Review of paper acp-2026-161: Linking In-Canopy Chemistry to Above-Canopy O3, BVOCs, and NOx 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, NOx 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 NOx 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, NOx 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 NOx 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.

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.

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.

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?

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?

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 NOx 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 NOx 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.

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).

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 canopy-top NOx fluxes.

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).

Line 212: “To estimate a canopy exchange of NOx and O3 (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?

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).

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).

Line 244: “Measurements show windspeeds are maintained around 2–4 m s-1 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 mentioned/known that turbulent transport between the canopy and overlaying atmosphere is so crucial on determining the efficient canopy exchange of these reactive species.

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 O_3 deposition is mostly dominated by the surface uptake efficiency, expressed by the deposition velocity (v_d), 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 v_d. 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.

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.

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.

Around lines 295 and Figure 3, you discuss the NO2 concentrations and the changes in the NO/NO2 ratios but not so much the absolute simulated versus observed NO and NO2 mixing ratios. How does the supply of NO2 by advection compare to the contribution by the soil NO emissions?? If you would have some 5-10 ppb NO2 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 NOx ventilated out of the canopy; one of the main reasons to apply multi-layer exchange models).

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 O3 deposition/role of chemistry. Possible should start from a hypothesis; what drives O3 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.

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 O3 deposition. But then those other controls should be properly analysed on the combined use of the model experiments and measurement data.

Line 331: I had to read the following statement a couple of times " Figure 4b shows the equivalent losses scaled by O3 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 v_d values in cm s^{-1}, a common unit used by the deposition community. It becomes clear that the role of chemistry in the O3 removal is quite small but that there might be differences between the years and also between the model simulated and measurement inferred v_d. 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 O3 deposition in your model experiments (vs observations), this explanation becomes totally speculative.

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 O3 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 O3 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 O3 removal?). (Still you need to substantially improve on more properly evaluating the other drivers of processes involved in O3 removal by a tropical forest canopy).

Line 381: " The significant diurnal variability in O3 production suggests that canopy escape efficiencies of precursors (especially NOx and sesquiterpenes) should be investigated across the diurnal cycle"; see also my previous comment on carefully checking the role of temporal (diurnal) variability in the NOx 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 NOx 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).

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.

Reading section 3.4, I really wonder how you have tackled the NOx 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 NO2 (when upwind biomass burning has happened) which changes the gradient from an emission to a deposition gradient (assuming that in the in-canopy NOx 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 NOx).

Line 431; " and enhanced deposition"; this stresses again that a lot of relevant information is missing; how does the model treat NOx deposition?? Role of compensation point? Stomatal versus non-stomatal removal?

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 NO2 during stagnant conditions overnight and may therefore underestimate NOx 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 NOx 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??).

Line 499/500 “This suggests that increased transport of biomass burning pollution reduces the ability of the canopy to remove O3 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 v_d.

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.

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.

Line 550: Reading the statement “Differences in in-canopy O3 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.

Line 564: I strongly support your closing statement “We further highlight that a diurnally varying parameterisation of soil NOx escape could improve representation of variability in NOx chemistry; the diurnal cycle of soil NOx 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 O3 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).