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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A model-based analysis of foliar NO_x deposition" *by* Erin R. Delaria and Ronald C. Cohen

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We are very grateful for the constructive comments and valuable suggestions offered by the three reviewers. The reviewers' comments appear in **bold** followed by our responses to each comment in *italics*. Line numbers in our responses refer to the edited manuscript. Please see attached supplement for revisions referred to.

Reviewer 1

General:

1. While I appreciate that NO-NO2 cycling is rapid, non-linear and highly

complex, I would like to authors to be explicit in precisely which molecule they are considering the dry deposition of. They rather inconsistently refer to deposition of NO2 and of NOx. Presumably they are assuming that NO deposition is negligible and hence deposition of NO2 can be used as a proxy of NOx deposition. If so, this should be explicitly stated early in the manuscript and a single term used from that point on.

We have gone through the manuscript and have corrected mention of "NOx deposition" to explicitly refer to "NO2 deposition". We also do use NO2 as a proxy of NOx deposition. A statement was added to P3, L17 clarifying that we consider NO deposition to be negligible.

2. The study purports to use two field sites, Blodgett Forest (BEARPEX campaign 2009) and University of Michigan Biological Station (UMBS campaign 2012). However, the authors almost exclusively focus their model description, parameterizations, sensitivity tests, results and discussions on Blodgett with scant details given to the results from UMBS other than to corroborate (or highlight differences) those from Blodgett. The authors should either reduce their analysis to a single site or, preferably, give similar attention to UMBS. The differences between model outcomes for the two sites is, to my mind, of real importance to enable the modelling and measurements communities to understand the processes that require further elucidation.

We have considered the reviewers comment. We believe similar giving similar attention to UMBS would distract from our focus on the conceptual conclusions of this paper. The purpose of including the UMBS data is to further corroborate the ideas in the model and to demonstrate that the model is applicable to multiple sites and not simply tuned for Blodgett Forest observations. The overall purpose of this manuscript is not *to argue that observations should exactly match our model predictions, but rather to illustrate trends and key ideas that field observations and modelling studies should pay further attention to in future observational and modelling research. We added to P11, L30: "Similar trends (not shown) were also observed using parameters for UMBS."*

We also chose to focus our attention on Blodgett Forest for comparing the Wesely and Emberson models because this is a region subject to frequent dry conditions in the summer and fall, and view this site as an example of a region where our findings may be of particular importance.

3. While the authors explicitly quantify the differences in NOx concentrations and fluxes between the two deposition schemes and between the perturbed parameter sensitivity tests, they do not similarly evaluate the relative performances against observations, relying instead on qualitative, descriptive differences. The results would be far stronger if this aspect of the model outcome were better explored and presented.

We agree with the reviewer that it will be important in the future to directly and quantitatively compare models to observations. However, at this point in time, we believe clarifying key variables that govern NOx fluxes is an important advance even without such a quantitative comparison. Moreover, we are not aware of observations for a location during both dry and wet conditions. We call for more long-term observations of stomatal behaviour and dry deposition processes over a variety of meteorological conditions.

Specific:
Introduction

Throughout: All of the deposition models and studies presented here are specifically focused on the dry deposition of O3. The authors need to build a stronger argument that NO2 deposition should be assumed to follow the same process. In particular, in the case of O3, there still remain questions around the relative contributions of stomatal vs cuticular fluxes to the total leaf conductance. Most O3 deposition calculations assume that mesophyllic conductance is zero, is there evidence that this is the case for NO2.

We added a statement to P2, L27-29 with citations arguing NO2 deposition is also controlled by stomatal opening. Mesophyllic resistance in models is indeed assumed to be comparatively small. However, this is a question we are actively researching with laboratory chamber measurements. This will be followed up in a future publication currently in preparation.

p2, L19 (and elsewhere): VPD is a convenient proxy for leaf water potential as it can be calculated from routinely measured meteorological variables but it is often not a good metric to use under conditions of drought.

We agree with the reviewer comment. However, the focus that we take on VPD is indeed because it is a convenient proxy that we believe is practical. Consideration of VPD is a substantial improvement over current CTMs that do not include such a parameterization. We note that this does not completely tell the whole picture, which we discuss later P13, L19-31.

p2, L20: make clear that "season" and "seasonality" refers to plant phenology

"season" was changed to "seasonality of leaf phenology".

p3, L4-5 (and elsewhere): Technically, the DO3SE model estimates stomatal conductance for use in deposition schemes to calculate deposition velocities and hence O3 fluxes.

Line was changed to "...estimating stomatal conductance to predict ozone deposition velocities,...", now P3, L5-6.

p3, L12: Could the authors explicitly state some of these "other molecules"

P3, L19-20 now reads: "... other molecules such as NO2, NO, H2O2, HNO3, hydroxy nitrates, alkyl nitrates, peroxyacyl nitrates, etc...."

p3, L15-17: YES!!! This should be emphasised!

We agree, but are unsure what more we could do to emphasize this point.

2 Model description

p3, L21: A value of 100m for the PBL height during the peak growth season (summer) seems low, particularly for Blodgett. Under clear skies and high insolation I would expect to see values of 1500-2000m. Is their value based on observations at the two sites? If so, please provide references; if not please justify.

References to Wolfe and Thornton, (2011) and Wolfe et al., (2011) were added to P3, L29.

p3, 21: "Gaussian"

fixed

p3, L30: △h is surely the height / depth of the box. I assume that the model has a horizontal scale of 1m2 or 1cm2, but please clarify this.

Each box layer is treated as well-mixed and homogenous.

p4, L1-19: This paragraph (which should really be split in two for BEARPEX and UMBS) is not a description of the model, rather the two field sites and should have a separate section.

The paragraphs describing the two sites were separated into two paragraphs and a separate section added (2.2, P5, L17–P6, L12).

p4, L7: I am surprised that UMBS was modelled here without a separate understory, see e.g. Bryan et al (2015) Atmos Environ.

There is a separate understory. This has been clarified in P5, L28 and Table 1. Citation to Bryan et al., 2015 was also added.

p4, L20-21: Make clear here that this is simply following Beer's Law.

"...following Beer's law:" was added to P6, L9.

p4, L30: What are tau and TL in this context?

Please see Wolfe and Thornton, (2011). We added an additional citation of this paper following P6, L21. A definition was also added to P6, L20 : ".. defined as the ratio of the "time since emission" of a theoretical diffusing plume (τ) and the Lagrangian timescale (TL)..."

p4, L30 (and Table 1): Where is the value of u* taken from and why is it a constant value?

We used for u the average daytime value reported by Wolfe and Thornton, (2011). The range of u* during the BEARPEX-2009 campaign was $\sim$ 0.1–0.8. We decided to use the daytime average as a constant value, as for the most part we restricted our analysis to daytime results. We ran a scenario with our model in which u* above the canopy varied based on a sinusoidal fit to average diurnal observations at Blodgett Forest, and observed negligible changes to the canopy fluxes and above-canopy NOx mixing ratios. Based on this, and our sensitivity test to τ/T_L, we decided to leave out this additional complication in our model so that it would be easily extendable to forests where observations of u* are not readily available.*

p5, L15: Please explain why the rate constants require adjustable parameters to make them site-specific. Are the authors assuming segregation? recycling?

To P7, L23 we added the statement: "kOH and kNO3 are effective values adjusted in the model based on site-specific VOC composition and observations of OH reactivity."

p5, L21: Where are the basal emission rates taken from? Are they average values for deciduous and evergreen mid-latitude forests, site-specific, dominant-species specific?

Citations of the emissions rates and other parameters were added as a table caption for Table 1.

p5, L22: Deposition should be described in a separate section. In fact, given it is the main focus of the study, it should be the first.

We have rearranged the manuscript so Deposition appears in its own section and first in the section 2.1.

p5, L26-p6, L5: This is the Baldocchi parameterisation of total resistance. Why have the authors not used the subsequent Gao et al (1993) update?

The Baldocchi parameterization of total resistance is used because our model has been built to scale up laboratory observations of leaf-level deposition to the canopy scale. A similar approach was taken for CAFE model development (Wolfe and Thornton, 2011), on which this simplified model was based. In our opinion, the Gao update adds complexity without changing the aspects that are key to the discussion here.

p6, L5-7: If all processes are correctly included and parameterized there should be no need to use a compensation point; this is merely a formulation that is

used when the production and loss terms are not fully represented in a model.

We changed the sentence (P4, L21-22) to say: "We do not allow for emission of NO or NO2 from leaves, consistent with recent laboratory observations that have observed negligible compensation points for these molecules (Chaparro-Suarez et al., 2011; Breuninger et al., 2013; Delaria et al., 2018)."

p6, L13: The authors have not defined SR

A definition of SR has been added P5, L2.

p6, L14: Eqn 12 is essentially the Jarvis (1976) parameterisation of stomatal conductance. It has been modified since, with additional adjustment factors. It forms the basis of the DO3SE model, but really the DO3SE model is about the damage and therefore incorporates an additional modifying factor fo3 to the Jarvis expression for gs.

The Emberson et al. (2000) paper we refer to does not include this fO3 term. We added a citation of Jarvis et al. (1976) to P4, L28.

p7, L6 L8: VOC or BVOC?

BVOC. This has been updated p 7, L22.

p7, L16: Please expand on how fluxes are calculated within this model.

Fluxes are calculated according to Eq. 14 (updated manuscript). We added a reference to Wolfe and Thornton (2011) P6, L15, as the same method of calculating fluxes was used here. Reference to Eq. 14 was also added to P8, L14.

p7, L17: How is the PAN formation / NOx removal incorporated? It is not clear if or how these processes are included in the authors' considerations of chemical production and loss, lifetime calculations and OPE.

As shown in the Romer et al. reference, during the day at high temperatures, PAN is in steady state with NOx and a constant PAN/NOx ratio occurs. PANs role in these circumstances is to sequester NOx in a different form. In this paper, we neglect the possibility of direct PAN deposition. Upon deposition of NO2, PAN dissociates maintaining the fixed PAN/NOx ratio set by the steady-state. At night, PAN is assumed to be a permanent sink of NOx and not available to return to the NOx pool when NO2 is removed by deposition.

We have removed this discussion of night time chemistry/deposition as it is not important to the conclusions of the paper.

3 Sensitivity to parameterizations:
As previously noted, this section appears only to consider Blodgett Forest (unless all parameters were the same at both sites, which other parts of the manuscript suggest was not the case)

p7, L22-23: How were these values of total deposition velocity chosen?

We edited P8, L21-23 to read: "...based on values of gmax and gmin chosen for Blodgett forest (discussed above) and typical values for deposition velocity observed for a variety of species in the laboratory (Teklemariam and Sparks, 2006; Chaparro Suarez et al., 2011, Breuninger et al., 2013, Delaria et al., 2018). "

p8, L10: Why have the authors chosen a value of 2 for tau/TL; Wolfe and Thornton (2011) used a value of 4 for this site when developing the CAFE model.

In our simplified model, a value of 2 resulted in the residence time in the canopy most similar to what was observed at Blodgett Forest. The simplified model gave a different residence time with a value of 4 than in the CAFE model.

p8, L10: "resulting in a canopy residence time of 152s" at both sites? Or just Blodgett?

"...for Blodgett Forest,..." has been added to P9, L11 for clarification. We have also added the applicable UMBS residence time.

p8, L22: Please explain why Rb and specifically lw has a larger impact on species with high rates of leaf deposition.

At higher deposition velocities, the stomatal resistance is lower and Rb makes a greater contribution to the total resistance. We expect small changes in Rb under these conditions to have a greater overall effect. We have added to P9, L23: "...where Rb makes a greater contribution to the total resistance."

p9, L14: I realise this is taken from a previous study but it is not clear why UMBS should be modeled using parameters for a European beech species when it is dominated by aspen.

We agree with the reviewer that parameters for aspen would have been more appropriate. However, there is no available data we are aware of for the specific tree species found at UMBS. As the site also contains American beech trees, and other hardwood deciduous tree species, a European beech species was chosen as a "best guess" for how trees at UMBS would behave. We realize this is not ideal, and call for more studies of stomatal regulation of North American trees. We note that the resulting predictions are in plausible agreement with observations and that the parameters used are distinct form those at Blodgett Forest, serving our purpose of showing that the model parameters we identify as important are flexible enough to represent different ecosystems.

p9, L19-p10, L4: Please quantify the model-obs fit rather than providing simply a qualitative overview.

We added references to figures 3 and 4 where appropriate, as well as parentheticals describing quantitative differences to P10, L18-P11, L6.

p9, L25: Please explicitly state what is meant by NOx enhancement. I think it is the difference between in-canopy and above canopy concentrations. But these will differ between levels in the canopy and PBL

This has been clarified in P10, L16: "... ,relative to above-canopy mixing ratios, ...". A definition has also been added to the caption for Figure 3.

p10, L6: Wesely

Fixed.

p10, L26-28: How do these deposition velocities compare with observations? In L10, the authors state that values of 1.4, 0.77 and 1 are used in global models. Do the author have site-specific measurements on which they have based their choice of 0.3 and 1.4 as upper and lower bounds?

An upper bound of 1.4 was chosen from the upper bound of the global model listed above. Our lower-bound estimate was 0.1 cm s-1, but we believe 0.3 cm s-1 is a more reasonable lower bound estimate based on chamber studies we have recently conducted. Quantitative data for 0.1 cm s-1 was added P11, L29-30 for consistency.

p11, L1: The authors are comparing 2 sites with a range of differences so I'm not sure they can claim "regional" differences. Surely it's more to do with different forest types, different soils, different meteorology, . . . Please could the authors be a little more specific.

We have made edits for accuracy on P12, L 2-3. The manuscript now reads: "The relative importance of including parameterizations of VPD and SWP in the calculation of stomatal conductance and overall deposition velocity is expected to be regionally variable, along with regional variations in dominant tree species, soil types, and meteorology."

P11, L2: I have a problem with the use of "wet" and "dry" in this context as deposition itself is referred to as wet or dry. Perhaps the authors can find an alternative way to describe wet and dry environments (I couldn't think of an obvious alternative I'm afraid)

We have considered the reviewers point and understand how referring to conditions as "wet" and "dry" is less than ideal. However, we also were unable to come up with a more appropriate way of referring to these conditions.

p11, L4-7: Do these values of SWP and RH match long-term observations?

Citations have been added to P12, L9-12 for our choices of "wet" and "dry" conditions.

p11, L20-25: It would be good to see a more considered discussion of the results and the reasons (i.e the processes) behind the similarities and differences between the sites.

The current discussion serves our purpose of showing that the model is plausibly related to a second location. More detailed analysis of similarities and differences strikes us as more appropriate when more extensive observations of NOx fluxes are available at a location.

p12, L6-7: Suggest the authors extend their view beyond the USA. Surely their findings are GLOBALLY applicable?

We considered the reviewer's suggestion, but we decided to leave as-is. We do not *feel that giving an example of a region with frequent droughts in the US implies our finding will not be applicable globally. Our intention was to give one such example of a type of environment that our findings may be important for.*

p12, L9: CLM includes a specific parameterization of stomatal conductance and is the land surface model for both regional and global models of chemistry-climate (see Lombardozzi et al, various). Models with a full land surface module already calculate stomatal conductance and plant physiology so have no need to incorporate either the Wesely or Emberson approaches for estimating gs.

p12, L21-22: Following on from the above point, this point about the relative simplicity of the Emberson approach should be made explicitly clear from the outset by the authors.

We have added a line to the introduction to highlight the simplicity of the Emberson model. "We consider here both the Wesely model and the similarly simplistic approach of Emberson et al. (2000) that incorporates effects of VPD and SWP." We have also added a reference to the CLM P13, L24-26.

p13, L2: How is OPE defined? As molecule of O3 produced per "molecule" of NOx lost?

This definition is correct. Please see Eq. 26.

p13, L8: PBL

The suggested change has been made to P14, L18.

p13, L20-p14, L10: Parameterized for BEARPEX again?

All relevant parameterizations have been listed in this section. However, the values chosen for α, VOC reactivity and PHOx were similar to conditions at BEARPEX-09. A clarification has been made in L17 of P14.

p13, L26: Is PBL height fixed?

Yes, this section describes a simple box-model that does not evolve in time.

p14, L1 and L3: The plots of observed NOx concentrations for both sites suggest they are $\sim\leq 1$ ppb so why have the authors explored up to 100 ppb here?

In our view, the purpose of a mechanistic model is to permit prediction outside the range of observations and to identify circumstances where a process is uniquely important. In this section, we explore the role of deposition in near-urban forests where NOx concentrations are significantly higher than the two forests we focus on as our test examples. We find that NOx loss via stomatally controlled deposition is the primary loss mechanism in cities. To our knowledge that idea is not described previously in the literature, at least not with a tool that has the potential for incorporation into quantitative modelling.

6 Conclusions

p14, L25: missing closing parenthesis.

Fixed.

p14, L30-31: It's also imperative to accurately measure gs in a way that reflects differences between leaf-level and canopy-scale gs.

We agree with the reviewer.

p14, L31-32: DO3SE is NOT a deposition model; it is a model of stomatal conductance that can be used in a deposition scheme so effectively it also uses the resistance in series approach.

The wording has been changed for accuracy on P16, L9.

p15, L1-4: Why is this important? What does this miss? Do we know that is wrong?

The text in the conclusions and paper points to several items that are important, including a mechanistic explanation for CRF, explicit modelling of stomatal opening, and recognition of NOx fluxes as a significant control over the NOx lifetime in a range of different circumstances. We do not believe it would help the reader for us to be repetitive on these points at this place in the text.

p15, L8: think GLOBAL!

Locations outside the US have been references P16, L17-18.

p15, L8-9: Please could the authors be more specific in their recommendations? Precisely what do they mean by explore? More measurements? More modeling? And specifically of what, when and where?

We have added a sentence to the end of the concluding paragraph:

"... explored with observations of NOx fluxes and concurrent models to confirm the role of deposition in a wider range of environs and more thoroughly vet the conceptual model proposed here."

Figures and Tables

p24, Fig 1: I am surprised that the authors have chosen only to vary PBL for the top two layers in the active mixed layer. I would expect the lower 2 of these layers to similarly evolve over the course of the day but with lower amplitude.

We do not believe this additional complication would change the general themes presented here, although they would certainly change things in detail.

p24, Fig 1: Right-hand labels on plot say "remnant" and caption says "residual". Would personally use the latter.

Fixed.

p25, Fig 2: Not sure that this figure (or Fig S9) add anything to the paper. The

authors have given the lat-long coordinates for both sites so readers could look for them on a map and they do not refer more than in passing to the figure from the text.

It is our impression that other readers may appreciate having the maps. Particularly for observing the relative proximity to urban centers.

p26, Fig 3(d): Clarify what is meant by NOx enhancement in this context.

This has been clarified in the figure caption. NOx enhancement is defined as NOx at each height – NOx above the canopy.

p27, Fig 4: A panel showing a time series of NOx would be helpful for direct comparison between the two sites.

We prefer to only show the diurnal average and variance.

p32, Fig 9: PAN? Daylight hours or 24-hour average?

This figure shows an average of daylight hours. This has been clarified in the figure caption. PAN is included in NOx, as it is in steady-state with NOx during the day (Romer et al., 2016).

Reviewer 2

We have added additional legends to some of the figures. We have also gone through

our figure captions and tried to be as clear as possible about symbol meanings and more detailed in our descriptions where applicable.

Reviewer 3

We thank reviewer 3 for pointing out some of the complexities in representing canopy exchange. Here we have focused on a fairly simple representation because a model of this complexity is comparable to those utilized in regional or global models. We intend to focus less on the quantitative agreement and emphasize the key conceptual advances. We argue that to correctly represent the degree of complexity in atmosphere-biosphere interactions the new ideas we present are needed. With these ideas alone, we are able to reach some significant insightâĂŤespecially that CRF's are not necessary. We do not intend to suggest that the ideas we present alone are adequate to describe canopy scale mixing. The parameterization used here is designed to simulate conditions in two forests. In response to reviewer 3, we have added the following text P6, L25-32.

> *Our model is a simple parameterization of turbulent processes and as such will only capture mean vertical diffusion. Other work (Collineau and Brunet, 1993a; Raupach et al., 1996; Brunet and Irvine, 2000; Thomas and Foken, 2007; Sörgel et al., 2011; Steiner et al., 2011) has shown that "near-field" effects of individual canopy elements and coherent turbulent structures can play an important role in canopy exchange. These more intricate processes are not captured explicitly by our simple model. Previous work (Gao et al., 1993; Makar et al., 1999; Stroud et al., 2005; Wolfe et al., 2011) have also utilized fairly simple representations of canopy exchange in local and regional models As such, K-theory is likely sufficient to represent average vertical diffusion for the purposes of our study.*

In response to the concerns presented by Reviewer 3, on page C3, we have added a more detailed description of the representation of mixing that we use in our model, along with specific citations of the works cited by Wolf and Thornton (2011) and Reviewer 3. We have added the following to the text P6, L20-24:

> *The details of the parameterization of turbulent diffusion fluxes is documented elsewhere (Wolfe and Thornton, 2011) and based on the works of Raupach (1989) and Makar et al. (1999). The height dependent friction velocity (u(z)*) is attenuated from the above-canopy u* according to Yi et al. (2008). Although Finnigan et al. (2015) identified flaws in this treatment, we believe it is sufficient for our focus on illustrating generalizable qualitative trends.*

The following statement was added to P12, L30-33:

> *We recognize that the multibox model presented in this work is a simplified representation of physical processes, and as such is not likely to (and is not intended to) provide quantitative exactitude for the trends described above. However, we argue for the necessity of incorporating these conceptual advances for accurately representing canopy processes and predicting their effect on the NOx cycle.*

Specific comments:
P6 L4: "and are dependent upon plant physiology." => They also depend on the physical and chemical properties of the compounds.

On page 4, L19-20 (originally P6, L4), we have included the statement: "Rleaf is dependent upon plant physiology and the chemical and physical properties of the

deposition compounds".

P8 L31: Did the different canopy shapes change the residence times or was this kept constant? Are canopy structure and LAI independent from the residence time in the model?

The different canopy shapes did change the residence time. The residence time for UMBS was added to P9, L11.

P9 second paragraph:
Here again the question how much influence has the "advection correction" here?

Specifics for how advection was treated in the model was added to P7, L10-11 and P11, L9.

Technical comments:
P3 L21: "below the boundary layer" => replace by either "within the pbl" or "below pbl top".

We changed this to "...within the planetary boundary layer (PBL)".

P8 L31: "is was" => is

Fixed

Fig.3 and 4: Please use same spacing of time axis for all panels. Makes it easier to compare.

Fixed

Figure 3d): which time intervals are used for "morning" and "afternoon"?

Interval definitions were added to the figure caption.

Figure 4b): Move NO2 label in graph as the subscript 2 is hidden within the data points.

Fixed

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-538/acp-2019-538-AC1-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-538, 2019.