

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

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1 **Abstract:** Dry deposition process refers to flux loss of an atmospheric pollutant due to uptake of
2 the pollutant by the earth's surfaces including vegetation and underlying soil and any other surface
3 types. In chemistry transport models (CTMs), dry deposition flux of a chemical species is typically
4 calculated as the product of its surface-layer concentration and its dry deposition velocity (V_d), the
5 latter is a variable that needs to be highly empirically parameterized due to too many
6 meteorological, biological and chemical factors affecting this process. The gaseous dry deposition
7 scheme of Zhang et al. (2003) parameterizes V_d for 31 inorganic and organic gaseous species. The
8 present study extends the scheme of Zhang et al. (2003) to include additional 12 oxidized volatile
9 organic compounds (oVOCs) and hydrogen cyanide (HCN), while keeping the original model
10 structure and formulas, to meet the demand of CTMs with increasing complexity. Model
11 parameters for these additional chemical species are empirically chosen based on their
12 physicochemical properties, namely the effective Henry's law constants and oxidizing capacities.
13 Modeled V_d values are compared against field flux measurements over a mixed forest in the
14 southeastern U.S. during June 2013. The model captures the basic features of the diel cycles of the
15 observed V_d . Modeled V_d values are comparable to the measurements for most of the oVOCs at
16 night. However, modeled V_d values are mostly around 1 cm s^{-1} during daytime, which is much
17 smaller than the observed daytime maxima of $2\text{-}5 \text{ cm s}^{-1}$. Analysis of the individual resistance
18 terms/uptake pathways suggests that flux divergence due to fast atmospheric chemical reactions
19 near the canopy was likely the main cause of the large model-measurement discrepancies during
20 daytime. The extended dry deposition scheme likely provides conservative V_d values for many
21 oVOCs. While higher V_d values and bi-directional fluxes can be simulated by coupling key
22 atmospheric chemical processes into the dry deposition scheme, we suggest that more
23 experimental evidence of high oVOC V_d values at additional sites is required to confirm the

24 broader applicability of the high values studied here. The underlying processes leading to high
25 measured oVOC V_d values require further investigation.

26

27 **1. Introduction**

28 Atmospheric pollutants impact human health and can also cause detrimental effects on sensitive
29 ecosystems (Wright et al., 2018). Quantifying atmospheric deposition for atmospheric pollutants
30 is needed to estimate their lifetimes in air and deposition rates to ecosystems. In mass continuity
31 equation of a chemistry transport model (CTM), atmospheric deposition is calculated separately
32 for dry and wet deposition fluxes. Dry deposition refers to the removal process through which
33 pollutants are taken up by the earth's surface, and this process, while being quite slow, is a
34 continuous process happening all the time, even during precipitation. In contrast, wet deposition
35 is fast but episodic, and pollutants need to be first incorporated into hydrometeors before being
36 delivered to the surface via precipitation. The amount of dry deposition of a pollutant of interest is
37 typically calculated as the product of its ambient concentration and its dry deposition velocity (V_d),
38 with V_d being calculated using empirically developed dry deposition schemes (Wesely & Hicks,
39 2000). In most V_d formulations, turbulent and diffusion effects are parameterized as aerodynamic
40 and quasi-laminar resistance, respectively, above and sometimes also inside the canopy. Uptake
41 effects by canopies and underlying soils and any other surface types are parameterized as canopy
42 (or surface) resistance, which include several flux pathways such as stomatal, cuticle and soil.
43 All of these flux pathways can be simultaneously affected by meteorological, biological and
44 chemical factors, most of which cannot be explicitly considered and thus are highly empirically
45 parameterized in existing dry deposition schemes, which are known to have large uncertainties
46 even for the most commonly studied chemical species such as O_3 , SO_2 and more commonly

47 measured nitrogen species with relatively rich flux datasets (Flechard et al., 2011; Wu et al., 2012;
48 Wu et al., 2018).

49 Existing dry deposition schemes have thus far considered a small number of oxidized
50 volatile organic compounds (oVOCs). Due to the lack of field flux data of oVOCs, V_d of these
51 species is typically parameterized based on physicochemical properties, taking SO_2 and O_3 as
52 references (Wesely, 1989; Zhang et al., 2003). In these existing schemes, V_d of most oVOCs were
53 on the similar order of magnitude to or slightly smaller than that of V_d of O_3 . However, higher
54 daytime V_d values for certain oVOCs than predicted by these schemes were reported lately by two
55 studies (Karl et al. 2010; Nguyen et al., 2015). In one study Karl et al. (2010) found that V_d of
56 oVOCs calculated using existing schemes are about a factor of 2 lower than those based on canopy-
57 level concentration gradient measurements over six forest and shrubland sites. V_d in their study
58 was calculated from an inverse Lagrangian transport model with concentration gradient data as
59 model input. The ratios of magnitudes between $V_d(\text{oVOCs})$ and $V_d(\text{O}_3)$ in the study of Karl et al.
60 (2010) are similar to those of Zhang et al. (2003) in that $V_d(\text{oVOCs})$ are slightly smaller than $V_d(\text{O}_3)$
61 in both cases. However, the typical daytime $V_d(\text{O}_3)$ over vegetated canopies is around 1 cm s^{-1} in
62 the literature from numerous studies (see summary in Silva & Heald, 2018), and the value in Karl
63 et al. (2010) is much higher (e.g., up to 2.4 cm s^{-1} at canopy top). One hypothesis explaining both
64 high $V_d(\text{O}_3)$ and high $V_d(\text{oVOCs})$ would be the reaction of O_3 with oVOC, which depends on the
65 chemical structure of the oVOC, but data required for validating this hypothesis are still lacking.
66 We thus suspect that the very high $V_d(\text{oVOCs})$ presented in Karl et al. (2010) were likely caused
67 by atmospheric chemical processes not typically considered in the dry deposition process. High
68 $V_d(\text{oVOCs})$ values were also observed over a temperate mixed forest in the southeastern U.S. in a
69 more recent short-term study (Nguyen et al., 2015), which again were suspected to be caused by

70 atmospheric chemical reactions near vegetation surface. The flux measurements themselves also
71 contain uncertainty. For example, Wu et al. (2015) showed that different measurement methods
72 (e.g., flux-gradient versus eddy correlation) resulted in very different daytime $V_d(\text{O}_3)$ over the same
73 forest canopy.

74 Hydrogen cyanide (HCN) is one of the most abundant cyanides present in the atmosphere
75 (Singh et al., 2003) and is considered a biomass burning marker (Bunkan et al., 2013), but few
76 existing studies have considered its dry deposition, which is critical to estimating the total sinks
77 and atmospheric lifetimes of cyanides.

78 To meet the demands of modeling a large number of organic compounds in CTMs (Kelly
79 et al., 2019; Moussa et al., 2016; Paulot et al., 2018; Pye et al., 2015; Xie et al., 2013), existing or
80 newly developed air-surface exchange/dry deposition schemes need to be expanded to include
81 additional oVOCs. At this stage with very limited knowledge on oVOC V_d , air-surface exchange
82 models based on various theoretical and/or measurement approaches should be developed, so that
83 these models can be made available to the scientific community where such models are urgently
84 needed, and for future evaluation and improvement should more flux measurements become
85 available. For example, Nguyen et al. (2015) modified the Wesely (1989) scheme to fit the flux
86 data. A more sophisticated model, with a bottom-up approach, was adopted in Nizzetto and
87 Perlinger (2012) to handle air-canopy exchange of semivolatile organic compounds.

88 The original dry deposition scheme of Zhang et al. (2003) includes 9 inorganic species and
89 22 organic species. Most of these 22 organic species are oVOCs formed from oxidation of
90 nonmethane hydrocarbons. To take advantage of the recent flux dataset of a large number of
91 oVOCs and HCN collected over a temperate forest (Nguyen et al., 2015), the present study extends
92 the Zhang et al. (2003) scheme by including 12 additional oVOC species and HCN while keeping

93 the same original model structure and theory. These additional oVOCs include hydroxymethyl
 94 hydroperoxide, peroxyacetic acid, organic hydroxy nitrates, and other multifunctional species that
 95 are mainly formed from the oxidation of biogenic VOCs (e.g., isoprene and monoterpenes). Model
 96 parameters for these newly-included species are theoretically constrained based on the effective
 97 Henry's law constants and oxidizing capacities of the individual species and by considering the
 98 measured V_d values as well. Such an approach provides a top-down determination of V_d through
 99 comparison with measured (bottom-up) fluxes. Model-measurement comparison is conducted for
 100 V_d as well as resistance components/uptake pathways, results from which identify the major causes
 101 of model-measurement discrepancies. This study provides a computer code that is potentially
 102 useful for CTMs handling these oVOCs.

103 **2. Methodology**

104 *2.1 Brief description of the V_d formulation*

105 In the scheme of Zhang et al. (2003), V_d is calculated as follows:

$$106 \quad V_d(z) = (R_a(z) + R_b + R_c)^{-1}, \quad (1)$$

107 where R_a is the aerodynamic resistance, R_b the quasi-laminar sub-layer resistance, R_c the surface
 108 resistance, and z the reference height above the vegetation. R_c is parameterized as:

$$109 \quad \frac{1}{R_c} = \frac{1 - W_{st}}{R_s + R_m} + \frac{1}{R_{ns}}, \quad (2)$$

$$110 \quad \frac{1}{R_{ns}} = \frac{1}{R_{ac} + R_g} + \frac{1}{R_{cut}}, \quad (3)$$

111 where R_s is the canopy stomatal resistance, R_m the mesophyll resistance, R_{ns} the non-stomatal
 112 resistance including resistance for uptake by leaf cuticles (R_{cut}) and by soil or ground litter (R_g),

113 R_{ac} in-canopy aerodynamic resistance, and W_{st} the fraction of stomatal blocking under wet
114 conditions.

115 R_s is calculated as follows:

$$116 \quad \frac{1}{R_{s,i}} = G_s(PAR) f(T) f(D) f(\Psi) \frac{D_i}{D_{H_2O}}. \quad (4)$$

117 Here $G_s(PAR)$ is the unstressed canopy stomatal conductance for water vapor, a function of
118 photosynthetically active radiation (PAR). The dimensionless functions $f(T)$, $f(D)$ and $f(\psi)$ range
119 from 0 to 1, representing the fractional degree of stomatal closure caused by the stress from
120 temperature, water vapor pressure deficit, and leaf water potential, respectively. D_{H_2O} and D_i are
121 the molecular diffusivities for water vapor and the gas of interest, respectively.

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

$$124 \quad \frac{1}{R_{cut/g}(i)} = \frac{\alpha(i)}{R_{cut/g}(SO_2)} + \frac{\beta(i)}{R_{cut/g}(O_3)}. \quad (5)$$

125 Details of the R_s related formulas were described in Zhang et al. (2002), R_{ns} related formulas in
126 Zhang et al. (2003), and R_a and R_b formulas in Wu et al. (2018).

127

128 *2.2 Extension of the scheme to additional chemical species*

129 Dry deposition of a gaseous compound to most canopy types is mainly through nonstomatal uptake
130 during nighttime and through both nonstomatal and stomatal uptake during daytime. The
131 nonstomatal uptake depends on water solubility and reactivity of the species, which can be
132 quantified by its effective Henry's Law constant (H^*) and oxidizing capacity, respectively (Wesely,
133 1989; Zhang et al., 2002).

134 In the Supporting Information (SI) document, Table S1 lists H^* values and Table S2 lists
135 the oxidizing capacities for oVOCs and HCN considered in the present study. As shown in Eq. 5
136 above, two model parameters (α and β) are needed for every chemical species to calculate the
137 nonstomatal uptake, with α being dependent on H^* and β dependent on oxidizing capacity. Initial
138 α values were first given based on the relative magnitudes of H^* of all the chemical species and
139 that of SO_2 . Considering that the majority of the chemical species are very reactive, a value of 1.0
140 was used for β for most species and smaller values for a few less reactive species. α and β values
141 were then adjusted based on the agreement of nighttime V_d between modeled values and measured
142 fluxes obtained from a forest site in the southeastern US during summer (Nguyen et al., 2015).
143 When adjusting α and β values, two rules were first applied: (1) the trends in α (or β) values
144 between different chemical species should be consistent with the trends of their $\log(H^*)$ (or
145 oxidizing capacity) (see Figure S1 for the finalized α versus $\log(H^*)$); and (2) modeled mean and
146 median nighttime V_d should be mostly within a factor of 2.0 of the measured values (see discussion
147 in Section 3.2 below). Only after these two rules were satisfied, then the possible maximum α and
148 β values were chosen to reduce the gap between the modeled and measured daytime V_d , knowing
149 that model predicted V_d were mostly lower than the measured ones. The finalized α and β values
150 for the additional 12 oVOCs and HCN are listed in Table 1.

151 Model parameters chosen for the additional oVOCs and HCN can produce the magnitude
152 of nighttime V_d for nearly all the chemical species, but inevitably underpredicted daytime V_d for
153 several oVOCs species with very high measured daytime V_d values. We designed the model
154 parameters this way due to the following considerations: (1) some of the chemical processes
155 causing flux loss at the surfaces may be treated separately in the mass continuity equation in
156 chemical transport models, (2) some of the oVOCs may also experience bi-directional air-surface

157 exchange, and (3) more flux measurements are needed to confirm if the very high daytime flux for
158 certain oVOCs is an universal phenomenon, noting that the existing data used here were from a
159 short period of several days and over only one surface type.

160 Besides α and β , another chemical species-dependent parameter that needs to be arbitrarily
161 chosen is R_m . R_m for HCN was set to 100 s m^{-1} based on its effective Henry's law constants and
162 oxidizing capacities. Karl et al. (2010) found that enzymatic conversion can be an efficient pathway
163 for the immobilization of oVOCs (e.g., methacrolein and methyl vinyl ketone, acetaldehyde,
164 methacrolein) within leaf interior, besides dissolution and oxidation, which suggests that the
165 magnitude of R_m for oVOCs is minimal. Thus, the R_m for the oVOCs was set to 0 s m^{-1} (Table 1).

166

167 2.3. Field flux data

168 The fluxes of 16 atmospheric compounds (including 13 oVOC species, HCN, hydrogen peroxide
169 (H_2O_2), and nitric acid (HNO_3)) were measured using the eddy covariance (EC) technique at the
170 Centreville ("CTR") Southeastern Aerosol Research and Characterization Study (SEARCH) site
171 (hereinafter referred to as CTR). Note that Formic acid (HCOOH) is the only overlapping oVOC
172 species between the original Zhang et al. (2003) scheme and the flux measurement dataset. The
173 CTR site (Brent, Alabama; 32.90°N , 87.25°W) is surrounded by a grassy field to the south and a
174 temperate mixed forest that is part of the Talladega National Forest in all the other directions. The
175 forest canopy is comprised of needleleaf coniferous (shortleaf, longleaf, and loblolly pine; ~40%)
176 and broadleaf deciduous (primarily oak, sweetgum, and hickory; ~60%) tree species. The canopy
177 height near the tower is on average ~10 m with a leaf area index (LAI) of $\sim 4.7 \text{ m}^2 \text{ m}^{-2}$. A 20 m
178 metal walk-up tower is used as the main structure supporting instruments that measured the eddy
179 covariance fluxes and related meteorological variables. The sonic anemometer and the gas inlet

180 were mounted at a height of about 22 m, facing north toward the forest. Mixing ratios of gas-phase
181 compounds were measured with negative-ion chemical ionization mass spectrometry (CIMS) at 8
182 Hz or faster. A database of half-hourly V_d for 16 atmospheric compounds covering 5 non-
183 continuous days in June 2013 was obtained at the site. During these periods, the predominant winds
184 were northerly which is ideal to sample air from the forest (Figure S2) and the requirement on
185 energy balance closure was met (see Nguyen et al. (2015)). At CTR, it was typically humid (RH
186 50-80%) and warm (28-30 °C) in the daytime during the experiment (Figure S3). A comprehensive
187 description of the V_d dataset, data processing protocols, the instrumental methods, uncertainty
188 analysis, and the site characterizations can be found in Nguyen et al. (2015).

189

190 **3. Results and Discussion**

191 *3.1. Comparison of modeled resistance components*

192 *3.1.1. Atmospheric resistances (R_a and R_b)*

193 For very reactive and soluble substances such as HNO_3 and H_2O_2 , R_c is often assumed to be close
194 to 0 (Hall & Claiborn, 1997; Meyers et al., 1989; Valverde-Canossa et al., 2006; Wesely & Hicks,
195 2000). The analysis of the measurement data showed that the daytime averaged V_d for HNO_3 and
196 H_2O_2 fitted well the rate of deposition without surface resistance ($V_d = 1/[R_a+R_b]$) (Nguyen et al.,
197 2015), which supports the assumption of near zero R_c for HNO_3 and H_2O_2 over the mixed
198 deciduous-coniferous CTR site under humid environment. Therefore, the measured V_d of HNO_3
199 and H_2O_2 can be used to evaluate the modeled atmospheric resistances for those species (the sum
200 of R_a and R_b). R_a represents the resistance for turbulent transport between the reference height and
201 the surface and is not chemical compound specific. R_b quantifies the resistance for the mass transfer

202 across the thin layer of air in contact with surface elements and is a function of the molecular
203 diffusivity of a specific compound (Wesely & Hicks, 1977). In theory, the differences in R_b
204 between any two gaseous species are only determined by differences in their molecular diffusivity
205 at any given turbulent condition.

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

221

222 3.1.2. Stomatal resistance (R_s)

223 Over vegetative areas, gas molecules can exit and enter the leaf through the stomata by molecular
224 diffusion, similar to the leaf-air exchange of water vapor and CO_2 . In dry deposition models, R_s

225 for water vapor is estimated using evapotranspiration stomatal submodels, an approach that is also
226 popular in the land surface and climate communities. R_s is extended to any gas species using the
227 ratio of molecular diffusivity of the species of interest to that of water vapor (Pleim & Ran, 2011;
228 Wesely & Hicks, 2000). Figure 2 compares the modeled canopy stomatal conductance ($G_s = 1/R_s$)
229 for water vapor against the observation-based estimates. The observation-based G_s was estimated
230 by using the inversion of the Penman-Monteith (P-M) equation (Monteith & Unsworth, 1990)
231 which calculates R_s for water vapor by using measured water vapor fluxes and related
232 meteorological data (e.g., humidity, temperature). The evaporation from soil water and liquid
233 water on the vegetation surfaces is usually a minor contribution to the total water vapor flux
234 observed above a forest canopy during summer daytime. It was assumed that 85% of the water
235 vapor flux originated from transpiration in this study, following that used in the study of
236 Turnipseed et al. (2006) at Duke Forest, North Carolina. Note that a value of 90% was used by
237 Clifton et al. (2017) at Harvard Forest, Massachusetts. The uncertainty of the calculated R_s related
238 with the uncertainty in water vapor flux portion (on an order of 10%) is much smaller than the
239 differences between the modeled and the observation-based stomatal conductance (by a factor of
240 two) as discussed below.

241 As shown in Figure 2, the model reproduced the basic diel pattern in G_s (i.e., highest values
242 between 08:00 and 11:00) but the peak value is only about half of the observation-based values.
243 The Jarvis-type stomatal submodel (Jarvis, 1976) is known for its linear dependence on the
244 prescribed minimum stomatal resistance ($R_{s,min}$), a term that is subject to large uncertainties
245 (Kumar et al., 2011; Wu et al., 2018; Wu et al., 2011). A series of tests conducted by iteratively
246 adjusting the $R_{s,min}$ values showed the modeled G_s to be in better agreement with observations if
247 $R_{s,min}$ was decreased by 40% (Figure 2). Modeled G_s with the adjusted $R_{s,min}$ was in good agreement

248 with the observation-based values for most of the time, though the modeled values were slightly
249 smaller than the observation-based estimates around noon. Analysis of the R_s parameterization
250 indicates that this discrepancy was related to the stress function for water vapor pressure deficit
251 (VPD) used in the Jarvis-type stomatal submodel, which may overpredict the stress on stomatal
252 opening due to high VPD around noon.

253

254 3.1.3. Non-stomatal resistance (R_{ns})

255 To assess if the non-stomatal resistance (R_{ns}) parametrization (Eq. 3) is reasonable, modeled $1/R_{ns}$
256 (defined as G_{ns}) values are compared with the non-stomatal portion of the flux, the inverse of
257 which is termed the residual conductance ($G_{residual}$). $G_{residual}$ includes all processes influencing
258 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
259 from the observations, R_a and R_b are calculated by the model driven by the observed meteorology,
260 R_s is the observation-based estimates by the P-M method, adjusted by the molecular diffusivity of
261 each gas (similar to Eq. 4), and R_m is listed in Table 1. The uncertainties in individual resistance
262 terms of Zhang et al. (2003) and several other dry deposition schemes have been thoroughly
263 assessed by Wu et al. (2018), from which we believe $G_{residual}$ estimated using the above formula is
264 meaningful although with large uncertainties. The estimated $G_{residual}$ can provide useful
265 information on the flux/ V_d resulting from processes such as deposition to the leaf cuticle and
266 ground (i.e., non-stomatal) or chemical loss due to reactions within and near the canopy that lead
267 to flux divergence.

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

271 dry (no dew), the $G_{residual}$ for oVOC species ranged from 0.08 to 0.18 cm s^{-1} and the modeled G_{ns}
272 was comparable in magnitude. When the surface was wet from dew formation on leaves and
273 needles, the oVOC species showed an increase in $G_{residual}$ by 55%-440% compared to the nighttime
274 dry surface. The model captured the increases in non-stomatal uptake when the surface become
275 wet with dew, although it may underestimate (e.g., HDC₄, INP, HCN) or overestimate (e.g., PAA,
276 DHC₄, HCOOH) the wetness effects. During the daytime of the study period, no precipitation was
277 recorded at the CTR site (Figure S3) and the canopy surface was dry. The mean $G_{residual}$ for oVOCs
278 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
279 species (0.2 - 1 cm s^{-1}). Figure S4 presents the diel variations of $G_{residual}$ and G_{ns} and it shows that
280 the modeled G_{ns} showed smaller diel variations than those of $G_{residual}$ and large differences in
281 magnitude can be seen during the daytime. The modeled G_{ns} showed a peak during the early
282 morning (around 7:00) which may be due to the enhanced non-stomatal uptake by dew wetted
283 surfaces.

284

285 3.2. Evaluation of modeled deposition velocities

286 Figure 4 shows model-measurement comparison of diel V_d of the oVOCs and HCN and Table 2
287 presents the statistical results of the comparison. As described in Section 2, the assigned α and β
288 values should first produce reasonable nighttime V_d . Modeled nighttime mean V_d were very close
289 to measurements for the majority of the chemical species, although the differences were somewhat
290 larger for the median values (Table 2). Three species (HAC, HPALD, PROPNN) still had 50%
291 lower modeled than measured nighttime mean V_d , but had slightly higher modeled than measured
292 nighttime median V_d . In contrast, modeled daytime mean V_d were more than 50% lower than the
293 measured values for four species (HMHP, PAA, HPALD, ISOPOOH/IEPOX) and were also

294 significantly lower for several other species. Only three species (MTNP, HCN, HCOOH) had
295 comparable modeled and measured V_d for both day- and nighttime. One species (DHC₄) had
296 slightly lower of modeled than measured daytime mean or median V_d , but with an opposite trend
297 for nighttime V_d .

298 The model reproduced the basic features of the diurnal pattern of the observations, showing
299 highest values during the day and lowest values at night. Correlation coefficients between the
300 measurement and the model ranged from 0.52 to 0.77. At night, the measured V_d for the oVOCs
301 remained relatively low, typically ranging from 0.1-0.5 cm s⁻¹, and the model produced the same
302 magnitudes for most of the species. During the daytime, the model can only capture the magnitudes
303 of the measured V_d for a few species (e.g., HCN, HCOOH, MTNP, DHC₄), of which the peak V_d
304 values were less than 1.5 cm s⁻¹. For the other species, the measured peak V_d values were in the
305 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,
306 the modeled G_s was likely underestimated when compared to the simultaneous measurements of
307 water vapor flux. Adjusting G_s higher by 67% (through reducing $R_{s,min}$ by 40%) can only increase
308 the modeled V_d of the oVOCs by 10-40% during the daytime (see the sensitivity test in Figure 4),
309 and the peak values were still mostly below 1 cm s⁻¹. Figure 5 shows that the model captured the
310 differences in measured V_d for the oVOCs to some extent. The model-measurement agreements
311 were good for species with the measured mean V_d below 0.5 cm s⁻¹, above which the discrepancy
312 increased. For the measurements, the mean values were significantly larger than the median values,
313 especially for the fast-deposited species, indicating that the distribution of the measured V_d values
314 skewed to the right (high values). The model has a better agreement with the measurements by
315 comparing the median versus mean values.

316

317 *3.3. Fast chemical reactions as potential causes of the daytime model-measurement discrepancies*

318 At night when stomata are mostly closed and atmospheric chemical reactions are largely inhibited,
319 the measured fluxes above the canopy should better represent non-stomatal surface uptake. In the
320 presence of sunlight, fast chemical reactions between the inlet and canopy could make a significant
321 or even dominant contribution to the measured fluxes of reactive species (Cape et al., 2009; Farmer
322 & Cohen, 2008; Wolfe et al., 2011). The impact of fast chemical reactions on surface fluxes should
323 be different for different chemical species. To verify this hypothesis, two chemical species (HAC
324 and PAA) having similar molecular weights (74 Da and 76 Da, respectively) but very different
325 daytime fluxes were compared (Figure 6). Their similar molecular diffusivities (controlled by
326 molecular weight) suggest that they should be transferred through the quasi-laminar sub-layer and
327 taken up through leaf stomata at similar rates, resulting in similar resistance components of R_b and
328 R_s . Note that R_a is universal to any trace gases and R_m is assumed to be negligible. Thus, the
329 differences between their V_d should be caused by their different non-stomatal sinks. At night, V_d
330 values were similar between HAC and PAA (median values: 0.04 cm s^{-1}) over dry surfaces. When
331 the surfaces were wet due to dew formation, V_d for both HAC and PAA increased (median values:
332 $0.30\text{-}0.48 \text{ cm s}^{-1}$). In contrast, $V_d(\text{PAA})$ was much higher than $V_d(\text{HAC})$ during daytime,
333 suggesting additional or larger sinks exist for PAA compared to HAC. The reactivity parameters
334 listed in Table S2 in Supporting Information also suggest PAA is more reactive than HAC. Thus,
335 fast chemical processing and subsequent flux divergence above the canopy likely caused the large
336 discrepancies between the measured and modeled V_d for the reactive oVOC compounds during the
337 daytime.

338 Chemical processes indeed can cause flux divergence or convergence at the surface, which
339 has been supported by growing evidence from field measurements (e.g., Farmer and Cohen, 2008;

340 Min et al., 2014; Wolfe et al. 2009). For example, Wolfe et al. (2009) suggested that the differences
341 in loss rate between the inlet and canopy may be an important contributor to the measured net flux
342 of peroxyacetyl nitrate, irrespective of turbulent timescales. Photochemical OH production is
343 reduced within canopies, which in turn slows down the oxidation of volatile organic compounds
344 and the photolysis of organic nitrates. The oVOCs measured at the CTR site are mainly produced
345 from the oxidation of isoprene and monoterpenes (Nguyen et al., 2015). Most of the oVOCs are
346 quite chemically reactive and can undergo fast oxidation (e.g., multifunctional carbonyls),
347 decomposition (e.g., HMHP), or photolysis (e.g., organic nitrates) (Müller et al., 2014; Nguyen et
348 al., 2015). Vertical gradients in the chemical production and loss rates below the inlet can exhibit
349 chemical flux divergence, which contributes to the net flux above canopy. Quantifying the effects
350 of chemical processing on the net flux would require a multi-layer model with resolved emission,
351 deposition, turbulent diffusion, and chemical processes throughout the canopy, which is
352 recommended for future studies (e.g., Ashworth et al., 2015; Bryan et al., 2012; Stroud et al., 2005;
353 Wolfe & Thornton, 2011; Zhou et al., 2017).

354 Quantifying V_d as the ratio of flux to concentration at one measurement height only ($V_d =$
355 F/C_{zr}), rather than as the ratio of flux to the concentration difference at the measurement height
356 and the surface ($V_d = F/[C_{zr} - C_0]$), although commonly employed in analyzing eddy covariance
357 flux measurements, is a simplification. It is valid for 1) matter that disappears nearly completely
358 by reactions at the surface, and 2) unstable or neutral conditions. Most chemical species considered
359 here may satisfy the first condition. With regards to the second condition, our analysis is based on
360 the assumption that, under stable conditions at nighttime, concentrations observed at the
361 measurement height change in relation to the fluxes measured at this height. However, no relation
362 between measured concentration and flux is typically observed due to the presence of a shallow

363 stable boundary layer, connection between the stable free atmosphere and stable boundary layer
364 by internal gravity waves, ground inversions, and low-level jets, leading to intermittent turbulence
365 at the measurement height containing a gravity wave signal, and non-steady-state conditions
366 (Foken, 2017). Future efforts to model oVOC and HCN deposition velocities above forest canopies
367 should be based on neutral or unstable boundary layer flux measurements only, or, for example,
368 on modified Bowen ratio flux measurement in which concentrations are measured at two heights
369 in the constant flux layer. Such an approach can provide a means to compute a measured deposition
370 velocity of a surface reactive substance as proportional to the ratio between the measured flux and
371 the measured concentration difference.

372

373 **4. Summary and recommendations**

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

386 The modeled nighttime V_d agrees well with the measured data for most of the oVOCs,
387 suggesting that the current non-stomatal parameterization scheme is a reasonable approach. The
388 stomatal conductance for water vapor, with adjusted (reduced) $R_{s,min}$, also agrees well with
389 measured values. However, the modeled peak V_d values during daytime are only a fraction (0.2-
390 0.5) of the measured values for some of the oVOCs, suggesting that fast atmospheric chemical
391 processes likely contributed to the total measured fluxes. In practice, these additional fluxes during
392 daytime can be modeled as non-stomatal uptake and better model-measurement agreement can be
393 obtained by adjusting the non-stomatal parameterization scheme (e.g., Müller et al., 2018; Paulot
394 et al., 2018). However, using this approach will produce unreasonably high values for the solubility
395 parameter and overpredict V_d during nighttime if the same non-stomatal formulas are used for both
396 day and nighttime (as is the case in the existing schemes). More importantly, the high measured
397 V_d have only been observed at relatively few sites during very short periods (Karl et al., 2010;
398 Nguyen et al., 2015). More evidence is needed to parameterize V_d for oVOCs to different land use
399 categories over entire seasons. Until then, the conservative estimates of V_d such as modeled in this
400 study are still recommended for use in chemical transport models. The model parameters chosen
401 for V_d of these oVOCs provide the best-known representation of their respective physicochemical
402 properties, and the modeled V_d values fall within the range of the low-end values of the available
403 measurements.

404 Future field studies should focus on conducting flux measurements of oVOC compounds
405 with highest uncertainties, such as those that are most chemically reactive in the atmosphere or
406 most rapidly taken up by wet surfaces. Additional measurements are also needed in different
407 ecosystems to inform the representativeness of the high oVOC V_d reported by Nguyen et al. (2015)
408 and Karl et al. (2010). Furthermore, concurrent chemical measurements of oxidants such as O_3 and

409 radicals are needed to quantify flux divergence due to fast within-and near-canopy chemical
410 reactions. Future dry deposition schemes should include additional biochemical processes and
411 species-dependent parameters for non-stomatal uptake, including enzymatic reactions (Karl et al.,
412 2010), the octanol-air partitioning coefficients to account for the cavity formation and polar
413 intermolecular interactions with leaf surfaces and reservoirs (Nizzetto and Perlinger, 2012), and
414 the enhancement/reduction effects due to soil and leaf moisture. Chemical processes within the
415 canopy airspace could also be coupled with emission and deposition schemes to realistically
416 simulate chemicals fate and transport, including bi-directional fluxes of reactive compounds
417 discussed here, as well as less reactive compounds such as methanol. Such an approach would
418 require specification of chemical conditions within and near the canopy as well as in-canopy
419 radiation and air flow. While more computationally intensive, the results presented here reinforce
420 the need for such advanced models to explicitly resolve the non-stomatal processes contributing
421 to the net atmosphere-biosphere exchange of reactive compounds. Above all, intercomparison
422 studies should be first conducted for existing models that can handle oVOC dry deposition
423 processes to quantify the magnitudes of uncertainties in the simulated V_d as well as the associated
424 ambient concentration and deposition fluxes.

425

426 **Code and data availability**

427 The computer code and data used in this study can be obtained from contacting the
428 corresponding author. The code is also available from (DOI:10.5281/zenodo.4697426):
429 <https://zenodo.org/record/4697426#.YHmzu5-Sk2w>

430 **Competing interests**

431 The authors declare that they have no conflict of interest.

432 **Author contributions**

433 ZW conducted model run and data analysis and drafted the manuscript. LZ designed the project,
434 finalized computer code, drafted part of the manuscript and finalized the paper. JTW contributed
435 to manuscript writing and commented on the manuscript. PAM generated chemistry data that are
436 used in the supporting document and commented on the manuscript. JAP contributed to model
437 design and manuscript writing and commented on the manuscript. XW contributed to the project
438 design and commented on the manuscript.

439

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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.

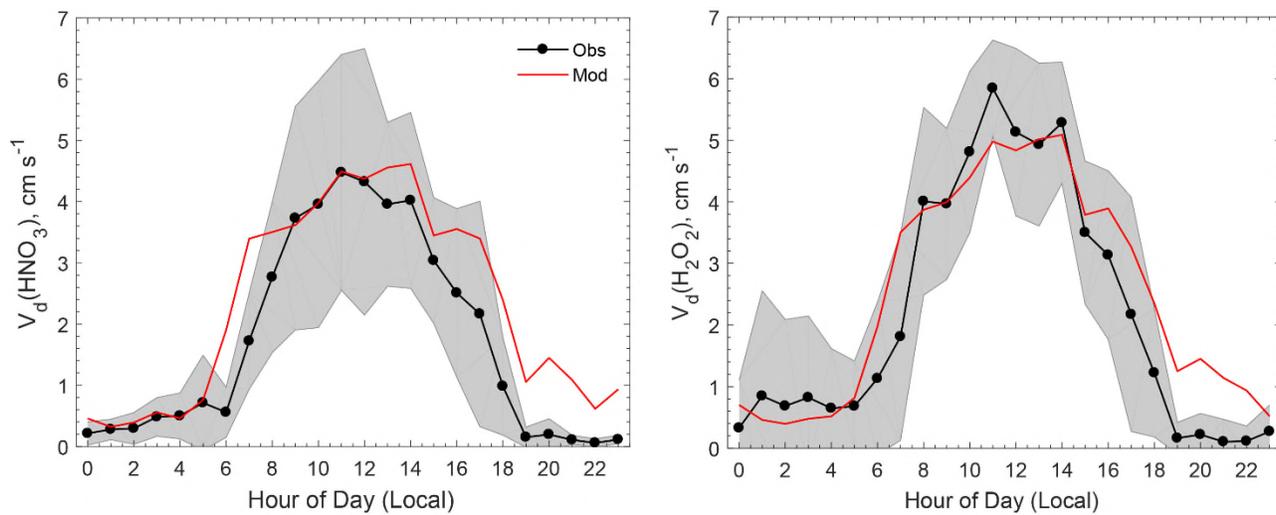


Figure 1. Comparison of the observed and modeled average diel variations of dry deposition velocities (V_d) for HNO_3 and H_2O_2 . The shaded area indicates the standard deviation of the observations. The model assumes that surface resistances (R_c) for HNO_3 and H_2O_2 are zero.

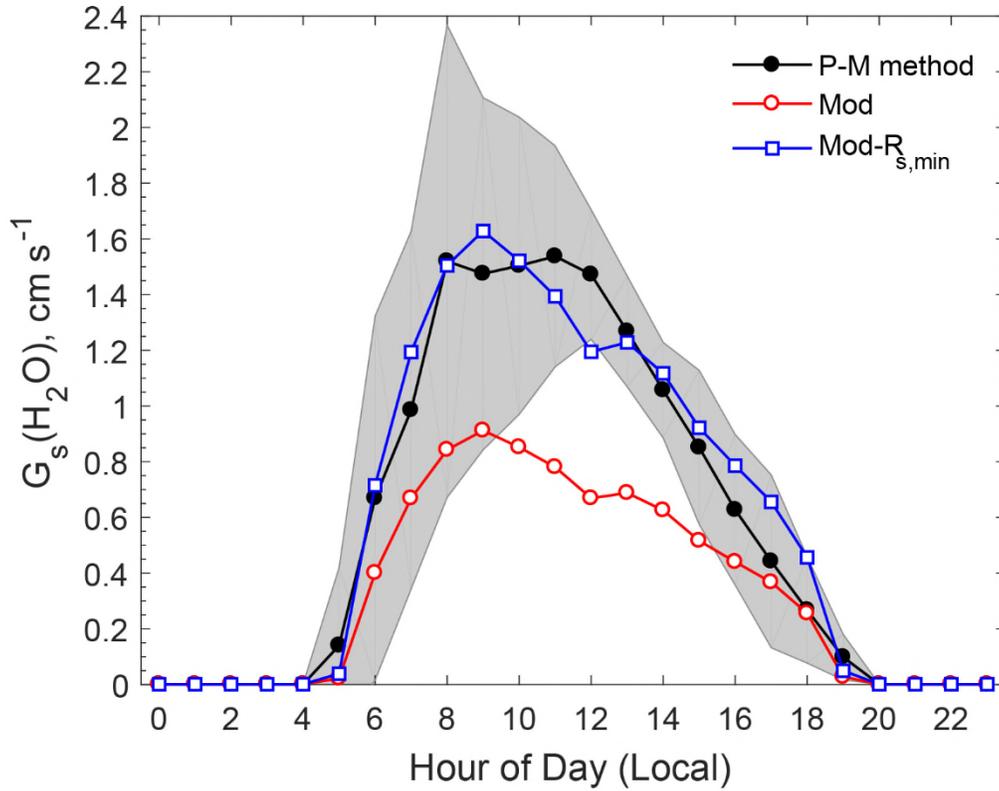


Figure 2. Comparison of observation-based and modeled averaged diel variations of stomatal conductance (G_s) for water vapor. The shaded area indicates the standard deviation of the observation-based $G_s(H_2O)$ estimated by the P-M method. “Mod- $R_{s,min}$ ” refers to a model sensitivity test in which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

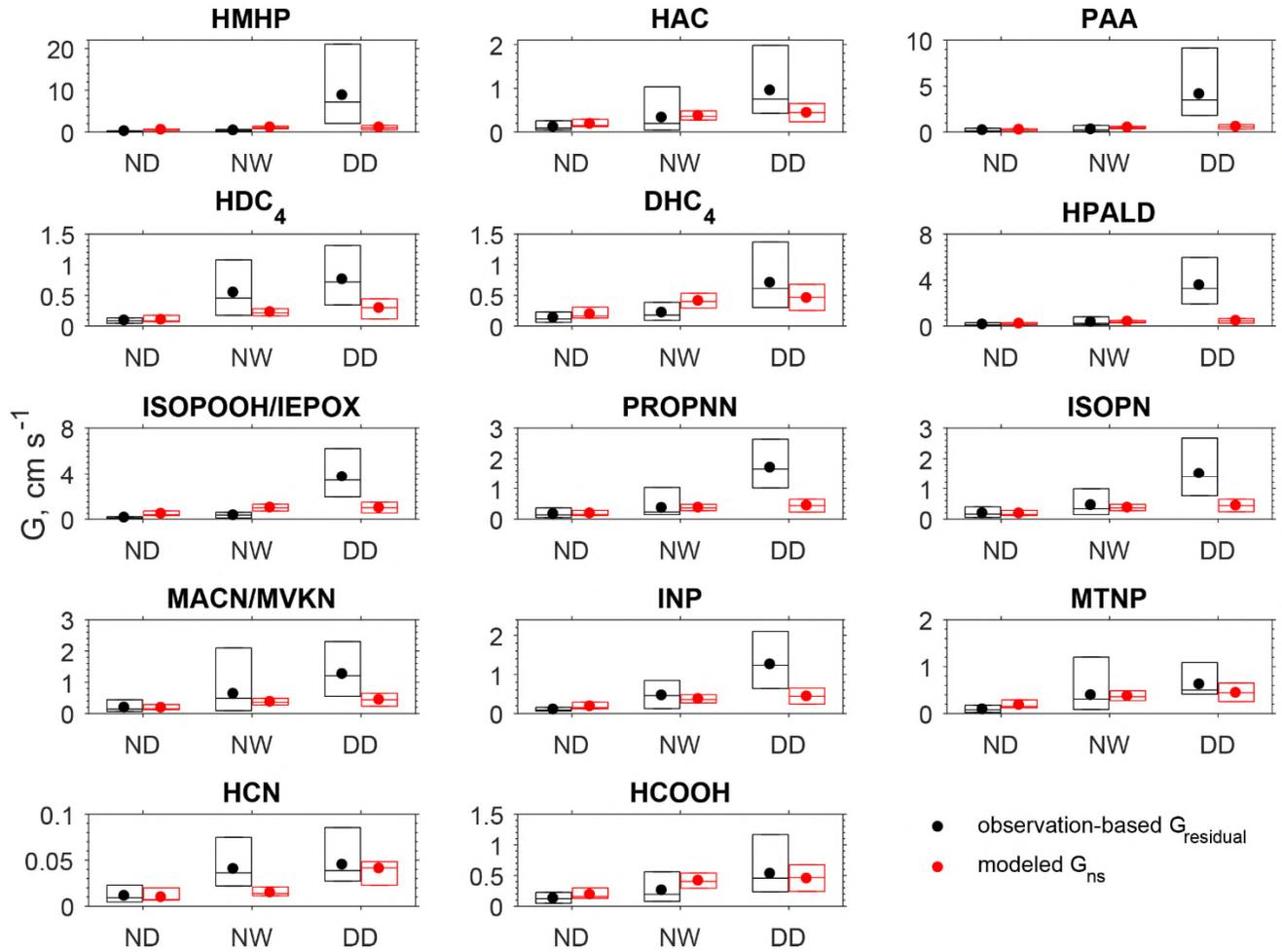


Figure 3. Box plot of the observation-based residual conductance ($G_{residual}$) and the modeled non-stomatal conductance (G_{ns}) during nighttime dry period (ND, $n=88$), nighttime wet period (NW, $n=40$), and daytime dry period (DD, $n=85$). In each box, the central mark is the median, and the edges 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.

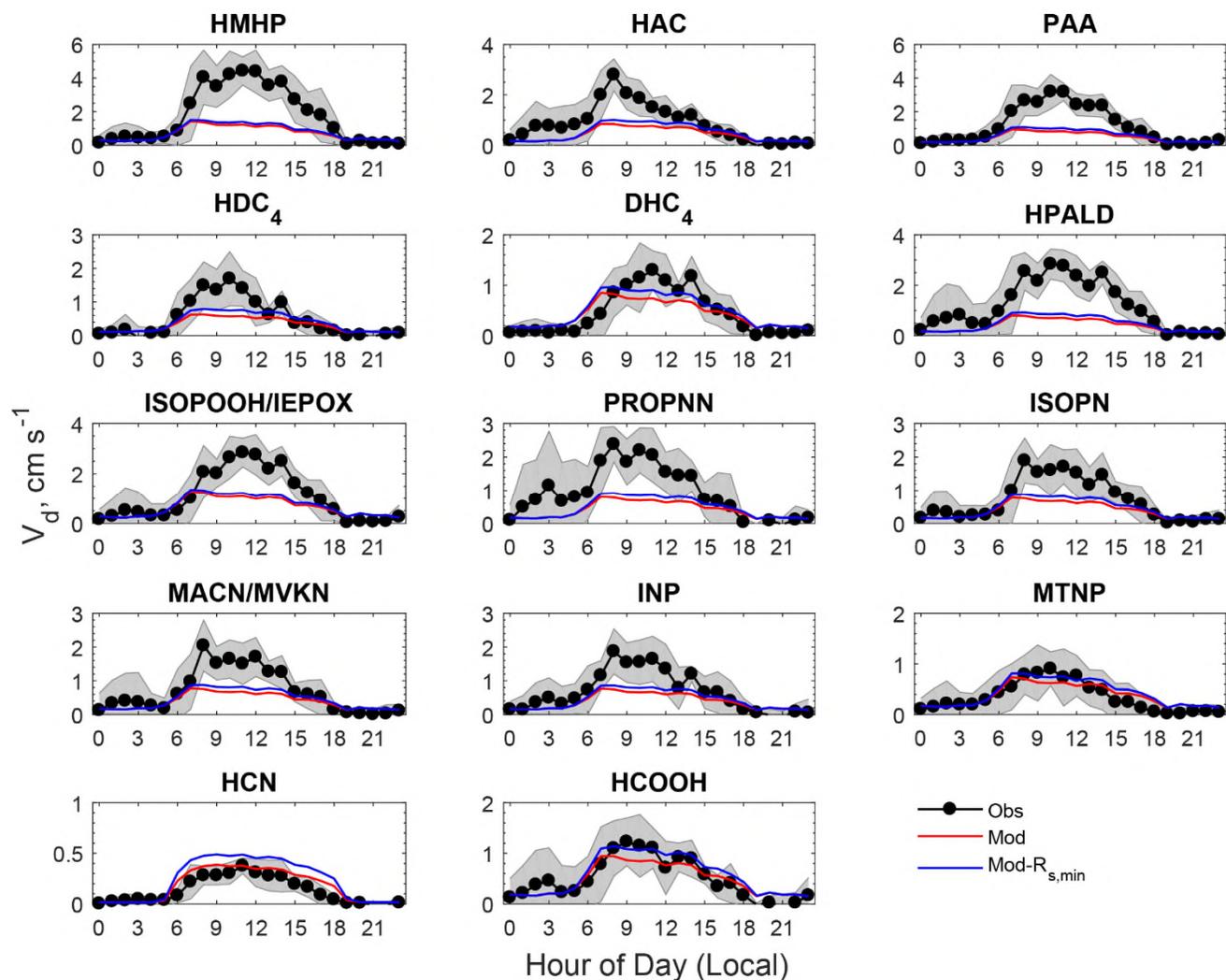


Figure 4. Comparison of averaged diel cycles of observed and modeled dry deposition velocities (V_d) of oVOCs and HCN. The shaded area indicates the standard deviation of the observations. “Mod- $R_{s,min}$ ” refers to a sensitivity test in which $R_{s,min}$ was reduced by 40%.

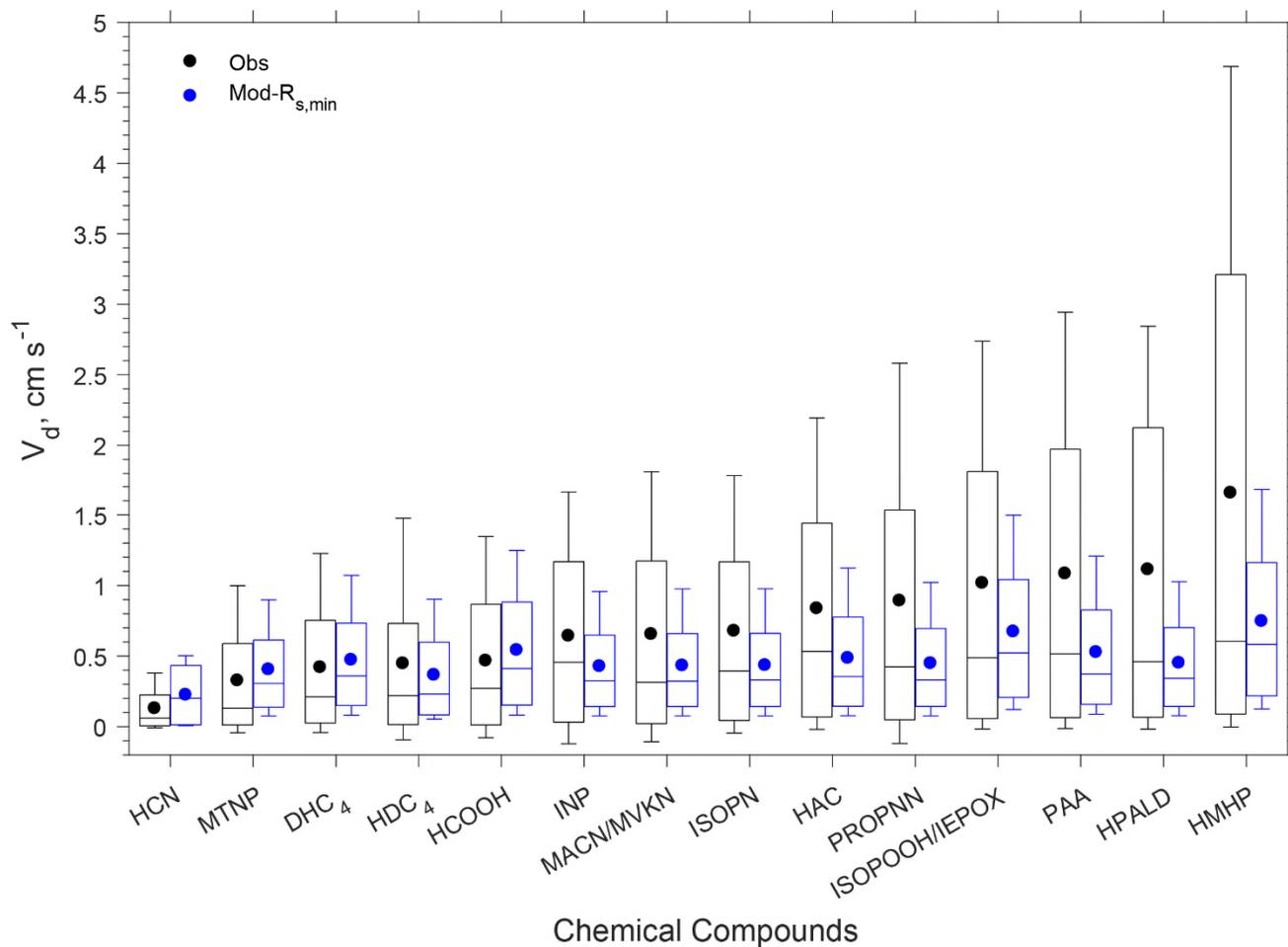


Figure 5. Box plot of observed and modeled hourly dry deposition velocities (V_d) of oVOCs and HCN. In each box, the central mark is the median, the edges of the box are the 25th and 75th percentiles, and the whiskers extend to the 10th and 90th percentiles. The filled dots represent the arithmetical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

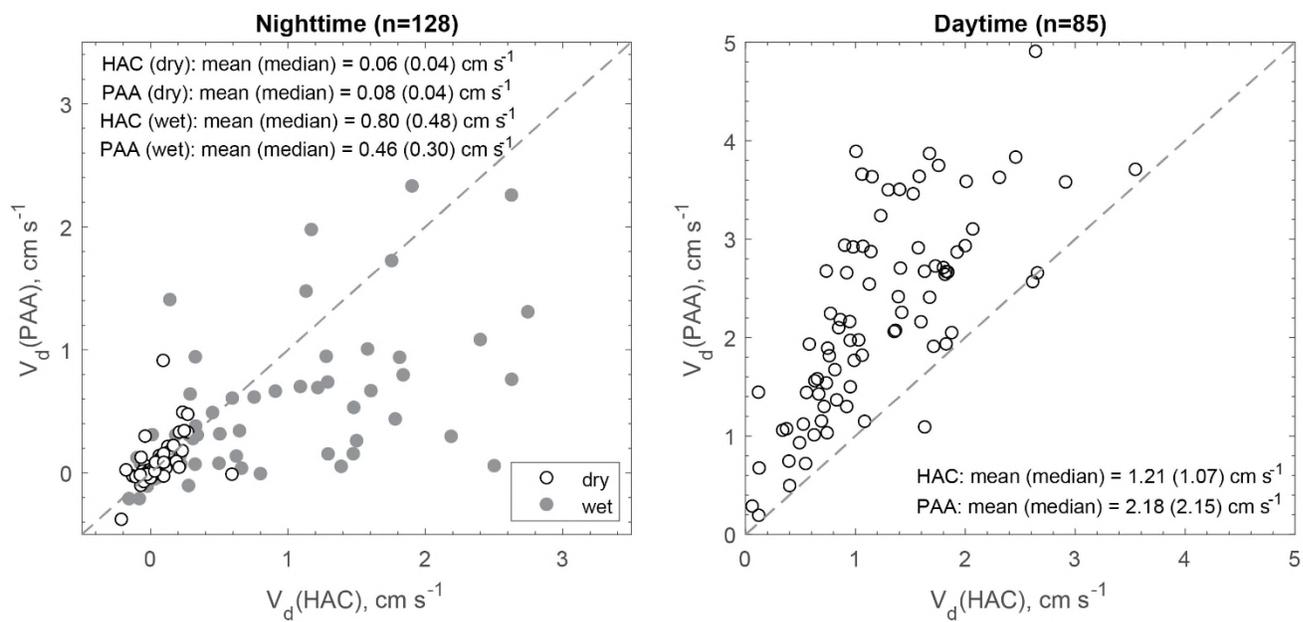


Figure 6. Scatter plot of the measured dry deposition velocities (V_d) for hydroxyacetone (HAC) and peroxyacetic acid (PAA) during nighttime (20:00-06:00, local time) and daytime (09:00-17:00, local time). The shaded (white) cycles correspond to the wet (dry) surface conditions.