

We thank the reviewers for their detailed reading of our manuscript and the expertise they have brought to our analysis. Our response is given in red with quotation marks used to highlight the changes we have made in the manuscript. All comments have been addressed below.

#### Reviewer #1

Overall comment and rating:

This paper has some interesting results in Sections 3 and 4, but Section 2 provides an inadequate description of the model for me to recommend publication at this time. My overall rating is therefore “major revisions”: the description of the model needs to be considerably more detailed, in order for readers to be able to place the subsequent results in context. Care needs to be taken to describe components such as the gas-phase mechanism and the means by which gas-phase chemistry is solved numerically, the manner in which boundary conditions for emissions and deposition are included into the model’s diffusion equation and the numerical means for solving the diffusion equation, and the deposition parameterization and its component resistances and the algorithm approach used (big leaf / layered/ other). Several pages of model descriptive information need to be supplied, in Section 2, to better bolster the subsequent analysis and findings. A concise precis of the model is needed in order for this paper to be suitable for ACP.

Similarly, more details are needed on some of aspects of model setup, boundary conditions, and treatment of advected NO<sub>2</sub> is needed, as described in my detailed comments below. I’ve placed an asterisk beside some of the more important points

Having said that, I think that the strength of the paper in sections 3 and 4 will make publication (once Section 2 has been properly updated), likely. I look forward to seeing the revised manuscript.

We note that the model is described in complete detail in the original model development papers cited in the text (Ashworth et al., 2015; Wei et al., 2021). To address the reviewer’s comments, we have substantially expanded Sect. 2.2 and added even further information to the supplementary. We believe the restructuring and additional information has addressed several comments below.

Specific comments by page and line number:

Page 3, line 76: Another reference is Makar et al., 1998, <https://agupubs.onlinelibrary.wiley.com/doi/epdf/10.1029/1998JD100065>): removal rates of O<sub>3</sub> within a mixed forest in North America there had rapid changes with height, maximum oxidation rates of 0.80 ppbv/hour; that paper was aimed at the biogenic emissions, but the oxidation rate applies to both the monoterpenes present and O<sub>3</sub> (see Figure 4 of that paper).

This reference has been added.

Page 3, line 78: Some chemical transport models are including surrogate monoterpenes and sesquiterpenes; while the details of the products for sesquiterpenes aren’t known, the approach taken is usually to include at least the emitted precursor monoterpene and an organic radical, to get the first stage of oxidation correct.

A sentence has been added to acknowledge this (Line 79):

*“As these species are considered key to representing the biogenic chemical environment, some studies have included simple sesquiterpene mechanisms (Zhang et al., 2022).”*

Page 3, line 84: perhaps also worth noting that Makar et al (2017) found that an adequate representation of forest canopies for regional modelling purposes can be done with three layers, representing the below foliage, within foliage, and near-top of the canopy. More recent work suggests that at least some of the canopy effects can be captured at the relatively low vertical resolution of numerical transport models by generating integrated or averaged values of diffusion and photolysis taking place within forest canopies (Tang et al., ACP, 2025, <https://doi.org/10.5194/acp-25-16631-2025>). The latter paper shows one approach for parameterizing canopy effects without significant changes to the regional modelling framework, though the effects are likely underestimated due to the use of lower resolution in the vertical.

We have added a sentence to acknowledge this (Line 86):

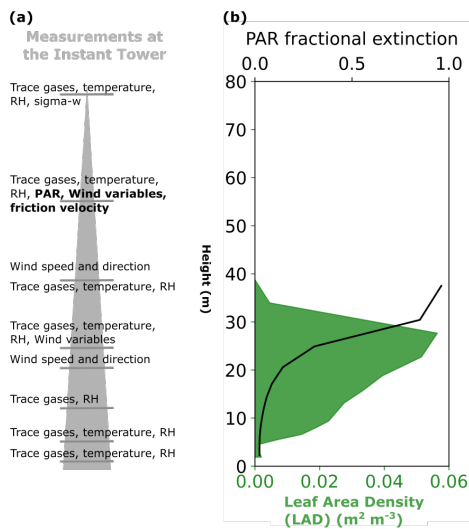
*“These studies find that only a few layers are needed to improve simulations, suggesting multilayer canopies could arise more frequently in global models in the future. (Ganzeveld et al., 2002a; Makar et al., 2017; Vermeul et al., 2024; Wang et al., 2025).”*

Page 4, line 114: a small nit-picking correction: its better to use “evaluate” rather than “validate” here – validation implies that the model is “valid” thereafter, “evaluate” is better in that it describes the model performance without giving judgement on the outcome of the evaluation.

Thanks. We have made the change.

Page 4, lines 104-125: the description of the site would benefit from an additional Figure with a to-scale sketch of the tower noting the heights at which the different quantities were observed, as well as the LAI profile of the canopy.

Good suggestion. We have included this as Figure 1.



*“Figure 1: (a) The observed variables used for model evaluation throughout this paper and their approximate measurement heights. Variables in bold are used as driving data in the simulations. (b)*

*prescribed leaf area density (green shading) and fractional extinction of PAR (black solid line) within the canopy (model simulated average). The height scale on both figures is the same.”*

Deleted: (b)

\*Page 4, line 130: The model's vertical extent is to 5km, and the text mentions that the model is forced by observations at 30 minute intervals, but it's not clear where the forcing conditions for the upper part of the model domain are originating. I'm wondering in particular about the magnitude and strength of the horizontal and vertical components of wind, and the K theory values that are used in the bulk of the 5km that are above the canopy. The SI has information from 55 m for the above-canopy environment – what was done for higher elevations above the surface? The paper needs a paragraph or two description of how the K values above the canopy are derived using K-theory, how wind speeds are determined, and how the above and below-canopy values are blended together (to replace the sentence on line 155).

In reworking Section 2.2, we have included details of model boundary conditions, K values and vertical wind. In the supplementary, we have now explicitly included equations for K values above the canopy and horizontal wind magnitudes.

The paper also needs a paragraph or two explaining how the variables in S5 through S9 were used in the simulations. For example, S4a shows a K value vertical profile for each year, and a shaded region – shaded region is not explained in the SI or in the main paper text – is this max and minimum at the given height over the year, a 90% limit on variability, a daily average maximum and minimum for the two years, or something else, and more importantly, what was used in the model itself, for the period the authors are simulating, and where did it originate?

The Methods section now describes the choice of parameters in more detail, but we direct the reviewer to the supplementary for further description of the parameter selection used in sensitivity tests.

Fig. S4 (now fig S16) shows the average K values used in the simulation. The figure caption is now updated, and the K value calculation is described in detail in the methods section.

Figure S3 shows a good correspondence between equation 2 and the 21 m sigma-w and the observed values; what values of tau/TL was used in this case?

The sigma-w profile is calculated using the equation given in the text :

$$\sigma_{w(z)} = 0.5 \times \sigma_{w(55)} + 0.45 \times \sigma_{w(55)} \times \cos\left(\pi \times \left(1 - \frac{z}{55}\right)\right)$$

Which does not use tau/TL. This value is then passed to equations to calculate K, where tau/TL is introduced. The new description should now make this clear.

\*Page 5, lines 158-165, and equation (1): The details have been moved to the SI, but I think they should appear in the main document, since this is a central part of their model construction. Re: “The equation describes the reduction in K explicitly” I assume this is “reduction in K from the above canopy values”? – but from what value of K? i.e. how were the above-canopy values of K determined? (see above comment). There needs to be a few more paragraphs describing model setup. As part of that description, there needs to be some discussion on what tau/TL represents (with reference to Raupach's work), and whether the parameterized values in table S2 are within a reasonable range or not. Similarly, how do the temperature and/or light dependent emission factors in Table S2 compare to those appearing in the literature for

databases such as BEIS or MEGAN? What were the temperature and light dependent functions used (the tabulated values in S2 are for basal emission rates – I’m wondering whether the exponential decay constants used in the authors functions are similar to ones appearing elsewhere in the literature.

The equations describing the calculation of K now appears in the main text, and describes the reduction in K based on observed sigma-w and u\* at the canopy top. (Line 323)

*“The value of K used to describe both heat and mass transport is computed at each level, with separate equations for the surface layer, the boundary layer and the free atmosphere. K-theory is a first-order closure theory that assumes that turbulent flow leads to transfer down a concentration gradient (Raupach, 1989), where K dictates the efficiency of turbulent mixing based on atmospheric stability. The equations for the above-canopy profile of K are described in the SI and in Wei et al. (2021).*

*Below the canopy, K is a function of sigma\_w at height z:*

$$K = Tl \times \sigma_{w(z)}^2 \times R \text{ (Eq. 15)}$$

*Tl is a scaling factor with units of length:*

$$Tl = \frac{0.3 \times h}{u_*} \text{ (Eq. 16)}$$

*Raupach et al. (1989) suggests scaling by an R factor within the canopy to account for near-field effects, which describes changes to conditions close to an emissions source or boundary, especially from a non-uniform source:*

$$R = \frac{1 - e^{-\frac{z}{\tau Tl}} \times (\tau Tl)^{3/2}}{(\tau Tl \times e^{-\frac{z}{\tau Tl}})^{3/2}} \text{ (Eq. 17)}$$

*The R factor describes the reduction of K within the canopy explicitly. However, tau is undefined and must be estimated. We perform 3-day sensitivity studies to select tau/Tl = 1.6 and evaluate the effect on concentration profiles of O3 and isoprene (Fig. S8, S9).*

*K is first calculated above the canopy using observed sigma\_w at 55 m (Sect. 2.1). The in-canopy K values are derived at each model level using a function that modifies the observed sigma\_w to decrease with height z (a result of surface friction and interception by the canopy). For the ATTO site, we adapt the function for sigma\_w(z) within the canopy from Wei et al. (2021), which uses observations at two heights (above and within the canopy) and interpolates linearly at heights in between. As the ATTO site has limited measurements within the canopy, it is advantageous to describe the in-canopy mixing using only above canopy measurements. To achieve this, we calculate the variation in sigma\_w(z) with height within the canopy as in Raupach et al. (1989) (Eq. 18), changing the relationship from a linear to a sine-based function. This results in a faster reduction in mixing with height, reflecting a greater separation between the canopy and above-canopy in the tropical forest. With this adjustment, measured in-canopy sigma\_w(z) is reproduced from above-canopy sigma\_w, giving confidence in our estimation at other heights (Fig. S10). This implies that the vertical mixing can be described using only above-canopy observations, and therefore simulations can be performed during periods when in-canopy measurements are missing. For height z below canopy height, wind deviation sigma\_w(z) is calculated from sigma\_w(55) at 55m:*

$$\sigma_{w(z)} = 0.5 \times \sigma_{w(55)} + 0.45 \times \sigma_{w(55)} \times \cos\left(\pi \times \left(1 - \frac{z}{55}\right)\right) \text{ (Eq. 18)}$$

*Between the canopy height and 55 m, K is smoothed to transition to above canopy values of K (see Supplementary model description) without discontinuity. Figs. S1 and S2 show sigma\_w(55) and u\* used to produce K below the canopy.”*

Tau/Tl is described in reference to other values in the supplementary, and the chosen value in these simulations was determined from sensitivity studies.

A comparison to MEGAN emission factors (basal rates) is now included in the supplementary but we feel matching the observed concentrations and emission rates is more important than the emission factor values compared to MEGAN. (Supplementary Methods)

*“These emission factors are somewhat lower than parameters suggested by Guenther et al. (2012) for tropical evergreen forest. Calculations of  $\epsilon_s$  for isoprene at the ATTO site by Gomes Alves et al. (2023) also found significant reductions from values suggested by Guenther et al. (2012) were required to reproduce observations. Furthermore, parameter suggestions in Guenther et al. (2012) include additional values which decrease the final emission flux including canopy reduction factors, leaf age factors and soil moisture and  $\text{CO}_2$  parameters that are not included in this formulation. As a result, the emission factors here are not directly comparable.”*

The temperature and light response functions are the same as Guenther et al. (2012). This is stated in the text and readers are directed to this paper for details. The calculation of the emissions are now presented with the equations used for pool and synthesis emissions and a table of the emission factors: (Line 218).

	Isoprene	$\alpha$ -pinene	Limonene	$\beta$ -caryophyllene
$\epsilon_s$ (nmol m <sup>-2</sup> s <sup>-1</sup> )	6.0	0.4	0.0	0.0
$\epsilon_p$ (nmol m <sup>-2</sup> s <sup>-1</sup> )	0.0	0.0	0.017	0.08
$\beta$ (K <sup>-1</sup> )	0.13	0.1	0.1	0.1

*Table 1: Emission factors for synthesis ( $\epsilon_s$ ) and pool ( $\epsilon_p$ ) emissions selected from sensitivity tests and the  $\beta$  temperature parameters from Guenther et al (2012).*

Overall, there needs to be better description of the model's input formulae and choice of parameters used in the paper. There's insufficient information at present to allow a reader to be able to reproduce the authors' work.

Sect. 2 now describes many of the input parameters and the rationale behind selecting them. We also provide the input files and model with a link to the relevant GitHub in the data access section.

\*Page 5, equation 2: There are some problems with open brackets that do not have closing brackets in this equation. Please correct the equation. Also, the reader has not been told the vertical extent over which the equation applies. I'm assuming that this is between the surface and  $z=0$  and the top of the canopy at  $z=h$ , but this is not clear from the text ( $h$  also needs to be defined, I think, prior to this equation).

Thanks for identifying this. The corrected version already appears in response to a comment above.

Page 5, line 174: Authors have mentioned something called the “Arc of Deforestation” – they need to define this, for readers unfamiliar with the area.

We have defined this where it is first introduced (Line 274):

*“Biomass burning during the southern Amazon dry season (August–October) mostly occurs in the Arc of Deforestation in the E–SE Amazon border, a location named for the agriculture, logging and infrastructure expansion that occurs.”*

\*Page 6, lines 174 to 176: the “adding NO<sub>2</sub> to heights 75 m – 200m when the wind direction comes from 90° - 150°” has been stated without describing the amounts of NO<sub>2</sub> or the observational evidence justifying the approach taken. This section needs to clearly explain where these boundary conditions originated and give reasoning for why they are appropriate. For example, were these based on past observations as a function of wind direction using sonde measurements, or something similar? The boundary conditions could have an important influence on the model results, but the information presented makes the values sound a bit arbitrary. What’s the rationale for a wind-strength-based scaling of the NO<sub>2</sub> values at higher levels? The authors need to describe the information sources used and present a justification for the procedure used for “adding NO<sub>2</sub>” in more detail.

We have described the idealized advection component more explicitly and given justification for the choices. We agree that this NO<sub>2</sub> advection is indeed an uncertainty and we consider simulations with and without including the term to quantify its influence (Line 266):

“Advection

*A basic advection scheme must be included for input of nearby heat and trace gas sources since 1-D models do not simulate horizontal atmospheric transport. There is insufficient data at this remote forest site to reliably include a complete mass-balance advection scheme, so FORCAST v2 includes a simple parameterisation based on wind speed and direction developed by Bryan et al. (2012). The advection rate in ppbv s-1 is proportional to wind speed (U; m s-1) scaled by a coefficient k. The calculation of the U profile from observed u\* is described in the SI (Supplementary model description).*

*For the ATTO site, we investigate the inclusion of advection of NO<sub>2</sub> from biomass burning to heights 73 m – 200 m when the wind direction comes from 90° – 150°. Biomass burning during the southern Amazon dry season (August–October) mostly occurs in the Arc of Deforestation in the E – SE Amazon border, a location named for the agriculture, logging and infrastructure expansion that occurs. Measurements at a site close to ATTO have identified increases of NO<sub>2</sub> coincident with increases in black carbon, attributed to biomass burning transport from this region (Cordova et al., 2004). Furthermore, back trajectories from HYSPLIT show air masses to the ATTO site arriving from 90° – 150° often originate from biomass burning locations (Pöhlker et al., 2018). Although NO<sub>2</sub> was not measured, Pöhlker et al. (2018) identify clear increases in biomass burning aerosol when winds arrive from these directions during months August–November. Although November is considered a transition month, biomass burning in the Arc of Deforestation sometimes still occurs. We select a value of k that best improves representation of observed O<sub>3</sub> concentrations in 2015 ( $k=2 \times 10^{-6}$  ppbv m-1). The inclusion of upwind transport of NO<sub>2</sub> by advection is explored further in the main simulations below (Sect. 2.3).”*

Page 6, line 187: is “light-dependent emission factor” the same as “basal emission rate”?

Yes. This is now defined more clearly with the emission equations given in the new Sect. 2.

Page 6, line 188: do the authors mean “measured emission rates ->at this site-”, rather than just “measured emission rates, here”?

Yes, we have added this to the sentence.

Page 6, lines 190, 191, 195 – what are the temperature dependence values? Maybe this is in the SI?

This is now included in Table 1 (shown above) but the values are identical to MEGAN (Guenther et al., 2012)

Page 7, line 201: "We run 3-day sensitivity studies to identify the optimal vertical mixing parameter ( $\tau/TL$ )," etc.:

This is neither a question or a statement but, in rewriting Sect. 2, we have given more context to the sensitivity studies and introduced them in a more logical way.

Page 7, line 199: how are soil emissions added into the model? For example, this can be done as a flux boundary condition on the lower boundary vertical diffusion equation, or as a direct injection of mass into the lowest model layer. The former is a better approach numerically.

It is a direct injection of mass as the flux boundary condition; this was incorrectly applied in previous model versions, now described in the text (Line 307):

*"In this version, we move soil NO emissions from being a lower boundary condition to a mass injected into the lowest atmosphere layer. Surface emissions and deposition are now treated explicitly within the chemical source terms prior to the transport step. To ensure that turbulent transport redistributes species within the column without introducing additional sources or sinks at the domain boundaries, the transport solver applies zero-flux (Neumann) boundary conditions at both the lower and upper boundaries. At each timestep, new concentrations of all chemical species are calculated at each level using an implicit method to solve the partial differential equations required in calculation of mixing. The zero-flux upper boundary means there is no representation of entrainment but O<sub>3</sub> concentrations in our simulations equilibrate within a day to 20 ppb at 1 km and 50 ppb at 3 km and remain stable. As this is the first time the model has been used to simulate a longer time period without nudging (Otu-Larbi et al., 2021), improvement of the upper boundary concentrations should be considered in future."*

\*\*Page 7, equation 3: at this point the reader/reviewer does not know how the model carries out chemistry, deposition or emissions, and that needs to be included in the model description. I'm assuming the terms in the equation are for the ->rates of change<- of each of these variables at each level, at a given time (please clarify – add this to the text or otherwise define what is meant by "chemistry" "deposition" "emission" and "storage")? What is meant by "storage"? in the context of Equation (3)?

Descriptions of how the chemistry and emissions are treated and combined to calculate the concentrations at each timestep is now included in the methods section. The equation has now been explained more completely with units (Line 366):

*"To estimate a canopy exchange flux of NO<sub>x</sub> and O<sub>3</sub> ( $E_x$ ;  $nmol\ m^{-2}\ s^{-1}$ ) from the canopy to the atmosphere, we use the formula defined in Rummel et al. (2007), which specifically accounts for temporary storage of trace gases within the canopy:*

$$E_x = \int_0^h Chem_{net}(z)dz - \int_0^h Dep(z)dz + \int_0^h Emission(z)dz + \frac{d}{dx} \int_0^h [x](z)dz \quad Eq. 19$$

*Where  $x$  is either O<sub>3</sub> or NO<sub>x</sub> and each term describes the integrated sum of chemistry, deposition, emission rates and storage across the vertical canopy levels  $z$  from soil level to canopy height  $h$ .  $Chem_{net}(z)$  refers to the net chemical production and loss rates at each height  $z$ . The storage term  $\frac{d}{dx} \int_0^h [x](z)dz$  represents any gas that is formed within the canopy or otherwise trapped within the canopy, that causes the in-canopy concentration to change. For example, soil-emitted NO does not immediately become an above-canopy flux, for a time it is trapped within the canopy and can be identified by an increase in within-canopy NO<sub>x</sub> concentrations."*

What are the numerical methods used by the model to determine these rates of change? E.g. what was the numerical approach to solve the equation of vertical diffusion, and how were the above-canopy K values determined?

The details of the mass flux is now described with an equation and greater detail (Line 300):

*"The mass flux for gas-phase species is described by:*

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left( K \frac{\partial c}{\partial z} \right) + S_c + C$$

*where  $c$  is the concentration or mixing ratio of a chemical species,  $S_c$  represents the sum of emissions, deposition, and advection ( $s^{-1}$ ),  $C$  is net chemical production ( $s^{-1}$ ), and  $K$  is the turbulent exchange coefficient ( $m^2 s^{-1}$ ).*

*Emissions, deposition and advection contributions are summed for each layer to calculate the concentration injection at each layer and are passed to the vertical transport solver. The chemical solver is applied subsequently. This operator splitting is described and evaluated in Wei et al. (2021).*

The K value description is now included as stated above.

\*Page 7, line 219: This is the first instance that the reader learns that the upwind NO<sub>2</sub> transport into the column is provided as an "emissions" term. Is there a similar downwind removal term? How are these terms used in the net equation describing the rates of change of chemical concentrations? The paper would benefit from a background theory section describing the rate of change of chemical concentration as an equation, and a few sentences on how each component is solved numerically, and how boundary conditions such as this are incorporated into the model.

Model boundary conditions, NO<sub>2</sub> advection and net equation are now included in the methods section and given elsewhere in this document.

\*Page 8, line 239: it's a bit frustrating as a reviewer to get to this point in the code and see that temperature and wind are prognostic variables of the 1-D model, without having seen equations describing how the temperature or wind speeds are being predicted. It's not clear to the reader how the model is predicting temperature, from the information presented about the model prior to this point. The equations in section 2 deal with diagnostics of the model, but not about the model itself, or that it is predicting meteorological in addition to chemical variables. There needs to be a better description of the model than currently appears in the paper before I can recommend it for publication. I'm not suggesting reproducing work appearing in past papers, but a several page summary of the main prognostic equations in the model along with the references, to place the current work in context, and their numerical implementation, is needed. This information could possibly be summarized in a single large table. The information presented prior to section 3 is insufficient for a reader (or a reviewer) to understand how the model works, its theoretical basis for its predictions, what it's using as input, etc.. For example, gas-phase reactions are important for ozone formation and destruction, but there's no description of the gas-phase mechanism or the numerical method used for predicting future concentrations. Ozone (and other gas) deposition is an important process – but I don't see a description of how deposition is handled (either the calculation of deposition fluxes or how those fluxes are incorporated numerically into the model). Is ozone a completely prognostic variable of the model, or are there O<sub>3</sub> boundary condition terms in the model as well (e.g. similar to the NO<sub>2</sub> "transport" term)? Biogenic emissions are going into the layers (I think), but how this is done numerically, as a height dependent flux condition on the diffusion equation or an injection into layers – and how the parameters such as LAI are being used, are absent from the standpoint of a layer-dependent equation describing these terms. The biogenic emissions are stated to be temperature dependence, but the formulae for that temperature dependence is not given. How or if operator splitting is used to combine the different terms in

the equations being solved need to be described. My point with all these questions: this information is necessary in order for the reader (and this reviewer) to understand the model and its good points versus weaknesses, and also to put the parameter fitting in Table S2 and Table 1 into context. Several pages of background information describing the canopy model employed, its processes and how they are parameterized, with the relevant equations, needs to be added to the main document in section 2.

Several pages have been added to Section 2, with a complete rewriting of the model description to cover these details. For conciseness, we refer the reviewer to the revised manuscript.

Page 8: somewhere earlier in the document (section 2) the period being simulated needs to be more clearly stated. At one point in the document mention is made of previous simulations of a few days in duration, whereas Figure 1 shows month-long simulations.

This was stated in section 2, including a table of simulations carried out. For clarity, we have now given this text a new section header '2.3. simulations' and explicitly stated the study motivations (Line 352):

### **"2.3. Simulations**

*Using the parameters above, we produce five simulations of the ATTO site for the periods 1–13 November 2013 and 11–23 November 2015 to explore effects of meteorology, sesquiterpenes and upwind transport of NO<sub>2</sub> in more detail (Table 2). The model uses observations of wind direction,  $\sigma_w$ ,  $u^*$  and PAR recorded above the canopy (55 m) as described in Sect. 2.1. (Figs. S1, S2). For simulations of 2013, we duplicate  $\sigma_w$  from 2015 due to missing observations, assuming that the average turbulence was similar between years. November 2013 is considered to represent an average November, whereas the 2015 period is used for comparison to an El Niño period in which increased biomass burning occurred.*

<b><u>Simulation name</u></b>	<b><u>NO<sub>x</sub> source</u></b>	<b><u>Sesquiterpene emission</u></b>
<b><u>2013</u></b>	<b><u>Soil NO</u></b>	<b><u>Yes</u></b>
<b><u>2013 No SOT</u></b>	<b><u>Soil NO</u></b>	<b><u>No</u></b>
<b><u>2015</u></b>	<b><u>Soil NO, transport of NO<sub>2</sub></u></b>	<b><u>Yes</u></b>
<b><u>2015 No SOT</u></b>	<b><u>Soil NO, transport of NO<sub>2</sub></u></b>	<b><u>No</u></b>
<b><u>2015 pristine</u></b>	<b><u>Soil NO</u></b>	<b><u>Yes</u></b>

*Table 2: Variables in five simulations investigating effects of NO<sub>x</sub> sources and sesquiterpene emissions.*

*We test the hypothesis that sesquiterpene emissions have an important role in canopy-scale O<sub>3</sub> deposition fluxes via chemical removal inside the canopy by including simulations with and without sesquiterpene emissions. We also consider if transported NO<sub>2</sub> from biomass burning in 2015 could impact O<sub>3</sub>, BVOC and NO<sub>x</sub> exchange at the canopy top."*

Page 9, Figure 1 caption, Horizontal is misspelled.

Thanks, this has been corrected.

\*Page 9, line 257: its not clear how the NO<sub>2</sub> used for transport from upwind was determined in the first place, or how it is incorporated into the model. It sounds like on lines 219-220 that the NO<sub>x</sub> due to transport is some sort of free parameter of the model, added until the predicted concentrations are about right, but I may be mistaken. Please clarify how horizontally transported species are included into the 1D model, in a few more sentences by equation (4).

This is now described in the new Section 2.2 and quoted above.

Page 10, Figure 2: its not clear to me why sensitivities to sesquiterpene concentrations were examined for 2013, and to NO2 transport in 2015, and not both aspects in both years? Less NO2 transport in 2015 from observations?

Sesquiterpenes were examined in both years, and both are included in the figure.

NO2 transport is assumed to have only occurred in 2015. November 2015 had higher fire activity than normal as it was an el nino year (described at the start of Sect. 3.1), which was likely advected to the site. 2013 was an 'average' year and observations are reproduced without needing to consider advection. We clarify the link (Line 564):

*"This suggests that advected biomass burning air masses, resulting from higher fire activity in November 2015 compared to average (Ribeiro Neto et al., 2022; Silva Junior et al., 2019), are the main driver of higher O<sub>3</sub> concentrations at the site in 2015 rather than other meteorological differences such as higher temperature."*

Deleted: the

Page 10, lines 270-275: More information earlier in Section 2 on the model would help in diagnosing the cause of the ozone underestimates at night. The formulae for biogenic emissions including the temperature dependence would be useful at this point - this is an exponential decay equation relative to a base temperature like 300K - and whether some of the overestimates might be a result of the exponential decay constant used, as opposed to the basal emission rate employed. Same possibility for surface NO emissions - if the temperature constants in the emission equations are not right, the NO emissions at night could be overestimated, leading to excess NO<sub>x</sub> titration. The other possibility is that the nighttime diffusion constants in the lower part of the canopy are too weak. The authors description of how Raupach's formula have been employed (equations 1 and 2) with respect to the diffusion equation K values need to be clarified. For example, by showing the diffusion equation first, then how K is determined as a function of height more explicitly with equations would make it easier to determine what's happening with the model at night. Perhaps the sigma-w term in equation (2) is underestimating K values at night leading to too-high NO<sub>x</sub> titration. A model description including the gas-phase mechanism or a reference to same is needed in order and a corrected version of equation (2) is needed in order to suggest possible causes.

These points are all true, however within the canopy, the model evaluates well against observations. The above-canopy elevated O<sub>3</sub> is more likely related to O<sub>3</sub> mixed down from above on nights with intermittent turbulence. We evaluated indicators of turbulence and added the following text (Line 489):

*"Divergence between friction velocity and horizontal wind speed above the canopy has implications on vertical mixing within the model. Observed wind speeds are low in the canopy at night, but remain high above the canopy. This indicates decoupling between the canopy and above under stable, stratified nighttime conditions. Frequently in 2013 and on several nights in 2015, nights show high wind shear and sustained wind speeds above the canopy (Fig. S13). Richardson numbers in both periods are above 0.25 at night, which suggests turbulence is suppressed and intermittent (Fig. S14). However, the model likely overestimates the degree of turbulence suppression in 2013. The simulated flow has very low shear at night, meaning shear-driven mixing in the boundary layer is underestimated (Fig. S13a, S14c). This arises from the model reliance on friction velocity to constrain turbulent exchange, meaning intermittent turbulence is not captured when friction velocity is low. As a result, vertical mixing in the above-canopy space is overly weak on some nights in the simulations, with possible implications for the representation of exchange with the canopy".*

Line 589:

*"In both 2013 and 2015 simulation periods, the model performs worst overnight, often failing to capture nights in which O<sub>3</sub> is maintained at high concentrations, including in the lower canopy on three nights in 2015 (Fig. 3). High nighttime O<sub>3</sub>, such as on November 14<sup>th</sup> 2015, are most likely related to missing turbulent features in our model. Nights with high O<sub>3</sub> concentrations above the canopy are often associated with high wind shear that is not reproduced by the model, suggesting turbulence within the boundary layer that brings O<sub>3</sub> to the canopy top (Fig. S13). Below the canopy, nighttime O<sub>3</sub> concentrations are reproduced on most nights in the model. The model captures the O<sub>3</sub> diurnal cycle more closely in the tropics compared to previously simulated temperate forests (Ashworth et al., 2015; Wei et al., 2021) due to the smaller influence from transported air masses at this site.*

*Figures 4a and 4b confirm that, whilst the daytime O<sub>3</sub> profiles are a good match to observations, nighttime profiles are underestimated, especially above the canopy. The step-change in O<sub>3</sub> gradient below the canopy in observations of the 2013 period suggests some decoupling between the canopy and above occurs, as also indicated by the sustained wind and low friction velocity above the canopy, described above (Figs. S12b, S12c). The lack of intermittent turbulence above the canopy in the simulations leads to underestimation of the above canopy O<sub>3</sub> profile, but decoupling results in a smaller bias below the canopy. The shape of the daytime vertical profile in the 2015 period is better captured than in the 2013 period; the observed 2013 vertical concentration gradient is steeper than 2015 but this is not replicated by the model."*

Page 11, lines 279 – 284: I'm not sure I agree that this a lack of decoupling – the NO and O<sub>3</sub> behavior of the model at night (line 290) implies that either NO emissions are too high or that the vertical mixing is insufficient...it would be helpful for the paper to include more details earlier, which could then be used to bolster the arguments made here. Lack of decoupling could mean that the cosine function employed in equation (2) is insufficiently "steep" in the vertical to describe the observed shelf in diffusivity shown in Raupach's work, but the 100% NO near the surface at night (line 289) implies that there is strong decoupling of below-canopy versus above canopy. Question: were the observations in Figure S4(a) available such that day and night values could be determined separately? This might show that a different functional dependence, perhaps a variation between day and night in the TL values might account for the ozone differences. It might be worthwhile to compare to other parameterizations of Raupach's work in the literature if sufficient information is available – for example, the Makar et al reference quoted by the reviewers has a vertical coordinate dependence of the value of TL, while the authors are apparently not including any variation in TL with height. In the reference the sigma-w went to 0.25u\* at z=0 and the TL went to 0.3 \* canopy height / u\* - how do these numbers compare to the authors' equation (2) and their tau/TL assumption (assuming u\* is available for their forest)?

**First some clarifying points:**

- K profiles given in Fig. S4a (now S16) are the simulated versions – there is no observational profile.
- The difference between day and night K values in the simulations can be seen in Fig. S15
- The NO:NO<sub>2</sub> ratio states equal amounts of NO and NO<sub>2</sub> at the surface, not 100% NO

Nonetheless, we agree that there is in fact sufficient decoupling from the above canopy and this is not the issue. We have taken a closer look at other indicators of mixing that could be evaluated in our simulation and improved our model evaluation (above).

We show later on that NO emissions play a minor role in controlling O<sub>3</sub> concentrations. In any case, the issue is with the above canopy concentrations not the below canopy values.

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- Deleted: Sensitivity tests in which sesquiterpene emissions are switched off are 1–2 ppbv higher at night, providing a better match to observations on average but not necessarily capturing the day-to-day variability better (Figs. 1, 2a, 2b). This may suggest that sesquiterpene emissions or their reactivity with O<sub>3</sub> are overestimated in the model, although h...
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- Deleted: that is not reproduced in the simulations.
- Deleted: The lack of decoupling in the simulations likely contributes to the faster decline in above-canopy O<sub>3</sub> concentrations overnight compared to observations
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As for the mixing parameterisations, we cover some sensitivity tests for tau/Tl in the supplementary and find that increased mixing decreases the above canopy O3 concentrations (as more O3 is brought into the canopy and deposited). Outside of the manuscript, many different mixing profiles were considered and tested, however we did not identify any improvement that would warrant choosing a more complicated parameterization over the existing choice. With a longer period of observations, or more observed profiles of different variables, a better choice may be discovered in the future.

Another possibility: how well did the authors' model simulate near-surface nighttime temperatures? Perhaps the nighttime NO and sesquiterpene emissions might have been too high as a result?

Near surface temperatures are now mentioned (Line 483):

*"The surface-level temperatures, which affect the soil NO emissions, reproduce night-time observations but underestimate the maximum temperatures in the daytime."*

We use the simulations without sesquiterpenes to consider how likely a sesquiterpene emission issue could explain the underestimation. However, we find it does not satisfactorily improve the simulation, implying the issue cannot be resolved by manipulating sesquiterpene parameters.

Page 11, line 290: Does "NO2 transport" reset the concentration of NO2 in the model at every timestep?

This should now be clear in Section 2. It is an injection of mass at the model timestep rather than nudging.

Page 11, line 290: total conversion of NO to NO2 at night, along with ozone underestimates at night implies that the diffusivity values near the surface are too low, or the gradient in diffusion in the near-surface environment is too steep.

We tested in detail changing the mixing near the surface but total loss of NO at 10 m seems to occur in all cases except with exceptionally low O3 that is not observed (these tests are not included in the manuscript as they do not add any information). We also note that O3 in the canopy is reproduced quite well, it is the above canopy values that are underestimated. Similar to comments above, it is likely that mixing within the canopy can be improved but we do not have sufficient evidence to change the parameterisation.

Page 12, Figure 3: I'm wondering what was used for the lower boundary condition on the diffusion equation in the authors' model? Zero concentration or zero gradient? The latter might force the concentrations further from the observations. It occurred to me that the boundary condition might be affecting the model results (ditto for the top boundary condition). How boundary conditions have been applied to the model should be added to Section 2.

Here is our added description of the boundary conditions (Line 309):

*"To ensure that turbulent transport redistributes species within the column without introducing additional sources or sinks at the domain boundaries, the transport solver applies zero-flux (Neumann) boundary conditions at both the lower and upper boundaries. At each timestep, new concentrations of all chemical species are calculated at each level using an implicit method to solve the partial differential equations required in calculation of mixing. The zero-flux upper boundary means there is no representation of entrainment but O3 concentrations in our simulations equilibrate within a day to 20 ppb at 1 km and 50 ppb at 3 km and remain stable. As this is the first time the model has been used to simulate a longer time period without nudging (Otu-Larbi et al., 2021), improvement of the upper boundary concentrations should be considered in future."*

Page 13, line 324: Suggest “reduce deposition to vegetation” should be “reduce the deposition flux to vegetation through reducing the ozone available for deposition”.

This is a better phrasing as we have edited the text.

Page 14, Figure 4: how were the numbers derived from the layered structure of the model? For example, are these vertically averaged values throughout the forest canopy vis-à-vis equation (3)?

Yes it is a sum of all the fluxes at each level to get a total canopy flux as in Eq. 3 (now Eq. 19), averaged over the simulation period. This is now referenced in the section (and Eq. 19 is described in more detail above). (Line 692)

*“Figure 5a shows the mean total canopy flux of O<sub>3</sub> over the simulation period, divided into net chemical loss and deposition (as in Eq. 19).”*

Page 14, lines 330 to 336: interesting. One aspect of the authors work worth highlighting is the estimate of ozone loss rates. What drives the difference in deposition velocity between the two years? Having a description of the deposition algorithm in Section 2 that could be referred to here would help.

We now show daily deposition velocities and canopy conductance in the supplementary to answer some of these questions. The differences mostly result from a change in the O<sub>3</sub> distribution through the canopy combined with some days of low canopy conductance in 2013.

Line 769:

*“Our simulations show high relative humidity (Fig. S21) and daytime temperatures (Fig. 2) close to the simulation optimum parameter for stomatal conductance (301 K), suggesting little stomatal limitation and therefore “wet season” behaviour. This is consistent with evaluation of the energy balance and Bowen ratio described above (Sect. 3.1, Fig. S17). Day-to-day variability in deposition velocity in the simulations follows variability in temperature and PAR (Fig. S22). The 2013 period exhibits lower average PAR and greater daily variability (including a cool, cloudy day on the 4<sup>th</sup>), resulting in lower average stomatal conductance than the 2015 period (Fig. S23). However, differences in deposition velocity between simulations are likely also related to changes in O<sub>3</sub> distribution within the canopy.”*

Deleted: This may be due to reduced stomatal limitation as November is a transition month into the wet season.

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The deposition scheme is now also described in more detail in sect. 2

Page 14, line 336: I’m wondering to what extent the simulated ozone fluxes are dependent on how the above-canopy concentrations are determined for both ozone and its precursors. If ozone is a free variable, then the NO<sub>2</sub> profile used for the transport term may have a large influence on the calculated flux of ozone (and if this profile is a time average of many observations, then the resulting smoothing might reduce the calculated ozone flux). The NO<sub>2</sub> profile should be discussed more in Section 2.

We have further discussed the advection scheme in section 2. Most models are nudged to the above canopy values, implying that adequate simulation of above canopy concentrations is a reasonable starting point to explore the fluxes. As we have mostly good agreement of above canopy concentrations, this seems sufficient to explore the fluxes.

Page 15, line 341, good discussion on Figure 5. It would also be worthwhile to provide a similar figure for the net diffusion transport and the deposition removal of ozone, to see how the three terms interact.

We would like our manuscript to focus on the chemistry occurring in the canopy. Although these other features must be accurately represented to gain confidence in the modelling system, we do not want to focus on deposition here. We considered the figure for deposition differences between simulations but, as the difference between simulations in comparison to the total deposition rate were small, differences were not very visible.

The net diffusion transport is not easy to isolate from the model outputs and we feel it would not contribute substantially to the findings made in the paper.

As quoted above, we have evaluated daily variability in deposition and conductance which we feel gives more insight into the processes and included these figures in the supplementary.

Line 350: the convergence of chemical losses between the two years may reflect model boundary conditions more than year to year variability, or that the surface is relatively decoupled from the layers above.

This is in relation to chemical losses in 2013 and 2015 having similar below canopy profiles in simulations without sesquiterpenes. The reasons above could well be the case (although the boundary conditions do not force any concentrations), however the point here is to highlight that differences between years occur only when sesquiterpenes are included. This is a starting point to examine the role of sesquiterpenes.

Page 16, Figure 6 and related analysis through the end of section 3.2 is also good. Line 365: why is there an 8-fold increase in deposition of ozone during the day rather than the night? I'm guessing that this is the stomatal term in the author's deposition code – it would be good to include a description of the algorithm, and how it is employed in Section 2 (see Clifton et al 2023, <https://doi.org/10.5194/acp-23-9911-2023> for an overview of recent deposition algorithms). With regards to how the algorithm is employed - are the authors calculating a layer-dependent deposition flux of ozone? I ask since many larger scale (regional) models make use of a "big leaf" assumption in which deposition fluxes effectively go to an equivalent surface at the ground; the authors' parameterization might be of interest to the larger community. Again, a sketch of the tower including the observation heights and the model levels would be good to have at the start of the paper, along with the variation in LAI with height on the same figure; this would aid the reader in visualizing where the 25m is with respect to the canopy.

This has been clarified in the text and the methods section has been updated to describe the deposition terms, which are multilayer. It is the stomatal conductance that acts as the main sink for ozone. We also show daytime stomatal and cuticular total canopy conductance in the supplementary to compare magnitudes. The soil of course also contributes. (Line 826).

*"During the day, the contribution diminishes to 5%, which is in response to an 8-fold increase in deposition flux as stomatal pathways become available, rather than a significant change in chemistry."*

Page 18, lines 400-403: It could be that a dependence of the escape efficiency on a function of  $u^*$ , canopy height, and height within the canopy, rather than  $u^*$  itself, might yield a higher correlation. Note that some parameterizations of Raupach's work have both  $\sigma_w$  and  $T_l$  parameterized as functions of  $u^*$  and canopy height, as noted above, with the net value of  $K$  being dependent on  $u^*$  plus these other terms.

This is interesting and worth exploring further in future. We here aimed to find a simple relationship that could be used to parameterize single-layer models and have added clarification (Line 868):

*"The escape efficiency of sesquiterpenes ranges from 45%–55% between simulations. The highest escape efficiency of 55% occurs in 2015 pristine conditions. When transport of  $NO_2$  is included, this decreases to 48% as a result of higher  $O_3$  concentrations. Both simulations of the 2015 period have a higher escape*

efficiency than the 45% in 2013. The MEGAN 2.0 BVOC emissions model includes an escape efficiency to account for BVOC losses within the canopy, based on chemical lifetime,  $u^*$  and canopy depth (Guenther et al., 2006). This parameterisation results in canopy escape efficiencies from 10% (in the presence of high  $O_3$ ) to 60%. Our results, in relatively low  $O_3$  conditions compared to global averages, fit realistically within this wide range. We find a significant correlation exists between daily mean escape efficiency and  $u^*$  ( $r^2=0.69$ ,  $p<<0.05$ ; Fig. S25). This indicates that, for single-layer canopy models seeking a simple parameterisation, the current equation in MEGAN 2.0 is functional.”

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Page 18, lines 404 – 405: Escape efficiencies likely will likely inversely correlate with the oxidation rate (oxidant concentration x reaction rate constant) where the oxidants are OH,  $O_3$  and  $NO_3$ : the fastest reacting VOCs present at the site would have the lower escape efficiencies, the slower reacting VOCs would have the higher escape efficiencies. A plot of oxidant rate using typical concentrations of those species versus escape efficiency would probably show this.

This is true and we considered including the figure you suggest, however as sesquiterpenes are much more reactive than the other BVOCs the figure was mostly empty space. We have instead chosen to describe the relationship as an introduction to the paragraph and find this a useful addition. The remainder of the section describes differences between simulations in greater detail. (Line 863)

*“BVOC escape efficiency is controlled by their oxidation rate with respect to OH,  $O_3$  and  $NO_3$ , such that the faster a species can be removed (dependent on reaction rate and oxidant concentration), the lower the escape efficiency. For the oxidant concentrations at this site, escape efficiencies of primary emitted BVOCs increase in the order: sesquiterpenes << limonene <  $\alpha$ -pinene < isoprene. Furthermore, depending on transport and oxidant concentration between simulations, BVOC escape efficiencies vary among simulations.”*

Page 19, line 415: it’s worth reminding the reader how the soil  $NO_x$  contribution was isolated here, by turning the transport source off.

We have added a description: (Line 898)

*“The soil  $NO_x$  escape efficiency is different than the canopy  $NO_x$  flux (described in the next section) in that it excludes the contribution from upwind transported  $NO_2$  into the canopy. To exclude this, we estimate the contribution from transported  $NO_2$  entering the canopy using a simulation with no soil  $NO$  source and subtract this from the simulation of 2015 with transported  $NO_2$  (as described in Sect. 2.4; Eq. 20). The motivation for isolating only the soil  $NO$  that leaves the canopy is to inform how soil  $NO$  emission should be represented by a single-layer canopy model. The comparison between 2015 and pristine 2015 reveals changes in soil  $NO$  emission resulting from a change in chemical environment (e.g., the  $NO_x$  production and loss terms depend on the background environment).”*

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Figure 7: also explain or remind the reader here what the “store” component represents and how it is calculated. Storage? What is meant by storage, in the context of the equations governing the rate of change of the chemical concentration? Section 2 would benefit from a discussion on how the terms are calculated.

We have added a short explanation and more detail in section 2: (Line 923)

*“We first consider the role of storage in the diurnal pattern, which refers to  $NO_x$  that becomes trapped in the canopy space due to slow vertical mixing.”*

Page 20, line 430-431: note that the sentence “Daylight hours have...” would seem to indicate a pretty strong separation between above and below canopy environment.

True. Discussion of thoughts on vertical turbulence are addressed above but we have added your comment here as well: (Line 927)

*“This indicates strong separation between the below and above-canopy environment overnight.”*

Page 21, line 457-458: Not sure what the authors mean by “not described by K” here. Did the authors do a separate correlation at morning hours and find it was zero? Or just different from the correlation over all?

It can be seen in Fig. S17 that the morning increase in NO is disproportionate relative to the change in K. We have changed the text: (Line 967)

*“The morning spike in NO<sub>x</sub> escape is proportionally greater than the morning increase in K (Fig. S27) but is the main driver of O<sub>3</sub> production above-canopy in pristine conditions (Fig. 7).”*

(although we removed the morning hours and the correlation did increase by 0.1)

Page 22, section 3.4.2: Very interesting results. Storage in this context I assume means “trapped within the lower canopy once it reaches that level due to the lower K values there”? Yes, makes sense. Note that figure 9 also is likely influenced by lower deposition velocities at night, due to the stomatal resistance shutting down (I assume – please make sure the revision includes details on the deposition parameterization’s component resistances): you can see the deposition component is lower at night. It’s worth mentioning this in the write-up at this point, since its another factor resulting in more nighttime storage of NO<sub>x</sub> within the below-canopy environment.

We have added some details on NO<sub>2</sub> deposition to the previous sections that are relevant to your comment: (Line 933)

*“NO emitted from the soil is rapidly oxidized to NO<sub>2</sub> when O<sub>3</sub> is present, but during the night, NO accumulates near the ground. At night, there is a significant flux to the soil and lower canopy surfaces (Fig. S26). As stomata are closed, this is likely non-stomatal deposition to the soil and cuticles that is high due to build-up of NO<sub>2</sub> in the lower canopy originating from the soil in low turbulence. With the onset of turbulent mixing under daylight, O<sub>3</sub> oxidises NO to NO<sub>2</sub>, which is transported upwards but partially taken up by deposition to vegetation (Gut et al., 2002; Breuninger et al., 2013; Chaparro-Suarez et al., 2011). The greatest daytime deposition flux therefore also occurs at the onset of mixing as NO<sub>x</sub> at the surface is brought to heights with greater leaf area (Fig. S26). However, the daytime deposition flux is lower than nighttime on average due to lower daytime concentrations.”*

We have also described the storage term (quoted above) and the deposition scheme in earlier sections.

Page 23, line 494. Section 2 needs to mention the time span(s) used for simulations and include a sentence like “Hereafter, ‘2013’ is used to represent the two week simulation period from November 1<sup>st</sup> through November 14<sup>th</sup> of the year 2013, and ‘2015’ refers to the two week period from November 11<sup>th</sup> through November 24<sup>th</sup> of the year ‘2015’.” It might also be better to use phrases like “in the 2013 and 2015 simulation periods” rather than “2013 and 2015”, since the latter may be indirectly confused with the entire year in the minds of the readers.

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Good point, thanks for this suggestion. We have signposted the simulation periods better in Sect. 2.3 (shown above) and changed the phrasing to '2013 periods' etc. throughout the manuscript.

Page 23, lines 499-500: "This suggests that ...". I think this phrase overstates the case; it's not a matter of the ability of the canopy being reduced, per se, but the ozone concentration due to chemistry associated with transport being greater than the canopy's capacity to reduce through terpene emissions". Something like "biomass burning pollution generates ozone in sufficient quantities to be greater than the canopy's ozone destruction capacity due to terpene oxidation". How dependent is this conclusion on the accuracy of the sesquiterpene emission rates?

We have actually removed this sentence as the effect is quite small even with the sesquiterpene emission rate and reactivities used (which we feel are an upper estimate).

Page 23, line 501: "Biomass burning therefore increases stomatal O<sub>3</sub> flux, leading to a heightened risk of O<sub>3</sub> damage to the forest (e.g., Cheesman et al., 2024)." This is something that could be tracked in the model; see Galmarini et al., ACP, 2021; <https://doi.org/10.5194/acp-21-15663-2021>, Figure 4 and related discussion). The relative contributions of each deposition pathway towards the net deposition velocity can be tracked in models using effective conductances, and the contributions towards net deposition fluxes can be tracked via effective fluxes.

This would indeed be interesting but currently is considered beyond the scope of this study as several model diagnostics would need to be added and evaluated.

Page 24, line 509-511: The authors mention deposition schemes as being highly parameterized here, without describing theirs, aside from referring to it as a simple parameterization at the end of this paragraph; is it a "big leaf" parameterization, leaf or soil level parameterization? A more detailed description of deposition is needed in Section 2, which could then place the authors statement here in context. Both the Galmarini et al and Clifton et al references provide good examples of overview descriptions of different deposition algorithms used in regional models – what was used here?

We now describe the deposition scheme in greater detail. It is a multilayer scheme with a Jarvis style conductance model. Compared to existing schemes, it is a standard formulation and the main limitation is lack of site specific deposition measurements and general uncertainty around non-stomatal processes that would exist regardless of the choice of scheme.

Page 24, line 524: The authors should mention that the monoterpene and sesquiterpene basal emission rates of their own scheme were effectively a free parameter of the model at this point; the initial values for sesquiterpenes came from another Amazon site, and the values were varied to help get the best fit for O<sub>3</sub>, correct?

The basal emission rates were fitted to match observed monoterpene and sesquiterpene concentrations. The effect on O<sub>3</sub> is evaluated in the manuscript to give an uncertainty range on the effect of sesquiterpenes on O<sub>3</sub> concentrations but was not used in the fitting. However, it is true that these parameters were not well-constrained due to lack of emissions measurements at this site. We add words to this effect: (Line 1089)

*"Nonetheless, further measurements of sesquiterpene species and reactivity are needed to accurately quantify the impact on O<sub>3</sub> concentrations. Sesquiterpene measurements are not currently available at the ATTO site, such that the emission factors used here could be better constrained if measurements become available. Similarly, monoterpene emissions can include highly reactive species that have not been accurately characterised and our emission factors are estimated from observed concentration profiles rather than emission rate observations."*

Page 25, line 559-560: what about the assumed shape of the vertical profile of NO<sub>2</sub> due to transport as another factor worth considering? What is being used at the moment (another thing to clarify in Section 2).

We have added a sentence highlighting this feature as a contributing uncertainty: (Line 1132)

*“We also identify a possible influence from biomass burning transport of NO<sub>2</sub> into the above-canopy space, so NO<sub>x</sub> concentration measurements, especially during biomass burning months (the dry season), would help to refine this parameterisation.”*

Page 25, line 565-567: I’m wondering about the model’s lower level air temperatures. At some parts of the paper they seem to be a prognostic variable, at other parts possibly a boundary condition driven by observations. This needs to be clarified in Section 2. If the lower canopy temperatures do not match well with observations, especially at night, the NO emissions will be affected.

We have clarified that temperatures are prognostic in the methods and add some comments evaluating lower canopy temperatures in sect. 3.1. (quoted above).

We also want to highlight that the above canopy NO release is mainly controlled by in-canopy factors, such as turbulence, in our simulation (as described in Sect. 3.4, the escape cycle mostly looks like the mixing cycle much more than it resembles the emissions). This is identified in other studies, such that we feel our statement is accurate: (Line 1156)

*“We further agree with existing studies of pristine environments (e.g., Ganzeveld et al., 2002) that a diurnally varying parameterisation of soil NO<sub>x</sub> escape could improve representation of variability in NO<sub>x</sub> chemistry; the diurnal cycle of soil NO<sub>x</sub> escape is strongly related to vertical turbulence, combined with an additional spike in morning escape efficiency that is important to consider for accurate simulation of O<sub>3</sub> production (Fig. 8).”*

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We do agree that soil NO temperature dependency is uncertain, such that the temperature emissions parameterization is likely a greater uncertainty than the simulated temperatures themselves. This is discussed in sect. 2. (Line 231)

*“NO emission fluxes and their sensitivity to driving variables remains a significant uncertainty. Global studies indicate increased emission with temperature (Luo et al., 2013; Ke et al. 2022), however studies on isolated tropical soils tend to show weaker temperature dependence (Cardenas et al., 1993). Water status is also likely a driving factor of soil NO emission, with limited NO fluxes in water-logged or dry soils and heavy rainfall triggering NO emission pulses (Yienger and Levy, 1995), which is not considered here.”*

## Reviewer #2

Review of paper acp-2026-161: Linking In-Canopy Chemistry to Above-Canopy O<sub>3</sub>, BVOCs, and NO<sub>x</sub> Gas Fluxes in the Amazon Rainforest by Brown et al. The paper describes application of a multi-layer canopy model system (FORCAsT) for analysis of the ATTO tower vertical profile and flux measurements on ozone, NO<sub>x</sub> and BVOCs to diagnose the role of in-canopy interactions in the observed above canopy fluxes of these reactive compounds. Overall, this reads as a nice study making a point about some interesting features on tropical forest atmosphere-biosphere exchange of ozone, BVOC and NO<sub>x</sub> and how these findings support further need to experiments and development of models to study atmosphere-biosphere interactions under changing/increasing human/climate forcing in the Amazon (biomass burning). My main concerns, as also reflected by the long list of comments on especially many model aspects, is how to fully appreciate the conclusions drawn from the model experiments given that some of the simulated processes, essential to evaluate atmosphere-biosphere exchange of ozone, NO<sub>x</sub> and BVOCs, are not well evaluated (e.g., surface energy balance including partitioning of energy over LE (stomatal conductance) / H also relevant for simulation of atmospheric boundary layer, soil NO<sub>x</sub> emissions (soil moisture, T), non-stomatal deposition, etc). I am aware that some of these details might be available in other papers and that, showing that this features of the model performance are satisfactory, this might require even another paper. But these are according to me essential aspects to benchmark application of such a model to assess the role of processes explaining the role of processes in atmosphere-biosphere exchange. Given this long list of comments, I would be eager to see the response by the authors to the shared feedback and hope, it will overall be appreciated as constructive feedback. Below you can find my more specific comments.

Thank you for taking the time to provide these detailed comments. Most points raised here are addressed in response to specific comments below. We have also included a brief evaluation of LE and H from the model: (Line 536)

*“As a final evaluation of the model, we consider the partitioning of energy into latent and sensible heat fluxes above the canopy (Fig. S17). Average maximum hourly latent heat fluxes are 250 W m<sup>-2</sup> in 2013 and 310 W m<sup>-2</sup> in 2015, in good agreement with observations from the nearby LBA-k34 flux tower, which recorded hourly maxima of 250 and 300 W m<sup>-2</sup> for wet and dry season means, respectively (Gerken et al., 2018). Sensible heat fluxes are 80 W m<sup>-2</sup> and 100 W m<sup>-2</sup> in 2013 and 2015, respectively, compared to 110–150 W m<sup>-2</sup> in the nearby observations for wet and dry seasons. As a result of the lower magnitude and differences in the sensible heat flux diurnal cycle compared to observations, the Bowen ratio is higher in the morning and lower in the evening relative to the flux site values. However, the mean values of 0.4 in 2013 and 0.32 in 2015 (Fig. S17c) are close to observations (0.5) and represent an improvement over many land surface models (Restrepo-Coupe et al., 2021). These values suggest 2015 was not strongly water-limited in our simulations, with energy partitioning primarily responding to radiation. Observations of pristine tropical forests typically show seasonal cycles driven by radiation, with water stress rarely limiting, making the model behaviour plausible, despite lacking directly comparable observations.”*

Pp2, line 94/95: “ This acts as a first step towards identifying the important processes for improved parameterisation of tropical forest behaviour in global models”; This is a very general statement. This is not about the role of tropical forests in the global C and water cycle. According to me this study is about explicit consideration of the tropical forest canopy processes compared to the commonly applied big-leaf approaches in atmospheric chemistry (and climate) interactions. And honestly, see that further parameterization should not be the end goal; to properly represent forest-atmosphere reactive trace gas and

aerosol exchange in large-scale models the big-leaf approach should be replaced by including multi-layer model representations, as has already been done. And yes, some of the processes (turbulent mixing) might reflect a quite high level of parameterization.

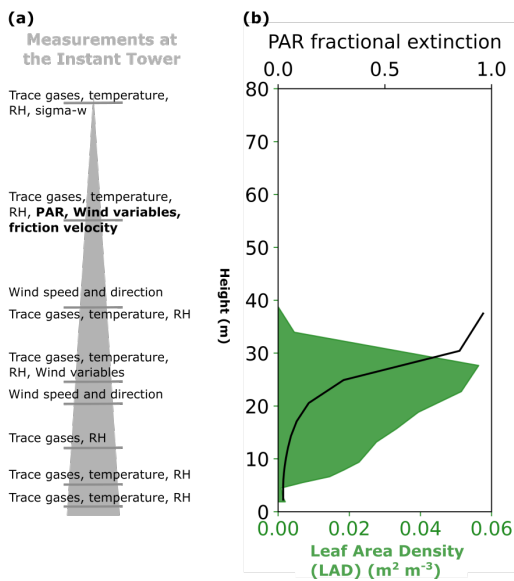
We have changed the text so as to not imply parameterization is the only option and to describe the study more accurately: (Line 99)

*“This acts as a first step towards identifying the important features of trace gas exchange required for improved representation of tropical forest canopy chemistry in global models.”*

Line 104; here you mention only the availability of measurements at 80m but then below it becomes clear that there are measurements at multiple heights. So, refer to this 80m measurement height as the highest measurements above the forest canopy.

We have clarified that this is the height of the tower and a profile is available. We also create a new Figure 1, showing which heights have measurements of which variables. (Line 112)

*“Figure 1a summarises the ATTO measurements used in this study as driving data and for model evaluation. Measurements were taken at various heights along the 80 m tower”*



*Figure 1: (a) The observed variables used for model evaluation throughout this paper and their approximate measurement heights. Variables in bold are used as driving data in the simulations, (b) prescribed leaf area density (green shading) and fractional extinction of PAR (black solid line) within the canopy (model simulated average). The height scale on both figures is the same.*

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Line 109; the focus period is mentioned giving as a major motivation the availability of data needed to constrain the model experiments and where this availability is also further discussed afterwards. Here it would be nice to read also implications of selecting these two November case study periods; where there some contrasts in the prevailing conditions and how representative are November results for the longer-term atmosphere-biosphere exchange regime?

We agree and have added additional information here: (Line 134)

*“November 2013 reflects typical background conditions at ATTO, with moderate temperatures, clean air masses, and biogenic-dominated chemistry, whereas November 2015 represents a perturbed regime characterised by El Niño-driven warming, biomass burning influence, and enhanced atmospheric oxidation (Ribeiro Neto et al., 2022; Silva Junior et al., 2019). Consequently, 2013 observations are representative of the broader atmosphere–biosphere exchange during this period, while 2015 is used to investigate how climate extremes and fire activity may shift the chemical regime. Indeed, November 2015 may be more representative of dry season conditions.*

...

*November 2013 is considered to represent an average November, whereas the 2015 period is used for comparison to an El Niño period.”*

Line 134-135: “since many other canopy chemistry models are nudged by above-canopy Observations”; mentioning this feature of different approaches in using multi-layer canopy model approaches (online versus offline simulation of the processes driving emissions, deposition, chemistry and turbulence), it is important to indicate the potential implications of these different approaches. And you might like to shortly mention what is being meant by nudging (not familiar to all, e.g. experimentalists?) but also which parameters are being nudged, only the meteorological variables are also long-lived tracer concentrations? The previous comment is also relevant given this description of how advection of air masses with different physical and composition characteristics is being considered. How does this approach differ from the nudging approach? How do you consider the role changes in advection contributions as a function of altitude, time and where did you define your boundary conditions?

These questions on model structure (advection, boundary conditions, initial concentrations) are now included in the methods section. This has been rewritten so details are not included here to save space. We also describe nudging and the pros and cons of different set ups: (Line 156)

*“All other variables including temperature, wind speed, chemistry, water and energy fluxes are prognostic variables in the model after specifying initial conditions. The minimal number of forcing variables is a feature of this canopy model, since many other canopy chemistry models are nudged by above-canopy observations. Nudging gradually forces model variables towards observations and is commonly applied to constrain above-canopy long-lived gas concentrations and meteorology. This has the advantage of holding the above-canopy environment as close to the true values as possible with the aim that the below-canopy environment is more likely to be well-represented and analysis can focus on below-canopy processes. However, as nudging is a correction rather than an explicit representation of transport, it can mask transport or chemistry errors in the model. To represent lateral transport of air masses in a process-based way, FORCASTv2 includes an advection parameterisation as a prescribed tendency inside the column. The model is described in detail by Ashworth et al. (2017), Wei et al. (2021) and Bryan et al. (2012); we provide an overview in what follows.”*

Section 2.3: “We modify the vertical mixing profile within the canopy to create a faster reduction in mixing with height, reflecting a greater separation between the canopy and above-canopy in the tropical forest”. This comes completely out of the blue; what is the motivation/hypothesis behind this modification of the turbulent transport component in the model? Is this because first model experiments indicated that the model simulated metrics were clearly indicating a misrepresentation of the canopy mixing regimes? Then reading over the specific details regarding the consideration of the NO<sub>x</sub> advection contribution, it further seems that first results were showing some issues on capturing some of the observations. But this now all reads too much as simply tweaking the model to get it reproduce those observations without a clear explanation about what could be obvious motivation to do so; what explains that for a particular wind direction there is a significant source of NO<sub>x</sub> as a function of altitude?? Is this reflecting the role of biomass burning footprints as also inferred from the observations? I am aware that these might be features even part of the discussion but now some major adjustments seem to miss completely a sound justification based on process insights.

We have substantially reworked this section to offer a more logical description of the model set up.

For turbulent transport: (Line 337)

*“K is first calculated above the canopy using observed  $\sigma_w$  at 55 m (Sect. 2.1). The in-canopy K values are derived at each model level using a function that modifies the observed  $\sigma_w$  to decrease with height z (a result of surface friction and interception by the canopy). For the ATTO site, we adapt the function for  $\sigma_w(z)$  within the canopy from Wei et al. (2021), which uses observations at two heights (above and within the canopy) and interpolates linearly at heights in between. As the ATTO site has limited measurements within the canopy, it is advantageous to describe the in-canopy mixing using only above canopy measurements. To achieve this, we calculate the variation in  $\sigma_w(z)$  with height within the canopy as in Raupach et al. (1989) (Eq. 18), changing the relationship from a linear to a sine-based function. This results in a faster reduction in mixing with height, reflecting a greater separation between the canopy and above-canopy in the tropical forest. With this adjustment, measured in-canopy  $\sigma_w(24)$  is reproduced from above-canopy  $\sigma_w$ , giving confidence in our estimation at other heights (Fig. S10). This implies that the vertical mixing can be described using only above-canopy observations, and therefore simulations can be performed during periods when in-canopy measurements are missing.”*

For advection: (Line 273)

*“For the ATTO site, we investigate the inclusion of advection of NO<sub>2</sub> from biomass burning to heights 73 m – 200 m when the wind direction comes from 90°–150°. Biomass burning during the southern Amazon dry season (August–October) mostly occurs in the Arc of Deforestation in the E–SE Amazon border, a location named for the agriculture, logging and infrastructure expansion that occurs. Measurements at a site close to ATTO have identified increases of NO<sub>2</sub> coincident with increases in black carbon, attributed to biomass burning transport from this region (Cordova et al., 2004). Furthermore, back trajectories from HYSPLIT show airmasses to the ATTO site arriving from 90°–150° often originate from biomass burning locations (Pöhlker et al., 2018). Although NO<sub>2</sub> was not measured, Pöhlker et al. (2018) identify clear increases in biomass burning aerosol when winds arrive from these directions during months August–November. Although November is considered a transition month, biomass burning in the Arc of Deforestation sometimes still occurs. We select a value of k that best improves representation of observed O<sub>3</sub> concentrations in 2015 ( $k=2 \times 10^6$  ppbv m<sup>-1</sup>). The inclusion of upwind transport of NO<sub>2</sub> by advection is explored further in the main simulations below (Sect. 2.3).*

Line 194: “ an upper limit on reactivity”, possibly this feature of reactivity (OH) should be properly introduced and do you consider this feature of OH reactivity in your analysis; were there measurements taken and does the model calculate the OH reactivity? Am raising this issue since it is used as motivation to justify selection of some of the VOC emission settings having potentially important implications for the in-canopy chemistry (ozonolysis, aerosol formation efficiency).

This is actually about the consequences of using 100% beta-carophyllene SQT emissions on O3 reactivity. We adapt the text: (Line 210)

*“Terpenoids react with oxidants NO<sub>2</sub>, O<sub>3</sub> and OH; isoprene dominates OH reactivity due to its abundance and some sesquiterpenes demonstrate high reactivity with O<sub>3</sub>. Comparison of diurnal cycles of OH reactivity at 80 m to observations in 2018 by Pfannerstill et al. (2018) show the daily variability of OH reactivity is captured by the model, but the model underestimates the magnitude by 5–10 s<sup>-1</sup>, likely because we do not include a full suite of BVOCs and the simulation length prevents oxygenated products from accumulating (Fig. S6). β-caryophyllene is one of the most reactive sesquiterpenes with respect to O<sub>3</sub> and it is often measured to be among the most abundant (e.g., Costa et al., 2025; Gomes Alves et al., 2022; Jardine et al., 2011). Thus, by including only this species of sesquiterpene our results represent an upper limit on sesquiterpene O<sub>3</sub> reactivity.”*

Line 199: “Soil NO emissions are corrected from previous model versions so that emissions are added to the lowest model layer”. I was already curious about this important feature of tropical forest O3/NOx/VOC exchange having read that these emission are included in FORCAsT as a function of T (only?) whereas the few measurements might show a lower T dependence (also not having large temporal Tsoil differences) and where other features such as water status might be more relevant. Given some of the presented results on analysis of the NOx CRF, this feature should be much better explained and am curious to see the final results on simulated soil NO and canopytop NOx fluxes.

Here we now define the NO emission calculation in the model: (Line 220)

*“Soil NO emissions are temperature-dependent (Forkel et al., 2006) such that the emission factor (0.02 nmol m<sup>-2</sup> s<sup>-1</sup>) is scaled by an exponential dependency on the top layer soil temperature (β):*

$$\beta = e^{0.071 \cdot T(^{\circ}\text{C})} \text{ (Eq. 3)}$$

*Observed soil NO emission fluxes in undisturbed tropical forests span a large uncertainty range from 3 to 100 μg m<sup>-2</sup> hr<sup>-1</sup> (Bakwin et al., 1990, Erikson et al., 2002; Rummel et al., 2002; Lee et al., 2024). Most models of soil NO estimate values of 3 – 7 μg m<sup>-2</sup> hr<sup>-1</sup> (Yan et al., 2005; Yienger and Levy 1995) for tropical soils. We select an emission factor of 0.02 nmol m<sup>-2</sup> s<sup>-1</sup> for an average emission of 9 μgN m<sup>-2</sup> hr<sup>-1</sup> following sensitivity tests described in the supplementary (Fig. S7). This is at the upper end of previously simulated ranges (Yienger and Levy, 1995; Hudman et al., 2012) as suggested by Lee et al. (2024) but towards the lower end of the large range in observed NO emissions from tropical soils (Lee et al., 2024). Sensitivity tests considering the effect on NO<sub>x</sub> concentrations in comparison to observations at other tropical locations is included in the supplementary (Fig. S7).*

*NO emission fluxes and their sensitivity to driving variables remains a significant uncertainty. Global studies indicate increased emission with temperature (Luo et al., 2013; Ke et al. 2022), however studies on isolated tropical soils tend to show weaker temperature dependence (Cardenas et al., 1993). Water status is also likely a driving factor of soil NO emission, with limited NO fluxes in water-logged or dry soils and heavy rainfall triggering NO emission pulses (Yienger and Levy, 1995), which is not considered here.”*

Lines 203-204: “ with model drift (e.g., build-up of species) as with previous uses of the model, which were limited to 2-days” Here we see some of the text that you put at the beginning; that you have done initial experiments and that have resulted in some of the main changes in the setting as all described all before this paragraph. But also bring up this issue since your statement indicates that there might be structural problem with FORCAst/the followed approach of prescribing the advection. Is there any insight in why the model is showing a drift? Is this limited to continuous increases/decreases in trace gases or is also something seen in the physical metrics; moisture, energy (T) etc.? (given the online simulation of most of the energy/water balance/other processes in this column model approach).

We have changed the paragraph order and methods structure completely to improve readability and add model details, also placing sensitivity studies in a more appropriate location. We remove this paragraph as this model drift in temperature was observed in previous applications in the temperate site. Our simulations did not drift so we cannot confirm the origin or details.

Line 212: “To estimate a canopy exchange of NO<sub>x</sub> and O<sub>3</sub> (Ex) from the canopy to the atmosphere”; I should go back to the Rummel et al paper but what is expressed here with this canopy exchange, a flux (units?) or efficiency (ratio relative to..) or rate?

This has been clarified as a flux.

Section 3.1: you provide here at the beginning some more context that would be useful to shortly include at an earlier stage (e.g. to motivate the selected time frames being focus of the study).

Thanks for you suggestion, we agree that this should be introduced earlier to motivate the study. We have added text (quoted above).

Line 235; here you indicate something quite essential on differences in model simulated mixing conditions between the two years and which triggers straightaway the question why this is. But then you describe more the specific feature of turbulent mixing (daily cycles in coupling regimes) as a inferred from the observations. First describe those features and then start to discuss what the model simulates (and how this compares to those observations).

We have restructured this paragraph to first describe the mean condition and then describe the differences between years, which we think is the most logical process. (Line 529)

*“Below the canopy, vertical turbulent exchange in our simulations shows strongly decreased vertical mixing at night, with stable air throughout the canopy especially between 1:00–5:00 local time (5:00–9:00 UTC) in both years. By midday, the canopy is well-mixed down to the lowest 20%–30%, which remains more separated from the air above (Fig. S15). Mixing below the canopy is enhanced in the 2015 period compared to the 2013 period during daytime on average across the simulation periods (Fig. S16). In observations, Pfannerstill et al. (2018) also found increased turbulent features during 2015.”*

Line 244: “Measurements show windspeeds are maintained around 2–4 m s<sup>-1</sup> overnight at 70 m, whereas friction velocity, which controls simulated wind speed, drops substantially, driving this underestimation”. This is a very important statement; the measured wind speeds are maintained but the observed  $u^*$  (and used to constrain the turbulence calculations in FORECAST) is strongly reduced; how to reconcile this both on the measurements but also in the model. How high are the Richardson numbers?? And about what time averaging you are talking? Is there a role of intermittent exchange? And how do the model simulated wind speeds and  $u^*$  (prescribed) compare?? What is the model calculated  $Ri$ ? I am raising this since it is

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*Vertical turbulent exchange shows strongly decreased vertical mixing at night, with stable air throughout the canopy especially between 1:00–5:00 local time (5:00–9:00 UTC) in both years. By midday, the canopy is well-mixed down to the lowest 20%–30%, which remains more separated from the air above (Fig. S11 ...*

mentioned/know that turbulent transport between the canopy and overlaying atmosphere is so crucial on determining the efficient canopy exchange of these reactive species.

Thank you for these helpful diagnostics to consider. We evaluated this now and have added the following paragraph: (Line 489)

*“Divergence between friction velocity and horizontal wind speed above the canopy has implications on vertical mixing within the model. Observed wind speeds are low in the canopy at night, but remain high above the canopy. This indicates decoupling between the canopy and above under stable, stratified nighttime conditions. Frequently in 2013 and on several nights in 2015, nights show high wind shear and sustained wind speeds above the canopy (Fig. S13). Richardson numbers in both periods are above 0.25 at night, which suggests turbulence is suppressed and intermittent (Fig. S14). However, the model likely overestimates the degree of turbulence suppression in 2013. The simulated flow has very low shear at night, meaning shear-driven mixing in the boundary layer is underestimated (Fig. S13a, S14c). This arises from the model reliance on friction velocity to constrain turbulent exchange, meaning intermittent turbulence is not captured when friction velocity is low. As a result, vertical mixing in the above-canopy space is overly weak on some nights in the simulations, with possible implications for the representation of exchange with the canopy.”*

Line 254/255: “day-to-day variability driven by mixing cannot be fully represented”. This raises the question to what extent mixing conditions explain the day-to-day variability; given that O3 deposition is mostly dominated by the surface uptake efficiency, expressed by the deposition velocity (vd), and then also by concentration differences due to supply of different air masses, it would be good see a comparison of the day-to-day variability in simulated and observed vd. This would indicate about differences in the simulated and observed physical drivers of surface uptake (radiation as a function of cloud cover, moisture). Possibly this is tackled later on this ms.

We have tried to clarify that we are not stating that mixing is definitely an important part of the O3 concentrations: (Line 559)

*“One of the vertical mixing components ( $\sigma_w$ ) is not available for 2013, so any contribution to day-to-day variability ~~that may occur from~~ mixing cannot be fully represented.”*

We do not have observed vd at this site but we now discuss daily variability later in Sect. 3.2. and add additional figures to the supplementary. The additional text can be found later in this response.

Line 275: you are directly bringing in a misrepresentation of SQT emissions as a likely explanation for a misrepresentation of nocturnal O3 mixing ratios. This is really a large step requiring a more detailed analysis of a potential misrepresentation by the model of the turbulent mixing conditions. How does the model simulated wind speed/ $u^*$  for those nights compare to the observations? I anticipate those for those nights, with still relatively high O3 values, that there is not much a stratification and where O3 concentration changes might be dominated by advection, deposition and not so much by any of this chemistry (including the titration by soil emitted NO) also with those emitted gases being efficiently diluted due to the ongoing mixing.

We did not intend to suggest this as a likely explanation. We fully agree with your hypothesis, implied with the sentence ‘high nighttime O<sub>3</sub>, such as on November 14<sup>th</sup> 2015, are more likely related to turbulent features’. However, we feel it is worth acknowledging the uncertainty relating to sesquiterpene concentrations in the model since this manuscript is about chemistry, with a large focus on sesquiterpene chemistry. To resolve this, we have moved the sentence about sesquiterpene chemistry and changed the paragraph to reflect the further analysis: (Line 589)

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"In both 2013 and 2015 simulation periods, the model performs worst overnight, often failing to capture nights in which O<sub>3</sub> is maintained at high concentrations, including in the lower canopy on three nights in 2015 (Fig. 3). High nighttime O<sub>3</sub> such as on November 14<sup>th</sup> 2015, are most likely related to missing turbulent features in our model. Nights with high O<sub>3</sub> concentrations above the canopy are often associated with high wind shear that is not reproduced by the model, suggesting turbulence within the boundary layer that brings O<sub>3</sub> to the canopy top (Fig. S13). Below the canopy, nighttime O<sub>3</sub> concentrations are reproduced on most nights in the model. The model captures the O<sub>3</sub> diurnal cycle more closely in the tropics compared to previously simulated temperate forests (Ashworth et al., 2015; Wei et al., 2021) due to the smaller influence from transported air masses at this site.

Figures 4a and 4b confirm that, whilst the daytime O<sub>3</sub> profiles are a good match to observations, nighttime profiles are underestimated, especially above the canopy. The step-change in O<sub>3</sub> gradient below the canopy in observations of the 2013 period suggests some decoupling between the canopy and above occurs, as also indicated by the sustained wind and low friction velocity above the canopy, described above (Figs. S12b, S12c). The lack of intermittent turbulence above the canopy in the simulations leads to underestimation of the above canopy O<sub>3</sub> profile, but decoupling results in a smaller bias below the canopy. The shape of the daytime vertical profile in the 2015 period is better captured than in the 2013 period; the observed 2013 vertical concentration gradient is steeper than 2015 but this is not replicated by the model."

Line 285: seeing here a reference to the simulated OH concentrations, how do these numbers compare to previously reported OH estimates for tropical rainforest. Do you have any measurements available on OH for these 2013/2015 measurements? Am asking since we know from past work on Amazon forest oxidation chemistry that many AC models were generally largely underestimating OH also associated with a misrepresentation of some of the VOC chemistry.

There are unfortunately no ATTO measurements available of OH for a direct comparison. We compare to the GoAmazon measurements, which give midday peak OH concentrations. We use only 3 BVOC emissions species and do not initialize the model with any long lived VOCs so we expect that our chemistry has the same limitations as other AC models: (Line 616)

"Simulations of 2015 with transported NO<sub>2</sub>, which produces additional O<sub>3</sub>, consequently have a higher oxidative capacity. In pristine conditions, midday peak OH concentrations above the canopy are on average  $1.3 \times 10^6 \text{ cm}^{-3}$ , decreasing to  $0.4 \times 10^6 \text{ cm}^{-3}$  within the canopy (not shown). The addition of transported NO<sub>2</sub> increases OH by 2x above the canopy, with diminishing differences between simulations below the canopy. Literature values from recent site measurements report  $1 \times 10^6 \text{ cm}^{-3}$  (Jeong et al., 2021), of similar magnitude to our simulations."

Around lines 295 and Figure 3, you discuss the NO<sub>2</sub> concentrations and the changes in the NO/NO<sub>2</sub> ratios but not so much the absolute simulated versus observed NO and NO<sub>2</sub> mixing ratios. How does the supply of NO<sub>2</sub> by advection compare to the contribution by the soil NO emissions?? If you would have some 5-10 ppb NO<sub>2</sub> being present in the surface/mixed layer than I would expect that there would be a reduced role of soil NO emissions but for any surface concentrations ~1ppb, the soil emissions might provide a relevant source and impacting the in- and above concentration profiles also as a function of the mixing conditions (nighttime, little mixing? strong accumulation, resulting in a morning burst of NO<sub>x</sub> ventilated out of the canopy; one of the main reasons to apply multi-layer exchange models).

Your predictions are all in agreement with our simulation results, so it seems the model is working as expected. We now add some description of the NO<sub>x</sub> concentrations relative to measurements at other locations in the Amazon, as there are no reliable NO and NO<sub>2</sub> measurements available at ATTO currently. We also show the above-canopy NO<sub>x</sub> concentrations in the supplementary to show that we are not enhancing NO<sub>2</sub> by 5 – 10 ppb even with advection events. (Line 627)

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*“Even with the inclusion of transported NO<sub>2</sub>, NO<sub>x</sub> concentrations above the canopy remain below 1 ppbv (Fig. S18). Transported NO<sub>2</sub> can increase the above-canopy nighttime NO<sub>2</sub> concentrations from ~300 pptv to up to 600 pptv (e.g., on the 16<sup>th</sup> November 2015), increasing daytime NO as well. The values in pristine conditions compare well to observations at another Amazon site that measures pristine nighttime values of 350 pptv but find pollution enhancements of up to 1800 pptv (Cordova et al., 2004). Simulations show a distinct NO peak at sunrise as soil emissions are released from the canopy. These peaks show significant daily variability from 25 pptv to over 100 pptv, with daytime mean concentrations of 25 pptv without transported NO<sub>2</sub> and 50 pptv when NO<sub>2</sub> transport is included (Fig. S18c). The addition of transported NO<sub>2</sub> results in a less steep decay in NO from the midday peak. These values fit with observations recording 20 pptv – 50 pptv above the Amazon forest canopy (Bakwin et al., 1990; Kuhn et al., 2010). Soil NO emissions therefore affect above-canopy NO<sub>x</sub> concentrations significantly across all simulations.*

*Ground-level concentrations of NO depend strongly on O<sub>3</sub> concentrations, with even a few ppbv of O<sub>3</sub> rapidly removing emitted NO. Our simulations show very low nighttime O<sub>3</sub> concentrations (in agreement with observations), resulting in NO concentrations of 2 pptv – 4 ppbv. This is consistent with observations from Rummel et al., (2002) who record lower NO concentrations of up to 2 ppbv but higher nighttime O<sub>3</sub> values. Conversely, ground-level daytime O<sub>3</sub> at the ATTO site is higher than measured by Rummel et al. (2002) and simulated daytime NO concentrations are below their measurements of 1.2 ppbv. Our daytime ground-level NO concentrations are closer to those of Bakwin et al. (1990) at 450 pptv.”*

We analyse the role of soil vs transported NO<sub>x</sub> in Sect. 3.4. including accumulation and bursts of NO from morning ventilation.

Line 317: “This implies the chemistry in the canopy is not strongly affected by the temperature changes between years, nor the deposition affected by other meteorological differences.” This sentence suggests that temperature differences are the main explanation for differences in O<sub>3</sub> deposition/role of chemistry. Possible should start from a hypothesis; what drives O<sub>3</sub> deposition and how much is the anticipated role of chemistry and on what physical/dynamical drivers does this depend. The chemistry might also depend on changes in radiation (photolysis), water vapour (OH production) but the ozone sinks also likely depend on soil water regulation of stomatal control (and energy partitioning and ABL dynamics through impact on evapotranspiration). So far in the analysis, no information on differences between the seasons or on model simulated physical drivers of all these processes have been presented.

We apologise that this was not clearly phrased. We simply intended to mention that, without transported NO<sub>x</sub>, 2013 and 2015 have practically identical deposition fluxes, despite having different meteorology (particularly temperature, which is described earlier on). We have changed this to be clear we are giving an overview of the total canopy flux in this paragraph, and not assigning any explanation at this stage. (Line 692)

*“Figure 5a shows the mean total canopy flux of O<sub>3</sub> over the simulation period, divided into net chemical loss and deposition (as in Eq. 19). The O<sub>3</sub> mostly originates from above the canopy, meaning the canopy is a net O<sub>3</sub> sink. The total flux in 2013 is -2.4 nmol m<sup>-2</sup> s<sup>-1</sup> compared to -3.9 nmol m<sup>-2</sup> s<sup>-1</sup> in 2015, whereas the total flux in the 2013 simulation period and an idealised 2015 period with no transported NO<sub>2</sub> are very similar (i.e. the main difference between 2013 and 2015 simulation periods is related to effects of transported NO<sub>x</sub>). Simulations without sesquiterpene emissions have very little effect on the total flux.”*

We assume, when you say differences between seasons have not been presented, that you mean the impact on meteorological differences have not been analysed with respect to their effect on chemistry and deposition fluxes. Some analysis comes later in the text. We do introduce differences between the seasons (temperature, mixing) in Sect. 3.1.

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Line 325; the statement makes clear that you were working from a hypothesis that T differences would result in changes in sesquiterpene emissions impacting ozone deposition (which is interesting but which could have been supported by previous findings indicating that this is a relevant term), relative to other controls on tropical forest O<sub>3</sub> deposition. But then those other controls should be properly analysed on the combined use of the model experiments and measurement data.

The start of this paragraph simply describes Fig. 4a, which includes sensitivity tests with and without sesquiterpene emissions and transported NO<sub>2</sub>. The aim of these tests was precisely to identify if there was an effect on O<sub>3</sub> deposition and whether they are relevant terms. We have attempted to express this explicitly in a new 'Sect 2.3. Simulations' (shown in a later comment when this issue appears again).

We have signposted this paragraph to indicate we are now describing the proportion of chemical vs depositional losses for each simulation. The analysis of these results follows on for several more paragraphs. (Line 697)

*"Considering the breakdown of the flux into chemical and depositional components, we find that deposition accounts for the majority of O<sub>3</sub> losses in all simulations."*

Line 331: I had to read the following statement a couple of times " Figure 4b shows the equivalent losses scaled by O<sub>3</sub> concentration to obtain a canopy loss velocity". The way I interpreted it now also checking the figures is that you are comparing the flux/concentration (= canopy-scale deposition velocity) differences for the various runs in/excluding SQTs, for the different years. First of all, better to report these vd values in cm s<sup>-1</sup>, a common unit used by the deposition community. It becomes clear that the role of chemistry in the O<sub>3</sub> removal is quite small but that there might be differences between the years and also between the model simulated and measurement inferred vd. Then it would be good to discuss why the model simulated vd values are higher than those reported by Rummel et al. You address this partly in the discussion by referring to moisture transitions (dry to wet season) but since you have not presented in the previous sections anything on how the role of moisture status is affecting O<sub>3</sub> deposition in your model experiments (vs observations), this explanation becomes totally speculative.

We described it as a loss velocity to indicate that it includes chemistry and dry deposition and to make it clear when we are describing the total vs just the deposition component. We have changed it to 'canopy-scale deposition velocity' as it seems that will be more understandable to the community.

We have now additionally analysed the daily deposition velocity and stomatal and cuticular conductances to show that there is likely very little stomatal limitation in our simulations (and high observed relative humidity implying this is correct behaviour from the model), all of which point to 'wet season' behaviour: (Line 764)

*"Diurnal patterns of individual flux terms (chemistry, deposition and storage) show the same features identified by Rummel et al. (2007) such as an increase in storage in the morning as vertical transport brings O<sub>3</sub> into the canopy from above (Fig. S20). Observed fluxes are also similar in magnitude to our simulations but cannot be directly compared as they depend strongly on O<sub>3</sub> concentration. Observations of canopy deposition velocities are larger in the wet season compared to the dry season, attributed to humidity-driven stomatal limitation in the dry season. Our simulated deposition velocities are within the range of wet season observations but are higher than dry season averages of  $-0.5 \text{ cm s}^{-1}$  (Rummel et al., 2007). Our simulations show high relative humidity (Fig. S21) and daytime temperatures (Fig. 2) close to the simulation optimum parameter for stomatal conductance (301 K), suggesting little stomatal limitation and therefore 'wet season' behaviour. This is consistent with evaluation of the energy balance and Bowen ratio described above (Sect. 3.1, Fig. S17). Day-to-day variability in deposition velocity in the simulations follows variability in temperature and PAR (Fig. S22). The 2013 period exhibits lower average PAR and greater daily variability (including a cool, cloudy day on the 4<sup>th</sup>), resulting in lower average stomatal*

**Deleted:** Whilst the simulated O<sub>3</sub> fluxes are lower than measurements recorded in the Amazon by Rummel et al. (2007), the

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*conductance than the 2015 period (Fig. S23). However, differences in deposition velocity between simulations are likely also related to changes in O<sub>3</sub> distribution within the canopy.”*

Line 343: “The chemical loss velocity profiles for simulations without sesquiterpene emissions show that loss by reaction with soil NO is of similar magnitude to O<sub>3</sub> removal by other BVOCs and the in-canopy profiles are very similar between years, which suggests sesquiterpenes are responsible for the differences in net chemistry” Now that I read these findings it becomes more and more clear. It seems that you did the model experiments and then found these results, it becoming clear about these differences in especially the BVOC emissions (between 2013/2015, model versus observations?) explaining some of the differences in O<sub>3</sub> deposition (or am I wrong?). You could tackle some of my main criticism, making this clear from the beginning (starting with the hypothesis on the important role of changing SQT emissions impacting O<sub>3</sub> removal?). (Still you need to substantially improve on more properly evaluating the other drivers of processes involved in O<sub>3</sub> removal by a tropical forest canopy).

We have reorganised section 2 to clearly outline our motivation for the simulations and study goals from the beginning. We are testing how sensitive O<sub>3</sub> chemistry is to sesquiterpenes: (Line 352)

“2.3. Simulations

*Using the parameters above, we produce five simulations of the ATTO site for the periods 1–13 November 2013 and 11–23 November 2015 to explore effects of meteorology, sesquiterpenes and upwind transport of NO<sub>2</sub> in more detail (Table 2). The model uses observations of wind direction,  $\sigma_w$ ,  $u^*$  and PAR recorded above the canopy (55 m) as described in Sect. 2.1. (Figs. S1, S2). For simulations of 2013, we duplicate  $\sigma_w$  from 2015 due to missing observations, assuming that the average turbulence was similar between years. November 2013 is considered to represent an average November, whereas the 2015 period is used for comparison to an El Niño period in which increased biomass burning occurred.*

<i>Simulation name</i>	<i>NO<sub>x</sub> source</i>	<i>Sesquiterpene emission</i>
<u>2013</u>	<u>Soil NO</u>	<u>Yes</u>
<u>2013 No SQT</u>	<u>Soil NO</u>	<u>No</u>
<u>2015</u>	<u>Soil NO, transport of NO<sub>2</sub></u>	<u>Yes</u>
<u>2015 No SQT</u>	<u>Soil NO, transport of NO<sub>2</sub></u>	<u>No</u>
<u>2015 pristine</u>	<u>Soil NO</u>	<u>Yes</u>

*Table 2: Variables in five simulations investigating effects of NO<sub>x</sub> sources and sesquiterpene emissions.*

*We test the hypothesis that sesquiterpene emissions have an important role in canopy-scale O<sub>3</sub> deposition fluxes via chemical removal inside the canopy by including simulations with and without sesquiterpene emissions. We also consider if transported NO<sub>2</sub> from biomass burning in 2015 could impact O<sub>3</sub>, BVOC and NO<sub>x</sub> exchange at the canopy top.”*

This paper aims to evaluate whether and how in-canopy chemistry is important. Therefore, we do not intend to focus on dry deposition (which could in itself be another paper). We have developed the paragraph to better describe and evaluate deposition in our simulation, confirming that to the best of our knowledge the deposition scheme is performing as expected (provided in the response above).

Line 381: “ The significant diurnal variability in O<sub>3</sub> production suggests that canopy escape efficiencies of precursors (especially NO<sub>x</sub> and sesquiterpenes) should be investigated across the diurnal cycle”; see also

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**Deleted:** *Diurnal patterns of individual flux terms (chemistry, deposition and storage) show the same features identified by Rummel et al. (2007) such as an increase in storage in the morning as vertical transport brings O<sub>3</sub> into the canopy from above (Fig. S14). ... Diurnal patterns of individual flux terms (chemistry, deposition and storage) show the same features identified by Rummel et al. (2007) such as an increase in storage in the morning as vertical transport brings O<sub>3</sub> into the canopy from above (Fig. S...*

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my previous comment on carefully checking the role of temporal (diurnal) variability in the NO<sub>x</sub> exchange regime (soil emissions vs turbulent exchange vs canopy-scale fluxes). By the way, this triggers straightaway a relevant question; does the model capture observations of bi-directional NO<sub>x</sub> exchange (am pretty convinced that this is happening where deposition might prevail during polluted conditions and the canopy is a source for the clean conditions expressed by a positive CRF).

We also thought these were interesting things to investigate and Sect. 3.4 is dedicated to exploring these relationships.

Around line 400: I am now wondering how K versus u\* would be a better approximation of the escape efficiency (or canopy residence time). Where do the differences arise with both parameters being strongly connected and expressing a measure of turbulent transport.

We state in the text that it may be the inclusion of sigma-w, but as this is not a major point of the paper, we are happy to remove it. The paragraph now reads: (Line 867)

*“The escape efficiency of sesquiterpenes ranges from 45%–55% between simulations. The highest escape efficiency of 55% occurs in 2015 pristine conditions. When transport of NO<sub>2</sub> is included, this decreases to 48% as a result of higher O<sub>3</sub> concentrations. Both simulations of the 2015 period have a higher escape efficiency than the 45% in 2013. The MEGAN 2.0 BVOC emissions model includes an escape efficiency to account for BVOC losses within the canopy, based on chemical lifetime, u\* and canopy depth (Guenther et al., 2006). This parameterisation results in canopy escape efficiencies from 10% (in the presence of high O<sub>3</sub>) to 60%. Our results, in relatively low O<sub>3</sub> conditions compared to global averages, fit realistically within this wide range. We find a significant correlation exists between daily mean escape efficiency and u\* (r<sup>2</sup>=0.69, p<<0.05; Fig. S25). This indicates that, for single-layer canopy models seeking a simple parameterisation, the current equation in MEGAN 2.0 is functional.”*

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Reading section 3.4, I really wonder how you have tackled the NO<sub>x</sub> escape efficiency diagnostics. This also refers to some of the previous raised points. I would see that the advection component brings in air enhanced in NO<sub>2</sub> (when upwind biomass burning has happened) which changes the gradient from an emission to a deposition gradient (assuming that in the in-canopy NO<sub>x</sub> concentrations are dominated by the in-canopy sources and sinks) and with the canopy escape efficiency, expressed by the Canopy Reduction Factor (CRF, canopy/surface layer flux/soil NO emission flux), changing from a positive to a negative value. But are you results indicating that the contribution by advection was never that large that deposition occurred?? Was it only indeed reducing the escape efficiency (therefor I asked to potentially mention/show the changes in the simulated/observed surface layer NO<sub>x</sub>).

The equations are given in the first section and it is simply a case of summing the correct terms together that are directly output for the model and taking care to scale for grid size / units etc. We have added to the equation description (shown above). Here we also attempt to explain the soil NO escape efficiency as it is not the same as the NO<sub>x</sub> flux or CRF. Sect. 3.4.1 focuses on the soil NO flux: (Line 897)

*“Figure 8a shows the NO<sub>x</sub> budget terms below the canopy and the overall escape efficiency of soil NO<sub>x</sub>. The soil NO<sub>x</sub> escape efficiency is different than the canopy NO<sub>x</sub> flux (described in the next section) in that it excludes the contribution from upwind transported NO<sub>2</sub> into the canopy. To exclude this, we estimate the contribution from transported NO<sub>2</sub> entering the canopy using a simulation with no soil NO source and subtract this from the simulation of 2015 with transported NO<sub>2</sub> (as described in Sect. 2.4; Eq. 20). The motivation for isolating only the soil NO that leaves the canopy is to inform how soil NO emission should be represented by a single-layer canopy model. The comparison between 2015 and pristine 2015 reveals*

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*changes in soil NO emission resulting from a change in chemical environment (e.g., the NO<sub>x</sub> production and loss terms depend on the background environment)."*

As for the NO<sub>x</sub> flux, we actually don't find the canopy often becomes a net sink as advection does not increase NO<sub>x</sub> concentrations significantly enough (we now include this information on NO<sub>x</sub> concentrations in Sect 3.1.). The NO<sub>x</sub> flux is now addressed in Sect. 3.4.2: (Line 980)

*"Here, we consider how transported NO<sub>2</sub> above the canopy in the 2015 period affects the total canopy NO<sub>x</sub> flux. When NO<sub>x</sub> concentrations above the canopy are high, as can happen when NO<sub>2</sub> is transported, the canopy can become a net sink. This bi-directional exchange means the canopy flux can switch from positive to negative in polluted conditions.*

*Figure 10a highlights the first 6 days of the simulation to show that even with transport of NO<sub>2</sub>, the canopy largely remains a NO<sub>x</sub> source. This is likely because NO<sub>x</sub> concentrations at the canopy top are not significantly enhanced in our simulations (Fig. S18). Exceptions occur when NO<sub>2</sub> transport occurs during the night; the transfer into the canopy at individual moments are greater than the soil NO escape, making the canopy a NO<sub>x</sub> sink (also see Fig. S27b). This implies the canopy must remain a substantial depositional sink overnight."*

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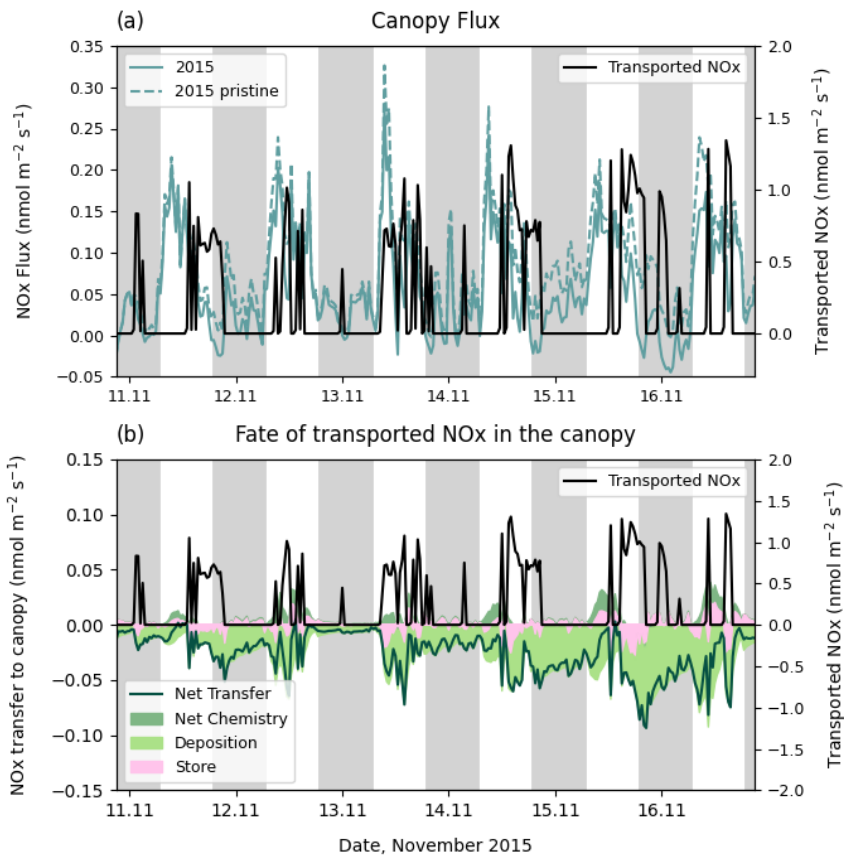


Figure 10: (a)  $\text{NO}_x$  transported from upwind above the canopy (black solid line) compared to the canopy-scale  $\text{NO}_x$  flux in 2015 for simulations with transported  $\text{NO}_x$  (teal solid line) and with pristine conditions (teal dashed line). (b)  $\text{NO}_x$  transported from upwind above the canopy (black solid line) compared to transported  $\text{NO}_x$  entering the canopy (green solid line), divided into deposition (light green shading), net chemistry (dark green shading) and storage (pink shading). Tick marks on the x axis are placed at midnight.

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Line 431; "and enhanced deposition"; this stresses again that a lot of relevant information is missing; how does the model treat  $\text{NO}_x$  deposition?? Role of compensation point? Stomatal versus non-stomatal removal?

The deposition scheme is now explained in the methods and the stomatal and cuticular conductances for water are shown in the supplementary. Of course these change with each species, but the deposition scheme implemented is quite standard. We do not include a compensation point for  $\text{NO}_2$  (assuming you

mean a point at which leaves emit NO<sub>2</sub> rather than deposit) and only consider deposition. This paper is not intended to evaluate the deposition scheme (as we do not have any deposition measurements at the site).

We add some extra analysis and clarifying information to communicate that deposition fluxes increase because NO<sub>2</sub> concentrations within the canopy markedly increase overnight. We hope this provides a greater picture of the canopy process: (Line 921)

*“Daylight hours have the highest escape efficiency, whereas NO<sub>x</sub> release overnight is suppressed by in-canopy storage and enhanced deposition fluxes.*

*We first consider the role of storage in the diurnal pattern, which refers to NO<sub>x</sub> that becomes trapped in the canopy space due to slow vertical mixing. Our simulations find the greatest transfer of stored NO<sub>x</sub> from the canopy occurs at sunrise when stable separation between the canopy and above breaks down and photochemistry is initiated (Fig. 8, pink shading). This is very pronounced in 2015 when the escape from the canopy is greater than the instantaneous soil emission rate. This indicates strong separation between the below and above-canopy environment overnight that allows NO<sub>x</sub> to build up.*

*NO emitted from the soil is rapidly oxidized to NO<sub>2</sub> when O<sub>3</sub> is present, but during the night, NO accumulates near the ground. At night, there is a significant flux to the soil and lower canopy surfaces (Fig. S26). As stomata are closed, this is likely non-stomatal deposition to the soil and cuticles that is high due to build-up of NO<sub>2</sub> in the lower canopy originating from the soil in low turbulence. With the onset of turbulent mixing under daylight, O<sub>3</sub> oxidizes NO to NO<sub>2</sub>, which is transported upwards but partially taken up by deposition to vegetation (Gut et al., 2002; Breuninger et al., 2013; Chaparro-Suarez et al., 2011). The greatest daytime deposition flux therefore also occurs at the onset of mixing as NO<sub>x</sub> at the surface is brought to heights with greater leaf area (Fig. S26). However, the daytime deposition flux is lower than nighttime on average due to lower daytime concentrations.”*

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Line 481: “Most resistance-based deposition schemes include an aerodynamic resistance that is lower when vertical turbulence is higher, however this does not account for enhanced deposition of NO<sub>2</sub> during stagnant conditions overnight and may therefore underestimate NO<sub>x</sub> losses to the canopy”. I have been reading over this sentence a couple of times wondering what to make of it; are you indicating resistance based deposition schemes would have strongly reduced deposition over night whereas in the canopy models, considering deposition inside the forest canopy, this Ra would not limit deposition?? But inside the forest canopy, the NO<sub>x</sub> also needs to overcome the (strongly reduced or enhanced (with a warmer soil than crown-layer) turbulent transport to the leaf/other surfaces. It raises an additional question how FORCAST treats the layer-scale deposition process (including also the turbulent and quasi-molecular diffusion term in calculating leaf uptake??).

The deposition scheme is more clearly explained in Sect. 2. The resistance scheme includes R<sub>b</sub> but does not have an R<sub>a</sub> term since turbulent transport, the concentration profile and resistances are resolved at each layer. Omitting R<sub>a</sub> is standard with a multi-layer canopy. We have tried to clarify our statement: (Line 1033)

*“Most single-layer canopy deposition schemes do not account for continued deposition of NO<sub>x</sub> stored within the canopy overnight. The resistance term includes an aerodynamic resistance that is lower when vertical turbulence is higher, describing enhanced transport into the canopy. However, a single layer canopy cannot account for canopy storage, missing possible enhanced deposition of NO<sub>2</sub> during stagnant conditions overnight and may therefore underestimate NO<sub>x</sub> losses to the canopy.”*

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Line 499/500 “This suggests that increased transport of biomass burning pollution reduces the ability of the canopy to remove O<sub>3</sub> from the atmosphere”. I think this is a too strong claim; yes there is some impact of

changes in the SQT ozonolysis contribution to O3 deposition but this term seems to be really small and you would need to compare this to the uncertainty in the model-simulated and observation derived vd.

We agree that this is in fact a minor effect and have removed the sentence

Lines 509: “ Deposition schemes are highly parameterised and remain a substantial uncertainty in canopy modelling, and this study did not explore the leaf- or soil level parameterisations in detail. As the majority of simulated O3 and NOx canopy losses occur via this pathway, greater focus is needed on accurately representing deposition within the canopy and its response to changing meteorological conditions”. This statement of the discussion actually expresses what I think it the main issue with the presented analysis; to make claims on the role of other drivers of O3 deposition to tropical forests, you need to know well how your modelling system, used to make sense of the field observations, performs on these key drivers.

We hope information provided earlier in this document helps to inform the deposition scheme and its effect. Compared to existing schemes, it is very standard and the main limitation is lack of site specific deposition measurements and general uncertainty around non-stomatal processes that would exist regardless of the choice of scheme.

We have added another statement on the NO2 deposition in our simulation, as this arose in response to an earlier comment: (Line 1078)

*“Our simulations estimate sustained NO<sub>2</sub> deposition occurring overnight via non-stomatal pathways, leading to net canopy deposition when NO<sub>2</sub> is transported to the site (Fig. 10). Greater understanding of the partitioning between stomatal, cuticular and soil deposition is required to evaluate these conclusions.”*

Line 543: “Similarly, the absence of reliable NOx emissions and concentration measurements at the ATTO site prevents a direct evaluation of NOx concentrations in the model.”. I wonder about this. Possibly these data are not available for the specific periods but in many of the Amazon forest campaigns (LBA) but also at ATTO, there have been many measurements collected on NOx canopy concentration profiles (and soil NO emissions) that could serve to at least show some representation by the model in reasonable agreement with the observations.

We have thoroughly searched the literature for amazon profiles and found data from ABLE and LBA. Data recorded at ATTO was advised not to be used as instrument errors were identified. We have added text in the main results and supplementary showing comparison to observations. The main text is here: (Line 628)

*“Even with the inclusion of transported NO<sub>2</sub>, NO<sub>x</sub> concentrations above the canopy remain below 1 ppbv (Fig. S18). Transported NO<sub>2</sub> can increase the above-canopy nighttime NO<sub>2</sub> concentrations from ~300 pptv to up to 600 pptv (e.g., on the 16<sup>th</sup> November 2015), increasing daytime NO as well. The values in pristine conditions compare well to observations at another Amazon site that measures pristine nighttime values of 350 pptv but find pollution enhancements of up to 1800 pptv (Cordova et al., 2004). Simulations show a distinct NO peak at sunrise as soil emissions are released from the canopy. These peaks show significant daily variability from 25 pptv to over 100 pptv, with daytime mean concentrations of 25 pptv without transported NO<sub>2</sub> and 50 pptv when NO<sub>2</sub> transport is included (Fig. S18c). The addition of transported NO<sub>2</sub> results in a less steep decay in NO from the midday peak. These values fit with observations recording 20 pptv – 50 pptv above the Amazon forest canopy (Bakwin et al., 1990; Kuhn et al., 2010). Soil NO emissions therefore affect above-canopy NO<sub>x</sub> concentrations significantly across all simulations.*

*Ground-level concentrations of NO depend strongly on O<sub>3</sub> concentrations, with even a few ppbv of O<sub>3</sub> rapidly removing emitted NO. Our simulations show very low nighttime O<sub>3</sub> concentrations (in agreement with observations), resulting in NO concentrations of 2 pptv – 4 ppbv. This is consistent with observations*

*from Rummel et al., (2002) who record lower NO concentrations of up to 2 ppbv but higher nighttime O<sub>3</sub> values. Conversely, ground-level daytime O<sub>3</sub> at the ATTO site is higher than measured by Rummel et al. (2002) and simulated daytime NO concentrations are below their measurements of 1.2 ppbv. Our daytime ground-level NO concentrations are closer to those of Bakwin et al. (1990) at 450 pptv.”*

Line 550: Reading the statement “Differences in in-canopy O<sub>3</sub> chemistry between 2013 and 2015 in our simulations only cause a small change in total loss velocity, suggesting there is not an urgent need for in-canopy chemical loss parameterisations that vary with environmental conditions” reminds me of some of the main conclusions drawn in a study on the use of a global chemistry-climate model including an explicit representation of the canopy interactions to study the impact of land cover and land use changes on composition and climate (Ganzeveld et al., 2010); the overall impact of the considered land use and cover as well as emission changes is not that large due to the role of compensating effects as considered in the multi-layer representation of the forest canopy environment.

We have added the following text: (Line 1143)

*“These compensating effects of the canopy on above-canopy chemical composition in fact arise in multilayer canopies for several species and in response to various perturbations (Ganzeveld et al., 2010).”*

Line 564: I strongly support your closing statement “We further highlight that a diurnally varying parameterisation of soil NO<sub>x</sub> escape could improve representation of variability in NO<sub>x</sub> chemistry; the diurnal cycle of soil NO<sub>x</sub> escape is strongly related to vertical turbulence, combined with an additional spike in morning escape efficiency that is important to consider for accurate simulation of O<sub>3</sub> production” since this was also a feature that we already demonstrated in the Ganzeveld et al. 2002 studies. I though would argue we don’t need so much further improved parameterization of this process. It has already been shown that inclusion of multi-layer canopy model representation, replacing the commonly applied big-leaf approaches is feasible but also very much justified for many scientific reasons (see also Vermeuel et al., 2025).

We have added the following text: (Line 1136)

*“Whilst inclusion of multilayer canopies is becoming more common (e.g., Vermuel et al., 2024), there remain many cases where single layer canopies are still (and will continue to be) in use due to computational constraints... We further agree with existing studies of pristine environments (e.g., Ganzeveld et al., 2002a,b) that a diurnally varying parameterisation of soil NO<sub>x</sub> escape could improve representation of variability in NO<sub>x</sub> chemistry; the diurnal cycle of soil NO<sub>x</sub> escape is strongly related to vertical turbulence, combined with an additional spike in morning escape efficiency that is important to consider for accurate simulation of O<sub>3</sub> production (Fig. 8).”*

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