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Evaluating the calculated dry deposition velocities of reactive nitrogen oxides and ozone from two community models over a temperate deciduous forest

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Hourly measurements of O₃, NO, NO₂, PAN, HNO₃ and NOx concentrations, and eddy-covariance fluxes of O₃ and NOx over a temperate deciduous forest from June to November, 2000 were used to evaluate the dry deposition velocities (Vd) estimated by the WRF-Chem dry deposition module (WDDM), which adopted Wesely (1989) scheme for surface resistance (Rₛ), and the Noah land surface model coupled with a photosynthesis-based Gas-exchange Evapotranspiration Model (Noah-GEM). Noah-GEM produced better Vd(O₃) variations due to its more realistically simulated stomatal resistance (Rₛ) than WDDM. Vd(NOₓ) is very sensitive to the minimum canopy stomatal resistance (Rₛ) which is specified for each seasonal category assigned in WDDM. Treating Sep-Oct as autumn in WDDM for this deciduous forest site caused a large underprediction of Vd(O₃) due to the leafless assumption in ‘autumn’ seasonal category for which an infinite Rₛ was assigned. Reducing Rₛ to a value of 70 s m⁻¹, the same as the default value for the summer season category, the modeled and measured Vd(NOₓ) agreed reasonably well. HNO₃ was found to dominate the NOx flux during the measurement period; thus the modeled Vd(NOₓ) was mainly controlled by the aerodynamic and quasi-laminar sublayer resistances (Rₛ and Rₛ), both being sensitive to the surface roughness length (zₒ). Using an appropriate value for zₒ (10% of canopy height), WDDM and Noah-GEM agreed well with the observed daytime Vd(NOₓ). The differences in Vd(NOₓ) between WDDM and Noah-GEM were small due to the small differences in the calculated Rₛ and Rₛ between the two models; however, the differences in Rₛ of NOₓ and PAN between the two models reached a factor of 1.1–1.5, which in turn caused a factor of 1.1–1.3 differences for Vd. Combining the measured concentrations and modeled Vd, NOₓ, PAN and HNO₃ accounted for 19%, 4%, and 70% of the measured NOₓ fluxes, respectively.

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1. Introduction

Global atmospheric emissions of nitrogen oxide have increased dramatically during the past 150 years, and the supply of reactive nitrogen to ecosystems has doubled due to anthropogenic activities such as nitrogen fertilization, biomass burning, and fossil fuel combustion (Galloway et al., 2008). Dry deposition is responsible for a significant portion of the total (wet and dry) nitrogen deposition (e.g. 34%, Munger et al., 1998; 58%, Sparks et al., 2008). Up to 43% of NOₓ—N emissions over North America have been estimated to be removed from the atmosphere by dry deposition (Shannon and Sisterson, 1992). Reactive nitrogen oxides, called NOₓ, is a class of oxidized nitrogen compounds including NO, NO₂, NO₃, N₂O₅, HNO₃, PAN (peroxycetyl nitrate), other organic nitrates, and particle nitrate, which supply significant nutrient and acidic quantities to ecosystems. Augmented atmospheric deposition of NOₓ associated with increased emissions of NOₓ poses many environmental threats, including acidification of soil and surface water, eutrophication of lake, river and estuary, loss of biodiversity, damage to forests, and global climate change (Galloway et al., 2008). Increased anthropogenic emissions of NOₓ combined with hydrocarbons have produced high levels of surface O₃ concentration. O₃ can penetrate the tissues...
of leaves easily through stomatal uptake, causing stomatal occlusion and leaf damage. The direct uptake by vegetation through the stomata is also a major sink of O$_3$ in the lower troposphere (Turnipseed et al., 2009).

Given the significant impacts of NO$_x$ and O$_3$ deposition on atmospheric chemistry and ecosystem health, it is desirable to quantify the deposition amount and assess the effects. Measuring deposition fluxes for reactive nitrogen compounds and O$_3$ with the eddy-covariance technique (e.g., Munger et al., 1996; Turnipseed et al., 2006) or the gradient method (e.g., Meyers et al., 1989; Sievering et al., 2001) have formed the basis for deposition models aimed at predicting dry depositions of reactive nitrogen compounds and O$_3$.

Models have been developed (e.g., Wesely, 1989; Meyers et al., 1998; Zhang et al., 2002, 2003; Niyogi et al., 2009; Wu et al., 2003) to estimate the dry deposition velocity ($V_d$) by commonly utilizing the resistance approach analogous to Ohm’s law in electrical circuits. Accurately parameterizing the complex surface-atmosphere exchange process remains challenging for $V_d$ modeling due to large variability in surface conditions (e.g., vegetation types, and soil contents) at model sub-grid scales. It is difficult to describe the physiological processes concerning the vegetation stomatal responses to various environmental conditions, leaf age, injury, and so on. The rapid within-canopy chemical reactions are not often considered in simple single-layer models, neither for the role of horizontal flow to receptor surfaces over non-uniform surfaces and terrains (Wesely and Hicks, 2000). Therefore, large uncertainties still exist in modeling $V_d$. A recent study (Flechard et al., 2010) modeled the $V_d$ of inorganic reactive nitrogen species (i.e., NH$_3$, NO$_2$, HNO$_3$, and HONO and aerosol NH$_4$ and NO$_3$) over 55 monitoring sites throughout Europe, using four existing dry deposition models. Their result revealed that differences between models can reach a factor 2—3 and are even greater than differences between monitoring sites. Hence, there is a continuous need to evaluate modeled $V_d$ over different land-cover types and for different chemical compounds.

Observational deposition fluxes of SO$_2$ and O$_3$ are often used to evaluate models (Zhang et al., 2002; Wu et al., 2003). However, few studies have evaluated modeled $V_d$ for nitrogen species primarily because accurate quantifications of dry deposition fluxes and speciation of the reactive nitrogen species are difficult and expensive to obtain (Horii et al., 2005). Munger et al. (1996) demonstrated that the dry deposition fluxes of NO$_x$ can be measured reliably using the eddy-covariance technique and year-round observations have been conducted at the Harvard Forest Environmental Measurement Site (HFEMS) since 1990. In a campaign attempting to estimate NO$_x$ concentration and deposition budget, concentrations of individual NO$_x$ species (i.e., NO, NO$_2$, PAN and HNO$_3$) have been measured at HFEMS. The reactive nitrogen dataset along with the O$_3$ fluxes/concentrations available at HFEMS are used to evaluate two community dry deposition models here.

One model is the Weather Research and Forecasting-Chemistry model (WRF-Chem) dry deposition module (hereafter WDDM). WRF-Chem is a state-of-the-art, regional atmospheric chemistry model (Grell et al., 2005) and has been successfully applied for regional air quality studies (Wang et al., 2009). Due to lack of observational data, few studies have evaluated the ability of the WDDM for calculating nitrogen $V_d$, even though dry deposition is one of the most important sinks for pollutants. The other model is the Noah land surface model (LSM) (Chen and Dudhia, 2001) coupled with a photosynthesis-based Gas-exchange Evapotranspiration Model (Niyogi et al., 2009) (hereafter Noah-GEM). The Noah LSM has been used to provide surface heat fluxes as boundary conditions for WRF. It is of broad interest to develop capacities of computing $V_d$ in Noah LSM (Charusombat et al., 2010). This evaluation effort is part of a broader effort to eventually integrate the balance of hydrosphere, biosphere, and atmosphere with environmental modeling such as atmospheric nitrogen input for the ecosystems in Noah. There are also plans to couple surface deposition and emission information more closely in Noah by linking with biogenic emission models such as MEGAN (Model of Emissions of Gases and Aerosols from Nature; Guenther et al., 2006). So one main purpose of this paper is to document current deficiencies in WDDM and raise the awareness of such problems. Also, because an investigation of nitrogen deposition calculation has not been done for these models, this study takes advantage of recently available nitrogen flux data to investigate nitrogen-deposition algorithms, which can serve well in the deposition models. The objectives are to: 1) assess the performances of WDDM and Noah-GEM in calculating $V_d$ of NO$_x$ and O$_3$ over a temperate deciduous forest, 2) understand the sensitivity of modeled $V_d$ to the key variables/parameters, and 3) improve the models by comparing with the field observations.

We will first describe the measurements used in this study (Section 2) and the modeling framework and formulations of WDDM and Noah-GEM (Section 3). Next, the observation data and model results and discussions are presented in Section 4, which is followed by the conclusions in Section 5.

2. Field measurements used in this study

2.1. Site description

The HFEMS is located in a temperate 80—100 year-old mixed deciduous forest in central Massachusetts (42.54 N, 72.18 W elevation, 340 m), which consists of red oak (Quercus rubra), red maple (Acer rubrum) with scattered hemlock (Tsuga canadensis), red pine (Pinus resinosa), and white pine (Pinus strobus). The canopy height near the observation tower is approximately 20 m with a peak leaf area index (LAI) of 3.4 m$^2$ m$^{-2}$ during summer. The nearest sources of significant pollution are a secondary road about 2 km west of the site and a main highway about 5 km north of it.

A permanent 30-m Rohn 25 G tower has been used at HFEMS to measure eddy-covariance fluxes of CO$_2$, NO$_x$, and O$_3$, along with vertical profiles of NO, NO$_2$, and O$_3$ since 1990. Measurements of PAN concentrations were added to the tower in 2000. A temporary 23-m steel scaffolding tower, situated about 100 m to the southeast of the Rohn tower, was configured with a Tunable Diode Laser Absorption Spectrometer (TDLAS) to measure concentrations of HNO$_3$ from June—November 2000. Due to physical constraints, the second tower did not match the measurement height of HNO$_3$ (22 m) with the measurement height of O$_3$, NO, NO$_2$, and PAN (29 m) on the first tower. However, Horii et al. (2005) confirmed that the two datasets are spatially coherent on the hourly timescale. Details on the site and the instrumental methods can be found in Munger et al. (1996) and Horii et al. (2005). Data used in this study are available online at http://atmos.seas.harvard.edu/lab/data/nigec-data.html.

2.2. Calculations of flux and dry deposition velocity

The fluxes ($F$) of O$_3$ and NO$_2$ were measured using the eddy-covariance technique. The ratio of observed heat flux and heat flux mathematically smoothed to simulate the attenuation of high-frequency variations by the instruments was used to account for loss of scalar covariances at high frequencies. Corrections were typically less than 20% (Munger et al., 1996; Horii et al., 2005). Flux data were also omitted during periods
of very low turbulence intensity (when the friction velocity, \( u^* < 0.2 \text{ m s}^{-1} \)), resulting in approximately 18% and 21% of the data being omitted for O3 and NOy, respectively. In addition, periods with \([\text{O}_3] < [\text{NO}_y]\) (1%) were excluded for O3 to avoid periods when O3 chemical reactions may exceed O3 deposition (Munger et al., 1996).

Assuming a zero concentration on the absorbing surface, the dry deposition velocity \( (V_d) \) can be determined as

\[
V_d(z) = -\frac{F}{C(z)}
\]

where \( C(z) \) is the gas concentration at a reference height, \( z \).

3. Description of models

3.1. Modeling framework

The resistance method determines \( V_d \) as the reciprocal of a total resistance \( (R_t) \) which consists of a series of resistances to perform gas transport from the atmosphere down to the surface.

\[
V_d(z) = R_t^{-1} = (R_a(z) + R_b + R_c)^{-1}
\]

Table A.1 describes each resistance component, and Table A.2 compares the formulations between WDDM and Noah-GEM.

3.2. Further developments of GEM

The GEM model (Niyogi et al., 2009) was further developed here (see Appendix B), but the parameters were kept the same and not specifically tuned for this study. \( R_s \) is the primary output of GEM and since direct measurements of \( R_s \) were not available at HFEMS, examining modeled surface heat fluxes provides an independent assessment of \( R_s \). The new results from the Noah-GEM model with modified \( R_s \) substantially improved calculations of heat fluxes for both summer and autumn (Fig. 1), implying that it produced more reasonable \( R_s \) and better surface energy partitioning between sensible and latent heat fluxes. In section 4, we discuss the performance of Noah-GEM in calculating \( V_d(\text{O}_3) \) and \( V_d(\text{NO}_y) \), based on this modified version.

3.3. Model configuration

The WDDM was extracted from the WRF-Chem model V3.1.1 and executed in a 1-D mode, and the Noah LSM V3.1 plus GEM was executed in the same fashion. Hourly tower measurements of air temperature \( (T_a) \), relative humidity (RH), wind speed (WS), wind direction (WD), atmospheric pressure \( (P_a) \), downward shortwave radiation \( (R_{g,\text{in}}) \), downward long-wave radiation \( (R_{\text{long, in}}) \), and precipitation rate \( (P_{\text{recip}}) \) at the height of 29 m were used to drive Noah-GEM. The \( u^* \) and \( L \) are obtained in Noah via an iterative process, using \( T_a, \text{RH}, \text{WS}, \text{and } P_a \) (Chen et al., 1997). WDDM requires inputs of \( T_a, R_{g,\text{in}}, \text{RH and } P_{\text{recip}} \) at the height of 29 m were used to drive Noah-GEM. Hourly \( V_d \) were computed for O3, NO, NO2, PAN and HNO3.

3.4. Modeling analysis

Model results are evaluated using descriptive statistics such as the degree of agreement \( (d) \) and fractional bias (FB) (e.g., Charusombat et al., 2010):

\[
d = 1 - \sum_{i=1}^{n} \left[ (o_i - m_i)^2 / \left( \sum_{i=1}^{n} |o_i| + |m_i| \right)^2 \right],
\]

\[d = 0.86 \quad FB = 0.59 \]

\[d = 0.97 \quad FB = 0.01 \]

\[d = 0.87 \quad FB = -0.94 \]

\[d = 0.94 \quad FB = -0.42 \]

\[d = 0.89 \quad FB = -0.9 \]

\[d = 0.93 \quad FB = -0.56 \]

Fig. 1. Comparison of averaged diurnal cycles of observed and modeled heat fluxes by Noah-GEM. (a) Latent heat flux for June—August, (b) sensible heat flux for June—August, (c) latent heat flux for September—October, and (d) sensible heat flux for September—October. \( d \) and FB were calculated from the original hourly data.
regulating stomatal openings.

4. Results and discussion

4.1. The observations of O3 deposition and its environmental drivers

Fig. 2 shows the time series of hourly-averaged \([O_3]\) and \(F(O_3)\) from June–October 2000. There was a distinct seasonal cycle of \([O_3]\) showing maxima in summer, associated with the high solar radiation and temperature. The peak values ranged from 40 to 80 ppbv, slightly lower than the observations in 1991–1994 (Munger et al., 1996). \(F(O_3)\) followed the same seasonal trend with maxima during summer, closely coinciding with high concentrations and canopy growth (Munger et al., 1996). As shown in Fig. 3, \(V_d(O_3)\) augmented with increasing PAR (when \(<1400 \mu\text{mol m}^{-2} \text{s}^{-1}\) and decreased with increasing VPD. At moderate temperature (8–24 °C), \(V_d(O_3)\) exhibited relatively small variations, but declined at more extreme temperature conditions. The environmental factors are often not independent from each other, e.g., high PAR often accompanying high temperature and VPD. \(V_d(O_3)\) tended to decrease with increasing PAR above 1400 \(\mu\text{mol m}^{-2} \text{s}^{-1}\), suggesting that temperature and VPD, rather than light, take controls in regulating stomatal openings. \(V_d(O_3)\) increased almost linearly with increasing latent heat flux (LE), consistent with stomatal control of the \(O_3\) uptake and plant evapotranspiration. These trends agree with the analysis by Turnipseed et al. (2009) over a subalpine forest. \(V_d(O_3)\) had a strong diurnal cycle. During summer, mean \(V_d(O_3)\) peaked before 1200 LST at 0.9 cm s\(^{-1}\) and dropped throughout the day to minimum value of 0.2 cm s\(^{-1}\) at night (Fig. 4), as seen in Munger et al. (1996).

4.2. Evaluation of modeled \(V_d(O_3)\)

Fig. 4 compares the modeled summer \(V_d(O_3)\) by WDDM and Noah-GEM against observations. Table 1 presents the statistical results of the comparison. WDDM and Noah-GEM produced low values of \(V_d(O_3)\) at night (\(\sim 0.1 \text{ cm s}^{-1}\)), much smaller than the observations (FB = 0.43–0.82). Zhang et al. (2002) and Charusombat et al. (2010) reported a similar bias, indicating an overestimation of nighttime non-stomatal resistance (R\(_{\text{ns}}\)). Wesely (1989) scheme estimates R\(_{\text{ns}}\) mainly using constant values specified for each season and each land-use category, while a recent R\(_{\text{ns}}\) scheme developed by Zhang et al. (2003) is a function of u*, RH, LAI and canopy wetness for non-stomatal uptake. As the main purpose of this paper is to compare the performance of different algorithms for stomatal uptake, Noah-GEM deploys the same R\(_{\text{ns}}\) parameterization as WDDM for convenience of comparison. The performance of Noah-GEM and WDDM can be improved by utilizing the more realistic and accurate R\(_{\text{ns}}\) parameterization (e.g. Zhang et al., 2003) in the future work.

\(V_d(O_3)\) increased in the morning as canopy photosynthesis became active. In Fig. 4, WDDM and Noah-GEM produced \(V_d(O_3)\) with similar magnitude. However, WDDM did not capture the peak and underestimated morning \(V_d(O_3)\) by \(\sim 0.2 \text{ cm s}^{-1}\). Noah-GEM, on the other hand, was able to capture the \(V_d(O_3)\) decline possibly as a result of stomatal closure at noon. Noah-GEM also produced a second peak in \(V_d(O_3)\) in the late afternoon that was not observed. Zhang et al. (2006) also observed the early morning peak of \(V_d(O_3)\) over two forest sites and proposed a threshold of accumulated \(O_3\) stomatal flux for leaves, above which stomatal uptake of \(O_3\) is slowed down probably due to an increased substomatal CO2 concentration or non-zero \(O_3\) concentrations inside the stomata. However, those factors are not considered in the current deposition models. In Fig. 5, the observed \(V_d(O_3)\) showed expected patterns of behavior with respect to the main environmental drivers (PAR, temperature and VPD) and, therefore, exhibited both unimodal (June 03, 16, and 18) and bimodal diurnal patterns (June 04, and 17). Noah-GEM captured the bimodal diurnal pattern on June 04 and 17, while under the unimodal conditions it reproduced the peak before noon but overestimated the afternoon \(O_3\) uptake. WDDM was found to hardly capture the diurnal behaviors of \(V_d(O_3)\), probably due to its Jarvis-type R\(_{i}\) (Eq. (A8)). However, it should be pointed out that Wesely (1989) R\(_{i}\) scheme was developed for general application, which requires very little data to use and intends to produce average estimate for a long time over large areas, rather than a period of days at a particular site.

WDDM considerably underestimated \(V_d(O_3)\) in autumn (Fig. 6), and the minimum canopy stomatal resistance (R\(_{i}\), which is also broadly denoted as R\(_{\text{min}}\) in the atmospheric and plant modeling community) was found to be responsible for this large discrepancy. The R\(_{i}\) parameter in WDDM for deciduous broadleaf forests was assigned to be an infinite value (10\(^{25} \text{ s m}^{-1}\) was used) for early autumn (Wesely, 1989). Here we defined the season classification for June—August as category 1(summer) and September—October as seasonal 2 (early autumn) respectively, based on the general climate at HFEMS (see also Munger et al., 1998). The infinite R\(_{i}\) implies that there is no air-surface exchange via the stomatal pathway (Wesely, 1989) and is only valid for leafless condition. However, this was not the case for the Harvard Forest during September—October, as indicated by the observations of net ecosystem exchange of CO2 and also LAI (Urbanski et al., 2007). The dominant effect of R\(_{i}\) on modeled R\(_{i}\) has been emphasized (e.g. Cooter and Schwede, 2000) and is well illustrated in Fig. 6. For this particular study, the value of R\(_{i}\) for summer (70 s m\(^{-1}\)) seems appropriate for the early autumn.

\[
FB = 2 \left( \frac{\sum_{i=1}^{n} o_i - \sum_{i=1}^{n} m_i}{\sum_{i=1}^{n} o_i + \sum_{i=1}^{n} m_i} \right) \tag{4}
\]

where \(o_i\) is the observation, \(m_i\) the model result, and \(n\) the number of samples.

![Fig. 2. Time series of (a) O3 mixing ratio, and (b) O3 fluxes.](image-url)
Fig. 6 shows that neither model captured the rising of $V_d(O_3)$ in the early morning hours (0300–0600 LST). The early morning rising is possibly due to some factors (e.g., episodic mixing events and transport) which are not adequately represented by the resistance analogy, and also note that the small number of observations available during this period is likely hard to smooth those effects.

As illustrated by Fig. 6, the uncertainty in specifying $R_i$ is one main reason for modeled bias in $R_s$ and $V_d$ of gases that are under stomatal control for WDDM. However, the prescription of $R_i$ inherently has significant uncertainty because $R_i$ cannot be measured or determined independently in the laboratory (Niyogi et al., 2009) and also the assumption of a constant $R_i$ value within a season is inappropriate because of its temporal variations including diurnal cycle (Avissar, 1993). Better approaches have been proposed to solve the issue related with seasonal category classification, such as using continuous LAI without the need of defining different seasonal categories (e.g., Zhang et al., 2003), which could avoid the abrupt change of input parameters (e.g., $R_i$) from one season to the next. Charusombat et al. (2010) identified LAI as the first-order parameter affecting Noah-GEM estimates of $R_s$. The Noah LSM prescribed a maximum value of 3.3 m$^2$ m$^{-2}$ for LAI in this case, slightly lower than the field measurement (3.4 m$^2$ m$^{-2}$). Model performance can be improved by assimilating more accurate and seasonally-varying LAI data in the future work.

$R_s$ is a complex and dynamic variable representing the coupled effects of resistance imposed by plants to vegetation-atmosphere exchange through leaf stomata (Niyogi et al., 2009). The difference between modeled $V_d(O_3)$ by WDDM and Noah-GEM is mainly caused by the use of different $R_s$ schemes. Noah-GEM simulates the response of stomata to various environmental variables (e.g., PAR, canopy temperature, soil moisture, CO2 concentration and relative humidity at the leaf surface) (Niyogi et al., 2009). A significant feature of Noah-GEM is that it is structured to consider the impacts of physiological

| Table 1 |
| --- |
| Statistical results of the observed and modeled $V_d(O_3)$ and $V_d(NO_y)$.

|          | All | Daytime | Nighttime |
|----------|-----|---------|-----------|
|          | $d$ | $FB$    | $d$       | $FB$    |
| $V_d(O_3)$ WDDM | 0.90 | 0.18 | 0.93 | 0.01 |
| Noah-GEM | 0.90 | -0.09 | 0.93 | -0.18 |
| $V_d(NO_y)$ WDDM | 0.86 | 0.48 | 0.92 | 0.16 |
| WDDM* | 0.88 | 0.38 | 0.94 | 0.04 |
| Noah-GEM | 0.88 | 0.37 | 0.94 | 0.02 |

* Note: Daytime is 0900–1700 (LST); Nighttime is 1900–0600 (LST). The sample numbers are 1134, 551 and 430 for $V_d(O_3)$, and 170, 80 and 70 for $V_d(NO_y)$, respectively.
processes including CO₂ assimilation rate on the responses of leaves to environmental parameters, which can predict R₂ better than the Jarvis-style approach that is based on the minimum canopy stomatal resistance parameter (Niyogi et al., 2009).

4.3. The observations of NOₓ deposition and its environmental drivers

HFEMS experienced minor pollution events during the selected period (Fig. 7). [NO₂] was generally lower than 5 ppbv, occasionally reaching 15 ppbv. f(NO₃) and V_d(NOₓ) showed large day-to-day variations, with maximum values of 22 µmol m⁻² h⁻¹ and 4.5 cm s⁻¹, respectively. f(NO₃) and V_d(NO₃) tended to peak during midday, consistently following similar diurnal behavior to those of turbulence development. Large values of V_d(NOₓ) on October 02, 04, 07 and 08 accompany large ratios of HNO₃/NOₓ, inferring a key role HNO₃ played in the NOₓ deposition and V_d(NOₓ) (see also Munger et al., 1996).

The measured V_d(NOₓ) represent averaged V_d of the total NOₓ species. But, in current gas dry deposition models, V_d values are estimated for individual species (see Section 3). Similar to Michou et al. (2005), the concentrations and V_d of individual NOₓ species were used to derive a composite V_d(NOₓ), which can be more directly compared to observations. Simulated V_d(NOₓ) can be defined as

\[ V_d(NO_x) = \sum_{i=1}^{n} |x_i| V_d(x_i) / \sum_{i=1}^{n} |x_i|, \]  

where \( x_i \) is the member of the NOₓ family, and \( n \) the number of the members.

Modeling-wise, the unique value of this data set at HFEMS lies in the availability of the simultaneous concentrations of the main NOₓ species (e.g., NO, NO₂, PAN, HNO₃) and the high temporal resolution (1 h). However, data gaps exist in the concentration measurements especially for HNO₃, which is very difficult to measure at a short integration time (e.g., at hourly interval) due partially to its tendency to adsorb onto surfaces (Horii et al., 2005). All the gaps in the concentrations will be reflected in the simulated V_d(NOₓ) (see Eq. (5)). To obtain a less patchy simulation of V_d(NOₓ), a “x/NOₓ” ratio method was used to fill the gaps. The average diurnal cycles of “x/NOₓ” were derived from the measurements from June–November 2000 (not shown here). Along with the NOₓ concentrations, inferred concentrations of NO, NO₂, PAN, and HNO₃ were derived as

\[ [x_{D,H}^{\text{inferred}}] = [NO_x]^{D,H} \times \text{Ratio}(\{x_i\}/[NO_x])^{H}, \]  

where \( D \) indicates the date, \( H \) is the hour of day \((H = 0,1,2,...23)\), \([NO_x]^{D,H}\) is the measured concentration of NOₓ at the hour of \( H \), on the date of \( D \), \([x_{inferred}]\) is the inferred concentration of \( x \), and \( \text{Ratio}(\{x_i\}/[NO_x])^{H} \) is the averaged ratio at the hour of \( H \).

The inferred concentrations were used to fill the gaps in the measured concentrations. Observations at HFEMS suggested that HNO₃ played a critical role in V_d(NOₓ). To minimize the errors in simulated V_d(NOₓ) that result from inferred concentrations, the period (October 1–12, shown in Figs. 7 and 8) with the fewest gaps in HNO₃ concentrations was selected.

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**Fig. 5.** Time series of (a) observed and modeled O₃ deposition velocities by WDDM and Noah-GEM, (b) air temperature, (c) vapor pressure deficit, and (d) photosynthetically active radiation.

**Fig. 6.** As in Fig. 4, but for September–October. ‘WDDM’ indicates the simulation results with \( R_i \) of 10² s m⁻¹, which was assigned to early autumn in WDDM. ‘WDDM*’ indicates the simulation results with \( R_i \) of 70 s m⁻¹, which was assigned to summer in WDDM.
Fig. 8 presents the measured concentrations of the NOy species and also the gap-filled data from the “x/NOy” ratio method. A few gaps existed for NO and NO2 while PAN concentrations were all inferred. Given that PAN usually showed a relatively small Vd, and the averaged PAN/NOy ratio had a relatively small deviation, the simulated Vd(NOy) should not be significantly affected by the uncertainties in the inferred PAN concentrations. The relative differences between the concentrations of NOy and the sum of gap-filled NO, NO2, PAN and HNO3 were typically less than 30% (Fig. 8a).

4.4. Evaluation of modeled Vd(NOy)

The roughness length for momentum (z0) is an essential parameter in calculating Ra in LSMs and can be prescribed as a function of land-cover type, as in Noah where the value of 0.5 m is assigned for deciduous broadleaf forest. Alternatively, if information about the vegetation morphology (e.g., canopy height (hc), and LAI) is known, z0 can be calculated following Meyers et al. (1998):

\[ z_0 = h_c \left( 0.215 - \text{LAI}^{0.25} / 10 \right) . \]  

or simply assumed 0.1 hc (e.g., Chen and Zhang, 2009). In our sensitivity simulations, the model was run with three z0 values: 1) 0.5 m (Noah default), 2) 1.6 m (Eq. (7)) and 3) 2 m (0.1 hc). As z0 increased from the initial model value of 0.5 to 1.6 and 2 m, modeled u* increased significantly and approached observations (Fig. 9). Increased z0 and u* can reduce Ra and Rb (Eqs. (A3) and (A7)), which, in turn, leads to an increase of up to 1.5 cm s\(^{-1}\) in modeled Vd(NOy). This exercise demonstrates that adjusting z0 can substantially alter the Vd of compounds sensitive to Ra and Rb (e.g. HNO3). Ultimately, a value of 2 m for z0 seems a reasonable representation of the canopy structure for HFEMS in this scenario.

WDDM showed similar response to the parameter z0, and the results are not presented here. Hereafter, we assessed the models performance with z0 set to 2 m.

These sensitivity tests highlight the importance of treating the atmospheric surface layer in modeling the biosphere-atmosphere exchange. Indeed, current LSMs (including WDDM and Noah) employ the Monin–Obukhov Similarity Theory (MOST) to parameterize surface exchange coefficients. While MOST provides a dimensionally-based set of relationships that links the vertical fluxes of scalars to the gradients of the mean profiles within the...
atmospheric surface layer, it is only valid well above the rough surface (Högström, 1996) and fails in the so-called roughness sublayer, which is above tall canopies and within canopies (e.g., Harman and Finnigan, 2008). Simply adjusting parameters such as \( z_0 \) used in MOST may not solve this fundamental problem, and future work to improve the models will involve the use of vertically-varying profiles of mean scalar concentration (e.g., Harman and Finnigan, 2008) or a multi-layer canopy model that explicitly resolves the radiative, dynamical, and thermal transport within vegetation canopies.

Fig. 10 compares the modeled \( V_d(NO_2) \) by WDDM and Noah-GEM against the observations. Table 1 presents the statistical results of the comparison. As described in section 4.2, WDDM prescribed an infinite value for \( R_i \), which results in no air-surface exchange via stomata during autumn. To assess the sensitivity of \( R_s \) parameterization to \( V_d(NO_2) \) estimate, we conducted an additional simulation, reducing \( R_i \) to 70 s m\(^{-1}\) as validated in \( V_d(O_3) \) study. The WDDM modeled daytime \( V_d(NO_2) \) increased from 1.2 cm s\(^{-1}\) to 1.37 cm s\(^{-1}\) (on average), closer to the observations of 1.41 cm s\(^{-1}\) (also see Table 1, FB decreased from 0.16 to 0.04). This result is consistent with Munger et al. (1996) in that the stomatal influence on NO\(_2\) dry deposition at HFEMS is relatively small. WDDM with corrected \( R_i \) presented quite similar results with Noah-GEM (Table 1 and Fig. 10), as WDDM has the same expressions for \( R_m \) and \( R_{ns} \) with Noah-GEM and the predicted \( R_a \) values by the two models are generally close.

Although the models are generally in good agreements with the observations \((d = 0.88)\), they seem to underestimate the nighttime value of \( V_d(NO_2) \) significantly \((FB = 1.09–1.18)\). Overestimation of nighttime \( R_a \) may be a chief reason for this unsatisfactory model performance as the conventional micrometeorological equations (e.g., Eqs. (A2), (A3)) have been known to have poor \( R_a \) estimate for nighttime stable regime (Wesely and Hicks, 2000). The underestimation of \( V_d(HNO_3) \) in turn caused the poor performance of \( V_d(NO_2) \) during nighttime. Part of these model deficiencies can also be attributed to the fact that both models do not have a multiple canopy scheme to represent a realistic wind shear within forest canopies.

Models reproduced the daytime \( V_d(NO_2) \) with satisfactory statistic results \((d = 0.94, FB = 0.02–0.04)\), and captured most variations in the observation (Fig. 10a), while the bias occurred...
mainly on October 04, 07 and 08. The underestimation of \( \dot{V} \) on October 07 and 08 (Fig. 9a) led to a too high \( R_f \), which could be one reason for the \( V_d(\text{NO}_3) \) underestimation. A large ratio of \( \text{HNO}_3 \) to \( \text{NO}_2 \) was observed (Fig. 7) on October 04, which caused the large \( V_d(\text{NO}_3) \) in the observations. The models appear to substantially underestimate the \( \text{HNO}_3 \) deposition on this particular day.

At HFEMS, \( \text{HNO}_3 \) dominated the \( \text{NO}_x \) deposition, so the modeled \( V_d(\text{NO}_3) \) did not show much sensitivity to \( R_f \), but mostly depended on \( R_e \) and \( R_h \). However, a recent field study over a coniferous forest (Turnipseed et al., 2006; Sparks et al., 2008) estimated that \( \text{HNO}_3 \) accounted for only \(~24\%\) of the \( \text{NO}_x \) flux and \( \text{PAN} \) exhibited a close portion of \(~35\%\). Those new findings of fast deposition of \( \text{PAN} \) modeled by Noah-GEM reached a factor of \( 1.1 \) on the order of \( 3 \) to \( 6 \) cm s\(^{-1} \), on the same order with the gradient-method measurements by Meyers et al. (1989) over a dense deciduous forest (2.2 to 6.0 cm s\(^{-1} \)) and Sievering et al. (2001) over a conifer forest (7.6 cm s\(^{-1} \)).

We estimated the deposition fluxes of individual \( \text{NO}_x \) species by multiplying the predicted \( V_d \) (using \( z_0 = 2 \) m) with the observed concentrations (Eq. (1)). On average, \( \text{NO}_2 \), \( \text{PAN} \) and \( \text{HNO}_3 \) accounted for 19%, 4%, and 70% of the measured \( \text{NO}_x \) fluxes, respectively. In the current models we only considered the unidirectional fluxes (deposition), and this assumption is not valid for gases with emission fluxes from the surface. Emissions of \( \text{NO} \) from soils at HFEMS are negligible (Horii et al., 2005). But Horii et al. (2004) observed bi-directional fluxes of \( \text{NO}_2 \) and suggested a compensation point for \( \text{NO}_2 \) near 1.5 ppbv at HFEMS, the ambient concentration below which \( \text{NO}_2 \) is emitted from stomata. Given that \( [\text{NO}_2] \) approached this level occasionally during the daytime within the selected period (Fig. 8), the estimate of the contribution of \( \text{NO}_2 \) to \( \text{NO}_x \) fluxes should be overestimated at some degree. This uncertainty can be narrowed by incorporating a parameterization of the compensation point within the models in the future work. Because the overestimated nocturnal \( R_f \) resulted in understimation of \( V_d(\text{HNO}_3) \), the contribution of \( \text{HNO}_3 \) to \( \text{NO}_x \) fluxes presented here should be considered more of a lower limit.

5. Summary and conclusions

We evaluated the ability of two models (WDDM and Noah-GEM) to calculate \( V_d(\text{O}_3) \) and \( V_d(\text{NO}_x) \) against direct observations at HFEMS, and identified key variables/parameters and uncertainties in the two models. WDDM employs Wesely (1989) parameterization for \( R_f \), which uses a simple \( R_i \) scheme based on the \( R_i \) parameter prescribed for each season and land-cover category. The uncertainty in prescribed \( R_i \) dominates the errors in estimating \( V_d \) for \( \text{O}_3 \) and other gases that are controlled by the stomatal pathway. An infinite \( R_i \) value for deciduous forest in autumn in the default WDDM was not appropriate and resulted in low values of \( V_d(\text{O}_3) \), while using \( R_i \) values originally prescribed for summer (70 s m\(^{-1} \)) produced better \( V_d(\text{O}_3) \). More evaluations of WDDM for \( R_i \) at different seasons are needed to mitigate the underestimation of \( V_d(\text{O}_3) \). Several revisions to the
original GEM formulations were justified by comparing the formulations with other literature and also by evaluating modeled surface sensible/latent heat fluxes against observations. Compared with WDDM, Noah-GEM has a more sophisticated $R_s$ scheme considering the response of physiological processes to environmental variables (such as soil moisture, vapor pressure deficit, and CO$_2$ concentration at the leaf surface) and shows a better ability to capture the variations in $\text{V}_d(\text{O}_3)$ than WDDM. The models still need to be improved to better represent the nocturnal $\text{O}_3$ dry deposition process. On the other hand, results showed that $\text{V}_d(\text{NO}_3)$ calculation was not sensitive to $R_s$ as expected, because $\text{V}_d(\text{NO}_3)$ was mainly affected by the rapidly depositing species such as HNO$_3$ and controlled by the atmospheric resistances (i.e. $R_a$ and $R_b$). The difference in calculated $\text{V}_d(\text{NO}_3)$ by WDDM and Noah-GEM was small as these two models produced similar $R_a$ and $R_b$. WDDM and Noah-GEM agreed well with the observed daytime $\text{V}_d(\text{NO}_3)$, but underestimated it under nighttime stable conditions. A modest adjustment in the $z_0$ values can significantly alter and/or improve the predicted $\text{V}_d(\text{NO}_3)$. Daytime $\text{V}_d(\text{NO}_3)$ was more sensitive to $z_0$. These sensitivity tests regarding $z_0$ and inferior performance of WDDM and Noah-GEM models under stable conditions illustrate the simplicity and difficulties in modeling the biosphere–atmosphere exchange within the forest canopies, the layer known as roughness sub-layer where the traditional MOST theory is not valid. Therefore, our future model development effort will involve utilizing vertically-varying profiles of mean scalar concentration including chemical species such as PAN, NO and NO$_2$ or a multi-layer canopy model that explicitly resolves the radiative, dynamical, and thermal transfer within vegetation canopies. Finally, with a combination of the observed concentrations and modeled $\text{V}_d$, it was estimated that NO$_3$, PAN, and HNO$_3$ were 19%, 4%, and 70% of the measured NO dry deposition fluxes, respectively. Comparison of the simulated $R_c$ and $\text{V}_d$ for NO$_3$ and PAN shows that differences of $R_c$ estimates between WDDM and Noah-GEM were large and would cause differences in $\text{V}_d$ reach a factor of 1.1–1.3.

Very few studies were done in the past to extensively focus on evaluating nitrogen-deposition models, which are critical to estimating the surface and atmospheric nitrogen budget in atmospheric chemistry models, primarily due to lack of observations. This is particularly true regarding the WRF-Chem model, because its dry deposition calculation has not been systematically evaluated despite its popularity in atmospheric air quality community. This work is a first step and yet a preliminary study to evaluate the effects of two modules with different treatment of canopy resistance on deposition estimation. The implementation of Noah-GEM calculated $\text{V}_d$ in WRF-Chem is underway. And more comprehensive studies at different seasons and locations (for different forest types) will be done in the future.

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**Appendix A. Resistance description and formulation comparisons between WDDM and Noah-GEM**

Table A1 gives the definition of each resistance component. Among the three resistances ($R_a$, $R_b$ and $R_c$), $R_a$ is generally the most dynamic and difficult to estimate, varying with the properties of the surface and properties of the depositing gas. For many gases such as O$_3$ and SO$_2$, $R_a$ is dominant in the deposition process as it is typically the largest in magnitude among the three resistances. However, for very reactive and soluble substances such as HNO$_3$, $R_b$ can be neglected. Therefore, the deposition of HNO$_3$ is governed by the atmospheric resistances ($R_a$ and $R_b$) while the deposition of other species considered in this study is dominated by $R_d$ during daytime.

The deposition may take place through stomata and onto exterior surface (including soil surface). $R_c$ can be generalized from both models discussed here as

$$\frac{1}{R_c} = \frac{1}{R_a} + \frac{1}{R_m} + \frac{1}{R_{NS}}$$  \hfill (A1)

For the $R_c$-dominant species, a large fraction of the deposition is through direct uptake by vegetation through the stomatal pores (Wesely, 1989).

Table A2 presents the comparison of the formulations used in WDDM and Noah-GEM. WDDM and Noah-GEM both calculate $R_a$ primarily as a function of surface properties, such as surface roughness, and atmospheric stability through the use of the Monin–Obukhov similarity theory as documented in Chen et al. (1997).

The fundamental difference between WDDM and Noah-GEM exists in the $R_s$ scheme. WDDM employs Wesely (1989) $R_s$ parameterization that estimates $R_s$ based on the parameter of minimum canopy stomatal resistance for water vapor ($R_s$), which is regulated by two environmental factors, namely solar irradiation (G) and surface air temperature ($T_s$) (see Eq. (A8)). Niyogi et al. (2009) developed the Gas-exchange Evapotranspiration Model (hereafter referred to as GEM), based on the Ball–Berry stomatal scheme (Eq. (A9)) that describes the response of stomatal conductance for water vapor ($g_s$), the inverse of $R_s$ of a single leaf to the rate of net CO$_2$ uptake ($A_{ref}$), the relative humidity fraction at the leaf surface ($h_s$), and CO$_2$ partial pressure at the leaf surface ($C_{i_s}$). In GEM, a photosynthesis sub-model calculates $A_{ref}$ by considering the effects of PAR, canopy temperature and soil moisture in a non-linear way. A leaf boundary layer sub-model calculates $C_{i_s}$ and $h_s$ as a function of the ambient CO$_2$ concentration, relative humidity, air temperature and wind speed. Both sub-models are coupled with the Ball–Berry stomatal sub-model to obtain $g_s$.

The expressions for $R_m$ and $R_{NS}$ can be found in Wesely (1989) and are not reproduced here for brevity.

**Table A1** Description of the resistance components in the framework of gas dry deposition models.

| Symbol | Name                          | Definition                                                                 |
|--------|-------------------------------|---------------------------------------------------------------------------|
| $R_a$  | Aerodynamic resistance        | Turbulent transport between the reference height, $z$, and the surface.   |
| $R_b$  | Quasi-laminar sub-layer resistance | Mass transfer across the thin layer of air in contact with surface elements. |
| $R_c$  | Surface resistance            | Efficiency of the surface to capture gases.                                |
| $R_{NS}$ | Canopy stomatal resistance   | A measure of the aperture size of the canopy stomata.                     |
| $R_m$  | Mesophyll resistance          | Ability of the compounds to be absorbed by the moist cells and mesophyll. |
| $R_{NS}$ | Non-stomatal resistance      | Uptake to other surfaces, including leaf cuticles, bark, soil, or ground litter (grouped together as non-stomatal). |
Appendix A. Formulation updates of GEM

The formulation updates of GEM are presented here, however, all original ones used in GEM, and their descriptions can be found in Appendix A and B of Niyogi et al. (2009).

\[
W_e = \frac{\text{PAR} (1 - \omega_e) \left( C_l - I^* \right) / \left( C_l + 2I^* \right)} {1 + \frac{1}{2(G + 0.1)^2} \left( \frac{D_{3,0}}{D_x} \right) 400 (T_s - T_e) / x}
\]  

(B1)

where \( w_e \) is the photosynthesis limiting factor due to amount of PAR absorbed by the leaf chlorophyll, PAR is the photosynthetically active radiation, \( \varepsilon \) is the quantum efficiency for CO2 uptake, \( \omega_e \) is the leaf-scattering coefficient for PAR, \( C_l \) is the CO2 partial pressure (Pa) in the leaf intercellular spaces, \( I^* \) is the CO2 compensation point (Pa).

\[
S_m = 1 - \frac{2}{3} \left[ \frac{W_2 - W_{\text{wilt}}}{W_{fc} - W_{\text{wilt}}} \left( 0.03 + 1.5 \frac{1}{B} + 1.5 \frac{1}{B} \right) \right]^{1/2}
\]  

(B2)

where \( S_m \) is a soil moisture stress factor, \( W_2 \) is the root-level soil moisture content, \( W_{\text{wilt}} \) and \( W_{fc} \) are root-level soil moisture wilting and field capacity values, \( B \) is the slope of the soil moisture retention curve.

\[
V_m = V_{\text{max}} f(T) f(w_2)
\]  

(B3)

where \( V_m \) is the maximum catalytic Rubisco capacity for the leaf, \( V_{\text{max}} \) is the maximum \( V_m \) of \( f(T) \) and \( f(w_2) \) are the stress functions of temperature and soil moisture, respectively.

\[
f(T) = 2Q_t \frac{1}{1 + \exp(0.3[T_s - S_2])} \frac{1}{1 + \exp(0.3[S_4 - T_s])}
\]  

(B4)

where \( Q_t \) is the temperature dependency taken as \( 0.1(T_s - 298.0) \), \( T_s \) is the surface or canopy temperature, \( S_4 \) and \( S_2 \) are low and high temperature stress parameters.

\[
g_m = g_{\text{mp}} \left[ \frac{2Q_t \frac{1}{1 + \exp(0.3[T_s - S_2])} \frac{1}{1 + \exp(0.3[S_4 - T_s])}} {W_2 - W_{\text{wilt}} \frac{W_{fc} - W_{\text{wilt}}}{W_{fc} - W_{\text{wilt}}}} \right]
\]  

(B5)

where \( g_m \) is the mesophytic conductance, which is based on the modulation of a potentially maximum value \( g_{\text{mp}} \).

\[
C_s = C_a - A_n \frac{P}{g_0}
\]  

(B6)

where \( C_s \) is the CO2 partial pressure at the leaf surface, \( C_a \) is the ambient CO2 partial pressure, \( A_n \) is the rate of net CO2 uptake, \( P \) is the atmospheric pressure, and \( g_0 \) is the leaf boundary conductance.

\[
w_2 = \sum_{i=1}^{3} \frac{\text{SMC}(i) \times |\text{SLDPTH}(i)|}{\sum_{i=1}^{3} |\text{SLDPTH}(i)|}
\]  

(B7)

where SMC is the multiple levels of soil moisture content, SLDPTH is the thicknesses of each soil layer, and the 3rd level of soil reaches to 1 m down from the surface.

Eqs. (B1)–(B7) are used to replace Eqs. (A1b), (B5), (A3), (A4), (A2b), and (B3), and Fig. B1 in Niyogi et al. (2009), respectively.

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