

## Response to Reviewer #1

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.

### Summary:

In “Extension of a gaseous dry deposition algorithm to oxidized volatile organic compounds and hydrogen cyanide for application in chemistry transport models”, Wu et al. describe an extension of an existing dry deposition algorithm to 12 additional oxidized VOCs and evaluation of the model against field data. The effort shows that some oVOCs are well-represented by this formulation, but others severely underestimate the observed deposition rates, suggesting a second sink is also important that the authors suggest is chemical reactivity. Overall, the important content is included, but the manuscript would be improved with a reorganization to introduce important background information earlier on. Specific comments aim to improve this and other areas of the work.

### Major comments:

As an overall comment, the manuscript would benefit from reorganization in ways that present relevant background information earlier in the introduction and methods, and not waiting in some cases to present this information in the results and discussion. An additional section heading after 3.2 could help indicate that the discussion has shifted from evaluation of modeled deposition velocities to the role of other loss mechanisms, namely chemical reactions. The comments below give more specific examples for this organization along with other notes.

We have added some additional materials in Abstract and Introduction based on reviewer’s comments. We have reorganized Introduction and methods section as suggested by the reviewer. We have split 3.2 into sections 3.2 and 3.3 as recommended by the reviewer.

(1) I suggest defining dry deposition early on in the abstract and introduction. Which processes are considered dry deposition? Are they all dependent on concentration to first order (L24 states how it is calculated, could you state what it represents)? Why is it ‘dry’ vs ‘wet’, and how relevant is the distinction for different gases/processes? For many gases with uptake fluxes into the biosphere, the term ‘deposition’ is a bit misleading, because rather than depositing like a dust particle or aerosol, gases are often taken up by gradient-driven biochemical reactions that vary in time and space in ways that are not consistent with the idea of simple deposition on a surface. I understand the historical use of this term, and my suggestions here is just to add more description of the involved processes that are referred to collectively as dry deposition earlier in the manuscript.

In the revised manuscript, dry deposition is defined in the abstract and introduction. Major factors affecting dry deposition process is briefly mentioned (which includes meteorological, biological and chemical factors). The concept of dry versus wet deposition has been added in the introduction. Here are some revised texts:

In Abstract: “Dry deposition process refers to flux loss of an atmospheric pollutant due to uptake of the pollutant by the earth’s surfaces including vegetation and underlying soil and any other surface types.”

“ $V_d$ , the latter is a variable that needs to be highly empirically parameterized due to too many meteorological, biological and chemical factors affecting this process.”

In Introduction: “In mass continuity equation of a chemistry transport model (CTM), atmospheric deposition is calculated separately for dry and wet deposition fluxes. Dry deposition refers to the removal process through which pollutants are taken up by the earth’s surface, and this process, while being quite slow, is a continuous process happening all the time, even during precipitation. In contrast, wet deposition is fast but episodic, and pollutants need to be first incorporated into hydrometeors before being delivered to the surface via precipitation.”

abstract: Instead of relying on the citation of Zhang et al. (2003) to describe the nature and extent of the dry deposition scheme, please be more descriptive in this second sentence of the abstract and describe in simple terms what dry deposition processes are, what the Zhang version includes, and was anything in the scheme fundamentally changed except adding new gas species?

We have modified the first half of the abstract to include descriptions of the dry deposition process and how the model of Zhang et al. (2003) is modified in this study to include additional oVOCs. The revised text reads: “Dry deposition process refers to flux loss of an atmospheric pollutant due to uptake of the pollutant by the earth’s surfaces including vegetation and underlying soil and any other surface types. In chemistry transport models (CTMs), dry deposition flux of a chemical species is typically calculated as the product of its surface-layer concentration and its dry deposition velocity ( $V_d$ ), the latter is a variable that needs to be highly empirically parameterized due to too many meteorological, biological and chemical factors affecting this process. The gaseous dry deposition scheme of Zhang et al. (2003) parameterize  $V_d$  for 31 inorganic and organic gaseous species. The present study extends the scheme of Zhang et al. (2003) to include additional 12 oxidized volatile organic compounds (oVOCs) and hydrogen cyanide (HCN), while keeping the original model structure and formulas, to meet the demand of CTMs with increasing complexity. Model parameters for these additional chemical species are empirically chosen based on their physicochemical properties, namely the effective Henry’s law constants and oxidizing capacities.”

Methods: Is dry deposition to canopy/vegetation only or does it also include soil? This information should be given in introduction, instead of only being first mentioned in L119.

The following explanation has been added in the first paragraph of Introduction: “In most  $V_d$  formulations, turbulent and diffusion effects are parameterized as aerodynamic and quasi-laminar resistance, respectively, above and sometimes also inside the canopy. Uptake effects by canopies and underlying soils and any other surface types are parameterized as canopy (or surface) resistance, which include several flux pathways such as to stomatal, cuticle and soil.”

L90 give the model equations/formulation in this paper earlier in the methods, instead of relying on the reader accessing Zhang et al. 2002 or waiting to L134. Does  $H^*$  enter into the model formulation directly, or just inform the parameterization of alpha and beta? The ‘scaling parameter’ terminology is helpful for understanding these factors in Table 1, and could be used in the text to make their meaning clearer. Give a formula for how you scaled alpha for oVOCs relative to that of SO<sub>2</sub>.

We have reorganized section 2 into the following three sub-sections: *2.1 Brief description of the  $V_d$  formulation*; *2.2 Extension of the scheme to additional chemical species*; and *2.3. Field flux*

*data*. Materials are adjusted accordingly. After this reorganization, formulas appeared first as recommended by the reviewer.

$H^*$  is not used directly in any formula, instead, it is used for choosing the alpha value. This has been describe clearly in section 2.2: “Initial  $\alpha$  values were first given based on the relative magnitudes of  $H^*$  of all the chemical species and that of  $\text{SO}_2$ ” “When adjusting  $\alpha$  and  $\beta$  values, two rules were first applied: (1) the trends in  $\alpha$  (or  $\beta$ ) values between different chemical species should be consistent with the trends of their  $\log(H^*)$  (or oxidizing capacity) (see Figure S1 for the finalized  $\alpha$  versus  $\log(H^*)$ ); and (2) modeled mean and median nighttime  $V_d$  should be mostly within a factor of 2.0 of the measured values.”

L196-201: this is really helpful background information for the model that might be more useful in the introduction or methods section, rather than only being presented in the results. Same comment regarding the introduction material on stomatal conductance and transpiration fluxes.

After careful considerations we feel that it is not a good space in the Introduction section to discuss model theories. This is because 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 update process) in the introduction will loose the major focus of the study. We do have added a simple description of the model theory that mentions stomatal uptake in Introduction, which reads: “Uptake effects by canopies and underlying soils and any other surface types are parameterized as canopy (or surface) resistance, which include several flux pathways such as to stomatal, cuticle and soil.”

Because of the same reason (no change in model structure or theory), we feel there is no need to add detailed description of the model theory in the Methods section either, especially considering such theory is well known in the air-surface exchange scientific community. The theory was only briefly mentioned in the Results section where it is needed to explain the results (as an introductory sentence in each topical discussion).

L230: give some examples of what other processes can affect deposition earlier in this paragraph, rather than leaving it to the end as “leaf cuticle and ground (more specifically soil/litter) or reactions within and near canopy”.

As mentioned in several responses above, we have added brief statements in Abstract and Introduction, mentioning the many process affecting deposition. For this particularly comment, we have further added this statement: “All of these flux pathways can be simultaneously affected by meteorological, biological and chemical factors, most of which cannot be explicitly considered and thus are highly empirically parameterized in dry deposition models.”

(2) Appropriate context for the current state of understanding is lacking. Give examples of the oVOCs relevant to this paper and their properties before L31, so we can understand how suitable it may be to use  $\text{SO}_2$  or  $\text{O}_3$  as references. For example, you state that the  $\text{O}_3$  reaction with oVOCs should depend on chemical structure—please describe this in more detail and list the oVOCs you will consider beforehand so we have context. L50-53 on HCN feels like an orphan sentence—suggest to make a different paragraph where oVOC and HCN properties are discussed together. Define IEPOX in Table 1 or text referring to it the first time.

Field flux measurement data on oVOC are extremely rare, and currently we do not have a very good understanding on the deposition process of oVOCs. The approaching of using SO<sub>2</sub> and O<sub>3</sub> as base species for scaling the non-stomatal uptake of other chemical species including oVOCs has been used in several widely used community dry deposition schemes (e.g., Wesley et al, 1989; Zhang et al., 2003). The impact of reactivity on dry deposition cannot be quantitatively assessed or applied in dry deposition schemes due to the limited knowledge at present. It is their relative reactivity that are important for choosing model parameters (such as beta used in this model). All related chemical reactions are listed in Table S2 of Supporting Information. Because of these reasons, we do not have much to add to the existing discussion in Introduction regarding their reactivity.

I would suggest re-writing L32-L50 to make more general statements that are illustrated by the discrepancy between Zhang and Karl studies, rather than being so specific about these papers. Otherwise, the introduction reads more like a discussion and feels very narrow, and the expectation (L43) is written more like a conjecture. Give a range of ratios for oVOCs and O<sub>3</sub> V<sub>d</sub> so we can more clearly compare how they differ.

Here we tried to convey these facts: There are only two studies reporting higher V<sub>d</sub> for oVOC than those predicted by existing dry deposition schemes. Discussing some details revealed in one of the studies (Karl et al., 2010) can then illustrate (i) the possibly of chemical effect on dry deposition flux, and (ii) the potential large uncertainty in their flux data (which was not directly measured, but generated from concentration gradient using a model). We have modified the introductory sentences so that these discussions can be read in a logic way. The revised text reads: “In these existing schemes, V<sub>d</sub> of most oVOCs were on the similar magnitude to or slightly smaller than that of V<sub>d</sub> of O<sub>3</sub>. However, higher daytime V<sub>d</sub> values for certain oVOCs than predicted by existing schemes were reported lately by two studies (Karl et al. 2010; Nguyen et al., 2015). In one study Karl et al. (2010).....”

(3) L64: what specifically do you mean by ‘this approach’? The last sentence ends with the inability of the model to match high daytime values... making it unclear what approach you are referring to because the last description of the approach was a negative one. Give model context. L65, consideration 1: the introduction did not give sufficient context for what you mean here, please describe this more clearly. It is unclear how your approach addresses these considerations.

We have modified and moved this part to the third paragraph of section 2.2 *Extension of the scheme to additional chemical species*. This particularly sentence has been changed to this: “Model parameters chosen for the additional oVOCs and HCN can produce the magnitude of nighttime V<sub>d</sub> for nearly all the chemical species, but inevitably underpredicted daytime V<sub>d</sub> for several oVOCs species with very high measured daytime V<sub>d</sub> values.”

(4) End of introduction. L71-74: very general, long sentence. Reads more like a conclusion/future outlook. As does most of this paragraph. Much of this final paragraph does not appear to be relevant to the specific approach taken in this study, so it belongs earlier in the introduction or maybe in the conclusions. Be specific about what the contribution of your effort here is.

We have moved some of the materials in this paragraph to the place before describing our own approach in the Introduction, and rewritten the last two paragraphs of Introduction accordingly so the material can be presented in a logic way. We also feel that it may fit into conclusion, but we need such a discussion to support why we choose our approach, so we think it is better to

keep it in Introduction, and in a place before describing our approach. The revised text reads: “To meet the demands of modeling a large number of organic compounds in CTMs (Kelly et al., 2019; Moussa et al., 2016; Paulot et al., 2018; Pye et al., 2015; Xie et al., 2013), existing or newly developed air-surface exchange/dry deposition schemes need to be expanded to include additional oVOCs. At this stage with very limited knowledge on oVOC  $V_d$ , 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. For example, Nguyen et al. (2015) modified the Wesely (1989) scheme to fit the flux data. A more sophisticated model, with a bottom-up approach, was adopted in Nizzetto and Perlinger (2012) to handle air-canopy exchange of semivolatile organic compounds.

The original dry deposition scheme of Zhang et al. (2003) includes 9 inorganic species and 22 organic species. Most of these 22 organic species are oVOCs formed from oxidation of nonmethane hydrocarbons. To take advantage of the recent flux dataset of a large number of oVOCs and HCN collected over a temperate forest (Nguyen et al., 2015), the present study extends the Zhang et al. (2003) scheme by including 12 additional oVOC species and HCN while keeping the same original model structure and theory. These additional oVOCs include hydroxymethyl hydroperoxide, peroxyacetic acid, organic hydroxy nitrates, and other multifunctional species that are mainly formed from the oxidation of biogenic VOCs (e.g., isoprene and monoterpenes). Model parameters for these newly-included species are theoretically constrained based on the effective Henry’s law constants and oxidizing capacities of the individual species and by considering the measured  $V_d$  values as well. Such an approach provides a top-down determination of  $V_d$  through comparison with measured (bottom-up) fluxes. Model-measurement comparison is conducted for  $V_d$  as well as resistance components/uptake pathways, results from which identify the major causes of model-measurement discrepancies. This study provides a computer code that is potentially useful for CTMs handling these oVOCs.”

(5) Since the measurement of VOCs is highly dependence on the instruments used, state the instrumentation used to measure the 13 VOCs, HCN, H<sub>2</sub>O<sub>2</sub>, and HNO<sub>3</sub> in this paper instead of relying on the Nguyen et al., 2015 paper alone.

We have added a sentence to specify the instrument of oVOCs measurement, which reads “Mixing ratios of gas-phase compounds were measured with negative-ion chemical ionization mass spectrometry (CIMS) at 8 Hz or faster.”

(6) Were there ever net emissions of these compounds from the ecosystem, and how did that factor into  $V_d$  calculations? Please comment on what role soil uptake might or might not play in the large observed residual uptake of oVOCs during daytime dry conditions.

As mentioned above, field flux measurement data on oVOC are extremely rare. For most oVOCs considered here, dry deposition should dominate over emission so only net dry deposition is considered in the model.

Soil uptake should not be a dominate non-stomatal or residual uptake of oVOCs as it can be limited by the weak in-canopy turbulence especially for a closed canopy such as the forest site in this study.

(7) How is  $G_{ns}$  calculated, and how does that differ from  $G_{residual}$ ? An equation is only given for the latter (L231). The difference between the two, and why we must assume that  $G_{ns}$  terms are correctly estimated is not clear. Please elaborate and justify.

$G_{ns}$  is calculated according to Eq (3) in the manuscript ( $G_{ns} = 1/R_{ns} = 1/(R_{ac}+R_g) + 1/R_{cut}$ ). The  $R_{ac}$ ,  $R_g$ , and  $R_{cut}$  terms are from the modeling result of the Zhang scheme. As described in the manuscript,  $G_{residual}$  is estimated as  $[V_d^{-1} - (R_a + R_b)]^{-1} - (R_s + R_m)^{-1}$  where  $V_d$  is from the eddy-covariance measurements,  $R_s$  is calculated by the Penman-Monteith equation using measured water vapor flux,  $R_a$  and  $R_b$  rely on conventional micrometeorological approaches driven by measured meteorology (e.g.,  $u^*$ ). These formulas are clearly presented in the manuscript.

#### **Minor comments:**

L33: cite the existing schemes or describe how they are different from what you do here.

The existing schemes refer to those mentioned in the preceding sentence (Wesely, 1989; Zhang et al., 2003). We have added a sentence before this sentence and we think it is now clear. The revised text reads: “Due to the lack of field flux data of oVOCs,  $V_d$  of these species is typically parameterized based on physicochemical properties, taking  $SO_2$  and  $O_3$  as references (Wesely, 1989; Zhang et al., 2003). In these existing schemes,  $V_d$  of most oVOCs were on the similar magnitude to or slightly smaller than that of  $V_d$  of  $O_3$ . However, higher daytime  $V_d$  values for certain oVOCs than predicted by these schemes were reported lately by two studies (Karl et al. 2010; Nguyen et al., 2015)”

L54: be more specific, what does ‘community demands’ mean?

We have modified the sentence to this: “To meet the demands of modeling a large number of organic compounds in CTMs (Kelly et al., 2019; Moussa et al., 2016; Paulot et al., 2018; Pye et al., 2015; Xie et al., 2013), existing or newly developed air-surface exchange/dry deposition schemes need to be expanded to include additional oVOCs.”

L263: had instead of have

Corrected.

L270: discussion starts?

This paragraph starts interpolating the model evaluation results and discusses the possible causes of the model-measurement discrepancies using knowledge from literature. We have split this section into two separate sections for easy reading. The additional section is given a title of “3.3. *Fast chemical reactions as potential causes of the daytime model-measurement discrepancies.*”

L110: specify if you mean formic acid is the only species available in the original Model.

The original Zhang scheme (Zhang et al., 2003) includes 9 inorganic species and 22 organic species. Most of these 22 organic species are also oVOCs produced from nonmethane hydrocarbons (NMHCs) oxidation process. In this study, we extended the model to include 12 new oVOCs for which flux measurements over a temperate forest were available. These additional oVOCs include hydroxymethyl hydroperoxide, peroxyacetic acid, organic hydroxy nitrates, and other multifunctional species and are mainly formed from the oxidation of biogenic VOCs (e.g., isoprene and monoterpenes). Formic acid is the only overlapped species between the original model and the measurement data set. We have added the above information in the Introduction.