



**Extension of a gaseous dry deposition algorithm to oxidized volatile organic compounds
and hydrogen cyanide for application in chemistry transport models**

Zhiyong Wu^{1,2}, Leiming Zhang^{1,*}, John T. Walker³, Paul A. Makar¹, Judith A. Perlinger⁴,
Xuemei Wang⁵

¹Air Quality Research Division, Science and Technology Branch, Environment and Climate
Change Canada, Toronto, ON, M3H 5T4, Canada

²ORISE Fellow at US Environmental Protection Agency, National Risk Management Research
Laboratory, Research Triangle Park, NC, 27711, USA

³US Environmental Protection Agency, National Risk Management Research Laboratory,
Research Triangle Park, NC, 27711, USA

⁴Civil & Environmental Engineering Department, Michigan Technological University,
Houghton, MI, 49931, USA

⁵Institute for Environmental and Climate Research, Jinan University, Guangzhou, 510632, China

*Correspondence to: Leiming Zhang (leiming.zhang@canada.ca)



Abstract: With increasing complexity of air quality models, additional chemical species have been included in model simulations for which dry deposition processes need to be parameterized. For this purpose, the gaseous dry deposition scheme of Zhang et al. (2003) is extended to include 12 oxidized volatile organic compounds (oVOCs) and hydrogen cyanide (HCN) based on their physicochemical properties, namely the effective Henry's law constants and oxidizing capacities. Modeled dry deposition velocity (V_d) values are compared against field flux measurements over a mixed forest in the southeastern U.S. during June 2013. The model captures the basic features of the diel cycles of the observed V_d . Modeled V_d values are comparable to the measurements for most of the oVOCs at night. However, modeled V_d values are mostly around 1 cm s^{-1} during daytime, which is much smaller than the observed daytime maxima of $2\text{--}5 \text{ cm s}^{-1}$. Analysis of the individual resistance terms/uptake pathways suggests that flux divergence due to fast atmospheric chemical reactions near the canopy was likely the main cause of the large model-measurement discrepancies during daytime. The extended dry deposition scheme likely provides conservative V_d values for many oVOCs. While higher V_d values and bi-directional fluxes can be simulated by coupling key atmospheric chemical processes into the dry deposition scheme, we suggest that more experimental evidence of high oVOC V_d values at additional sites is required to confirm the broader applicability of the high values studied here. The underlying processes leading to high measured oVOC V_d values require further investigation.



19 1. Introduction

20 Atmospheric pollutants impact human health and can also cause detrimental effects on sensitive
21 ecosystems (Wright et al., 2018). Quantifying atmospheric deposition for atmospheric pollutants
22 is needed to estimate their lifetimes in air and deposition rates to ecosystems. The amount of dry
23 deposition of a pollutant of interest is typically calculated as the product of its ambient
24 concentration and its dry deposition velocity (V_d), with V_d being calculated using empirically
25 developed dry deposition schemes (Wesely & Hicks, 2000). Existing dry deposition schemes are
26 known to have large uncertainties even for the most commonly studied chemical species such as
27 O_3 , SO_2 and more commonly measured nitrogen species with relatively rich flux datasets (Flechard
28 et al., 2011; Wu et al., 2012; Wu et al., 2018).

29 Existing dry deposition schemes have thus far considered a small number of oxidized
30 volatile organic compounds (oVOCs). Due to the lack of field flux data of oVOCs, V_d of these
31 species is typically parameterized based on physicochemical properties, taking SO_2 and O_3 as
32 references (Wesely, 1989; Zhang et al., 2003). However, Karl et al. (2010) found that V_d of oVOCs
33 calculated using existing schemes are about a factor of 2 lower than those based on canopy-level
34 concentration gradient measurements over six forest and shrubland sites. V_d in their study was
35 calculated from an inverse Lagrangian transport model with concentration gradient data as model
36 input. The ratio of magnitudes between $V_d(\text{oVOCs})$ and $V_d(O_3)$ in the study of Karl et al. (2010)
37 are similar to those of Zhang et al. (2003) in that $V_d(\text{oVOCs})$ is slightly smaller than $V_d(O_3)$ in both
38 cases. However, the typical daytime $V_d(O_3)$ over vegetated canopies is around 1 cm s^{-1} in the
39 literature from numerous studies (see summary in Silva & Heald, 2018), and the value in Karl et
40 al. (2010) is much higher (e.g., up to 2.4 cm s^{-1} at canopy top). One hypothesis explaining both
41 high $V_d(O_3)$ and high $V_d(\text{oVOCs})$ would be the reaction of O_3 with oVOC, which depends on the



chemical structure of the oVOC, but data required for validating this hypothesis are still lacking. We thus suspect that the very high $V_d(\text{oVOCs})$ presented in Karl et al. (2010) were likely caused by atmospheric chemical processes not typically considered in the dry deposition process. High $V_d(\text{oVOCs})$ values were also observed over a temperate mixed forest in the southeastern U.S. in a more recent short-term study (Nguyen et al., 2015), which again were suspected to be caused by atmospheric chemical reactions near vegetation surface. The flux measurements themselves also contain uncertainty. For example, Wu et al. (2015) showed that different measurement methods (e.g., flux-gradient versus eddy correlation) resulted in very different daytime $V_d(\text{O}_3)$ over the same forest canopy. Hydrogen cyanide (HCN) is one of the most abundant cyanides present in the atmosphere (Singh et al., 2003) and is considered a biomass burning marker (Bunkan et al., 2013), but few existing studies have considered its dry deposition, which is critical to estimating the total sinks and atmospheric lifetimes of cyanides.

To fulfill community demands of modeling dry deposition of organic compounds (Kelly et al., 2019; Moussa et al., 2016; Paulot et al., 2018; Pye et al., 2015; Xie et al., 2013) and to take advantage of the recent flux dataset of a large number of oVOCs and HCN (Nguyen et al., 2015), the present study extends the current Zhang et al. (2003) scheme by including 12 additional oVOC species and HCN. The parameterization for these newly-included species is based on the effective Henry's law constants and oxidizing capacities of the individual species and by considering the measured V_d values as well. Model-measurement comparison is conducted for V_d as well as resistance components/uptake pathways, results from which identify the major causes of model-measurement discrepancies. Model parameters were chosen to produce the magnitude of nighttime V_d for nearly all the chemical species, but this approach inevitably underpredicted daytime V_d values for several oVOCs species with very high measured daytime V_d values. This approach is



recommended due to the following considerations: (1) some of the chemical processes causing flux loss at the surfaces may be treated separately in the mass continuity equation in chemical transport models, (2) some of the oVOCs may also experience bi-directional air-surface exchange, and (3) more flux measurements are needed to confirm if the very high daytime flux for certain oVOCs is an universal phenomenon, noting that the existing data used here were from a short period of several days and over only one surface type.

At this stage with very limited knowledge on oVOC V_d , air-surface exchange models based on various theoretical and/or measurement approaches should be developed, so that these models can be made available to the scientific community where such models are urgently needed, and for future evaluation and improvement should more flux measurements become available. For example, Nguyen et al. (2015) modified the Wesely (1989) scheme to fit the flux data, while in the present study a more theoretically constrained approach was used. A more sophisticated model for handling air-canopy exchange of semivolatile organic compounds is also available in the literature (Nizzetto and Perlinger, 2012). Note that a bottom-up approach was adopted in Nizzetto and Perlinger (2012) to estimate fluxes as compared to the present study, which provides a top-down determination of deposition velocity through comparison with measured (bottom-up) fluxes. oVOC V_d values from all the existing models may all be within the uncertainty range.

2. Methodology

Dry deposition of a gaseous compound to most canopy types is mainly through nonstomatal uptake during nighttime and through both nonstomatal and stomatal uptake during daytime. The nonstomatal uptake depends on water solubility and reactivity of the species, which can be



quantified by its effective Henry's Law constant (H^*) and oxidizing capacity, respectively (Wesely, 1989; Zhang et al., 2002). In the Supporting Information (SI) document, Table S1 lists H^* values and Table S2 lists the oxidizing capacities for oVOCs and HCN considered in the present study. Following the approach described in Zhang et al. (2002), two model parameters (α and β) are needed for every chemical species to calculate the nonstomatal uptake, with α being dependent on H^* and β dependent on oxidizing capacity. Initial α values were first given based the relative magnitudes of H^* of all the chemical species and that of SO_2 . Considering that the majority of the chemical species are very reactive, a value of 1.0 was used for β for most species and smaller values for a few less reactive species. α and β values were then adjusted based on the agreement of nighttime V_d between modeled values and measured fluxes obtained from a forest site in the southeastern US during summer (Nguyen et al., 2015). When adjusting α and β values, two rules were first applied: (1) the trends in α (or β) values between different chemical species should be consistent with the trends of their $\log(H^*)$ (or oxidizing capacity) (see Figure S1 for the finalized α versus $\log(H^*)$); and (2) modeled mean and median nighttime V_d should be mostly within a factor of 2.0 of the measured values (see discussion in Section 3.2 below). Only after these two rules were satisfied, then the possible maximum α and β values were chosen to reduce the gap between the modeled and measured daytime V_d , knowing that model predicted V_d were mostly lower than the measured ones. Model theory and field data used for model evaluation are briefly described below.

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2.1. Parameterization scheme for V_d of oVOCs and HCN

The gaseous dry deposition scheme of Zhang et al. (2003) (hereinafter referred to as the Model) was originally designed to model V_d for 31 chemical compounds including 9 inorganic species and



22 organics. Formic acid (HCOOH) is the only oVOC species that is available in both the Model and the flux measurement dataset used here (described in the next section). In this study, the Model was extended to include 12 new oVOC species and HCN. Briefly, V_d is calculated according to:

$$V_d(z) = (R_a(z) + R_b + R_c)^{-1}, \quad (1)$$

where R_a is the aerodynamic resistance, R_b the quasi-laminar sub-layer resistance, R_c the surface resistance, and z the reference height above the vegetation. R_a and R_b can be estimated using the conventional micrometeorological approaches based on similarity theory and the equations used in the Model can be found in Wu et al. (2018). R_c is parameterized as:

$$\frac{1}{R_c} = \frac{1 - W_{st}}{R_s + R_m} + \frac{1}{R_{ns}}, \quad (2)$$

$$\frac{1}{R_{ns}} = \frac{1}{R_{ac} + R_g} + \frac{1}{R_{cut}}, \quad (3)$$

where R_s is the canopy stomatal resistance, R_m the mesophyll resistance, R_{ns} the non-stomatal resistance including resistance for uptake by leaf cuticles (R_{cut}) and by soil or ground litter (R_g), R_{ac} in-canopy aerodynamic resistance, and W_{st} the fraction of stomatal blocking under wet conditions.

R_s for any gaseous oVOCs (i) or HCN is also calculated using the sunlit/shade stomatal resistance approach as was done in Zhang et al. (2002):

$$\frac{1}{R_{s,i}} = G_s(PAR) f(T) f(D) f(\Psi) \frac{D_i}{D_{H_2O}}. \quad (4)$$

Here $G_s(PAR)$ is the unstressed canopy stomatal conductance for water vapor, a function of photosynthetically active radiation (PAR). The dimensionless functions $f(T)$, $f(D)$ and $f(\psi)$ range from 0 to 1, representing the fractional degree of stomatal closure caused by the stress from



temperature, water vapor pressure deficit, and leaf water potential, respectively. D_{H_2O} and D_i are the molecular diffusivities for water vapor and the gas of interest, respectively.

R_{cut} and R_g for any oVOCs or HCN are scaled to those of SO_2 and O_3 with two species (i)-dependent scaling parameters $\alpha(i)$ and $\beta(i)$:

$$\frac{1}{R_{cut/g}(i)} = \frac{\alpha(i)}{R_{cut/g}(SO_2)} + \frac{\beta(i)}{R_{cut/g}(O_3)} . \quad (5)$$

$\alpha(i)$ and $\beta(i)$ values for all the chemical species are listed in Table 1, which are assigned using the method described above.

The R_m for HCN was set to 100 s m^{-1} based on its effective Henry's law constants and oxidizing capacities. Karl et al. (2010) found that enzymatic conversion can be an efficient pathway for the immobilization of oVOCs (e.g., methacrolein and methyl vinyl ketone, acetaldehyde, methacrolein) within leaf interior, besides dissolution and oxidation, which suggests that the magnitude of R_m for oVOCs is minimal. Thus, the R_m for the oVOCs was set to 0 s m^{-1} (Table 1).

2.2. Field flux data

The fluxes of 16 atmospheric compounds (including 13 oVOC species, HCN, hydrogen peroxide (H_2O_2), and nitric acid (HNO_3)) were measured using the eddy covariance (EC) technique at the Centreville ("CTR") Southeastern Aerosol Research and Characterization Study (SEARCH) site (hereinafter referred to as CTR). The CTR site (Brent, Alabama; 32.90°N , 87.25°W) is surrounded by a grassy field to the south and a temperate mixed forest that is part of the Talladega National Forest in all the other directions. The forest canopy is comprised of needleleaf coniferous (shortleaf, longleaf, and loblolly pine; ~40%) and broadleaf deciduous (primarily oak, sweetgum, and hickory; ~60%) tree species. A 20 m metal walk-up tower is used as the main structure supporting



instruments that measured the eddy covariance fluxes and related meteorological variables. The sonic anemometer and the gas inlet were mounted at a height of about 22 m, facing north toward the forest. The canopy height near the tower is on average ~10 m with a leaf area index (LAI) of ~4.7 m² m⁻². A database of half-hourly V_d for 16 atmospheric compounds covering 5 non-continuous days in June 2013 was obtained at the site. During these periods, the predominant winds were northerly which is ideal to sample air from the forest (Figure S2) and the requirement on energy balance closure was met (see Nguyen et al. (2015)). At CTR, it was typically humid (RH 50-80%) and warm (28-30 °C) in the daytime during the experiment (Figure S3). A comprehensive description of the V_d dataset, data processing protocols, the instrumental methods, uncertainty analysis, and the site characterizations can be found in Nguyen et al. (2015).

3. Results and Discussion

3.1. Comparison of modeled resistance components

3.1.1. Atmospheric resistances (R_a and R_b)

For very reactive and soluble substances such as HNO₃ and H₂O₂, R_c is often assumed to be close to 0 (Hall & Claiborn, 1997; Meyers et al., 1989; Valverde-Canossa et al., 2006; Wesely & Hicks, 2000). The analysis of the measurement data showed that the daytime averaged V_d for HNO₃ and H₂O₂ fitted well the rate of deposition without surface resistance ($V_d = 1/[R_a + R_b]$) (Nguyen et al., 2015), which supports the assumption of near zero R_c for HNO₃ and H₂O₂ over the mixed deciduous-coniferous CTR site under humid environment. Therefore, the measured V_d of HNO₃ and H₂O₂ can be used to evaluate the modeled atmospheric resistances for those species (the sum of R_a and R_b). R_a represents the resistance for turbulent transport between the reference height and



the surface and is not chemical compound specific. R_b quantifies the resistance for the mass transfer across the thin layer of air in contact with surface elements and is a function of the molecular diffusivity of a specific compound (Wesely & Hicks, 1977). In theory, the differences in R_b between any two gaseous species are only determined by differences in their molecular diffusivity at any given turbulent condition.

Figure 1 compares the modeled average diel variations of V_d for HNO_3 and H_2O_2 against observations. The measured V_d for HNO_3 and H_2O_2 peaked around noon at about 4 cm s^{-1} and 6 cm s^{-1} , respectively, and were less than 1 cm s^{-1} during the night. The model reproduced the diel pattern and captured the peak V_d values at noon well. During the early night time (hours 19-23), the modeled V_d for HNO_3 and H_2O_2 were on the order of 1 cm s^{-1} , much higher than the measurements ($<0.2 \text{ cm s}^{-1}$). During the night, R_a dominates atmospheric resistance as it is usually much larger than R_b in magnitude. This discrepancy between the measurement and the model during the early night could be due to the stability correction functions used in the R_a calculation (the equations can be found in the article by Wu et al. (2018)) which is subject to large uncertainties under nocturnal stable conditions (Högström, 1988). The measurements indicated that H_2O_2 deposited slightly faster than HNO_3 , and the model reproduces well, as shown in Figure 1. Modeled R_b for H_2O_2 is always smaller than that for HNO_3 due to the smaller molecular weight and the larger molecular diffusivity. Overall, the model was in good agreement with the measurements regarding V_d for HNO_3 and H_2O_2 , implying that the parameterization for atmospheric resistances (R_a and R_b) was reasonable for the site during the study period.

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195 *3.1.2. Stomatal resistance (R_s)*



196 Over vegetative areas, gas molecules can exit and enter the leaf through the stomata by molecular
 197 diffusion, similar to the leaf-air exchange of water vapor and CO₂. In dry deposition models, R_s
 198 for water vapor is estimated using evapotranspiration stomatal submodels, an approach that is also
 199 popular in the land surface and climate communities. R_s is extended to any gas species using the
 200 ratio of molecular diffusivity of the species of interest to that of water vapor (Pleim & Ran, 2011;
 201 Wesely & Hicks, 2000). Figure 2 compares the modeled canopy stomatal conductance ($G_s = 1/R_s$)
 202 for water vapor against the observation-based estimates. The observation-based G_s was estimated
 203 by using the inversion of the Penman-Monteith (P-M) equation (Monteith & Unsworth, 1990)
 204 which calculates R_s for water vapor by using measured water vapor fluxes and related
 205 meteorological data (e.g., humidity, temperature). The evaporation from soil water and liquid
 206 water on the vegetation surfaces is usually a minor contribution to the total water vapor flux
 207 observed above a forest canopy during summer daytime. It was assumed that 85% of the water
 208 vapor flux originated from transpiration in this study, following that used in the study of
 209 Turnipseed et al. (2006) at Duke Forest, North Carolina. Note that a value of 90% was used by
 210 Clifton et al. (2017) at Harvard Forest, Massachusetts. The uncertainty of the calculated R_s related
 211 with the uncertainty in water vapor flux portion (on an order of 10%) is much smaller than the
 212 differences between the modeled and the observation-based stomatal conductance (by a factor of
 213 two) as discussed below.

214 The model reproduced the basic diel pattern in G_s (i.e., highest values between 08:00 and
 215 11:00) but the peak value is only about half of the observation-based values. The Jarvis stomatal
 216 submodel (Jarvis, 1976) used in the Model is known for its linear dependence on the prescribed
 217 minimum stomatal resistance ($R_{s,min}$), a term that is subject to large uncertainties (Kumar et al.,
 218 2011; Wu et al., 2018; Wu et al., 2011). A series of tests conducted by iteratively adjusting the



219 $R_{s,min}$ values showed the modeled G_s to be in better agreement with observations if $R_{s,min}$ was
 220 decreased by 40% (Figure 2). G_s from the Model with the adjusted $R_{s,min}$ was in good agreement
 221 with the observation-based values for most of the time, though the modeled values were slightly
 222 smaller than the observation-based estimates around noon. Analysis of the R_s parameterization
 223 indicates that this discrepancy was related to the stress function for water vapor pressure deficit
 224 (VPD) used in the Jarvis stomatal submodel, which may overpredict the stress on stomatal opening
 225 due to high VPD around noon.

226

227 3.1.3. Non-stomatal resistance (R_{ns})

228 To assess if the non-stomatal resistance (R_{ns}) parametrization (Eq. 3) is reasonable, modeled $1/R_{ns}$
 229 (defined as G_{ns}) values are compared with the non-stomatal portion of the flux, the inverse of
 230 which is termed the residual conductance ($G_{residual}$). $G_{residual}$ includes all processes influencing
 231 deposition aside from R_a , R_b , R_m , and R_s , calculated as $[V_d^{-1} - (R_a + R_b)]^{-1} - (R_s + R_m)^{-1}$. Here V_d is
 232 from the observations, R_a and R_b are calculated using the Model driven by the observed
 233 meteorology, R_s is the observation-based estimates by the P-M method, adjusted by the molecular
 234 diffusivity of each gas (similar to Eq. 4), and R_m is listed in Table 1. Although considerable
 235 uncertainties in the calculated $G_{residual}$ exist (in this form of back-calculation, we must assume that
 236 the G_{ns} terms are correctly estimated), it can provide useful information on the flux/ V_d resulting
 237 from processes such as deposition to the leaf cuticle and ground (i.e., non-stomatal) or chemical
 238 loss due to reactions within and near the canopy that lead to flux divergence.

239 Figure 3 compares the observation-based $G_{residual}$ for each oVOC species or HCN against
 240 the corresponding modeled non-stomatal conductance (G_{ns}) under different conditions. The mean
 241 and median values are presented in Table S3. During the nighttime when the canopy surface was



242 dry (no dew), the $G_{residual}$ for oVOC species ranged from 0.08 to 0.18 cm s⁻¹ and the modeled G_{ns}
 243 was comparable in magnitude. When the surface was wet from dew formation on leaves and
 244 needles, the oVOC species showed an increase in $G_{residual}$ by 55%-440% compared to the nighttime
 245 dry surface. The model captured the increases in non-stomatal uptake when the surface become
 246 wet with dew, although it may underestimate (e.g., HDC₄, INP, HCN) or overestimate (e.g., PAA,
 247 DHC₄, HCOOH) the wetness effects. During the daytime of the study period, no precipitation was
 248 recorded at the CTR site (Figure S3) and the canopy surface was dry. The mean $G_{residual}$ for oVOCs
 249 ranged from 0.5 cm s⁻¹ to 8.7 cm s⁻¹ during the daytime, much higher than the modeled G_{ns} for most
 250 species (0.2 - 1 cm s⁻¹). Figure S4 presents the diel variations of $G_{residual}$ and G_{ns} and it shows that
 251 the modeled G_{ns} showed smaller diel variations than those of $G_{residual}$ and large differences in
 252 magnitude can be seen during the daytime. The modeled G_{ns} showed a peak during the early
 253 morning (around 7:00) which may be due to the enhanced non-stomatal uptake by dew wetted
 254 surfaces.

255

256

257 3.2. Evaluation of modeled deposition velocities

258 Figure 4 shows model-measurement comparison of diel V_d of the oVOCs and HCN and Table 2
 259 presents the statistical results of the comparison. As described in Section 2, the assigned α and β
 260 values should first produce reasonable nighttime V_d . Modeled nighttime mean V_d were very close
 261 to measurements for the majority of the chemical species, although the differences were somewhat
 262 larger for the median values (Table 2). Three species (HAC, HPALD, PROPNN) still had 50%
 263 lower modeled than measured nighttime mean V_d , but have slightly higher modeled than measured
 264 nighttime median V_d . In contrast, modeled daytime mean V_d were more than 50% lower than the



measured values for four species (HMHP, PAA, HPALD, ISOPOOH/IEPOX) and were also significantly lower for several other species. Only three species (MTNP, HCN, HCOOH) had comparable modeled and measured V_d for both day- and nighttime. One species (DHC₄) had slightly lower of modeled than measured daytime mean or median V_d , but with an opposite trend for nighttime V_d .

The model reproduced the basic features of the diurnal pattern of the observations, showing highest values during the day and lowest values at night. Correlation coefficients between the measurement and the model ranged from 0.52 to 0.77. At night, the measured V_d for the oVOCs remained relatively low, typically ranging from 0.1-0.5 cm s⁻¹, and the model produced the same magnitudes for most of the species. During the daytime, the model can only capture the magnitudes of the measured V_d for a few species (e.g., HCN, HCOOH, MTNP, DHC₄), of which the peak V_d values were less than 1.5 cm s⁻¹. For the other species, the measured peak V_d values were in the range of 2 to 5 cm s⁻¹, while the modeled results were below 1 cm s⁻¹. As shown in section 3.1.2, the modeled G_s was likely underestimated when compared to the simultaneous measurements of water vapor flux. Adjusting G_s higher by 67% (through reducing $R_{s,min}$ by 40%) can only increase the modeled V_d of the oVOCs by 10-40% during the daytime (see the sensitivity test in Figure 4), and the peak values were still mostly below 1 cm s⁻¹. Figure 5 shows that the model captured the differences in measured V_d for the oVOCs to some extent. The model-measurement agreements were good for species with the measured mean V_d below 0.5 cm s⁻¹, above which the discrepancy increased. For the measurements, the mean values were significantly larger than the median values, especially for the fast-deposited species, indicating that the distribution of the measured V_d values skewed to the right (high values). The model has a better agreement with the measurements by comparing the median versus mean values.



288 At night when stomata are mostly closed and atmospheric chemical reactions are largely
289 inhibited, the measured fluxes above the canopy should better represent non-stomatal surface
290 uptake. In the presence of sunlight, fast chemical reactions between the inlet and canopy could
291 make a significant or even dominant contribution to the measured fluxes of reactive species
292 (Farmer & Cohen, 2008; Wolfe et al., 2011). The impact of fast chemical reactions on surface
293 fluxes should be different for different chemical species. To verify this hypothesis, two chemical
294 species (HAC and PAA) having similar molecular weights (74 Da and 76 Da, respectively) but
295 very different daytime fluxes were compared (Figure 6). Their similar molecular diffusivities
296 (controlled by molecular weight) suggest that they should be transferred through the quasi-laminar
297 sub-layer and taken up through leaf stomata at similar rates, resulting in similar resistance
298 components of R_b and R_s . Note that R_a is universal to any trace gases and R_m is assumed to be
299 negligible. Thus, the differences between their V_d should be caused by their different non-stomatal
300 sinks. At night, V_d values were similar between HAC and PAA (median values: 0.04 cm s^{-1}) over
301 dry surfaces. When the surfaces were wet due to dew formation, V_d for both HAC and PAA
302 increased (median values: $0.30\text{-}0.48 \text{ cm s}^{-1}$). In contrast, $V_d(\text{PAA})$ was much higher than $V_d(\text{HAC})$
303 during daytime, suggesting additional or larger sinks exist for PAA compared to HAC. Thus, fast
304 chemical processing and subsequent flux divergence above the canopy likely caused the large
305 discrepancies between the measured and modeled V_d for the reactive oVOC compounds during the
306 daytime.

307 Chemical processes indeed can cause flux divergence or convergence at the surface, which
308 has been supported by growing evidence from field measurements (e.g., Farmer and Cohen, 2008;
309 Min et al., 2014; Wolfe et al. 2009). For example, Wolfe et al. (2009) suggested that the differences
310 in loss rate between the inlet and canopy may be an important contributor to the measured net flux



311 of peroxyacetyl nitrate, irrespective of turbulent timescales. Photochemical OH production is
 312 reduced within canopies, which in turn slows down the oxidation of volatile organic compounds
 313 and the photolysis of organic nitrates. The oVOCs measured at the CTR site are mainly produced
 314 from the oxidation of isoprene and monoterpenes (Nguyen et al., 2015). Most of the oVOCs are
 315 quite chemically reactive and can undergo fast oxidation (e.g., multifunctional carbonyls),
 316 decomposition (e.g., HMHP), or photolysis (e.g., organic nitrates) (Müller et al., 2014; Nguyen et
 317 al., 2015). Vertical gradients in the chemical production and loss rates below the inlet can exhibit
 318 chemical flux divergence, which contributes to the net flux above canopy. Quantifying the effects
 319 of chemical processing on the net flux would require a multi-layer model with resolved emission,
 320 deposition, turbulent diffusion, and chemical processes throughout the canopy, which is
 321 recommended for future studies (e.g., Ashworth et al., 2015; Bryan et al., 2012; Stroud et al., 2005;
 322 Wolfe & Thornton, 2011; Zhou et al., 2017).

323 Quantifying V_d as the ratio of flux to concentration at one measurement height only ($V_d =$
 324 F/C_x), rather than as the ratio of flux to the concentration difference at the measurement height
 325 and the surface ($V_d = F/[C_x - C_0]$), although commonly employed in analyzing eddy covariance
 326 flux measurements, is a simplification. It is valid for 1) matter that disappears nearly completely
 327 by reactions at the surface, and 2) unstable or neutral conditions. Most chemical species considered
 328 here may satisfy the first condition. With regards to the second condition, our analysis is based on
 329 the assumption that, under stable conditions at nighttime, concentrations observed at the
 330 measurement height change in relation to the fluxes measured at this height. However, no relation
 331 between measured concentration and flux is typically observed due to the presence of a shallow
 332 stable boundary layer, connection between the stable free atmosphere and stable boundary layer
 333 by internal gravity waves, ground inversions, and low-level jets, leading to intermittent turbulence



at the measurement height containing a gravity wave signal, and non-steady-state conditions (Foken, 2017). Future efforts to model oVOC and HCN deposition velocities above forest canopies should be based on neutral or unstable boundary layer flux measurements only, or, for example, on modified Bowen ratio flux measurement in which concentrations are measured at two heights in the constant flux layer. Such an approach can provide a means to compute a measured deposition velocity of a surface reactive substance as proportional to the ratio between the measured flux and the measured concentration difference.

341

4. Summary and recommendations

The number of chemical species simulated in chemical transport models (CTMs) has been increasing with increasing computer power. Among these, oVOCs and HCN are an important groups of atmospheric pollutants for which dry deposition processes need to be treated as accurately as possible, so that their inputs to ecosystems (noting that some oVOCs are organic nitrogen) and their roles on other atmospheric chemistry processes (e.g., formation of ozone and secondary organic aerosols) can be assessed. Earlier dry deposition schemes have considered very few oVOCs and need to be extended for more species. Dry deposition of HCN was assumed to be negligible in some CTMs (e.g., Moussa et al., 2016). The present study first generated effective Henry's law constant and oxidizing capacity, the two key physical and chemical properties that are considered to control the dry deposition process (Wesely & Hicks, 2000), for 12 oVOCs species and HCN. Two scaling factors for the non-stomatal resistance and one for the mesophyll resistance were applied to individual oVOCs and HCN for calculating their respective V_d .

The modeled nighttime V_d agrees well with the measured data for most of the oVOCs, suggesting that the current non-stomatal parameterization scheme is a reasonable approach. The



357 stomatal conductance for water vapor, with adjusted (reduced) $R_{s,min}$, also agrees well with
358 measured values. However, the modeled peak V_d values during daytime are only a fraction (0.2-
359 0.5) of the measured values for some of the oVOCs, suggesting that fast atmospheric chemical
360 processes likely contributed to the total measured fluxes. In practice, these additional fluxes during
361 daytime can be modeled as non-stomatal uptake and better model-measurement agreement can be
362 obtained by adjusting the non-stomatal parameterization scheme (e.g., Müller et al., 2018; Paulot
363 et al., 2018). However, using this approach will produce unreasonably high values for the solubility
364 parameter and overpredict V_d during nighttime if the same non-stomatal formulas are used for both
365 day and nighttime (as is the case in the existing schemes). More importantly, the high measured
366 V_d have only been observed at relatively few sites during very short periods (Karl et al., 2010;
367 Nguyen et al., 2015). More evidence is needed to parameterize V_d for oVOCs to different land use
368 categories over entire seasons. Until then, the conservative estimates of V_d such as modeled in this
369 study are still recommended for use in chemical transport models. The model parameters chosen
370 for V_d of these oVOCs provide the best-known representation of their respective physicochemical
371 properties, and the modelled V_d values fall within the range of the low-end values of the available
372 measurements.

373 Future field studies should focus on conducting flux measurements of oVOC compounds
374 with highest uncertainties, such as those that are most chemically reactive in the atmosphere or
375 most rapidly taken up by wet surfaces. Additional measurements are also needed in different
376 ecosystems to inform the representativeness of the high oVOC V_d reported by Nguyen et al. (2015)
377 and Karl et al. (2010). Furthermore, concurrent chemical measurements of oxidants such as O_3 and
378 radicals are needed to quantify flux divergence due to fast within-and near-canopy chemical
379 reactions. Future dry deposition schemes should include additional biochemical processes and



species-dependent parameters for non-stomatal uptake, including enzymatic reactions (Karl et al., 2010), the octanol-air partitioning coefficients to account for the cavity formation and polar intermolecular interactions with leaf surfaces and reservoirs (Nizzetto and Perlinger, 2012), and the enhancement/reduction effects due to soil and leaf moisture. Chemical processes within the canopy airspace could also be coupled with emission and deposition schemes to realistically simulate chemicals fate and transport, including bi-directional fluxes of reactive compounds discussed here, as well as less reactive compounds such as methanol. Such an approach would require specification of chemical conditions within and near the canopy as well as in-canopy radiation and air flow. While more computationally intensive, the results presented here reinforce the need for such advanced models to explicitly resolve the non-stomatal processes contributing to the net atmosphere-biosphere exchange of reactive compounds. Above all, intercomparison studies should be first conducted for existing models that can handle oVOC dry deposition processes to quantify the magnitudes of uncertainties in the simulated V_d as well as the associated ambient concentration and deposition fluxes.

Code and data availability

The computer code and data used in this study can be obtained from containing the corresponding author.

Competing interests

The authors declare that they have no conflict of interest.

Author contributions

ZW conducted model run and data analysis and drafted the manuscript. LZ designed the project, finalized computer code, drafted part of the manuscript and finalized the paper. JTW contributed



402 to manuscript writing and commented on the manuscript. PAM generated chemistry data that are
 403 used in the supporting document and commented on the manuscript. JAP contributed to model
 404 design and manuscript writing and commented on the manuscript. XW contributed to the project
 405 design and commented on the manuscript.

406

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Table 1. List of model parameters needed in the scheme of Zhang et al. (2003) for simulating dry deposition velocity of additional oVOCs species and HCN: α and β are scaling parameters for non-stomatal resistance, and R_m is mesophyll resistance.

Symbol	Name	Molecular Weight (Da)	Scaling Parameters		R_m (s m ⁻¹)
			α	β	
HMHP	hydroxymethyl hydroperoxide	64	5	1	0
HAC	hydroxyacetone	74	1.5	1	0
PAA	peroxyacetic acid	76	2	1	0
HDC ₄	the C4 hydroxy dicarbonyl from IEPOX oxidation	102	1	0.2	0
DHC ₄	the C4 dihydroxy carbonyl from IEPOX oxidation	104	2	0.2	0
HPALD	isoprene hydroperoxy aldehydes	116	1.5	1	0
ISOPOOH/IEPOX ^a	isoprene hydroxyhydroperoxide and isoprene dihydroxyepoxide	118	5	0.2	0
PROPNN	propanone nitrate or propanal nitrate	119	1.5	1	0
ISOPN	isoprene hydroxy nitrates	147	1.5	1	0
MACN/MVKN ^a	methacrolein and Methyl vinyl ketone hydroxy nitrate	149	1.5	1	0
INP	isoprene nitrooxy hydroperoxide	163	1.5	1	0
MTNP	monoterpene nitrooxy hydroperoxide	231	1.5	1	0
HCN	hydrogen cyanide	27	0	0.1	100
HCOOH ^b	formic acid	46	2	0.2	0

^a Treated as one group of compounds in the field measurements due to instrument limitation and have the same parameter values in the model.

^b Beta value for HCOOH in Zhang et al. (2003) is 0.0, and here is given as 0.2 to be consistent to other oVOC species here (which would make no difference since the alpha value of 2 would dominate the nonstomatal resistance).



Table 2. Statistical results of the observed and modeled dry deposition velocity (V_d) for oVOCs and HCN (cm s^{-1})^a

Compound	All					Daytime				Nighttime		
	N	Obs	Mod	Mod- $R_{s,min}$	R	N	Obs	Mod	Mod- $R_{s,min}$	N	Obs	Mod
HMHP	247	1.66 (0.61)	0.69 (0.54)	0.75 (0.58)	0.63	85	3.42 (3.49)	1.05 (1.04)	1.19 (1.17)	128	0.33 (0.13)	0.37 (0.24)
HAC	245	0.84 (0.53)	0.41 (0.31)	0.49 (0.36)	0.61	84	1.21 (1.07)	0.65 (0.62)	0.81 (0.78)	128	0.44 (0.12)	0.21 (0.15)
PAA	243	1.08 (0.52)	0.46 (0.34)	0.53 (0.37)	0.74	85	2.18 (2.15)	0.71 (0.69)	0.86 (0.83)	128	0.28 (0.09)	0.24 (0.17)
HDC ₄	205	0.45 (0.22)	0.30 (0.20)	0.37 (0.23)	0.64	66	0.91 (0.78)	0.51 (0.49)	0.66 (0.65)	111	0.10 (0.06)	0.15 (0.10)
DHC ₄	247	0.42 (0.21)	0.41 (0.31)	0.47 (0.36)	0.61	85	0.92 (0.85)	0.63 (0.61)	0.76 (0.73)	128	0.08 (0.06)	0.22 (0.16)
HPALD	247	1.11 (0.46)	0.39 (0.29)	0.45 (0.34)	0.67	85	2.08 (2.17)	0.60 (0.58)	0.73 (0.70)	128	0.40 (0.10)	0.21 (0.15)
ISOPOOH/IEPOX	247	1.02 (0.49)	0.63 (0.48)	0.67 (0.52)	0.59	85	2.11 (2.06)	0.94 (0.94)	1.05 (1.05)	128	0.28 (0.09)	0.34 (0.23)
PROPNN	246	0.89 (0.43)	0.39 (0.29)	0.45 (0.33)	0.53	84	1.40 (1.38)	0.60 (0.58)	0.73 (0.70)	128	0.46 (0.13)	0.21 (0.15)
ISOPN	247	0.68 (0.39)	0.38 (0.28)	0.43 (0.33)	0.62	85	1.27 (1.29)	0.58 (0.57)	0.70 (0.67)	128	0.21 (0.09)	0.21 (0.15)
MACN/MVKN	246	0.65 (0.32)	0.38 (0.28)	0.43 (0.32)	0.57	84	1.19 (1.15)	0.58 (0.57)	0.70 (0.66)	128	0.22 (0.06)	0.21 (0.15)
INP	247	0.64 (0.46)	0.38 (0.28)	0.43 (0.33)	0.63	85	1.12 (1.17)	0.57 (0.56)	0.68 (0.65)	128	0.24 (0.10)	0.20 (0.15)
MTNP	246	0.33 (0.13)	0.36 (0.27)	0.40 (0.31)	0.54	84	0.55 (0.57)	0.54 (0.54)	0.64 (0.62)	128	0.16 (0.04)	0.20 (0.15)
HCN	234	0.13 (0.06)	0.17 (0.15)	0.22 (0.20)	0.77	84	0.26 (0.24)	0.33 (0.34)	0.43 (0.45)	117	0.03 (0.01)	0.03 (0.01)
HCOOH	244	0.47 (0.27)	0.46 (0.35)	0.54 (0.41)	0.52	83	0.82 (0.75)	0.72 (0.68)	0.91 (0.88)	127	0.20 (0.05)	0.23 (0.16)

^a Note: N is the number of samples; R is the correlation coefficient between observation (Obs) and model simulation (Mod); “Mod- $R_{s,min}$ ” refers to a sensitivity test in which $R_{s,min}$ was reduced by 40%; Daytime is 09:00-17:00 (local time) and nighttime is 20:00-06:00 (local time). Median values are provided in parentheses, following arithmetic mean values.

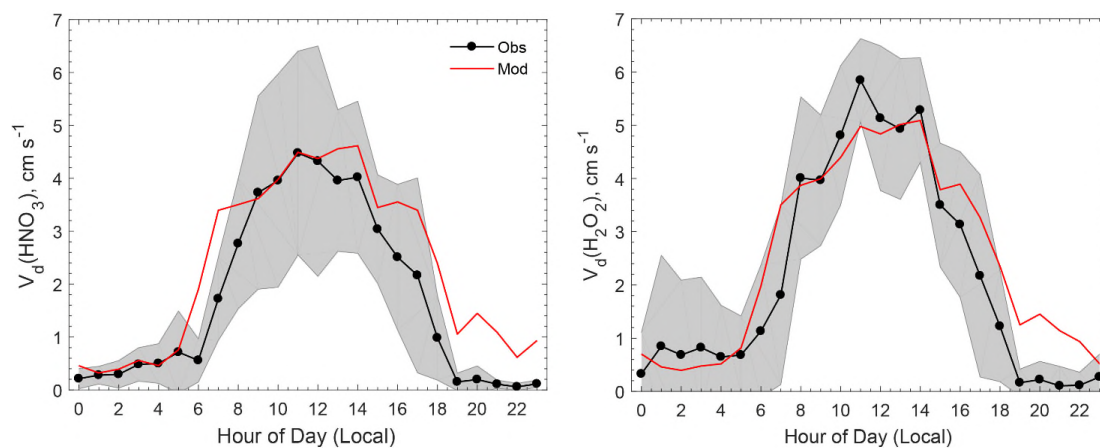


Figure 1. Comparison of the observed and modeled average diel variations of dry deposition velocities (V_d) for HNO_3 and H_2O_2 . The shaded area indicates the standard deviation of the observations. The model assumes that surface resistances (R_c) for HNO_3 and H_2O_2 are zero.

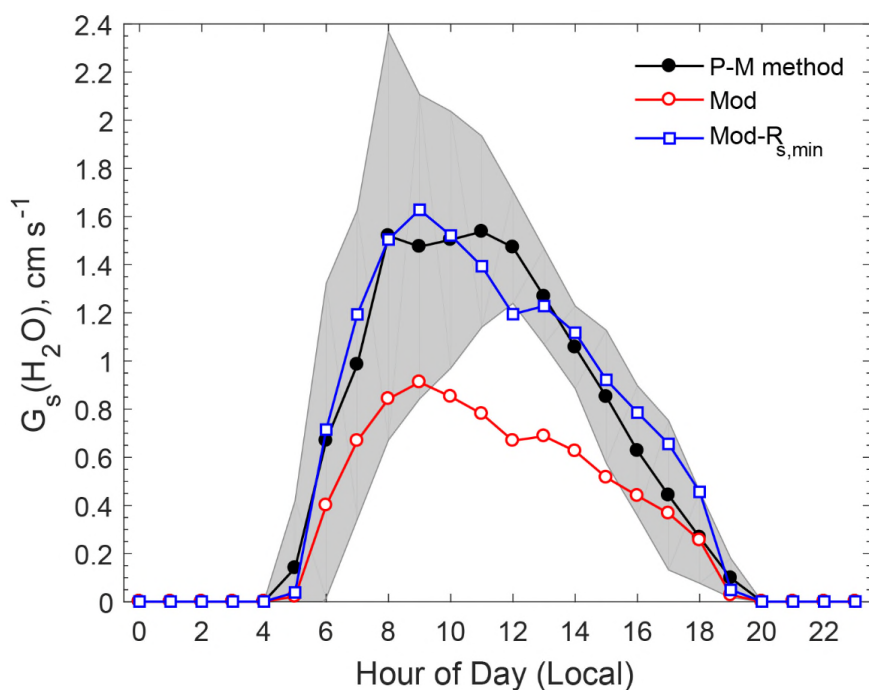


Figure 2. Comparison of observation-based and modeled averaged diel variations of stomatal conductance (G_s) for water vapor. The shaded area indicates the standard deviation of the observation-based $G_s(H_2O)$ estimated by the P-M method. “Mod- $R_{s,min}$ ” refers to a model sensitivity test in which $R_{s,min}$ was reduced by 40%.

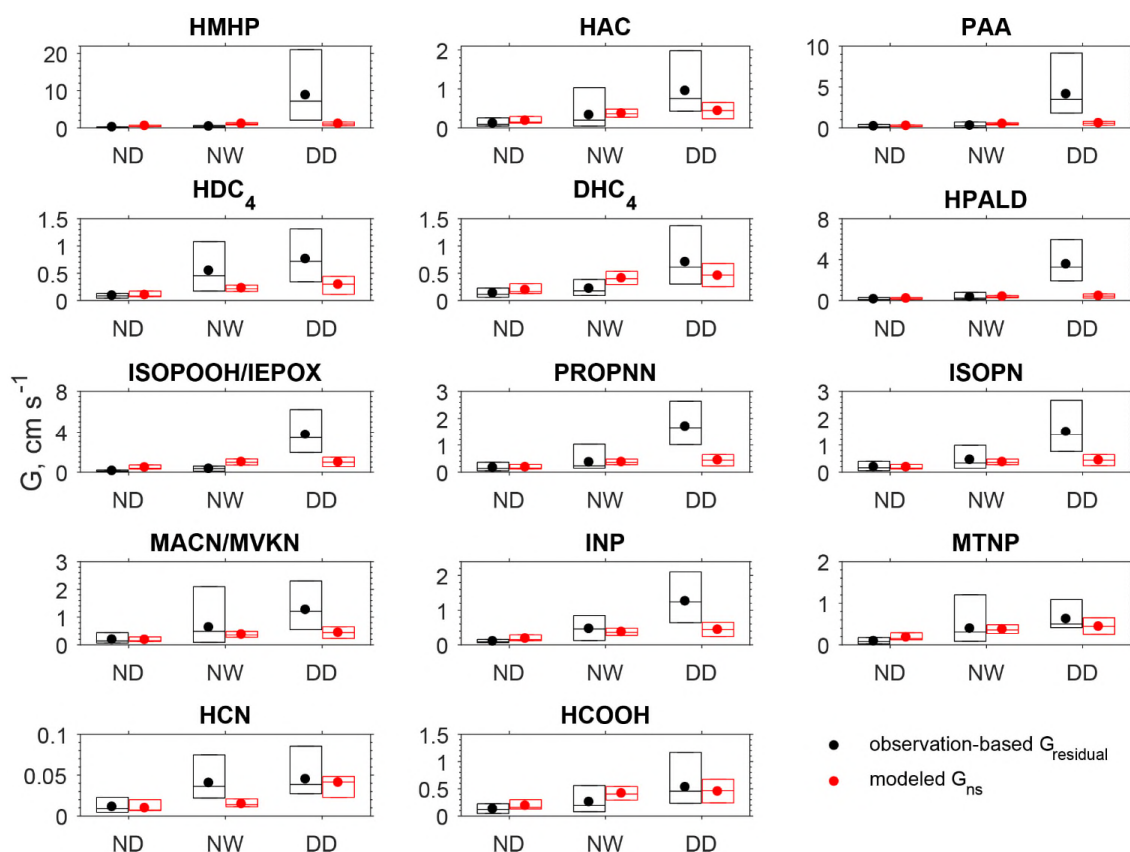


Figure 3. Box plot of the observation-based residual conductance (G_{residual}) and the modeled non-stomatal conductance (G_{ns}) during nighttime dry period (ND, $n=88$), nighttime wet period (NW, $n=40$), and daytime dry period (DD, $n=85$). In each box, the central mark is the median, and the edges of the box are the 25th and 75th percentiles. The filled dots represent the arithmetical mean of data between 25th and 75th percentiles. Daytime is 09:00-17:00 (local time) and nighttime is 20:00-06:00 (local time). The wet surface conditions were determined in the model driven by the observations of relative humidity, precipitation rate, friction velocity, and temperature.

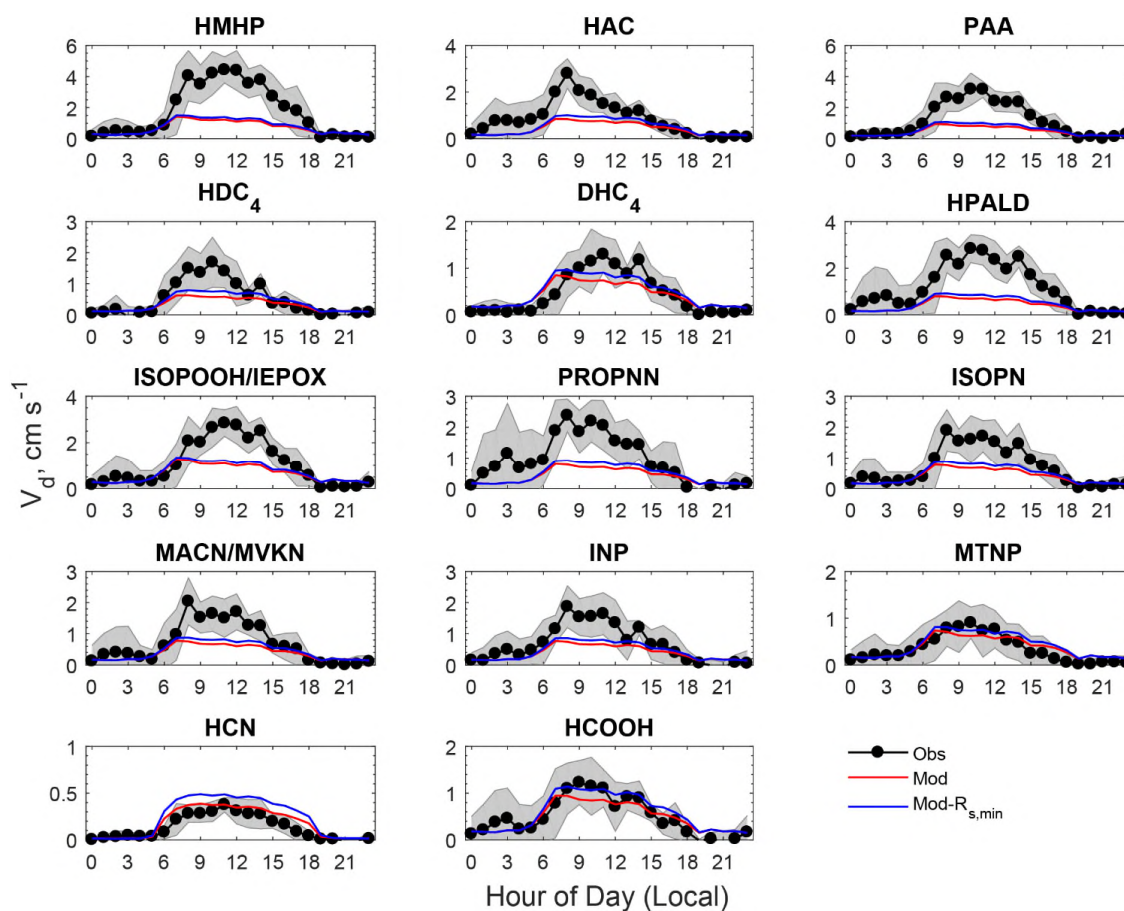


Figure 4. Comparison of averaged diel cycles of observed and modeled dry deposition velocities (V_d) of oVOCs and HCN. The shaded area indicates the standard deviation of the observations. “Mod- $R_{s,min}$ ” refers to a sensitivity test in which $R_{s,min}$ was reduced by 40%.

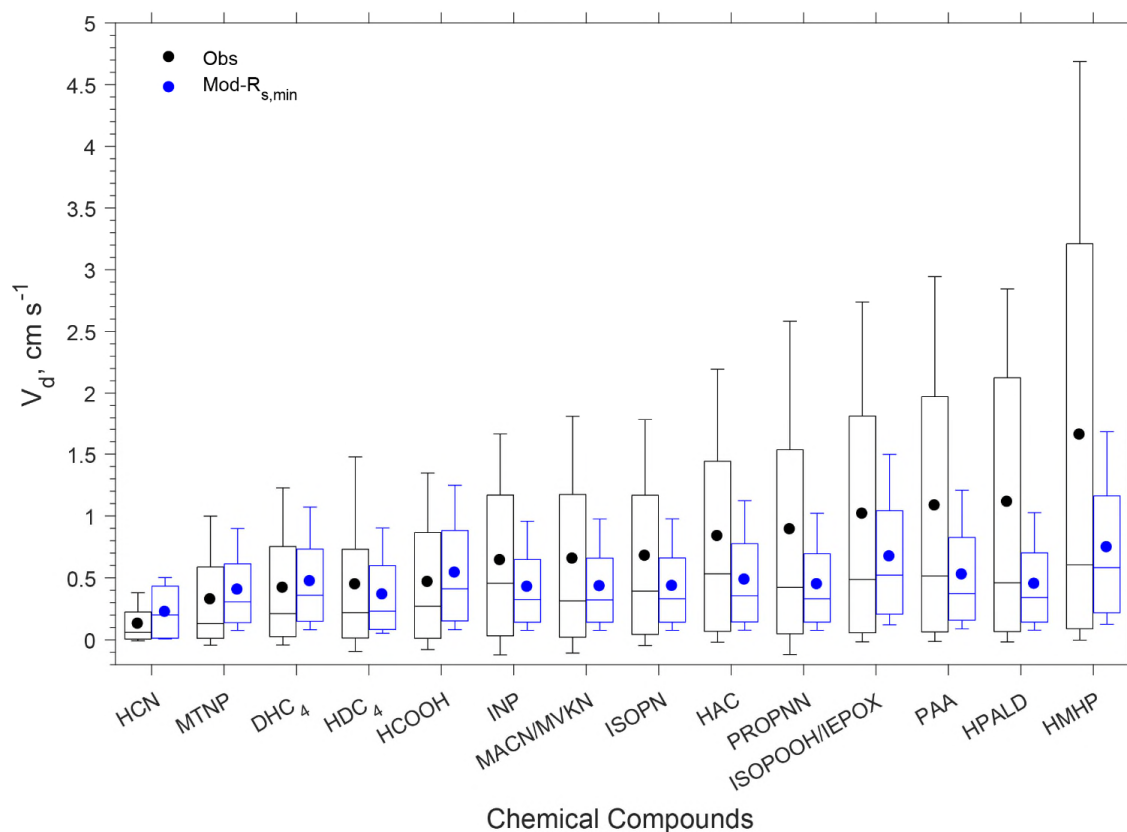


Figure 5. Box plot of observed and modeled hourly dry deposition velocities (V_d) of oVOCs and HCN. In each box, the central mark is the median, the edges of the box are the 25th and 75th percentiles, and the whiskers extend to the 10th and 90th percentiles. The filled dots represent the arithmetical mean of all the data. “Mod- $R_{s,min}$ ” refers to a sensitivity test in which $R_{s,min}$ was reduced by 40%.

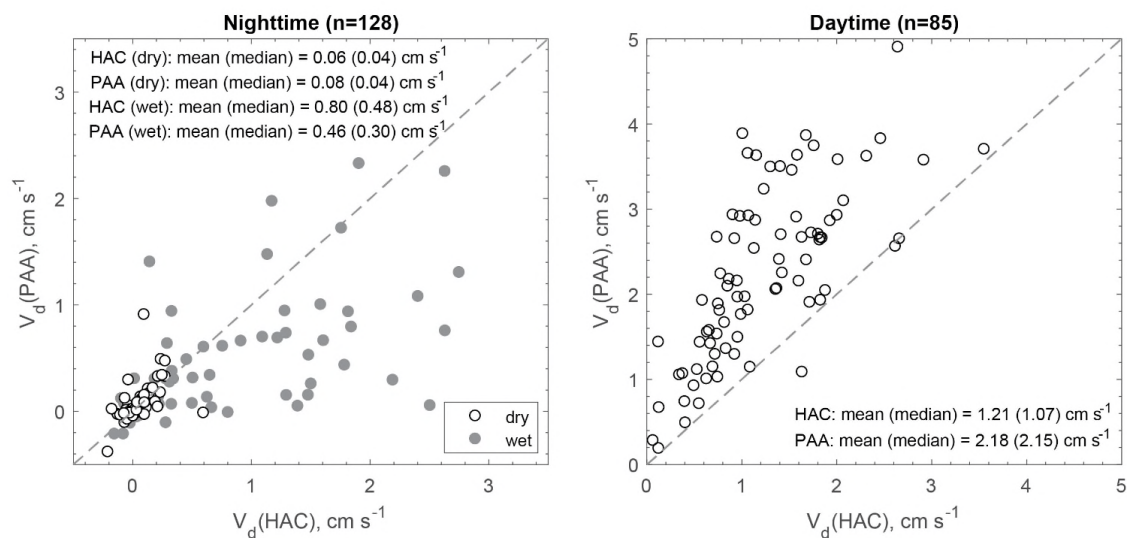


Figure 6. Scatter plot of the measured dry deposition velocities (V_d) for hydroxyacetone (HAC) and peroxyacetic acid (PAA) during nighttime (20:00-06:00, local time) and daytime (09:00-17:00, local time). The shaded (white) cycles correspond to the wet (dry) surface conditions.