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

Zhiyong Wu\textsuperscript{1,2}, Leiming Zhang\textsuperscript{1,*}, John T. Walker\textsuperscript{3}, Paul A. Makar\textsuperscript{1}, Judith A. Perlinger\textsuperscript{4}, Xuemei Wang\textsuperscript{5}

\textsuperscript{1}Air Quality Research Division, Science and Technology Branch, Environment and Climate Change Canada, Toronto, ON, M3H 5T4, Canada
\textsuperscript{2}ORISE Fellow at US Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC, 27711, USA
\textsuperscript{3}US Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC, 27711, USA
\textsuperscript{4}Civil & Environmental Engineering Department, Michigan Technological University, Houghton, MI, 49931, USA
\textsuperscript{5}Institute 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 process refers to flux loss of an atmospheric pollutant due to uptake of the pollutant by the earth’s surfaces including vegetation and underlying soil and any other surface types. In chemistry transport models (CTMs), dry deposition flux of a chemical species is typically calculated as the product of its surface-layer concentration and its dry deposition velocity ($V_d$), the latter is a variable that needs to be highly empirically parameterized due to too many meteorological, biological and chemical factors affecting this process. The gaseous dry deposition scheme of Zhang et al. (2003) parameterize $V_d$ for 31 inorganic and organic gaseous species. The present study extends the scheme of Zhang et al. (2003) to include additional 12 oxidized volatile organic compounds (oVOCs) and hydrogen cyanide (HCN), while keeping the original model structure and formulas, to meet the demand of CTMs with increasing complexity. Model parameters for these additional chemical species are empirically chosen 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 2-5 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.

1. Introduction

Atmospheric pollutants impact human health and can also cause detrimental effects on sensitive ecosystems (Wright et al., 2018). Quantifying atmospheric deposition for atmospheric pollutants is needed to estimate their lifetimes in air and deposition rates to ecosystems. In mass continuity equation of a chemistry transport model (CTM), atmospheric deposition is calculated separately for dry and wet deposition fluxes. Dry deposition refers to the removal process through which pollutants are taken up by the earth’s surface, and this process, while being quite slow, is a continuous process happening all the time, even during precipitation. In contrast, wet deposition is fast but episodic, and pollutants need to be first incorporated into hydrometeors before being delivered to the surface via precipitation. The amount of dry deposition of a pollutant of interest is typically calculated as the product of its ambient concentration and its dry deposition velocity ($V_d$), with $V_d$ being calculated using empirically developed dry deposition schemes (Wesely & Hicks, 2000). In most $V_d$ formulations, turbulent and diffusion effects are parameterized as aerodynamic
and quasi-laminar resistance, respectively, above and sometimes also inside the canopy. Uptake
effects by canopies and underlying soils and any other surface types are parameterized as canopy
(or surface) resistance, which include several flux pathways such as to stomatal, cuticle and soil.
All of these flux pathways can be simultaneously affected by meteorological, biological and
chemical factors, most of which cannot be explicitly considered and thus are highly empirically
parameterized in existing dry deposition schemes, which are known to have large uncertainties
even for the most commonly studied chemical species such as O₃, SO₂ and more commonly
measured nitrogen species with relatively rich flux datasets (Flechard et al., 2011; Wu et al., 2012;
Wu et al., 2018).

Existing dry deposition schemes have thus far considered a small number of oxidized
volatile organic compounds (oVOCs). Due to the lack of field flux data of oVOCs, V_d of these
species is typically parameterized based on physicochemical properties, taking SO₂ and O₃ as
references (Wesely, 1989; Zhang et al., 2003). In these existing schemes, V_d of most oVOCs were
on the similar order of magnitude to or slightly smaller than that of V_d of O₃. However, higher
daytime V_d-values for certain oVOCs than predicted by these schemes were reported lately by two
studies (Karl et al. 2010; Nguyen et al., 2015). In one study Karl et al. (2010) found that V_d of
oVOCs calculated using existing schemes are about a factor of 2 lower than those based on canopy-
level concentration gradient measurements over six forest and shrubland sites. V_d in their study
was calculated from an inverse Lagrangian transport model with concentration gradient data as
model input. The ratios of magnitudes between V_d(oVOCs) and V_d(O₃) in the study of Karl et al.
(2010) are similar to those of Zhang et al. (2003) in that V_d(oVOCs) are is slightly smaller than
V_d(O₃) in both cases. However, the typical daytime V_d(O₃) over vegetated canopies is around 1 cm
s⁻¹ in the literature from numerous studies (see summary in Silva & Heald, 2018), and the value in
Karl et al. (2010) is much higher (e.g., up to 2.4 cm s\(^{-1}\) at canopy top). One hypothesis explaining both high \(V_d(O_3)\) and high \(V_d(oVOCs)\) 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 \(V_d(oVOCs)\) presented in Karl et al. (2010) were likely caused by atmospheric chemical processes not typically considered in the dry deposition process. High \(V_d(oVOCs)\) 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 \(V_d(O_3)\) 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 a large number of organic compounds in CTMs (Kelly et al., 2019; Moussa et al., 2016; Paulot et al., 2018; Pye et al., 2015; Xie et al., 2013), existing or newly developed air–surface exchange/dry deposition schemes need to be expanded to include additional \(oVOCs\). 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. A more sophisticated model, with a bottom-up approach, was adopted in Nizzetto and Perlinger (2012) to handle air-canopy exchange of semivolatile organic compounds is also available in the literature (Nizzetto and Perlinger, 2012).

The original dry deposition scheme of Zhang et al. (2003) includes 9 inorganic species and 22 organic species. Most of these 22 organic species are oVOCs formed from oxidation of nonmethane hydrocarbons. To take advantage of the recent flux dataset of a large number of oVOCs and HCN collected over a temperate forest (Nguyen et al., 2015), the present study extends the current Zhang et al. (2003) scheme by including 12 additional oVOC species and HCN while keeping the same original model structure and theory. These additional oVOCs include hydroxymethyl hydroperoxide, peroxyacetic acid, organic hydroxy nitrates, and other multifunctional species that are mainly formed from the oxidation of biogenic VOCs (e.g., isoprene and monoterpenes). The parameterization for these newly-included species are theoretically constrained 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. Such an approach provides a top-down determination of $V_d$ through comparison with measured (bottom-up) fluxes. 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. This study provides a computer code that is potentially useful for CTMs handling these oVOCs.

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

2.1 Brief description of the \(V_d\) formulation

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

\[ \frac{1}{R_c} = \frac{1}{R_s + R_m} + \frac{1}{R_{ns}} \]  

(2)

\[ \frac{1}{R_{ns}} = \frac{1}{R_{ac} + R_{g}} + \frac{1}{R_{sur}} \]  

(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.

$R_s$ is calculated as follows: using the sunlit/shade stomatal resistance approach as detailed in Zhang et al. (2002):

\[ \frac{1}{R_{s,i}} = G_s(PAR) f(T) f(D) f(\Psi) \frac{D_{i}}{D_{H_2O}} \]  

(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 chemical species are scaled to those of SO$_2$ and O$_3$ with two species ($i$)-
dependent scaling parameters $\alpha(i)$ and $\beta(i)$:

\[
\frac{1}{R_{cat/g}(i)} = \frac{\alpha(i)}{R_{cat/g}(SO_2)} + \frac{\beta(i)}{R_{cat/g}(O_3)} \quad (5)
\]

Details of the $R_3$ related formulas were described in Zhang et al. (2002), $R_{ns}$ related formulas in Zhang et al. (2003), and $R_a$ and $R_b$ formulas in Wu et al. (2018).

2.2 Extension of the scheme to additional chemical species

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) as shown in Eq. 5 above, two model parameters ($\alpha$ and $\beta$) are needed for every chemical species to calculate the nonstomatal uptake, with $\alpha$ being dependent on $H^*$ and $\beta$ dependent on oxidizing capacity. Initial $\alpha$ values were first given based on 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 $\beta$ for most species and smaller values for a few less reactive species. $\alpha$ and $\beta$ 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 $\alpha$ and $\beta$ values,
two rules were first applied: (1) the trends in $\alpha$ (or $\beta$) values between different chemical species should be consistent with the trends of their $\log(H^*)$ (or oxidizing capacity) (see Figure S1 for the finalized $\alpha$ 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 $\alpha$ and $\beta$ 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. The finalized $\alpha$ and $\beta$ values for the additional 12 oVOCs and HCN are listed in Table 1.

Model parameters chosen for the additional oVOCs and HCN can produce the magnitude of nighttime $V_d$ for nearly all the chemical species, but inevitably underpredicted daytime $V_d$ for several oVOCs species with very high measured daytime $V_d$ values. We designed the model parameters this way 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.

Model theory and field data used for model evaluation are briefly described below.

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:

\[
V_d(z) = \left( R_a(z) + R_b + R_s \right)^{-1},
\]

where \( R_a \) is the aerodynamic resistance, \( R_b \) the quasi-laminar sub-layer resistance, \( R_s \) 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). \( R_s \) is parameterized as:

\[
\frac{1}{R_s} = \frac{1 - W_{st}}{R_s + R_m} + \frac{1}{R_{ns}},
\]

\[
\frac{1}{R_{ns}} = \frac{1}{R_{ac} + R_g} + \frac{1}{R_{cut}},
\]

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):

\[
\frac{1}{R_{s,i}} = G_s(PAR) f(T) f(D) f(\psi) \frac{D_i}{D_{H,0}},
\]

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.

**Besides** \( \alpha \) and \( \beta \), another chemical species-dependent parameter that needs to be arbitrarily
chosen is \( R_m \). 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).

**2.32 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). Note that Formic acid \((HCOOH)\) is the only overlapping oVOC
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. The canopy height near the tower is on average ~10 m with a leaf area index (LAI) of ~4.7 m² m⁻². 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. Mixing ratios of gas-phase compounds were measured with negative-ion chemical ionization mass spectrometry (CIMS) at 8 Hz or faster. 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 Vd 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 Vd 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 (Rₐ and Rₜ)
For very reactive and soluble substances such as HNO$_3$ and H$_2$O$_2$, $R_c$ 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 HNO$_3$ and H$_2$O$_2$ 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 HNO$_3$ and H$_2$O$_2$ over the mixed deciduous-coniferous CTR site under humid environment. Therefore, the measured $V_d$ of HNO$_3$ and H$_2$O$_2$ 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$_2$O$_2$ against observations. The measured $V_d$ for HNO$_3$ and H$_2$O$_2$ 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$_2$O$_2$ were on the order of 1 cm s$^{-1}$, much higher than the measurements (<0.2 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$_2$O$_2$
deposited slightly faster than HNO₃, and the model reproduces well, as shown in Figure 1. Modeled

\[ R_b \text{ for } H_2O_2 \text{ is always smaller than that for } HNO_3 \text{ due to the smaller molecular weight and the larger molecular diffusivity. Overall, the model was in good agreement with the measurements regarding } V_d \text{ for } HNO_3 \text{ and } H_2O_2, \text{ implying that the parameterization for atmospheric resistances } (R_a \text{ and } R_b) \text{ was reasonable for the site during the study period.}

3.1.2. Stomatal resistance (\( R_s \))

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

As shown in Figure 2, the model reproduced the basic diel pattern in $G_s$ (i.e., highest values between 08:00 and 11:00) but the peak value is only about half of the observation-based values. The Jarvis-type stomatal submodel (Jarvis, 1976) used in the Model is known for its linear dependence on the prescribed minimum stomatal resistance ($R_{s,min}$), a term that is subject to large uncertainties (Kumar et al., 2011; Wu et al., 2018; Wu et al., 2011). A series of tests conducted by iteratively adjusting the $R_{s,min}$ values showed the modeled $G_s$ to be in better agreement with observations if $R_{s,min}$ was decreased by 40% (Figure 2). Modeled $G_s$ from the Model with the adjusted $R_{s,min}$ was in good agreement with the observation-based values for most of the time, though the modeled values were slightly smaller than the observation-based estimates around noon. Analysis of the $R_s$ parameterization indicates that this discrepancy was related to the stress function for water vapor pressure deficit (VPD) used in the Jarvis-type stomatal submodel, which may overpredict the stress on stomatal opening due to high VPD around noon.

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

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

Figure 3 compares the observation-based $\mathcal{G}_{\text{residual}}$ for each oVOC species or HCN against the corresponding modeled non-stomatal conductance ($\mathcal{G}_{\text{ns}}$) under different conditions. The mean and median values are presented in Table S3. During the nighttime when the canopy surface was dry (no dew), the $\mathcal{G}_{\text{residual}}$ for oVOC species ranged from 0.08 to 0.18 cm s$^{-1}$ and the modeled $\mathcal{G}_{\text{ns}}$ was comparable in magnitude. When the surface was wet from dew formation on leaves and needles, the oVOC species showed an increase in $\mathcal{G}_{\text{residual}}$ by 55%-440% compared to the nighttime dry surface. The model captured the increases in non-stomatal uptake when the surface become wet with dew, although it may underestimate (e.g., HDC$_4$, INP, HCN) or overestimate (e.g., PAA, DHC$_4$, HCOOH) the wetness effects. During the daytime of the study period, no precipitation was recorded at the CTR site (Figure S3) and the canopy surface was dry. The mean $\mathcal{G}_{\text{residual}}$ for oVOCs ranged from 0.5 cm s$^{-1}$ to 8.7 cm s$^{-1}$ during the daytime, much higher than the modeled $\mathcal{G}_{\text{ns}}$ for most species (0.2 - 1 cm s$^{-1}$). Figure S4 presents the diel variations of $\mathcal{G}_{\text{residual}}$ and $\mathcal{G}_{\text{ns}}$ and it shows that the modeled $\mathcal{G}_{\text{ns}}$ showed smaller diel variations than those of $\mathcal{G}_{\text{residual}}$ and large differences in magnitude can be seen during the daytime. The modeled $\mathcal{G}_{\text{ns}}$ showed a peak during the early morning (around 7:00) which may be due to the enhanced non-stomatal uptake by dew wetted surfaces.
3.2. Evaluation of modeled deposition velocities

Figure 4 shows model-measurement comparison of diel $V_d$ of the oVOCs and HCN and Table 2 presents the statistical results of the comparison. As described in Section 2, the assigned $\alpha$ and $\beta$ values should first produce reasonable nighttime $V_d$. Modeled nighttime mean $V_d$ were very close to measurements for the majority of the chemical species, although the differences were somewhat larger for the median values (Table 2). Three species (HAC, HPALD, PROPNN) still had 50% lower modeled than measured nighttime mean $V_d$, but had slightly higher modeled than measured 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 (DHC$_4$) 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, DHC$_4$), 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 $R_{s,\text{min}}$ 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.

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

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

Chemical processes indeed can cause flux divergence or convergence at the surface, which has been supported by growing evidence from field measurements (e.g., Farmer and Cohen, 2008; Min et al., 2014; Wolfe et al. 2009). For example, Wolfe et al. (2009) suggested that the differences in loss rate between the inlet and canopy may be an important contributor to the measured net flux of peroxyacetyl nitrate, irrespective of turbulent timescales. Photochemical OH production is reduced within canopies, which in turn slows down the oxidation of volatile organic compounds and the photolysis of organic nitrates. The oVOCs measured at the CTR site are mainly produced from the oxidation of isoprene and monoterpenes (Nguyen et al., 2015). Most of the oVOCs are quite chemically reactive and can undergo fast oxidation (e.g., multifunctional carbonyls), decomposition (e.g., HMHP), or photolysis (e.g., organic nitrates) (Müller et al., 2014; Nguyen et al., 2015). Vertical gradients in the chemical production and loss rates below the inlet can exhibit chemical flux divergence, which contributes to the net flux above canopy. Quantifying the effects of chemical processing on the net flux would require a multi-layer model with resolved emission, deposition, turbulent diffusion, and chemical processes throughout the canopy, which is
recommended for future studies (e.g., Ashworth et al., 2015; Bryan et al., 2012; Stroud et al., 2005; Wolfe & Thornton, 2011; Zhou et al., 2017).

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

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

Future field studies should focus on conducting flux measurements of oVOC compounds with highest uncertainties, such as those that are most chemically reactive in the atmosphere or most rapidly taken up by wet surfaces. Additional measurements are also needed in different ecosystems to inform the representativeness of the high oVOC \( V_d \) reported by Nguyen et al. (2015) and Karl et al. (2010). Furthermore, concurrent chemical measurements of oxidants such as O\(_3\) and radicals are needed to quantify flux divergence due to fast within-and near-canopy chemical 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 contacting the corresponding author. The code is also available from (DOI:10.5281/zenodo.4697426):

https://zenodo.org/record/4697426#.YHmzu5-Sk2w

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

**Acknowledgments**
We thank Tran Nguyen for the field flux data and Glenn Wolfe and Christopher Groff for the tree survey data. We also greatly appreciate helpful comments from Tran Nguyen, Chris Geron and Donna Schwede. X. Wang was supported by the Chinese National Key Research and Development Plan (2017YFC0210100) and the State Key Program of National Natural Science Foundation of China (91644215). The SouthEastern Aerosol Research and CHaracterization (SEARCH) network was sponsored by the Southern Company and the Electric Power Research Institute. The field data during the SOAS 2013 campaign is available at https://esrl.noaa.gov/csd/groups/csd7/measurements/2013senex/Ground/DataDownload/.

Disclaimer: The research presented was not performed or funded by U.S. Environmental Protection Agency and was not subject to EPA’s quality system requirements. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

References:


