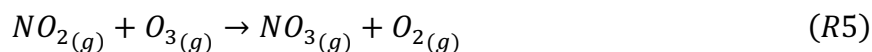
Throughout the day, as the production of OH continues from other sources, a gas-phase loss of HONO can become meaningful through the oxidation of HONO with OH (R3), which is a pressure-dependent third body (M = N₂ + O₂) reaction, where with the loss rate of HONO much smaller than that of R2 (Jenkin and Cox, 1987).



Several laboratory studies have identified alternative daytime reaction pathways for HONO production by reacting NO₂ on photoexcited aerosol surfaces such as soot, humic acid, and TiO₂ (i.e. paint pigment). However, the characterization of these reactions in real atmospheric observations have been proven to be challenging (Aubin and Abbatt, 2007; Stemmler et al., 2006; Monge et al., 2010; El zein et al., 2012; Sörgel et al., 2011).



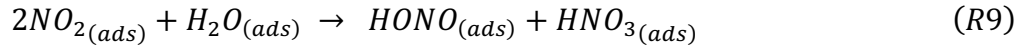
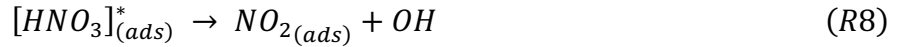
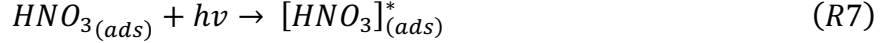
During nighttime at lower temperatures and at high NO_x, a potential sink for NO₂ could be the reaction with O₃ to form the nitrate radical (NO₃), where an equilibrium favours dinitrogen pentaoxide (N₂O₅) under lower temperatures and at high NO_x (R5-R6) (Brown and Stutz, 2012; Platt et al., 1980a, 1980b; VandenBoer et al., 2013). Given that the nocturnal production of HONO is mainly dictated by ground uptake of NO₂, a potential nocturnal sink for NO₂ in R5-R6 results in less gas-phase HONO production from NO₂.



Recent studies have shown that the calculated HONO formation rate required to sustain a PSS HONO mixing ratio in the day (i.e. minimum daily mixing ratio of HONO) far exceeds the observed gas-phase source rate of HONO and the heterogenous uptake of NO₂ on aerosol and ground surfaces, with the calculated HONO formation rate ranging from 100 pptv per hour to over 1000 pptv per hour. Given that homogenous gas-phase mechanisms of HONO have been studied extensively and a missing source(s) of HONO still exists, studies have postulated that contribution from heterogeneous sources of HONO to the daytime production of HONO are significantly greater than homogeneous sources.

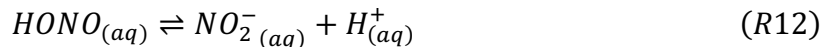
A daytime heterogeneous source of HONO can be the photolysis of surface adsorbed and/or particulate nitrate (R7- R10), where adsorbed HONO at the surface can desorb in R10 to yield gas-phase HONO under low mixing ratios of NO_x (NO₂ + NO). It has been shown that the

photolysis rate coefficient of surface adsorbed HNO_3 can be as much as 45 times greater than that of gas-phase HNO_3 , permitting the photolysis rate of adsorbed HNO_3 to occur 1-4 orders of magnitude greater than gas-phase photolysis of HNO_3 (Karamchandani et al., 2014; Baergen and Donaldson, 2013; Ye et al., 2016; Zhou et al., 2003).

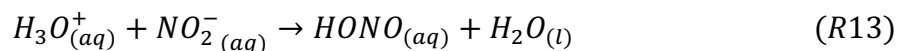


Given that HONO is also a water-soluble weak acid, its gaseous concentration can be influenced by uptake to bulk water. This is often a nocturnal heterogeneous sink governed by meteorological conditions and surface chemical properties. It has been shown in both laboratory and observational studies that the formation of dew can act as a nocturnal reservoir for HONO in both urban (Ren et al., 2020) and rural sites (He et al., 2006). Field measurements of gas-phase HONO using a canopy surface revealed that mixing ratios of HONO increased significantly during the day when dew formation was observed on the canopy surface during the night (He et al., 2006). The nocturnal uptake of HONO can be defined by the adsorption of gas-phase HONO into bulk water on the ground surface or canopy (R11) and the acid dissociation of HONO into nitrite and hydronium ion (R12). At sunrise, when the temperature at a given surface increases as a result of terrestrial radiation, evaporation of dew is likely to begin, at which point nitrite can be released back into gas-phase HONO upon protonation through these dynamic equilibria (**Figure 1.5**).





Recent studies have shown that the role of the ground surface is an important nocturnal sink of gas-phase HONO, which can form a reservoir in the form of nitrite (NO_2^-) that has the potential to be emitted back into gas-phase HONO during the day (Donaldson et al., 2014; VandenBoer et al., 2013). With the deposition velocity of strong atmospheric acids such as HNO_3 and HCl reaching a maximum by midday, VandenBoer et al. (2014), suggested that the nitrite reservoir can be displaced by these atmospheric acids and revert back to gas-phase HONO, accounting up to 30 % of the daytime gas-phase HONO source in Bakersfield, California (R13,R14).



Vertical profile studies of HONO and NO_2 have shown that when comparing ground versus aerosol surfaces, ground surfaces are the dominant source of HONO from the heterogeneous uptake of NO_2 on the ground and a nocturnal sink of HONO by dry deposition. (Villena et al., 2011; Zhang et al., 2009; Wong et al., 2011; VandenBoer et al., 2013). From these studies, vertical gradients of HONO and NO_2 during the night were observed to increase in concentration at the surface, with the production of HONO increasing as gas-phase NO_2 builds up in the absence of photolysis within a lower BL, resulted in dry deposition and chemical transformation of NO_2 (Villena et al., 2011; Zhang et al., 2009; Wong et al., 2011; VandenBoer et al., 2013). Given that vertical turbulent mixing via the aerodynamic resistance term has a significant impact on transport of gas-phase HONO and NO_2 near the surface, the change in aerosol surface area over volume ratio (S/V) over the course of the day should be considered. The S/V decreases during the day as the height of the PBL increases, while during the night, the S/V increases during the night when the PBL is at its minimum (Sörgel et al., 2011). Aerosols can also be found above the PBL (i.e. free troposphere) but are most concentrated within the PBL, as they are emitted from surface emissions. Vertically-resolved measurements from the NACHTT campaign revealed that the surface area of the ground surface (i.e. $6700 \mu m^2 cm^{-3}$ in a 150 m NBL) was more than an order of magnitude greater than

the surface area of aerosols (i.e. $146 \mu\text{m}^2\text{cm}^{-3}$). To evaluate the importance of uptake to ground or aerosols surfaces on HONO production, the reported NO_2 uptake coefficients gathered from modelling studies (Wong et al., 2011), field measurements (VandenBoer et al., 2013), and laboratory studies (Broske et al., 2003, Kleffmann et al., 1998) were found to small ranging between 10^{-6} and 10^{-5} . Assuming that these reported literature values are true, VandenBoer et al. (2013) stated that in order to force the production of HONO to arise only from aerosol surfaces, the estimated uptake coefficient of NO_2 would have to be in the range of $1.7 \times 10^{-4} - 8 \times 10^{-4}$ to explain the observed variability between vertical profile measurements, which ranges from a factor of 12 to 875 greater than those reported in literature. This suggests that the ground surface dominates the production of HONO over aerosols and that more attention should be placed to study the production of HONO from ground surface heterogeneous processes.

1.6. NACHTT campaign:

Given the importance of the ground surface as a reservoir for gas-phase HONO, identifying the missing source of HONO in the atmosphere requires an explicit understanding of the evolution of the vertical structure of HONO near the ground surface, a characterization of the boundary layer height, and defined meteorological profiles, which until recently were not attainable as high-resolution vertically-resolved studies were limited (Kleffmann et al., 2003; Tuite et al., 2021; Wong et al., 2011; Cesler-Maloney et al., 2024). In this thesis, the 1D model framework is based on measurements made in the 2011 Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) campaign, which took place from 2011-02-15 to 2011-03-15 at the Boulder Atmospheric Observatory (BAO) – a rural field site in Erie, Colorado (40.050 N, 105.040 W, 1500 m) (Brown et al., 2013). The BAO tower was first established in 1977 by NOAA, NCAR, and CIRES; its purpose was to first monitor the real-time vertical distribution of meteorological variables, specifically within the boundary layer and has since hosted several large international and national scale campaigns with over 2500 publications since 2005. A unique feature of the 2011 NACHTT campaign at BAO is the rare use of high-resolution vertically resolved measurements mounted on a 300 m steel tower to study the vertical distribution of reactive gas-phase species, particulates, and micrometeorology near the ground surface (**Figure 1.6**). A description of all the instruments, methodology, and time resolution used during the NACHTT campaign and for this thesis has been tabulated in Table 1.1. From

VandenBoer et al. (2013), it was found that on nights where a NBL was identified during the NACHTT campaign, there was an enhancement in the production of gas-phase HONO, with maximum mixing ratios reaching greater than 1000 pptv. This showcased the formation of a stable NBL is a critical factor that influences the time course of the nighttime chemistry of HONO. The variation in HONO production between nights where a NBL was observed was attributed to differences in NO₂ emissions, the stability of the atmosphere affecting the depth of the NBL and the ASL, and RH near the ground surface. To reconcile the observations of HONO during the NACHTT campaign, a 0D box model framework was developed using observational constraints that accounted for gas-phase chemistry of HONO, the heterogeneous production of HONO via NO₂ hydrolysis, and loss by dry deposition. When heterogeneous processes included an RH-dependent factor that was multiplied by the uptake coefficients of NO₂ and HONO in the production of HONO via NO₂ hydrolysis (RH/50) and dry deposition (RH/20), the 0D box model was able to reproduce the nighttime observations to within 30 %, with the greatest unknown source rate of HONO occurring during the early morning periods of the NACHTT campaign (5 accounts). The high-time and high-vertical resolution measurements of gas-phase species, aerosols and particulates, and meteorology allows a unique opportunity to develop a 1D model framework from a bottom-up approach and include surface source parametrizations already employed in the previous 0D box model study to highlight the role of a dynamic vertical transport term on setting the correct vertical distribution of HONO throughout the NACHTT campaign.

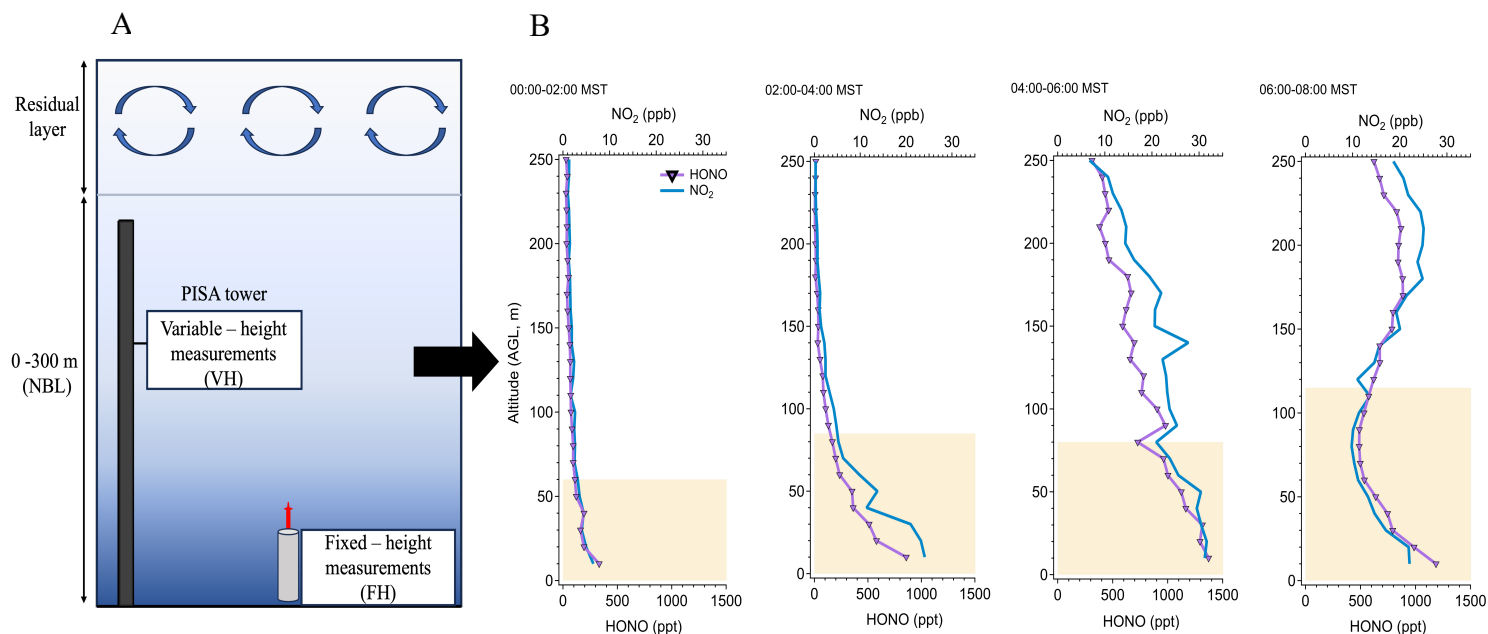


Figure 1.6. (A) Schematic of the layout of the NACHTT campaign featuring a vertical tower that extends up to 300 m and the Portable Instrument Shelter with Amentities (PISA) that houses all the instruments that were measured at a variable height (VH). On the ground surface, there is also a set of measurements that were made at a fixed height (FH), including a ceilometer (shown in the grey cylinder), which was not part of the NACHTT campaign. The blue background gradient represents the vertical stratification of negative gradient gas-phase species like HONO and NO_2 , where concentrations increase near the ground surface. A complete description of the instruments used has been tabulated in Table 1.1). (B) The high-resolution vertically-resolved measurements of gas-phase species and meteorology made during the NACHTT campaign between 0-250 m AGL, which allowed us to visualize the evolution in vertical gradients of HONO (purple line) and NO_2 (blue line) within the ASL (yellow shaded) in two hour bins over the course of the night (00:00-08:00 MST). For this series of plots, the vertically-resolved measurements of gas-phase HONO (lower x-axis; ppt) and NO_2 (upper x-axis; ppbv) were gathered during February 19th, 2011.

Table 1.1. Instrumentation used during the NACHTT campaign (Brown et al., 2013).

<i>Variable height (VH) measurements from the 2011 NACHTT campaign</i>			
Measurement	Method	Time resolution	Height resolution (m)
Meteorology	Weather Station on carriage	1 min	10 – 250
HONO, HNO ₃ , HCl, organic Acids	Chemical Ionization Mass spectrometer using acetate ion (CIMS)	0.1 Hz	10 – 250
NO ₂ , NO, NO ₃ , O ₃ , N ₂ O ₅	Cavity Ring-Down Spectrometer (CRDS)	0.1 Hz	10 – 250
Aerosol number and surface area	Ultra-high sensitivity Aerosol Spectrometer (UHSAS)	1 sec	10 – 250
<i>Fixed Sampling Platform at 10 m from the 2011 NACHTT campaign</i>			
VOCs (8 species)	Proton Transfer Reaction Mass spectrometry (PTR-MS)	1 Hz	10
VOCs (15 species)	Gas cannister retrieval Gas Chromatography Mass Spectrometry (GCMS)	1 hour	10
Photolysis rate coefficients (jO ₃ , jNO ₂ , jNO ₃)	Radiometer	1 min	10
Meteorology	Weather station fixed	1 min	10, 100, 300
<i>Auxiliary Observations from the BAO Tower</i>			
Ceilometer	Light Detection and Radar (LIDAR)	1 Hz	1

1.7. 1D Box Modelling:

One of the three main pillars in atmospheric chemistry is the realm of atmospheric box modelling, where the selection of the dimensionality of the box model (i.e. 0D, 1D, or 3D) and resolution depend on the research question at hand and its suitability to the input dataset (**Figure 1.7**). The simplest form of box modelling is zero-dimensional box modelling, where a single well-mixed box is represented as a point space, represented by any volume of air from 1 cm³ to the entire atmosphere.

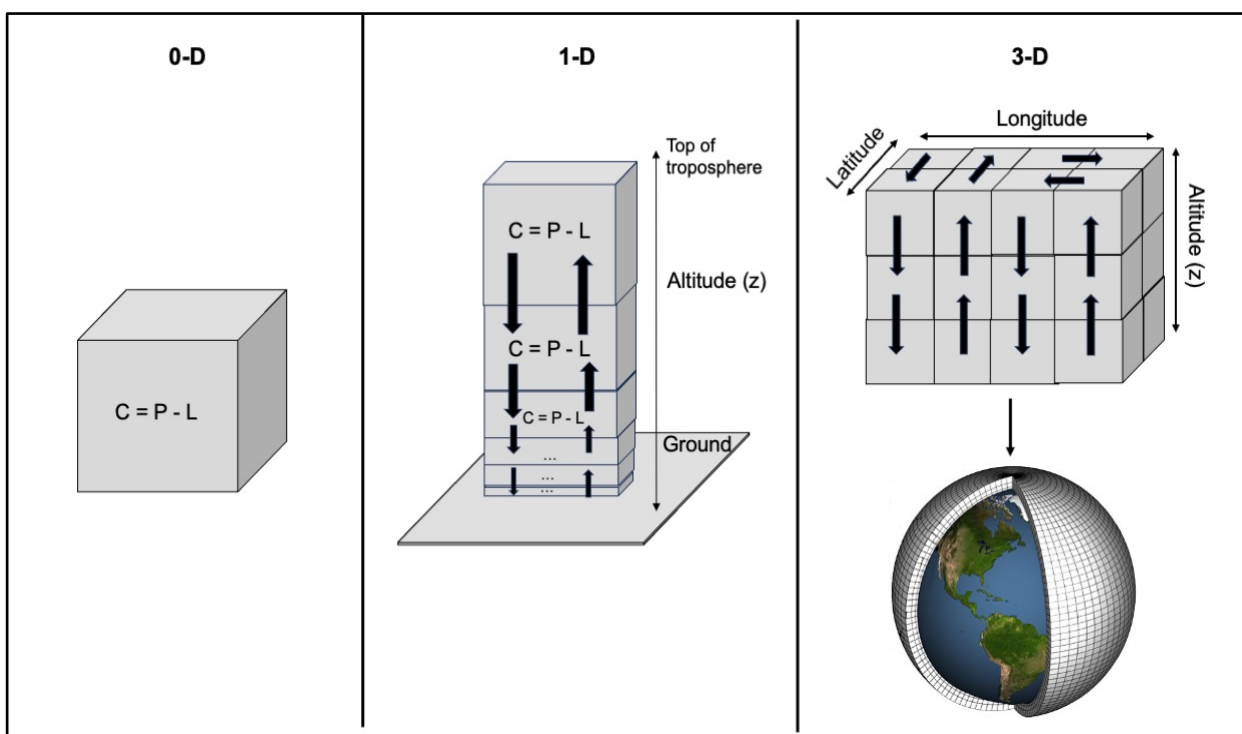


Figure 1.7. Schematic of various atmospheric models with their dimensionalities represented, including zero-dimensional point source model (left panel), one-dimensional mixing and transport model (middle panel), and three-dimensional global transport model (right panel). The black arrows in 1D and 3D modelling schematics represent mixing between box levels in the form of vertical diffusion and horizontal advection (for 3D models only). Chemistry (C) can be represented explicitly in 0D and 1D models as the sum of chemical production (P) minus the sum of chemical loss (L; includes dry deposition). The final 3D model represented as a globe was adapted from Kotamarthi et al. (2021).

With this constraint, a 0D box model can only study the temporal changes in the mixing ratios of target gas-phase species (i.e. HONO) by ignoring the vertical diffusion mixing term using a simple

PBL parametrization method that dilutes the box contents by simulating changes in box dimensions as a function of time. For example, many HONO models are 0D and use increases monotonically from morning to noon that reflect average meteorology and keeps the NBL constant during the night (VandenBoer et al., 2013). It has been shown in field and modelling studies that the formation of a stable NBL is a critical factor to be considered for studying the nighttime chemistry of HONO (Geyer and Stutz, 2004; Kleffmann, 2007; Tuite et al., 2021; Wong et al., 2013). In a 1D box model, a series of boxes are vertically stacked upon one another from the ground surface to a defined vertical height, where the vertical resolution of each box increases (i.e. depth of the box decreases) as we approach the lowest box level. The dimensions of a 1D box model are generally defined in the microscale, with horizontal resolution from a few meters up to a kilometer (Wiersema, 2019). Unlike 0D modelling, where the chemistry of HONO is represented in a single box and physics parametrizations are simplified, the significance of 1D modelling lies in the utilization of complex numerical solving methods that account for both physical and chemical parameterizations to be derived from in-field observations, other models, or from representative theory (**Figure 1.7**). In a 3D global transport model, the dimensions of each box is defined in the mesoscale, with coarse grid typically ranging in resolution from one kilometer up to ten kilometers. Each coarse grid is coupled with a vertical gradient component that when connected represents a regional land mass or the entire globe, where horizontal advection is accounted for in the model. Given that mesoscale simulations are often used to resolve large-scale meteorological effects and understand the long range transport of air pollutants, they are unable to resolve micrometeorological effects and chemical transformations on local time scales. A study by Zhang et al (2023), showed that parametrizations of HONO chemistry were misrepresented in WRF-Chem, which results in a lack of understanding of haze pollution events due to underestimations in the production of OH. Global and regional 3D Chemical Transport Models (CTMs) such as WRF-CHEM and CMAQ have yet to update the dry deposition scheme of NO₂ to account for the heterogeneous uptake of NO₂ on ground surfaces. This underestimates the deposition velocity of NO₂ at night when the influence from the aerodynamic transport term is greatest, resulting in the misrepresentation of vertical chemistry of nighttime HONO (Boys et al. 2024; Stelle et al., 2013). To better understand how to explicitly parametrize the individual processes pertaining to the loss and production of HONO, we have to first understand where the missing daytime source of HONO is arising from at the microscale using a 1D box model. The

purpose of this study was to parametrize the known nocturnal ground surface sources and sinks of HONO by accounting for vertical diffusion mixing to explain the missing daytime source of gas-phase HONO, which makes 1D box modelling an ideal framework for this study (Wong et al., 2013; VandenBoer et al., 2013; Tuite et al., 2021; Geyer and Stutz, 2004, 2010). Given the challenge of measuring high-resolution vertical profiles of a suite of relevant gas-phase species and meteorology, there have been limited large-scale campaigns conducted to generate an observational dataset for 1D modelling and vertical transport related to HONO production and loss (Tuite et al., 2021; Kleffmann et al., 2003; VandenBoer et al., 2013; Wong et al., 2011; Cesler-Maloney et al., 2024; Villena et al., 2011). In this thesis, we utilized the Platform for Atmospheric Chemistry and vertical Transport in One Dimension (PACT-1D) model, which has incorporated a new module to study the chemistry of HONO on the ground surface, run using constraints from vertically resolved observations from the NACHTT-11 campaign in Erie, CO. A full description of the PACT-1D model and its components will be discussed in Chapter 2 but briefly, a unique feature of the PACT-1D model is the addition of a ground surface storage term, in which gas-phase species can be stored in the lowest box level (i.e. an infinitesimal layer) upon molecular collision with the ground surface via a prescribed ground uptake coefficient and calculated deposition velocity (Ahmed et al., 2022; Tuite et al., 2021). This makes the PACT-1D model paired with the unique NACHTT dataset an ideal framework to comprehensively study formation and loss processes of HONO throughout the atmospheric surface layer via the ground surface by coupling heterogeneous parameterizations of known processes of HONO with an explicit vertical diffusion and mixing term. A recent study by Tuite et al. (2021) analyzed coarsely resolved (33 – 556 m intervals) vertical profiles of HONO in an urban center in Pasadena, California and utilized a PACT-1D model to test whether parametrizations of HONO surface production terms resulted in better agreement with observations during the CalNex campaign during the summer of 2010. Their model run was found to be in good agreement with observations for target species including HONO, NO_x , and O_3 , especially when ground surface source routines of HONO were implemented into the model, including: the photolysis of surface HNO_3 , the daytime photo-enhanced conversion of NO_2 , the hydrolysis of NO_2 , soil emissions of NO represented as biogenic emissions of HONO, and the nocturnal uptake of HONO to form nitrite followed by acid displacement with a strong acid such as HNO_3 or HCl (Tuite et al., 2021).

Until recently, there have been limited 1D modelling studies of HONO based on rural measurements during the winter than in the summer, given there is much less OH• radicals produced from photochemical precursors of OH• due to the lower intensity of sunlight. To our knowledge, this will be the first study to incorporate vertically-resolved measurements of HONO from a rural site during the winter into a 1D model framework, which would allow us to better understand heterogeneous parameterization of HONO during colder conditions.

1.8. Objectives/Aims:

We developed a 1D model that takes into account vertical diffusion mixing, regional meteorology, and all individual processes pertaining to the loss and production of HONO, with an emphasis on validating the physics component of the 1D model (i.e. vertical mixing and meteorology), which are described in chapter two. In chapter three, I explored the vertical distribution of reactive nitrogen species (N_r), Ozone, meteorological variables (temperature, pressure, and RH), as well as ground-level VOCs observed during the NACHTT campaign to select a 48-hour timeframe that was used to initialize the 1D model. This selected timeframe will henceforth be defined as **Model Period (MP)**, which was chosen using a selection criteria that were based on the following constraints in order of increasing importance: 1) Elevated nighttime mixing ratios of HONO (≥ 1 ppbv), 2) evidence for the formation of a stable nocturnal boundary layer, 3) data availability with all instruments and 4) wind speed near the ground ≤ 6 m/s.

In this modelling study, there was a great effort to ensure that the physics parametrizations, including the vertical diffusion mixing and meteorological profiles of the PACT-1D model, were reflective of the BAO measurement site during the NACHTT campaign. Given the importance of the ground surface as a dominant source of HONO, the physics parametrizations were constrained to permit the diffusion of gas-phase species to the ground surface. We first validated the physics parametrizations by assessing whether the modelled meteorological profiles are in agreement with vertically-resolved observations of temperature, pressure, and relative humidity from the BAO tower. All the other components of the PACT-1D in the BASE model configuration (see section 2, Chapter 2 for a full description of model initialization), including the photolysis rate coefficients, initial vertical profiles of gas-phase species, observationally constrained emissions, surface source

processes of HONO, and relevant tropospheric mechanisms, rate constants, and quantum yields from the **Regional Atmospheric Chemistry Model Version 2** (RACM2) were defined and initialized.

In Chapter 4, The validated physics parametrizations were employed in the BASE model and we compared the modelled vertical profiles of 20 gas-phase species, including N_r species, VOCs, and O_3 with observations during the MP of the NACHTT campaign to assess the predictability of the BASE model. we produced three model outputs with PACT-1D, each employed with unique heterogeneous HONO ground surface source routines (or lack thereof) to further explore the importance of the ground as the dominant source of HONO and the role of vertical diffusion mixing on the removal and enhancement of HONO during the 48-hour MP. These heterogeneous ground surface parametrizations include 1) Turning off the ground surface source routines (i.e. NO_GSS), 2) The production of gas-phase HONO from the conversion of NO_2 on surface adsorbed water and loss of HONO from dry deposition (i.e. BASE), and 3) Similar to the BASE model, except with an RH-dependent ground reactive uptake coefficient applied to HONO and NO_2 using observationally-constrained measurements from the NACHTT campaign (i.e. BASE_WET), developed by VandenBoer et al (2013). The purpose of this chapter was to investigate the chemical dynamics of currently known heterogeneous mechanisms and their relative contributions to the diurnal variability of HONO. Furthermore, we aim to explore whether the inclusion of an RH-dependent surface parameter, integrated into a 1D model framework, could result in better agreement with observations from NACHTT when compared to a 0D model framework.

Chapter II: The Platform for Atmospheric Chemistry and vertical Transport in One Dimension Model (PACT-1D Model)

Abstract:

In this chapter, the PACT-1D model and the parametrization method for each component, including the vertical dimensions of the box model and integration timestep, the vertical diffusion mixing profile, the vertical meteorological profiles, the emissions term, the photolysis rate coefficients, the initial concentrations and chemistry are defined explicitly. Before the heterogeneous ground surface processes of HONO can be explored with this model, a great deal of validation has been conducted with the physics parametrizations of the PACT-1D model, which is a critical step in constraining the chemistry and ensuring that the atmospheric conditions in the model are representative of the measurement location at the BAO tower in Boulder, Colorado.

2.1. 1D Model Description (PACT-1D):

The Platform for Atmospheric Chemistry and vertical Transport in One Dimension (PACT-1D) is based on an Eulerian mass balance framework, where a series of interconnected boxes are stacked vertically, and the volume of each box is spatially fixed (**Figure 2.1**). To account for the law of conservation of mass with an Eulerian framework (i.e. stationary 1D model), the change in concentration in each box should be defined as the sum of all sources of a molecule, from which the sum of all sinks is subtracted, where the general 1D differential equation used to describe how 1D models solve chemical composition can be represented using **Equation 2.1**.

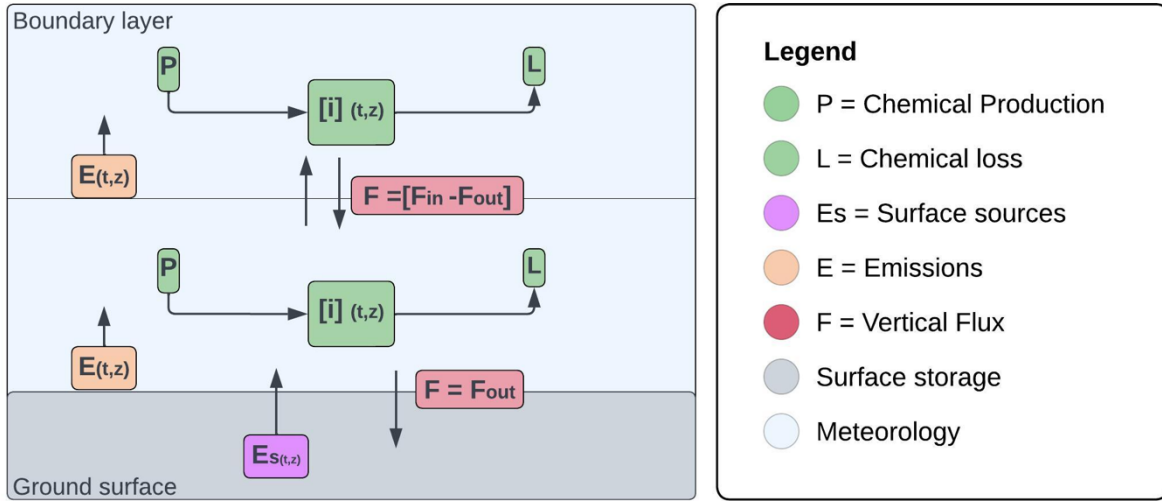


Figure 2.1. Schematic of the lowest two boxes of the PACT-1D model between the ground surface and the boundary layer representing various terms from the general 1D differential equation, including the chemical production and loss (green) terms, the vertical flux term (red), the ground surface storage term (grey), the emissions (brown), and surface sources (purple). Meteorology (blue) influences each term but is not incorporated into the 1D general differential equation.

$$\frac{dC}{dt}(i, t, z) = P_{(i,t,z)} - L_{(i,t,z)} + F_{(i,t,z)} + E_{(i,t,z)} \quad (Eq. 2.1)$$

where dC/dt is the change in concentration of a gas-phase species, P is the chemical production term, L is the chemical loss term, F is the flux term, and E is the emission term all as a function of height (z), time (t) for each chemical species (i) considered in the chemistry framework.

Based on the computational layout of the PACT-1D model shown in **Figure 2.2**, several components must be initialized and fall under physics or chemistry parametrizations. The physics parameterizations must be defined for the entire duration of the model run and include the vertical dimensions of the box model, meteorology (i.e. vertical profiles of ambient temperature, RH, and pressure), vertical transport (i.e. eddy diffusion coefficient, K_z), and photolysis rate coefficients.

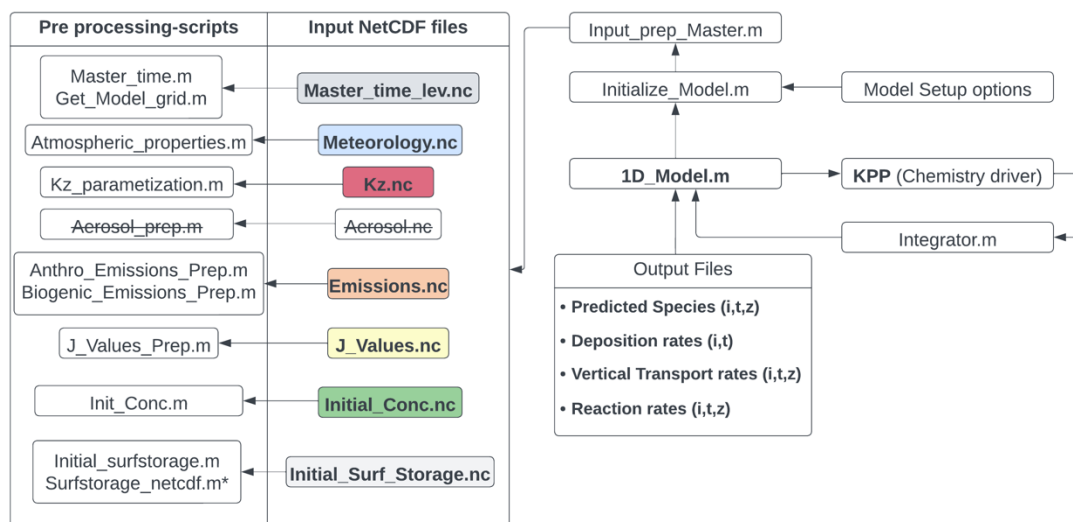


Figure 2.2. The computational layout of the PACT-1D model, where the pre-processing scripts, input files, the 1D model, and the output files are shown in sequence with each arrowhead directed to a prerequisite script that is required to run the 1D model. During the pre-processing stage, data from in-situ measurements or parameterizations based on observations will be imported, cleaned, and converted to input NetCDF files, where each row represents a component of the 1D model. After initialization of the NetCDF files (i.e. Initialize_model.m), the model setup options define the integrated timestep, the internal chemistry timestep (i.e. KPP timestep), and the number of vertical diffusion timesteps per chemistry timestep. The 1D model then communicates alongside KPP (i.e. the chemistry integrator) at a defined rate and the time evolution, deposition rates, and vertical transport rates of all species are defined in the output NetCDF file.

In contrast, the chemistry parameterizations only include the initial concentrations of species at the lowest box level (i.e. $t = 0$), where it is the combination of **K**inetic **P**re **P**rocessor (KPP; a chemical integration software that solves the chemical production and loss terms of the general 1D equation), the physics parameterizations, and ground-level emission rates that drive the predicting power of the PACT-1D. A unique feature of the PACT-1D model for this study is that the emissions ($E_{(t,z)}$) term were derived explicitly using observational constraints, which allowed horizontal advection to be accounted for near the surface (**Figure 2.1**). This is the first PACT-1D study to incorporate an observationally-constrained emissions term, which was an important

requirement to study the case studies during the NACHTT campaign with high-time resolution. An overview of the initialization period for each component of PACT-1D relative to the 48-hour **Model Period (MP)** can be illustrated in **Figure 2.3**, where MP1 (February 18th to February 19th, 2011, 17:00-17:00 MST) and MP2 (February 19th to February 20th, 2011, 17:00-17:00 MST) can be classified as the first and second day of the MP, respectively (Tuite et al., 2021).

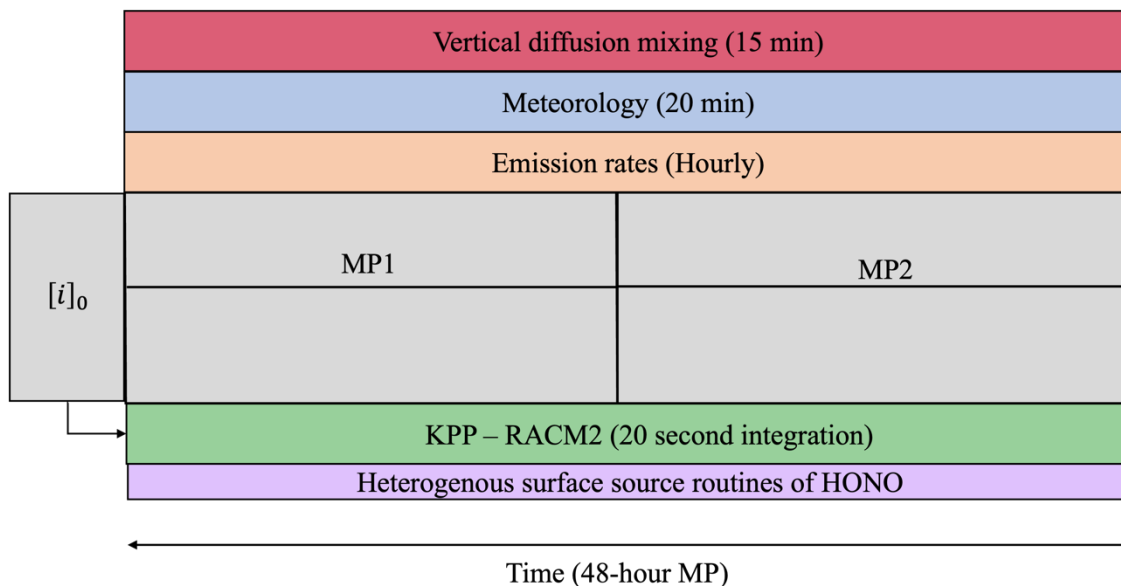


Figure 2.3. A schematic representing the initialization period of all components of the PACT-1D during the 48-hour MP is shown, where vertical diffusion mixing, meteorology, emission rates, and chemistry (composed of homogenous chemical mechanisms from KPP and heterogenous surface routines of HONO) are initialized for the entire 48-hour MP. The raw time resolution for each component of the PACT-1D model is also shown before interpolating to the 15-minute time resolution for PACT-1D inputs. The only component of PACT-1D that is initialized at the start of the 48-hour MP ($t=0$) is the initial concentration of all defined gas-phase species, which is imported into KPP upon integration of the PACT-1D model.

All data processing was performed in MATLAB, IGOR, and Linux Bash scripting in order of increasing use, where the script for the PACT-1D model and processing of matrices was run using MATLAB, data averaging and height filtering of vertically-resolved observations was executed in IGOR with macros written by Donna Sueper, Ken Aikin, and Trevor VandenBoer (i.e. GeneralMacros2022.ipf), and KPP was initialized via Linux Bash Scripting (i.e. Linux Terminal). Input processing scripts in MATLAB for all the components of the PACT-1D model were either

adapted from Ahmed et al. (2022) or custom-made to tailor to the measurements incorporated in this study. A comprehensive standard operating procedure (SOP) of the PACT-1D has been written in Appendix B to support future 1D modelers drawing on this work. The SOP highlights all the important steps from the installation guide and defines all the scripts in each component of the model through to running the final model output (**Appendix C**).

2.2. Initializing The Vertical Dimensions and Model Run Time of PACT-1D:

The vertical dimensions and model run time (i.e., start and stop time) of PACT-1D were defined in the *Master_time_lev.m* file, which is a master script that is embedded into every other component of the model and is responsible for setting the vertical resolution for all other input components of PACT-1D to be interpolated to a defined vertical grid. In the *Master_time_lev.nc* file, two variables account for vertical dimensions and differentiating between the two is important. The junction between box levels is defined as BOX_WALL, and the midpoint height between box levels is defined as BOX_CH (**Figure 2.4**). The physics parametrizations, including the vertical diffusion mixing and meteorology, will be interpolated to the vertical grid of PACT-1D using BOX_WALL, while chemistry parametrizations, including the emissions and initial concentrations of gas-phase species, will be interpolated to the vertical grid of PACT-1D using BOX_CH. This ensures that the gas-phase species inserted at the centre point of each box level have maximum time to undergo chemical and physical perturbations. For this model configuration, there are a total of 54 levels, which can be categorized into four different sections based on vertical resolution. The first nine levels are logarithmically spaced from 1×10^{-3} to 1 m and are required as a foundational characteristic of 1D models to represent the ground surface, which is rooted in both physical principles and computational efficiency. Given that the surface layer of the **Boundary Layer (BL)** experiences sharp gradients in both meteorological and chemical variables such as wind speed, temperature, and pollutant concentrations, accurately characterizing the surface layer requires higher resolution. The sharp gradients occurring near the ground surface are caused by surface friction and shear wind effects, where wind speeds decrease substantially near the ground surface due to friction (or drag), leading to a logarithmic wind profile. To accurately model these sharp gradients and allow for computational efficiency, we represent the first nine levels of the box model using logarithmic spacing. For the next 35 levels **Above Ground Level (AGL)**, a 10 m linear spacing was used to represent the observational limit of vertically-resolved measurements

from the **B**oulder **A**tmospheric **O**bservatory (BAO) tower from 1 to 250 m, followed by a linear 50 m spacing from 250 to 1000 m. The final ten levels of the model are defined by non-linear spacing from 1000 m to the upper boundary of the model at 5000 m. The model run time was defined as the 48-hour MP chosen from the **N**itrogen, **A**erosol **C**omposition, and **H**alogens on a **T**all **T**ower (NACHTT) campaign, where the start and stop times were set at 2011-02-18 17:00 MST and 2011-02-20 17:00 MST, respectively. For this model configuration, the *Master_time_lev.nc* file was defined as a matrix with 193 time and 54 vertical dimensions, where all raw input data from other components of the PACT-1D model were interpolated with respect to *Master_time_lev.nc*. This ensures that upon initialization of the PACT-1D model, all the input NetCDF files are the same size before integration of the model begins (**Figure 2.2**).

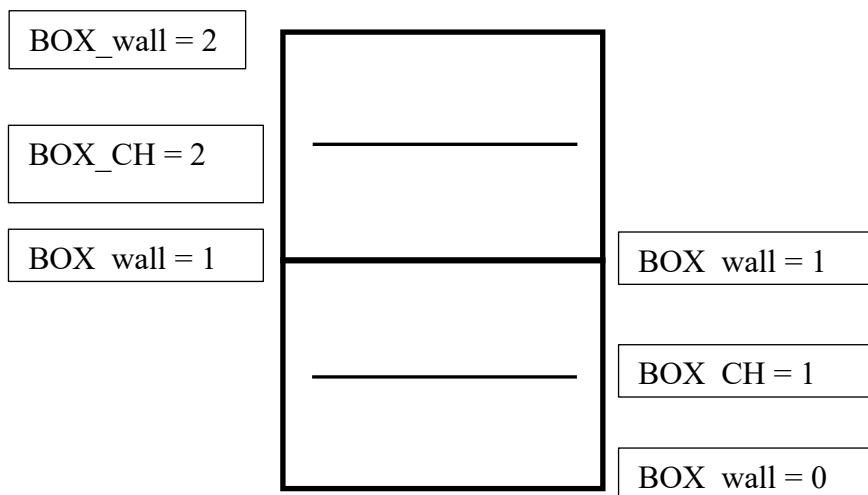


Figure 2.4. Representation of defining the height of box levels (BOX_wall) and their associated centre height (BOX_CH) in the PACT-1D model.

2.3. Initializing The Vertical Diffusion Mixing Term:

The eddy diffusion coefficient (K_z , m^2/s) is a physical term that is used to describe the vertical distribution and dispersion of gas-phase species due to turbulent mixing. To allow heterogeneous chemistry to take place on the ground surface in the model, gas-phase molecules in the open atmosphere must be allowed to diffuse through stagnant air layers to reach the ground, which can only occur if the K_z term is limited such that molecular diffusion can dominate. In the

PACT-1D model, the total diffusion profile (K_D) can be defined as the sum of eddy diffusion and molecular diffusivity for each target gas-phase species, where contributions from the eddy diffusion coefficient decreases as we approach the ground surface (**Equation 2.2**).

$$K_D(t, z) = K_z(t, z) + D(t, 1) \quad (Eq\ 2.2)$$

where K_D is the total diffusion profile as a function of time in $m^2\ s^{-1}$, K_z is the eddy diffusion coefficient profile as a function of time in $m^2\ s^{-1}$, and D is the molecular diffusivity to the ground surface in $m^2\ s^{-1}$.

Depending on the type of measurements used as input, the PACT-1D model utilizes three methods for determining the vertical profile of K_z , including deriving the vertical profile of K_z solely from the **Weather Research Forecasting with Chemistry (WRF_CHEM)** 3D model, deriving the vertical profile of K_z using parametrizations developed by Cao et al. (2016), and lastly, a combination of the first and second method such that the vertical profile of K_z is defined by the WRF_CHEM model above 50 m and parametrized using Cao et al. (2016) below 50 m (**Appendix C, section 3.2**). To define the vertical profile of K_z for the NACHTT campaign MP, we followed parameterizations developed by Cao et al. (2016), which coupled boundary layer height (BLH), ground wind speed measurements, and land surface physical properties to represent vertical mixing in three vertically-spaced boundaries. These boundaries were defined within the free troposphere (**Equation A1**), between the top of the boundary layer and the surface layer height (SLH) (**Equation A2**), and below the SLH, where the influence of turbulent drag increases and transports gas-phase species to the surface dependent on atmospheric stability parameters (**Equation 2.3**).

$$K_{Z_{SL}} = (\kappa \cdot u^*(t, 1) \cdot SLH(t, 1)) \quad (Eq. 2.3)$$

where $K_{Z_{SL}}$ is the vertical diffusion coefficient profile below the ASL, κ (Von Karman constant) is 0.43, u^* is the friction velocity in m/s derived from observational constraints, and SLH is the surface layer height in m.

This method was the only available option, as our configuration of WRF_CHEM did not include a K_z product. Wind speed measurements were gathered at fixed heights of 10, 100, and

300 m from the BAO tower (<https://downloads.psl.noaa.gov/psd3/bao/Special-Datasets/CU/10mTower/>), where the friction velocity (u^* , m/s) and surface roughness length (z_0 , m) were calculated via the logarithmic wind profile equation (**Equation 2.4** and **2.5**). Wind speed measurements at each height interval were averaged over the course of the 48-hour MP and plotted against the natural logarithm of height, where a linear regression was used to calculate $\ln(z_0)$, which was equal to the negative value of the y-intercept divided by the slope $-\frac{(\frac{u^*}{\kappa} \ln(z_0))}{\frac{u^*}{\kappa}}$.

$$u^* = \frac{\kappa \cdot u}{\ln\left(\frac{z}{z_0}\right)} \quad (\text{Eq. 2.4})$$

$$u(z) = \frac{u^*}{\kappa} \ln\left(\frac{z}{z_0}\right) \quad (\text{Eq. 2.5})$$

where κ (Von Karman constant) is 0.43, u is windspeed (m/s) obtained from observations, surface layer height (SLH, m) is defined as 10 % of the BLH, z is the height in meters, and z_0 is the surface roughness length, which was calculated as 0.0024 m.

Given the strong dependency of the BLH on parameterizations of the vertical diffusion mixing term (**Appendix A, Equation A1-A3**), explicitly defining the BLH for the PACT-1D model was of utmost importance. Daytime aerosol backscatter profiles were gathered from a ground-based LIDAR ceilometer (<https://downloads.psl.noaa.gov/psd3/bao/Ceilo/processed/>) near the BAO tower for the duration of the NACHTT campaign, where timeframes were processed between February 18-25 and March 1-10 using the BL-View (Vasaila, Vantaa, Finland) to get an estimation of the BLH. These timeframes were chosen based on selection criteria, where precipitation was absent, a gradual increase in the BLH was observed early in the day, and due to data availability. The BL-view software utilizes an aerosol backscatter gradient retrieval method for determining BLH, which stems from two assumptions, such that the concentration of aerosols at the top of the boundary layer is much greater than in the free troposphere and between the top of the BLH and the free troposphere, a negative gradient exists in which the BLH is defined at a local maximum (**Figure A3**). One common disadvantage with ground-based LIDAR ceilometers

coupled with aerosol backscatter gradient method is that it may misrepresent or be unable to identify the Nocturnal Boundary Layer Height (NBLH) due to the absence of irradiation and scattering of light at night. The molecular diffusion coefficients of HONO and NO₂ at STP were found to be $7.2 \times 10^{-5} \text{ m}^2/\text{s}$ (Hirokawa et al., 2008) and $1.5 \times 10^{-5} \text{ m}^2/\text{s}$ (Langenberg et al., 2019), respectively. Given that the magnitude of these molecular diffusion coefficients is on the order of 10^{-5} , the vertical diffusion mixing term near the ground level of the model was constrained to permit molecular diffusion to occur during the 48-hour MP.

To account for missing values of BLH from ceilometer measurements during the 48-hour MP, a BLH of 1000 m during the day and a NBLH of 300 m at night was assumed, where this was defined as the preliminary vertical diffusion parametrization in PACT-1D, hereinafter referred to as $K_{z_{\text{ceil}}}$. In order to check the parametrizations of $K_{z_{\text{ceil}}}$, the PACT-1D model was run with $K_{z_{\text{ceil}}}$ parametrizations included, where modelled mixing ratios of C₂-C₈ hydrocarbons were compared with ground-level observations from NACHTT (red-dashed trace, **Figure A4**). Given that these hydrocarbons are inert and their mixing ratios vary diurnally over the course of the 48-hour MP, only direct emissions and vertical diffusion mixing terms contribute to their modelled mixing ratios, making them ideal species to determine the estimated BLH throughout the model period. Time series of modelled mixing ratios of C₂-C₈ hydrocarbons with $K_{z_{\text{ceil}}}$ parametrizations were compared to ground-level observations, where placeholder values of daytime BLH from $K_{z_{\text{ceil}}}$ were increased from 1000 m to a maximum of 3000 m to better match observations over the 48-hour MP. This was the final vertical diffusion parameterization defined in PACT-1D, hereinafter referred to as $K_{z_{\text{final}}}$, which was also found to be in better agreement with simulated BLH values from WRF (**Figure A4, A**). As the wind speed increases above 6 m/s during the daytime of MP2, its influence on the value of K_z becomes more important than the depth of the BL, hence there is very little change between modelled mixing ratios of C₂-C₈ hydrocarbons in $K_{z_{\text{ceil}}}$ and $K_{z_{\text{final}}}$ at this time period.

2.4. Initializing The Meteorological Profiles of Ambient Temperature, Relative Humidity, and Pressure:

To define the meteorological profiles (i.e. ambient temperature, °C; relative humidity, %; and pressure, Pa) for a model grid in PACT-1D, only one method has been developed and it requires the use of a WRF simulation. The importance of using a WRF 3D model as input for meteorology in PACT-1D is that it captures regional meteorological trends for a given model location to improve the predicting power of the model. A common disadvantage of 3D models to study interfacial chemistry is the lack of resolution near the ground surface due to non-explicit parametrization of the ground surface. To correct for this, simulated temperature, RH and pressure profiles from WRF were interpolated from the upper boundary (i.e., 5000 m) down to a height of 10 m (levels 10–54) and merged with meteorological observations at a fixed height of 10 m, representing the lowest levels (levels 1–9) of the PACT-1D vertical grid (**Figure 2.5**). In this study, the WRF model was initialized based on defining the domain of the measurement site at BAO tower, Erie, Colorado (40.050 N, 105.040 W, 1500 m) using a 6-day model spin-up time from 2011-02-14 20:00 to 2011-02-20 17:00 MST, with a 20 minute integration time. Within the domain configuration of WRF (**Figure B1**), two grids predict the meteorological profiles with varying horizontal resolution, such that the inner grid (i.e. main grid, *d02*) and outer grid (i.e. *d01*) are defined by 3x3 km and 9x9 km horizontal resolution, respectively, with a vertical resolution of 49 levels, extending from 1×10^{-4} m to 8×10^4 m. The purpose of utilizing two grids with varying horizontal resolution is to ensure that simulated meteorological profiles at the border of the inner grid have reduced stochasticity.

Ten 4D products were imported from the output of the WRF simulation, where the dimensions were defined as longitudinal grids ($n = 99$), latitudinal grids ($n = 99$), vertical grids ($n = 49$), and a 6-day time dimension with a 20-minute integration loop ($n = 433$). The longitudinal and latitudinal grids were centered on a single box at $n = 59$ and $n = 48$, respectively, with coordinates representing at 39.9761 N and 104.5748 W. Due to the 3 km by 3 km coarse grid resolution in WRF, the longitudinal and latitudinal grids were filtered to a single box closest to the measurement location (the BAO tower). After filtering the time of all WRF products to the 48-hour MP, the 4D products were constrained to 2D height and time matrices. The names and definitions of each WRF product used to derive meteorological profiles have been tabulated in

Table 2.1, including the latitude ($XLAT$, °), longitude ($XLONG$, °), time, perturbation potential temperature (θ , K), terrain height (HGT , m), perturbation geopotential (PH , m^2/s^2), base-state geopotential (PHB , m^2/s^2), perturbation pressure (P , Pa), and base-state pressure (PB , Pa), and the mixing ratio of water vapour ($QVAPOR$, kg/kg).

Table 2.1. The definitions and matrix dimensions of imported WRF products and their relation to precursors of PACT-1D meteorology inputs.

WRF Products	Matrix _{pre} [*] (x,y,z,t)	PACT-1D Meteorology Inputs	Matrix _{post} [*] (z,t)
Longitude ($XLONG$, °)	99x99x433	-	-
Latitude ($XLAT$, °)	99x99x433		
Time ($TIME$, s)	1x433		
Perturbation Potential Temperature (θ , K)	99x99x49x433	Vertical Ambient Temperature profile (Eq. 2.4)	49x145
Perturbation pressure (P , Pa)	99x99x49x433	Vertical Pressure profile (Eq. 2.5, 2.6)	49x145
Base-state pressure (PB , Pa)	99x99x49x433		
Mixing ratio of water vapour ($QVAPOR$,	99x99x49x433	Vertical RH profile (Eq. B1-B3)**	49x145
Terrain height (HGT , m)	99x99x433	Altitude (AGL) (Eq2.7)	49x145
Perturbation geopotential (PH , m^2/s^2)	99x99x49x433		
Base-state geopotential (PHB , m^2/s^2)	99x99x49x433		

* Matrix_{pre} are 4D matrixes defined for WRF products consisting of longitude(x), latitude(y), height(z), and time(t) and after processing for input to PACT-1D, Matrix_{post} are 2D matrixes of height and time for the PACT-1D meteorology inputs.

** Refer to Appendix B to view how the vertical RH profile was derived from the vertical profile of water vapour.

The vertical profile of ambient temperature was calculated using the Poisson theorem (**Equation 2.6**), which relates potential temperature gathered from WRF to ambient temperature and pressure by accounting for the adiabatic lapse rate.

$$T_{(z,t)} = \frac{\theta_{(z,t)}}{\left(\frac{P_{(z,t)}}{P_0}\right)^{\frac{R}{c_p}}} \quad (Eq\ 2.6)$$

where P is the pressure (Pa), P_0 is the standard atmospheric pressure equivalent to 101325 Pa, θ is the potential temperature (K), R is the universal gas constant of air equivalent to 287 J/kg·K, and c_p is the specific heat capacity of air at constant pressure and equal to 1005 J/kg·K.

The vertical pressure profile was calculated by taking the sum of the perturbation and base-state pressure from imported WRF products, where P_B is a location-dependent forecast of pressure constant with height, and P is the difference between the total pressure (P_T) and the hydrostatic pressure (P_H) (**Equations 2.7 and 2.8**).

$$P_{(z,t)} = P_{PB(z,t)} + P_{P(z,t)} \quad (Eq. 2.7)$$

$$P_{P(z,t)} = P_{T(z,t)} - P_{H(z,t)} \quad (Eq. 2.8)$$

Given the output of WRF did not include a product for the vertical RH profile, the vertical water vapour profile ($QVAPOR$) was imported instead and converted to RH by calculating the saturated water vapour profile, followed by taking the quotient of $QVAPOR$ over $Q_s Vapour$ to equate RH (**Appendix B, Equation B1-B3**). After processing the meteorological profiles using imported WRF products and constraining them based on the measurement location and the 48-hour MP, the matrix dimensions post-processing were filtered to a 2D height and time matrix of 49x145 (**Table 2.1**). Defining the altitude for WRF products was needed in order to properly scale the vertical grid of the WRF model to PACT-1D (**Figure 2.5**). To determine the altitude of the WRF model AGL, the elevation (m) was subtracted by the terrain height via **Equation 2.9**, where elevation is equivalent to the sum of the base-state geopotential and the perturbation geopotential over the acceleration due to gravity ($g = 9.81 \text{ m/s}^2$).

$$Z_{AGL} = \left(\frac{PHB + PH}{g} \right) - HGT \quad (Eq. 2.9)$$

The meteorological profiles of RH, ambient temperature, and pressure were then interpolated to the vertical grid and model time dimensions of PACT-1D, yielding a matrix of 54x196 for height and time, respectively. This satisfies the requirement that the meteorological

component and all other components of PACT-1D are initialized with the same number of matrix dimensions prior to model integration. To validate the predicted meteorological profiles defined for the PACT-1D model, modelled meteorological profiles were first binned into 6-hour intervals to determine if the diurnal trends are in agreement with known physical phenomena in the troposphere, mainly in the presence and absence of terrestrial radiation (**Figure 2.11**). Sequentially, a time series of modelled meteorological variables of RH, pressure, and ambient temperature were compared with observations at heights of 10 and 300 m from the BAO tower (**Figure 2.12**).

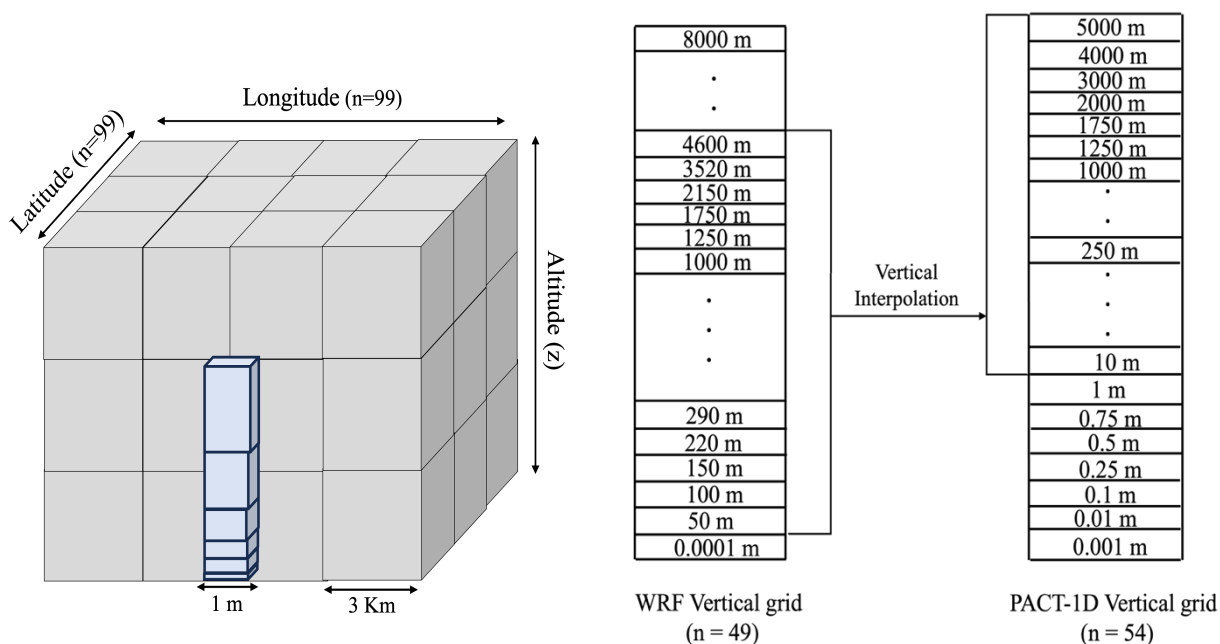


Figure 2.5. From the left schematic, the horizontal resolution between the PACT-1D (in blue) and the inner grid of the WRF model (in grey) is shown, each with 1 m² and 3 km² grid resolution, respectively. Note that the vertical dimensions of PACT-1D nested in the WRF model grid are not to scale. From the right schematic, the vertical grid of WRF (n= 49) and PACT-1D (n= 54) are shown, where meteorological profiles imported from WRF (50 – 4600 m) were interpolated to the vertical grid of the PACT-1D model above 10 m. Below 10 m, meteorological profiles were defined using fixed meteorological measurements at a height of 10 m.

2.5. Initializing Concentrations of Gas-Phase Species and Chemistry for BASE Model Run:

The PACT-1D model defines an initial vertical profile for any species by representing a constant mixing ratio within the boundary layer, assuming a uniformly mixed boundary layer. Above the boundary layer, we defined the initial vertical profile using an exponential decay curve to represent

a simple dilution scheme, where the mixing ratio of any gas-phase species at the top of the boundary layer is diluted to one-fifth of the value at the upper boundary of the box model (i.e. 5000 m). Unlike all other input components of the PACT-1D that were defined using observational constraints for the 48-hour MP, the initial vertical profile of all gas-phase species was initialized only at $t = 0$ (**Figure 2.3**). The initial concentration input file serves as a base state to define all gas-phase species, where contributions of vertical mixing and meteorology profiles from physics parametrizations, as well as chemical mechanisms and rate constants from chemistry parameterizations, drive the predicting power of the model. The initial ground-based concentrations for all gas-phase species were defined using two methods, depending on the diurnal variability of the target gas over the 48-hour MP. For all Volatile Organic Carbon (VOCs) species, hourly-based average diurnal mixing ratios (ppb) were measured over the campaign period ($n = 22$ days), where initial ground-based concentrations were defined at the start of the MP (17:00 MST). For reactive nitrogen species and ozone, the ground-level mixing ratios were initialized based on the 24-hour average measured from the previous day (2011-02-17), as mixing ratios of ozone and reactive nitrogen species (i.e., HONO, NO₂, NO, and O₃) varied greatly over the NACHTT campaign and are the focus of this study.

To simulate tropospheric chemistry in the PACT-1D model, we used 363 relevant homogenous chemical mechanisms, quantum yields, and rate constants within the Regional Atmospheric Chemical Mechanism V2 (RACM2) scheme, which includes definitions for photolysis, thermal reactions, three-body pressure-dependent reactions, and equilibrium reactions for 20 gas-phase species defined in the RACM2 nomenclature (W.S. Goliff, W.R. Stockwell, and C.V. Lawton, 2013). The RACM2 scheme is embedded in the Kinetic PreProcessor (KPP) module of PACT-1D. The KPP is an open-sourced software that solves chemical production and loss terms in the general 1D differential equation by temporal integration (Sander et al. 2005). During a model run, KPP performs the chemistry with an integrated timestep of 10 seconds, whereas the integrator in the PACT-1D module runs with a 20-second integrated timestep (**Figure 2.2**). A complete description of the initialization of KPP coupled to RACM2 and its integration into the PACT-1D structure has been defined in the PACT-1D SOP (**Appendix C, section 4.0**). To ease the computational effort of numerical integration in KPP, RACM2 sums species with similar reactivity and chemical classification (i.e., the HC3 group represents n-propane, n-butane, and i-butane identically; **Table 2.2**). The rate constants for each mechanism type (i.e. thermal reaction,

pressure-dependent reactions) were described in the chemical mechanism definition file in KPP and gathered from RACM. For all model runs, the vertical profiles of 20 gas-phase species from RACM2 were initialized using 23 species measured during the NACHTT campaign, which included reactive nitrogen species, a range of anthropogenic and biogenic VOCs, and tropospheric O₃ (Table 2.2).

Table 2.2. List of chemical formulas and initial mixing ratios defined for all species in PACT-1D.

Chemical Formula	RACM2 name	[X] _i (ppb)	Initialization method
HONO	HONO	0.152	24-hour average before MP (02-17-2011)
NO ₂	NO2	6.03	
NO	NO	0.33	
N ₂ O ₅	N2O5	0.2	
HNO ₃	HNO3	0.615	
O ₃	O3	40	
C ₆ H ₅ CH ₃	TOL	0.25	Initialized at start time of MP, using hourly diurnal mixing ratios over the entire campaign period.
C ₆ H ₆	BEN	0.24	
C ₂ H ₆	ETH	22.22	
C ₃ H ₈ + C ₄ H ₁₀	HC3	30.70	
C ₅ H ₁₂ + C ₆ H ₁₄	HC5	4.53	
C ₇ H ₁₆ + C ₈ H ₁₈	HC8	0.04	
C ₂ H ₄	ETE	0.53	
C ₄ H ₈ O	MEK	0.27	
HCHO	HCHO	0.93	
C ₃ H ₆ O	ACT	1.29	
CH ₃ CHO	ACD	0.72	
CH ₃ COOH	ORA2	0	
CH ₃ OH	MOH	4.7	

A complete description of the measurement site setup and a list of all instruments used in the NACHTT campaign are discussed in **Chapter III**. A total of 15 VOCs were selected based on data availability, oxidative capacity, and fit with RACM2 nomenclature. The VOCs can be classified as C₂-C₈ alkanes, alkenes (ethene), ketones (acetaldehyde, acetone, formaldehyde, and methyl ethyl ketone), and aromatics (benzene and toluene). Photolysis rate coefficients for 62 reactions were initialized hourly for the MP, using the Tropospheric Ultraviolet-Visible (TUV, Version 5.4) radiative transfer model via the Fortran-based source code. Input parameters for the TUV model included defining the geographical coordinates (i.e. latitude, longitude, ground elevation; 40.050 N, 105.040 W, 1500 m) and the start time, which was equivalent to the start time of the PACT-1D model. A method employed by Tuite et al. (2021) was used to account for light scattering due to clouds throughout the model period, where NO₂ photolysis rates from radiometer measurements were scaled against all photolabile species (**Equation 2.10**).

$$J_x(t, z) = J_{TUV, x} \left(\frac{J_{Obs, NO_2}}{J_{TUV, NO_2}} \right) \quad (Eq\ 2.10)$$

2.6. Initializing Emission Rates of Gas-Phase Species for BASE Model Run:

The multitude of high-time resolution and vertically-resolved measurements of gas-phase species, coupled with BLH measurements, during the NACHTT campaign were used to derive hourly input emission rates for all defined gas-phase species during the 48-hour MP. This is the first PACT-1D modelling study to derive input emission rates explicitly by being observationally-constrained by measurements. For high-resolution tower-based measurements of reactive nitrogen species and VOCs, the observed profiles of their number density were filtered to timeseries captured within the lowest 50 m at the BAO tower, where they were then averaged to hourly intervals to match the resolution of the ground-based VOC measurements via the gas-canisters and GC-MS. The hourly input ground emission rates (mol/m²/hr) of 17 primary gas-phase species were calculated by multiplying the hourly change in number density (Δn_x , molecules/cm³/hr) of each gas-phase species by the BLH (cm), assuming that each species is well mixed within the boundary layer (**Equation 2.11**).

$$E_x(t) = \frac{\Delta n_x(t) \cdot BLH(t)}{N_A} \cdot 10^4 \quad (Eq\ 2.11)$$

where E_x is the input emission rate (mol/m²/hr), Δn_x is the hourly-averaged number density of each species (molecules/cm³/hr), BLH is the boundary layer height (cm), N_A is Avogadro's number, and the unit factor of 10^4 is to convert cm² to m².

In previous modelling studies using PACT-1D, emission rates were derived from national or regional emission inventories and used as input in 3D transport models (i.e. WRF-CHEM), where some species were scaled by more than 50% to match observations and account for differences between coarse grid resolution and finer horizontal and vertical grid resolution to represent the model location relative to the inventory and for the necessary chemistry (Tuite et al. 2021). The WRF-CHEM model accounts for horizontal and vertical advection terms and regional meteorology, scaled over a larger coarse grid resolution (i.e. greater than 3x3 km) to generate input emission rates. In this study, the input emission rates were derived directly from observations, therefore the scaling of emissions was not required. The calculated input emission rates of NO₂, NO, HNO₃, and HONO were constrained to within 0.1 – 1 m of the PACT-1D model, while the input emission rates of all VOCs were constrained to within 0.1-10 m of the PACT-1D model. Given the input emission rates were derived from observations, the output of the PACT-1D model would account for horizontal advection and dilution near the surface, which raises the predictive capability of the PACT-1D model as 1D models typically do not account for horizontal advection. The parametrization of the input emission rate serves as the final component to be added to the PACT-1D model, after the physics parametrizations and chemistry have been implemented.

A top-view schematic of the Front Range urban corridor of Colorado adapted from Brown et al. (2013) is shown in **Figure 2.6**, highlighting all the emission sources, including the agricultural farms, oil and gas wells, power plants, and urban regions (i.e. Denver and Boulder) relative to the measurement site in Erie, Colorado. The closest emission source (< 1 km) to the measurement site is the oil and gas wells, which surround the measurement site in all directions and extend to Greeley, located 50 km NW of the measurement site (**Figure 2.6**). A study by Pétron et al. (2012) characterized the summertime hydrocarbon emissions by sampling from the BAO, where the greatest emission fluxes from oil and gas wells were found to be methane, ethane, C₃-C₆ alkanes, and benzene, in decreasing order.

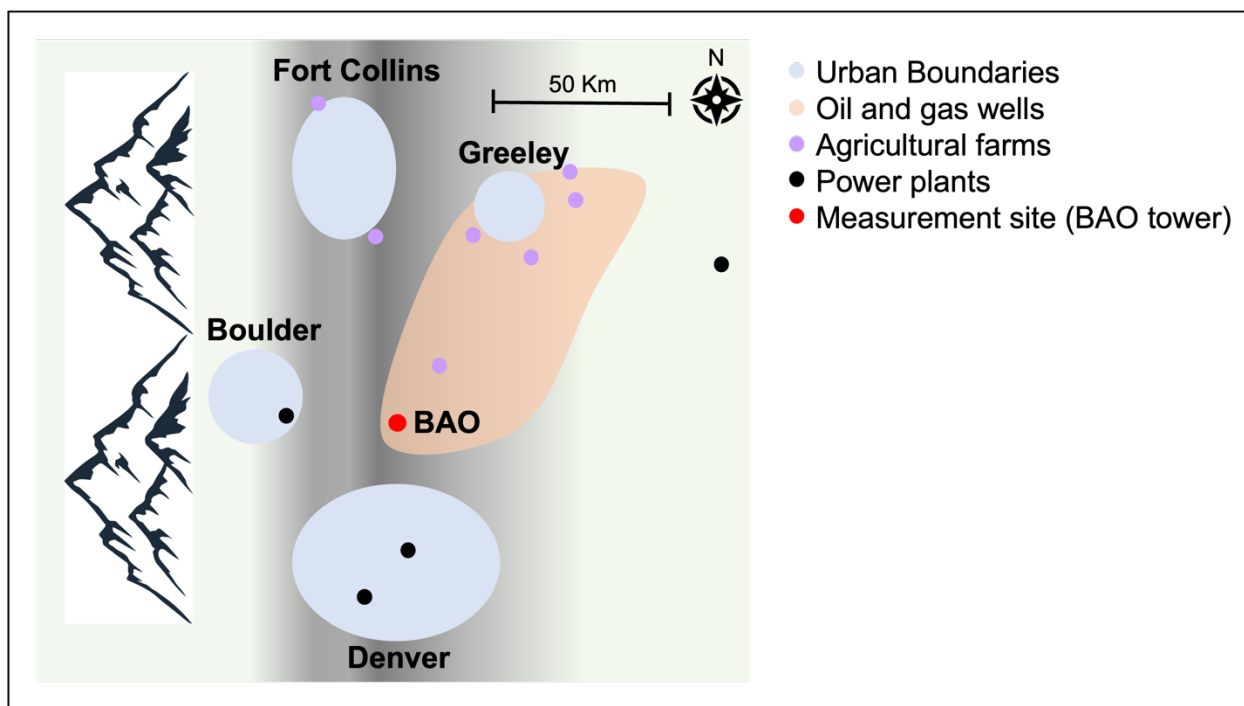


Figure 2.6. A top-view schematic of the Front Range urban corridor of Colorado is shown with various point emission sources, including oil and gas wells (orange), power plants (black), agricultural farms (purple), and urban boundaries (blue; Denver, Boulder, Greeley, Fort Collins) relative to the measurement site (red). The density of roads is shaded in a grey-black gradient, where road density is greater in darker regions. This schematic is adapted from a figure originally presented in Brown et al. (2013).

Based on the time series of emission fluxes required for all primary gas-phase species defined in PACT-1D, two emission source types influenced the measurement location during the 48-hour MP (**Figure 2.7** and **Figure 2.8**). These include a strong emission source of C_2 - C_8 alkane hydrocarbons due to proximity to oil and gas wells and a regional emission source for all other VOCs and NO_x , respectively. The direct emission rate of HONO from traffic sources was derived using a scaling factor of $0.003(NO + NO_2)$, which was obtained from a tunnel study by Kurtenbach et al. (2001), assuming a lower limit estimate for the emission of HONO from NO_x given the higher propensity of gasoline vs. diesel engines in North America.

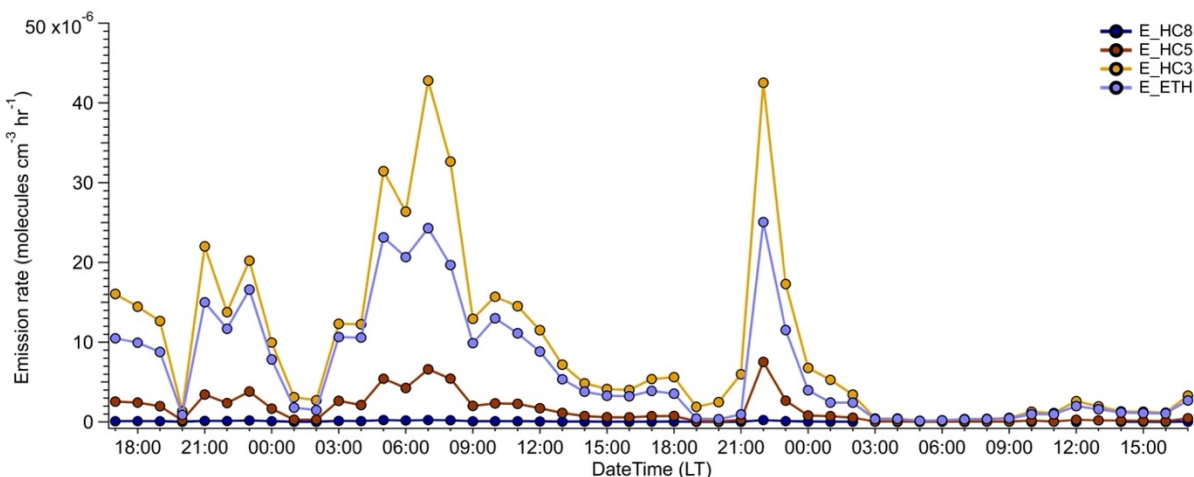


Figure 2.7. Time series of calculated emission rates ($\text{molecules cm}^{-3} \text{hr}^{-1}$) of ETH (purple, ethanol), HC3 (yellow, propane + n-butane + i-butane), HC5 (red, pentane + hexane), and HC8 (indigo, heptane + octane) during the 48-hour MP. Due to the proximity of oil and gas wells to the measurement location, $\text{C}_2\text{-C}_8$ alkanes have the greatest emission rates and follow a diurnal trend that is distinct from other primary gas-phase species.

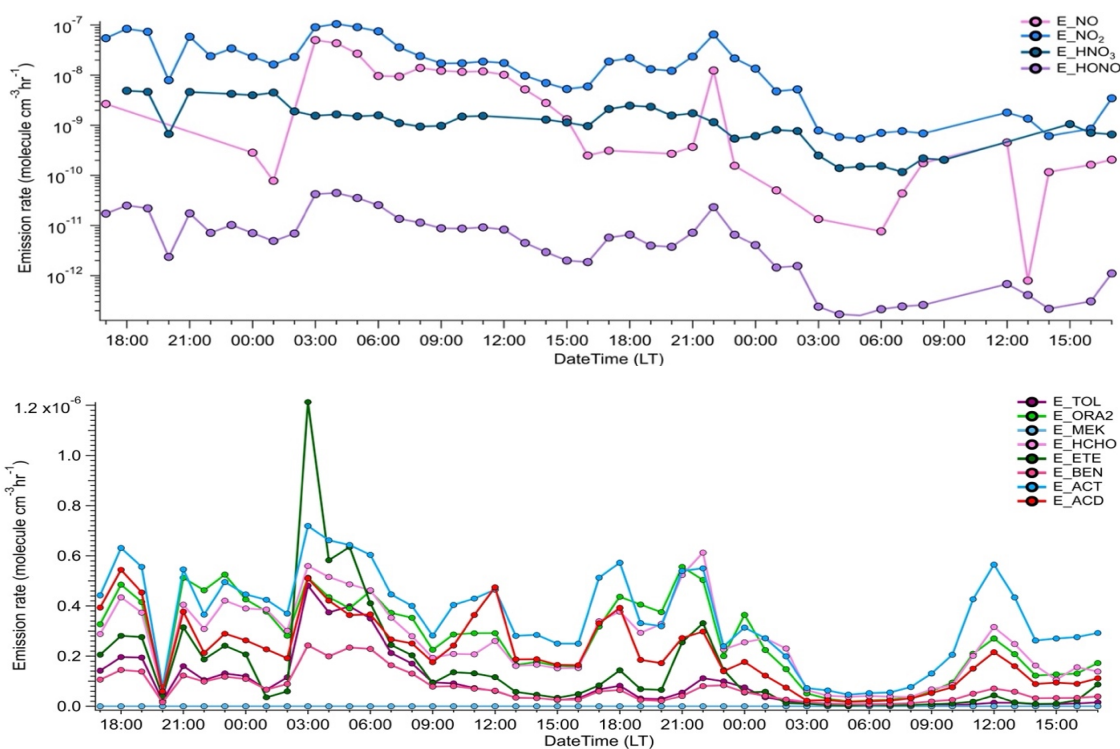


Figure 2.8. (A) Time series of calculated emission rates ($\text{molecules cm}^{-3} \text{s}^{-1}$) of reactive nitrogen species during the 48-hour MP. The y-axis is log-scaled to fit the relative emission rates of all reactive nitrogen species, including NO_2 (blue), NO (pink), HNO_3 (indigo), and HONO (purple). (B) Time series of calculated emission rates of all other primary VOCs representing background emissions during the 48-hour MP.

2.7. Surface Source Parametrizations of HONO in The BASE model:

In the PACT-1D model, the deposition of gas-phase species was calculated by tracking the number of molecules colliding at the ground surface in the lowest grid level at every timestep, with a prescribed ground uptake coefficient for HONO and NO₂. This allowed for an explicit representation of the interfacial chemistry of HONO between the ground surface and the troposphere. One assumption that was made in PACT-1D was that deposition rates were calculated assuming a uniform surface roughness, which may introduce bias, as it does not account for the variability in terrain and land use surrounding the measurement site. The presence of grasslands (i.e. measurement site), oil and gas wells, farmlands, and the nearby mountainous topography could result in spatially varying surface roughness lengths, which would influence deposition and vertical mixing, especially under the most turbulent periods when horizontal advection becomes more prominent during the 48-hour MP. All model outputs from PACT-1D in this study will have the same physical parametrizations but will differ in surface source chemistry parametrizations, where the first model output is hereinafter referred to as the BASE model. Prior to setting the surface source routines of HONO in the BASE model of PACT-1D, a 3-day spin-up from a previous model run was initialized, where molecules that were deposited on the ground surface at the end of the model period were built up in the ground storage term of PACT-1D for use in the BASE model run. In the BASE model, there were two mechanisms postulated for the heterogeneous parametrizations of HONO in PACT-1D. The first mechanism is the most dominant nocturnal source of gas-phase HONO, which is formed from the conversion of NO₂ on surface-adsorbed water (Finlayson-Pitts et al., 2003; Kleffmaan, 2003; Sorgel et al., 2011; VandenBoer et al., 2013). For this parametrization, we assumed for every two molecules of gas-phase NO₂ that collided with the ground surface, one molecule of gas-phase HONO is produced, and one molecule of HNO₃ is added to the ground surface storage term (**Chapter I, R4**). The deposition rate of NO₂ was calculated using **Equation 2.12**, where the ground uptake coefficient of NO₂ was set to 8×10^{-6} using average of the observational constraints from the NACHTT campaign at nights when NBLH were detected (VandenBoer et al. 2013).

$$V_{dep,NO_2} = \frac{1}{8} \gamma_{NO_2,ground} \bar{C}_{NO_2} \quad (Eq. 2.12)$$

where $\gamma_{NO_2,ground}$ is the unitless observationally-constrained reactive ground uptake coefficient of NO_2 describing the reaction probability per surface collision and $\bar{C}_{NO_2}$ is the mean molecular speed of NO_2 ($m\ s^{-1}$).

The second HONO parametrization describes the nighttime loss of HONO by dry deposition into an aqueous film (i.e. ground storage term) and subsequent acid dissociation into nitrite and hydronium ions (**Chapter I, R9-R10**). The deposition rate of HONO was calculated using **Equation 2.13**, where the ground uptake coefficient of HONO was set to 7.3×10^{-5} , using nighttime observational constraints from the NACHTT campaign. In this model, an assumption is made that all gas-phase HONO molecules deposited onto the ground will convert to nitrite as a reservoir.

$$V_{dep,HONO} = \frac{1}{4} \gamma_{HONO,ground} \bar{C}_{HONO} \quad (Eq. 2.13)$$

where $\gamma_{HONO,ground}$ is the unitless observationally-constrained reactive ground uptake coefficient of HONO and $\bar{C}_{HONO}$ is the mean molecular speed of HONO ($m\ s^{-1}$).

Both laboratory and field studies have highlighted the chemistry of semi-volatile molecules when drying aqueous solutions of salts, where weak acid ions like nitrite were either converted back into gas-phase HONO by evaporation or formed a non-volatile nitrite salt depending on the number of non-volatile cations and anions (Takenaka et al. 2009; Wentworth et al. 2016). In the BASE model, the fraction of HONO that is emitted back into the atmosphere was zero, assuming a greater abundance of non-volatile cations to anions, where irreversible loss occurs via the formation of nitrite salts (**Equation 2.14**).

$$F_{HONO} = \frac{C_{NO_2^-} - (\sum C_{cations} - \sum C_{anions})}{C_{NO_2^-}} \quad (Eq. 2.14)$$

Where F_{HONO} is the fraction of HONO formed from the evaporation of nitrite, $C_{NO_2^-}$ is the concentration of nitrite in mg/L, $C_{cations}$ and C_{anions} are the sum of all cations and anions in the aqueous system in mg/L, respectively.

After running the PACT-1D with chemical integration via KPP, the BASE model output included predicted vertical profiles for each gas-phase species defined, where each profile consisted was a matrix of height and a 20-second timestep (54x8641). In addition, the model output of PACT-1D included several other products, described in **Table 2.4**, including the vertical a transport rate profiles, the deposition rates, and reaction rates for all 363 mechanisms defined in RACM2.

Table 2.4. Names, dimensions, and units of all PACT-1D products after model integration.

PACT-1D products	Dimensions	Units
Predicted vertical profile of gas-phase species	(54x8641)	molecules·cm ³ s ⁻¹
Deposition rates	(1x8641)	molecules·cm ⁻² s ⁻¹
Reaction rates	(54x8641)	molecules·cm ³ s ⁻¹
Vertical transport rates	(54x8641)	molecules·cm ³ s ⁻¹

2.8. Validating Parametrizations of The Vertical Diffusion Coefficient (K_z):

To facilitate heterogeneous mechanisms of HONO on the ground surface, target gas-phase species, including HONO and NO₂ found in the first level of the model, were explicitly represented so they were able to diffuse to the ground surface. In the troposphere, the exchange of molecules between the ground surface and the immediate atmosphere is governed by turbulence and molecular diffusion, which are driven by changes in regional and mesoscale transport, respectively. These two forces function on different timescales, where the former force must be limited for the latter to take effect. In the absence of a physically explicit 1D transport and chemistry model, the deposition velocity of gas-phase HONO and NO₂ in the absence of a canopy is often represented as a series of resistances controlling the transport and deposition of molecules to Earth's surface (Seinfeld and Pandis, 2006). This includes aerodynamic transport (R_a) to the ground surface and molecular diffusion (R_b). The parametrization of K_z in the ASL in a 1D model represents the R_a term, which directly impacts the deposition velocity of all gas-phase species, independent of their chemical properties. The R_b term of gas-phase HONO and NO₂ on the ground surface is dependent on their respective reactive uptake coefficients ($\gamma_{HONO} = 7.3 \times 10^{-5}$, $\gamma_{NO_2} = 8.0 \times 10^{-6}$) and the surface roughness length ($z_0 = 0.0024$ m), which stays constant throughout the MP. During the day,

the R_a term decreases with increasing vertical mixing, potentially facilitating greater deposition velocities of HONO and NO₂ if they are diffusion limited at other times. During the night, when vertical mixing decreases, the R_a term increases drastically over land, reducing transport of HONO and NO₂ from aloft, resulting in a surface system that is more diffusion limited. The resistance from the R_a term is known to be greater in magnitude under more stable (i.e. formation of a NBL) or neutral conditions compared to unstable atmospheric conditions (Seinfeld and Pandis, 2006). Several studies involving vertically-resolved measurements of HONO and NO₂ in both urban and rural regions highlighted that the presence of a stable NBL is a critical factor for being able to observe the accumulation of HONO at night as it results in the vertical stratification of HONO (Kleffmann et al., 2003; VandenBoer et al., 2013; Wong et al., 2011; Zhang et al., 2009). In order to permit molecular diffusion on the ground surface when a NBL is formed, the K_z near the ground must be constrained during the night to properly represent the influence and/or limitation of aerodynamic transport on the deposition velocity of HONO and NO₂, with respect to the molecular diffusion resistance (R_b) term.

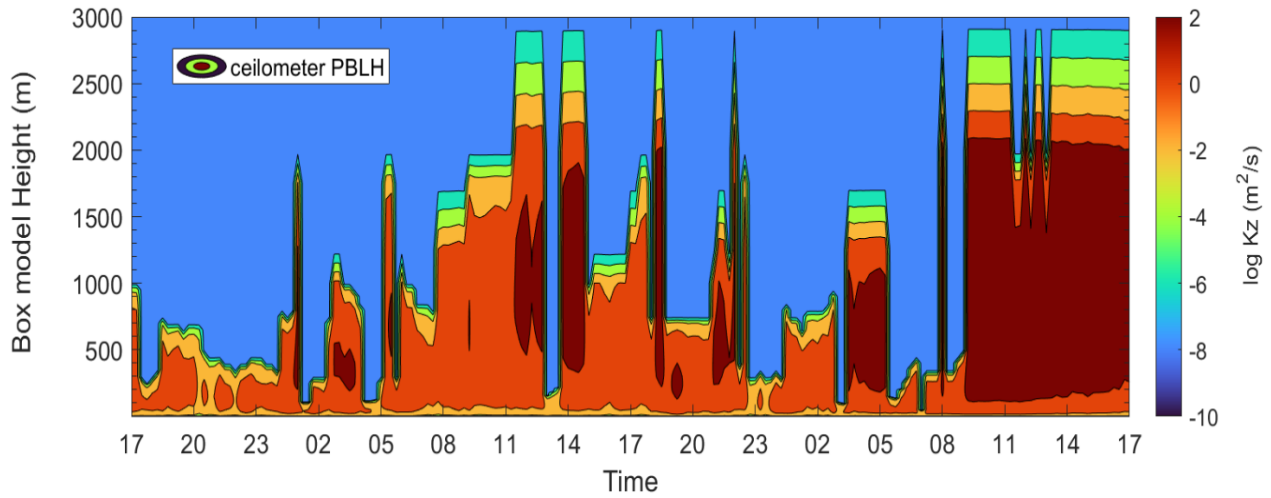


Figure 2.9. Logged contour plot of the modeled vertical diffusion mixing term (K_z) during the 48-hour MP, ranging between 10^{-5} to 10^2 m²/s within 3000 m of the box model height. The junction between the coloured contour and the free troposphere (blue background) represents the boundary layer height (m). Using parametrizations of K_z from Cao et al. (2016), the BLH controls the vertical depth of mixing while ground-level wind speeds controls the intensity of vertical mixing.

Based on the vertical diffusion mixing (K_z) parameterizations developed for PACT-1D (**Figure 2.9, Figure A1-A2**), there is clear evidence to support that the average K_z expressed in the first layer of the BASE model (i.e. 10^{-3} m) lies in the same magnitude as the molecular diffusion coefficients of HONO and NO₂ at all times of MP1 but is limited on MP2. From the logged contour plot of the K_z term defined in PACT-1D (**Figure 2.9**), there is a clear transition between daytime and nighttime K_z coefficients on both dates due to differences in mixing layer height and wind speeds, with K_z generally ranging from 10^{-2} - 10^2 m²/s and 10^{-5} – 1 m²/s during daytime and nighttime periods, respectively. During MP1 (February 18th to February 19th, 2011, 17:00-17:00 MST), the formation of a stable NBL occurred below 400 m at 20:00 to 05:30 MST, coupled with low wind speeds (i.e. ≤ 6 m/s), resulting in an average K_z , ranging from 1 m²/s at the top of the NBL to 10^{-5} m²/s at the ground surface (**Figure A1**). During MP2 (February 19th to February 20th, 2011, 17:00-17:00 MST), the formation of a stable NBL occurred below 550 m from 23:00 – 03:00 MST, where the average K_z ranged from 10^1 m²/s at the top of the NBL to 10^{-4} m²/s at the ground surface (**Figure A2**). This shows that the average K_z coefficient near the ground surface in MP2 was an order of magnitude greater than the molecular diffusion of HONO and NO₂ at STP, thereby increasing the influence of the R_a term on the deposition velocity and making the uptake HONO and NO₂ to the ground surface less diffusion limited. The formation of a stable NBL still occurred during MP2 but was shorter-lived due to the influence of stronger wind speeds (i.e. ≥ 6 m/s) creating a deeper mixing layer, which continued well after 03:00 MST until the end of the MP. The development of a stable NBL on both nights of the 48-hour MP has also been confirmed by VandenBoer et al. (2013) from the 2011 NACHTT campaign using an alternate method, where the depletion of O₃ coupled with inversions in potential temperature from vertical profile measurements was used as a marker to determine the presence of a stable NBL (Brown et al., 2013; Fuchs et al., 1970). The 48-hour MP can be classified under two different vertical mixing regimes. On MP1, the coefficient of K_z was found to be less turbulent than MP2 due to differences in meteorology, which gives an opportunity to study the chemistry of modelled HONO under non-ideal mixing conditions. It was also determined that limited vertical mixing under the development of a NBL in MP1 likely contributed to the accumulation of HONO on the ground surface at the same time interval when a morning burst of gas-phase HONO were observed, where the term burst was used to describe a sustained enhancement of HONO mixing ratios observed near the surface despite active photolysis and expected breakup of the NBL (VandenBoer et al., 2013). The

parametrization of K_z employed in this 1D model study explicitly represents the resistance to the aerodynamic transport to the ground, in addition to permitting molecular diffusion to the surface to take place. Given that the initial step (i.e. deposition) for nocturnal heterogeneous surface processes is controlled by the R_a and R_b terms, a correct parametrization of K_z serves as the critical component controlling the deposition velocity of HONO and NO₂, ultimately dictating the capacity with which surface chemistry can take place.

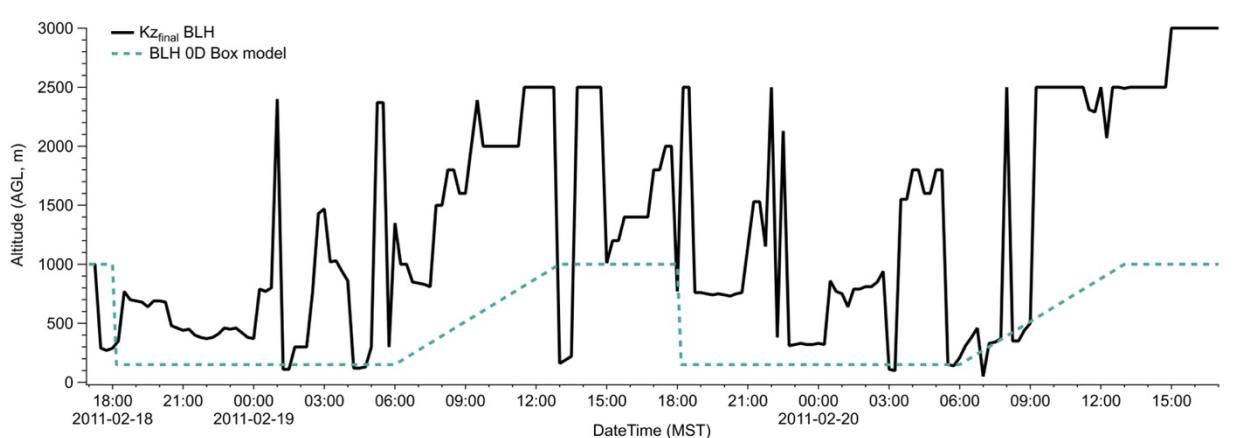


Figure 2.10. Time series of the BLH estimations derived from ceilometer measurements (black) in this study and a 0D parametrization of BLH (green) that assumes a constant nighttime BL and increases monotonically during the transition from a NBL to a convective mixing layer to a maximum of 1000 m.

In **Figure 2.10**, the estimated BLH from ceilometer measurements used during the 48-hour MP of the PACT-1D was compared to the estimated BLH parametrization from a 0D box model, which was applied during the NACHTT campaign on periods with stable atmospheric conditions. It was found that both BLH parametrizations follow the same diurnal trend but they differ clearly in magnitude, with the ceilometer-derived BLH found to be at times an order of magnitude greater than the 0D box model BLH parametrization. During the night of MP1 and MP2, ceilometer-derived BLH measurements can be observed with stochastic trends, which is an inherent limitation in the aerosol backscatter gradient method of determining the NBL height which could lead to the overestimation of the NBL height. In the default setting, the BL-view software (i.e. program that estimates BLH from ceilometer aerosol backscatter gradients) estimates the NBL at a single height as a function of time. In reality, under a formation of a stable vertically

stratified NBL, there could be several vertical gradients of aerosols observed, resulting in the stochastic nature of the BLH.

2.9. Comparing Modelled Meteorological Profiles with Observations:

To validate the predicted meteorological profiles parametrized in the WRF model, predicted ambient temperature profiles were first filtered into 6-hour periods to ensure diurnal trends were followed based on known physical phenomena for a given period (**Figure 2.11**). From 00:00-06:00 MST (**Figure 2.11, A**), the earth's radiative cooling effect occurs in the sun's absence, where the ground surface cools faster than the air aloft until a temperature inversion is observed within the NBLH. As a result of radiative heating following sunrise (**Figure 2.11, B**), the ground surface warms faster than the air aloft, increasing the turbulence near the ground and thereby elevating the BLH (i.e. temperature inversion observed above 500 m). From 12:00-17:00 MST, (**Figure 2.11, C**), a stability transition was observed near the ground surface, where surface temperatures begin to cool after peak solar radiation exposure (i.e. noon). The four blue traces with near-constant vertical temperature profiles between 0-400 m indicate the development of a temperature inversion, which eventually result in the formation of a stable NBL.

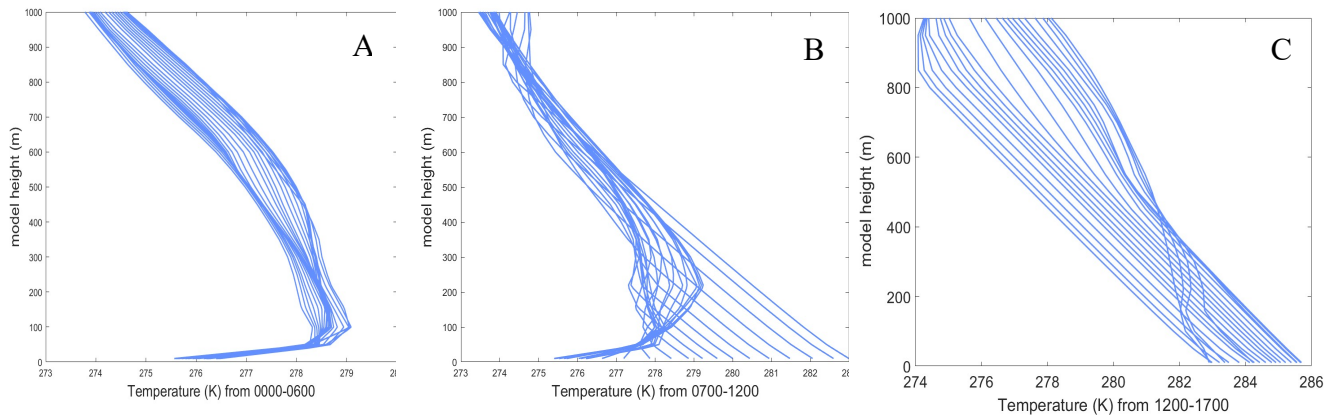


Figure 2.11. Vertical profiles of temperature from the output of WRF binned in 6-hour intervals overnight (A, 00:00-06:00), morning to noon (B, 07:00-12:00), and afternoon till late evening (C, 12:00-17:00) for the first 24 hours of the MP between February 18, 17:00 MST to February 19, 17:00 MST. Note that each trace represents a 15-minute interval.

In **Figure 2.12**, a time series of modelled ambient temperature from WRF was compared to observations constrained at 10 and 300 m to validate the predictive power of WRF and determine if the model captures diurnal trends from observations and lies in the same magnitude. Overall, it was found that the modelled ambient temperature from WRF was in excellent agreement with observations at both heights during the 48-hour MP, ranging from 268 – 285 K and 274 – 287 K, respectively. A comparison of modelled temperatures at 10 and 300 m follows an inverse relationship with height, which is expected for temperature profiles in the troposphere. The greatest deviance in temperature (≤ 5 K) between the model and observations occurs during both nights. From 03:00-06:00 MST of MP1 (**Figure 2.12, A**), the modelled ambient temperature remains constant at 275 K, while the observed ambient temperature decreases to 270 K (< 0 °C) at a height of 10 m. This deviation could be due to the formation of frost on the ground surface, thereby further decreasing temperatures near the ground surface compared to modelled temperatures from WRF, which simulated the formation of dew during this timeframe. From 03:00-09:00 MST of MP2 (**Figure 2.12, A**), the modelled ambient temperature decreases to a minimum of 268-270 K, while the observed ambient temperature remains above 275 K. In the WRF model, temperature perturbations at a single vertical grid point can vary more greatly between adjacent grid points, especially under more turbulent K_z regimes caused by wind speeds ≥ 6 m/s near the ground, which is shown in **Figure 2.12**. Furthermore, given that WRF simulations were run using a 3 km by 3 km horizontal resolution, it is expected that the spatial variability in surface roughness between the chosen coordinates of the WRF model and observations could also differ, resulting in the underestimation of the modelled ambient temperature at 10 m. To limit this underestimation in future studies, one suggestion would be to average the temperature perturbations from WRF using four vertical grid points, which would yield a more regional representation of meteorology, especially under turbulent conditions.

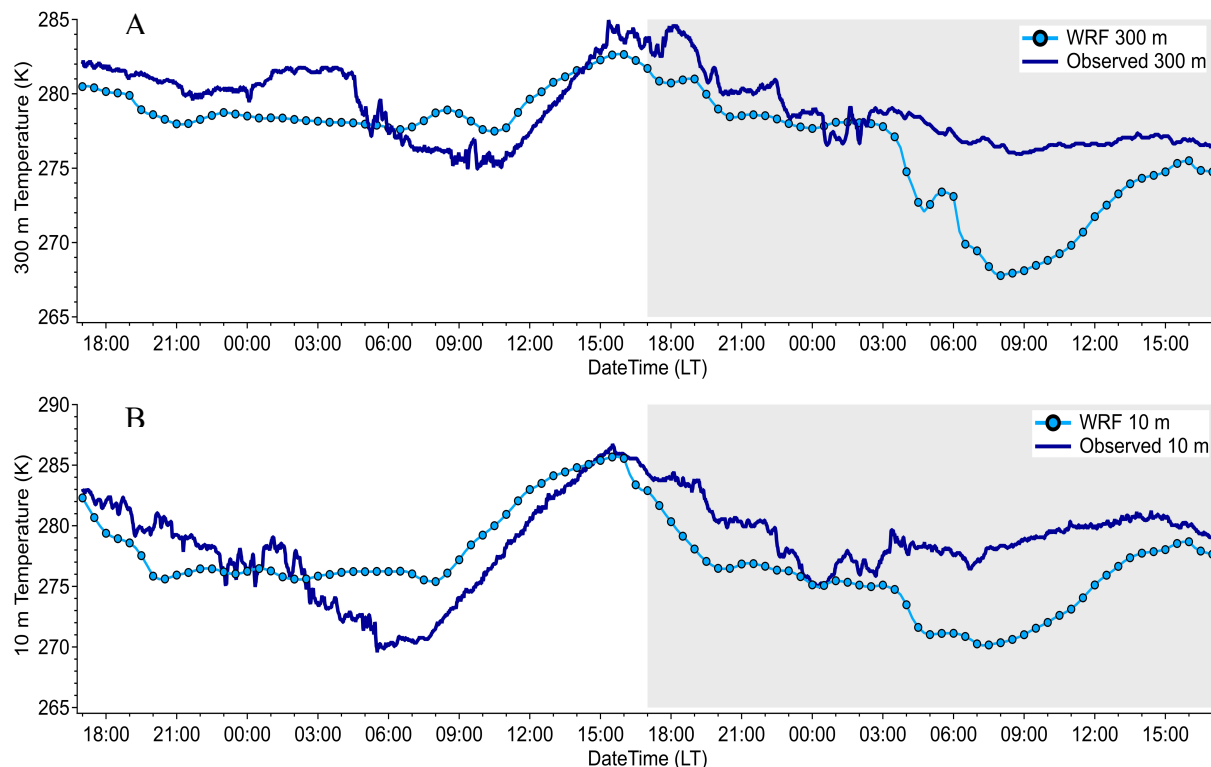


Figure 2.12. Time series of WRF predicted (light blue) vs observed (dark blue) ambient temperature (K) from 300 m (A) down to 10 m (B). The non-shaded region represents MP1 from February 18th 17:00 MST to February 19th 17:00 MST and the grey shaded region indicates the start of MP2 (2nd model period day), from February 19th 17:00 MST to February 20th 17:00 MST.

2.10. Conclusion:

In this chapter, a detailed explanation of every component of the PACT-1D model and their parametrization method were defined. A great deal of effort was made to validate the physics parametrizations, including the vertical diffusion mixing (K_z) term, meteorological profiles, emission rates, and photolysis rate frequencies to constrain the chemistry of the PACT-1D model. This was the first PACT-1D study to incorporate observationally-constrained measurements of gas-phase species from the NACHTT campaign and utilize a BLH dilution scheme to represent the emission rates of primary gas-phase species, without the need to ascribe scaling factors as in the case of emission rates derived from national emission inventories. The K_z parametrized in the PACT-1D model captured the development of an NBL on both nights during the 48-hour MP, with a more well-defined NBL forming during MP1 compared to MP2. This was a result of lower K_z values during MP1, which was influenced by low wind speeds (≤ 6 m/s) and a shallow mixing layer. During MP2, wind speed during the day reaches 15 m/s, which could have resulted in greater

uncertainties in K_z as the parametrization developed by Cao et al. (2016) was intended for application under stable boundary conditions. Modelled vertical temperature profiles were influenced by terrestrial radiation throughout the 48-hour MP, where strong temperature inversions were formed within 500 m, indicating the formation of an NBL on both nights during the 48-hour MP. The diurnal evolution of modelled ambient temperature was in excellent agreement with the observed ambient temperature, ranging from 268 – 285 K and 270 – 287 K, respectively.

Chapter III: Vertically-Resolved Measurements from The NACHTT Campaign

3.1. Introduction:

Given the importance of the ground surface as a reservoir for gas-phase HONO, identifying the missing source of HONO in the atmosphere requires an explicit understanding of the evolution of the vertical structure of HONO near the ground surface, a characterization of the boundary layer height, and defined meteorological profiles, which until recently were not attainable as high-resolution vertically-resolved studies were limited (Kleffmann et al., 2003; Tuite et al., 2021; Wong et al., 2011; Cesler-Maloney et al., 2024). In this thesis, the 1D model framework is based on measurements made in the 2011 Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) campaign, which was composed of 31 days that took place from 2011-02-15 to 2011-03-15 at the Boulder Atmospheric Observatory (BAO) – a rural field site in Erie, Colorado (40.050 N, 105.040 W, 1500 m) (Brown et al., 2013). A unique feature of the 2011 NACHTT campaign at the BAO is the rare use of high-resolution vertically resolved measurements mounted on a 300 m steel tower to study the vertical distribution of reactive gas-phase species, particulates, and micrometeorology near the ground surface (**Figure 3.1**).

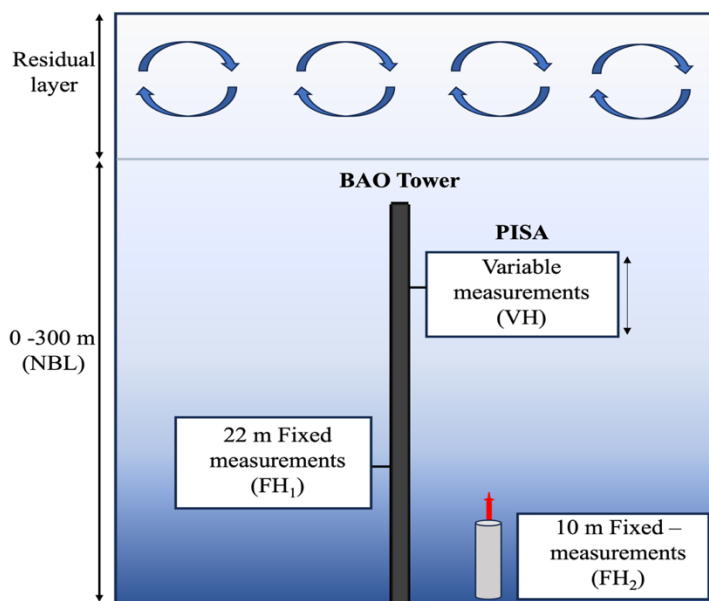


Figure 3.1. Schematic of the instrumentation setup during the 2011 NACHTT campaign, showcasing the expansive set of vertically-resolved (VH) measurements from the BAO tower and fixed measurements at 22 m (FH₁) and 10 m (FH₂) utilized.

The 2011 NACHTT campaign was the first campaign that introduced continuous high-time and high-vertically resolved measurements of gas-phase HONO, which when coupled with boundary layer dynamics was able to characterize chemical transformations of HONO that occurred during this wintertime study (VandenBoer et al., 2013). The diurnal trend of HONO from the NACHTT campaign was in agreement with known theory for urban through rural sites impacted by substantial anthropogenic NO_x emissions, in that mixing ratios of HONO accumulated during the night and were depleted by photolysis during the day (**Figure 3.2**).

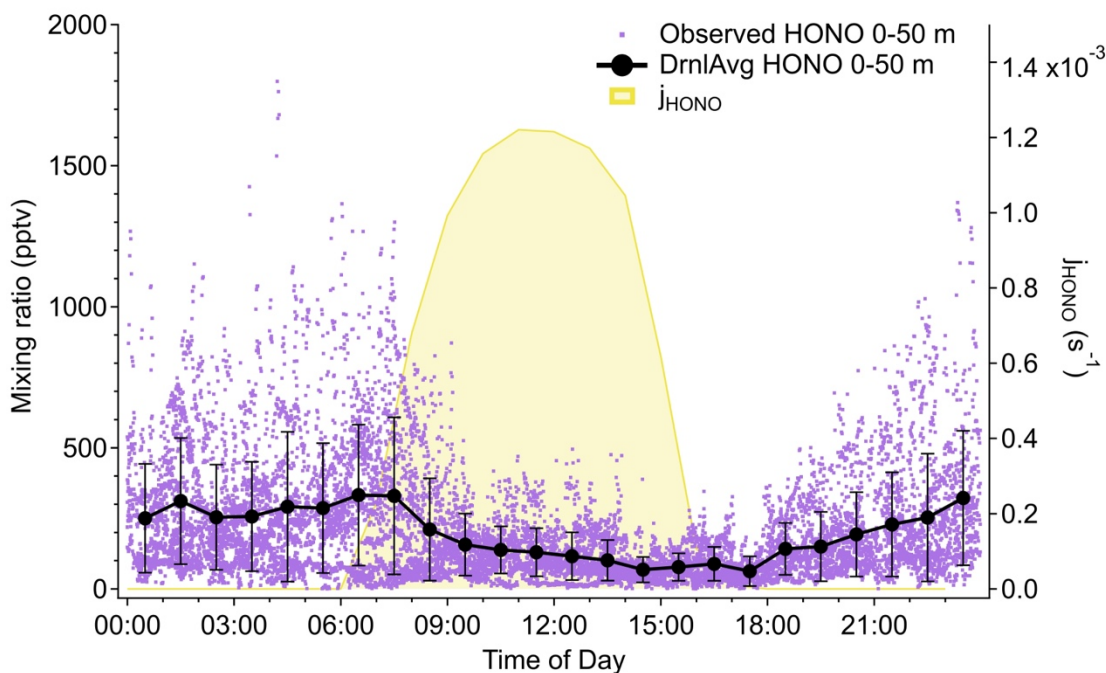


Figure 3.2. The diurnal trend of HONO from the entire NACHTT campaign (2011-02-15 to 2011-03-15) showing the measured mixing ratios of HONO (purple trace) and the 30 min averaged mixing ratios of HONO (black trace) at a height of 0-50 m AGL overlaid with the photolysis rate coefficient of HONO (yellow shaded area).

There were several objectives that were set with respect to the measurements of gas-phase HONO during the NACHTT campaign, including to evaluate the nocturnal heterogeneous sources and sinks of HONO, to understand the daytime production of HONO, and the potential for the ground surface to act as a nocturnal reservoir and a daytime source of HONO (VandenBoer et al., 2013). From this study, it was found that on nights that a stable NBL was formed, strong vertical gradients of HONO were observed within the NBL, which resulted in the accumulation and stratification of HONO near the ground surface. During the NACHTT campaign, the ground

surface dominated the heterogeneous production of HONO by the hydrolysis of NO₂ during the night, and loss of HONO by dry deposition on the ground surface was found to potentially account for 25 % to over 100 % of the unknown source of HONO required to match the observations made during the day. The variability in the ground surface production of HONO at night can be attributed to the relative magnitude of NO_x, the depth of the NBL, and the relative humidity at night. The dependency of RH on the production of HONO has been suggested in several field measurements, where the production of HONO was enhanced when RH increased above 60 % (Stutz et al., 2004; Wojtal et al., 2011; VandenBoer et al., 2013). To understand the observations of HONO from the NACHTT campaign, a 0D box model using observational constraints was produced that accounted for gas-phase chemistry of HONO, the heterogeneous production of HONO via NO₂ hydrolysis, and the heterogeneous loss of HONO via dry deposition. The heterogeneous processes were parameterized using an RH-dependent factor, in which the uptake coefficient of HONO was multiplied by a factor of RH/20 and the uptake coefficient of NO₂ was multiplied by a factor of RH/50. The 0D box model developed for the NACHTT campaign was able to reproduce the nighttime observations of gas-phase HONO within 30 %, with the greatest unknown source rate of 600 pptv hr⁻¹, which occurred during the early morning period of the NACHTT campaign. An important limitation in 0D box models is that they ignore the vertical diffusion mixing as it is only represented as a single box, given its focus is to solely focus on atmospheric chemistry. This limitation in 0D box models is attributed to the inability to capture the morning burst period of HONO, which was previously observed during the NACHTT campaign (VandenBoer et al., 2013). For gas-phase species that exhibit a negative vertical gradient profile (i.e. greater near the surface than aloft) like HONO, the addition of a dynamic vertical diffusion mixing term is critical in setting the correct vertical distribution of HONO in a diurnal period to study the surface chemistry. Another disadvantage in 0D box models is that the availability of case studies to select during the NACHTT campaign is only limited to stable atmospheres to minimize the influence of meteorology on the box model. The PACT-1D model framework in this thesis incorporated an explicit term for the vertical diffusion mixing coefficient during the NACHTT campaign, giving an opportunity to expand the number of possible days in which HONO chemistry can be constrained and studied. In this section, a 48-hour case study was selected that was under the influence of two varying vertical mixing regimes, in both stable and unstable atmospheric conditions, allowing an opportunity to constrain and compare the surface chemistry between both

periods – a key advantage of a 1D model. Vertically-resolved measurements of HONO and NO₂ at a height of 1 – 250 m were compared between the two 24-hour observation periods in order to evaluate the magnitude of several factors that control the heterogeneous production of HONO on the ground surface during the NACHTT campaign. Meteorological measurements, including wind speed, RH, and NBL heights were also utilized to characterize the atmospheric conditions between the two 24-hour observation periods. The 48-hour case study period from the NACHTT campaign will then be incorporated into a PACT-1D model framework that includes known gas-phase and heterogeneous chemistry of HONO (and an overview of the main gas-phase atmospheric mechanisms; RACM2), an explicit vertical diffusion mixing term, direct emissions, photolysis rate coefficients, and meteorology to determine how the 1D model matches with observed vertical gradients of HONO during the 48-hour case study.

3.2. Field Site Description and Instrumentation:

A detailed overview of the NACHTT campaign at the BAO, including its regional topography, and measurements made previously at Erie, Colorado are described in Brown et al. (2013). The NACHTT campaign at the BAO has three distinctive components in which measurements were made. The main sampling platform featured a motorized carriage (**Portable Instrument Shelter with Amenities, PISA**) which was mounted on a 300 m stainless-steel vertical tower that extended from an upper boundary of 270 m AGL to a lower boundary of 1 m AGL. For safety, the PISA unit was kept below 40 m when wind speeds exceeded 12 m/s throughout the NACHTT campaign (VandenBoer et al., 2013; Brown et al., 2013). The time taken for the PISA unit to reach the top of the tower and return to the ground (i.e. the total transect time) was less than 20 minutes. The quick total transect time of the carriage coupled with high time resolution (i.e. < 10 seconds) measurements allowed for the opportunity to study the evolution of vertically-resolved gas-phase species, particulates, and micrometeorology (**Table 3.1**).

The PISA unit housed several instruments including a meteorology station for the measurement of air temperature (°C), pressure (Pa), RH (%), wind speed (m/s), and wind direction (°), with a 10 second time resolution. For measuring the number size distributions of aerosols with diameter between 0.07 μm – 0.8 μm , a laser-based Ultra-High Sensitivity Aerosol Spectrometer (UHSAS) with a 1 second time resolution was used (Brock et al., 2012). To determine the composition of aerosols with diameter 0.07 μm – 0.8 μm during the NACHTT campaign, an

Aerosol Mass Spectrometer (AMS) was utilized with a 10 second time resolution (Bahreini et al., 2009). For the measurement of gas-phase species in the PISA unit, two chemical ionization mass spectrometers (CIMS) each with 10 second time resolutions were included for the quantitative measurement of gas-phase HCl, HBr, HONO, HNO₃, formate, and HNCO with a CH₃COO⁻ ionization source (Robert et al., 2010; Veres et al., 2008) and gas-phase ClNO₂, N₂O₅, and Cl₂ with an I⁻ ionization source (Riedel et al., 2012). A Cavity-ring down spectrometer (CRDS) was also utilized for the quantitative measurement of gas-phase NO, NO₂, O₃, NO₃, and N₂O₅ with a 1 second time resolution (Wagner et al., 2011). Another sampling platform at a fixed height of 22 m AGL was used for aerosol collection and as the point for air sample to be delivered to an instrument trailer positioned below the BAO tower with a tandem mist chamber used to measure inorganic and organic acids, including HCl, HNO₃, NH₃, HCOOH, CH₃COOH, and soluble bromide over 2 hour intervals via high-performance ion-chromatography (IC) (Keene et al., 2009). The ionic and elemental composition of size-resolved aerosols with diameter between 0.25 μm – 20 μm were also sampled on the elevated platform and collected with Whatman 41 cellulose filters in 12 hour intervals, where they were stored frozen and subsequently analyzed for 13 ions via IC at the University of Virginia (Young et al., 2013). Another sampling platform was positioned south of the BAO tower at a fixed height of 2 m to 10 m, where several trailers were housed for near surface-level measurements of Volatile Organic Compounds (VOCs), hydroxyl radicals (OH[•]), ozone (O₃), HCl, and photolysis rate coefficients of NO₂, NO₃, and O₃. There were two online and one offline techniques used to measure over 100 speciated VOCs during the NACHTT campaign, with inlets of the online techniques positioned at a height of 10 m. A Time-of-Flight Proton Transfer Reaction Mass Spectrometry (TOF-PTRMS) was used to mainly measure 14 aromatic and oxygenated VOCs with a high time resolution of 1 min. A suite of 43 speciated primary VOCs, including alkanes, alkenes, and aromatics were measured using an in-situ Gas-Chromatography Mass Spectrometry (GC/MS) instrument that sampled every 30 minutes with a 5 minute integration time per sample (Gillman et al., 2009). The offline technique included the collection of gas canisters every hour, where they were each analyzed by a GC/MS instrument at the University of New Hampshire for the detection and quantification of 82 speciated VOCs (Swarthout et al., 2013). In addition, a filter radiometer was used to measure the photolysis rate coefficients of NO₂, NO₃, and O₃ (Stark et al., 2007) at a height of 10 m AGL, while a CIMS instrument was used for the quantification of OH[•] during the NACHTT campaign with a time resolution of 10 minutes (Tanner

et al., 1997; Kim et al., 2013). Apart from measurements at NACHTT, auxiliary ground-based measurements near the BAO tower were used to estimate the BLH using a LIDAR ceilometer (Chapter 2, Section 2.3).

Table 3.1. Measurements used in the NACHTT campaign (Brown et al., 2013).

<i>Variable measurements on the PISA unit</i>			
Measurement	Method	Time resolution	Height resolution (m)
Meteorology	Weather Station on carriage	10 s	10 – 250
HONO, HNO ₃ , HCl, organic Acids	Chemical Ionization Mass spectrometer using acetate ion (CIMS)	0.1 Hz	10 – 250
NO ₂ , NO, NO ₃ , O ₃ , N ₂ O ₅	Cavity Ring-Down Spectrometer (CRDS)	0.1 Hz	10 – 250
Aerosol number and surface area*	Ultra-high sensitivity Aerosol Spectrometer (UHSAS)	1 s	10 – 250
<i>Fixed Sampling Platform at 10 m (FH₂)</i>			
VOCs (14 species)	Proton Transfer Reaction Mass spectrometry (PTR-MS)	1 min	10
VOCs (82 species)	Gas canister retrieval Gas Chromatography Mass Spectrometry (GC/MS)	1 hr	10
VOCs (43 species)	In-situ GC/MS	5 min	10
OH•	CIMS	10 min	10
Photolysis rate coefficients (jO ₃ , jNO ₂ , jNO ₃)	Radiometer	1 min	10
Meteorology	Weather station fixed at 10,100, and 300 m	1 min	10, 100, 300
<i>Auxiliary Observations from the BAO Tower</i>			
Ceilometer	Light Detection and Radar (LIDAR)	1 Hz	Ground

* Aerosol chemistry was not initialized in the PACT-1D model to reconcile observations from NACHTT campaign because heterogeneous production of HONO from aerosol chemistry was found to be negligible compared to the ground surface (VandenBoer et al., 2013).

3.3. Case Study Selection Criteria Justification:

To constrain the 1D model for a 48-hour case study, a selection criterion was used to determine the most suitable case study dates from the NACHTT campaign, using vertically-resolved mixing ratios of gas-phase HONO and NO₂ from 10 m to 250 m with a 10 s resolution that were collected from the BAO tower in Erie, Colorado. The criteria were chosen based on observing a sudden burst in concentrations of gas-phase HONO during the early morning (05:00-08:00 MST), evidence for formation of a stable NBL, minimizing the influence of plume transport (i.e. advection) into the box model by accounting for windspeeds ≤ 6 m/s, and data availability.

During the 2011 NACHTT campaign, there were a total of nine nights in which a stable NBL was formed within the vertical boundary of the BAO tower (i.e. within 300 m), including February 18-19, February 19-20, February 21-22, February 27-28, February 28 – March 1, March 1-2, March 2-3, March 4-5, and March 7-8. From these nine nights with an identifiable NBL, there were five nights when the mixing ratios of HONO were elevated to greater than 1 ppb, including February 19, 20, 28, and March 4 and 8 (VandenBoer et al., 2013). To maximize the PACT-1D model run time and to adhere to the selection criteria, the optimal case study date was defined as a 48-hour period from **February 18 17:00 MST to February 20 17:00 MST**.

To keep the nomenclature consistent with previous chapters, the first 24-hour period (February 18 17:00 MST to February 19 17:00 MST) shall be defined as **Observation Period I (OP1)**, while the second 24-hour period (February 19 17:00 MST to 20 17:00 MST) shall be defined as **Observation Period II (OP2)**. Both of these periods included nights with identifiable NBL and had HONO mixing ratios greater than 1 ppb. Due to limitations in data availability, wind speed measurements during OP1 followed the selection criteria with wind speeds found to be less than 6 m/s, while OP2 had instances during the daytime where the wind speed measurements exceeded 6 m/s. This gives an opportunity to study the nighttime surface chemistry of HONO under two meteorological conditions with varying vertical mixing dynamics.

3.4. Data Analysis:

For the purpose of this thesis, a curtain plot of the vertically-resolved measurements of gas-phase HONO and NO₂ are discussed, focusing on the 48-hour case study period as these species directly impacted the heterogeneous surface production and loss of gas-phase HONO (**Section 3.5**). To study the nighttime evolution of the vertical structure of each gas-phase species in more detail, vertically-resolved measurements of gas-phase HONO, NO₂, N₂O₅, NO₃, and O₃ with a 10 second time resolution collected during the 48-hour case study period were averaged to two-hour intervals. The two-hour mark was chosen to reduce stochasticity resulting from the physical movement of the motorized carriage and acts to combine three complete round trips from the motorized carriage to generate a representative vertical profile. Within each two-hour interval ($n = 720$), 10 second measurements were also vertically averaged at 10 m ($n = 25$) from 18:00 – 08:00 MST during OP1 and OP2 (**Section 3.6**). The spatial variability of gas-phase HONO, NO₂, and O₃ were assessed via a windrose plot in IGOR, using wind direction and wind speed as point coordinates color scaled with gas-phase mixing ratio of HONO, NO₂, and O₃ (**Appendix D**).

Vertically-resolved meteorology measurements of relative humidity (RH, %), dew point temperature (T_d , °C), air temperature (T_c , °C), wind speed (WS, m/s), potential temperature (θ , °C), and wind direction (WD, °) with a 10 second resolution were also collected from the NACHT campaign (**Table 3.1**) and averaged to two-hour bins similar to the vertical profiles of gas-phase species during the 48-hour case study period (**Appendix E**). The dew point temperature was calculated using the Weathermetrics package in R, using RH and air temperature. Given that air temperature profiles (and dew point) decrease towards the surface, we assumed that dew or frost formation occurred at intervals during the night when the difference in air and dew point temperature was less than 5 °C, as our lowest vertically-resolved measurement was at a height of 10 m. An assumption was made such that the lower boundary of vertically-resolved measurements at a height of 10 m were indicative of measurements at the ground surface.

To observe the depth of vertical mixing and turbulence within the boundary of the BAO tower throughout the 48-hour case study period, fixed wind speed measurements at heights of 10 m, 100 m, and 300 m were plotted with the 2-hour averaged estimation of the Nocturnal Boundary Layer (NBL) height, and ground-level RH (**Section 3.5**). Photolysis rate coefficients of HONO (j_{HONO})

were determined using an observationally constrained parametrization that linearly combines the observed photolysis rate coefficients of NO₂ and O₃ from the radiometer on the 10 m sampling platform (**Equation 3.1**). This parametrization of j_{HONO} was developed in Pasadena, California during the 2010 CalNex campaign and showed excellent agreement ($R^2 > 0.999$) with the TUV calculated j_{HONO} made during this campaign (VandenBoer et al. 2013; VandenBoer et al., 2014; Young et al., 2013).

$$j_{HONO} = (j_{NO_2} \cdot 0.1931 \pm 0.0002) + (j_{O_3} \cdot 2.50 \pm 0.07) \quad (Eq. 3.1)$$

where j_{HONO} is the calculated photolysis rate coefficient of HONO in s⁻¹, j_{NO_2} is the observed photolysis rate coefficient of NO₂, and j_{O_3} is the observed photolysis rate coefficient of O₃ in s⁻¹.

The **Nocturnal Boundary Layer (NBL)** was defined at a height where negligible change was observed with the potential temperature and O₃ profiles during the 48-hour case study period of the NACHTT campaign (VandenBoer et al., 2013, Brown et al., 2013; Fuchs et al., 1970). The decrease in the concentration profile of O₃ from the reaction with NO_x at the surface, coupled with the decrease in the potential temperature at the inversion of the NBL allowed an excellent estimation of the NBL height during the 48-hour case study period of the NACHTT campaign (**Appendix F**). Aerosol backscatter gradient estimations of the BL height via the LIDAR ceilometer were not utilized in this chapter for the determination of the NBL height as this method overestimated the NBL height during both nights of the 48-hour case study period. With the formation of a stable NBL when air (including aerosol) is vertically stratified, the identification of the NBL height can become a challenge for the BL-View software as multiple aerosol gradients can arise (Caicedo et al., 2017; Haman et al., 2012). The BL-View software was kept at default settings with the maximum observable BL height defined at 2500 m, which suggests that during the transition from a PBL to an NBL, the BL-View software utilized an upper boundary aerosol gradient that is not representative of the true NBL height. The aerosol backscatter gradient method can also lead to stochastic measurements of the BL height when calculated using shorter timeframes, as the evaluation of this method is typically based on months of data acquisition from field measurement campaigns to more broadly characterize the mixing climatology (Caicedo et al., 2017; Pandolfi et al., 2013; Haman et al., 2012).

3.5. The Spatial and Temporal Variability of HONO, NO₂, and Meteorology During the 48-Hour Case Study Period of the NACHTT Campaign

To constrain the PACT-1D model, a 48-hour case study was selected based on a selection criteria that prioritizes a sudden increase in the levels of HONO during the early morning, detection of a stable NBL, wind speeds ≤ 6 m/s, and data availability. The spatial and temporal evolution of gas-phase HONO, NO₂, and local meteorology that influence vertical mixing are discussed as these variables will have a direct impact on surface production and loss of gas-phase HONO during the 48-hour case study (**Figure 3.1**). During both OP1 (February 18 17:00 MST to February 19 17:00 MST) and OP2 (February 19 17:00 MST to February 20 17:00 MST), a stable NBL was formed during the night and included elevated nighttime mixing ratios of HONO (> 1 ppb), with early morning (05:00-08:00 MST) elevated mixing ratios of HONO only observed on OP1. There were differences in meteorology between OP1 and OP2, which gives an additional opportunity to study the impact of two varying vertical mixing regimes on the applicability of the parameterized nighttime surface chemistry of HONO, which was restricted only to stable conditions in the original analysis of this field dataset (VandenBoer et al., 2013). A time series showcasing the diurnal evolution of meteorological variables, including wind speed measurements at fixed heights of 10, 100, and 300 m, RH at 10 m, photolysis rate coefficient of HONO, and the two-hour binned averages of the NBL height during the 48-hour case study are shown in **Figure 3.3 A**. During the evening to early morning of OP1 (18:00 – 06:00 MST), wind speeds were lower at 10 m and 100 m ranging from 1-6 m/s) and greater at 300 m (3-10 m/s). RH measurements at the fixed height of 10 m increased gradually from 26 % at the start of the evening to peak of 76 % during the early morning. As the evening progressed, the NBL height was relatively constant near 120 m, growing to 210 m later in the night, and at sunrise before being broken up by the formation of the PBL the following day. The two-hour binned averages of NBL height were determined as 110 m, 130 m, 110 m, 90 m, 140 m, and 210 m, respectively. Given that the NBL height formed under stable atmospheric conditions when wind speeds ≤ 6 m/s, wind speed measurements at 10 m and 100 m were both supportive of winds speeds within the NBL. Above the NBL height at 300 m, wind speed lied in the residual layer, which is characterized by greater turbulence that is produced from wind shear. During morning to evening of OP1 (06:00-17:00 MST), wind speed measurements at all heights converge to between 1-3 m/s and RH steadily decreases, which is indicative of a transition into the convective PBL. The relatively low wind speeds during the daytime could be

attributed to a weak pressure gradient force gathered from synoptic-scale pressure gradients, resulting in negligible winds (i.e. horizontal advection) during the day of OP1. During the evening to early morning of OP2 (18:00 – 03:00 MST), a sudden increase in RH was observed from 31 % to 82 % as wind speeds at all heights diverged, indicating the formation of a stratified stable NBL. The sudden increase in RH could be attributed to the increase in the dew point temperature from -4 °C to 5 °C as the air temperature decreases from 10 °C to 4 °C (**Figure 3.3, A**). Wind speed measurements at a height 10 m and 100 m were found to be lower (1-8 m/s), while wind speed measurements at 300 m were found to be much greater (1-15 m/s) during this period. Similar to OP1, this indicates that the wind speeds at 10 m and 100 m are weaker as they are found within the NBL, while wind speeds at 300 m are greater and representative of the residual layer. The average depth of the NBL in OP2 was smaller than OP1, where its duration was shorter-lived, with two-hour binned averages of 60 m, 130 m, 130 m, 130 m, and 210 m over the evolution of the night, respectively. The NBL was broken up at 03:00 MST on OP2, as wind speed measurements at all heights increased by 5 m/s, reaching a maximum of 25 m/s at a height of 300 m by 09:00 MST.

From the vertically-resolved two-hour binned profiles of temperature and dew point during the 48-hour case study period, it was determined that OP1 experienced sub-zero temperatures (range: -4 °C to 10 °C) with a frost event likely occurring between 04:00-06:00 MST near the ground, while OP2 experienced warmer temperatures (range: 4 °C to 12 °C) with a dew event likely occurring between 20:00-00:00 MST near the ground (**Appendix E**).

The diurnal evolution of vertically-resolved mixing ratios of HONO and NO₂ at a height of 1 m to 250 m AGL are shown for the 48-hour case study period, with clear differences at night between OP1 and OP2 (**Figure 3.3, B and C**). These differences can be attributed to the degree of vertical mixing and NBL depth, local NO_x point sources generating plumes aloft, the magnitude of NO_x emissions at the ground surface, and RH near the ground. Throughout the 48-hour case study period, the vertical gradients of gas-phase HONO follows that of gas-phase NO₂, increasing near the ground surface and accumulating under the formation of a NBL until being lost due to photolysis or dilution and advection by high winds in the case of OP1 and OP2, respectively. It was also observed during both nights that the maximum mixing ratio of HONO is reached at the

same time interval when RH at 10 m reaches a maximum. The mixing ratio of HONO was greater near the ground surface of the BAO tower than aloft at all times of the 48-hour case study period, which is consistent with previous field studies that ground surfaces are the dominant source of gas-phase HONO from heterogeneous uptake of NO₂ on surface adsorbed water (Villena et al., 2011; Zhang et al., 2009; Wong et al., 2011; VandenBoer et al., 2013; Tuite et al., 2021).

During the evening of OP1 (18:00-03:00 MST), there is a plume of NO₂ residing in the NBL between 18:00-21:00 MST, with roughly 35 ppb near the ground surface reaching to about 20 ppb aloft that results in an increase of HONO vertical gradients below 50 m AGL with an average mixing ratio of 400 ppt (range: 50 – 650 ppt). Later, from 03:00-06:00 MST in OP1, a strong plume of gas-phase NO₂ transects the BAO tower, again extending to the top of the NBL, but disconnected from NO₂ detected near the surface. At the same time, a strong negative vertical gradient of HONO is observed from the top of the NBL to the ground surface with an average mixing ratio of 1500 ppt (range: 600 – 2016 ppt) below 50 m AGL. From the windrose plots of OP1 when wind speeds were less than 6 m/s during the night, mixing ratios of HONO and NO₂ were found to be arising from the origin (i.e. near the measurement site), which suggests these plumes are originating from natural gas or coal-fired powerplants and surround the measurement site (**Appendix D**). In either case, the plumes aloft were not mixing readily to the surface, as would be expected within a stable NBL. Given that the purpose of the PACT-1D model investigation here is to study the surface level production and loss processes of gas-phase HONO by accounting for vertical mixing, the NO_x and HONO containing plume aloft in OP1 is ignored as we aim to reproduce and explain the observations near the surface and know that the plume is not being entrained, but rather advects away from the site by sunrise. During the morning of OP1 (06:00-09:00 MST), vertical gradients of gas-phase HONO and NO₂ decreased within the 250 m vertical column as photolysis became the dominant loss pathway. Below 50 m AGL, we observe that negative profiles of HONO and NO₂ are still present well after the onset of photolysis with mixing ratios reaching 1300 ppt and 18 ppb by 7:30 MST, respectively. Previously, this observation could not be explained by the 0D box model used by VandenBoer et al. (2013), as daytime surface HONO sources were only just definitively identified in that study and a suitable 1D model did not exist. As such, these unusual HONO distribution features could not be extensively interrogated. Two explanations were possible, but remain outstanding to be tested. First, this morning burst of

gas-phase HONO could be attributed to suppressed vertical mixing near the ground surface, delaying the vertical transport HONO and NO₂ from near the ground surface, and thereby maintaining surface-level mixing ratios of HONO built up at night. The potential for surface frost formation is consistent with this potential explanation. Second, a strong surface source of HONO could become active in the morning, releasing HONO into the overlying air and perturbing the oxidative capacity of the surface layer as it photolyzes. The explicit mixing captured in the 1D model allows these two explanations to be explicitly tested, which will be explored in Chapter IV by focusing on model case studies during the 48-hour MP with different surface source routines of HONO.

During the evening of OP2 (18:00 – 03:00 MST), weaker vertical gradients of NO₂ were observed with average mixing ratios of 10 ppb (range 3 – 20 ppb) as there were no NO₂ plumes that intersected the BAO tower, given a shift in wind direction and wind speed arising from a storm system southeast of the BAO tower (**Appendix D**). During the same timeframe, strong vertical gradients of HONO were observed below 50 m with an average mixing ratio of 650 pptv (range: 350-1500 pptv), which suggests that HONO was accumulating near the ground under the formation of a stable NBL. From 03:00 MST – 17:00 MST of OP2, the mixing ratio of HONO and NO₂ decreased rapidly due to wind speeds ≥ 6 m/s near the ground surface, resulting in the loss of HONO and NO₂ by horizontal advection.

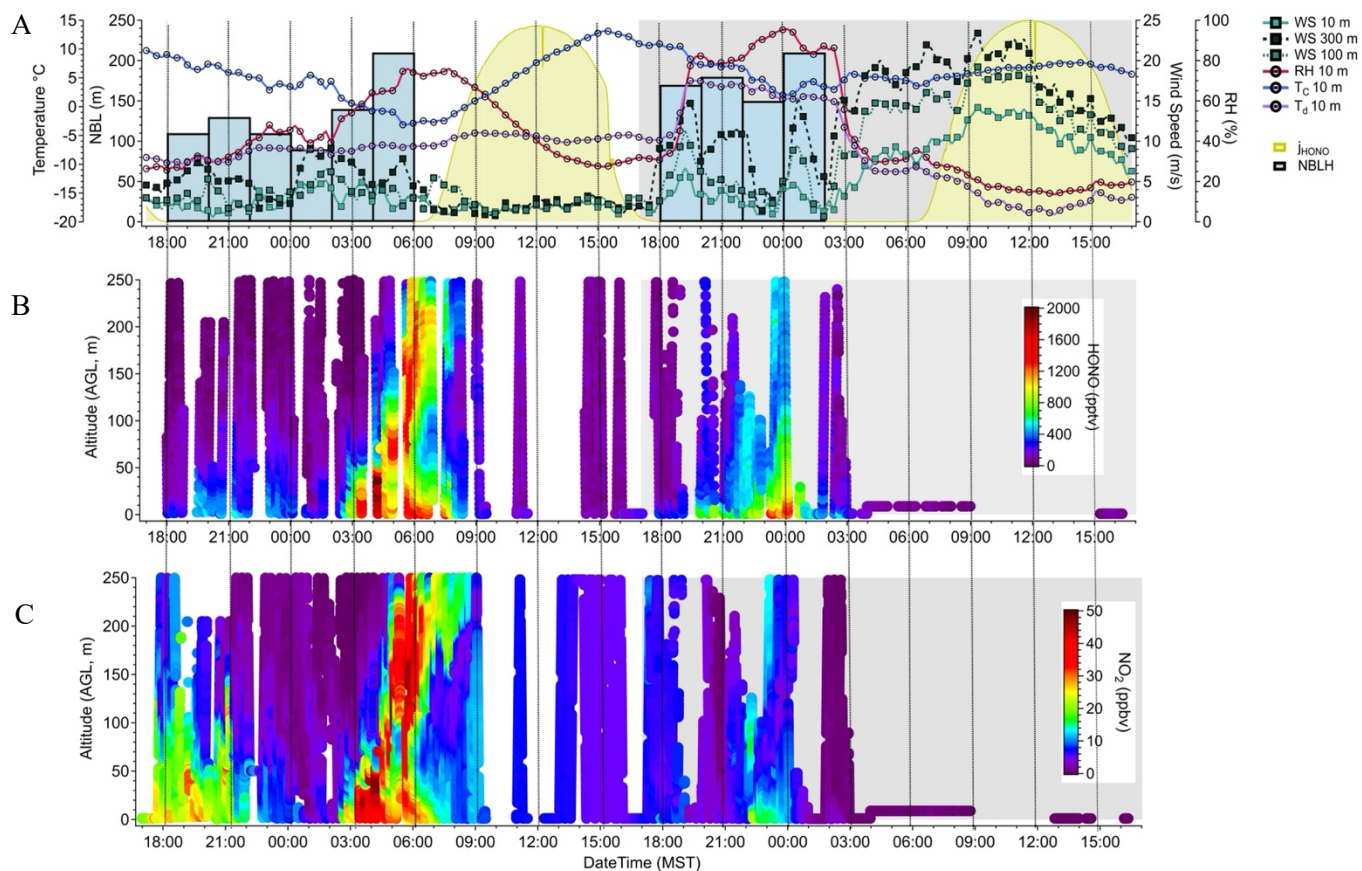


Figure 3.3. (A) Time series of meteorological variables that represent the degree of mixing (i.e. turbulence) within the lower troposphere, including fixed wind speed (right y-axis, m/s) measurements at a height of 10 m (square, light green trace), 100 m (square, dark green trace), and 300 m (square, black trace) from the BAO tower, fixed RH at a height of 10 m (circle, red trace), air (blue trace) and dewpoint (purple trace) temperature, and photolysis rate coefficients of NO₂ and O₃ from 10 m radiometer used to estimate the photolysis rate coefficient of HONO (shaded in yellow) during the NACHTT campaign (VandenBoer et al., 2013). The two hour binned estimates of the NBL height (blue bars) are also included for both nights of the 48-hour MP using potential temperature and O₃ profiles as indicators (Appendix C). (B) Vertically-resolved measurements of HONO (pptv) from 10 m to 250 m AGL, with mixing ratios changing from low (purple, sub -pptv) to high (red, >1200 pptv) and a 10 second time resolution during the 48-hour MP. (C) Vertically-resolved measurements of NO₂ (ppbv) from 10 m to 250 m AGL, with mixing ratios changing from low (purple, sub -ppbv) to high (red, > 30 pptv). On all panels, the grey shaded indicates the start of MP2.

3.6. Nocturnal Observations of HONO and NO₂ During The 48-Hour Case Study Period of The NACHTT Campaign

In order to study the nighttime evolution of gas-phase HONO and NO₂ and to contrast between vertical gradients within and above the NBL, vertically-resolved measurements of gas-phase HONO and NO₂ at a height of 10 m to 250 m were binned in two-hour averages and overlaid with the NBL height for both OP1 (**Figure 3.4**) and OP2 (**Figure 3.5**).

Based on the observations in OP1, it was found that the average mixing ratios of gas-phase HONO increased below 50 m AGL for all bins with an identifiable NBL height, changing from 400 ppt, 450 ppt, 480 ppt, 350 ppt, 850 ppt, and 1400 ppt during the time evolution of the night from 18:00 – 08:00 MST, respectively (**Figure 3.4**). For gas-phase NO₂ below 50 m, the average mixing ratio was more varied during the two hour binned time evolution of the night changing from 25 ppb, 18 ppb, 8 ppb, 6 ppb, 25 ppb, 30 ppb, and 20 ppb, respectively. Higher mixing ratios of surface-level HONO in OP1 can be attributed to an increase in the mixing ratio of NO₂. For the first four bins (18:00-02:00 MST), vertical gradients of HONO and NO₂ within the NBL approached a steady-state plateau due to limited vertical mixing, low availability of NO₂ and deposition loss of HONO. For the fifth and sixth bins (02:00-06:00 MST), a strong local source of NO₂ was present at the ground surface and trapped within the NBL, leading to strong vertical gradients of HONO being produced. During these periods, the sudden increase in HONO near the ground surface can be reasonably attributed to the heterogeneous production of HONO from the uptake of NO₂, increased availability of NO₂, and the enhancement of HONO under the formation of a NBL. For the last bin (06:00-08:00 MST), the photolytic loss of HONO and NO₂ dominates during the early morning as the NBL breaks up, leading to decreased quantities above 100 m AGL. But below 100 m AGL, the average mixing ratios of HONO and NO₂ did not change drastically. This might be attributed to vertical mixing suppression caused by low wind speeds and the potential for frost formation (**Appendix E**). The formation of frost on the ground surface acts as a thermal inversion reservoir where it has the potential to trap pollutants near the ground surface during the time required for solar heating to melt and/or evaporate the ice, resulting in the delay of the upward transport of surface-level HONO and NO₂.

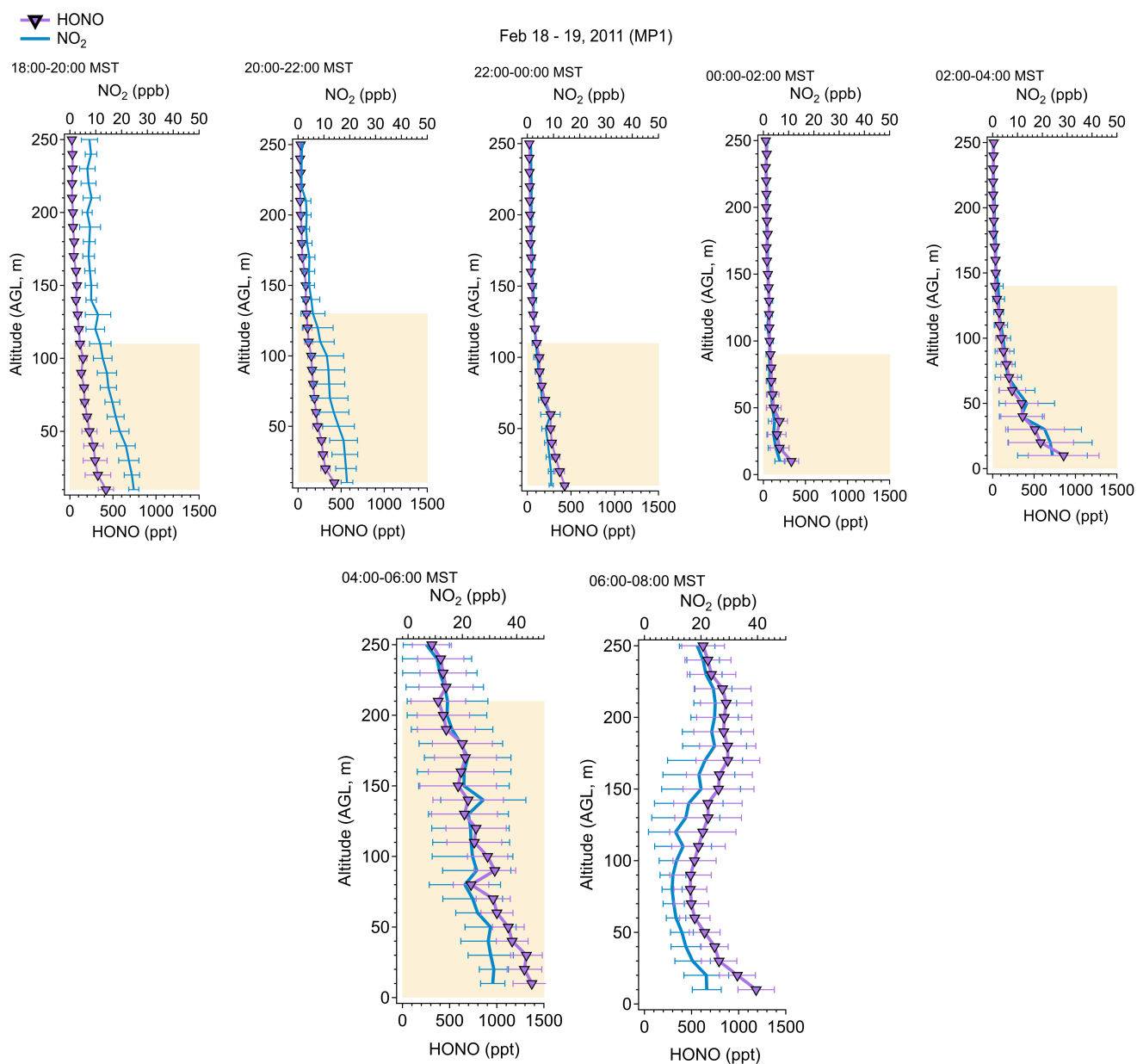


Figure 3.4. Two-hour binned average vertical profiles of HONO (purple, bottom x-axis, ppt) and NO₂ (blue, top x-axis, ppb) gathered from 10 m to 250 m AGL between 18:00 – 08:00 MST of OP1.

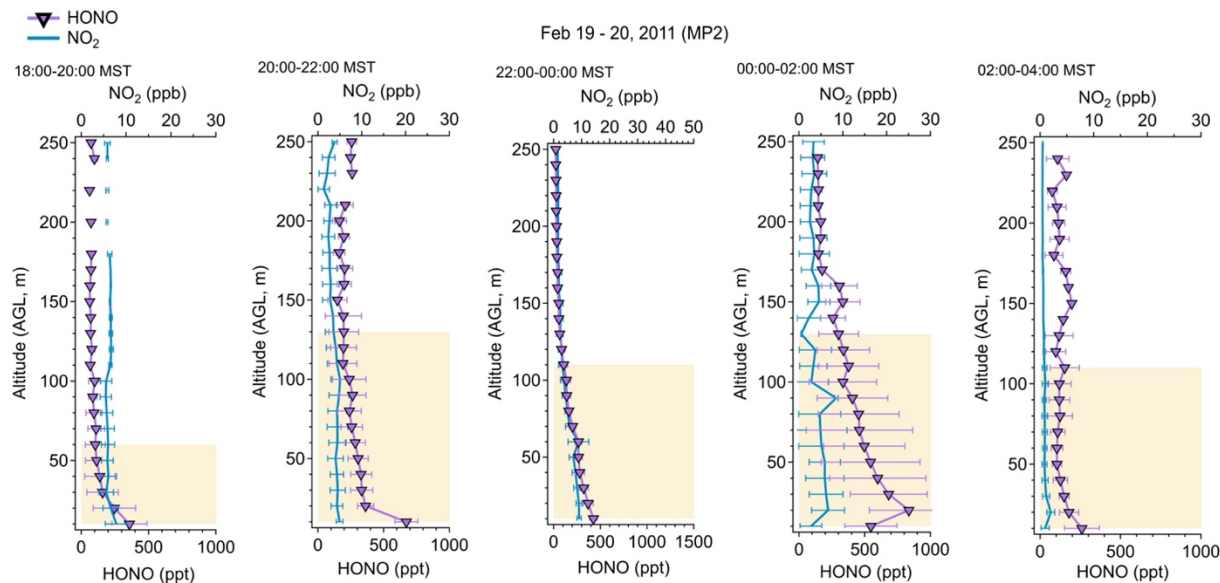


Figure 3.5. Two-hour binned average vertical profiles of HONO (purple, bottom x-axis, ppt) and NO₂ (blue, top x-axis, ppb) gathered from 10 m to 250 m AGL between 18:00 – 04:00 MST of OP2.

Based on the observations of OP2, it was found that HONO vertical profiles have strong vertical gradients within the NBL, with 2 hour interval mixing ratios below 50 m of 350 ppt, 685 ppt, 400 ppt, 850 ppt, and 385 ppt, respectively (**Figure 3.5**). Given these trends for surface-level mixing ratios of HONO and NO₂, it was found that during the nighttime evolution of OP2, both gas-phase HONO and NO₂ decreased near the ground due to dry deposition or by dilution through upward vertical transport. The only increase in the evolution of surface-level HONO occurs at the second bin (20:00-22:00 MST), where mixing ratios of HONO increases due to an increase in the depth of the NBL and the heterogeneous production of HONO from the ground uptake of NO₂. This highlights the importance that the availability of NO₂ near the surface is critical in the heterogeneous production of HONO, which is dominated by NO₂ hydrolysis.

3.7. The Importance of Vertical Mixing in Modelling Applications of HONO

The normalized number density was compared between observed HONO and the modelled HONO representing the hourly average integrated photolytic loss of HONO during the early morning (06:00 – 012:00 MST) of OP1 (**Section 3.6**). To determine the starting point for the integration of the modelled HONO ($t_0 = 1.95 \times 10^{10} \text{ molecules cm}^{-3} \text{ s}^{-1}$), the observed number density of HONO was filtered to a height of 0 – 50 m and averaged to a 15 minute time resolution

during sunrise between 06:45 MST to 07:00 MST. For each timestep, the number density of HONO was subtracted by the product of the measured hourly photolysis rate coefficient and the observed hourly number density of HONO (**Equation 3.2**). The observed hourly number density between 10:00 – 12:00 MST was missing due to the maintenance of the instruments in the PISA unit during the daytime, but we would expect that the normalized number densities between observations and the model at these timeframes to converge. The equation for the integrated photolytic loss of HONO was gathered from the 0D box modelling parametrization made during the 2011 NACHTT campaign (VandenBoer et al., 2013).

$$HONO_{model} = n_{(HONO,t=0)} - j_{HONO}[n_{HONO,obs}] \quad (Eq. 3.2)$$

where $HONO_{model}$ is the hourly average HONO quantity that changes only due to the integrated photolytic loss of HONO in molecules $\text{cm}^{-3} \text{ s}^{-1}$, $n_{(HONO,t=0)}$ is the average number density of HONO between 06:45 – 07:00 MST in molecule $\text{cm}^{-3} \text{ s}^{-1}$, j_{HONO} is the photolysis rate coefficient of HONO in s^{-1} , and $n_{HONO,obs}$ is the observed hourly number density of HONO in molecules $\text{cm}^{-3} \text{ s}^{-1}$.

For gas-phase species that exhibit a negative gradient profile such as HONO, it is important for models to include a parametrization that accounts for vertical diffusion mixing so that observations are accurately represented as it sets an appropriate vertical distribution of HONO thereby controlling the capacity in which heterogeneous chemistry on the ground can take place. The addition of a vertical diffusion mixing term becomes especially important during the early morning period, where a transition from a NBL to a convective PBL experiences the greatest change in vertical mixing. As depicted in **Figure 3.6**, the observed normalized number density of HONO was greater than the 0D modelled HONO term during the early morning when photolysis is known to be the dominant loss pathway. Given that the addition of a dynamic vertical diffusion mixing term is critical in setting the correct vertical distribution for surface chemistry of HONO to occur, the deviance between the two traces highlights the importance of including a vertical diffusion mixing parameter, which can only be incorporated in 1D models (**Figure 3.6**). For winter period measurements of HONO under stable atmospheric conditions, such as the early morning of OP1 from the NACHTT campaign, vertical mixing suppression could also lead to the enhancement

of gas-phase HONO. A 0D box model study of gas-phase HONO during the NACHTT campaign found that the greatest underestimations (4.6×10^6 molecules $\text{cm}^{-3} \text{ s}^{-1}$, 600 ppt hr^{-1}) between their model and observations occurred during the early morning (VandenBoer et al., 2013). Another 1D modelling study of HONO by Wong et al. (2011), found that the dominant source of HONO above 100 m was due to vertical transport, which highlights the importance of the role of vertical mixing in transporting newly formed HONO aloft, especially during the early morning. There have been numerous heterogeneous production mechanisms that have been proposed in 0D box models to explain the discrepancy between daytime field observations and the PSS of HONO, apart from the well-known hydrolysis of NO_2 (**Chapter I, section 1.4**). We argue that this discrepancy between daytime field observations and the Photostationary state (PSS) of HONO during the NACHTT campaign cannot be accurately compared as the coupling of chemistry with physical phenomenon such as vertical diffusion mixing is not accounted for in 0D box models.

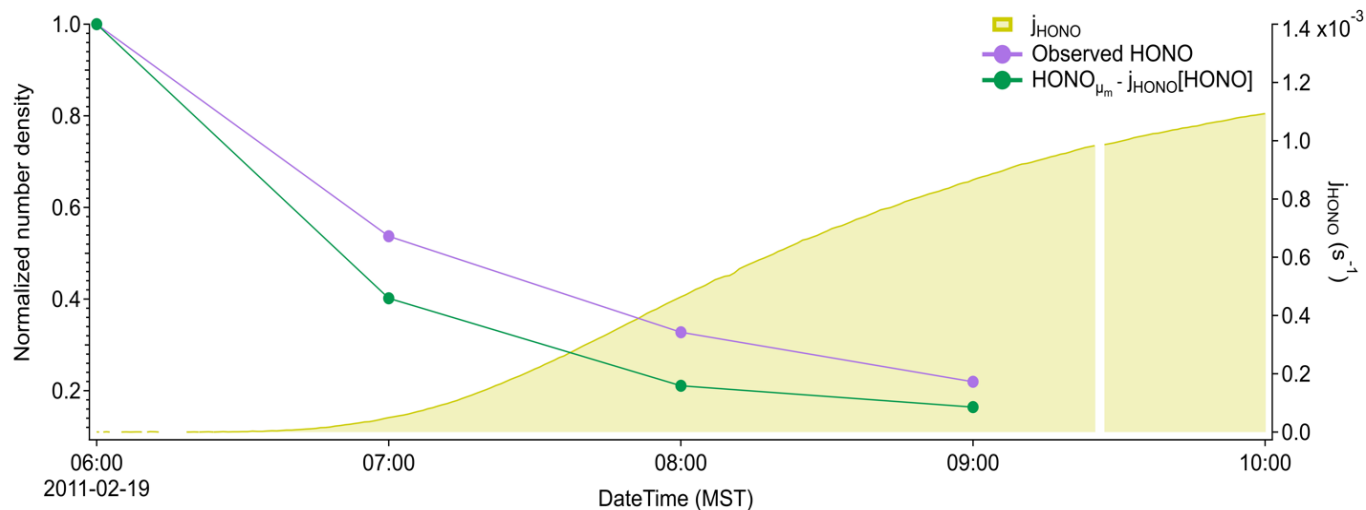


Figure 3.6. The normalized number density of observed HONO (purple trace) and modelled HONO (green trace) overlaid with the photolysis rate coefficient of HONO (yellow shaded area) depicted during the morning period of MP1 (06:00-10:00 MST).

3.8. Conclusion

The purpose of this section was to select a 48-hour period during the NACHTT campaign that was based on a selection criteria that prioritizes a sudden burst in the levels of HONO during the early morning, formation of a NBL, wind speeds ≤ 6 m/s, and data availability. Vertically-resolved measurements of HONO and NO₂ at a height of 1-250 m were characterized by negative gradient profiles during both OP1 and OP2, suggesting that the ground surface was the dominant nocturnal source and sink of HONO. The variability of HONO between the two observation periods can be attributed to the magnitude of NO_x either emitted on the ground or aloft via emission stacks from power plumes, the presence and depth of the NBL, and the time interval in which RH increases above 60 %. There were also differences in temperature between the two periods, where sub-zero temperatures (-5 to 12 °C) were observed during OP1, while temperatures (1 to 14 °C) during OP2 were warmer and above zero. The morning burst of HONO was only observed during OP1 as vertical mixing suppression were characterized by low wind speeds of 1-3 m/s during the day of OP1, which delayed the vertical transport of HONO and NO₂ on the ground, allowing a strong surface source of HONO to become active in the morning and get depleted by the onset of photolysis. The delay in the modelled vertical transport of HONO and NO₂ during the morning of OP1 was also supported by the potential formation of frost on the ground from observations of surface-level dew point and ambient temperature. In the next section, we will be testing the output of the BASE model after applying all the necessary chemical and physical parametrizations using observational constraints from the PACT-1D framework to reconcile the observations of 20 gas-phase species initialized, with a focus on gas-phase HONO. In order to test the relative contribution of heterogeneous ground mechanisms of gas-phase HONO and the importance of the ground surface as a dominant nocturnal source, three model outputs with varying surface source routines of HONO will be compared to observations during the 48-hour case study period.

Chapter IV: Case Studies in PACT-1D to Understand HONO Surface Sources During the NACHTT Campaign

4.1. Definitions of Output Model Runs and Configurations

This study was undertaken to produce a 1D transport model that takes into account the vertical diffusion mixing and current understanding of all the individual processes pertaining to the production and loss of HONO, with an emphasis on exploring the importance of HONO production and loss from heterogeneous ground surface mechanisms. To explore the dynamics between defined HONO surface sources (**Chapter II, section 2.7**) and vertical mixing parametrizations on the vertical gradient of HONO, we produced three PACT-1D model outputs and defined their names and model configurations in **Table 4.1**. Each model produced will have identical configurations for every component in PACT-1D (i.e. vertical mixing diffusion, meteorology, initial concentrations, photolysis rate coefficients, and emissions; Chapter II), but will differ in surface source routines.

Beginning with the most simplified chemical box model framework made in PACT-1D, ground surface routines were turned off in the No Ground Surface Source (**NO_GSS**) model, where the concentration of HONO near the ground can be attributed to net loss from homogeneous gas-phase chemistry, loss of HONO on the ground by vertical transport, and HONO production from direct emissions (**Equation 4.1**). The purpose of the NO_GSS model was to highlight that the ground surface dominates the nocturnal heterogeneous production of HONO by hydrolysis of NO₂ and to evaluate the relative contribution of direct emissions on the total nighttime budget of HONO during the 48-hour MP of the NACHTT campaign.

$$\frac{d[HONO]}{dt}_{50\text{ m}} = P_{gas,net} + P_E - P_{VT} \quad (Eq\ 4.1)$$

where $P_{gas,net}$ is the net contribution from all gas phase mechanisms, including the photolysis of HONO, formation of HONO by NO reacting with OH, and loss of HONO by reaction with OH. Hourly emission rates of HONO (P_E) and loss of HONO by vertical transport above 50 m AGL (P_{VT}) are additional source and sink terms, respectively.

As already described in detail in Chapter II, the production and loss terms of HONO below 50 in the **BASE** model have been described in **Equation 4.2** (VandenBoer et al., 2013).

$$\frac{d[HONO]}{dt}_{50\text{ m}} = P_{gas,net} + P_E - P_{VT} + \frac{1}{8}\gamma_{NO_2,grd}\bar{C}_{NO_2} - \frac{1}{4}\gamma_{HONO,grd}\bar{C}_{HONO} \quad (Eq\ 4.2)$$

The BASE_WET model extends on the chemical model framework of the BASE model by applying an *RH* factor to the heterogenous production and loss terms of HONO via the hydrolysis of NO₂ and dry deposition of HONO, respectively (**Equation 4.3**).

$$\frac{d[HONO]}{dt}_{50\text{ m}} = P_{gas,net} + P_E - P_{VT} + \frac{1}{8}\gamma_{NO_2,grd}\left(\frac{RH}{50}\right)\bar{C}_{NO_2} - \frac{1}{4}\gamma_{HONO,grd}\left(\frac{RH}{20}\right)\bar{C}_{HONO} \quad (Eq\ 4.3)$$

The last two terms in **Equation 4.2 and 4.3** describe the heterogeneous ground surface parametrizations for the production of gas-phase HONO via NO₂ hydrolysis and loss by dry deposition. Where $\gamma_{HONO,grd}$ ($= 7.3 \times 10^{-5}$) and $\gamma_{NO_2,ground}$ ($= 8 \times 10^{-6}$) are the unitless observationally-constrained reactive uptake coefficients of HONO and NO₂, respectively, and $\bar{C}_{HONO}$ and $\bar{C}_{NO_2}$ are the mean molecular speed of HONO and NO₂ in m/s. These ground surface sources and sinks are dependent on the deposition rate of NO₂ and HONO, which are described in detail in Chapter II, Section 2.7. In **Equation 4.3**, an *RH*-dependent factor of *RH*/50 and *RH*/20 was multiplied with the ground reactive uptake coefficient of NO₂ and HONO, respectively.

The *RH* dependency on the production of HONO has been suggested in the analysis of several field measurements, where the production of HONO was enhanced when *RH* increased above 60 % and soil water content decreased (Stutz et al., 2004; Wojtal et al., 2011; VandenBoer et al., 2013). In the 0D box model study from the NACHTT campaign, it was determined that when the heterogeneous production and loss terms of HONO included an *RH*-dependent factor, the early morning period was better matched with observations. Even with a more realistic chemical box model to represent the surface chemistry of water, the BASE_WET chemical model in a 0D framework was still not able to reproduce the early morning burst of HONO as vertical diffusion mixing and unknown chemical mechanisms at the time were not accounted for. In this thesis, we highlight that the selection of a 1D box for modelling applications of HONO is critical in setting

the correct framework for the vertical distribution of HONO, as this can identify whether additional surface sources are required to explain the observed HONO levels during this period of the day.

Table 4.1. List of PACT-1D model output names used in this study and their definitions.

Model Name	Configuration
BASE	Model configuration discussed in Chapter 2.
NO_GSS (No Ground Surface Source)	Same as BASE model except ground surface source routines of HONO are turned off.
BASE_WET	Same as BASE model except ground surface routines of HONO are defined using <i>RH</i> -dependent parametrizations from VandenBoer et al. (2013).

4.2. Validation of BASE Model: Comparing BASE Model Output of Reactive Nitrogen Species, VOCs, and O₃ with Observations

In this study, the output of the BASE model from PACT-1D was compared to both vertically-resolved (1 – 250 m) and ground-level observations to validate all the chemical and physical parametrizations, with an emphasis on HONO surface source parametrizations. Given the negative vertical gradient in the concentration profile of HONO in the troposphere and the importance of the ground surface as a source of HONO, the BASE model was used to set an initial condition on the formation and loss processes of HONO within the lowest atmospheric layers, using heterogeneous chemistry at the ground surface in addition to the known homogeneous gas phase chemistry (See Chapter 2.7). Time series of modelled mixing ratios of reactive nitrogen species (N_r = HONO, NO₂, NO, NO₃, N₂O₅, and HNO₃), ozone (O₃), and hydroxyl radical (OH•) at heights of 1, 10, and 50 m were compared to the available vertically-resolved measurements from the BAO tower and binned to a height up to 50 m AGL, with the exception of the modelled mixing ratio of OH•, which was only gathered at a height of 10 m (**Figures 4.1 and 4.2; Appendix H1 and H2**). The modelled mixing ratios of all 15 VOCs, including C₂-C₈ alkanes, benzene, toluene, formaldehyde, methyl ethyl ketone, acetaldehyde, acetic acid, methanol, acetone, and ethene, were also compared to ground-based measurements constrained to 1 m AGL (**Appendix H3-H6**).

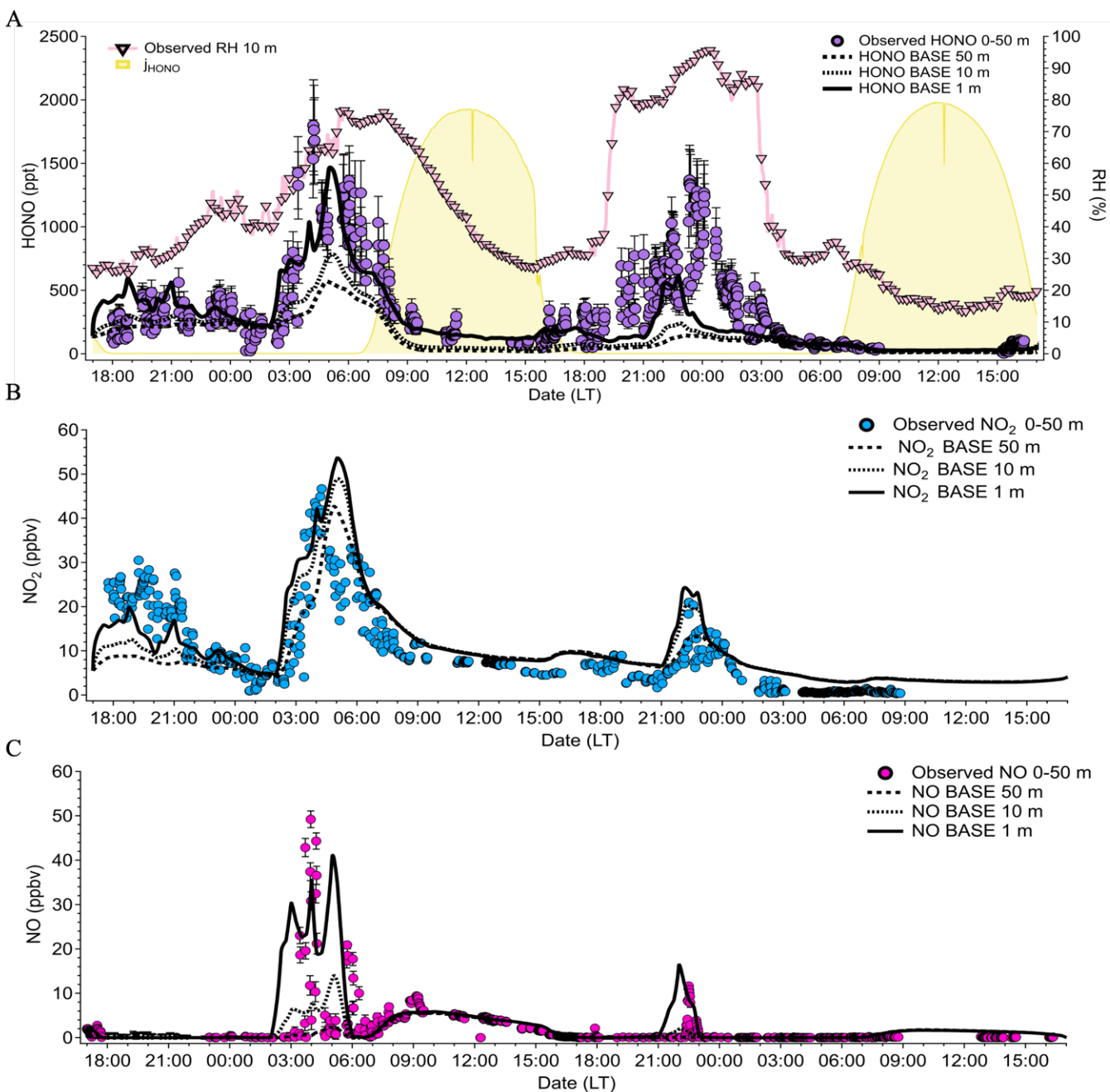


Figure 4.1. (A) Time series of vertically-resolved measurements of HONO (purple dot) filtered between heights of 0-50 m from the NACHTT campaign overlaid with modelled HONO from the PACT-1D BASE model at heights of 1, 10, and 50 m (black solid line, dotted line, and dashed line, respectively). Fixed measurements of *RH* (pink) and the photolysis rate coefficient of HONO (shaded yellow) are from 10 m at the fixed platform height on BAO tower. (B) Time series of vertically-resolved measurements of NO₂ (blue dot) filtered from 0-50 m overlaid with modelled NO₂ at 1, 10, and 50 m. (C) Time series of vertically-resolved measurements of NO (pink dot 0-50 m) overlaid with modelled NO.

Overall, it was found that the BASE model captures the diurnal trends of all 20 gas-phase species and was in good agreement with observations within 50 m AGL, suggesting that the parametrization of the vertical mixing term, meteorology, emissions, and homogeneous gas-phase chemistry are representative of real atmospheric conditions at the measurement location during the 48-hour MP. The BASE model clearly captured the temporal trends of observed NO₂, NO, and HONO, with modelled mixing ratios of all three species peaking during the early morning of MP1 (03:00-07:00 MST) and the late evening of MP2 (21:00-00:00 MST), driven by the absence of photolytic activity, an increase in local NO_x emissions, and the formation of a stable NBL that allows heterogeneous chemistry on the ground by dry deposition of NO₂ and HONO (**Figure 4.1**). Furthermore, the modelled mixing ratios of NO₂, NO, and HONO were found to increase near ground level, revealing a negative gradient profile for all three species, which was in agreement with vertically-resolved observations. When parametrizing the BASE model, the emission rates of NO₂, NO, and HONO were constrained at the 1 m model grid where HONO emissions were derived from a fraction of NO_x emissions ($\text{HONO} = 0.0003(\text{NO}_x)$) to simulate surface bound combustion sources (e.g. traffic, oil and gas well operations), which also contributed to their negative gradient profiles assuming horizontal homogeneity, especially during MP1. The time series of the calculated emission rates of HONO, NO₂, and NO during the 48-hour MP supports this (**Chapter II, Figure 2.8, A**), where the emission rates increased at the same time that modelled mixing ratios of NO, NO₂, and HONO peaked. The emission rates of NO_x and HONO were constrained to a height of 1 m, which may not be representative of realistic injection heights for all direct sources as emissions from power plants stacks were observed aloft during MP1, for example, rather than to only originating at the ground surface from transportation combustion sources (Riedel et al., 2012). Since HONO emissions in such plumes are even more poorly characterized, the model case studies here focus on surface-based emissions and chemistry. One limitation in the PACT-1D model is that the injection heights for gas-phase emissions must be fixed throughout the entire MP. As a result, elevated NO_x plumes observed from power plants stacks during the night of MP1 led to increased production of NO₂ and subsequent production of HONO aloft (i.e. above 100 m), which were not represented accurately in PACT-1D and produced clear discrepancies between the model and observations at higher altitudes due to this regional plume advection (**Figure J1**).

The most notable discrepancies between the BASE model and observations occurred during the night of MP2 (18:00-06:00 MST), particularly for modelled levels of O_3 , dinitrogen pentoxide (N_2O_5), and nitrate radical (NO_3), all of which are gas-phase species with measured positive vertical gradient profiles (**Figure 4.2**). For NO_3 and N_2O_5 , these discrepancies were a result of ignoring reactive uptake of NO_3 and N_2O_5 to aerosols and a underestimated temperature of 8 °C in the BASE model compared to observations, both of which led to overestimated modelled levels of NO_3 and N_2O_5 between 18:00 – 06:00 MST of MP2 (Wagner et al., 2013; Sander et al., 2011; VandenBoer et al., 2013). Given that the primary nocturnal sink of NO_3 and N_2O_5 is attributed to heterogeneous loss on aerosol surfaces and favored in colder conditions, the overestimations in modelled levels of NO_3 and N_2O_5 during the night of MP2 was a result of not including aerosol parameterizations and a having a temperature discrepancy of 8 °C in the BASE model. The uptake coefficient of N_2O_5 on aerosols also varies widely depending on the phase state of the aerosol, its liquid water content, aerosol nitrate, organics, and chloride content. The dynamic change in these factors in a day and variability between aerosols makes this parametrization very hard to model. Furthermore, the formation of N_2O_5 and NO_3 occur aloft and for the purpose of this thesis, they have minimal impact on the availability of NO_2 at the surface as the presence of NO from surface-bound NO_x emissions will revert any gas-phase N_2O_5 and NO_3 back into NO_2 . The mixing ratios of tropospheric O_3 from the BASE model were used to validate the chemistry and emissions parametrizations of modelled NO_x and VOCs, given that the production of O_3 (i.e. a secondary pollutant) is dependent on complex non-linear chemistry, influenced by the availability of VOCs, NO_x , and sunlight on a given day. From **Figure 4.2**, the modelled nocturnal loss of O_3 during MP2 (22:00-00:00 MST) was not in agreement with the observed O_3 , with mixing ratios of modelled O_3 sustained at 28 ppb at the ground level overnight, which could arise from a change in the background mixing ratios of O_3 due to the long range transport of O_3 which was not accounted for in the 1D model (Brown et al., 2013; Zhang et al., 2008; Lin et al., 2012). During the night of MP2 (18:00 - 06:00 MST), the formation of NO_3 from the BASE model increased in the presence of O_3 and NO_2 , while modelled N_2O_5 was in equilibrium with NO_3 and was favoured under lower temperatures and high NO_x conditions. This study did not incorporate aerosol parametrizations into the BASE model because of a previous 0D box modelling study from the NACHTT campaign, which found that the heterogeneous production of HONO from aerosol surfaces was negligible compared to the ground surface due to the greater surface area to volume ratio (VandenBoer et al.,

2013). Under low NO_x conditions during the early morning to the evening of MP2 (03:00-17:00 MST), modelled VOCs from the BASE model were all underestimated compared to observations due to enhanced vertical mixing from wind speeds greater than 10 m/s, which diluted surface emissions of VOCs by upward transport in the vertical column.

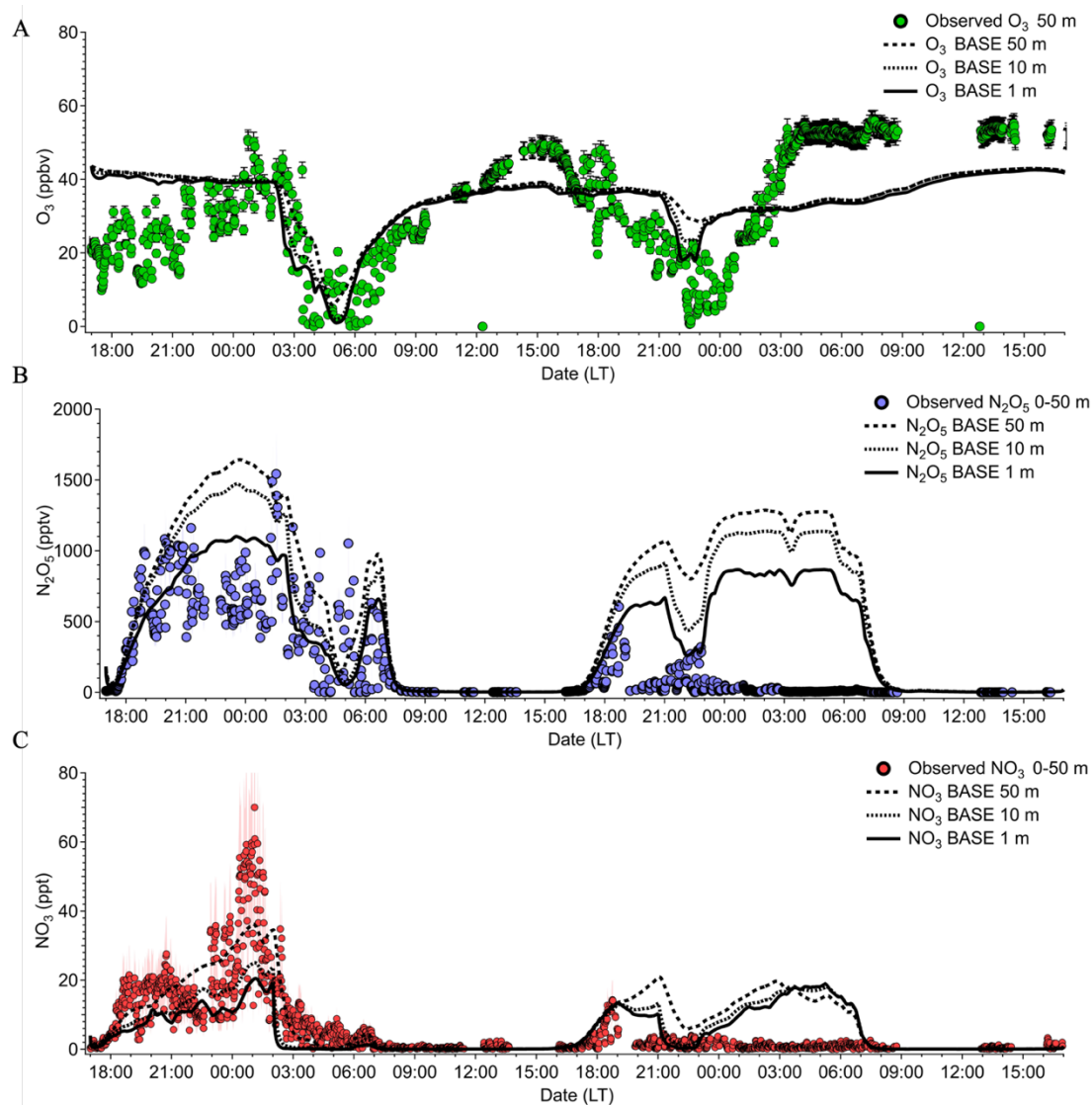


Figure 4.2. (A) Time series of vertically-resolved measurements of O₃ (green dot, ppbv) filtered between heights of 0-50 m from the NACHTT campaign overlaid with modelled O₃ from the PACT-1D BASE model at heights of 1, 10, and 50 m (black solid line, dotted line, and dashed line, respectively). (B) Time series of vertically-resolved measurements of N₂O₅ (purple, pptv) filtered between heights of 0-50 m overlaid with modelled N₂O₅ at 1, 10, and 50 m. (C) Time series of vertically-resolved measurements of NO₃ (red, pptv) filtered from of 0-50 m overlaid with modelled NO₃ at 1, 10, and 50 m.

Under low NO_x conditions during the early morning to the evening of MP2 (03:00-17:00 MST), modelled VOCs from the BASE model were all underestimated compared to observations due to enhanced vertical mixing from wind speeds greater than 10 m/s, which diluted surface emissions of VOCs by upward transport in the vertical column. The relative slower decrease in the levels of modelled VOCs from the BASE model compared to observations is that the model does not account for horizontal advection. Overall, the BASE model was able to capture the dynamic chemistry in all 20 gas-phase defined in the PACT-1D model, with excellent agreement especially with modelled negative vertical gradient species such as HONO, NO₂, and NO, which were the target gas-phase species in this thesis. Ultimately, this suggests that all the physical (vertical mixing term, meteorology, photolysis rate frequencies) and chemical (emissions, homogeneous gas-phase chemistry of all 363 mechanisms in RACM2, heterogeneous production of HONO by NO₂, and dry deposition of HONO) parametrizations initialized in the BASE PACT-1D model were representative of real atmospheric conditions during the 48-hour MP of the NACHTT campaign.

4.3. The Influence of Vertical mixing and Transport on HONO Chemistry in BASE model

To understand the influence of vertical mixing and boundary layer dynamics on modelled vertical gradients of HONO in the BASE model, a time series of the modelled surface flux loss rates of HONO and NO₂ were overlayed with the modelled vertical transport rate of HONO at a height of 1 m during the 48-hour MP (**Figure 4.3**). The vertical transport rate of HONO is a height-dependent term that is effectively defined by the change in concentration of HONO at each timestep, which is influenced by surface flux losses near the ground surface or by vertical diffusion mixing transport at all heights, respectively. These ground surface sources and sinks are dependent on the deposition rate of NO₂ (V_{dep,NO_2}) and HONO ($V_{dep,HONO}$), which is a temperature-dependent term that changes dynamically over the course of the MP (**Chapter II, Section 2.7**) and are represented as surface flux loss rates in **Figure 4.3**.

At the start of MP1 (17:00 MST), daytime vertical transport rates of HONO were on the order of $1 \times 10^8 - 3 \times 10^8$ molecules cm⁻² s⁻¹, indicating the presence of a convective mixing layer that exists until 23:00 MST (**Figure 4.3**). During the same timeframe, modelled mixing ratios of

HONO from BASE converge to 350 ppt at all heights, which indicates a homogenous vertical distribution within 50 m AGL while the vertical transport rate is more pronounced (**Figure 4.3**).

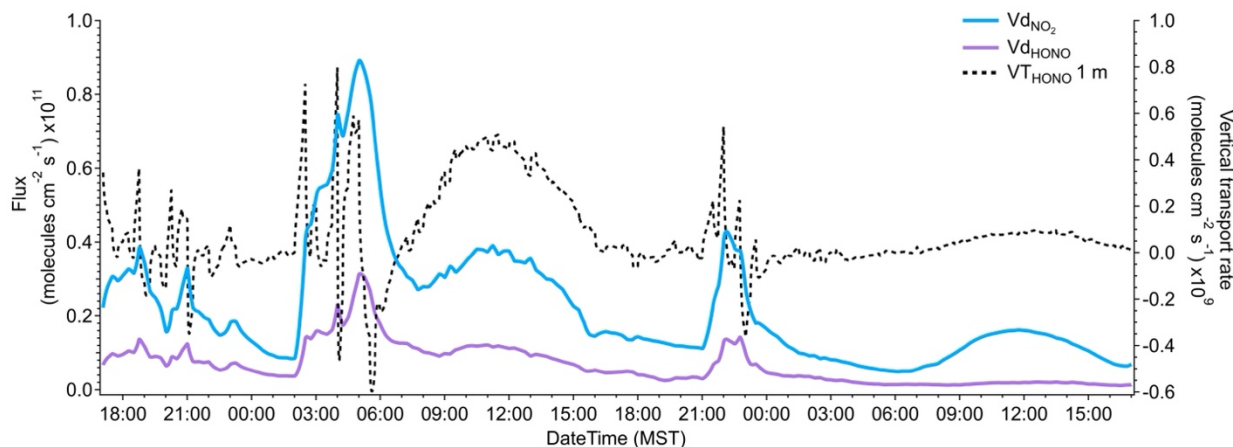


Figure 4.3. Time series of 1 m modelled surface flux loss rates (left axis, molecules $\text{cm}^{-2}\text{s}^{-1}$) of HONO (purple) and NO_2 (blue) overlaid with the 1 m modelled vertical transport rate (right axis, molecules $\text{cm}^{-2}\text{s}^{-1}$) of HONO (black dashed line) during the 48-hour MP of the BASE model. Note that a positive surface flux loss represents deposition to the ground surface, while a positive and negative vertical transport rate indicates upward transport and vertical stratification, respectively.

During the late night of MP1 (03:00-06:00 MST), the vertical transport rate of HONO decreased to a minimum (i.e. below zero) while the surface flux loss rates of HONO and NO_2 at a height of 1 m reached a maximum 3.1×10^{10} and 9.1×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$ at 05:00 MST, respectively. This indicates that a stable NBL developed as the vertical mixing weakened, leading to stratification near the ground, and inducing stronger dry deposition. Under these nocturnal conditions in MP1, the heterogeneous ground surface chemistry, particularly the hydrolysis of NO_2 and loss of HONO by dry deposition, dominates the net production of BASE HONO at 1 m, with mixing ratios reaching 1480 ppt when surface flux loss rates of HONO and NO_2 were at their maximum. With only two surface source processes parametrized, the BASE model reproduced 58 % (slope = 0.58; $R^2 = 0.84$) of the nocturnal production of HONO during MP1. As terrestrial radiation becomes active during the early morning of MP1 (06:00-09:00 MST), there is a gradual increase in the vertical transport of HONO, while the surface flux loss rates of HONO and NO_2 decreased due to the breakup of the NBL. During this timeframe, the modelled vertical transport rate of HONO begins at -6.0×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ and increases to near zero molecules $\text{cm}^{-2} \text{s}^{-1}$ by 7:30 MST, which shows a negative vertical transport rate, allowing the levels of HONO to accumulate below 50 m and confirming that the suppression of vertical mixing was identified (**Figure J1**). The BASE model was still not able to reproduce the morning burst observations of HONO during

the early morning period of MP1. This suggests that there was either an underestimation in the heterogeneous surface source parametrizations of HONO or in the parametrizations of vertical diffusion mixing. These processes, coupled with the daytime photolytic loss of HONO, led to a net loss of HONO, where modelled vertical gradients of HONO converge back to daytime mixing ratios within 50 m AGL. Without accounting for vertical mixing in a 0D box model framework, the greatest unknown surface source rate of HONO (roughly 4×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$) occurring at 06:00 MST overlaps with the expected onset time of boundary layer growth making the inference of chemical mechanisms only possible if the mixing is correctly represented (VandenBoer et al., 2013). Since a generic boundary layer growth term was used in the prior 0D model, it would not be expected to perform well on explicit case studies where this does not hold. It is important to accurately model the morning burst period of HONO that was observed during the NACHTT campaign as early morning processes (i.e. photolysis) initiate oxidation chemistry, where it can contribute to radical propagation via VOCs and ultimately increase the daytime production of secondary pollutants, such as O_3 and SOA. The inability to reproduce the morning burst period of HONO in our BASE model, or any other atmospheric chemistry model for that matter, can lead to an underestimation in $\text{OH}^\bullet$ radical production, which ultimately decreases the estimated oxidative capacity of the atmosphere during the 48-hour MP.

At the start of MP2 (17:00 MST), there is a sudden change between the proportionality of vertical transport and deposition, where the vertical transport rate of HONO and the deposition rates of NO_2 and HONO both decrease – a trend that was not observed in MP1 (**Figure 4.3**). This is due to a change in the regional meteorology of the measurement site, where wind speeds ≥ 6 m/s with a BLH extending up to 2500 m were observed, resulting in a turbulent regime with greater vertical diffusion mixing (**Chapter II, Figure 2.9**). This shift in meteorology occurs at the same time when a stable NBL should begin to form, delaying its development over the course of the evening until 22:00 MST. When compared to observations, the greatest underestimation of daytime BASE HONO occurred during the evening of MP2 (17:00-19:00 MST), which could arise from several confounding processes, including: horizontal transport of HONO to the measurement site, other daytime heterogeneous sources of HONO (Sarwar et al., 2008; Tuite et al. 2021), or misrepresentation of existing known chemistry. During MP2, vertical gradients from BASE HONO followed a similar trend to MP1, with uniform daytime distributions and negative

nighttime vertical gradients (i.e. decreases with height) at 50 m AGL. However, the nocturnal production of HONO was found to be less in MP2, with mixing ratios only reaching 700 ppt due to a more turbulent mixing regime, which dilutes HONO and NO₂ into a deeper surface layer by upward transport. Under these conditions, the BASE model was only able to reproduce 21 % (slope = 0.21; $R^2 = 0.64$) of the nocturnal production of HONO during MP2. These findings highlight the importance of vertical diffusion mixing and its impact on diluting the mixing ratios of HONO by upward transport (MP2) or by delaying the vertical transport of HONO via vertical mixing suppression (MP1). The vertical transport rate of HONO at a height of 1 m was on average two orders of magnitude less than the depositional surface flux loss of HONO and NO₂, which had a small loss contribution to the modelled mixing ratio of HONO near the ground from the BASE model. In the BASE model, assuming that 100 molecules of gas-phase HONO were being formed at the ground either by NO₂ hydrolysis, gas-phase chemistry, or direct emissions, 99 % of the molecules of gas-phase HONO would be lost by dry deposition, while 1 % of the molecules would be lost by vertical transport. The modelled vertical gradient of HONO from the BASE model was able to reproduce observations within 300 m AGL, which suggests that a small amount of vertical transport arising from ground surface chemistry is all that is required to reproduce observations during the 48-hour MP (**Figure I1**). The magnitude of the surface flux loss of HONO in the BASE model was in excellent agreement with previous 1D modelling studies of gas-phase HONO, while an important contrast was that vertical transport was a major loss at the ground in these urban sites (Wong et al., 2013; Tuite et al., 2021). The vertical mixing parametrization used in this study was still an important term to constrain during the 48-hour MP as it permits dry deposition of HONO and NO₂ to take place. In this thesis, the vertical mixing profile was defined by the sum of eddy diffusion and molecular diffusivity, where contributions from eddy diffusion was minimized near the ground surface to permit molecular diffusion of HONO and NO₂ on the ground surface (Cao et al. 2016).

Compared to the observed vertical gradients of HONO, the BASE model successfully captured most of the nocturnal production during the night of MP1, using NO₂ hydrolysis as the sole heterogeneous ground source (**Figure 4.3**). The nocturnal surface fluxes of HONO (2.2×10^{10} – 3.4×10^{10} molecules cm⁻² s⁻¹) and NO₂ (5.6×10^{10} – 9.4×10^{10} molecules cm⁻² s⁻¹) at a height of 1 m in the BASE model were consistent with values reported from literature, which is important

given that surface source routines were parametrized using the calculated reactive uptake coefficients of HONO and NO₂ (Geyer and Stutz, 2004; VandenBoer et al. 2013). These findings are in excellent agreement with previous modelling studies, which demonstrate that the ground surface is the most important nocturnal source of HONO, with NO₂ hydrolysis being the dominant production mechanism (Kleffmann et al., 2003; VandenBoer et al., 2013; Wong et al., 2013; Tuite et al., 2021). However, the BASE model was unable to capture the early morning burst of HONO during MP1 (04:00-08:00 MST), when vertical mixing was limited, and a stable NBL was present. The greatest absolute deviance of BASE HONO with respect to observations, is separate from the morning burst, occurring at 04:00 MST with an approximate 800 pptv difference. This discrepancy suggests enhanced production or an additional nighttime chemical source of HONO. Using a 0D box model framework and an *RH*-dependent surface parameter for the heterogeneous ground uptake of HONO and NO₂ during the NACHTT campaign, VandenBoer et al. (2013) showed greater agreement with observations when *RH*-dependent surface parameters were included in the model. The periods of disagreement in MP1 and MP2 here also happen to coincide with large changes in *RH* (**Chapter II, Appendix B1**). Thus, a case study was performed comparing the surface source routines of HONO from the BASE model with a surface source routine that includes an *RH*-dependent heterogeneous ground uptake of NO₂ and HONO (BASE_WET). In addition, to emphasize the importance of the ground surface in controlling the nocturnal HONO production, surface source routines were turned off in the NO_GSS model which was used as a reference point. The NO_GSS model was also used in validating the emission rates, which was important because this was the first PACT-1D study that incorporated an alternative method (i.e. observational constraints) to initialize the emission rates.

4.4. Comparing the modelled ground level of HONO from the output of NO_GSS, BASE, and BASE_WET with observations.

To evaluate the HONO surface source routines from the modelled outputs of HONO during the NACHTT campaign, a time series is shown comparing the dynamic chemistry between the NO_GSS, BASE, and BASE_WET model with that of vertically-resolved observations of HONO below 50 m AGL during the 48-hour MP (**Figure 4.4**). Between 50 m to a height of 250 m AGL, it was found that the modelled vertical gradients of HONO from NO_GSS, BASE, and BASE_WET were all underestimated compared to observations, but followed the same trend

(Figure J1), suggesting an error in the injection altitude of emissions employed in the model. A comparison of mixing ratio time series of HONO from NO_GSS, BASE, and BASE_WET found that ground surface chemistry explained the nocturnal production of HONO best when surface water and vertical mixing were taken into account during the 48-hour MP. (Figures 4.3 and 4.4).

The NO_GSS model output, as expected, greatly underestimated HONO when compared to observations, with peak mixing ratios of HONO reaching about 450 ppt and 200 ppt near ground-level during the night of MP1 and MP2, respectively. The chemical model in NO_GSS only includes homogeneous gas-phase chemistry and direct emissions as HONO source terms (Equation 4.1), so this clearly demonstrates that heterogeneous NO_2 hydrolysis on the ground dominates nocturnal HONO production, as has been suggested by several prior reports (Geyer and Stutz, 2004; VandenBoer et al., 2013; Tuite et al., 2021). This is also diagnostically important for the model, as it is utilized to validate the direct emissions parametrizations, which is important given that this study used a novel method to derive its emissions through observations.

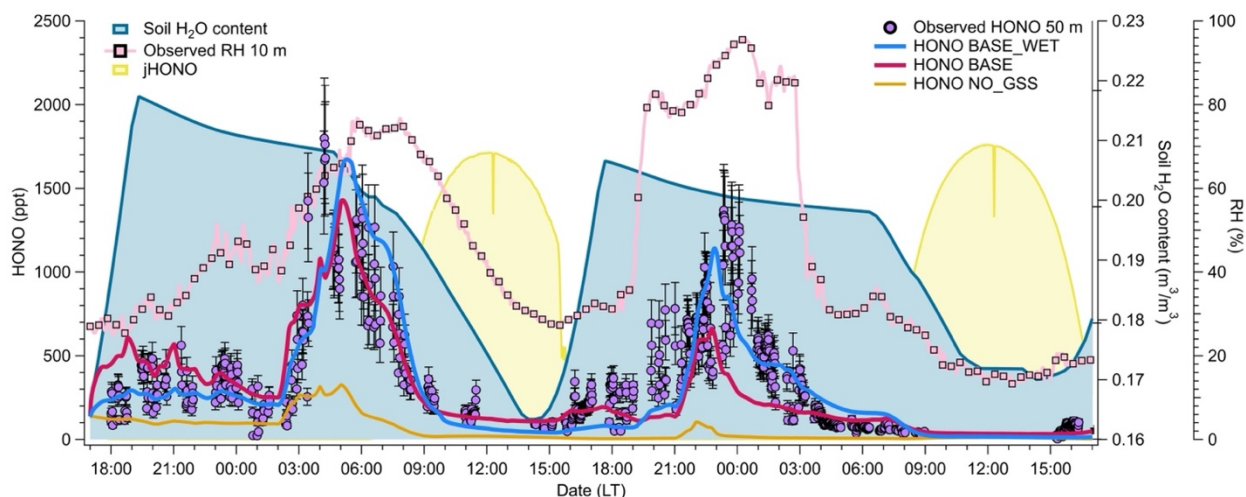


Figure 4.4. Time series of ground-level modelled mixing ratios of HONO from the NO_GSS (yellow trace), BASE (red trace), and BASE_WET (blue trace) model overlaid against the vertically-resolved mixing ratios of HONO from observations (purple dots) during the 48-hour MP. To track the soil moisture near the ground surface, WRF-derived soil water content (blue shaded area, m^3/m^3) at a height of 1 m was added in addition to the observed RH from a fixed height of 10 m. To differentiate between day and night, the observed photolysis frequencies of HONO were added for the 48-hour MP of the NACHTT campaign.

Between 06:00-09:00 MST during MP1, the BASE model was still unable to capture the observed morning burst event of HONO, which interestingly occurs at the same time period when ground level *RH* is greater than 60 %. The dependency of *RH* on the production of HONO has been shown in several field measurements, where the production of HONO was enhanced when *RH* increased above 60 % (Stutz et al., 2004; Wojtal et al., 2011; VandenBoer et al., 2013). Given that easiest known change to the surface chemistry is the *RH* dependent rate, it would make sense to modify currently known surface sources of HONO before adding novel daytime HONO sources. When an *RH*-dependent factor was included in the ground reactive uptake of NO₂ (*RH*/50) and HONO (*RH*/20) for the BASE_WET model, it was found that the modelled mixing ratios of HONO followed the dynamic chemistry from two 24-hour observation periods and more importantly, was able to reproduce the observed early morning burst of HONO during MP1 (**Equation 4.3**). The BASE_WET model accounted for 94 % (slope = 0.94; $R^2 = 0.90$) and 55 % (slope = 0.55; $R^2 = 0.69$) of the nighttime observations during MP1 and MP2, with mixing ratios of HONO reaching a peak of about 1750 ppt and 1100 ppt, respectively. The nocturnal heterogeneous ground production of HONO via the hydrolysis of NO₂ occurs in the presence of surface adsorbed water, when during the morning burst period (06:00-09:00 MST), it was observed that the WRF-derived soil water content on the ground gradually decreases from 0.21 m³/m³ to 0.18 m³/m³ and matches with the *RH* from observations. This reinforces the notion that the ground surface dominates the nocturnal heterogeneous production of HONO via NO₂ hydrolysis and that its production is enhanced when surface adsorbed water is present on the ground surface. When compared to observations, the modelled outputs of HONO were found to have greater discrepancies during MP2 than in MP1. This suggests that the 1D model fails to capture the observations of HONO when wind speeds becomes greater than 6 m/s, as contributions from horizontal transport become more important during MP2. This is exemplified between 19:00 – 23:00 MST of MP2, when nocturnal ground production of modelled HONO occurs only when wind speeds at heights of 10 m and 100 m from observations were less than 5 m/s (**Figure 4.4, Figure 3.2 A**). The PACT-1D model was in better agreement with observations and in predicting the dynamic chemistry of HONO than the 0D box model employed previously during the NACHTT campaign. One of the most important implications from the results of this thesis is that the incorporation of a vertical mixing term is critical in setting the correct vertical distribution of HONO. This suggests that for modelling applications of reactive gas-phase species with negative vertical gradients such as

HONO, the influence of vertical diffusion mixing must be accounted for before applying additional daytime HONO sources to explain the discrepancies between the model and observations. To study the chemical box framework of the BASE_WET model and its applicability to other environments (i.e. on urban surfaces), we can modify the deposition rate of NO₂ and HONO using ground uptake coefficients reported by researchers in other environments.

4.5. The Contribution of each Term From The 1D Continuity Equation To Modelled Levels of HONO from BASE and BASE_WET.

The modelled vertical gradients of HONO from BASE and BASE_WET are driven explicitly from the sum of terms defined in the 1D continuity equation (**Equation 2.1**) and not by observations from the NACHTT campaign. These terms were parametrized separately in the PACT-1D model and includes the net contribution from all gas-phase mechanisms of HONO, HONO emission rates derived from a fraction of observed NO_x emissions ($\text{HONO} = 0.003[\text{NO}_x]$), vertical transport rate of HONO, surface flux loss of HONO to the ground surface (i.e. dry deposition), and production and emission of HONO after deposition of gas-phase NO₂. In order to compare the contribution of each term in the 1D continuity equation during the 48-hour MP to the modelled mixing ratio of HONO from the BASE (**Figure 4.5**) and the BASE_WET (**Figure 4.6**) model, we constrained each term at a height of 1 m to ensure that all the units are equivalent and to focus on surface-based emissions and chemistry. In the PACT-1D model framework, the heterogeneous ground surface processes of HONO, including NO₂ hydrolysis and dry deposition of HONO were parametrized using deposition rates of NO₂ and HONO (**Chapter II, Section 2.7**), which changed as the average molecular speed of any gas-phase species is a temperature-dependent physical property that was calculated continuously over the MP. From the observationally constrained ground reactive uptake of HONO ($\lambda = 7.3 \times 10^{-5}$) and NO₂ ($\lambda = 8 \times 10^{-6}$) gathered from the NACHTT campaign, the deposition of HONO is about 9 times greater than the deposition of NO₂ (VandenBoer et al., 2013). When the RH-dependent factor was included in the BASE_WET model, the deposition of HONO becomes 23 times larger than NO₂. However, the relative mixing ratio of NO₂ was about four orders of magnitude greater than that of HONO during the 48-hour MP, with the greatest difference occurring during the nocturnal periods of MP1 and MP2. This is why the surface flux of NO₂ was greater than that of HONO during the BASE

and BASE_WET model, leading to net heterogeneous HONO production from the combined effects of NO₂ hydrolysis and dry deposition of HONO.

During the 48-hour MP, as expected, the net contribution from all gas-phase mechanisms of HONO (i.e. P – L term) was found to be negligible with respect to other terms from the 1D continuity equation near the ground surface, with the formation of HONO by NO and OH reaching an order of 10⁷ molecules cm⁻² s⁻¹ during the evening, while the loss by photolysis reaching an order of 10⁸ molecules cm⁻² s⁻¹ by midday (**Figure 4.5 and 4.6**).

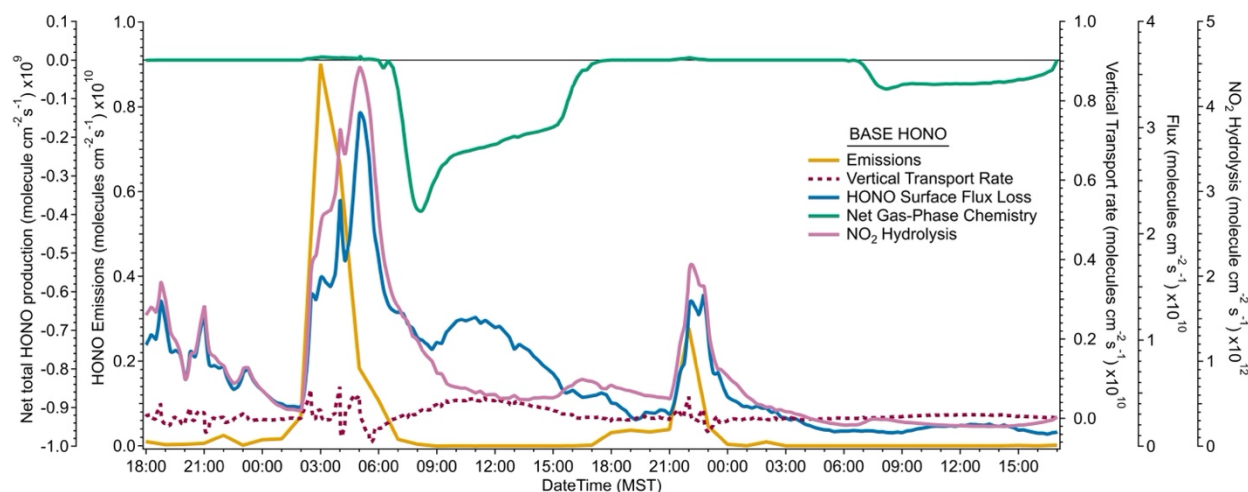


Figure 4.5. Time series of each term from the 1D continuity equation constrained at height of 1 m of the BASE model, including the net chemical production of HONO (far left axis; green line), emission rate of HONO derived from observed NO_x emissions (left axis; yellow trace), vertical transport of HONO (right ; red dashed trace), surface flux loss rate (right; blue trace), and NO₂ hydrolysis on the ground surface (far right axis; pink trace). For the units of the net gas-phase chemistry term, a positive and negative value imply a source and sink, respectively. The black line on the net gas-phase chemistry represents the zero line for net total HONO production. Note that the terms were all constrained at a height of 1 m to ensure all units were equivalent (molecules cm⁻² s⁻¹).

When surface source routines of HONO were turned on in the BASE and the BASE_WET model, net contribution from heterogeneous ground surface mechanisms was found to be the greatest contributor to the 1D continuity equation near the ground surface, with formation rates from NO₂ hydrolysis reaching an order of 10¹² molecule cm⁻² s⁻¹ and the loss of HONO by dry deposition reaching an order of 10¹⁰ molecules cm⁻² s⁻¹ during the 48-hour MP (**Figure 4.5 and 4.6**). It is important to note that all the terms derived from the 1D continuity equation of the BASE and BASE_WET model were constrained to the lowest 1 m of the box for relative comparison and the

absolute values of these terms will be diluted when considering the integrated contributions of each process throughout a larger atmospheric column, like the NBL.

For the BASE model, NO₂ hydrolysis was the most important term influencing the abundance of HONO in the 1D continuity equation during the 48-hour MP, followed by depositional surface flux loss of HONO, HONO emissions, and vertical transport. During the late night of MP1 (03:00-06:00 MST) in the BASE model, NO₂ hydrolysis was found to be 77 times (range: 66 – 114) greater than the depositional surface flux loss term of HONO, 740 times (range: 495 – 2400) greater than the HONO emissions term, and 4967 times (range: 4300 - 5600) greater than the vertical transport rate of HONO (**Figure 4.5**). During the late night of MP2 (21:00 – 00:00 MST) in the BASE model, NO₂ hydrolysis was found to be 37 times (range: 33 – 63) greater than the depositional surface flux loss term of HONO, 910 times (range: 769 – 1169) greater than the HONO emissions term, and 2735 times (range: 1530 – 3937) greater than the vertical transport rate of HONO.

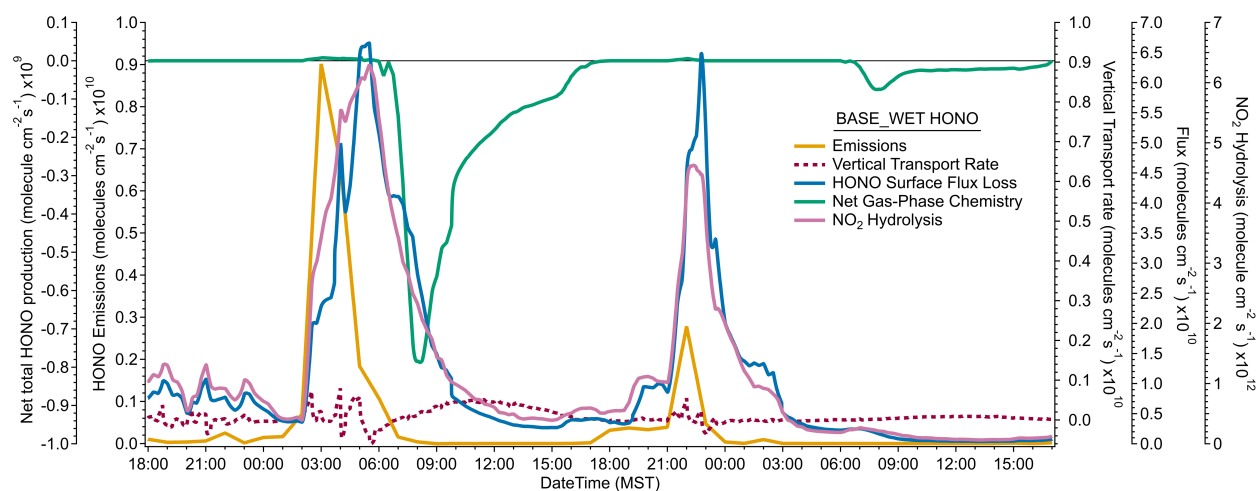


Figure 4.6. Time series of each term from the 1D continuity equation constrained at height of 1 m of the BASE_WET model, including the net chemical production of HONO (far left axis; green line), emission rate of HONO derived from observed NO_x emissions (left axis; yellow trace), vertical transport of HONO (right ; red dashed trace), surface flux loss rate (far right; blue trace), and NO₂ hydrolysis on the ground surface (far right axis; pink trace). For the units of the net gas-phase chemistry term, a positive and negative value imply a source and sink, respectively. The black line on the net gas-phase chemistry represents the zero line for net total HONO production. Note that the terms were all constrained at a height of 1 m to ensure all units were equivalent (molecules cm⁻² s⁻¹).

For the BASE_WET model, NO₂ hydrolysis was still the most important term influencing the abundance of HONO in the 1D continuity equation. The inclusion of an RH-dependent surface parameter further increased the depositional surface flux loss of NO₂ and HONO, while contributions from HONO emissions and vertical transport of HONO were identical to that of the BASE model. During the late night of MP1 (03:00-06:00 MST) in the BASE_WET model, NO₂ hydrolysis was found to be 115 times (range: 95 – 151) greater than the depositional surface flux loss of HONO, 1115 times (range: 700 – 3151) greater than the HONO emissions rate, and 6827 times (range: 5754 – 7900) greater than the vertical transport rate (**Figure 4.6**). During the late night of MP2 (21:00 – 00:00 MST) in the BASE_WET model, NO₂ hydrolysis was found to be 85 times (range: 71 – 115) greater than the depositional surface flux loss of HONO, 1790 times (range: 1663 – 1921) greater than the HONO emission rate, and 5654 times (range: 2795 – 8514) greater than the vertical transport rate of HONO.

Table 4.2. Tabulated contribution of NO₂ hydrolysis in both models relative to other terms in 1D continuity equation.

Model-Period	$\frac{NO_2 \text{ hydrolysis}}{\text{Surface flux loss HONO}}$	$\frac{NO_2 \text{ hydrolysis}}{\text{HONO Emissions}}$	$\frac{NO_2 \text{ hydrolysis}}{\text{HONO Transport}}$
BASE-MP1	77 (64 – 114)	740 (495 – 2400)	4967 (4300 – 5600)
BASE-MP2	37 (33 – 63)	910 (769 – 1169)	2735 (1530 – 3937)
BASE_WET-MP1	115 (95 – 151)	1115 (700 – 3151)	6827 (5754 – 7900)
BASE_WET-MP2	85 (75 – 115)	1790 (1663 – 1921)	5654 (2795 – 8514)

These results indicate that the depositional surface flux loss of NO₂ was the most influential term contributing to the modelled vertical gradient of HONO from the BASE and BASE_WET model within the NBL, with a greater influence found in the latter model when RH-dependent factors were applied to the ground reactive uptake of HONO and NO₂ (**Table 4.2**). This allowed the heterogeneous ground production via NO₂ hydrolysis to dominate HONO chemistry during the 48-hour MP in both models. In the BASE_WET model, when an enhancement in both the deposition of gas-phase HONO and NO₂ were observed, the deposition of HONO became 23 more effective than NO₂ over the course of the MP. Given the relative mixing ratio of gas-phase NO₂ was four orders of magnitude greater than gas-phase HONO over the course of the 48-hour MP,

the surface flux of NO_2 was greater than that of HONO, which increased the amount of HONO formed throughout the NBL, with the greatest increase occurring during the night when the relative mixing ratio of NO_2 increased and the RH was at maximum. Overall, when an RH-dependent surface parameter was applied to the ground reactive uptake of HONO and NO_2 in the BASE_WET model, this led to an enhancement in both the contribution of NO_2 hydrolysis and dry deposition of HONO such that the BASE_WET model was able to reconcile the nighttime observations of HONO without the need to parametrize other surface sources of HONO during the 48-hour MP (**Figure I1**).

4.4. Conclusions

In this section, the PACT-1D model was utilized to produce three modeled outputs (NO_GSS, BASE, BASE_WET) each with varying surface source routines of gas-phase HONO to understand the relative contribution of heterogeneous ground surface and loss processes of HONO. The chemical box model of BASE included a heterogeneous production of HONO via NO_2 hydrolysis and loss by dry deposition, homogeneous gas-phase chemistry, and direct emissions. It was found that the BASE model captured the dynamic chemistry of all 20 gas-phase species and was in excellent agreement with observations within 50 m AGL, which suggests that all the parametrization methods used to initialize each component of the PACT-1D model were representative of real atmospheric conditions at the BAO tower. There were some discrepancies between the BASE model and observations for some species including N_2O_5 , NO_3 , and O_3 , which could be due to the underestimation in modelled temperature, aerosols were not accounted for in the model, and the long range transport of O_3 was not accounted for in the model. For reactive gas-phase species with negative vertical gradients such as HONO, the influence of vertical mixing was found to be critical in setting the vertical distribution of HONO and for controlling the availability for which heterogeneous surface chemistry can take place, especially during the formation of a stable NBL. This is exemplified by the comparison between modelled surface flux loss rates of HONO and NO_2 and the modelled vertical transport of HONO during the 48-hour MP, where the modeled vertical transport rate of HONO influenced the timing and magnitude of HONO production and deposition. The NO_GSS model did not include any ground surface source routines and was just limited to gas-phase chemistry and direct emissions. This was an important model output to include as it confirmed that the direct emissions parametrizations employed in this study

were correctly initialized while also reinforcing the need to include a nighttime heterogeneous surface source of HONO. When an *RH*-dependent factor was included in the ground surface source routines of HONO and NO₂ in the BASE_WET model, it was found that the modelled mixing ratios of HONO accounted for 94 % (slope = 0.94; $R^2 = 0.90$) and 55 % (slope = 0.55; $R^2 = 0.69$) of the nighttime observations and was able to reproduce the observed early morning burst of HONO on MP1. Overall, the implications of this study reveal that in order to correctly evaluate the contributions of various heterogeneous ground surface of HONO in modelling applications, the vertical diffusion mixing term must be accounted for explicitly before exploring surface chemistry parametrizations. The most influential term that contributed to the modelled mixing ratio of HONO from the BASE and BASE_WET model was the production from NO₂ hydrolysis on the ground, which was further enhanced as a function of *RH* in the BASE_WET model.

5.0. Conclusion

To understand the PACT-1D model framework in its entirety, a great deal of effort was made to validate the physics (vertical diffusion mixing, meteorology, and photolysis rate coefficients terms) and chemical (emissions and initial concentrations terms) parametrizations of the PACT-1D model in **Chapter II**. Initializing the PACT-1D model was the most challenging and time consuming (>1 year) portion of my thesis, given that it required to learn about the fundamentals of every component of the PACT-1D framework and it was a computational challenge because each component of the BASE model had to be interpolated to the same time and height resolution, following the vertical dimensions and time component of the PACT-1D grid. Given the complexity and the availability of measurements from the NACHTT campaign, this was the first PACT-1D study to incorporate observational constraints for gas-phase species and utilize a BLH dilution scheme to represent the emission rates of primary-gas phase species defined in the model. The vertical diffusion mixing parametrization developed by Cao et al., (2016) correctly captured the development of a NBL on both nights during the 48-hour MP. Modelled vertical temperature profiles were influenced by terrestrial radiation throughout the 48-hour MP and resulted in excellent agreement with observed temperature profiles from the NACHTT campaign. The greatest discrepancy between the model and observed temperature profiles occurred during MP2 with an underestimation of -8°C .

In **Chapter III**, we explored the vertically-resolved observations made during the NACHTT campaign and utilized a selection criteria to select a 48-hour case study that prioritizes several constraints, including a sudden morning burst in the levels of HONO, the formation of a NBL, wind speeds ≤ 6 m/s, and data availability. The 48-hour case study period that adhered to the selection criteria was found to be February 18th 17:00 MST (OP1) to February 20th 17:00 MST (OP2) during the 2011 NACHTT campaign. Vertical gradients of HONO followed that of NO_2 during the 48-hour MP, with strong negative gradients of HONO observed when NO_2 mixing ratios are elevated near the ground either by surface-bound emissions of NO_x or by deposition of NO_2 . Colder temperatures (-4°C to 10°C) during OP1 resulted in the potential formation of frost on the ground surface during the early morning while warmer temperatures (4°C to 12°C) during OP2 suggested the potential formation of dew. Finally, the morning burst event was only observed during OP1 when vertical mixing was suppressed during the early morning transition of the NBL

to the convective PBL. This delayed the vertical transport of HONO and NO₂ on the ground, which allowed a strong surface source of HONO to become active during the early morning of OP1 and get depleted by photolysis.

In **Chapter IV**, the PACT-1D framework was utilized to produce three modelled outputs of gas-phase HONO (NO_GSS, BASE, and BASE_WET) with various ground surface source routines to highlight the relative importance of heterogeneous ground surface formation and loss processes of HONO, with the role of vertical diffusion mixing being critical for setting the vertical distribution of modelled HONO during the 48-hour MP of the NACHTT campaign. The BASE model had several formation and loss processes of HONO including, direct emissions, nocturnal heterogeneous ground surface production of HONO via NO₂ hydrolysis, net loss from homogeneous gas-phase chemistry, loss of HONO by upward transport, and heterogeneous loss of HONO by dry deposition. The NO_GSS model did not include any surface source routines to highlight the importance that the ground surface dominates the heterogeneous production of HONO. The chemical model of BASE_WET was the same as the BASE model, except it included an updated uptake coefficient for HONO and NO₂ that was dependent to RH, given that it has been shown in previous studies that the enhancement of HONO can occur when RH > 60 %.

The BASE model captured the dynamic chemistry of all 20 gas-phase species initialized in the model and was in excellent agreement with observations within 50 m AGL, suggesting that the physics and chemical parametrizations initialized in the PACT-1D framework are representative of real atmospheric conditions at the BAO tower during the 48-hour MP. The BASE model accurately captured the dynamic chemistry and vertical gradients of HONO, NO₂, and NO below 50 m, with a better match in MP1 then during MP2 due to differences in vertical mixing dynamics, emissions of NO_x, and RH on the ground. Although the vertical transport rate of HONO was suppressed during the morning burst event (06:00-09:00 MST) of MP1, the BASE model was unable to capture the full extent of the morning burst, suggesting that additional sources were at play. The modelled mixing ratios of NO₃ and N₂O₅ were all overestimated during MP2, which can be attributed to the lack of aerosol parametrizations and temperature differences of -8 °C between observations and the model resulting in the favored formation of N₂O₅. The modelled mixing ratio

of O_3 was greatly underestimated during MP2, which can be attributed to the potential for long range transport to increase the background mixing ratios of O_3 .

The influence of vertical diffusion mixing is critical in controlling the vertical gradients of HONO in the BASE model, especially during the night under the formation of a vertically stratified NBL. Throughout the time evolution of the 48-hour MP, the modelled surface flux loss rate of HONO followed the modelled surface flux loss rate of NO_2 from the PACT-1D BASE model. It was found that the magnitude of modelled surface flux loss rates of HONO and NO_2 during the 48-hour MP were consistent with modelled values reported from literature, given surface source routines were parametrized using observationally-constrained reactive uptake coefficients of HONO and NO_2 . The modelled vertical transport rate of HONO influenced the timing and magnitude of HONO deposition and production, which exemplifies the necessity to properly model the vertical mixing term before exploring the surface chemistry.

The NO_GSS model significantly underestimated the mixing ratios of HONO, which suggests that direct emissions and gas-phase chemistry alone are unable to reproduce the observations of HONO during the 48-hour MP. When surface source routines were turned on in the BASE model, modelled HONO accounted for 58 % (slope = 0.58; $R^2 = 0.84$) and 21 % (slope = 0.21; $R^2 = 0.64$) of the observations during the night of MP1 and MP2, respectively. This showcases that the heterogeneous surface production of HONO in the BASE model could not explain the total nighttime HONO budget during MP1 and MP2, which arises from the inability to parametrize surface water in the surface source routine of the BASE model, assuming that the presence of surface water is ubiquitous during both nights of the 48-hour MP. The BASE_WET model closely resembled the time evolution of gas-phase HONO from observations after applying an RH-dependent factor to the reactive uptake coefficient of HONO and NO_2 . The addition of the RH-dependent factor in the BASE_WET model allowed us to very clearly reproduce the observed nighttime of HONO during the 48-hour MP, with modelled HONO accounting for 94 % (slope = 0.94; $R^2 = 0.90$) and 55 % (slope = 0.55; $R^2 = 0.69$) of the observed nighttime budget of HONO in MP1 and MP2, respectively. This shows that the ground surface dominates the nocturnal heterogeneous production of HONO via NO_2 hydrolysis during the 48-hour MP, where the

production of gas-phase HONO is enhanced when surface adsorbed water is more readily available on the ground surface. An important confounding variable that impacts the model conversion of NO_2 and uptake of HONO on the ground surface is the amount of surface bulk water available and the composition of other ions present in the ground surface, which can change dynamically between different measurement locations and seasons. To test the chemical box framework of the BASE_WET, we can extend the model to study the heterogeneous chemistry of HONO to other environments with differences in the availability of surface bulk water and the abundance of other ions present in soil.

5.1. Future Work

The 48-hour MP was limited by data availability as the accommodation of 20 gas-phase species, photolysis rate frequencies, and meteorology measurements from the NACHTT campaign were difficult to navigate while also adhering to the selection criteria. For the purpose of measuring the vertical profiles of HONO and understanding the heterogeneous ground surface production and loss of HONO, the 2011 NACHTT was a world-class field campaign given its ability to incorporate high-time and highly vertically resolved measurements of HONO; coupling it with boundary layer dynamics. For future work, it would be advantageous to constrain the BASE model (or BASE_WET) to 24 hours and utilize this framework to model the four other periods during the NACHT campaign where a morning burst of HONO were observed. Given that the boundary layer dynamics were already explored for a 48-hour period during the OP of the 2011 NACHT campaign, we can extend the vertical mixing parametrization from the BASE model to the four other periods where a morning burst was observed. The parametrization of the vertical mixing term is dependent on the BLH and near-ground wind speed measurements, where the vertical mixing term was more strongly influenced by near-ground wind speed measurements, which was a measurement that was not limited by data availability during the NACHTT campaign. When expanding the BASE model framework to other morning burst periods of HONO, a new vertical mixing term can be defined that is defined by ground wind speed measurements from those new days, while the 24-hour BLH dynamics remains the same as the boundary layer dynamics in MP1.

There are several improvements that could be made to the future work of this thesis, from limitations of the NACHTT campaign to the initialization methods in the PACT-1D model framework. These improvements would aim to explain the stochasticity of the BLH from the ceilometer measurements, the absence of observed vertically-resolved data during the day, and gas-phase species and temperature discrepancies between the model and observations.

In this thesis, we utilized ceilometer aerosol backscatter gradients to estimate the BLH using the default configurations set in the BL-View software from Vaisala. One limitation in the determination of BLH using the aerosol backscatter method is the variability in aerosol gradients during the night under the formation of a stable NBL. There is a setting in BL-View to address this issue where instead of estimating a single height for the BL as a function of time, it resorts to identifying five different heights for the BL as a function of time. When initializing the BLH in the PACT-1D model for future work, it is recommended to select the daytime BLH as the greatest estimated height while the NBL height at the lowest estimated height. To test this parametrization, we could compare the vertical diffusion mixing terms between the BASE model and a model with the updated BLH scheme to their modelled HONO vertical gradients and observations.

The Initial concentrations of all gas-phase species during the 48-hour MP were initialized using observational constraints from the NACHTT campaign. Only gas-phase species that had data available during the 48-hour MP were included, while the rest was omitted. It is clear that the modelled OH• concentrations were about 4 times lower than the observed during the MP1 (**Figure H2**), which is most likely attributed due to the lack of biogenic VOCs (isoprene, alpha-pinenes, limonene or -diene terpenes,) and some anthropogenic VOCs (methacrolein, and M-,P-, O-Xylene) that were not initialized in the PACT-1D model. In this thesis, the focus was on understanding the nocturnal heterogeneous ground surface mechanisms of HONO, in which an accurate representation of modelled OH• chemistry was not needed. In a future updated version of the BASE model where understanding the daytime chemistry of HONO becomes relevant, we could increase the number of gas-phase species defined, which would be incorporated to both the initial concentration and emission rate components of the PACT-1D model.

In this thesis, ambient temperature profiles from WRF were found to be in great agreement with observations during MP1 but were greatly underestimated (-8 °C) during MP2. WRF-derived

temperature profiles were constrained to a single vertical grid point of 3x3 km, where they were then time and height interpolated to the PACT-1D grid. In future work, I would recommend taking the average of at least two (6x6 km) to four (12x12 km) vertical grids to better represent the regional meteorology for the model site and to reduce the stochasticity imposed at a single vertical grid.

The focus of this thesis was to understand the importance of the heterogeneous ground production and loss terms of HONO and the role of vertical diffusion mixing in setting the correct vertical distribution and influence in controlling the surface chemistry of HONO. In a future work, the parametrization of aerosols should also be incorporated into the PACT-1D model, in order to resolve some of the overestimations in the modelled levels of NO_3 and N_2O_5 that occurred during MP2 without being lost to aerosol uptake. With respect to HONO chemistry, the parametrization of aerosols in the PACT-1D model permits heterogeneous chemistry to occur on aerosol surfaces, either by loss of HONO or by formation of HONO via reactive uptake of NO_2 . The uptake of HONO and NO_2 on aerosol surfaces are dependent on the composition of aerosols, the aerosol diameter, and RH which vary both temporally and vertically during the 48-hour MP. From previous modelling studies of PACT-1D focusing on the parametrization of aerosols, the aerosol diameter was fixed throughout the model period due to limitations in computation and an assumption is set such that the composition of aerosols is uniform. During several days in the NACHTT campaign (including for two morning burst periods), the daytime measurements were also available, where continuous 24-hour vertical profiles of HONO were made. This gives an opportunity to utilize the PACT-1D model to evaluate the relative contribution of daytime heterogeneous ground and aerosol sources of HONO (i.e. nitrate photolysis, acid displacement by a strong acid), and its relevance during the 2011 NACHTT campaign, although many of the fundamental controls on some proposed mechanisms may still be beyond model assessment.

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Appendix A: Parametrizations and Initialization Methods Employed in the BASE model

The derivation of the vertical mixing term from Cao et al. (2016):

Free troposphere (red):

$$K_{Z_{FT}} = \text{constant} = 10^{-3} \frac{m^2}{s} \quad (Eq. A1)$$

Between BLH and SLH (green):

$$K_z(t) = \left(\left(\frac{BLH(t,1) - z}{BLH(t,1) - SLH(t,1)} \right)^2 \cdot \left(\frac{K_{Z_{SL}} - K_{Z_{FT}} + \left(z - SLH(i,1) \left(\frac{K_{Z_{SL}}}{SLH(i,1)} \right) + 2(K_{Z_{SL}} - K_{Z_{FT}}) \right)}{BLH(t,1) - SLH(t,1)} \right) \right) \quad (Eq. A2)$$

Below the SLH (blue):

$$K_{Z_{SL}} = (\kappa \cdot \mu^*(t, 1) \cdot SLH(t, 1)) \quad (Eq. A3)$$

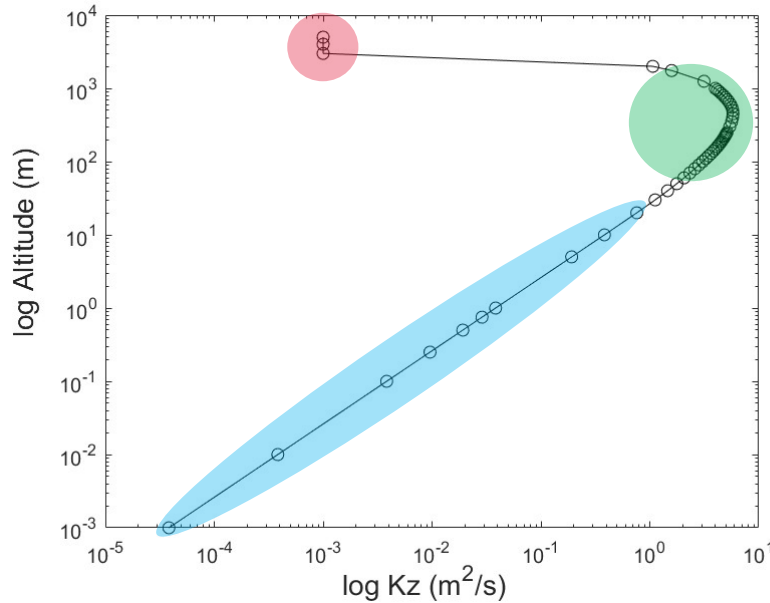


Figure A1: A loglog profile of altitude vs. the K_z term derived by parameterizations from Cao et al. (2016), where each dot represents an average K_z during MP1, expressed at each box level. The three colored regions are used to depict the various K_z parameterizations above the troposphere (red), between the top of the BL and the surface layer (green), and below the surface layer (blue).

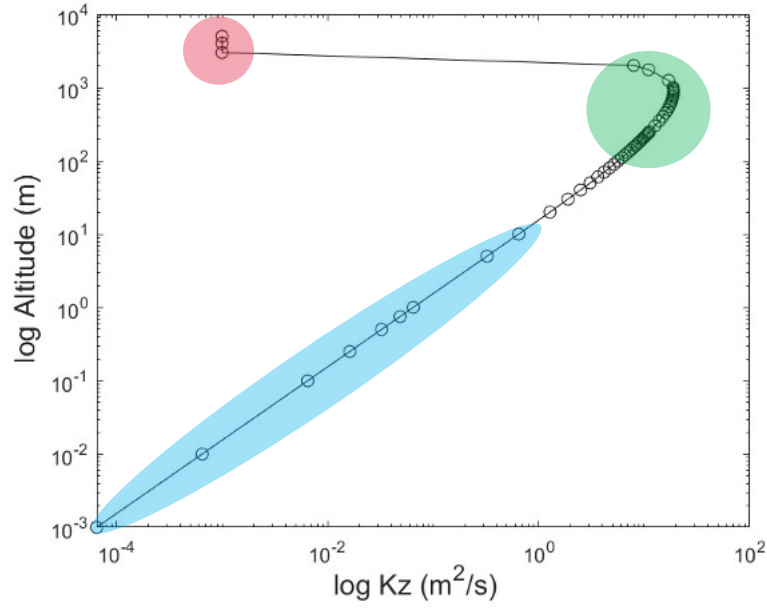


Figure A2. A loglog profile of altitude vs. the K_z term derived by parameterizations from Cao et al. (2016), where each dot represents an average K_z during MP2, expressed at each box level. The three colored regions are used to depict the various K_z parametrizations above the troposphere (red), between the top of the BL and the surface layer (green), and below the surface layer (blue).

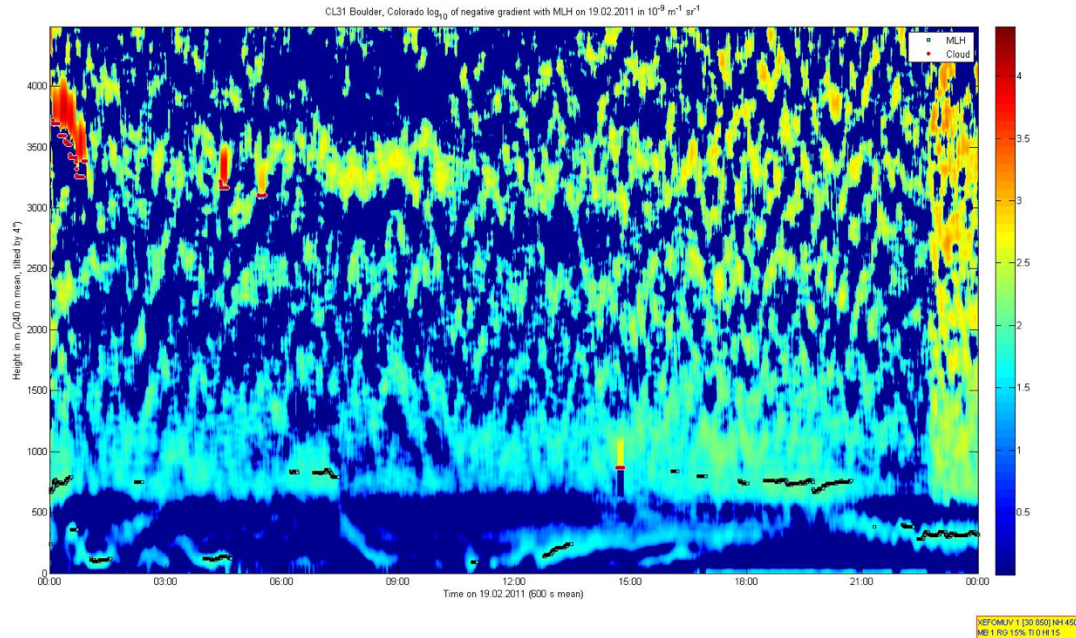


Figure A3. A sample contour plot of aerosol backscatter gradient (z-axis, colored) with the height AGL (y-axis, 0-5000 m) and time of day (x-axis, UTC) derived from BL-View software.

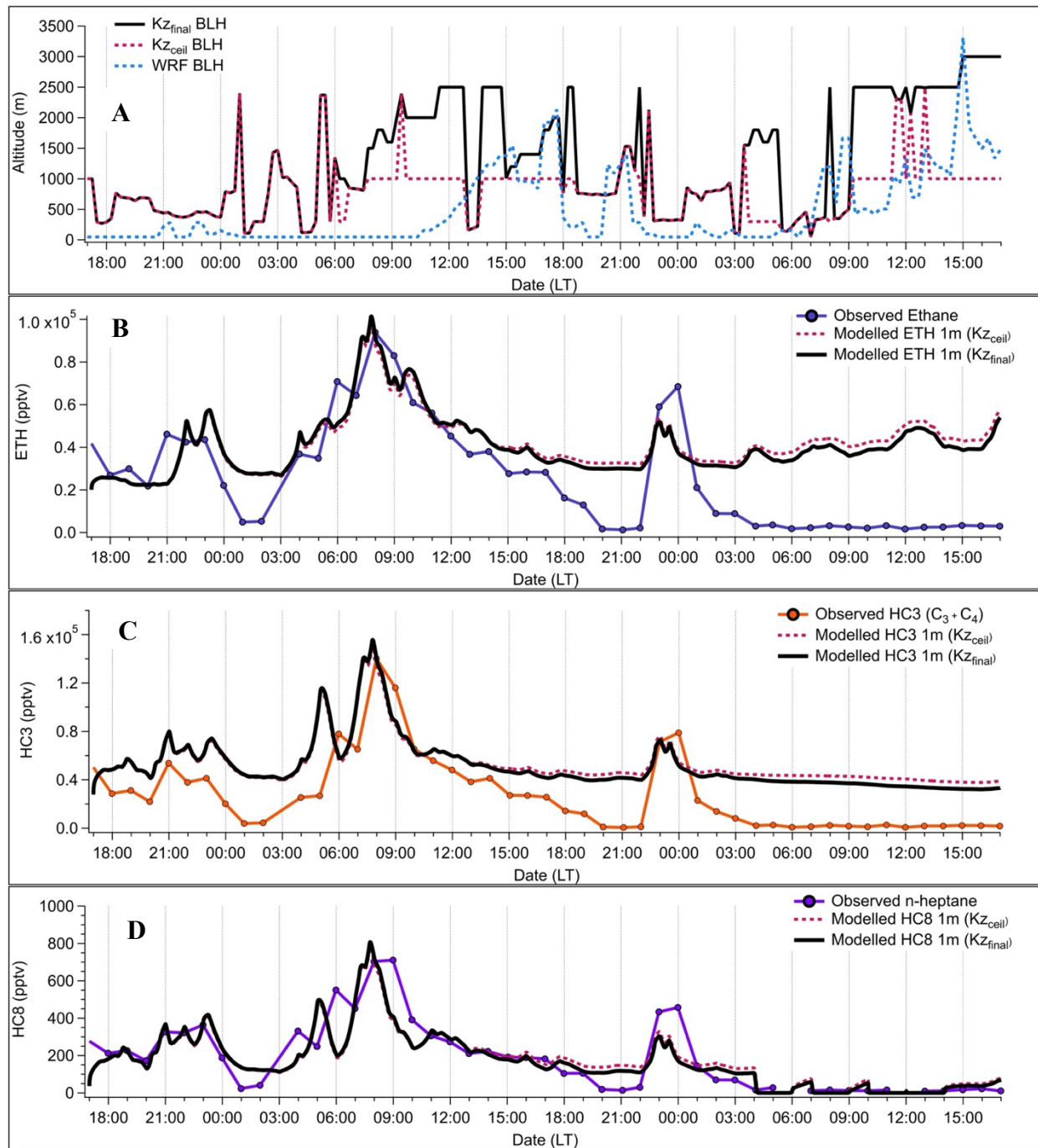


Figure A4. (A) Time series of BLH data from ceilometer measurements pre- (red dashed line) and post-processing (black line) with modelled BLH from WRF (blue dashed-line) during the 48-hour MP. (B, C, and D) Observed mixing ratios of ETH (blue), HC3 (orange), and HC8 (purple) overlaid with BASE (black line) model using pre-processed and post-processed BLH data from ceilometer measurements for parametrizing K_z .

Appendix B: Parametrizations of atmospheric properties and WRF

Calculating RH from the mixing ratio of water vapour:

Note: Similar to deriving K_z , a custom script was made in MATLAB with step-wise elementary operations because ambient temperature and pressure

RH can be expressed as the ratio of the mixing ratio of water vapour to its saturated mixing ratio:

$$\frac{Q_{vap}}{Q_{s vap}} \times 100 = RH = \frac{P_{vap}}{P_{s vap}} \quad (Eq. B1)$$

Where P_{vap} and $P_{s vap}$ are the vapour pressure and saturated vapour pressure of water, respectively. We can calculate the saturated mixing ratio of water using the following equation:

$$Q_{s vap} = 0.622 \left(\frac{P_{s vap}}{p} \right) \quad (Eq. B2)$$

Where 0.622 represents a dimensionless constant (specific gas constant of dry air over specific gas constant for water vapour) and p is the pressure (in Pa).

Using the Clausius-Clapeyron equation, we can derive the saturated vapour pressure as a function of temperature:

$$P_{s vap}(T) = P_{s vap}(T_0) e^{\left(\frac{L_v(T)}{R_v} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right)} \quad (Eq. B3)$$

Where $P_{s vap}(T_0)$ is the specific vapour pressure of water at reference temperature (273.15 K), $L_v(T)$ is the specific enthalpy of vapourization, and R_v is the specific gas constant for water vapour, all as a function of ambient temperature.

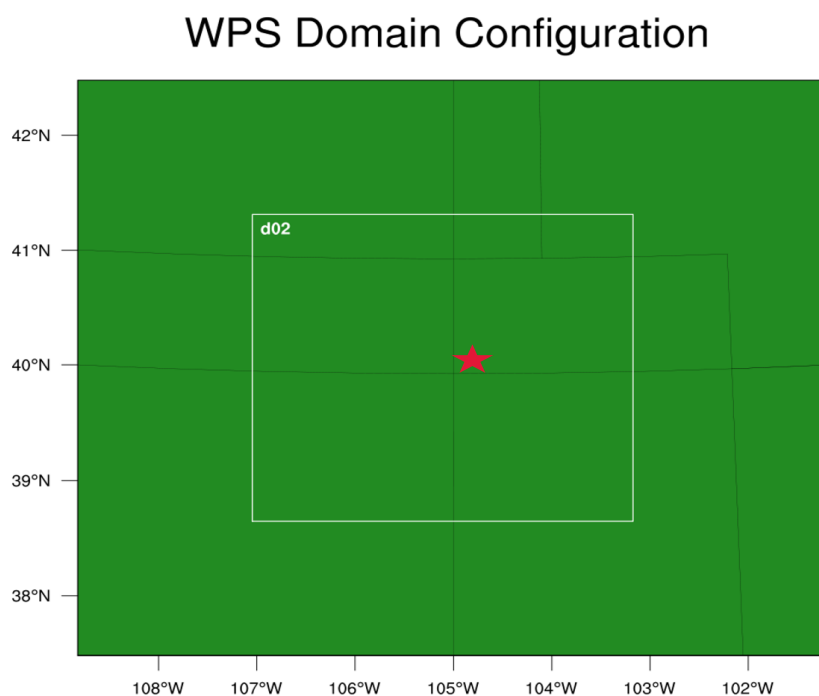


Figure B1. The domain configuration of WRF, where the red star shows the location of the measurement site.

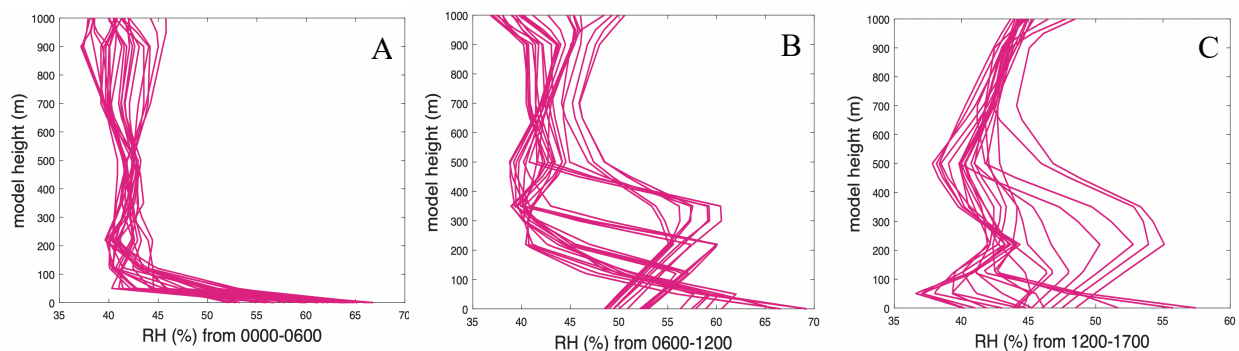


Figure B2. Vertical profiles of RH from the output of WRF binned in 6-hour intervals overnight (A, 00:00-06:00), morning to noon (B, 07:00-12:00), and afternoon till late evening (C, 12:00-17:00) for the first 24 hours of the MP between February 18, 17:00 MST to February 19, 17:00 MST. Note that each trace represents a 15-minute interval.

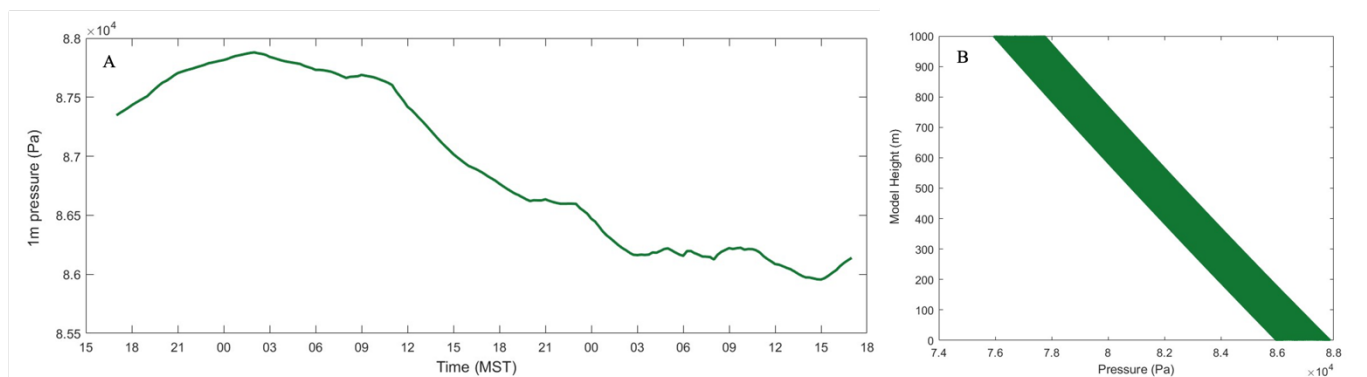


Figure B3. (A) Time series of pressure (Pa) from the WRF output at ground level (1 meter) over the course of the 48-hour MP. (B) Vertical profile of pressure of 1-1000 m from the WRF output over the course of the 48-hour MP. Note that each trace represents a 15-minute interval.

Appendix C: Standard Operating Procedure (SOP) of the PACT-1D model

The Platform for Atmospheric Chemistry and Vertical Transport in one Dimension (PACT-1D) SOP

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1.0. Getting Started/Installations

To run PACT-1D you would require several software installations and package installations before use. These software are the following:

- a) MATLAB (V2023Ra release; Run on Windows or LINUX)
- b) Kinetic Pre-processor (KPP V3.1.1)
(https://kpp.readthedocs.io/en/stable/getting_started/01_installation.html#download-kpp-from-github)
 - i. Needs to be run on LINUX OS or you can use the Windows Subsystem Linux (WSL) form on your windows terminal.
 - ii. LINUX: Follow the procedure using your Linux terminal to install KPP
 - iii. Windows: Go to your command prompt on Windows and type WSL, then follow the procedure to download KPP.
- c) IGOR Pro 8 (Windows or MacOSX)
 - i. IGOR Pro 8 will be utilized for data visualization and data processing.
 - ii. Ask Cora or Trevor for installation details.
- d) **PACT-1D Folder** (will be provided by Trevor VandenBoer)
- e) **Input processing Folder** (will be provided by Trevor VandenBoer)

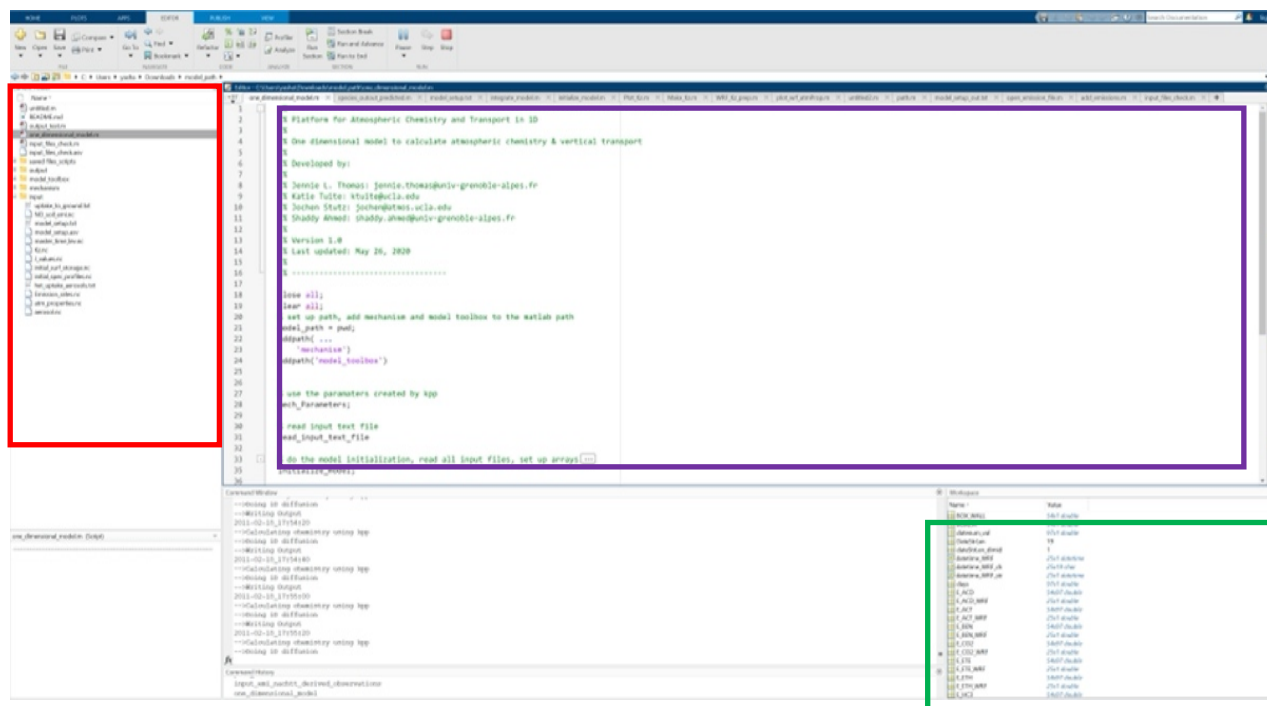


Figure C1. Layout of Matlab's user interface, where the MATLAB directory is shown in red, the script editor is shown in purple, and the workspace is highlighted in green.

2.0. PACT-1D Directory Architecture

When running .m files on MATLAB, ensure that your MATLAB directory is in the location of the .m file that you are running or else it won't run. The left-hand panel shows the MATLAB directory where you can find your .m file and run the script (**Figure C1**). In MATLAB, there are three types of file formats: 1) .m files which are scripts that you can run, 2) .m files with Fx marked are functions and they are not runnable, and 3) .txt files. In PACT-1D, we convert all MATLAB files (i.e. .m file) into a **Network Common Data Form** (NetCDF) file (i.e. .nc), which is a standardized format of storing scientific data with multi-dimensional fields with double precision capabilities. In the center of MATLAB is the script editor, where you can edit your scripts and scroll through already opened scripts. When you run a script successfully, the variables of that script will show up on the workspace (shown in the bottom right of Figure 1). The user of PACT-1D must understand effectively how to set up the proper virtual environment to maximize workflow as model simulations can take up to 12 hours each to complete. When you open the PACT-1D folder, there are four folders and the 1D model script itself (one_dimensional_model.m):

- i. /Model_toolbox: Houses all the auxiliary files required to run the PACT-1D model, where you can create surface source routines (i.e. surface_source_HONO.m).
- ii. /Mechanism: Houses all the files derived from KPP and whatever chemical mechanism scheme you are using (i.e. by default it is Regional Atmospheric Chemical Mechanism 2 [RACM2]).
- iii. /Output: After you run your simulation, all the products of your modelled run will be here and there are four .nc files each with their own respective .m file. To open an output product, you must open a .m file and customize the script to make your plots. These four outputs include:
 - a. VT_rates_plots.m: Plots vertical transport rates of specified gas-phase species x.
 - b. Depo_rates_plots.m: Plots deposition rates of specified gas-phase species x.
 - c. Species_output_predicted.m: Plots time-series of predicted concentration (contribution from emissions and chemistry) of specified gas-phase species x from spec.nc.
 - d. Rxn_rate_plots.m: For this product, it shows the contribution of each reaction from the RACM2 mechanism or otherwise added to your chemical scheme in plot form. The rxn rate products have not been multiplied by the mixing ratio of predicted species (from spec.nc)
- iv. /Input: The most important folder here is the input folder. This holds all the necessary input .nc files created from your input processing folders. See section 3 on what each .nc file does but below is an elaboration on the .txt files written here. There are three important .txt files:

- a. `Model_setup.txt`: Toggle ON (=1) and OFF (=0) options for the model such as initializing surface concentrations, adding emissions, vertical diffusion, setting up the timestep, the chemical (KPP) timestep, and the scaling of vertical diffusion.
- b. `Uptake_to_ground.txt`: Defined reactive uptake coefficients to the ground for species listed. You can always include species and define a respective uptake coefficient but it must follow RACM2 nomenclature.
- c. `Het_uptake_aerosols.txt`: Defined reactive and non-reactive uptake of gas-phase species to aerosols.

In the `Model_setup.txt` of the Input folder, when running the 1D model for the first time, make sure all the options are turned OFF, except running vertical diffusion (Option 2) as it is important to test the physics parametrization of the model before diving into the chemistry. In addition to the PACT-1D folder, you were also given an input processing folder that writes all the input .nc files for you. Once you have created your .nc input files in the input processing folder, you will then copy them to the `/PACT_1D/Input` folder. You will spend most of your time in the input processing folder while the PACT_1D folder is where you want to run your developed scripts.

3.0. Input Processing Directory

Within the Input processing folder, each folder (except for Observations or `pblh_NACHTT` folder) is an important component of the PACT-1D model which you can control. The `/Input` folder in this directory is the same as the PACT-1D folder. The Observations folder holds all the raw Excel files (in .csv format) for all the other input folders. Here are the brief definitions of each folder:

- i. **Aerosol**: Controls input processing of aerosols by observations of aerosol number concentration and radius.
- ii. **Atmos_properties**: Controls input processing of temperature, pressure, and RH from observations. Depending on your box model height (i.e. where the top of your box model is above the height of your observations, you might have to resort to using WRF simulations to get the full meteorological profile of your model.
- iii. **Emissions**: Controls the emission rates of each species x in your model. You can either derive the emission rates from observations or use a WRF_CHEM simulation to get the emission output at your model location.
- iv. **Kz**: Controls the vertical diffusion mixing in your model and utilizes observations of ground (or near ground) windspeed and Boundary layer height to determine the vertical diffusion mixing. Alternatively, you can also use a WRF_CHEM simulation to get the vertical diffusion mixing term as a product, although it will require a lot of storage to do so (> 200 GB).

- v. **J_Values:** Controls the photolysis rate coefficients of photolabile species x and is primarily gathered from the TUV model (https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/). Try to run TUV using the Fortran code and not the online version as there is a lot more control in the scripted version.
- vi. **Initial_conc:** Controls the initial concentrations of each of your species x following the nomenclature in mech.eqn file in the /PACT_1D/mechanism directory (or RACM2).
- vii. **Surface_storage:** Initializes the surface storage term based on the output of a prior model run. After initializing your first run with surface routines turned on, copy the surf_source.nc in the /PACT_1D/Output directory into this folder and run the init_surf_storage.m file to initiate the surface storage routine.
- viii. **Soil emissions:** Did not utilize this section yet.
- ix. **Make_master_time:** This .m file is rooted in the input processing folder and controls the most important aspect of your model – the number of boxes and their associated resolution, as well as the duration of the model. Note that each input file (i.e. Kz, aerosol, J_values, emissions, etc.) will extrapolate to the heights and time of your model, as needed (i.e. if you have BLH listed as 980 m and your box model height is increasing by 100 m, your BLH will be extrapolated to 1000 m to fit the box model height defined in the make_master_time.m file). The box model heights must be first defined correctly before doing any input processing.

Within each folder listed, there are .m files that are listed which are used to create the .nc files below. When combining the PACT-1D architecture with the Input processing directory, we get the entirety of the PACT-1D model from its processing to output (**Figure C2**).

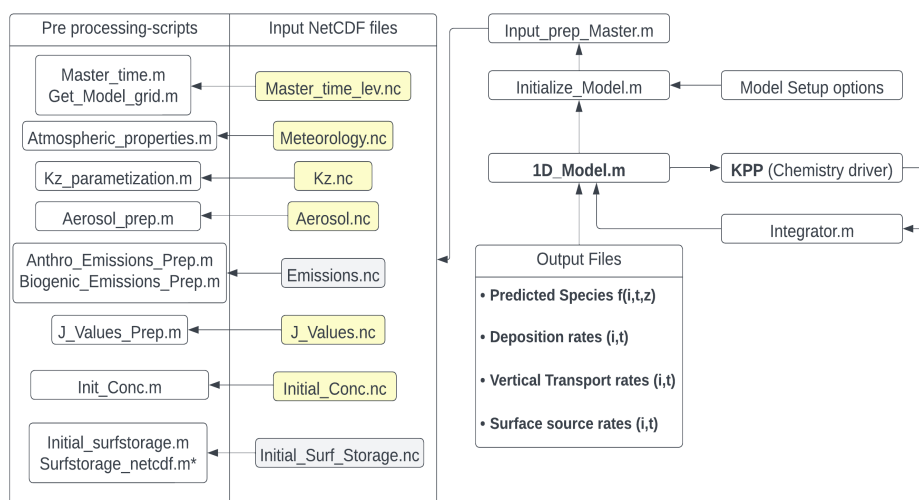


Figure C2. The computational layout of the PACT-1D model, where the pre-processing scripts, input files, the 1D model, and the output files are shown in sequence with each arrowhead directed to a prerequisite script that is required to run the 1D model.

3.1. Setting up the dimensions of the box model and time

The first and most important aspect to parametrize in the PACT-1D model is defining the vertical dimensions and resolution, as well as the start and stop date of your model. All other input components (i.e. Kz, Aerosols, J_Values, emissions, etc.) will be interpolated to match the matrix dimensions of height and time defined in this script. The question of determining how many vertical boxes and how much simulation time are needed for your model is dependent on the quality of the measurements you have and the research question at hand. Generally, the simpler the design of your box model with respect to the box levels and their resolution, the better the chemistry performed.

To manipulate the dimensions of the box model, go to the /Input_Processing directory and open the *make_master_time_file.m*. Set the start and stop date of your model period in the form that is mentioned in the script (YYYY-MM-DD HH:mm:ss) and then set the vertical grid of your box model. There are two height variables in this script termed BOX_WALL and BOX_CH, which are equivalent to the height of each box level and the center of each box level, respectively (Figure 3). The latter term will become useful later when adding emissions schemes, where we want to interpolate to the center of each box height, instead of at the starting edge. Once you have defined the BOX_wall terms, determine the midpoint between each BOX_wall term and define the BOX_CH terms appropriately (**Figure 3**). Once you have defined these terms, you can run the script and a .nc file should appear in the /Input_processing directory called *master_time_lev.nc*. Keep this file here and be ready to copy it into every folder in the /Input_processing folder later on.

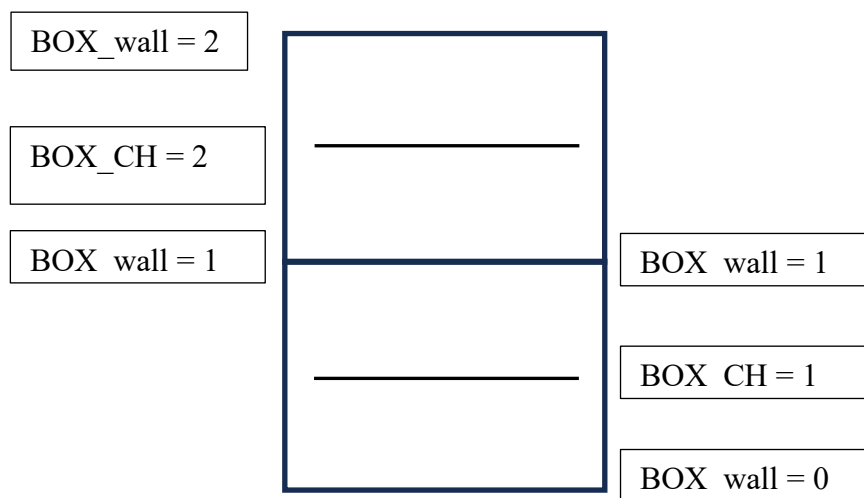


Figure C3. Representation of defining the height of box levels (BOX_wall) and their associated centre height (BOX_CH) in the PACT-1D model.

3.2. Setting up the vertical diffusion mixing term (Kz)

The PACT-1D model incorporates three different methods for calculating Kz depending on whether the user has a WRF simulation of Kz over its model location. If you have a WRF output of Kz, you can use all three methods. If not, you can resort to only one method. These files can be found in `Input_processing/Kz/WRF_Kz_prep` and they have the scripts for the three methods listed below.

- a. Creating Kz using observations only (*Kz_Cao_param.m*)
 - i. Parametrization of Kz made by Cao et al. (2016), where measurements of ground windspeed (<10 m) and BLH are needed to estimate a vertical profile of Kz. Look through *lines 103-129* for how Kz is defined at each junction.
 - ii. From *lines 96-100*, define the appropriate surface roughness of your box floor (i.e. use a logarithmic wind profile to estimate your surface roughness).
- b. Interpolating Kz from WRF to the ground (*Kz_interp_log.m*)
 - i. The limitation of the WRF output is that the minimum height is simulated at 50 m, therefore, this script extrapolates the Kz at 50 m logarithmically to the ground surface.
- c. Merging methods above observed Kz with WRF (*Kz_interp_Cao.m*)
 - i. Uses the lowest 50 m from parametrization of Kz (gathered from ground windspeed and BLH observations) and merges it with the WRF output of Kz above 50 m.

For method a, the script is built to fetch raw CSV files of ground windspeed and BLH from `Input/Observations` and interpolate them by time and height onto the model time grid. Before you run any of the three methods listed above, ensure that your modified *master_time_lev.nc* file is in the `Input_processing/Kz` directory.

After you have successfully run one of the methods above and have acquired a vertical Kz profile, check your current directory (`Input_processing/Kz/WRF_Kz_prep`) for a MATLAB variable called *Kz_Cao* (from method a) or *Kz_WRFcombined* (from method b and c). Copy the variable and paste it to the directory `/Kz`. Once in the `Kz` directory, find and run the scripts labelled *Make_Kz_CaoParam.m* (for method a) and *Make_Kz.m* (for method b and c) to get an output called *Kz.nc*. The *Kz.nc* file can then be copied to the `Input` folder in `Input_processing/Input`.

Check the output of your *Kz.nc* by running the script *Plot_Kz.m* in the `Input_processing/Kz` directory. For a stable boundary layer, ensure that the Kz term does not extend above 1-10 m²/s (depending on the geographical location of your model and its surface roughness) at the top of the BLH.

3.3. Setting up the Atmospheric Properties terms (Temp, Press, and RH)

In this section, the atmospheric properties scripts are used to determine the vertical profiles of temperature, pressure, and RH for the entire range of your model height. Having the correct physical characterizations of temperature, pressure, and RH at each height of the model will ensure that vertical diffusion mixing can occur correctly. This is a critical check point before proceeding to chemistry. There is only **one** method used in PACT-1D for determining the vertical profile of temperature, pressure, and RH – it involves the use of a WRF simulation. The advantage of WRF is that it provides insight into regional meteorological trends for a model location and drives the broader prediction power of the model output. A common disadvantage of this approach is a lack of near-ground surface resolution due to non-explicit parameterization of the surface roughness parameter within WRF.

The method below merges the WRF output of atmospheric properties from the top-of-the-box model to a minimum height of 50 m with observed meteorological measurements used in the lowest box model levels. Before beginning to run the scripts to define the atmospheric properties in your model and acquire an `atmos_properties.nc` file, ensure that your modified `make_master_time_lev.nc` file is in:

`Input_Processing/Atmos_properties/WRF_NACHTT_prep` and,
`Input_Processing/Atmos_properties`

and then proceed to the following:

- i. Load and define raw products from the WRF simulation into vertical profiles of temperature, RH, and pressure.

In the directory `Input_Processing/Atmos_properties/WRF_NACHTT_prep`, there is a script called `WRF_NACHTT_prep.m` which is responsible for loading the products from a `.nc` file and converting them into vertical profiles of temperature, RH, and pressure. Note that the WRF simulation outputs a multitude of physical products that are 4D matrixes (LON, LAT, Height, Time) and the user must isolate these products into 2D matrixes (Height, time) by accounting for the geographical location of their model, which is exactly what `WRF_NACHTT_prep.m` accomplishes. To change the script based on your model configuration, load your custom `WRF.nc` file by changing the directory name. Differences between WRF 3D models arises from time and spatial resolution, which is important to define for your model. In *line 45*, the user should change the coordinates of `XLONG` and `XLAT` to isolate the WRF products for their desired model site. All other nomenclature in WRF is universal so the names and definitions already defined in the script should be relevant for your case study.

- ii. Load observed ground measurements of temperature, RH, and pressure and then merge them with the WRF output

After you have obtained the vertical profiles of temperature, pressure and RH from WRF, the file *write_wrf_atmProp.m* in the directory Input_Processing/Atmos_properties uses a script to merge WRF simulated data with observations on the ground. From *lines 185 to 210*, measurements of temperature, pressure, and RH from a 10 m tower were loaded and interpolated onto the model time grid. From *lines 228 to 259* is an IF statement that merges the WRF vertical profiles of temperature, RH, and pressure with ground measurements. More specifically, *line 249* defines the model level at which the two measurements merge (**Equation 1**).

$$iRow < idxLev(x) \quad \text{Eq 1.}$$

Where x is the row number associated with BOX_WALL. For example, my ground-based measurements were derived from a fixed height of 10 m, which equates to a BOX_WALL row number of 9 (check the BOX_WALL variable). Any box level below row number 9 will be interpolated by ground-based measurements, while any box level above will be interpolated by WRF-simulated products.

Once the script *write_wrf_atmProp.m* is run successfully in the directory Input_Processing/Atmos_properties, an atm_properties.nc file should be created in the same directory. To check the output of the atm_properties.nc file, open the file *plot_wrf_atmProp.m* and run the script, where you would get vertical profiles of temperature, RH, and pressure throughout the entire model period. Ensure that the vertical meteorological profiles correctly follows a diurnal trend that is influenced by the absence or presence of terrestrial radiation, which is an important physical process affecting the troposphere. If everything checks out, you can copy the atm_properties.nc file in the Input_Processing/Input directory in preparation for running the PACT-1D model.

3.4. Setting up the Aerosol term

In this section, the vertical number profiles of aerosols are defined by the assumption that the number concentration of aerosols is constant within the boundary layer (BL), following an exponential decay fitting to 1/5 of the aerosol number concentration at the top of the box (i.e. the exponential decay term simulates the dilution of aerosols as they are above the BL). The aerosol radius (in nm) is fixed and can be adjusted depending on the range of aerosol sizes from observations and their relative mean log-normal distribution. All input processing files can be found in Input_Processing/Aerosol.

Before beginning to run any code, create a CSV file in the directory Input_Processing/Observations or Input_Processing/pblh_NACHTT with the following measurements: 1) ground-based aerosol number concentration and respective datetime, and 2) BLH and its respective datetime. In the Input_Processing/Aerosol directory, open the file *write_aerosol_data.m* and import the observed measurements by loading the CSV files before running the script. Also, remember to copy the modified *master_time_lev.nc* file to the Input_Processing/Aerosol directory. In the case of NACHTT-11, measurements of aerosols were highly resolved, so I had the opportunity to use 15-min averages as my input. It is important to

note that the datetime measurements that you import must include the start date and end date of your model period.

Once the script has successfully run, a file should be created in the directory called *Aerosol.nc*. To check the vertical number concentration profiles from the created *.nc* file, open and run the file labelled *plot_aer.m* and see how the script assumes the vertical number profile of aerosols by dilution above the BLH. If satisfied with the *Aerosol.nc* file, move this file to the *Input_Processing/Input* directory in preparation for running the PACT-1D model.

3.5. Setting up the Photolysis rate coefficient values (J values)

In this section, the molecular photolysis frequencies (s^{-1}) are defined entirely as input from the Tropospheric UltraViolet (TUV) model, which can be accessed from NCAR's website via a quick calculator (https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/), or be downloaded as a Fortran code separately for more control (<https://www2.acom.ucar.edu/modeling/tuv-download>). The TUV model outputs the hourly photolysis rate coefficients of 127 photolabile reactions by simulating the diurnal pattern of the solar actinic flux over 24 hours at a given coordinate (latitude, longitude). Once the zip file *TUV_5.3.2* has been downloaded, extract the contents into a local directory and the *README.txt* file. Read this file to get an understanding of how to get the program started, what options to select, the input parameters needed, and the output files of TUV that are executed (check this PDF for an in-depth overview of the input options that TUV offers https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/InstructionsWebTUV.pdf). It is important to note that the TUV model start and stop time should be equivalent to the *master_time_lev.nc* file (see section 3.1) from the PACT-1D model.

After the TUV model has run successfully, two output files will be created, labelled *tuvlog.txt* and *usrout.txt*, which will be required to parametrize the J values for the PACT-1D model. The first file (*tuvlog.txt*) is an output based on the input options selected for TUV, the list of photolysis reactions, and the solar zenith angle (SZA) of the sun at every hourly timestep. The second file (*usrout.txt*) is the hourly output of the molecular photolysis frequencies for the 127 photolysis reactions in the TUV model. Copy the two output files from the TUV model and paste them into the *Input_Processing/J_values* directory. Within the same directory, open the *.m* file named *J_values_prep.m*, which imports the photolysis rates from the *usrout.txt* file and its related datetime measurement. On *line 25* of the *J_values_prep.m* script, you have to define the line in the *usrout.txt* file which separates the photolysis rate coefficients from the photolysis reactions and then manually list out all the names of each J value in the correct order shown. (Figure C4).

1	%Modified by Katie Tuite April 2018 to account for multiday runs	94	93 = Br2 -> Br + Br
2		95	94 = BrO -> Br + O
3	clear; clc; close all;	96	95 = HOBr -> OH + Br
4		97	96 = BrNO -> Br + NO
5	% read in the master time and level file	98	97 = BrONO -> Br + NO2
6	% addpath('.../.../model_toolbox/')	99	98 = BrONO -> BrO + NO
7	addpath('.../');	100	99 = BrNO2 -> Br + NO2
8	time_level_file = ['./master_time Lev.nc'];	101	100 = BrONO2 -> BrO + NO2
9	[nlev, BOX_WALL, BOXCH, nhour, NTIM_INTEGRATION, Times] = get_model_grid_times(time_level_file);	102	101 = BrONO2 -> Br + NO3
10	[tmp DateStrLen] = size(Times);	103	102 = BrCl -> Br + Cl
11		104	103 = CH3Br -> Products
12	% define information from TUV file	105	104 = CHBr3 -> Products
13		106	105 = CF2Br2 (Halon-1202) -> Products
14	%%	107	106 = CF2BrCl (Halon-1211) -> Products
15	%this is the order of the J values in the TUV output	108	107 = CF3Br (Halon-1301) -> Products
16	%SA 25/03/20 - Added 6 extra reactions (to end of list) from OASIS 2009 campaign that are not in TUV	109	108 = CF2BrCF2Br (Halon-2402) -> Products
17	name = {'J_02','J_03_01D','J_03_03P','J_H02','J_H202','J_N02','J_N03_N0','J_N03_N02','J_N20','J_N205_	110	109 = I2 -> I + I
18	'J_HN02','J_HN03','J_HN04','J_N03aq_N02','J_N03aq_N02aq','J_CH20_HCO','J_CH20_CO','J_CH3CHO_CH3','	111	110 = IO -> I + O
19	'J_CH3CHO_CH3CO','J_C2H5CHO','J_CH3OOH','J_HOCH2OOH','J_CH3ON02','J_CH3_00N02','J_CH3CH2ON02','J_	112	111 = IOH -> I + OH
20	'J_1C4H9ON02','J_2C4H9ON02','J_CH3CHON02CH3','J_CH2OHCH2ON02','J_CH3COCH2_0N02','J_CCH33_0N02','J_	113	112 = perfluoro 1-iodopropane -> products
21	'J_CH3COON02_CH3CO_00','J_CH3COON02_CH3CO_0','J_CH3CH2COON02_CH3CH2CO_00','J_CH3CH2COON02_CH3	114	values at z = 1.564 km
22	'J_CH2CCH3CHO','J_CH3COCH2','J_HOCH2CHO_CH2OH','J_HOCH2CHO_CH3OH','J_HOCH2CHO_CH2CHO','J_CH3_CO	115	Columns: time, sza, photo-reactions
23	'J_CH2OHCOCH3_CH3CO','J_CH2OHCOCH3_CH3','J_CHOCHO_HCO','J_CHOCHO_H2','J_CHOCHO_CH2O','J_CH3COCH3'	116	time, hrs. sza, deg. 1 2 3 4 5
24	'J_CH3CO_00H','J_CH3COCO_0H','J_CH32NN0','J_CF20','J_C12','J_C10_01D','J_C10_03P','J_C100','J_OCL	117	0.0000 83.700 0.000E+00 2.625E-07 8.311E-05 0.000E+00 3.868E-07
25	'J_NOCL','J_C1N02','J_C1N0','J_C1ON02_N03','J_C1ON02_N02','J_CCL4','J_CH3OCL','J_CHCL3','J_CH3CL	118	1.0000 94.725 0.000E+00 9.315E-10 3.805E-08 0.000E+00 1.038E-09
26	'J_CCL3F','J_CCL2F2','J_CF2CLCF2CL','J_CF2CLCF2CL','J_CF3CF2CL','J_CHCLF2','J_CF3CHCL2','J_CF3CHF	119	2.0000 106.116 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
27	'J_CF3CF2CHCL2','J_CF2CLCF2CHFCL','J_Br2','J_BrO','J_OBrO','J_HOBr','J_BrNO','J_BrONO_Br','J_BrON	120	3.0000 117.556 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
28	'J_BrCl','J_CH3Br','J_CH2Br2','J_CHBr3','J_CF2Br2','J_CF2BrCl','J_CF3Br','J_CH2ClBr','J_CF2BrCF2Br	121	4.0000 128.669 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
29	'J_I0N02_IO','J_I0N02_I','J_I0N0','J_CH3CH2CH2I','J_I0N02','J_Icl','J_Ibr','J_perfluoro','J_BALD','	122	5.0000 138.863 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
30	[nrnxns ~] = size(name);	123	6.0000 147.014 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
31		124	7.0000 151.160 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
32	%information about the lines to skip in the file	125	8.0000 149.552 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
33	nskip = 136; %Start from 16/03/09 15:00 AKST	126	9.0000 142.947 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
34	nskip2 = nskip+1;	127	10.0000 133.495 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
35	% lines_per_altitude = nskip+nhour;	128	11.0000 122.697 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
36	lines_per_altitude = nskip+193; %End 21/03/09 00:00 AKST	129	12.0000 111.338 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
37	nday = 1;	130	13.0000 99.864 0.000E+00 1.601E-15 2.118E-11 0.000E+00 2.125E-14
38			
39	%Note you have to check by hand that the times and levels in the usROUT file match the		
40	%times in the master_time Lev.nc file		
41	%Note use space delimited txt file		
42	filename2 = ['./Merged_Jvalues.txt'];		
43			

Figure C4. The *J_values_prep.m* file (shown on the left) defines the location of the *UsROUT.txt* file (shown on the right) where photolysis rate coefficients are written. Note that the highlighted region in red in the *usROUT.txt* file shows the location in which the hourly photolysis rate coefficients for each species is defined.

After running this script successfully, a *TUV.mat* file will be created in the Input_Processing/*J_values* directory which contains the datetime, the photolysis rate coefficients, and the name of each photolysis reaction. To create the *J_values.nc* file, open and run the .m file called *write_jvalues.m*. The purpose of the *write_jvalues.m* file is to interpolate the TUV time with the PACT-1D time and to scale the *J* values from the TUV model to match observations by midday (Equation 2).

$$\frac{J_{NO_2,Obs}}{J_{NO_2,TUV}} \quad Eq\ 2.$$

If the user does not have photolysis rate measurements of NO₂ (*j*_{NO₂}), then it can be derived using irradiance measurements during a clear sky day. The scaling of *J* values from the TUV model is important as the TUV model does not incorporate clouds, which scatters light and reduces the observed *J* values. After successfully running *write_jvalues.m* with no errors, the *J_values.nc* file should be created in the Input_Processing/*J_values* directory. To check a time series plot of the photolysis rate frequencies over the span of the model period, open and run the file *plot_Jvalues.m* and ensure that the diurnal trend matches with observations. To finalize the *J* values for the PACT-1D model, copy *J_values.nc* from the current directory and paste it into Input_processing/Input directory for preparation of the PACT-1D model.

3.6. Setting up the initial concentration term

The initial concentration term is an important parameter related to the chemistry of the PACT-1D model as it sets the initial vertical profile of all defined gas-phase species in your model at $t = 0$. It is important to note that the species list whose initial concentrations are defined must follow naming nomenclature from KPP (i.e. based on RACM2; <https://ars.elsa-cdn.com/content/image/1-s2.0-S1352231012011065-mmc1.pdf>) and be defined in the same order as what is defined in the `mech.spc` file in the `PACT_1D/mechanism` directory. The initial concentration of any gas-phase species is assumed to be constant within the BL and then an exponential decay fit is applied above the BL to 1/20 its concentration at the top of the box model (i.e. simulating a simple diffusion scheme for each gas-phase species). The script for this parametrization can be found in the `Input Processing/Initial_conc` directory, under a file named `Init_conc_profile.m`.

i. Initializing concentrations of the PACT-1D model for the first time:

If this is your first time initializing concentrations for the PACT-1D model, open the `.m` file named `initial_conc.m` in the `Input Processing/Initial_conc` directory and read all the associated comments within the script. The function of this script can be segmented into two sections: 1) defining the species names from *lines 17 to 27* (depending on whether it is RACM2 or RACM) and 2) defining the initial ground surface concentrations (in ppbv) for each gas-phase species from *lines 32 to 217*. After successfully running this script, a `.nc` file should be created in your current directory labelled `initial_spec_profile.nc`. Copy this `.nc` file and paste it into the `Input_Processing/Input` directory for preparation of the PACT-1D model.

ii. Initializing concentrations of the PACT-1D model from a previous model run:

To make a new initial concentration input file based on a prior PACT-1D model run, first import the `spec.nc` (i.e. model output of predicted species) from the `PACT_1D/Output` directory into the `Input_Processing/Initial_conc` directory and run the `.m` file named `initial_conc_From_OutputFile.m`. After successfully running this script, a `.nc` file should be created in your current directory labelled `initial_spec_profile.nc`. Copy this `.nc` file and paste it into the `Input_Processing/Input` directory for preparation of the PACT-1D model.

Check the output of the `Initial_spec_profile.nc` file by running the script `test_plot_initial_conc.m` to get the initial vertical profile of your choice. The current script for `test_plot_initial_conc.m` is only set for CO_2 , however, you can modify the script to include the initial vertical profile of any gas-phase species that was defined in the scripts during initialization.

3.7. Setting up the Emission term

The emission term is the final term that is used to solve the 1D differential equation, where P and L are the chemical production and loss terms, F is the vertical flux, and E is the emission term as a function of height and time for any species i (**Equation 3**).

$$\frac{d[X]_{i,h}}{dt} = (P - L)_{i,h,t} + F_{i,t,h} + E_{i,t,h} \quad \text{Eq 3.}$$

There are currently two methods employed for determining the emission term, depending on the type of measurements being used:

I. Emission rates gathered from observations

The emissions term can be gathered from observations only if ground-based measurements of gas-phase species are coupled with an explicit reference to the BLH measurements, either from vertical radiosonde or through even more resolved techniques, such as ceilometers and Doppler LIDAR. The hourly emission rate (mol/cm²/hr) can be calculated by multiplying the ground-based number density (molecules/cm³) of gas-phase species with the BLH (m) as a vertical dilution factor (Equation 4), averaged over an hour (**Equation 4**).

$$E_t = \frac{n_{x(t)}(BLH)}{3600} \left(\frac{1}{N_a} \right) \left(100 \frac{cm}{m} \right) \quad \text{Eq 4.}$$

Where E is your emission rate (mol/cm²/hr) and N_a is Avogadro's number (6.022×10²³ molecules mol⁻¹). Once the hourly emission rates have been calculated for your gas-phase species of choice, save it as a CSV file in Input_processing/Observations directory, and then go to the file *input_emi_nachtt_derived_observations.m* in the Input_Processing/emissions directory. The purpose of this script is to import the calculated emission rates from observations, interpolate them to the time of the PACT-1D model, apply a scaling factor to obtain the overall emission rates (if needed), and then distribute the emissions to a defined box level. Note that the name of the emission rates must also match with the RACM2 nomenclature and must be speciated accordingly (i.e. HC3 = n-propane, n-butane) or else the emission routine will not work and the model will not run. To check the validity of your emissions (assuming the gas-phase chemistry mechanisms and vertical diffusion routine are correct) for a model run, do not include any explicit emission rates for O₃, N₂O₅, and NO₃ as the predicted concentrations of these species would strictly be related to the interaction between radicals, VOCs, and NO_x, as well as the nocturnal availability of NO_x and O₃, respectively. Once the script has run successfully, a .nc file named *Emission_rates.nc* will be created in the Input_processing/Emissions directory, where you can check the output of these files by running a script labelled *plot_emissions.m* in the same directory. Copy the *emission_rate.nc* file into the Input_processing/Input directory for preparation of the PACT-1D model run.

II. Emission rates gathered from simulations of WRF-CHEM

The alternative approach in the absence of either abovementioned measurements is to run a WRF-CHEM simulation to attain the emission rates for the PACT-1D model. The advantage of running a WRF-CHEM model is that it gives a simulated vertical profile of temperature, pressure, RH, vertical diffusion coefficient, and the emission rates all in one package which has been solved using the same numerical integration method. The disadvantage of a WRF-CHEM simulation is that it is computationally expensive because it has to be simulated for longer periods to be representative of the geographical location of interest, especially near the ground surface where the parametrizations of surface roughness may be poorly represented. Emission rates simulated from WRF-CHEM models are divided into anthropogenic and biogenic-based emissions, which are based on emission inventories such as the National Emission Inventory (NEI) and Model of Emissions of Gases and Aerosols from Nature (MEGAN), respectively.

To import the WRF-CHEM emission rate products into MATLAB, copy and paste the WRF-CHEM output (i.e. a .Dat file) into the Input_Processing/Emissions/WRF_files directory and open and read the file *WRF_emi_prep.m*. The purpose of this processing file is to convert the units of the emission rate from moles/Km²/hr to molecules/cm²/s and then speciate the WRF emission rates to fit the RACM2 nomenclature (i.e. $\text{WRF_NO}_2 = \text{WRF_NO}_x * 0.20$). Once the file has run successfully, open and run another file labelled *write_CalNex_emissions.m* in the Input_processing/Emissions directory, which is set to interpolate the time of the WRF-CHEM emissions with the PACT-1D, apply a scaling factor, and create a .nc file. After running this script successfully, a .nc file labelled *Emission_rates.nc* should be created in the current directory. You can check the output of the *emission_rates.nc* file by running a file labelled *plot_emission.nc*, which plots a time series of the emission rate for each gas-phase species defined in your model. Finally, copy the newly created *Emission_rates.nc* file and paste it into the Input_processing/Input directory for later processing of the PACT-1D model.

3.8. Setting up the initial surface storage term

The PACT-1D model features a ground surface storage term in which gas-phase molecules can react with the ground surface during a model run, where depending on their reactive uptake coefficients and the number of available molecules for collisions, they can be taken up by the ground storage term. The initial surface storage term is initialized after a prior run of the PACT-1D model, by equating the *surface_source.nc* file in the PACT_1D/output directory to an *initial_surf_storage.nc* file. To set up the initial surface storage term, copy the file labelled *surf_source.nc* in the PACT_1D/output directory and paste it into the Input_processing/surface_storage directory to get started. In the same directory, open the *init_surf_storage.m* script and define the name of the surface storage file (i.e. line 8 of the script) to import it into code. After running the script successfully, a .nc file should be created in the current directory labelled *initial_surf_storage.nc*, where we would copy this file into the Input_processing/Input directory for preparation of the final rendering of the PACT-1D model – with ground surface storage term included.

3.9. Initialization of the PACT-1D Model

Once the input NETCDF (i.e. .nc files) from each component of the PACT-1D has been initialized (except surface storage term for the first model run) and stored in the Input_Processing/Input directory, we can now move them to the PACT_1D/Input directory to run the model (**Figure C2**).

Note: copy the individual .nc files in the Input_Processing/Input directory instead of the entire folder itself. Once copied in the PACT_1D/Input directory, go to the *model_setup.txt* file and view all the options enlisted for the PACT-1D model (**Figure C5**) and their associated definitions (**Table C1**).

Table 1. Options of the PACT-1D model and their definitions.

#	Options	Definitions
1	Run chem	Run RACM2 chemistry routine using KPP
2	Run vert diff	Incorporate vertical diffusion mixing (Kz)
3	Addemissions	Run emission rate scheme
4	Initialize_surface_concentrations*	If = 1, utilizes Initial_spec_profile.nc (for first time run), else = 0 and utilize init_conc_from_outputFile.m
5	Add NO soil emission	Adds a separate soil emission scheme for NO (optional)
6	Add_surface_source_HONO	Adds surface production scheme of HONO based on heterogenous ground production mechanisms written in model_toolbox/surface_source_HONO.m
7	Add_surface_source_Cl_Br	Adds heterogenous surface production schemes of Cl and Br written in model_toolbox/surface_source_cl_br.m
8	Add_surface_source_Iodine	Adds heterogenous surface production scheme of Iodine written in model_toolbox/surface_source_iodine.m
9	xhet	Heterogenous chemistry on aerosol schemes controlled for species in input/het_uptake_aerosols.txt
10	xIod, xCl, xBr	Include gas-phase chemistry of iodine, chlorine, and bromine.
11	Chemistry timesteps	Timestep of the PACT-1D model (integrator.m)
12	KPP timestep	KPP timestep, where chem_timestep = n*KPP_timestep
13	n_step_diff	Controls the number of diffusion timesteps between box levels per chemistry timestep.
14	Output frequency	Number of outputs per chemistry timestep. Always keep this at 1.

During the first model run of the PACT-1D model (assuming chemistry has not been set up in KPP), turn off all options except options 2, 3, and 4 to test the physics parametrizations of your model using an inert gas such as ETH, HC3, HC5, HC8, or CO₂. After setting up these options in the model_setup.txt file, go to the /PACT-1D directory and run the *one_dimensional_model.m* file, which is the code for the PACT-1D model. Once you click on run in MATLAB, the command window should begin parsing all the individual options that have been activated and begin calculating the differential equation at every chemical timestep.

If a red error is displayed in the command window and the operation is halted, locate the error and fix the issue. These issues are usually related to not being on a file within the PACT_1D MATLAB directory when running the 1D model or incorrectly defining a directory name in the *integrator.m*, *read_input_text_file.m*, or *initialize_model.m*, which are all found in the PACT_1D/Model_toolbox directory. Another error that could show up during integration of the PACT-1D is if the number of matrix dimensions for each component of PACT-1D is not equivalent and their start and stop times do not match with the model time, which is defined in the Master_time_lev.nc file. Within the command window of MATLAB, this error is displayed in yellow (i.e. as a warning) and states that the command window

```
# options for running the model, timesteps, and output file comments
# do not change the order of the options, include all lines in this file
# use three comment lines for this file
1 %run_chem on=1 or off=0
1 %run_vert_diff on=1 or off=0
1 %addemissions on=1 or off=0
0 %initialize_surface_concentrations on=1 or off=0
0 %add_NO_soil_emissions on=1 or off=0
0 %add_surface_source_HONO on=1 or off=0
1 %add_surface_source_Cl_Br on=1 or off=0
0 %add_surface_source_Iodine on=1 or off=0
1 %xhet on=1 or off=0
0 %xIod on=1 or off=0, with or without iodine chemistry
1 %xCl on=1 or off=0, with or without chlorine chemistry
1 %xBr on=1 or off=0, with or without bromine chemistry
20 %chemistry timestep in seconds
10 %internal kpp timestep - (smaller than dt_chem) seconds, must follow dt_chem = n*dt_kpp, where n is an integer
500 %n_step_diff - number of diffusion timesteps per chemistry timestep
1 %output write frequency, write every X chemistry timesteps
'output_file_comment - Model start time: 18 March 2009 - 00:00 AKST'
'output_file_created_by - Shaddy AHMED - shaddy.ahmed@univ-grenoble-alpes.fr'

#NOTES
#1. - surface production of iodine, HONO, or other species are controlled in - model_toolbox/diffusion_1d.m and model_toolbox/
surface_source.m
#update this for your case! Currently only set up for HONO.

#2. We recommend a grid between about 10-20 meters that is log scale with decreasing box sizes close to the ground, with the lowest model
layer on the order of the millimeter scale, the scale appropriate for molecular diffusion. Between your lowest available Kz and the
ground, we recommend you interpolate such that for the lowest model level Kz = 0. We calculate online the molecular diffusivity and use it
to transport gases into the lowest model level
```

Figure C5. Screenshot of the *model_setup.txt* file in the PACT_1D/Input directory which controls the turning on and off options of the different components in the 1D model, as well as the chemistry and KPP timestep of the model. These options were defined and created by Shaddy Ahmed as an example.

4.0. Chemistry and setting up KPP

The Kinetic PreProcessor (KPP) is a numerical integration software that facilitates the PACT-1D model by characterizing the chemistry of all gas-phase species in the troposphere by defining their mechanisms and quantum yields. For all homogenous gas-phase mechanisms, the Regional Atmospheric Chemistry Mechanism 2 (RACM2) or any other peer-reviewed atmospheric chemistry mechanism scheme (i.e. MCM, RACM, RADM, etc.) can be incorporated into KPP.

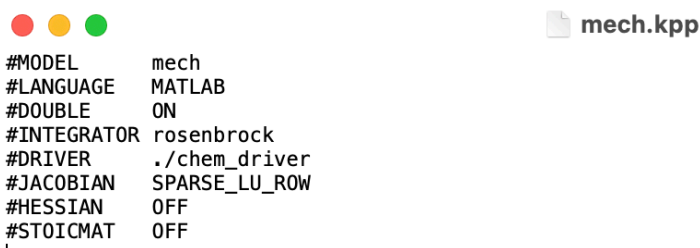
The most challenging aspect of KPP is installing the software on Linux, as it requires an understanding of building virtual environments within your Linux (or WSL) OS (link provided for installation guide in section 1.0). A virtual environment must be defined within your KPP directory or else the program will not parse. After downloading the KPP software on your Linux (or WSL) OS, I would highly recommend running KPP with an example mechanism provided as default in the KPP directory before making your own input files.

(https://kpp.readthedocs.io/en/stable/getting_started/02_running_kpp_sample_mech.html)

Within KPP, four input files are utilized to define KPP, each with a unique suffix: 1) *ROOT.kpp* (i.e. main console file), 2) *ROOT.eqn* (i.e. equation file), 3) *ROOT.spc* (i.e. species file), and 4) *ROOT.def* (i.e. rates defined by homogenous, third-body pressure-dependent, and equilibrium mechanisms), where the name ROOT is the name of the current KPP file. To look at specific examples of these files, I recommend going to the PACT_1D/mechanism directory and finding all the input files mentioned to get an idea of how they are defined (i.e. you can view these files by right-clicking and opening with a text editor).

4.1. Defining the ROOT.kpp file

The *ROOT.kpp* input file is a very simple text file (i.e. created outside of the KPP directory) that fetches files based on what is written in the KPP directory (**Figure C5**). Based on KPP syntax, each new line must begin with a # to let KPP know that you are fetching a new folder from the KPP directory. The names and definitions of each of these files are described in **Table 2**. For now, you can copy the *mech.KPP* file from the PACT_1D/mechanism directory and use it as a base case for your model, where the only input you should change is the name of the model (i.e. from mech to any name).



```
#MODEL      mech
#LANGUAGE   MATLAB
#DOUBLE     ON
#INTEGRATOR rosenbrock
#DRIVER     ./chem_driver
#JACOBIAN   SPARSE_LU_ROW
#HESSIAN    OFF
#STOICMAT   OFF
```

Figure C5. The *ROOT.kpp* file, controls all the output options for KPP, such as the output language (i.e. MATLAB), the integrator, the driver, and options for Jacobian routines.

Table C2. The components of the *ROOT.kpp* and their respective definitions.

Name	Definition
Model	Name of the model ROOT (all output files will also have ROOT name associated)
Language	The output language of KPP (i.e. MATLAB, Fortran, C+, etc.)
Double	The numbers we are using are classified as double precision, so that a large number of decimal places during integration is retained.
Integrator	In KPP/int directory, select from a wide variety of ordinary differential equations (ODEs)
Driver	In KPP/drv, select from a list of chemical drivers
Hessian	Always keep off
Stoicmat	Always keep off

4.2. Defining the ROOT.eqn file

The *ROOT.eqn* file is responsible for storing all the defined mechanisms that will be utilized in your model. In the PACT-1D/Mechanisms directory, open the file *mech.eqn* and view how each of these mechanisms was defined. Note that most of these equations were derived directly from the RACM2 mechanism (i.e. up until *reaction 363*) and Shaddy Ahmed's Chlorine and Bromine chemistry mechanisms (*reaction 364 – 486*). Note that in the PACT-1D/Input directory, the *model_setup.txt* file can automatically turn off select chemistry (i.e. chlorine, bromine, and iodine chemistry), therefore is no need to delete the mechanisms in the *ROOT.eqn* file that is utilized to characterize halogen chemistry, you can simply update the *ROOT.eqn* with the mechanisms of your choice, while actively turning off the halogen chemistry in the PACT-1D model setup txt file. Depending on the nature of your reaction mechanism, whether it is third-body pressure dependent, heterogenous on aerosols, in equilibrium, or simply homogenous, the notation of your mechanism will change. Each addition of a new mechanism begins with the row number of the mechanism enclosed in a curly bracket, followed by a description of the mechanism. Please note that the species names written in the *ROOT.eqn* file must match the nomenclature in the *ROOT.spc* file.

4.3. Defining the ROOT.spc file

The *ROOT.spc* file defines the names of all the species involved in the KPP routine and hence, the PACT-1D model. Depending on the atmospheric gas-phase chemical mechanism scheme you use (i.e. RACM2, RACM, RADM, or MCM), the names of species are defined in the *ROOT.spc* file must coincide with the nomenclature of the gas-phase chemical mechanism scheme. There are two types of classifications for species depending on whether they are fixed (i.e. DEFFIX) or variable (i.e. DEFVAR) over time.

4.4. Defining the ROOT.def file

The *ROOT.def* input file is responsible for defining the rate calculations within KPP based on the nature of the mechanism. To utilize the *ROOT.def* file used in my case scenario, go to the PACT-1D/mechanisms directory and open the *mech.def* file to visualize how each type of mechanism was defined. Notice that there are four different inline MATLAB rates defined in this file, including RACM_Thermal, RACM_Thermal_T2, RACM_TROE, and RACM_TROE_Equilibrium.

4.5. Running KPP from the Linux terminal (or WSL command prompt)

To create an instance of KPP for your model, open the Linux terminal (or the WSL command prompt in Windows) and type the following:

```
cd $HOME
mkdir example_directory
cd example_directory
```

The first line ensures that you are in your home directory (which is linked with the KPP directory), the second line creates a directory with the name of your choice (i.e. `example_directory`), and finally, the third line enters the newly made directory.

From the PACT-1D/mechanism directory, copy the file *mech.kpp* and paste it into the newly created example directory. Open the *mech.kpp* file and under `#Model`, change the name *mech* to the ROOT name of your choice (i.e. *test*), then save the file as the model name of your choice. To the same `example_directory`, add all of the other KPP input files, including the `.spc`, `.def`, and `.eqn` files. Within the `.def` file, ensure that the beginning of the script is changed to match the names of the `.spc` and `.eqn` files. Once all the KPP input files are in the example directory, go back to the Linux terminal and type the following code to begin an instance of KPP:

```
kpp test.kpp
```

If this instance of `kpp` ran successfully, the terminal should output the following message:

```
KPP has successfully created the model "test".
```

KPP will parse several output files within the example directory which will all be transferred to the PACT-1D/mechanisms directory and be ready to be used alongside PACT-1D model.

Appendix D: Spatial and Temporal Variability of HONO, NO₂, and O₃ During the 48-hour MP

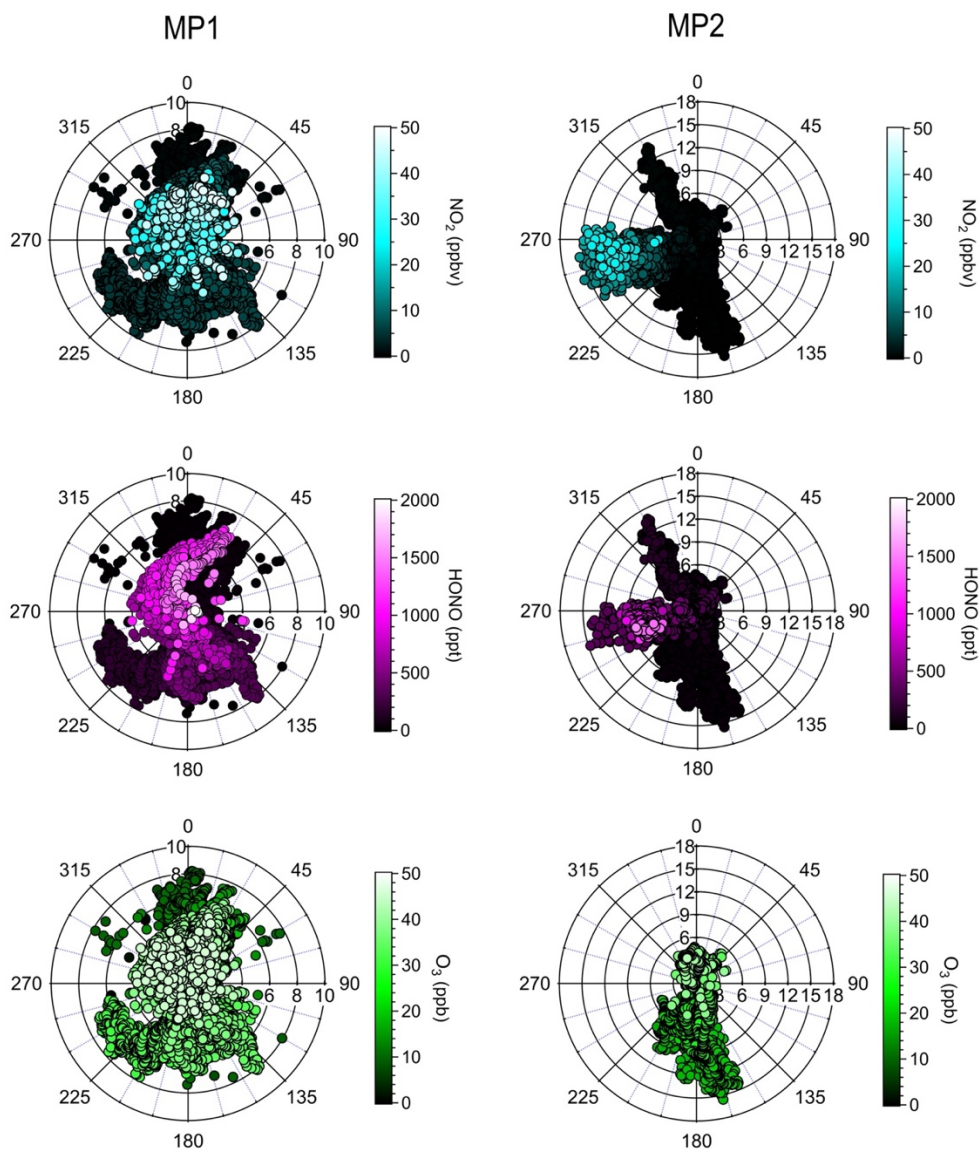


Figure D1. Windrose plots of gas-phase NO₂, HONO, and O₃ for both MP1 and MP2, where the rings depict the wind speed (m/s) interval and the declinations around the perimeters represent the wind direction (°).

Appendix E: Vertically-Resolved Meteorological Observations During the 48-hour MP

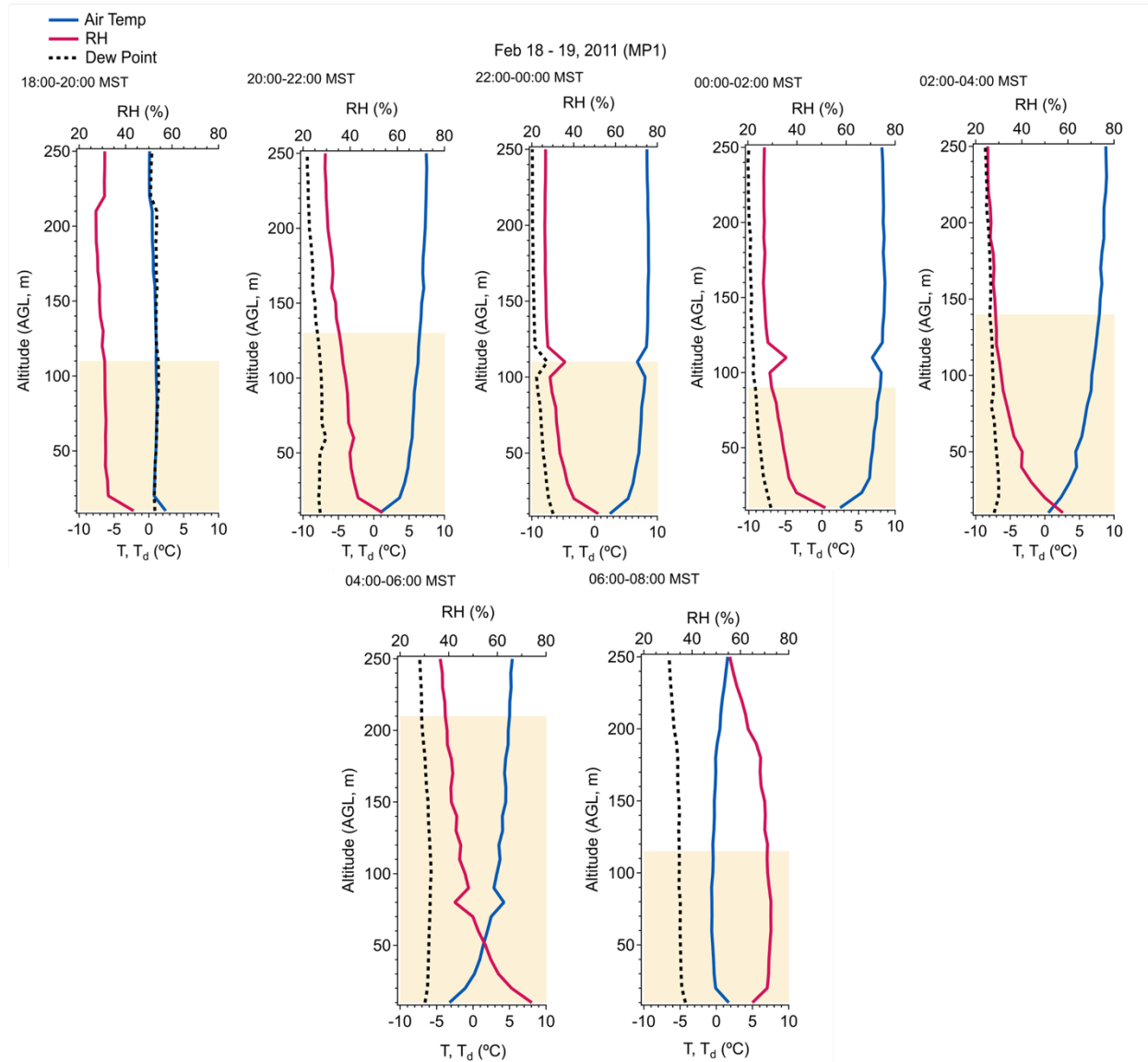


Figure E1. Two-hour binned average vertical profiles of RH (red, %), air temperature (blue, °C), and dew point temperature (black dash, °C) from a height of 10-250 m between 1800 - 0800 MST during OP1.

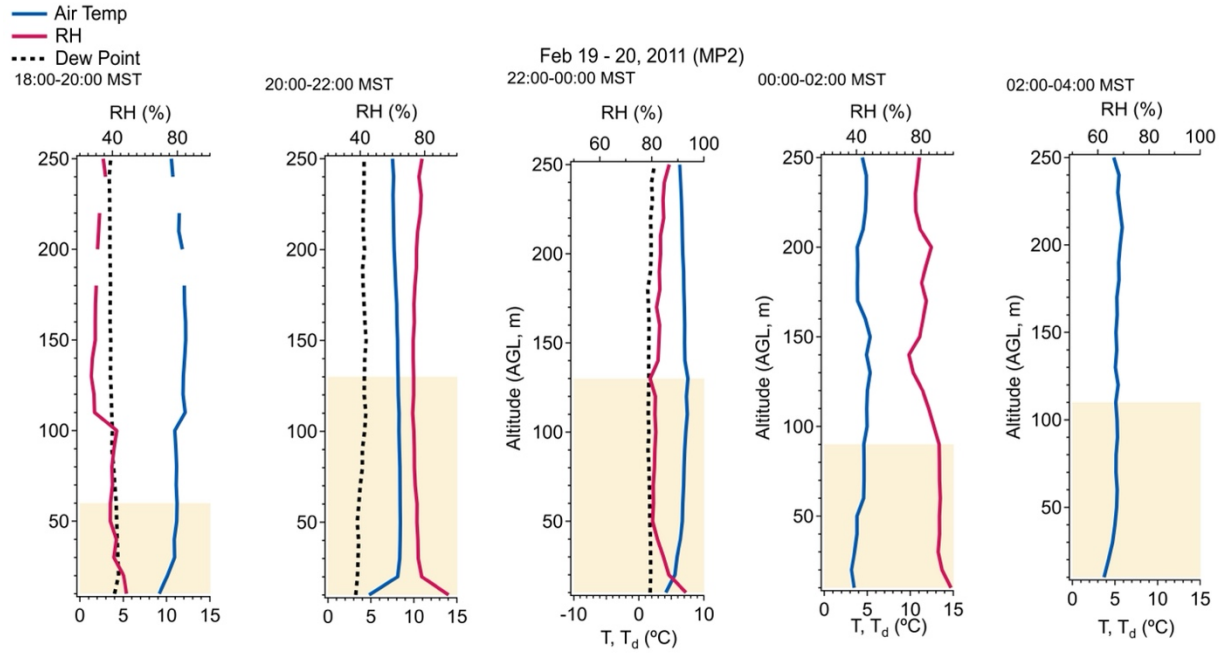


Figure E2. Two-hour binned average vertical profiles of RH (red, %), air temperature (blue, °C), and dew point temperature (black dash, °C) from a height of 10-250 m between 1800 - 0400 MST during OP2.

Appendix F: Determining the NBL Height Using Potential Temperature and O₃ Profiles

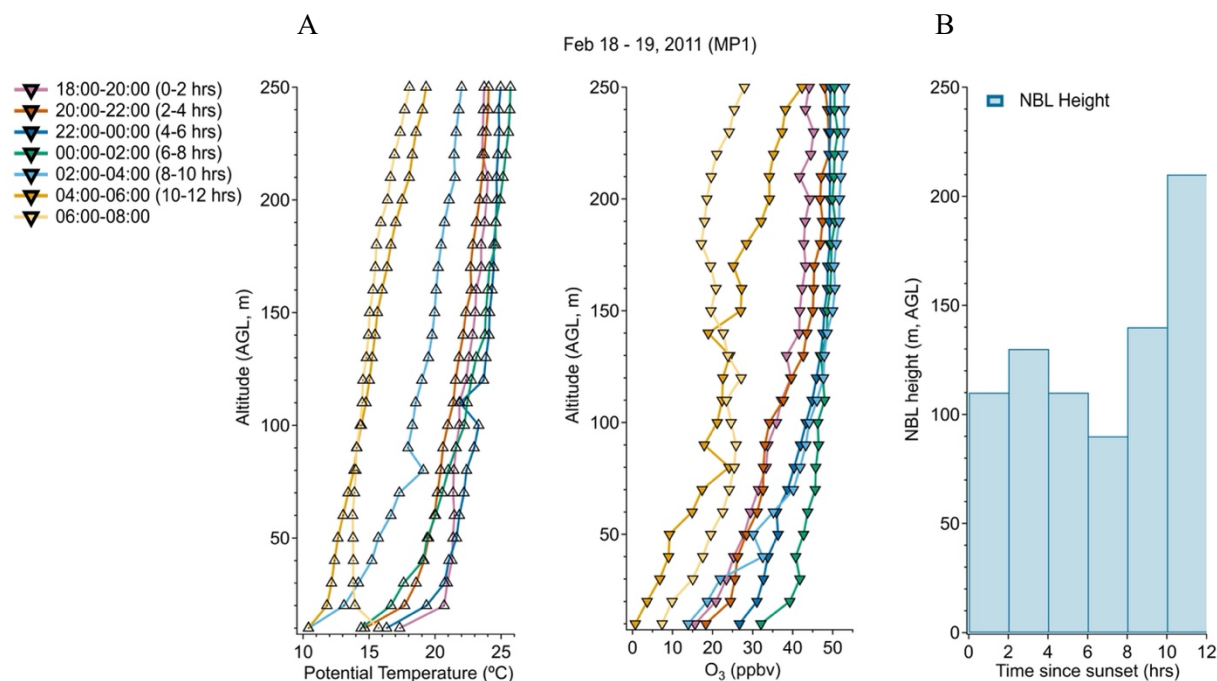


Figure F1. (A) Two-hour binned average vertical profiles of potential temperature (°C) and O₃ from a height of 10 m to 250 m during OP1 for the determination of the NBL height between 18:00-06:00 MST. (B) A bar graph showcasing the estimated NBL heights determined from the two-hour binned potential temperature and O₃ profiles in OP1.

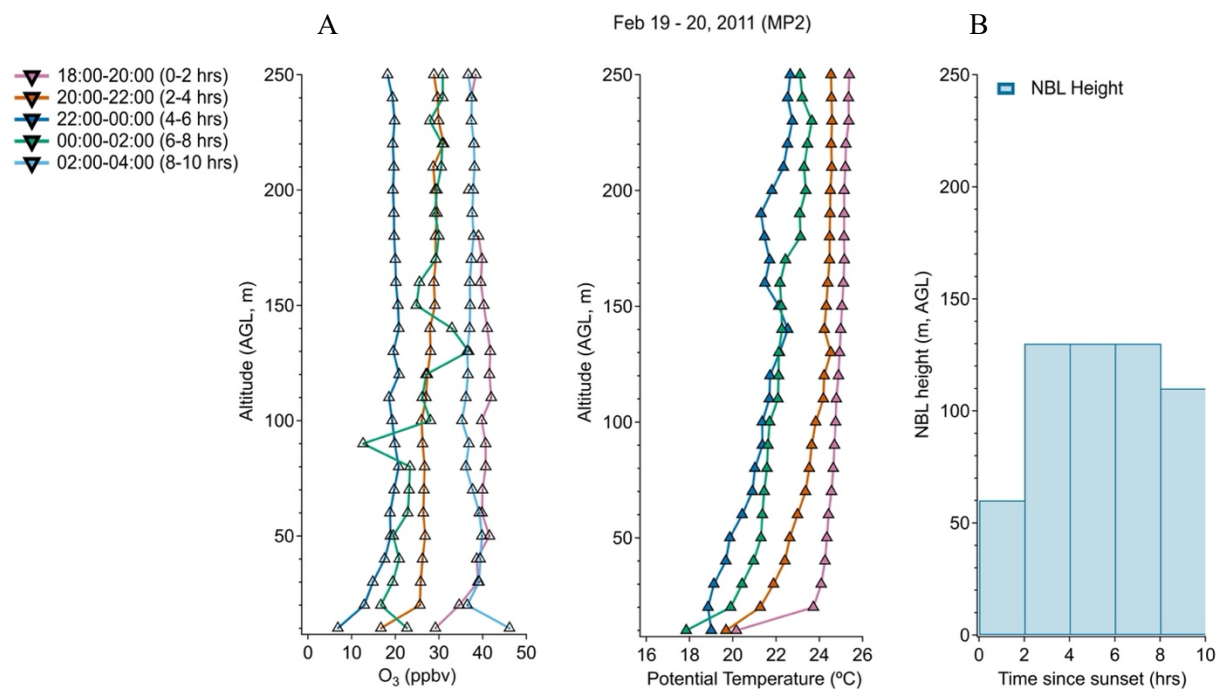


Figure F2. (A) Two-hour binned average vertical profiles of potential temperature ($^{\circ}\text{C}$) and O_3 from a height of 10 m to 250 m during OP2 for the determination of the NBL height between 18:00-04:00 MST. (B) A bar graph showcasing the estimated NBL heights determined from the two-hour binned potential temperature and O_3 profiles in OP2.

Appendix G: Modelled near surface-level mixing ratios of all other species from BASE

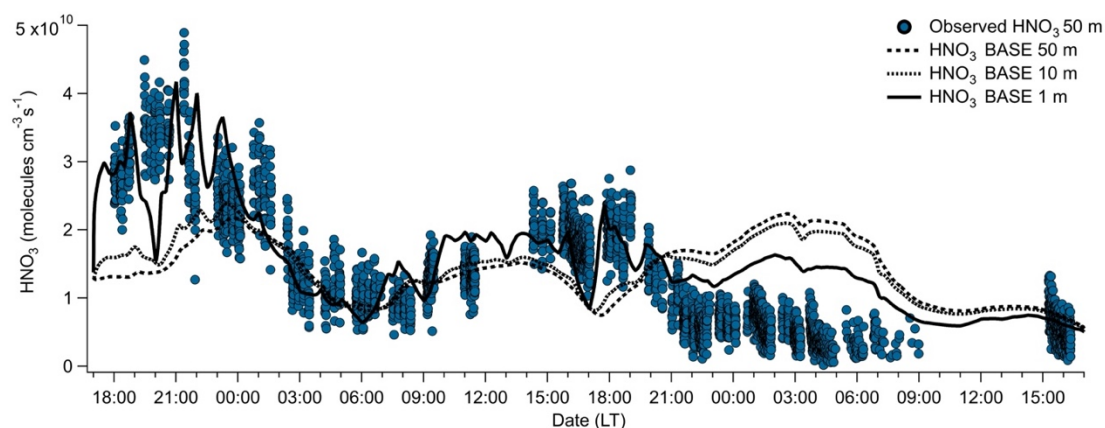


Figure G1. Time series of vertically-resolved measurements of HNO_3 (navy blue dot) filtered to a height of 50 m from the NACHTT campaign overlaid with modelled HNO_3 (black line, molecules $\text{cm}^{-3} \text{ s}^{-1}$) from the PACT-1D BASE model parametrization, at heights of 1, 10, and 50 m.

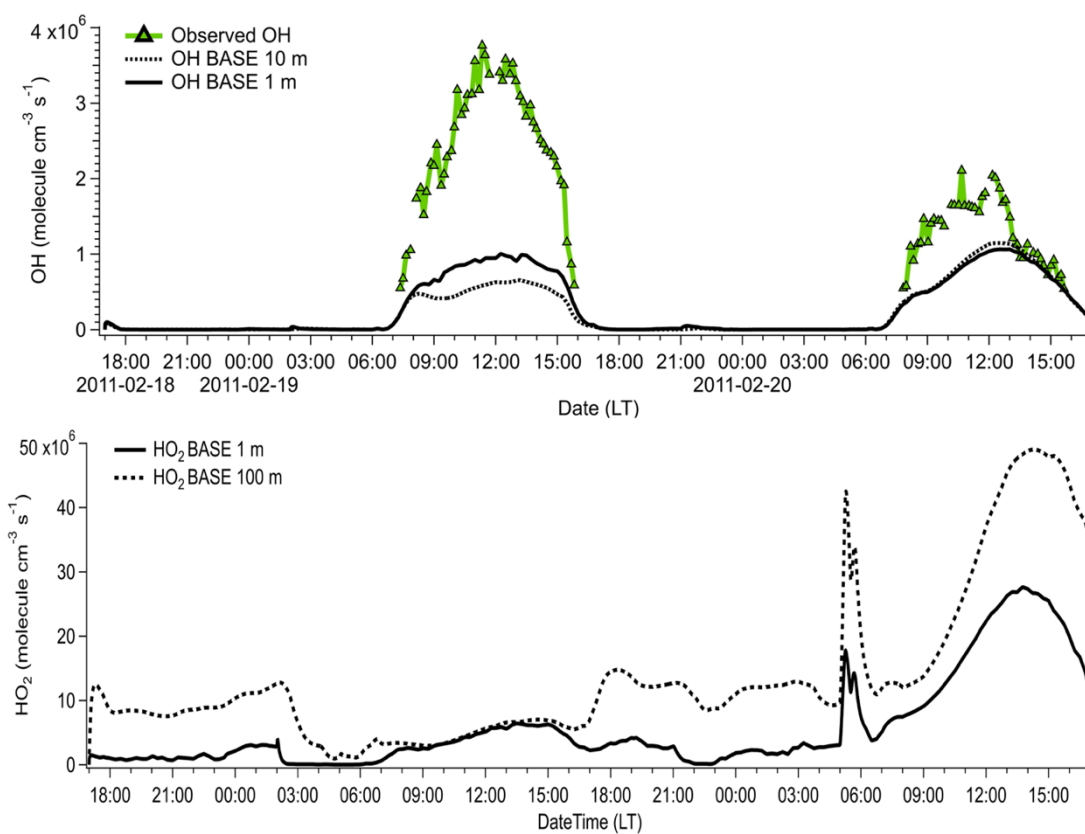


Figure G2. Time series of modelled number density of (A) OH and (B) HO_2 from the BASE model at the height of 1 (black line) and 100 m (black-dashed line) during the 48-hour MP.

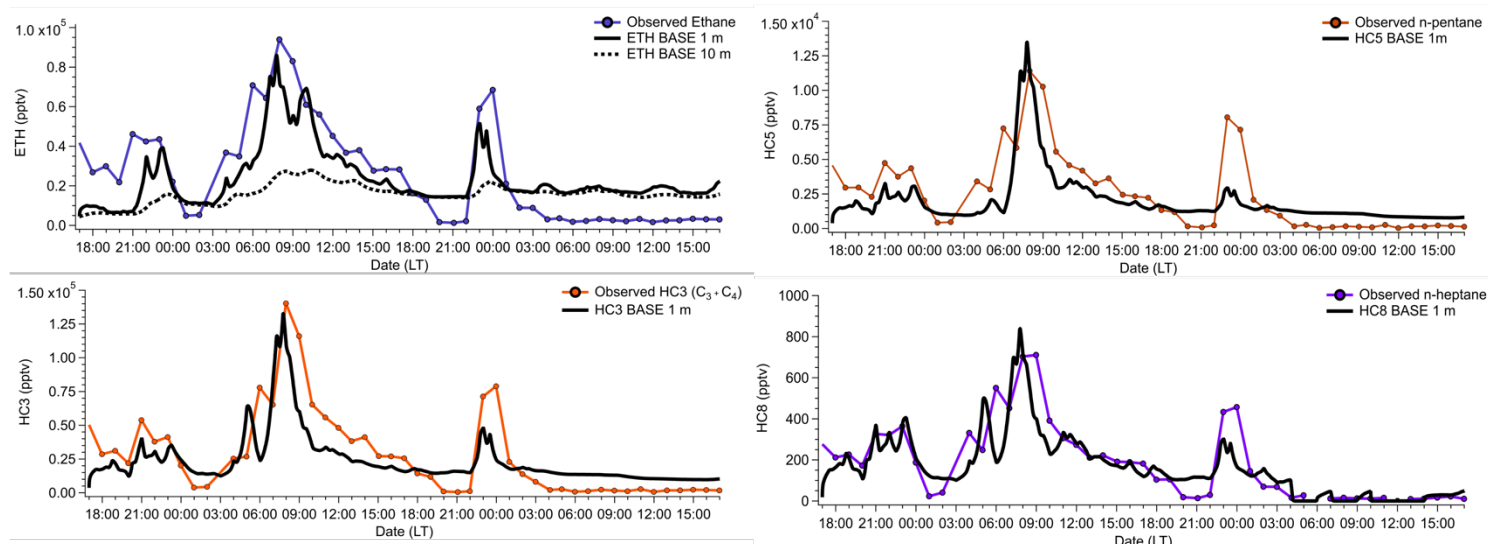


Figure G3. Time series of ground-level observations of C_2 (ETH), C_3+C_4 (HC3), C_5+C_6 (HC5), and C_7+C_8 (HC8) overlaid with respective modelled mixing ratios (black line) from the BASE model during the 48-hour MP.

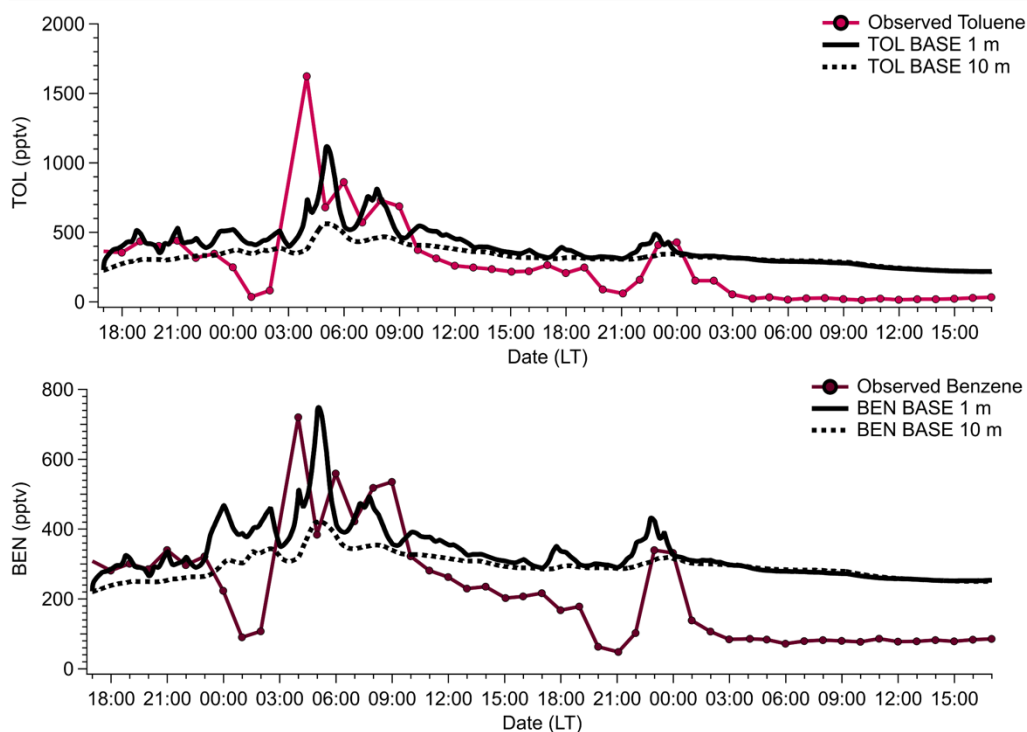


Figure G4. Time series of vertically-resolved measurements of aromatic VOCs, including benzene and toluene overlaid with modelled mixing ratios from the BASE model at a height of 1 and 10 m.

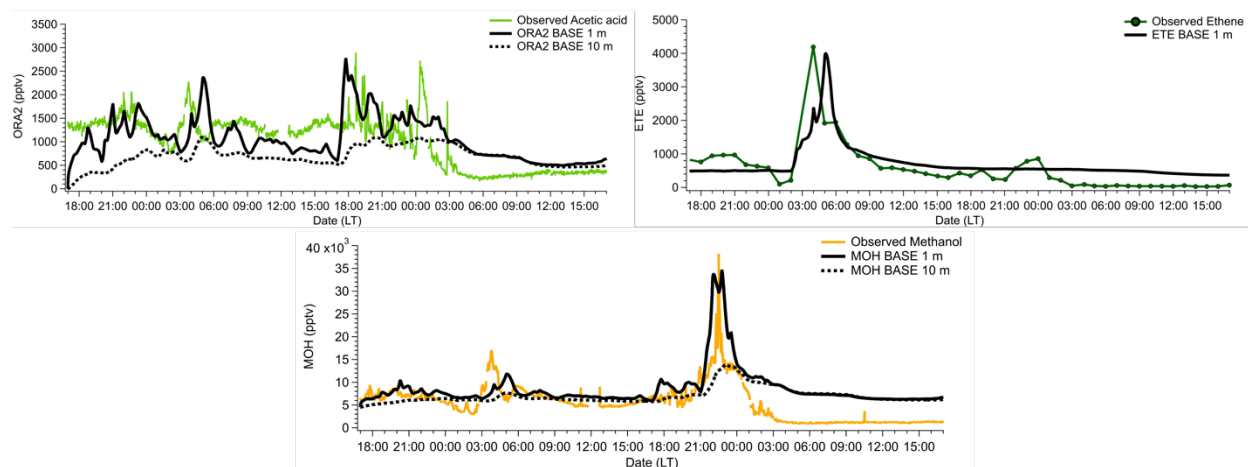


Figure G5. Time series of vertically-resolved and ground-based measurements of VOCs, including acetic acid (green) ethene (dark green), and methanol (yellow) overlaid with modelled mixing ratios from the BASE model at a height of 1 and 50 m.

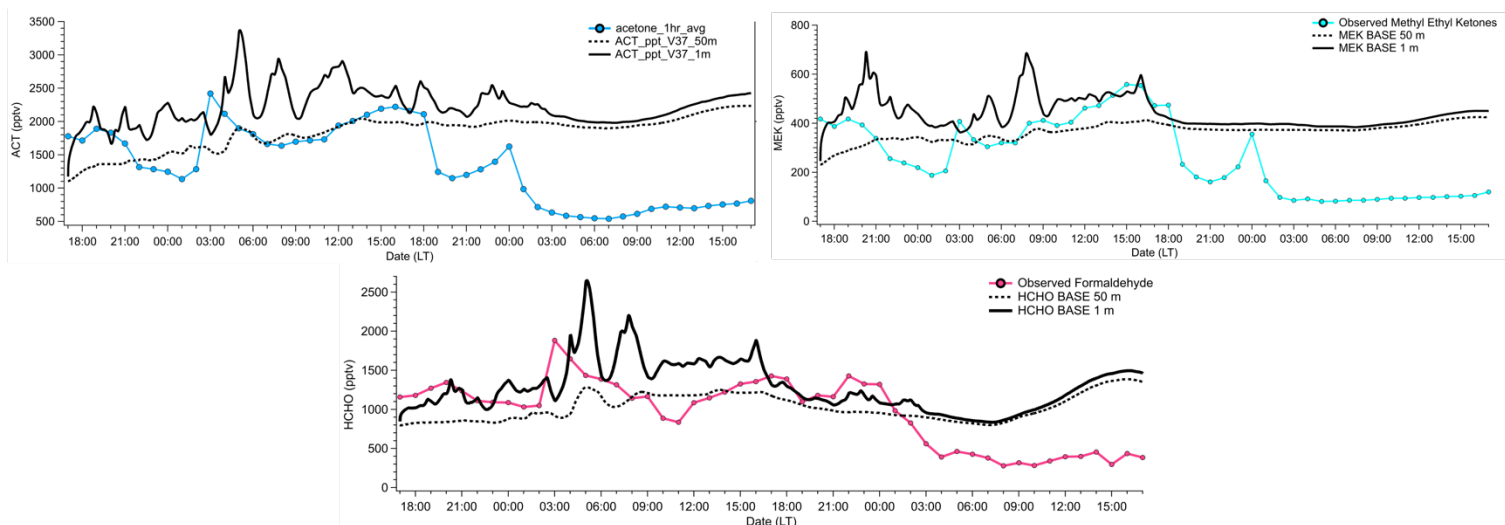


Figure G6. Time series of vertically-resolved measurements of VOCs containing carbonyl functional groups, including acetone (blue), methyl ethyl ketones (teal blue), and formaldehyde (pink) within 50 m AGL overlaid with their respective modelled mixing ratios from the BASE model at the height of 1 (black line) and 50 m (black-dashed line) during the 48-hour MP.

Appendix H: Modelled near surface-level mixing ratios of all species from BASE_WET

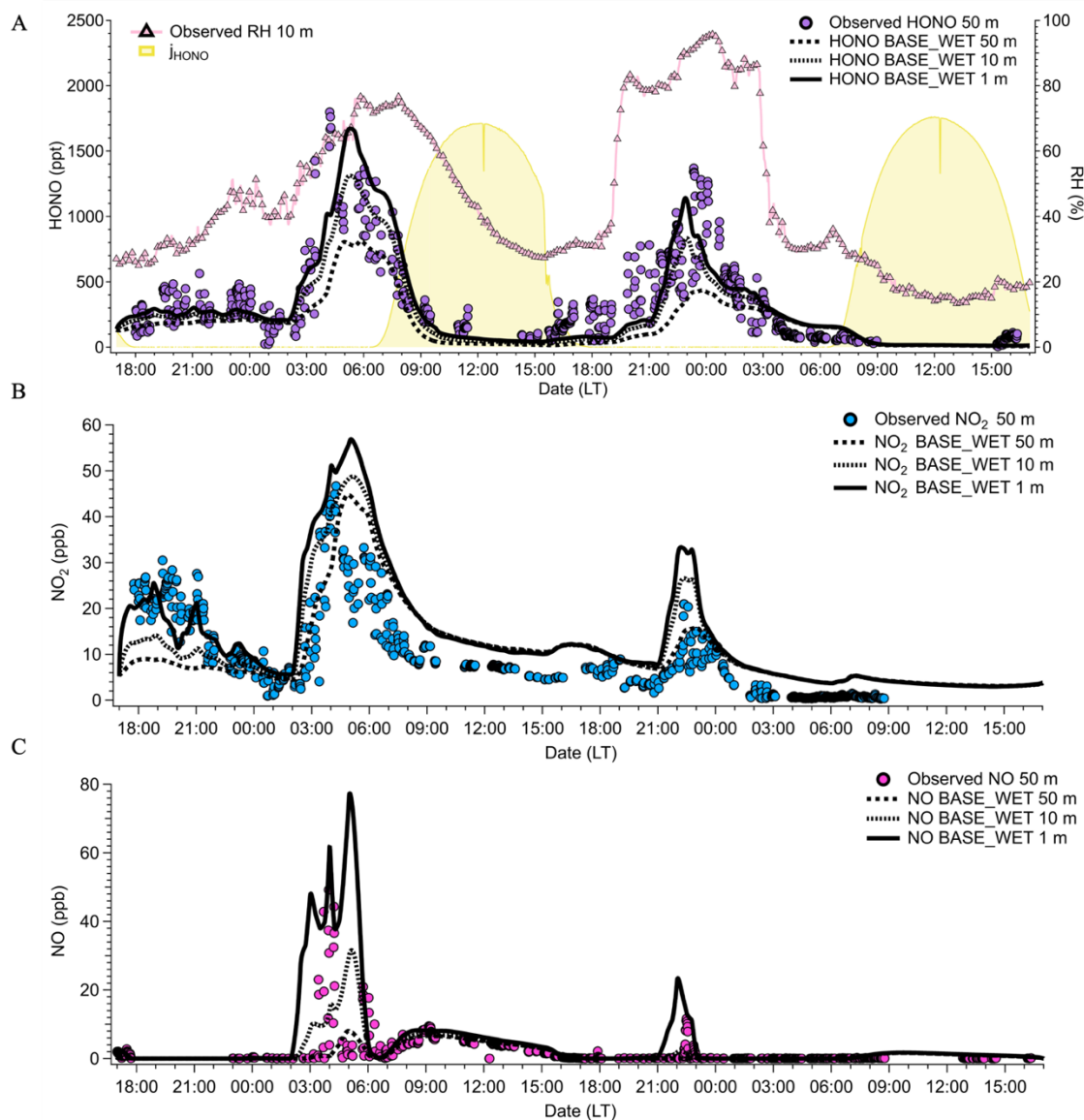


Figure H2. (A) Time series of vertically-resolved measurements of HONO (purple dot) filtered to a height of 50 m from the NACHTT campaign overlaid with modelled HONO from the PACT-1D BASE_WET model. Fixed measurements of RH (pink) and photolysis rate coefficient of HONO (shaded yellow) from a height of 10 m from BAO tower is also shown. (B) Time series of vertically-resolved measurements of NO₂ (blue dot) filtered to a height of 50 m from the NACHTT campaign overlaid with modelled NO₂ from the PACT-1D BASE_WET model. (C) Time series of vertically-resolved measurements of NO (pink dot) filtered to a height of 50 m from the NACHTT campaign overlaid with modelled NO from the PACT-1D BASE_WET model. Each modelled species was shown at heights of 1 (black line), 10 (black thin-dashed line), and 50 m (black thick-dashed line).

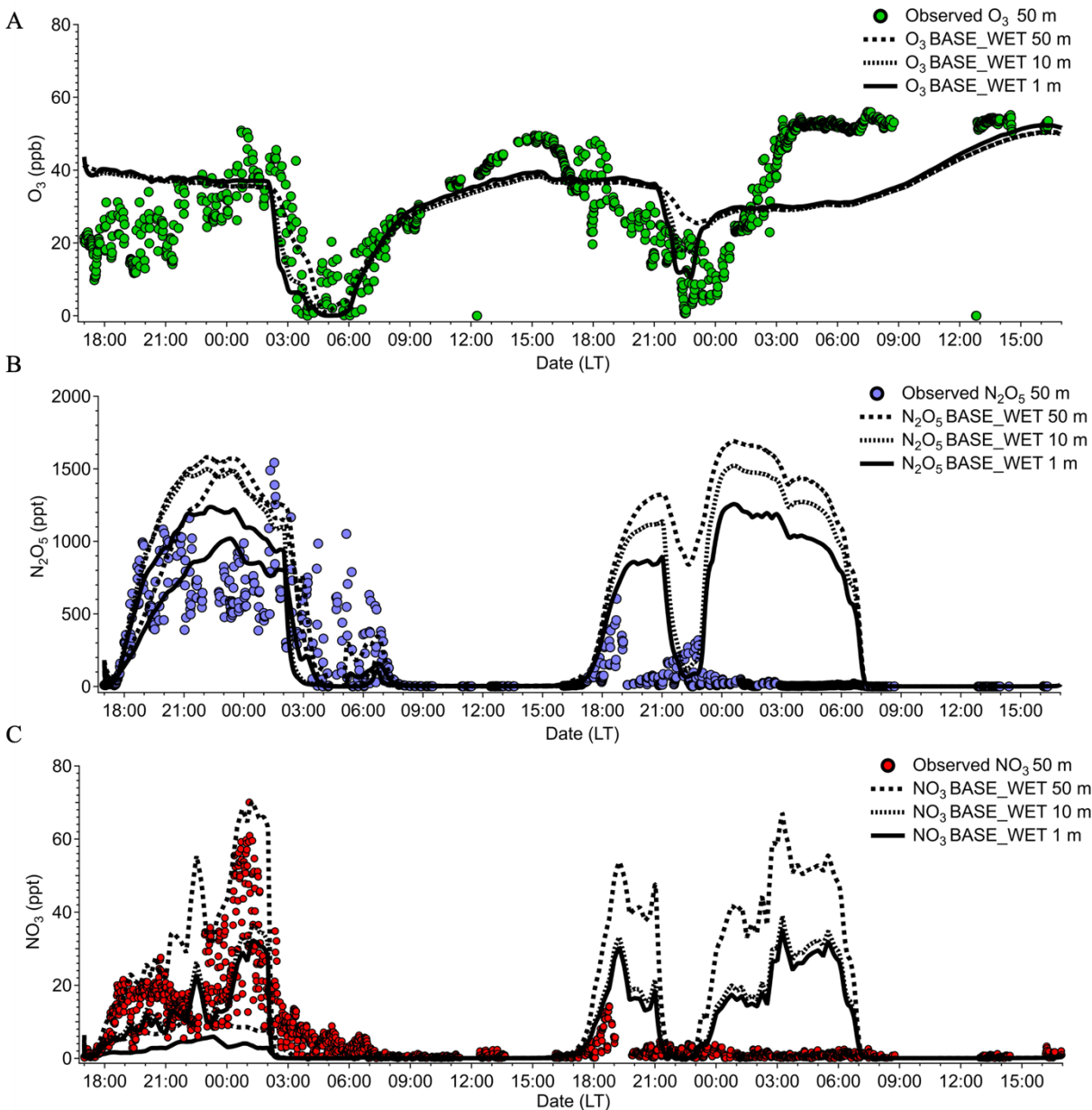


Figure H2. (A) Time series of vertically-resolved measurements of O_3 (green dot, ppbv) at a height of 50 m overlaid with BASE_WET modelled O_3 during the 48-hour MP of the NACHTT campaign. (B) Time series of vertically-resolved measurements of N_2O_5 (purple, pptv) at a height of 50 m overlaid with BASE_WET modelled N_2O_5 . (C) Time series of vertically-resolved measurements of NO_3 (red, pptv) at a height of 50 m overlaid with BASE_WET modelled NO_3 . Modelled outputs are shown at heights of 1 (line), 10 (thin-dashed line), and 50 (thick-dashed line) m during the 48-hour MP.

Appendix I: Curtain plots of modelled outputs of HONO within the BAO Tower Boundary

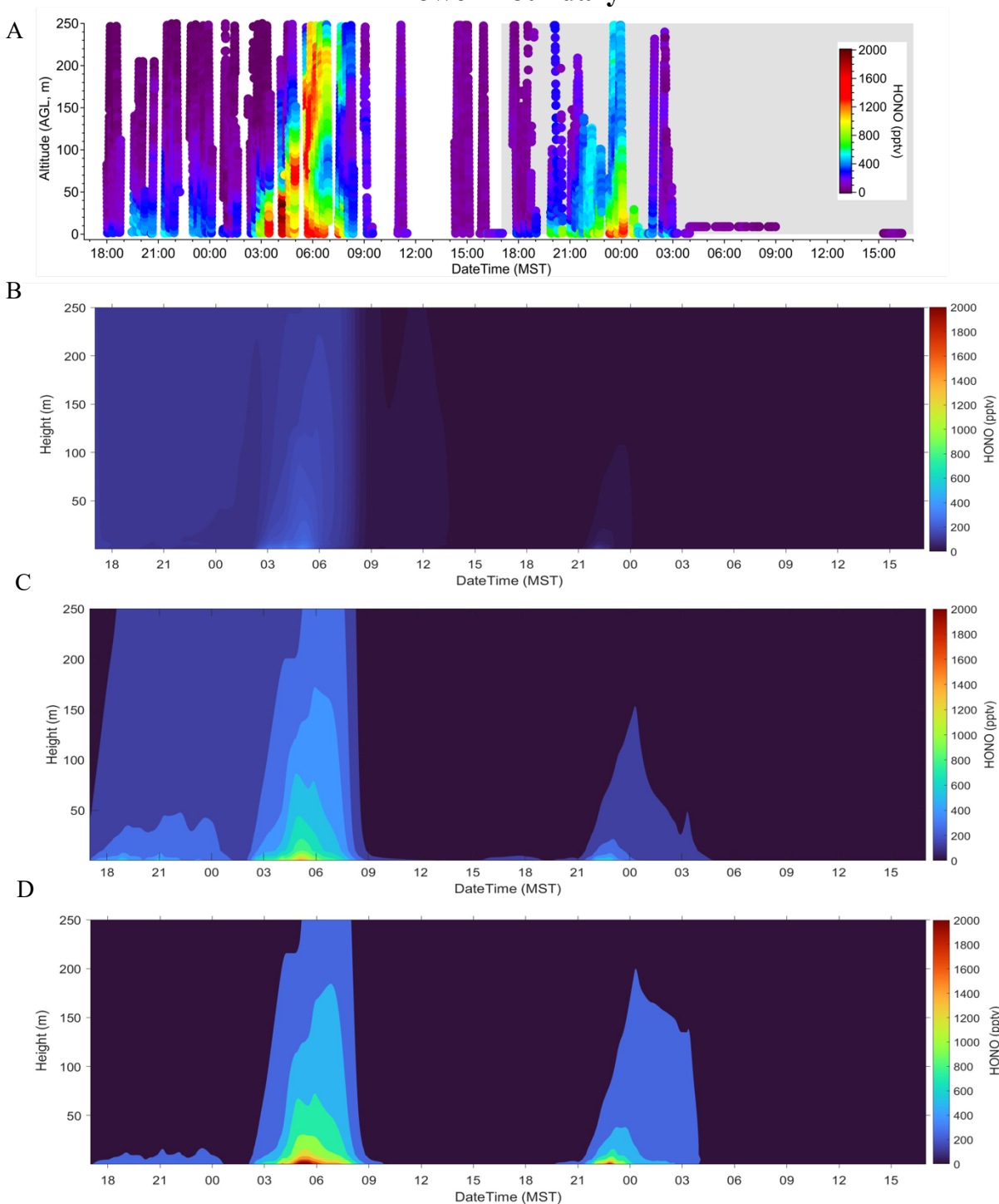


Figure I1. Curtain plots of HONO during the 48-hour MP comparing (A) the vertically-resolved observations of HONO, (B) the NO_GSS model, (C) the BASE model, and (D) the BASE_WET model at a height of 1-250 m.

Appendix J: Scatter plot Comparison of PACT-1D Modelled Outputs of HONO and Observations in OP1 and OP2

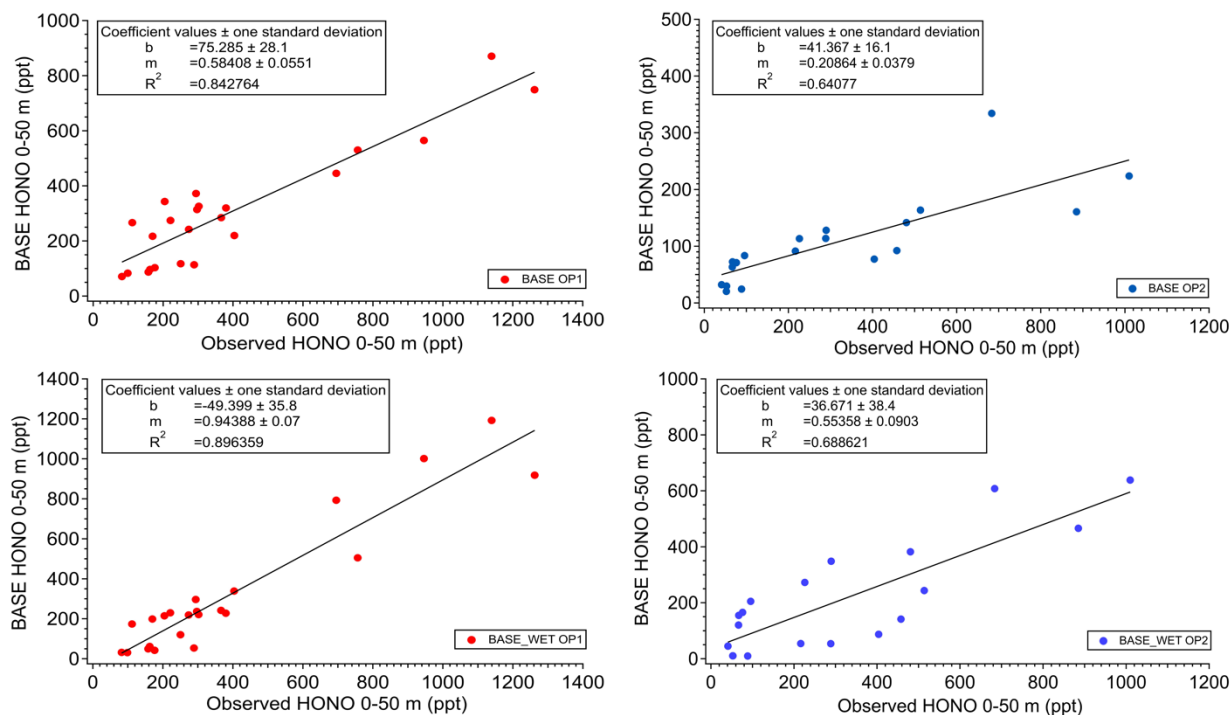


Figure J1. Scatter plot comparing the vertically-resolved measurements of HONO at a height of 0-50 m with respect to modelled HONO at a height of 0-50 m from the (A) BASE and (B) BASE_WET model separated between OP1 (February 18 17:00 MST to February 19 17:00 MST; red trace) and OP2 (February 19 17:00 MST to 20 17:00 MST; blue trace).