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Comment

# ***Interactive comment on “The effect of dry and wet deposition of condensable vapors on secondary organic aerosols concentrations over the continental US” by C. Knote et al.***

## **Anonymous Referee #1**

Received and published: 30 June 2014

Knote et al perform a sensitivity analysis to evaluate the impact of uncertainties in dry and wet deposition of SVOCs on SOA model predictions. They use the WRF-Chem model implemented with the VBS SOA formation scheme for this analysis. Recent work has suggested that Henry’s law constants for SVOC species may be substantially larger than what is typically used in models meaning that deposition would be enhanced. Knote et al, implement these new higher Henry’s law constants and evaluate their impact on wet and dry deposition separately and together. Due to the large uncertainty in this parameter they also conduct a series of sensitivity analyses using different Henry’s law constants, different SOA aging rates, and different reactivity factors. They

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Interactive Discussion

Discussion Paper

find that the use of the higher Henry's law constant can reduce SOA concentrations by 50% compared to no deposition of SVOCs, mostly due to enhanced dry deposition. This study addresses an important uncertainty in modeling SOA concentrations that has not previously received a great deal of attention. I have some suggestions for improvements, but recommend publication after revisions.

General comments:

Discussion of emissions on page 13736 and 13738: Emissions inputs have a large impact on any VBS results so it is essential to have a full description of what emissions were used in order for the reader to properly understand the results. The authors should add details on the emissions used including:

\*\*On page 13736, line 1, the authors mention mapping of SAPRC99 species to MOZART species but do not mention that the AQMEII emissions were originally available as CB05. A similar table in the supplement should show how the CB05 species were first mapped to SAPRC99 species before the second mapping to MOZART species could take place.

\*\*Please specify whether the 2010 AQMEII emissions are based on the 2005 or 2008 NEI. Substantial changes to methods (including switch of mobile emissions model from MOBILE6 to MOVES) occurred between these two inventories so it is important to state what base-year NEI was used to derive the AQMEII emissions.

\*\*Please describe how the organic emissions were apportioned to volatility bins. Were emissions of IVOCs and SVOCs included in these emissions? If so, what assumptions were used to derive these emissions since they were not part of the AQMEII emissions inputs? Many past VBS studies have apportioned POA emissions into different volatility bins and have assumed some additional IVOC/SVOC mass determined by applying a factor to the POA emissions (sometimes increasing POA emissions by up to a factor of 7.5 to account for "unmeasured" IVOC mass in the inventory). Were any such assumptions made here? The authors state that POA was treated as non-volatile. If

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this is the case, then previously developed factors for increasing organic mass before distributing POA into volatility bins may not be appropriate here. If no IVOCs or SVOCs were emitted, then state this explicitly. If emissions for these species were derived, please describe and justify the methods used.

Please provide more description of the Hodzic et al results used to determine  $H^*$ . Since the new Hodzic et al.  $H^*$  values are the basis for this work, more details are warranted. What specific compounds are used to create the weighted  $H^*$  values for each volatility bin? Are these compounds primary VOC oxidation products or are they the result of multiple oxidation steps? Is it reasonable to believe that such highly soluble compounds would be found universally in all ambient aerosol across the United States or might their prevalence vary based on spatially varying meteorology (humidity, insolation rates etc) and emissions sources?

The authors conduct simulations using the higher  $H^*$  values from Hodzic et al and compare those against simulations with no deposition. However, perhaps a fairer comparison would be the Hodzic  $H^*$  values compared to more typical assumptions of  $H^*$  in the photochemical models. I'd suggest that the authors conduct another sensitivity simulation using "traditional"  $H^*$  assumption. For instance, acetic acid is used as a surrogate for dry deposition of SVOC vapors in the CMAQ model ( $H^* = 4.1 \times 10^{-3}$ ) and adipic acid is used as a surrogate for wet deposition of SVOC vapors (see Carleton et al., 2010). Or, the authors could use the Ahmadov suggestion (0.25-0.5 times the  $\text{HNO}_3$  rate) for their "traditional"  $H^*$  sensitivity. Comparing against "no dep" baseline is a bit of a strawman.

The article would benefit from some more in depth model evaluation:

\*\*Why is model performance for  $\text{NH}_4$  wet dep worse than either  $\text{NO}_3$  or  $\text{SO}_4$  wet dep? It seems like these should be related. Some exploration of this question is warranted. Wet deposition is an important endpoint, but looking at ambient concentrations may be more informative in terms of model performance. Consider adding analysis

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of IMPROVE ambient nitrate and sulfate concentrations (IMPROVE measurements of ammonium are only available at a limited number of sites for limited time periods). The CSN network measures all three compounds, but may be less appropriate here since that is an urban-focused network and the grid resolution (36 km) may be too coarse to capture urban gradients. The last sentence on lines 18-20 of page 13740 may be a bit of an overstatement: “The model results . . . shows that the underlying processes are accurately modeled . . .” Compensating errors cannot be ruled out without a more thorough model evaluation.

\*\*The spatial and temporal averaging used in evaluation of OC concentrations may mask model performance issues. Wintertime OC concentrations are likely dominated by POA while summertime OC concentrations are largely due to SOA. Consequently looking only at annual average values may make interpretation of results difficult. In figure 5 (top left), I suggest that rather than looking at the annual average at each monitor location, you include daily (24-hr avg) data in the scatterplot. If data are too dense to be distinguished on the scatter plot a density scatter plot could be used. The R2 and NMB metrics should definitely be calculated using daily data in addition to (or in place of) annual average data. The map might be more informative if it was created by season since the physical and chemical processes governing OC fate and transport are different in summer and winter. Perhaps include a map of summertime average in the main paper and maps of other seasons in the supplemental information.

\*\*Spatial averaging used to create time series plots for figure 5 may also obscure spatially varying patterns. Consider grouping monitors into regions based on similar OC sources/concentrations (i.e. the OC in the Southeastern US is formed from different sources than the OC in the Northeast corridor or near Los Angeles). Consider creating time series plots for each region to see if different patterns emerge in different areas. Since these results are the meat of the paper, it is worth exploring them in a little more depth.

\*\*It might also be interesting to look at the diurnal cycle of OC and how that is impacted

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by the deposition scheme. This may give some insight into whether the volatility of OC is being properly captured in the modeling. I believe that hourly OC measurements are available at SEARCH network sites.

Minor comments: Page 13734, line 25: change “that” to “than”

Page 13736, line 25: The text references a  $C^*$  bin of 0.001 but Figure 1 represents the lowest volatility bin as  $10^{-4}$ . Which is it? Please fix either the figure or the text (note that the 0.001 value is stated other places in the text as well, for instance page 13739, line 4).

Page 13738, line 12: Rao et al, 2011 is not the appropriate reference for AQMEII phase 2 emissions inputs since this is an overview article on AQMEII phase 1 and does not include any technical details. Please find a more appropriate reference.

Page 13740, line 16: NMB should be -38%, not 0.69.

Page 13741, lines 8-10: Why doesn't wet deposition have a greater impact in the southeastern US where both OC concentrations and precipitation are high?

Page 13742, line 10: The modeled month-to-month evolution may be more similar to the observed evolution but it is still more pronounced than the observed annual pattern.

Page 13742, line 19-20: This statement is not accurate for wintertime underestimates which are not driven by SOA. The REF and NODEP results look similarly low during wintertime months.

Page 13744, lines 17-19: Others have also suggested this as well. For instance, Grieshop et al (2009) apply a more aggressive aging scheme (each oxidation step results in  $C^*$  drop of 2 volatility bins rather than 1 and rate constant  $K_{OH} = 2 \times 10^{-11}$ ) to match measured behavior.

Figure 5: This figure shows some unexpected results in that OC looks unbiased in August but not in other months. This is not what would be expected if SOA under-

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predictions were driving the model bias for OC. The persistent OC under-prediction in winter months also suggests that SOA/SVOC biases are only one factor in model performance issues for OC. A bit more discussion and interpretations of these results would be useful.

Figure 8: This is an informative plot. Could the authors make a similar plot for their WRF-Chem results comparing the volatility distributions in different sensitivity runs?

Refs: Carleton, A.M., Bhawe, P.V., Napelenok, S.L., Edney, E.O., Sarwar, G., Pinder, R.W., Pouliot, G.A., Houyoux, M. (2010) Model representation of secondary organic aerosol in CMAQv4.7, ES&T, 44, 8553-8560.

Grieshop, A.P., Logue, J.M., Donahue, N.M., Robinson, A.L. (2009) Laboratory investigation of photochemical oxidation from wood fires 1: measurement and simulation of organic aerosol evolution, ACP, 9, 1263-1277.

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[Interactive comment on Atmos. Chem. Phys. Discuss., 14, 13731, 2014.](#)

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