Response to Reviewer #2

We greatly appreciate the reviewer for providing valuable comments on our manuscript, which have helped us improve the paper quality. We have addressed all of the comments carefully as detailed below. The original comments are in black and our replies are in blue.

This is a generally well-written paper about a difficult scientific topic. The authors document how a well-know dry-deposition model can be extended to treat additional oVOC species. The authors are honest about limitations, and have good explanations for most of the issues. I do have concerns about the assumptions concerning Gns versus Gresidual, as well as some other points as given below. As long as these can be addressed satisfactory then the article, and in particular the changes to the deposition code, will be a useful addition to the literature.

General

The assumption that Gns is "correctly estimated" (L236) when looking at the Gresidual is of course a major problem. As noted by for example Massman (2004), or Cape et al (2009), these non-stomatal terms are very uncertain even for ozone. I would like to see a more thorough assessment of this issue.

"correctly estimated" should be replaced with "estimated with reasonable accuracy". We agree with the reviewer that the existing formulas for estimating non-stomatal terms have very large uncertainties. Compared to the other existing dry deposition schemes, the one used in Zhang et al. (2003) is actually the only one considering several key meteorological factors. For example, in Wesely (1989), constant values were used for this term for a specific land use. The uncertainties in individual resistance terms have been thoroughly discussed in Wu et al. (1028), which support this assumption: $G_{residual}$ estimated using the formula $[V_d^{-1} – (R_a + R_b)]^{-1} – (R_s + R_m)^{-1}$ is meaningful." We have modified this part to this: "The uncertainties in individual resistance terms of Zhang et al. (2003) and several other dry deposition schemes have been thoroughly assessed by Wu et al. (2018), from which we believe $G_{residual}$ estimated using the above formula is meaningful although with large uncertainties. The estimated $G_{residual}$ can provide…"

Also in this respect, the model assumes that surfaces are either wet or dry. Of course, the real world shows a high degree of variability, and it can be difficult to predict the thickness or coverage of moisture films on leaves (e.g. Wichink Kruit et al., 2008). How can the authors be confident that their Gns is correct when such basic factors as leaf-wetness (and its impacts on aqueous/surface reactions) are so hard to deal with?

I would have liked to see some analysis of the results with RH (or deficit D) as the driving variable, rather than just wet/dry.

In the figure below, we analyzed the nighttime $G_{residual}$ and G_{ns} under different RH conditions (similar to Figure 3 in the manuscript). Both $G_{residual}$ and G_{ns} tended to increase with higher RH, which is consistent with our findings with dry/wet surface at night.

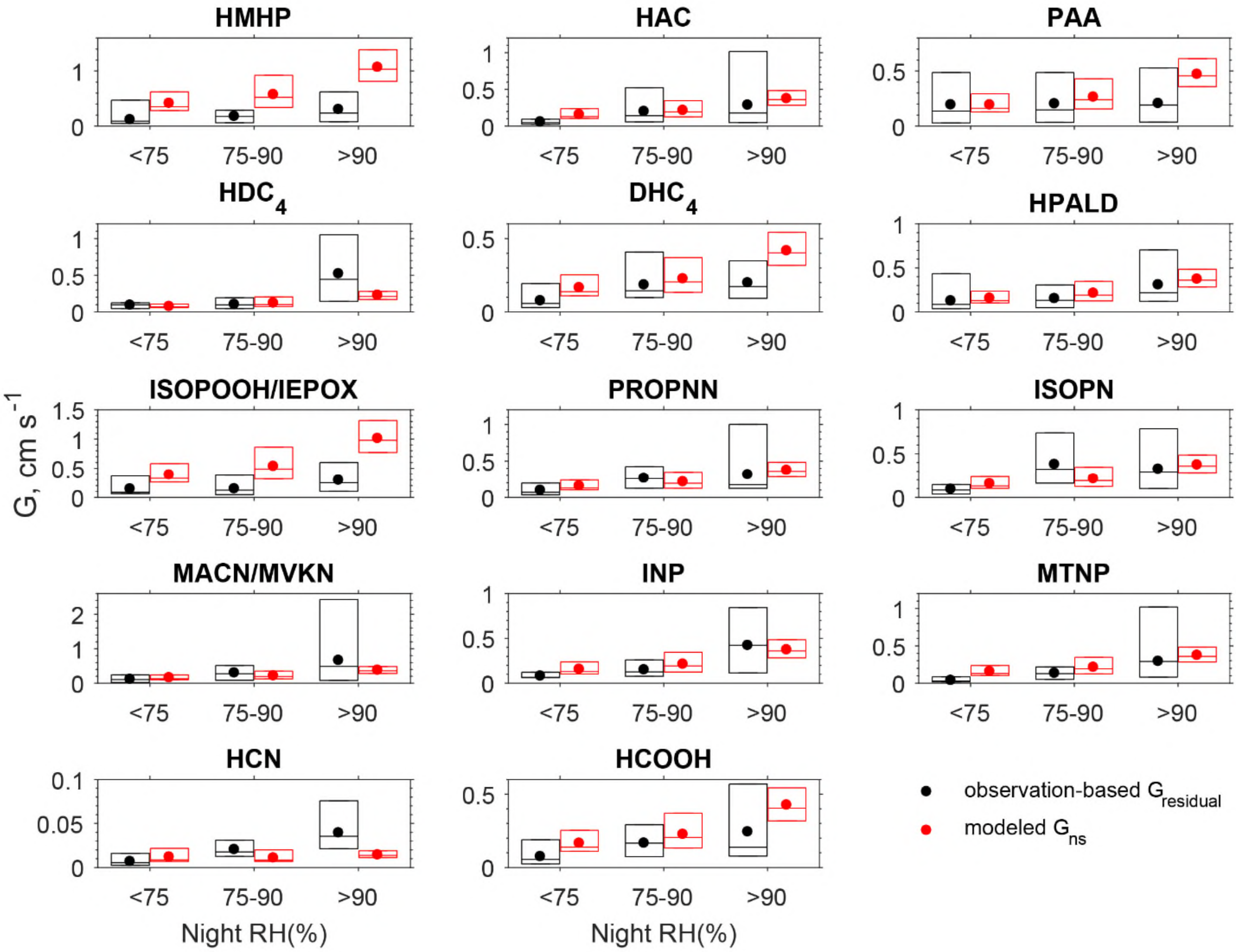

Figure. Observation-based residual conductance ($G_{residual}$) and the modeled nonstomatal conductance (G_{ns}) under different humidity conditions during nighttime. The sample sizes for RH <75, 75-90, and >90 are 20, 50, and 58, respectively. The box covers the 25-75th percentiles range with median (horizontal line) and the arithmetical mean (filled dot) of the 25-75th percentiles data also shown inside the box.

I would also have liked to see some indication and better discussion of the uncertainty of the flux measurements. These uncertainties are substantial, and presumably contribute to some of the differences seen in e.g. Fig. 4.

Nguyen et al. (2015) provided some discussions on the measurement uncertainties. For example, the Table S1 of Nguyen et al. (2015) showed that the sensor sensitivity uncertainties ranged from 20-50% for the oVOC species. We agree that the measurement uncertainties could contribute to the model-measurement discrepancies showed in this study, but the data we have are not enough for assessing the uncertainties in a quantitatively way.

When modeling the deposition of organic compounds, I wonder why water is the only solvent being considered when calculating Rns? Much of the SOA modeling conducted with CTMs assumes indeed that SOA species are absorbed in the organic rather than the water component of the particle. Perhaps complex thermodynamic models (e.g. Zuend et al, 2011) are required to cope with the deposition (or bi-directional exchange) of these compounds?

The organic matters could be an effective solvent for the oVOC compounds. Some studies in literature (e.g., Nizzetto and Perlinger, 2012; Wu et al., 2003) used the octanol-air partitioning coefficients to parameterize the absorption of the organic compounds in organic solvent. Currently the Zhang scheme doesn't include the octanol-air partitioning coefficients for the deposition compounds. In the future, new scheme can be further developed by including the octanol-air partitioning coefficients and coupling with complex thermodynamic models once the proper parameterizations and reliable parameter values are available. As we recommended in the Introduction: "At this stage with very limited knowledge on oVOC Vd, air-surface exchange models based on various theoretical and/or measurement approaches should be developed, so that these models can be made available to the scientific community where such models are urgently needed, and for future evaluation and improvement should more flux measurements become available."

Terminology: I must admit I don't like anybody referring to their own code as "the Model", with capital M, which makes it sound like it is the ultimate reference. Better to say "the model" or "the deposition model" or something similar.

The term "the Model" has been removed throughout the manuscript.

Other comments

L50: The sentence about HCN doesn't seem to fit with the rest of this paragraph, or the oVOC theme in general. Start a new paragraph maybe?

A separate paragraph is used for HCN discussion in the revised manuscript.

L117-, Do equations 2-3 ascribed to Wu et al. 2018 differ from those of equation 4 which is ascribed to Zhang et al 2002? (It is a little confusing here what is meant by "the Model", when the latter was stated on L108 to be Zhang et al 2003!)

Zhang et al. (2003) is an updated version of Zhang et al. (2002), where the non-stomatal resistance parameterizations were updated while the stomatal resistance sub-module was kept the same. R_a and R_b formulas were not provided in either Zhang et al. (2002) or Zhang et al. (2003) because various but very similar formulas are available in literature. In summary, the details of the R_s formulas were described in Zhang et al. (2002), R_{ns} formulas in Zhang et al. (2003), and R_a and R_b formulas in Wu et al. (2018). We thus have to cite different references for these resistance formulas. In the revised manuscript, we have removed the citation of Zhang et al. (2002) and Wu et al. (2018) in two places to avoid confusion, and instead, we have added this statement at the end of section 2.1 for clarification: "Details of the R_s related formulas were described in Zhang et al. (2002), R_{ns} related formulas in Zhang et al. (2003), and R_a and R_b formulas in Wu et al. (2018)."

L179-, Fig.1. The authors discuss the discrepancy in HNO3 Vd for hours 19-23. but not why Vd in hours 0-3 is so very different. What happens at midnight that could change Vd?

The figure below presents the averaged diel variation of measured friction velocity (u_*) which showed lower u_* at the early night (19-23) than the late night (0-3), consistent with the trend of the measured $V_d(HNO_3)$. One possible reason for the large model-measurement discrepancies in V_d for HNO_3 could be the poor performance of the R_a parametrization under low u_* conditions.

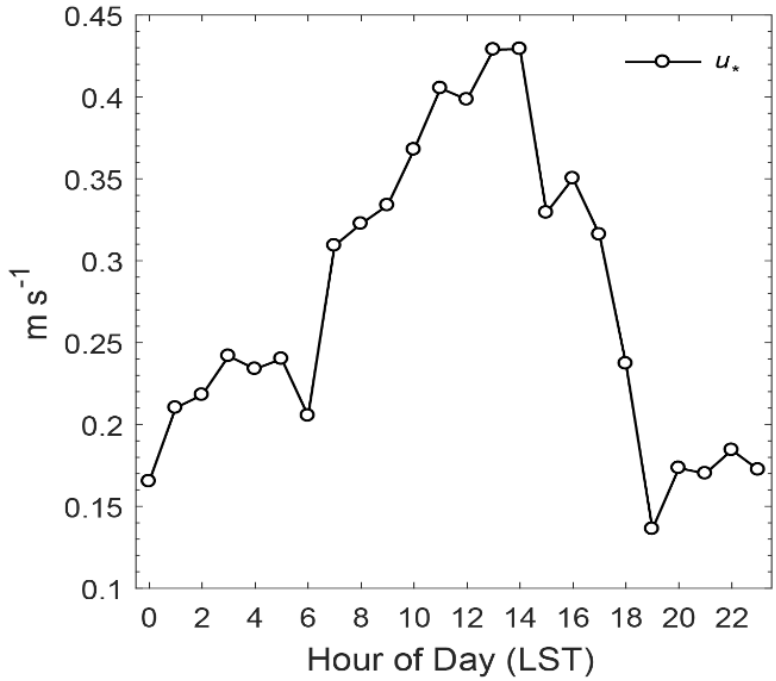

Figure. Averaged diel variations of measured friction velocity (u_*) at the CTR site during the study period.

L196- I agree with ref #1 that this material is background and should come earlier.

This paragraph describes the method for calculating the observation-based stomatal conductance so we can compare the observation-based and modeled stomatal conductance. Materials here are closely linked with the model-measurement comparison discussion presented in this section. We thus prefer not to move it to the Introduction.

As we responded to reviewer #1 on a similar comment: "The focus of the present study is to extend the model to additional chemical species without modifying the model structure or theory. Thus, the introduction section discusses the basic concept of dry deposition, the current knowledge status of oVOCs dry deposition, and the approach of extending the model to include additional oVOCs. Discussing too much details of model theory (such as including stomatal uptake process) in the introduction will loose the major focus of the study."

L214. Please add a ref to Fig. 2 here, so the reader knows what you are talking about.

We have added this: "As shown in Figure 2," at the beginning of the paragraph.

L216 claims that "the Jarvis" model is used, but are the Gs equations and parameters as used here (in "the Model") identical to those used in the 1976 Jarvis paper? If not, rephrase

We have rephrased it to "the Jarvis-type".

L223. Again, is the stress function used here identical to that from Jarvis 1976? In any case, all such stress functions are very sensitive to the very uncertain methods used to estimate soil water potential (or other metrics, e.g. Buker et al, 2012)

No, the stress functions mostly follow the SiB1 model (Sellers and Dorman, 1987) and the details can be found in Brook et al. (1999). In the case of this study, the stress factor from water vapor pressure deficit (VPD) was much lower than the other stress factors around noon and thus dominated the reduction of noon-time canopy stomatal conductance. Here we have also rephrased it to “the Jarvis-type”.

L241-242. The authors say that during night-time the "canopy surface was dry (no dew)", but presumably RH was high and some surface moisture was possible.

We agree that high RH at night could result in microscale water films on the canopy surfaces (invisible wetness). The Zhang et al. (2003) scheme follows the approach of Janssen and Romer (1991) to predict the occurrence of dew, which depends on wind speed, temperature and dew point temperature and this has been described in Brook et al. (1999). The prediction of microscale water films is much more uncertain and currently the Zhang’s scheme does not include such a parameterization. In a practical way, we classified the surface without predicted dew as dry condition and the surfaces with dew as wet condition. As shown in Figure 3, the nonstomatal conductance exhibited significant differences between the dry and wet conditions. The influence of the microscale wetness due to high RH is expected to be minimal and will not change any conclusions in this study.

L289. The paper states that the measured flux at night-time should better represent non-stomatal surface uptake, but it is also true that fluxes are very hard to measure at night-time. A brief discussion of this, and its implications, is warranted in the paper. (There are some comments starting on L330 that help in some regard, but these suggest that essentially one cannot trust the night-time Vd calculations; hence no relation with Gns can be established?)

We are aware of that the uncertainties in the measured fluxes are even larger in nighttime than daytime. This is the case even for the most commonly studies species such as O_3, SO_2, and some nitrogen species with rich flux data set, as also noted above by this reviewer in his/her general comment. That is why we provided a brief discussion/recommendation in L330 in the original manuscript. These large uncertainties making it difficult to obtain a good correlation between the modeled G_{ns} and measured nighttime flux. Nevertheless, we believe the magnitude of the campaign-averaged measured nighttime flux should be reasonable, so we aim to model G_{ns} to be within a factor of 2 of the measured flux on campaign-average time scale. Since this is a common issue to nearly all the chemical species (not just applying to oVOCs studied here), we feel we do not have any extra information to add, other than what has already been presented in L330 and below.

L303. So, what do the chemists tells about the reactivity of PAA versus HAC? I suggest giving some reaction rates and time-scales with OH, O3 and NO3.

According to Wesley (1989), oxidizing capacities can be described by redox reactions. We have generated related parameters and the details are provided in Table S2 of the Supporting Information. Based on their $pe^0(W)$ values, PAA is indeed more reactive than HAC (0.16 versus -2.35 $pe^0(W)$). We have added this statement in the revised manuscript where PAA and HAC are compared: “The reactivity parameters listed in Table S2 in Supporting Information also suggest PAA is more reactive than HAC.”

L395. Should give the doi

We have modified this statement to this: “The computer code and data used in this study can be obtained from contacting the corresponding author. The code is also available from (DOI:10.5281/zenodo.4697426): https://zenodo.org/record/4697426#.YHmzu5-Sk2w”

References mentioned in this response:

Brook, J., Zhang, L., Digiovanni, F., Padro, J., 1999. Description and evaluation of a model for routine estimates of air pollutant dry deposition over North America. Part I: Model devlopment. Atmospheric Environment 33, 5037–5051.

Janssen, L.H.J.M., Romer, F.G., 1991. The frequency and duration of dew occurrence over a year. Tellus 43B, 408-419.

Nguyen, T. B., Crounse, J. D., Teng, A. P., Clair, J. M. S., Paulot, F., Wolfe, G. M., et al. (2015). Rapid deposition of oxidized biogenic compounds to a temperate forest. Proceedings of the National Academy of Sciences, 112(5), E392-E401.

Nizzetto, L. & Perlinger, J.A. (2012). Climatic, biological, and land cover controls on the exchange of gas phase semivolatile chemical pollutants between forest canopies and the atmosphere. Environmental Science & Technology, 46(5), 2699-2707.

Sellers, P.J., Dorman, J.L., 1987. Testing the simple biosphere model (SiB) using point micrometeorological and biophysical data. Journal Climate Applied Metrology 26, 622-651.

Wesely, M. (1989). Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmospheric Environment, 23*(6), 1293-1304.

Wu, Y., B. Brashers, P. Finkelstein, and J. Pleim, A multilayer biochemical dry deposition model, 1 Model formulation, J. Geophys., 107, doi:10.1029/2002JD002293, in press, 2002.

Wu, Z. Y., Schwede, D. B., Vet, R., Walker, J. T., Shaw, M., Staebler, R., et al. (2018). Evaluation and intercomparison of five North American dry deposition algorithms at a mixed forest site. Journal of Advances in Modeling Earth Systems, 10(7), 1571-1586.

Zhang, L., Brook, J., & Vet, R. (2003). A revised parameterization for gaseous dry deposition in air-quality models. Atmospheric Chemistry and Physics, 3(6), 2067-2082.

Zhang, L., Moran, M. D., Makar, P. A., Brook, J. R., & Gong, S. (2002). Modelling gaseous dry deposition in AURAMS: a unified regional air-quality modelling system. Atmospheric Environment, 36(3), 537-560.