

We thank the reviewer for his/her comments on our paper. To guide the review process we have copied the reviewer comments *in black italics*. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (existing manuscript text **in bold text**, new/altered parts additionally **highlighted in yellow**).

Reviewer #3

General Comments: This is an interesting paper that has important implications for air quality modeling, particularly for prediction of secondary organic aerosol (SOA). The paper is well written and logically presented. The paper presents a modeling study where a new method for estimating Henry's law solubility constants (H) for gas-phase SVOCs is used in WRF-Chem to compute wet and dry deposition. They contend that this new method of estimating H for SVOCs according to volatility in the VBS SOA model in WRF-Chem reduces SOA concentrations by roughly half compared to modeling with no consideration of SVOC deposition.

R3.1 One problem is that the paper which describes the Henry's law estimates according to volatility is not yet published. Thus there should be more description of the parameterizations from the Hodzic et al. (2014) paper here.

The work by Hodzic et al. (2014) has now been published in Geophysical Research Letters and is available online. We would like to refer the reviewer to this publication for a detailed description of the parameterization. Given that this publication is now available, we deem the current description of the parameterization (p 13737, l 15ff) sufficient.

R3.2 While the study does a reasonable job of exploring various sources of uncertainty, a glaring exception is in the dry deposition calculations which is clearly a key process. The WRF-Chem uses the Wesely (1989) dry deposition model which parameterizes deposition with serial and parallel resistances. Many of the surface resistances are functions of Henry's law values for both wet and dry surfaces. The manuscript includes very little description of the dry deposition model and seems to assume that there is no significant uncertainty in its formulation. Wesely (1989) discusses many limitations and simplifications involved in his model and therefore makes it clear that the dry deposition estimates are very uncertain especially for chemical species other than ozone or SO₂. While the Wesely model was an important advance in dry deposition modeling when it was published it is now quite out of date. A particularly important aspect of the Wesely model is the pervasive influence of H in all conditions. More recent models parameterize resistance to wet surfaces as functions of solubility but not dry surfaces. Thus the

Wesely model is likely to be much more sensitive to H than other dry deposition models especially in dry climates. The resulting effects of including dry deposition on SOA as shown in Figure 4 seem unreasonable in that the effects are similar in the dry western part of the US as in the much wetter climate in the East. Even if it is hypothesized that dry cuticle resistance should scale on H there is so much less vegetation in most of the western areas that there should be little influence of solubility. There is certainly no reason that deposition to dry ground should scale on H. Thus I suggest that this study be re-modeled using a more up-to-date dry deposition model that has more realistic treatment of the effects of vegetation coverage and where the influence of solubility is primarily for wet surfaces (dew or rain).

We did not investigate the potential influence of uncertainties involved in the Wesely (1989) dry deposition scheme on our results, and we completely agree with the reviewer that this is an important question.

It was out of scope of our work to replace the dry deposition scheme in WRF-Chem. This would be a major undertaking and require rewriting substantial parts of the model, as well as involving a large amount of validation with measurements. Interestingly, most current chemistry-transport-models on both the regional as well as the global scale still use formulations of dry deposition based on Wesely (1989), though some included (considerable) modifications. The reviewer does not reference any of the “new” or “more recent” modeling systems, hence we were at a loss to understand which schemes the reviewer considers “current”.

We agree that the deposition velocities of surfaces like soil, rocks or built-up areas when dry should not scale with the Henry’s law constant. We still assume that the deposition velocities over vegetation are a function of Henry’s law constant even though the plants are not covered with rain or dew. H^* is used here for the exchange between the liquid water within a plant cell and the gas-phase in the stomatal cavity / above the cuticle, and not the wetted leaf surface.

With these assumptions and preconditions we conducted another simulation to assess the sensitivity of our results to the choice of the dry deposition scheme: in VEGFRA, dry deposition is assumed to be zero over non-vegetated areas, dry deposition velocities are hence scaled by the vegetated fraction of each grid cell. This represents the lower bound of the effect of dry deposition, considering dry deposition only over vegetated areas, and should address the reviewer’s concerns that the pervasiveness of H^* in the calculation of dry deposition velocities exaggerates the importance of dry deposition. Our results show that even under the assumption of no dry deposition at all onto surfaces other than

vegetation - clearly a lower bound for its effect - more mass is lost through gas-phase deposition than through the particle phase, and average surface level SOA concentrations are still reduced by -31 / -45 % compared to a simulation without considering dry deposition of SVOCs.

The revised section 5.3 now reads:

5.3 Dry deposition scheme

Removal of trace gases from the atmosphere through 'dry deposition' is modeled based on the resistance analogy developed in Wesely (1989). While the atmospheric and laminar sublayer resistances are functions solely of the meteorological conditions and the diffusivity of the trace gas, the bulk surface resistance depends firstly on the accuracy of properties of the land surface like e.g., the vegetated fraction, leaf area index, or the type of soil present (i.e. the input datasets), and, secondly, on how these properties are translated into a bulk surface resistance value (i.e., the dry deposition scheme). Uncertainty in both the datasets as well as the scheme used introduces considerable uncertainty in the contribution of dry deposition to total removal.

Improving the description of the Earth's surface in WRF-Chem is a major undertaking and not part of this investigation. It was also out-of-scope of this work to replace the dry deposition scheme included. However, we conducted another sensitivity study to elucidate the magnitude of uncertainty introduced through the assumptions made in the Wesely (1989) scheme.

A possible source of error is the dependency of the bulk surface resistance calculation on the Henry's law constant even under completely dry conditions in Wesely (1989). It is sensible to scale the mesophyll and leaf cuticle resistances of vegetation by the Henry's law constant even when it is dry, as the function of the Henry's law constant there is to describe the exchange of a gas with the water within a plant cell. However, this assumption does not necessarily hold true for the lower canopy and ground resistances, which are functions of H^* in Wesely (1989) as well. Dry deposition over structures, buildings, etc., will probably not be a function of the Henry's law constant under dry conditions. To consider this uncertainty and to provide a lower bound for the effect of dry deposition, we conducted a sensitivity study which we named 'VEGFRA'. There, we scale the dry deposition flux by the vegetated fraction in each grid cell, essentially assuming no dry deposition at all over surface types other than vegetation.

Our results show (Table 4) that, even if we do not dry deposit over land surface types other than vegetation, dry deposition through the gas-phase is still responsible for more than half of the total deposited mass (53/69 % in VEGFRA

instead of 59/74 % in REF for anthropogenic and biogenic precursors respectively), and still leads to reductions in average SOA concentrations over land of 31/45 % respectively.

Finally, the Wesely (1989) dry deposition scheme considers the effect of chemical processing of reactive VOCs within plants by adding a reactivity factor f_0 to the calculation of mesophyll and leaf cuticular resistances. An f_0 of 0 represents unreactive substances, whereas $f_0 = 1.0$ treats a species like O_3 (which immediately decomposes within the plant). In our work f_0 is set to 0.0, considering SVOCs to be unreactive. Karl et al. (2010) suggested based on flux measurements that oxidized organic trace gases should be considered reactive ($f_0 > 0$). To understand the effect of this treatment we conducted additional simulations where we set f_0 to 0.1 (F_0.1, slightly reactive) and 1.0 (F_1.0, reactive like O_3). We did not observe notable changes in the amount of deposited SVOCs or in SOA concentrations (not shown). This is reasoned by the fact that H^* values from GECKO used in our study are sufficiently high so that solubility dominates the mesophyll and cuticular resistances and the additional reduction in these resistances due to reactivity is negligible.

Specific comments:

R3.3 Page13734 line1: It should be noted that the CMAQ model uses acetic acid as a surrogate in the dry deposition calculation and adipic acid in the wet deposition calculation.

We have rephrased the sentence which now reads

Deposition of gas-phase SVOCs in current modeling systems is largely unconstrained and, if considered at all, typically scaled to the deposition of HNO_3 , CH_3COOH , or other reference compounds with known solubility.

It is unclear to us what the scientific basis might be to justify the use of different solubilities for dry and wet deposition processes, and no reference was provided by the reviewer that may contain such a justification. It would appear that they are just educated guesses.

R3.4 P13737 In11-12: How the Wesely model uses H in the parameterization of various surface resistances should be much more thoroughly described. Simply saying that H is used for “partitioning into plants and other wet surfaces” is incomplete and incorrect. If H were not also used in scaling of resistances to dry surfaces the effects shown in this paper would probably not be nearly so large. These issues need to be addressed.

The sentence has been rephrased and now reads:

[...] and a bulk surface resistance. The latter is a function of the Henry's law constant of a gas through its use in the calculation of the mesophyll and leaf cuticular resistance of vegetation. The lower canopy (representing structures, buildings, etc.) and ground resistances scale with the Henry's law constant as well, irrespective of whether the surface is wet or not. A reactivity factor [...]

We show (see our reply R3.2 and the new section 5.3 in the revised manuscript) that dry deposition is still the major loss process even if no dry deposition is considered at all over surfaces other than vegetation.

R3.5 P13738ln15: what is "the forcing data"?

The GFS analyses mentioned in the first part of the sentence. We have rewritten the sentence to clarify:

Each of these runs is preceded by a 6h meteorology-only spin up which is started from GFS analyses and nudged to this dataset above the planetary boundary layer.

R3.6 P13739lns12-16: The surface resistance should become negligible at very high H^ only when the ground and leaves are wet. I think this is a critical flaw in this study.*

We believe we sufficiently addressed this uncertainty - please refer to our replies R3.2, R3.4 and the corresponding updates to the manuscript.

R3.7 P13742ln2: I think the words "in summer" were left off the end of this sentence.

Corrected.

R3.8 P13745ln8: Please give reference for the H^ value for HNO_3 . Note that Wesely (1989) used $10e14$.*

For HNO_3 we used

Chameides, W. L. (1984), The photochemistry of a remote marine stratiform cloud, J. Geophys. Res., 89(D3), 4739–4755, doi:10.1029/JD089iD03p04739.

For the newly introduced sensitivity study using acetic acid we used

Johnson, B. J., Betterton, E. A., & Craig, D. (1996). Henry's law coefficients of formic and acetic acids. *Journal of Atmospheric Chemistry*, 24(2), 113-119.

Both references have been added to the text.

R3.9 P13746Ins10-11: please re-write this sentence.

The sentence now reads

We did not observe notable changes in the amount of deposited SVOCs or in SOA concentrations (not shown).

R3.10 P13746In22: should give units.

Fixed.

R3.11 P13747Ins27-29: This sentence should be qualified to state “for wet deposition only”. There is no such evaluation and confidence for dry deposition.

The sentence has been rephrased and now reads

We evaluated the modeling system against measurements of precipitation and wet deposition of inorganic ions, which lends confidence that the underlying wet removal process is accurately captured.

R3.12 Figure 5: these plots are way too small.

We have ensured that the plots are legible in the final version of the manuscript.