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 #1

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 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:

R1.1 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.

The mapping from SAPRC to MOZART mentioned in the text refers to SOA yields as provided in Lane et al. (2008). These are not emissions, but rather reflect the amount of SOA formed per oxidation reaction of a certain precursor.

We agree with the reviewer that conversion tables for emission species are helpful to other modellers. We have added two tables to the supplement that detail the conversion of gaseous and particulate emissions from CB05 / AER06 to MOZART / MOSAIC respectively. These are now referenced in the text as:

Emission conversion tables for the MOZART/MOSAIC setup used in this work are given in Tables S1 / S2 in the supplement. The simulations are split into 48 h long chunks of free running meteorology [...]

The tables are also reproduced at the end of this document.

R1.2 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.

The section has been updated to include more information about emissions preprocessing. A separate publication detailing the preparation process (Pouliot et al., 2014, currently under review) has been referenced as well. The updated paragraph reads

[...] conducted within the MACC project. Emissions of trace gases and aerosols are those provided in phase 2 of the Air Quality Model Evaluation International Initiative model intercomparison (AQMEII, Alapaty et al., 2012). For the United States, the 2008 National Emission Inventory (NEI) (version 2, released April 10, 2012) was used (http://www.epa.gov/ttn/chief/net/2008inventory.html). Updates for the following activity sectors were applied to reflect changes in emissions between 2008 and 2010: on-/off-road transport, wildfires and prescribed fires, and continuous emission monitoring equipped point sources. Preparation of the emission data is described in detail in Pouliot et al. (2014). Emission conversion tables [...]

R1.3 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 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.*

We consider POA as a non-volatile species, and therefore POA is emitted into the particle-phase and does not partition between gas- and particle-phase. We did not emit any additional S/IVOC gases in our runs, as we assumed that they are already partially included in our inert POA. POA is however considered as additional particle-phase organic material in the pseudo-equilibrium calculations.

All SOA mass is formed through the oxidation of gaseous precursors such as isoprene, monoterpenes, benzene, toluene, and so forth. Oxidation products (by OH and O3) of these precursors are distributed according to their volatility into the VBS bins.

We already stated in the manuscript that POA is inert (p 13736, l 23-25). To emphasize that we don't include SVOC/IVOC emissions we extended this sentence, which now reads

Direct emissions of organic particulates (primary organic aerosols, POA) are included as inert contribution to aerosol mass without consideration of evaporation and re-condensation. Direct emissions of semi / intermediate volatility organic compounds (SVOC/IVOC) are not considered in this study.

R1.4 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?*

As suggested by the reviewer we have provided a more detailed description of the solubility parameterization. H* values applied in this study were calculated by Hodzic et al. using the explicit chemical mechanism GECKO-A (Aumont et al., 2005) for the multi-generational oxidation products of individual SOA precursors. Values of H* were taken at the maximum of the SOA formation from each individual precursor, which is typically after 1-3 days of chemical processing (several steps of oxidation) depending on the precursor, and provided as a function of the volatility (VBS bins). In each volatility bin, a mass-weighted H* was calculated (see Table 1 in Hodzic et al. 2014). Using those values, we calculated in this study an averaged H* for both biogenic and anthropogenic precursor species. I.e. for biogenic species H* was averaged for isoprene and terpenes, whereas for anthropogenic species H* was averaged for short-chain alkanes and alkenes, and aromatics.

It is reasonable to consider that highly processed and oxygenated species (with 3-4 functional groups) will be highly soluble (Hodzic et al., 2013). The degree of chemical ageing/processing will of course depend on OH levels, as well as the type of precursors. As suggested by Hodzic et al., 2014, products of isoprene are typically more soluble than products of n-alkanes. The ageing that is considered in the VBS parameterization allows taking into account the amount of solar radiation through OH oxidation, and shifting the mass from volatile and less soluble VBS bins, into less volatile and more soluble ones. We acknowledge that large uncertainties still exist in the formation mechanisms of SOA (e.g. missing aqueous and in-particle phase reactions) that could impact the volatility of the oxidation products and our results, and we have tested the robustness of our results to changes in the volatility distribution.

This is now better explained on the manuscript:

Henry's law constants (H*, M atm^{-1}) used in this study for semi-volatile organic compounds were provided as a function of volatility by Hodzic et al. (2014a). They applied an explicit chemical mechanism (GECKO-A, Aumont et al., 2005) to generate the multi-generational oxidation products of individual SOA precursors and calculate the associated H* values using structure activity relationships (Raventos-Duran et al. 2010). Values of H* were taken at the maximum of the SOA formation from each individual precursor, which is typically after 1-3 days of chemical processing depending on the precursor, and provided as a function of the volatility (VBS bins). In each volatility bin, a mass-weighted H* was calculated (see Table 1 in Hodzic et al. 2014). Using those values, we calculated in this study an averaged H* for both biogenic and anthropogenic precursor species (Table 2). Dry and/or wet deposition of these volatile compounds is then considered by adding these species to the respective modules in WRF-Chem described above.

R1.5 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* = 4.1x10ˆ3) 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 HNO3 rate) for their "traditional" H* sensitivity. Comparing against "no dep" baseline is a bit of a strawman.*

The reviewer may have missed that simulations considering lower (but non-zero) Henry's law constants (H* = 1e5, H* = H*(HNO_3)) were already included and discussed in the manuscript (see the abstract, section 5.2, the conclusions, Figure 7, and Table 3). We showed that using H* = 1e5 leads to 25% and H* = H*(HNO_3) to 10 % overestimation of SOA concentrations vs. using the H* values derived in Hodzic et al., 2014. We agree with the reviewer that the simulation with no deposition is unrealistic, however it is a useful sensitivity case in that it provides an upper limit for quantifying the impact of this processus.

Given that the values for H* suggested by the reviewer are in between 0 and 1e5, the resulting overestimations will be between 50 and 25%. To estimate that value more precisely we conducted an additional simulation with H* = H* (CH_3COOH) (4.1e3, -dlnH/dlnT 6300, Johnson et al., 1996). This is now mentioned in the abstract

Assumptions about the water solubility of SVOCs made in some current modeling systems (H* = H*(CH_3COOH); H* = 10^5 M atm^{-1}; H* = H*(HNO_3)) still lead to an overestimation of 35% / 25% / 10% compared to our best estimate.

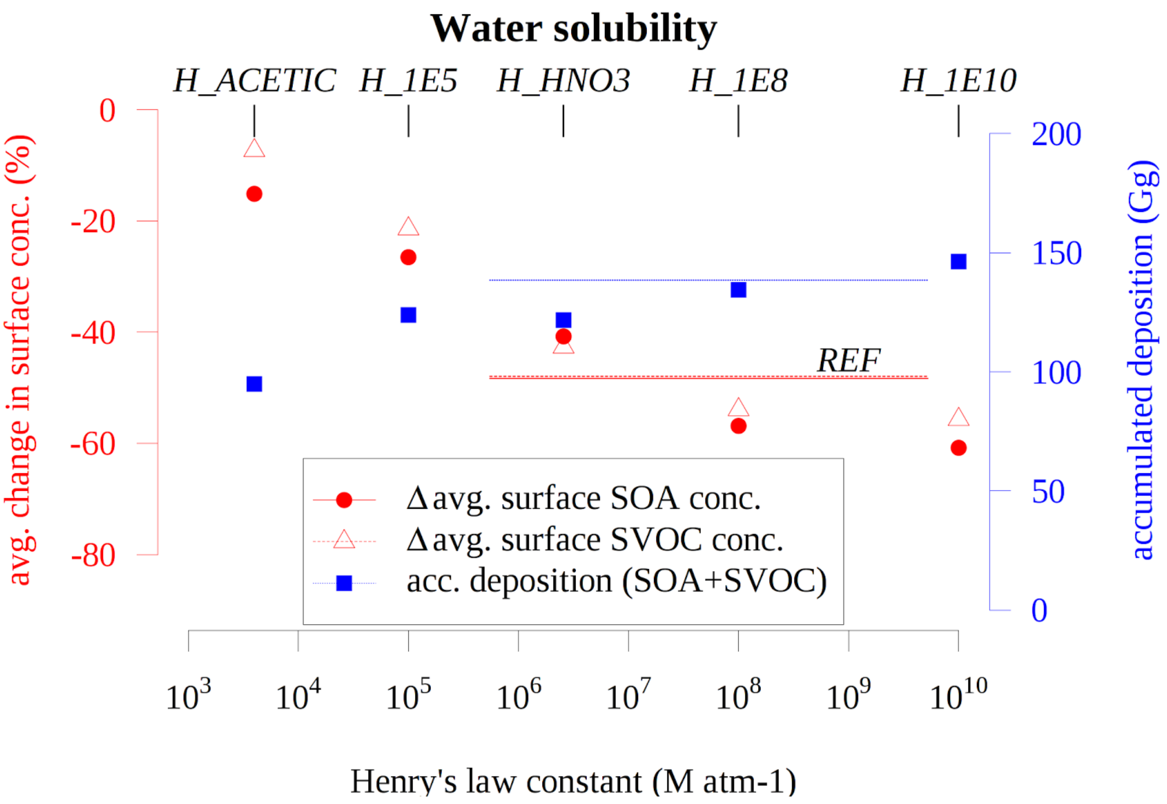
and in section 2.3

[...] but which are assumed to be very soluble. The fifth simulation (H_ACETIC) employs the Henry's law constant of acetic acid (CH_3COOH), as this is very similar to the values currently used in the Community Multi-Scale Air Quality Model (CMAQ, https://www.cmascenter.org/cmaq/, accessed July 18 2014). In the final two simulations [...]

and in section 5.2

[...] In these simulations we ignore the temperature dependence of the Henry's law constants. Additionally we included two simulations using Henry's law values derived for CH_3COOH (H* = 4.1 × 10^3 M atm^{-1} , d(ln H*)/d(1/T) = 6300) and HNO_3 (H* = 2.6×10^6 Matm−1, d(lnH*)/d(1/T) = 8700), commonly used in models as reference for very soluble compounds for which exact H∗ values are unknown. [...]

Figure 7 was updated accordingly:

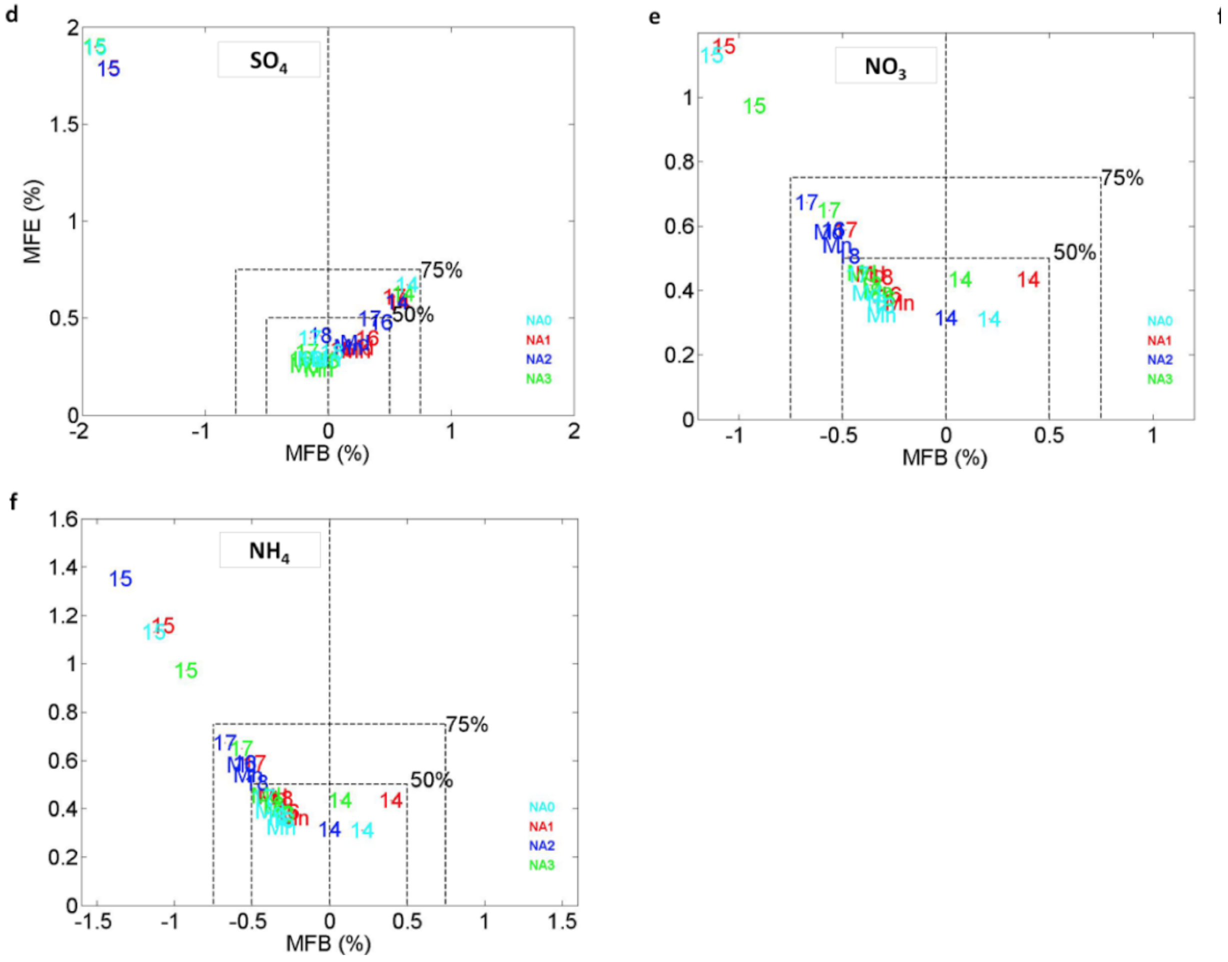


The article would benefit from some more in depth model evaluation:

R1.6 Why is model performance for NH4 wet dep worse than either NO3 or SO4 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 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.

For a more general model evaluation and intercomparison would like to refer the reviewer to the upcoming results of the AQMEII phase 2 model intercomparison, in which the model system used in our work was employed in a very similar configuration (same parameterizations, grid and input data, only differing in the way SOA is formed and removed). Two manuscripts describe the model evaluation of O_3 and particulate matter (Im et al., 2014a, 2014b).

The following Figure (adapted from Figure 12 in Im et al., 2014b) is a “soccer plot” (Appel et al., 2011) showing the performance of different setups of WRF-Chem (NCAR, North Carolina State University, University of Murcia / Spain), WRF-CMAQ (U.S. EPA), and GEM-MACH (Env. Canada) when compared against a combination of CASTnet, IMPROVE and the US E.P.A. AQS data (http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm) (SO_4 at 250, NO_3 at 148, and NH_4 at 149 stations). Our model simulations are marked by the number 17. The results are further broken down into subregions (Im et al., 2014b) NA1 (southwest), NA2 (southeast), and NA3 (northeast). NA0 are statistics over all stations.



These results in particular and the overall results of AQMEII phase 2 show that our model performance is on par with the suite of state-of-the-art modeling systems participating in AQMEII phase 2. We agree with the reviewer that there might be compensating errors that we could not identify with the limited evaluation done in this work.

We note that NH_3 (and subsequently NH_4^+) modeling has been notoriously difficult for current modeling systems as there is evidence that a more sophisticated parameterization of the bidirectional surface <-> atmosphere flux than simple emission fluxes is needed (e.g. Nemitz et al., 2001; Bash et al., 2013).

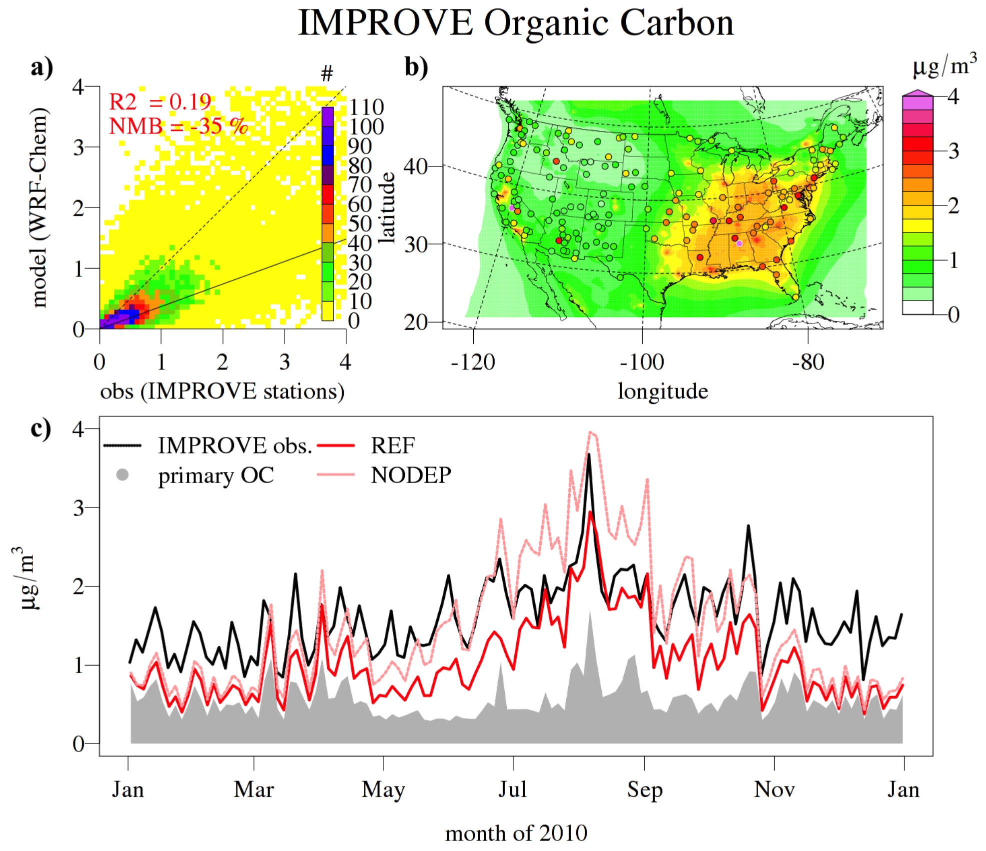
This discussion has been reflected in the text which now reads:

[...] wet deposition of ammonium is underestimated but still has a good correlation with measurements (R^2 = 0.69, NMB = −38). This deficiency could be related to the lack of a bi-directional exchange model in WRF-Chem to describe the flux of NH_3 at the surface (Nemitz et al., 2001; Bash et al., 2013). Measurements of water-soluble organics are not available so we could not directly evaluate the performance of WRF-Chem. The model results of wet deposition of inorganic ions however shows that the underlying processes are reasonably modeled, lending credibility to the accuracy of the wet deposition of organic substances.

R1.7 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.

We agree with the reviewer. We have accordingly modified Figure 5 (and added a new Figure 6, see R1.8). We now show a density scatterplot based on daily values. A scatterplot and map using only summer values has been added to the Supplementary Material, and is referenced in the revised text.

We identified an error in the plotting routine which erroneously showed SOA concentrations instead of POA concentrations as grey area in the time series, which is now corrected. This now even more clearly shows that wintertime is considerably more influenced by POA in the model as the reviewer already pointed out (see also our reply R1.18).



The revised figure caption now reads:

Evaluation of ground level total organic carbon (OC) concentrations against IMPROVE measurements. a) density scatterplot of daily average concentrations at each IMPROVE station against modeled concentrations (R^2 and NMB as defined in Fig. 3, again using the REF simulation). b) annual average OC surface level concentrations (REF simulation). Filled circles represent measured concentrations. c) time evolution of OC concentrations as average over all IMPROVE stations. Black solid line is measurement average. Grey area represents the POC contribution to total OC (from REF simulation). Light red and red lines are NODEP and REF simulation averages of total OC respectively.

R1.8 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 serious 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.

We have created an additional Figure 6 in which we show the performance when compared in the 3 subregions of most interest: the West coast, the Northeast, and the Southeast (see below). This plot is now referenced in the text:

In the REF simulation with removals, the overall concentrations of OC are underestimated compared to measurements, but the month-to-month evolution is considerably more similar to the observed evolution. We further disaggregated the analysis spatially and looked at the performance at stations at the west coast, the Northeast and the Southeast (Fig. 6). Our findings show that on the west coast, modeled OC is underestimated in all simulations, while in the Eastern US, both REF and LOWVOL results track observed OC concentrations well during July and August, but underestimate them in June.

We further [...]

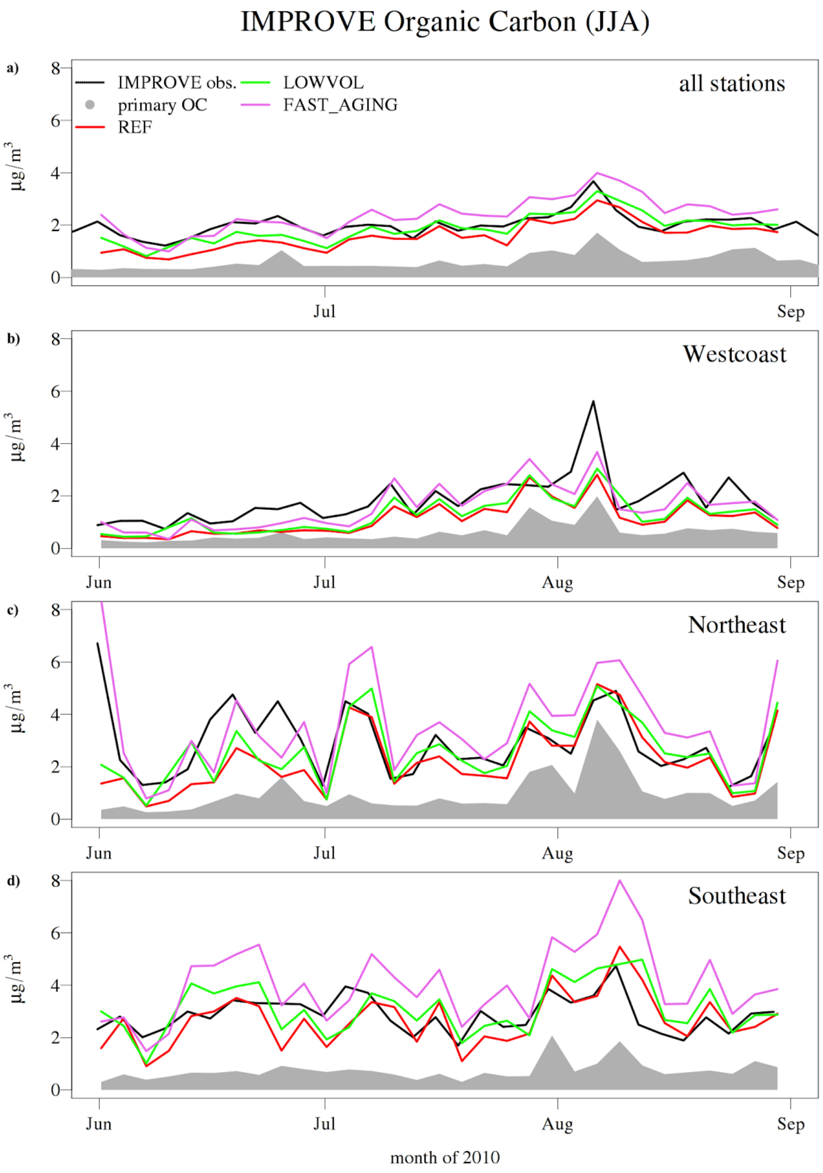


Fig. 6. Time lines of ground level total organic carbon (OC) concentrations against IMPROVE measurements like in Figure 5, but only for the summer period (June, July, August). Green and pink lines are for LOWVOL and FAST AGING sensitivity studies, respectively. a) all stations. b) west coast: California, Oregon, Washington. c) Northeast: Connecticut, Maine, Massachusetts, New Hampshire, Vermont, New Jersey, New York, Pennsylvania, Maryland, District of Columbia, Illinois, Indiana, Michigan, Ohio. d) Southeast: Alabama, Florida, Kentucky, Georgia, North Carolina, South Carolina, Tennessee, West Virginia, Virginia.

R1.9 It might also be interesting to look at the diurnal cycle of OC and how that is impacted 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.

We compared model results against OM measurements at the 4 stations in the SEARCH network that had hourly OM data (BHM, CTR, JST, YRK). The results of the average (JJA) diurnal cycles are shown in the Figure below. It appears that the inclusion of wet deposition of SVOCs has negligible effects on the diurnal cycle. Considering dry deposition of SVOCs slightly reduces the diurnal variability of OM concentrations. Interestingly, the sensitivity studies to access the effect of volatility (LOWVOL, FAST_AGING) lead to a slight shift in overall concentrations, but not to a visible change in the diurnal amplitude of OM concentrations.

The text has been amended in sections 4.1

[...] Our findings show that at the west coast, modeled OC is underestimated in all simulations, while in the Eastern US, both REF and LOWVOL results track observed OC concentrations well during July and August, but underestimate them in June. OC concentrations are overestimated in the FAST_AGING simulation, especially in the Southeast.

We further compared our results to hourly measurements of organic matter (OM) conducted within the Southeastern Aerosol Research and Characterization study (SEARCH, Hansen et al., 2012) to understand the effects of dry and wet deposition of SVOCs on the diurnal cycle of OM. Four stations in the Southeast (North Birmingham, AL - BHM; Centreville, AL - CTR; Yorkville, 270 GA - YRK; Jefferson Street, GA - JST) had measurements available (http://www.atmospheric-research.com/studies/search/SEARCHFactSheet.pdf, last accessed 11 Aug 2014, for site locationsand description). The resulting averaged diurnal cycles are shown in Figure 6. We find that including wet deposition of SVOCs has no effect on the diurnal cycle of OM at these stations, possibly due to the non-local nature of this removal process: washout affects the whole column up to the cloud where the precipitation originates, hence such an event also reduces concentrations aloft which are then advected. Dry deposition instead only acts on the lowest grid cell. Including dry deposition of SVOCs leads to a reduction in the diurnal amplitude of OM concentrations, and a better agreement with observations. In general, modeled diurnal amplitudes are larger than the observed ones. At all stations, with the exception of BHM, observed OM is more or less constant

throughout the day. Judging based on the observations at BHM and minor variations seen at the other stations we observe that the timing of diurnal maxima and minima differ between observations and model. Modeled diurnal cycles indicate a morning minimum in OM concentrations (possibly due to the rise of the boundary layer) and a maximum in the afternoon (maximum of photochemical SOA production), whereas the observed maximum OM concentrations occur in the early morning (around 6 LT) - arguably the time with the lowest boundary layer height and high primary emissions - and the observed minimum is during late afternoon hours (around 18 LT).

In our study we only consider "traditional" SOA formation mechanisms (pure gas-phase oxidation), [...]

and 5.1

[...] This suggests that VBS schemes currently used create a volatility distribution that is too volatile compared to the real atmosphere (observed before by e.g., Grieshop et al., 2009), although other effects may also be important.

Interestingly, when looking at the average diurnal cycles of OM (Figure 6), the effect of changing the volatility distribution leads to a mere shift in concentrations, but not to a change in the diurnal cycle, as it might have been expected.

5.2 Water solubility of SVOCs

And the following figure has been added:

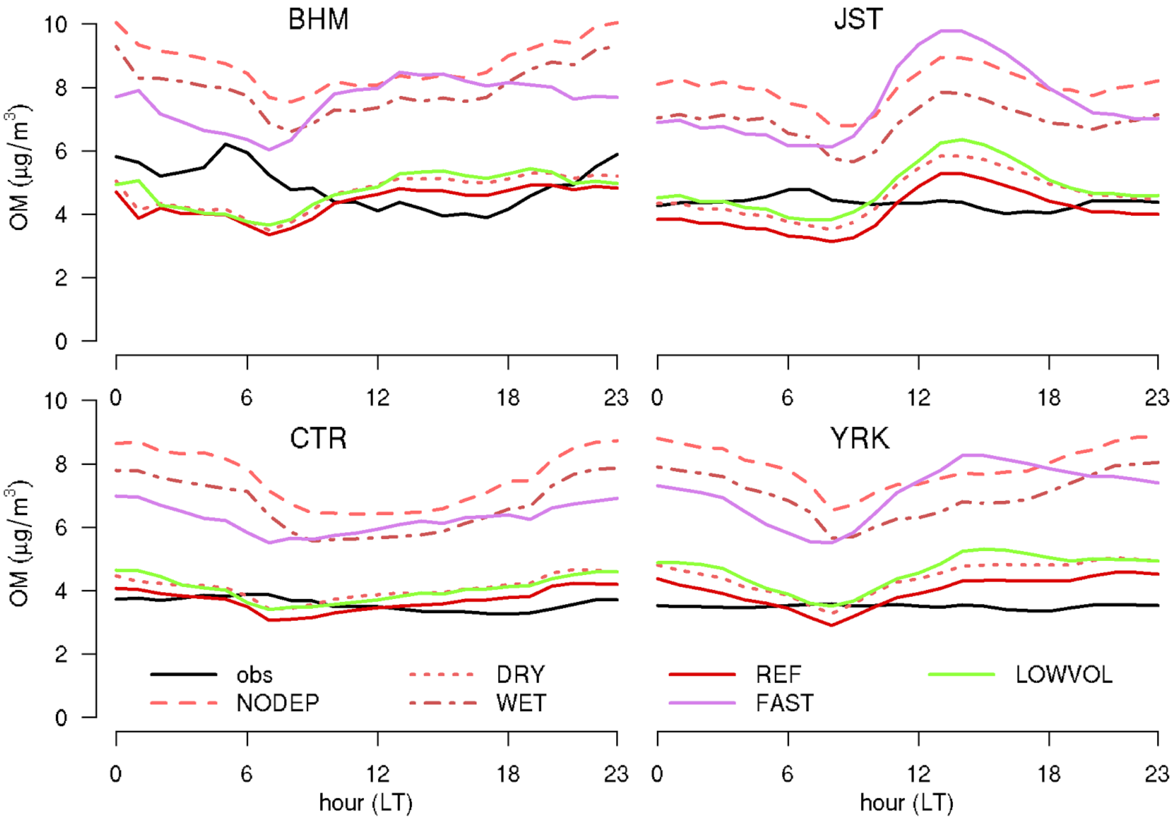


Fig. 6. JJA average diurnal cycles of organic matter (OM) concentrations at 4 field sites of the SEARCH network. Measurements assume an OM/OC ratio of 1.4 (Hansen et al., 2012).

Minor comments:

R1.10 Page 13734, line 25: change “that” to “than”

Changed.

R1.11 Page 13736, line 25: The text references a C bin of 0.001 but Figure 1 represents the lowest volatility bin as 10ˆ-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).*

It is 10^{-4}, as given in the schematic. The text has been updated accordingly.

R1.12 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.

The reference of AQMEII phase 2 has been updated, please refer to our response to R1.2 for detailed changes.

R1.13 Page 13740, line 16: NMB should be -38%, not 0.69.

Corrected.

R1.14 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?

It does have a greater impact in absolute terms, but the relative figures are very similar. We find that wet deposition of condensable organic vapors in general is much less effective than dry deposition (O(10%) vs. O(50%)), probably limited by the amount of liquid water available for partitioning.

R1.15 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.

We agree and have altered the sentence to emphasize that we are discussing the month-to-month evolution:

[...] In the REF simulation with removals, the overall concentrations of OC are underestimated compared to measurements, but the month-to-month evolution is considerably more similar to the observed evolution. [...]

R1.16 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.

We agree and have rephrased the sentence which now reads:

[...] will be similar. Including these processes would then increase concentrations shown in Fig. 5, predominantly during summer months where SOA contributes most to total OA, potentially closing the gap between

measurements and model results.

R1.17 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 = 2x10ˆ-11) to match measured behavior.*

We have included a number of references on this topic:

This suggests that VBS schemes currently used create a volatility distribution that is too volatile compared to ambient aerosols (observed before by e.g., Grieshop et al., 2009; Hodzic et al., 2010; Cappa and Jimenez, 2010; Lee-Taylor et al., 2011), although other effects may also be important.

R1.18 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-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.

We agree with the reviewer that this is indicates that SOA modeling is not the only factor impacting model performance. We have already addressed the discussion of model performance at several occasions throughout our replies to reviewers (R1.6, R1.7, R1.8, R1.9) and think this sufficiently discusses these comparisons.

R1.19 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?

We have created such a plot and included it in the Supplementary Material as Figure S1. It is reproduced below:

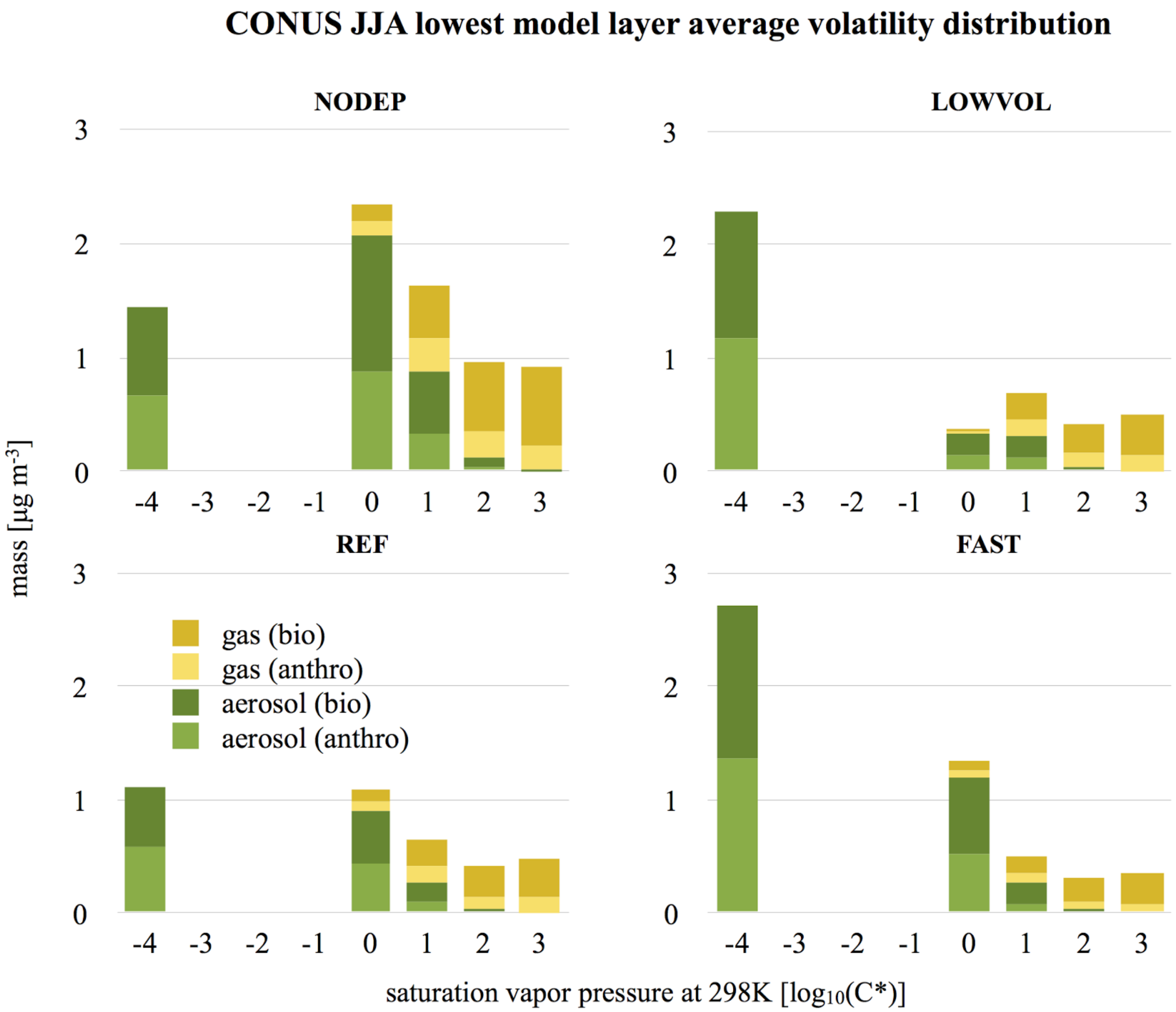


Figure S1. Continental United States, lowest model layer, summer months (June, July, August) average SOA volatility for the case without SVOC deposition (NODEP), the reference case (REF), and the two volatility sensitivity studies (FAST, LOWVOL).

We also reference this figure in the text (section 5.2):

[...] Both changes result in a much less volatile distribution of mass (see also Fig. S1 in the supplementary material) which is less susceptible to gas-phase removals. The reader is referred to the Appendix for a box model study on the effects of these changes. The resulting volatility distributions are comparable to what has been observed in the atmosphere (Cappa and Jimenez, 2010), hence we deem this to be a lower bound of the effect of gas-phase removal on SOA

concentrations. As expected, we find (Table 4) that the efficiency of gas-phase removal is sensitive [...]

Refs: Carleton, A.M., Bhave, 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 or organic aerosol evolution, ACP, 9, 1263-1277.

Reproduced tables S1 and S2 from the Supplement

Table S2. Mapping of emitted species as provided in the emissions input (AQMEII phase 2 data, Carbon Bond Mechanism Version 5 (CB05) speciation) onto the MOZART mechanism. Lumped structure species PAR, OLE and IOLE are converted into MOZART lumped molecules species assuming a (mole-wise) fractional contribution of 0.14, 0.02, and 0.84 of C3H6, BIGENE and BIGALK (based on measurements by Borbon et al., 2013) and the identities given in the table below.

MOZART species	**Emissions input species (CB05 speciated)**
MACR	ACROLEIN + BUTADIENE13
CH3CHO	ALD2 + ALDX
BENZENE	BENZENE
CH4	CH4
CO	CO
C2H6	ETHA
C2H4	ETH
C2H5OH	ETOH
CH2O	FORM
ISOP	ISOP
CH3OH	MEOH
NH3	NH3
NO2	NO2
NO	NO
HONO	HONO
SO2	SO2
SULF	SULF
C10H16	TERP
TOLUENE	TOL

XYLENE	XYL
C3H6	OLE + PAR
BIGENE	OLE + 2 × PAR, IOLE + 2 × PAR
BIGALK	5 × PAR
C3H8	1.12 × 10^{-2} × CO (Borbon et al., 2013)
CH3COCH3	1.18 × 10^{-2} × CO (Borbon et al., 2013)
MVK	2.40 × 10^{-4} × CO (Borbon et al., 2013)
C2H2	5.87 × 10^{-3} × CO (Borbon et al., 2013)

Table S3. Emissions mapping for aerosol species. Each WRF-chem species listed below is actually 2 variables, for emissions into the Aitken and the accumulation size mode respectively. This is based on a modal aerosol description like e.g. in MADE (Ackermann et al., 1998). We here distribute the emissions input that is not size resolved into the different modes by applying a mass fraction of 0.1 for the Aitken mode and 0.9 for the accumulation mode (based on the work of Elleman and Covert, 2010). Emissions into these two modes are then distributed within WRF-Chem into the size bins of the MOSAIC aerosol module.

WRF-Chem species	**Emissions input species**
PM25	PAL + PCA + PFE + PK + PMFINE + PMG + PMN + PMOTHR + PSI + PTI
NA	PNA
CL	PCL
EC	PEC
ORG	POC
SO4	PSO4
NO3	PNO3

NH4	PNH4
PM_10	PMC

Additional references

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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 #2

This is a well written, appropriately titled manuscript describing modeling efforts to quantify the effect that deposition of gas-phase semi-volatile organic compounds has on predictions of secondary organic aerosol. While it now appears from the literature that deposition/uptake of such compounds in smog chambers affects the ability of associated experiments to predict yields, only little effort has been aimed at quantifying this effect in the ambient atmosphere. Therefore, this is an appropriate topic for ACP. What work has been done previously is cited and provides the basis for this work, which provides a quantitative conclusion. The paper uses appropriate methodology and cites previous work liberally; methodologies (with the exceptions noted below) appear sound. The abstract is complete and accurate. That being said, there are a few issues that need to be addressed prior to my being able to recommend publication.

R2.1 Significant comments: Much of this work is predicated on the work of Hodzic et al. (2014a), which was not made available for review. Not enough information about this work is given to allow for an evaluation of whether this approach should be carried into WRF-Chem/VBS. Please provide more information.

The work by Hodzic et al. (2014) has been published in GRL and is available online. It contains detailed description of how the parametrization was derived and how it can be used within the VBS bins.

R2.2 Given that all biogenic and all anthropogenic species are lumped together, how accurate is the unweighted average that is used for their characteristics? For example, the compounds that result from isoprene or terpene or sesquiterpene oxidation that might be in the same bin of volatility are going to be very different structurally – how does this impact their water solubility/H? How widely do the individual H* vary? This needs to be explained more systematically in this manuscript. This would also then impact the deposition velocities, of course.*

We agree with the reviewer that oxidation products of isoprene and terpenes that fall into the same VBS bin have a very different structure and functional groups. We have averaged

H* values among all oxidation products of biogenic (anthropogenic) precursors located in the same bin due to computational constraints. This simplification is however not expected to significantly affect the accuracy of our results as for a given VBS bin, H* values vary by less than an order of magnitude e.g. for C*=10 ug m^3, H* varies from 3.5 x 10^8 for isoprene to 1.4 x 10^9 for monoterpenes in the low-NO_x case (Table 1 in Hodzic et al., 2014), and we used the average value of 7.0 x 10^8 in our study. In addition, as shown in the sensitivity studies, dry deposition is not very sensitive to small changes in H* values for H* values greater than 10^6 M atm^{-1}. Given that Hodzic et al. (2014) is published now we refer the reader and the reviewer to that publication for details.

R2.3 In the LOWVOL case (page 13739, line 4), what is the basis for using the C = 1 bin? I recognize that it is "shielding" but why C*= 1? Why not C* = 10? Or C* = 0.1?*

The first reason for choosing the C*=1 ug/m^3 bin is that this is the bin with the lowest volatility of the "original" VBS scheme (as described in Lane et al., 2008; Ahmadov et al., 2012) - which was the basis of our developments.
Secondly, we intended to create a sensitivity run in which secondary organic aerosol that has aged for a long time is of such low volatility that it does not partition into the gas-phase any more. Aside from some direct emission, the C* = 1 ug/m^3 is mostly comprised of mass moved into this bin through aging of material with higher volatility. It could hence be considered the bin with the "oldest" SOA, and hence the material we want to "shield" from removal in this study.

R2.4 Page 13742, line 10. By considering only "traditional" SOA pathways, I believe that the authors may have missed a good opportunity. Yes, their point was to emphasize that deposition of SVOCs should be included in models – and they state that including other SOA pathways would simply shift things around (that is, that the end effect will be similar). However, I would argue that models for the non-traditional pathways also exist – so when you include both traditional and non-traditional pathways AND the deposition pathways, it would be the best evaluation yet of how well we can model SOA – and it would tell us how far off we are and potentially give insight into what really is missing.

We completely agree with the reviewer that a combination of new formation pathways plus our new understanding of how SOA is removed in the atmosphere would be the most up to date modeling system and would show our current skill in SOA prediction. This is indeed what we are working on, and we will include this in upcoming publications. There are some intricacies in how to include these "new" formation pathways (namely formation in the aqueous-phase, and the correct description of S/IVOC emissions as well as semi-volatile POA) together with the removal pathways in a consistent framework, which need to be solved first before we can add these processes. This description will require a manuscript on itself, and is unfortunately out of scope for the work presented here.

Minor edits:
R2.5 Page 13734, line 14 – please define VBS here as this is the first use

changed

R2.6 Page 13741, line 13, I do not believe that the deposition cases has removed the local maximum. I believe it is still observed in Figure 4, left hand side.

The local maximum is removed, this becomes clearer with the revised figure in which the bars are colored differently.

R2.7 Page 13742, line 8. Strongly overestimating in summer? Strongly is probably too emphatic.

“strongly” has been removed.

R2.8 Page 13744, line 6, add “to” between “relative” and “simulations”; next line use “employ” rather than “employs”

fixed

R2.9 Page 13746, line 11 – change “and neither in the effect on” to “or in”

fixed

R2.10 Page 13747, line 1 – study should be studies

fixed

R2.11 Table 3, it could be my printed version, but it is difficult to see anything in bold?

fixed

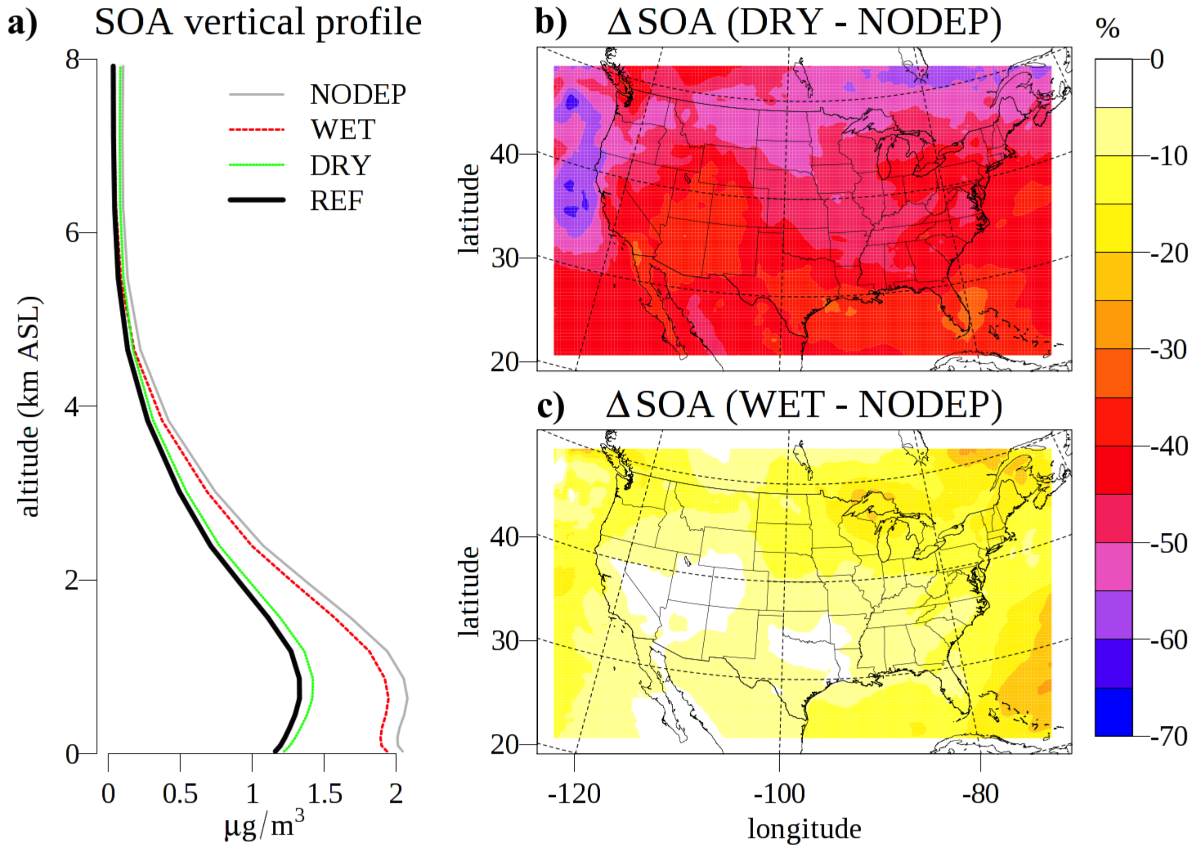
R2.12 Figure 2, update caption as there are no “left” and “right”

fixed

R2.13 Figure 3, small size makes it difficult to assess measurements versus model output in right hand side

The size of the figure will be increased in the published version.

R2.14 Figure 4, please use color in left hand side as the different lines are currently difficult to distinguish

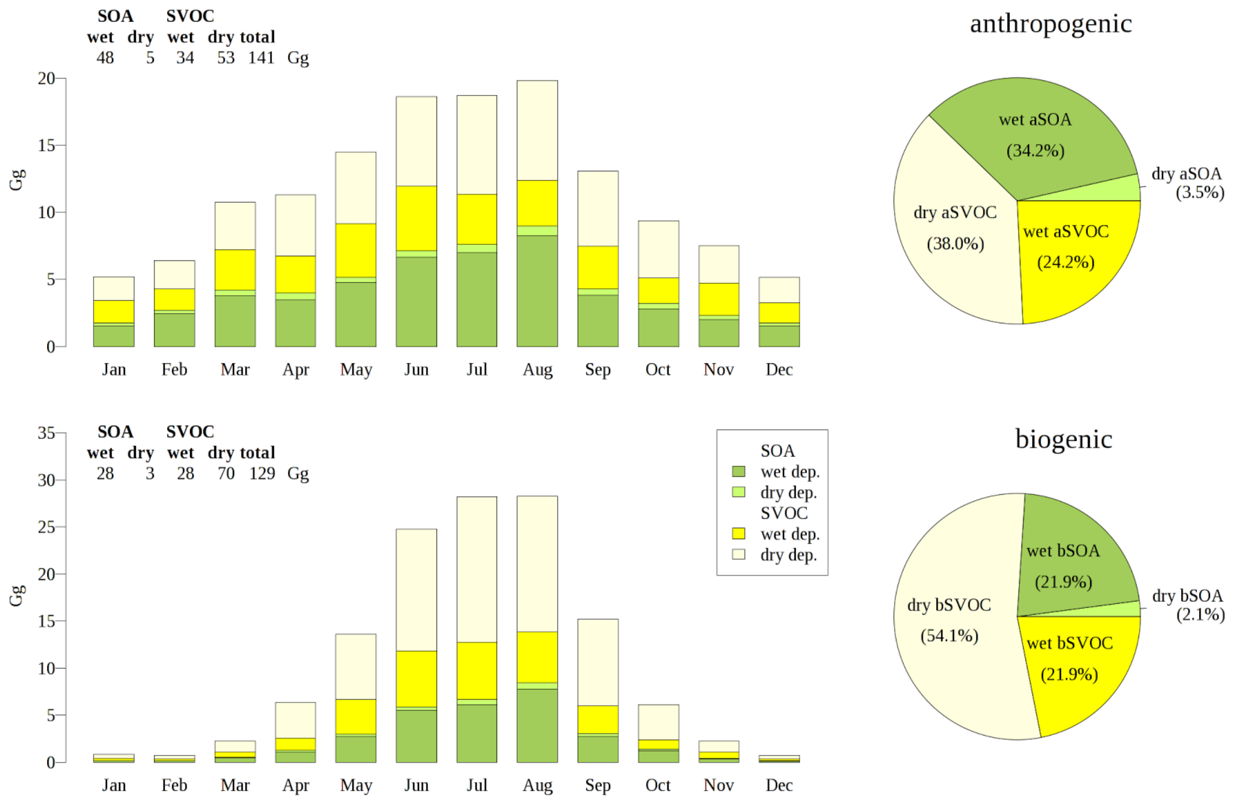


R2.15 Figure 5, same comment as Figure 3 for the top.

The size of the figure will be increased in the published version.

R2.16 Figure 6, dark font inside dark green pie slice is difficult to read.

The figure has been updated and the colors lightened:



R2.17 Should the figures associated with the Appendix be numbered differently?

The numbering has been changed to A1 and A2.

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 ln11-12: 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 HNO3. 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 P13746lns10-11: 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 P13746ln22: should give units.

Fixed.

R3.11 P13747lns27-29: 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.

[1,*]C.Knote [1]A.Hodzic [2]J. L.Jimenez

Manuscript prepared for J. Name
with version 5.0 of the LaTeX class copernicus.cls.
Date: 28 October 2014

The effect of dry and wet deposition of condensable vapors on secondary organic aerosols concentrations over the continental US

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Abstract. The effect of dry and wet deposition of semi-volatile organic compounds (SVOC) in the gas-phase on the concentrations of secondary organic aerosol (SOA) is reassessed using recently derived water solubility information. The water solubility of SVOCs was implemented as a function of their volatility distribution within the regional chemistry transport model WRF-Chem, and simulations were carried out over the continental United States for the year 2010. Results show that including dry and wet removal of gas-phase SVOCs reduces annual average surface concentrations of anthropogenic and biogenic SOA by 48 % and 63 % respectively over the continental US. Dry deposition of gas-phase SVOCs is found to be more effective than wet deposition in reducing SOA concentrations (−40 % vs. −8 % for anthropogenics, −52 % vs. −11 % for biogenics). Reductions for biogenic SOA are found to be higher due to the higher water solubility of biogenic SVOCs. The majority of the total mass of SVOC + SOA is actually deposited via the gas-phase (61 % for anthropogenics, 76 % for biogenics). ~~A number of sensitivity studies shows that this is a robust feature of the modeling system.~~ Results are sensitive to assumptions made in the dry deposition scheme, but gas-phase deposition of SVOCs remains crucial even under conservative estimates. Considering reactivity of gas-phase SVOCs in the dry deposition scheme was found to be negligible. Further sensitivity studies where we reduce the volatility of organic matter show that consideration of gas-phase SVOC removal still reduces average SOA concentrations by 31 % on average. We consider this a lower bound for the effect of gas-phase SVOC removal on SOA concentrations. A saturation effect is observed for Henry's law constants above 10^8 M atm^{-1}, suggesting an upper bound of reductions in surface level SOA concentrations by 60 % through removal of gas-phase SVOCs. Other models that do not consider dry and wet removal of gas-phase SVOCs would hence

overestimate SOA concentrations by roughly 50 %. Assumptions about the water solubility of SVOCs made in some current modeling systems ($H^* =$ $H^*(\mathrm{CH_3COOH})$; $H^* =$ 10^5 M atm^{-1}; $H^* = H^*(\mathrm{HNO_3})$) still lead to an overestimation of ~~25 %/10~~35 %/25 %/10 % compared to our best estimate. ~~A saturation effect is observed for Henry's law constants above 10^8 Matm^{-1}, suggesting an upper bound of reductions in surface level SOA concentrations by 60through removal of gas-phase SVOCs. Considering reactivity of gas-phase SVOCs in the dry deposition scheme was found to be negligible. Further sensitivity studies where we reduce the volatility of organic matter show that consideration of gas-phase SVOC removal still reduces average SOA concentrations by 31on average. We consider this a lower bound for the effect of gas-phase SVOC removal on SOA concentrations.~~

1 Introduction

Organic compounds represent a major, often dominant mass fraction of ambient aerosol (e.g. Murphy et al., 2006; Jimenez et al., 2009). Most of this mass results from the multigenerational oxidation of hydrocarbons forming products with lower volatility (Odum et al., 1996; Jimenez et al., 2009). The resulting oxygenated semivolatile organic compounds (SVOCs) equilibrate between the gas- and the particle-phase according to their saturation vapor pressure C^* ($\mu\mathrm{g\,m^{-3}}$, Pankow, 1994). Under ambient conditions in the troposphere, SVOCs with a C^* below 0.1 $\mu\mathrm{g\,m^{-3}}$ are predominantly found in the particle-phase, while products with saturation vapor pressure C^* between 0.1 and 10^3 $\mu\mathrm{g\,m^{-3}}$, are distributed between the gas- and the particle-phase with significant mass fractions in both phases. Aerosol volatility measurements during the MILAGRO campaign in Mexico City and similar observations for the Los Angeles area (Cappa and Jimenez, 2010) estimated that for organic material with $C^* \leq 10^3\,\mu\mathrm{g\,m^{-3}}$ the total amount in the gas-phase is between 0.7 to 2.4 times that of the mass in the particle-phase. Recent findings from explicit oxidation chemistry modeling (Hodzic et al., 2013, 2014a) with the Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A Aumont et al., 2005) together with structure-activity estimation of solubility (Raventos-Duran et al., 2010) suggests that many SVOCs are highly water soluble, with Henry's law constants H^* between 10^5 and 10^{10} $\mathrm{M\,atm^{-1}}$. This makes them very susceptible to removal processes in the atmosphere (wet deposition and dry deposition to wet surfaces/vegetation). Given that gas- and particle-phase are in equilibrium, this also implies that removal of gas-phase SVOCs could be an important indirect sink of SOA mass.

Currently, the removal of organic aerosols in 3-D models relies for the main part on wet deposition of aerosols (Tsigaridis et al., 2014) and the model's ability to accurately predict clouds and precipitation. Dry deposition of aerosols is a small contributor to this removal. Deposition of gas-phase SVOCs in current modeling systems is largely unconstrained and, if considered at all, typically scaled to the deposition of $\mathrm{HNO_3}$~~as a very soluble reference compound~~, $\mathrm{CH_3COOH}$, or other reference compounds with known solubility. Bessagnet et al. (2010) investigated the effect of dry deposition of gas-phase SVOCs on SOA concentrations over Europe. In their simulations they used Henry's law constants from different reference compounds (with H^* ranging from 10^5 to $10^{16}\,\mathrm{M\,atm^{-1}}$) and found that SOA concentrations are reduced by 20 to 30 % when including dry deposition of gas-phase SVOCs, mostly due to the removal of biogenic SVOCs. Pye and Seinfeld (2010) applied the global GEOS-chem model to look at the SOA formation from low volatile compounds. For SVOCs, they distinguished between freshly emitted ones with a very low Henry's law constant ($< 10\,\mathrm{M\,atm^{-1}}$) and oxidation products that are treated using a Henry's law constant of $10^5\,\mathrm{M\,atm^{-1}}$. They found that a considerable fraction is removed through the gas-phase, and that wet deposition dominates the removal pathways. In a sensitivity study they lowered the Henry's law constants for SVOCs and showed that the global OA budget is sensitive to this parameter, but they concluded that this does not decrease the model bias against observations. Ahmadov et al. (2012) implemented a ~~VBS~~ volatility basis set (VBS) model into WRF-Chem and found that SOA concentrations are very sensitive to the assumptions made on dry deposition of gas-phase SVOCs. They did not include wet deposition, and tentatively suggested to dry deposit SVOCs in the gas-phase 0.25 to 0.5 times the rate of $\mathrm{HNO_3}$ to optimize the agreement with observations. These studies show that treatment of gas-phase SVOC removal can significantly affect our ability to accurately predict SOA concentrations. Recently, Hodzic et al. (2014a) have provided a parameterization of the water solubility of SVOCs based on explicit oxidation chemistry modeling combined with estimation of Henry's law constants that is constrained from experimental data. Their results show that SVOC mixtures typically created through oxidation in the atmosphere are highly water soluble, 2–3 orders of magnitude higher ~~that~~ than e.g. assumed in Pye and Seinfeld (2010). No previous study investigated the combined effect of dry as well as wet deposition of SVOCs in the gas-phase with such high values for water solubility.

In this work we have integrated the new findings of Hodzic et al. (2014a) regarding the solubility of SVOCs into a state-of-the-art online modeling system (WRF-Chem) and perform a detailed assessment of the effects of the gas-phase SVOC wet and dry deposition on predicted SOA concentrations over North America. We ~~implement~~ implemented a volatility basis set (VBS) scheme with 5 volatility bins in our configuration of WRF-Chem based the work of Lane et al. (2008b) and Ahmadov et al. (2012) to consider the formation of compounds with lower volatility and their partitioning between gas- and aerosol phase. The dry and wet deposition schemes in WRF-Chem ~~are~~ were extended to consider removal of gas-phase SVOCs based on their estimated Henry's law constants for each volatility bin. Simulations ~~are~~ were performed for the full year of 2010 to understand the impact of these removal processes under very different ambient conditions, and test their robustness within the model parameter space.

In ~~Sect.~~Section 2 we present the modeling approach. Section 3 deals with the evaluation of model performance in terms of precipitation and removal of inorganic substances. ~~Finally, in Sect.~~In

Section 4, we address the effects of dry/wet removal of gas-phase SVOCs on SOA concentrations~~.~~, before we evaluate a number of uncertainties in our simulations in Section 5.

2 Modeling

WRF-Chem ~~v3.5~~ (Grell et al., 2005) in version 3.5 is used for all simulations. Meteorological processes and their parameterizations chosen for our simulations are summarized in Table 1.

The MOZART-4 gas-phase mechanism (Emmons et al., 2010) with more explicit treatment of aromatic compounds ~~(?)~~ (Knote et al., 2014) and monoterpenes (Hodzic et al., 2014b) is used together with the MOSAIC ~~4-bin~~ aerosol module (Zaveri et al., 2008) with 4 size bins.

2.1 The volatility basis set

MOSAIC has been extended by a volatility basis set parameterization to describe SOA formation based on the work of Lane et al. (2008a,b) and (Ahmadov et al., 2012). In Fig. 1 we present a schematic overview of the new module. Five volatility bins are considered (saturation concentrations C^* of ~~0.001~~10^{-4}, 1, 10, 100 and 1000 $\mu\mathrm{g\,m^{-3}}$ at 298 K) for both anthropogenic and biogenic precursors (see Table S1 for mapping SAPRC99 species to MOZART). The lowest volatility bin (C^* of ~~0.001~~10^{-4} $\mu\mathrm{g\,m^{-3}}$) has been added to avoid an unrealistically volatile mixture after substantial aging. We consider different SOA yields for low and high $\mathrm{NO_x}$ conditions, and the branching ratio B to determine the respective contributions is calculated according to Lane et al. (2008a) as

$$\beta = k_{(\mathrm{RO_2+NO})}[\mathrm{NO}]/(k_{(\mathrm{RO_2+NO})}[\mathrm{NO}] + k_{(\mathrm{RO_2+HO_2})}[\mathrm{HO_2}]) \qquad (1)$$

with $k_{(\mathrm{RO_2+NO})}$ and $k_{(\mathrm{RO_2+HO_2})}$ the reaction rate constants for the reaction of an organic peroxy radical ($\mathrm{RO_2}$) with NO vs. its reaction with $\mathrm{HO_2}$ respectively. OH and $\mathrm{O_3}$ act as oxidizing agents. To reduce the computational burden we sum up all mass formed from anthropogenic and biogenic precursors respectively and only keep track of total anthropogenic and total biogenic SVOC/SOA mass (called aSVOC/bSVOC and aSOA/bSOA in the following). Pseudo-ideal partitioning theory based on Pankow (1994) is used to estimate gas-aerosol partitioning as implemented in MOSAIC by Shrivastava et al. (2011). Values for the enthalpy of vaporization (ΔH) for each bin have been derived using the semi-empirical parameterization of Epstein et al. (2009) leading to values between 100 and 140 $\mathrm{kJ\,mol^{-1}}$ for the bins with C^* of 1, 10, 100, and 1000 $\mu\mathrm{g\,m^{-3}}$ (see Fig. 1 for exact values). The lowest volatility bin uses a ΔH of 40 $\mathrm{kJ\,mol^{-1}}$. “Aging” of condensable vapors through OH oxidation (mass transfer into the next lower volatility bin) is done with a fixed rate of $1.0 \times 10^{-11}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$ (Murphy and Pandis, 2009), and a 7.5 % mass increase due to the addition of oxygen atoms (e.g. Ahmadov et al., 2012). Secondary aerosol mass formed is assumed to have a density of 1.5 $\mathrm{g\,m^{-3}}$ (Lane et al., 2008a) and a molecular weight of 250 $\mathrm{g\,mol^{-1}}$. Direct emissions of organic particulates (primary organic aerosols, POA) are included as inert contribution to ~~organic~~ aerosol mass without consideration of evaporation and re-condensation. Direct emissions of semi-/intermediate volatility organic compounds (SVOC/IVOC) are not included.

2.2 Dry and wet deposition of gases and aerosols

Washout of gases and aerosols by convective precipitation is considered using the scheme included in WRF-Chem (based on Grell and Dévényi, 2002) which we modified to use Henry's law constants in gas-droplet partitioning. Grid-scale precipitation removes aerosols through the scheme implemented in MOSAIC (Easter et al., 2004; Chapman et al., 2009), while washout of trace gases is performed as described in (Neu and Prather, 2012). The Neu and Prather (2012) scheme also employs an equilibrium approach based on Henry's law constants to consider transfer into cloud droplets and subsequent conversion into rain droplets, as well as collection of gases by falling rain droplets. Both, washout through grid-scale and convective precipitation considers the same set of gas species with an identical set of Henry's law constants. Dry deposition of gases is parameterized in WRF-Chem based on Wesely (1989), modeling deposition as a series of resistors consisting of an atmospheric, a laminar sublayer, and a bulk surface resistance. The latter is a function of the Henry's law constant of a gas ~~to describe partitioning into plants and other wet surfaces~~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 f_0 (ranging from $f_0 = 0$ for non-reactive species to $f_0 = 1$ for species as reactive as O_3) is used in this scheme to consider oxidation of biological substances within plants once a species partitions into this volume. This is set to 0.0 for SVOCs.

~~Hodzic et al. (2014a) presented~~

Henry's law constants (H^*, $\mathrm{M\,atm^{-1}}$) used in this study for semi-volatile ~~oxidation products created from different anthropogenic and biogenic SOA precursors including alkanes, aromatics, or isoprene and terpenes which they derived from explicit oxidation chemistry simulations using the GECKO-A model (Aumont et al., 2005) . They also derived a parameterization~~ organic compounds were provided as a function of volatility by Hodzic et al. (2014a) . They applied an explicit chemical mechanism (GECKO-A, Aumont et al., 2005) to generate the multi-generational oxidation products of individual SOA precursors and calculate the associated H^* values using structure activity relationships (Raventos-Duran et al., 2010) . Values of H^* ~~as a function of precursor and saturation vapor pressure (C^*~~were taken at the maximum of the SOA formation from each individual precursor, which is typically after 1-3 days of chemical processing depending on the precursor, and provided as a function of the volatility (VBS bins). In ~~the VBS only total anthropogenic and biogenic SVOC mass is tracked – precursor information is lost. We hence calculated unweighted averages of~~ each volatility bin, a mass-weighted H^* ~~of the anthropogenic and biogenic precursors considered in the VBS parameterization to derive a value of~~ was calculated (see Table 1 in Hodzic et al., 2014a) . Using those values, we calculated in this study an averaged H^* for ~~anthropogenic and biogenic~~

~~SVOCs in each volatility bin~~ both biogenic and anthropogenic precursor species (Table 2). Dry and/or wet deposition of these volatile compounds is then considered by adding these species to the respective modules in WRF-Chem described above.

2.3 Model setup

Simulations were set up to cover the continental US at 36 km horizontal resolution and 33 levels up to 50 hPa. Meteorological parameters are initialized and forced at the boundaries by 6 hourly analyses (interlaced with 3 hourly forecasts) of the Global Forecasting System (GFS) of the National Center for Environmental Prediction (National Centers for Environmental Prediction/National Weather Service/NOAA/US Department of Commerce, 2010). Initial and boundary conditions for chemistry are provided by simulations of the IFS-MOZART global chemistry transport model (Stein et al., 2012) conducted within the MACC project. Emissions of trace gases and aerosols are ~~based on the US Environmental Protection Agency (US EPA) National Emission Inventory (NEI) updated for the year 2010 within the~~ those provided in phase 2 of the Air Quality Model Evaluation International Initiative ~~(AQMEII Rao et al., 2011) model intercomparison (phase~~ model intercomparison (AQMEII, Alapaty et al., 2012) . For the United States, the 2008 National Emission Inventory (NEI) (version 2~~).~~ , released April 10, 2012) was used (http://www.epa.gov/ttn/chief/net/2008inventory.html). Updates for the following sectors were applied to reflect changes in emissions between 2008 and 2010: on/off road transport, wildfires and prescribed fires, and Continuous Emission Monitoring (CEM)-equipped point sources. Preparation of the emission data is described in detail in Pouliot et al. (2014) . Emission conversion tables for the MOZART/MOSAIC setup used in this work are given in Tables S2 / S3 in the supplement.

The simulations are split into 48 h long chunks of free running meteorology (only forced at the boundaries) without nudging. Each of these runs is preceded by a 6 h meteorology-only spin up which is started from GFS analyses and nudged to ~~the forcing data~~ this dataset above the planetary boundary layer. Concentrations fields for trace gases and aerosol quantities resulting from the previous run are then used to initialize the following free run. Thereby, meteorology is restarted from analyses every 48 h, while chemistry is continuous over the whole period. All simulations have been conducted on NCAR's Yellowstone computing system (Computational and Information Systems Laboratory, 2012). The R language (http://www.r-project.org, last accessed October 06 2014) was used for postprocessing and analysis.

Table 3 lists all simulations conducted. In a first simulation (NODEP) we ignore both dry and wet deposition of SVOCs. In further three simulations we consider dry, wet, and dry + wet deposition of SVOCs (called DRY, WET and REF respectively) employing Henry's law values calculated by Hodzic et al. (2014a). The simulation with dry and wet deposition of SVOCs according to Hodzic et al. (2014a) is our best estimate and hence called REF. All these simulations were carried out for the full year 2010 with an additional 1 week of spin-up for chemistry (not used in the analysis).

A number of sensitivity studies were conducted to understand the sensitivity of the predictions to uncertainties in the process parameterizations. In LOWVOL and FAST_AGING we vary the SOA formation mechanism. In LOWVOL we decrease the overall volatility of the SOA formed by increasing the rate of aging from the volatility bin at $C^* = 1\,\mathrm{\mu g\,m^{-3}}$ to the one with ~~$C^* = 0.001$~~$C^* = 10^{-4}\,\mathrm{\mu g\,m^{-3}}$ by a factor of 10, thereby moving aged SOA to a bin with negligible partitioning into the gas-phase and hence leaving less SVOC that would be susceptible to the newly included removal processes. In FAST_AGING we increase the aging rate constants for all volatility bins to $4.0 \times 10^{-11}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$, thereby matching assumptions about the rate of aging used in previous modeling studies (e.g. Athanasopoulou et al., 2013), and again decreasing the amount of SVOC available for removal. ~~Four~~ Five additional simulations were conducted to determine the model sensitivity to assumptions about the Henry's law constants of SVOCs and identify a possible saturation effect at very high H^* values in the dry deposition scheme. The Wesely (1989) scheme used represents dry deposition as a series of resistances, with only the land surface/canopy resistance being affected by changes in H^*. At very high H^*, this resistance should become negligible and dry deposition would be governed by the remaining resistances. In H_1E5, H_1E8 and H_1E10 we employ Henry's law constants for SVOCs of 10^5, 10^8, and $10^{10}\,\mathrm{M\,atm^{-1}}$ respectively in both dry and wet deposition. The fourth simulation (H_HNO3) uses the Henry's law constant of $\mathrm{HNO_3}$ for SVOCs. The solubility of $\mathrm{HNO_3}$ (or a fraction of it) is often used in atmospheric modeling to treat compounds with unknown properties, but which are assumed to be very soluble. ~~In the final two~~ The fifth simulation (H SUBSCRIPTNBACETIC) employs the Henry's law constant of acetic acid (CH_3COOH), as this is very similar to the values currently used in the Community Multi-Scale Air Quality Model (CMAQ, https://www.cmascenter.org/cmaq/, accessed July 18 2014). In the VEGFRA simulation we assess uncertainties in the description of dry deposition by scaling dry deposition velocities with the vegetated fraction of each grid cell. Finally, two further simulations (F_0.1 and F_1.0) ~~we~~ were made to investigate the effect of the reactivity factor f_0 on predictions. Which SVOCs should be considered "reactive" is so far poorly constrained, but Karl et al. (2010) suggested that assuming $f_0 = 0.1$ or 0.0 as it is typically done for NMVOCs in current modeling systems might be too low. We vary it here to $f_0 = 0.1$ (F_0.1) and $f_0 = 1.0$ (F_1.0). All these sensitivity studies were conducted for the months of June, July and August of 2010 only.

3 Evaluation of predicted wet deposition

An accurate description of the spatiotemporal variability of precipitation is a prerequisite for modeling (wet) deposition. In Fig. 2 we compare our simulations against a composite of rain gauge and radar observations from the National Weather Service River Forecast Centers (http://water.weather.gov/precip/download.php) which provides daily accumulated precipitation amounts. Apart from a tendency of the model to overestimate rainfall amounts in the rather dry regions of the western United States the differences in the yearly accumulated precipitation are typically below ±25 %.

Wet deposition measurements from the National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu) are used to evaluate wet deposition of inorganic compounds (SO_4^{2-}, NO_3^-, NH_4^+). In Fig. 3 we compare monthly accumulated deposition of sulfate, nitrate and ammonium and find good agreement between model and measurements for sulfate (Pearson's correlation coefficient squared $R^2 = 0.62$, normalized mean bias NMB = 3 %) and nitrate ($R^2 = 0.65$, NMB = 7 %), while the amount of wet deposition of ammonium is underestimated but still has a good correlation with measurements ($R^2 = 0.69$, NMB ~~= 0.69).~~ $= -38$). This deficiency could be related to the lack of a bi-directional exchange model in WRF-Chem to describe the flux of NH_3 at the surface (Nemitz et al., 2001; Bash et al., 2013) . Measurements of water-soluble organics are not available so we could not directly evaluate the performance of WRF-Chem. The model results of wet deposition of inorganic ions however shows that the underlying processes are ~~accurately~~ reasonably modeled, lending credibility to the accuracy of the wet deposition of organic substances.

4 Effect of SVOC deposition on SOA concentrations

4.1 Effect on SOA concentrations

We first evaluate the differences in the average concentrations of SOA due to the removal of SVOCs. Dry deposition has a much stronger effect on SOA concentrations at the surface (top right map in Fig. 4) than does wet deposition (Fig. 4, bottom right map). As a yearly average over the continental US, dry deposition of SVOCs reduces SOA surface level concentrations by 46 % (aSOA: 40 %, bSOA: 52 %), whereas wet deposition leads to SOA concentrations at the surface that are lower by 10 % (aSOA: 8 %, bSOA: 11 %) vs. not considering this removal pathway (REF vs. NODEP ~~cases~~case). We find very similar results when analyzing changes averaged over the planetary boundary layer instead of changes in the surface layer. SOA seems to be most sensitive to dry removal of SVOCs over the Pacific Northwest coast, the northern Midwest (Montana, South/North Dakota) and parts of eastern Canada. Wet deposition is most effective around the Great Lakes area, and least effective over the Nevada/Utah/Arizona area as well as northeastern Texas. When looking at the average vertical profiles of SOA concentrations over land (Fig. 4, left panel) we find that the effects of these removal processes are visible throughout the vertical column. Dry deposition of SVOCs has the additional effect of removing a local maximum of SOA concentrations in the lowest model layers. When comparing the sum of the reductions due to only considering either dry (DRY) or wet (WET) deposition of SVOCs against the reductions in a simulation where we consider both processes (REF) we find that their effects are almost additive (not shown).

We evaluate the resulting total organic aerosol (OA) concentrations against measurements using measurements of the Interagency Monitoring of Protected Visual Environments network (IM-

PROVE, data hosted at http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm, accessed 6 February 2014). In Fig. ~~??~~ 5, 6 and S2 in the Supplementary Material we show comparisons of organic carbon (OC) in particles below 2.5 µm in diameter. Modeled concentrations are the sum of aSOA, bSOA and POA converted from organic aerosol mass to organic carbon assuming OA/OC ratios of 2.0 for a/bSOA and 1.4 for POA (comparable to findings of Aiken et al., 2008). When comparing the results from the REF run where we consider both dry and wet deposition of SVOCs we find ~~reasonable correlation ($R^2 = 0.58$) with measurements and an underestimation of the modeled amounts~~ low correlation ($R^2 = 0.19$) and a slight low bias in the model results (NMB ~~$= -34$~~$= -35$ %) ~~.~~ when looking at the full annual cycle (Fig. 5), and better correlation ($R^2 = 0.31$) and lower bias (NMB $= -22$ %) when using only values of June, July and August (Fig. S2) where SOA dominates OC. When analyzing the results from the simulation without SVOC removals (NODEP, ~~middle plot~~ bottom plot in Fig. 5) it is clear that the effect of these removals has a pronounced annual cycle, being almost negligible in winter (where POA dominates modeled OC concentrations) while reducing concentrations of secondary formed OC by half in summer. It is important to note that very different types of biases are observed here between the run without SVOC removals and the one where these are included: annually averaged, the OC mass predicted in the NODEP simulation would match annual averaged measured concentrations well, but there is a distinctly different evolution over the course of the year – the simulation shows a much stronger annual amplitude in OC than observed, underestimating measured values in winter and ~~strongly~~ overestimating in summer. In the REF simulation with removals, the overall concentrations of OC are underestimated compared to measurements, but the ~~annual~~ month-to-month evolution is considerably more similar to the observed evolution. We further disaggregated the analysis spatially and looked at the performance at stations at the west coast, the Northeast and the Southeast (Fig. 6). Our findings show that at the west coast, modeled OC is underestimated in all simulations, while in the Eastern US, both REF and LOWVOL results track observed OC concentrations well during July and August, but underestimate them in June. OC concentrations are overestimated in the FAST SUBSCRIPTNBAGING simulation, especially in the Southeast.

We also compared our results to hourly measurements of organic matter (OM) conducted within the Southeastern Aerosol Research and Characterization study (SEARCH, Hansen et al., 2012) to understand the effects of dry and wet deposition of SVOCs on the diurnal cycle of OM. Four stations in the Southeast (North Birmingham, AL - BHM; Centreville, AL - CTR; Yorkville, GA - YRK; Jefferson Street, GA - JST) had measurements available (http://www.atmospheric-research.com/studies/search/SEARCHFactSheet.pdf, last accessed Aug 11 2014, for site locations and description). The resulting averaged diurnal cycles are shown in Figure 7. We find that including wet deposition of SVOCs has no effect on the diurnal cycle of OM at these stations, possibly due to the non-local nature of this removal process: washout affects the whole column up to the cloud where the precipitation originates, hence such an event also reduces concentrations aloft which are then advected. Dry deposition instead only acts on the lowest grid cell. Including dry deposition of SVOCs leads to a reduction in the diurnal amplitude of OM concentrations, which is in line with observations. In general, modeled diurnal amplitudes are larger than the observed ones. At all stations, with the exception of BHM, observed OM is more or less constant throughout the day. Judging based on the observations at BHM and minor variations seen at the other stations we observe that the timing of diurnal maxima and minima differ between observations and model. Modeled diurnal cycles indicate a morning minimum in OM concentrations (possibly due to the rise of the boundary layer) and a maximum in the afternoon (maximum of photochemical SOA production), whereas the observed maximum OM concentrations occur in the early morning (around 6 LT) - arguably the time with the lowest boundary layer height - and the observed minimum is during late afternoon hours (around 18 LT).

In our study we only consider “traditional” SOA formation mechanisms (pure gas-phase oxidation), but a number of additional processes have been proposed (cloud-phase formation, e.g. Lim et al., 2010; in-aerosol formation, e.g. ~~?~~ Knote et al., 2014 ; evaporation of primary OA, e.g. Robinson et al., 2007; additional formation pathways from existing precursors like isoprene, e.g. Paulot et al., 2009). Assuming that the products formed from these new sources will exhibit similar volatility/water solubility relationships than the existing compounds, the effect of SVOC removal will be similar. Including these processes would then ~~lead to a general shift of the annual cycle of concentrations as~~ increase concentrations shown in Fig. ~~?? towards higher values,~~ 5, predominantly during summer months where SOA contributes strongest to total OA, potentially closing the gap between measurements and model results.

4.2 Total deposition for the different pathways

A comparison of the monthly and yearly accumulated deposition mass through the different removal pathways is shown in Fig. 8. We find that for the total of anthropogenic and especially for biogenic SVOC + SOA, more mass is removed as SVOCs (anthropogenics: 38.0 % via dry dep. and 24.2 % through wet dep. = 62.2 % total, biogenics: 54.1 % via dry dep. and 21.9 % through wet dep. = 76 % % total) than as particles (pie charts in the right column of Fig. 8). Dry deposition is the most efficient removal process for both types of organic species. Wet deposition of SVOCs and SOA is roughly equivalent, dry deposition of particles is small ($< 5\,\%$). The annual cycle of monthly accumulated deposition (left column, Fig. 8) shows a more pronounced annual variability of biogenic deposition. In winter, deposition of biogenic SVOC and SOA is negligible (due to the very low biogenic emissions), whereas deposition of anthropogenic SVOC + SOA in winter months is still about a quarter of the deposition in the summer months.

5 Discussion of uncertainties

The results presented above are valid for our particular model configuration. We investigated the sensitivity of these results to the model parameter space, considering uncertainties in the SOA formation mechanisms as well as in the treatment of deposition.

5.1 Volatility of the secondary organic aerosol formed

How susceptible SOA is to the removal of SVOCs in the gas-phase depends on the overall partitioning between gas- and particle-phase. In two sensitivity studies we change SOA volatility to investigate the impact: in LOWVOL we increase the aging rate constant into very low-volatility SOA (kOH of volatility bin with $C^* = 1$ to the bin with $C^* = 10^{-4}$) by a factor of 10, effectively hiding aged organic material from gas-phase removal. In FAST_AGING we increase the aging rate constants between all volatility bins by a factor of 4, reducing the time organic material is exposed to gas-phase removal during aging. Both changes result in a much less volatile distribution of mass (see also Fig. S1 in the Supplementary Material) which is less susceptible to gas-phase removals. The reader is referred to the Appendix for a box model study on the effects of these changes. The resulting volatility distributions are comparable to what has been observed in the atmosphere (Cappa and Jimenez, 2010), hence we deem this to be a lower bound of the effect of gas-phase removal on SOA concentrations. As expected, we find (Table ~~??~~4) that the efficiency of gas-phase removal is sensitive to the volatility distribution of the organic matter. Shielding aged material from gas-phase removal (LOWVOL) lowers the average reductions of SOA concentration at the surface from $-41/-56\,\%$ (aSOA/bSOA) to $-32/-48\,\%$ vs. the NODEP case, and accelerating the aging process in general (FAST_AGING) further reduces the changes to $-23/-39\,\%$. Note that each of these changes is relative to simulations where dry and wet deposition of SVOCs has been switched off, but which ~~employs~~ employ an otherwise identical VBS scheme (LOWVOL_NODEP and FAST_AGING_NODEP respectively). In all reductions except for anthropogenic organic matter in the FAST_AGING study, more mass is removed through the gas phase than through the particle phase. When looking at the resulting concentrations and their comparison against measurements (Fig. ~~??, bottom plot~~5, 6) we see that FAST_AGING exhibits a time evolution almost identical to the REF run, but shifted to higher concentrations. This leads to a strong overestimation during July and August. The concentrations predicted in the LOWVOL simulation lie in between REF and FAST_AGING. It is instructive to see that in LOWVOL, the variability of concentrations over the time period investigated is reduced. This actually resembles observations better, even though there is still a low bias in the mean. This suggests that VBS schemes currently used create a volatility distribution that is too volatile compared to the real atmosphere (observed before by e.g., Grieshop et al., 2009; Hodzic et al., 2010; Cappa and Jimenez, 2010; Lee-Taylor et al., 2011) , although other effects may also be important.

Interestingly, when looking at the average diurnal cycles of OM (Figure 7), the effect of changing the volatility distribution leads to a mere shift in concentrations, but not to a change in the diurnal cycle, as it might have been expected.

5.2 Water solubility of SVOCs

Hodzic et al. (2014a) showed based on explicit oxidation chemistry modeling that good correlation exists between the volatility of a compound (C^*) and its water solubility (H^*). Still, uncertainy remains in the accuracy of these values, which is further amplified by the simplifications made in this work to apply them in a 3-D modeling context. This warrants an investigation of the sensitivity of our results to H^*. As a second motivation, the Wesely (1989) dry deposition parameterization used here is based on the analogue of a series of resistances, with Henry's law constants only affecting the ~~canopy~~ bulk surface layer resistance. Once this resistance is sufficiently low (e.g. due to very high H^* values), the resulting dry deposition velocities are only determined by the value of the other resistances. This would imply that above a certain value of H^*, dry deposition of SVOCs should not increase anymore and no additional reduction of SOA concentrations will occur. At which values of H^* exactly this saturation effect is observed in a realistic 3-D simulation was unknown. We hence conducted additional simulations with different values of H^* assigned to the volatility bins: 10^5, 10^8, and $10^{10}\,\mathrm{M\,atm^{-1}}$. In these simulations we ignore the temperature dependence of the Henry's law constants. Additionally we included ~~a simulation~~ two simulations using Henry's law values derived for CH_3COOH ($H^* = 4.1 \times 10^3\,\mathrm{M\,atm^{-1}}$, $\mathrm{d}(\ln H^*)/\mathrm{d}(1/T) = 6300$, Johnson et al. (1996)) and HNO_3 ($H^* = 2.6 \times 10^6\,\mathrm{M\,atm^{-1}}$, $\mathrm{d}(\ln H^*)/\mathrm{d}(1/T) = 8700$, Chameidis (1984)), commonly used in models as reference for ~~very soluble~~ compounds for which exact H^* values are unknown. The resulting changes in average surface SOA concentrations and accumulated deposition (over the Continental US) are shown in Fig. 9. Results from the simulation using H^* values from explicit oxidation chemistry (REF) are included for reference. Changes in avg. SOA concentrations range from −~~25~~15 % for ~~$H^* = 10^5$~~ H^*=H^*(CH_3COOH) to −60 % for H^*=$10^{10}\,\mathrm{M\,atm^{-1}}$. A saturation effect is visible between the simulations with H^* at 10^8 and $10^{10}\,\mathrm{M\,atm^{-1}}$, where resulting SOA concentrations change by less than 5 % despite changes in H^* of two orders of magnitude. This suggests that the effect of deposition of SVOCs has an upper limit of −60 % reduction in avg. surface SOA concentrations for the region~~and time period~~, time period and model setup investigated here, corresponding roughly to Henry's law constants $> 10^{10}\,\mathrm{M\,atm^{-1}}$. It also shows that there is considerable variability in resulting SOA reductions within the range on H^* values used here, urging us to find ways to better constrain these removals to accurately describe the lifecycle of secondary organic aerosols. Note that these findings imply that, to be accurate, comparisons of SOA formation mechanisms implemented in 3-D models against measured concentrations will have to overestimate measured SOA concentrations by roughly 50 % if SVOC deposition is ignored (REF-NODEP), by 25 % if SVOC is deposited with $H^* = 10^5\,\mathrm{M\,atm^{-1}}$ (REF-H_1E5), and still by 10–15 % (REF-

H_HNO3) if dry and wet deposition of SVOCs is considered with H^* values of HNO_3.

5.3 ~~Reactivity factor f_0~~Dry deposition scheme

~~The Wesely (1989)~~ 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, ~~where as~~ 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 ~~and neither in the effect on~~ 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.

6 Conclusions

We investigated the effect of considering removal of semi-volatile organic compounds on secondary organic aerosols concentrations according to recent findings that suggest SVOCs are highly water soluble (Hodzic et al., 2014a). Simulations with the regional chemistry transport model WRF-Chem were conducted spanning the whole year 2010 over the domain of the continental US. Considering dry and wet deposition of SVOCs in the gas-phase with recently derived Henry's law constants reduces ground level SOA concentrations by 48 % (aSOA) / 63 % (bSOA) in the annual average over the continental US in 2010. Dry deposition is much more effective than wet deposition, reducing surface level concentrations -40 vs. -8 % for aSOA and -52 vs. -11 % for bSOA. More than half of the total mass of SVOCs + SOA (61 % for anthropogenics, 76 % for biogenics) is actually deposited via the gas-phase. In a number of sensitivity ~~study~~ studies spanning the months of June and July of 2010 we investigate the robustness of these findings by varying the volatility distribution of the organic matter, the Henry's law constants used, and ~~the effect of the reactivity parameter f_0~~ key parameters of the dry deposition scheme. We find that the efficiency of these removals is sensitive to the volatility of the mixture, reducing the resulting reductions in surface level SOA concentrations from -48 % (avg. of changes in aSOA and bSOA) in the standard simulation (REF) to -40 % when protecting aged SOA from gas-phase removal (LOWVOL), and to -31 % when accelerating the aging process in general (FAST_AGING). SOA is sensitive to the removal of SVOCs in the gas-phase through dry and wet deposition for the whole range of H^* values investigated, with average reductions in surface SOA concentrations of -25 % when assuming $H^* = 10^5\,\mathrm{M\,atm^{-1}}$, scaling up to -60 % for $H^* = 10^{10}\,\mathrm{M\,atm^{-1}}$. A saturation effect is clearly visible for $H^* \geq 10^8\,\mathrm{M\,atm^{-1}}$, suggesting that the upper bound of these processes on SOA concentrations is reached. These results are also sensitive to assumptions made in the dry deposition scheme, reducing the effect of considering dry deposition of SVOCs on changes in average surface SOA concentrations to -31 %/-45 % when dry deposition is only considered over vegetated areas. Considering reactivity of SVOCs in the dry deposition calculation over vegetation as suggested by Karl et al. (2010) had no observable effect as the high values of water solubility calculated by GECKO dominate the calculation of the vegetation-related resistances.

Our findings have important implications for the aerosol modeling community, as they show that considering dry as well as wet deposition of SVOCs in the gas-phase is an essential part of accurately modeling SOA. Any evaluation of regional SOA modeling against observed concentrations of particulate organic matter is biased high about 50 % if SVOC removal is neglected completely, about 25 % if SVOC removal is considered with a Henry's law constant $H^* = 10^5\,\mathrm{M\,atm^{-1}}$, and still 10 % if the water solubility of $\mathrm{HNO_3}$ is used. We also showed that the removal processes are still sensitive to the value of the Henry's law constant H^* used up to around $10^8\,\mathrm{M\,atm^{-1}}$. Finally, considerable uncertainty remains in the description of dry deposition. For all the uncertainties investigated we find that, while the actual resulting numbers vary, dry deposition of SVOCs remains an important pathway of SOA removal.

Including these processes suggests further that there is room for additional pathways (e.g. in-cloud, in-aerosol production) and precursors (evaporating POA, glyoxal) of SOA in order to close the gap with observations. We evaluated the modeling system against measurements of precipitation and wet deposition of inorganic ions, which lends confidence that the underlying ~~processes are~~ wet removal process is accurately captured. However, we are currently not able to observationally constrain the organic carbon budget until a network of long-term, routine measurements of dry and wet deposition of organic matter is established.

Appendix A

Box model simulations

How efficient the removal of gas-phase SVOCs is in decreasing SOA concentrations depends directly on the amount of SVOCs created by the oxidation of precursors (vs. the production of very low volatility compounds that partition predominantely in the particle phase), and the time it takes for subsequent chemistry to decrease the compound's volatility enough so that it remains in the particle phase. In VBS terminology it is a function of the yields distribution and the "aging" rate constant kaging. To investigate these sensitivites we simulate chamber experiments in a box model, employing VBS-type parameterizations with different assumptions. In Figs. A1 and A2 we show the results of the oxidation of 1 ppbv α-pinene (kOH(α-pinene) $= 5.2\times10^{-11}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$) and toluene (kOH(toluene) $= 1.7\times10^{-12}\times\exp(352/T)\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$), assuming constant OH of $2.0\times10^6\,\mathrm{molec\,cc^{-1}}$, and subsequent formation of SOA using the yields of Lane et al. (2008b). Four different VBS parameterizations are presented: as described in Lane et al. (2008b) (LANE), as described as base case in this work (NODEP), a low-volatility sensitivity study used in this work that "protects" aged material by moving into an "inert" volatility bin (LOWVOL), and a sensitivity study where the accelerate the overall aging of SVOCs (FAST_AGING). In all parameterizations we assume that chemistry of later generation compounds further reduces their volatility, which is approximated by reducing SVOC volatility by a decade (1 bin) with an "aging" rate constant of kaging $= 1\times10^{-11}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$. In the LOWVOL sensitivity study, kaging from the bin with

$C^* = 1.0$ to $C^* = 1.0 \times 10^{-4}$ is increased to $1 \times 10^{-10}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$. In FAST_AGING, the aging rate constants for all bins are increased to $4 \times 10^{-11}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$. A first-order loss (e-folding lifetime of 1 day) is applied to the vapor phase in all bins to simulate SVOC deposition. Temperature varies as sine function around 298 K with a 10 K amplitude and a wave-length of 24 h.

SOA formation from α-pinene peaks in the first hours of the simulation due to faster reaction with OH (Fig. A1, third row) and higher yields. After α-pinene is depleted, toluene provides addqitional condensable vapors mass almost throughout the 120 h simulated. Clearly visible from the volatility distributions after 24 h (Fig. A1, top row) is that in REF, LOWVOL, and especially in FAST_AGING, a substantial amount of mass is shifted into the particle phase due to aging into the "inert" bin at $C^* = 1 \times 10^{-4}$ compared to LANE. We compare these results to the thermodenuder experiments of Cappa and Jimenez (2010) where they find that the semi-volatile fraction of oxygenated organic aerosol (SV-OOA, Fig. 5f in Cappa and Jimenez, 2010) has $2/3$ of the total mass (gas+particle) of compounds with $C^* \leq 2$ in the particle phase. It is evident that the three different parameterizations exhibit very different sensitivities to changes in temperature. LANE uses a relatively low enthalpy of vaporization (dH) of $30\,\mathrm{kJ\,mol^{-1}}$, and consequently the total SOA mass (Fig. A1, second row) does not vary strongly. In the REF, LOWVOL and FAST_AGING parameterizations the higher dH of $> 100\,\mathrm{kJ\,mol^{-1}}$ (parameterization of Epstein et al., 2009) are used, and these simulations intially react much stronger to changes in temperature. It is notable, however, that in the LOWVOL and FAST_AGING cases, temperature sensitivity quickly decreases and the result is almost completely insensitive to temperature after 72 h. This is obviously the result of moving mass more quickly into the "inert" bin (Fig. A2).

As the four parameterizations exhibit very different volatility distributions, application of a loss process to simulate SVOC deposition leads to very different total mass concentrations (Fig. A1, second row) and volatility distributions after 120 h (Fig. A2). While LANE only has $0.5\,\mathrm{\mu g\,m^{-3}}$ of SOA left (down from $> 1\,\mathrm{\mu g\,m^{-3}}$ after 42 h), REF ends up with $2\,\mathrm{\mu g\,m^{-3}}$, LOWVOL with almost $3\,\mathrm{\mu g\,m^{-3}}$, and FAST_AGING with $5\,\mathrm{\mu g\,m^{-3}}$ of SOA after 120 h. The inert bin protects SOA mass from being depleted via equilibration with the gas-phase and subsequent removal through deposition. This effect is even stronger in the LOWVOL and FAST_AGING cases, as the overall exposure time (from initial formation to ending up in the inert bin) is shorter.

Supplementary material related to this article is available online at:
http://\@journalurl/\@pvol/\@fpage/\@pyear/\@journalnameshortlower-\@pvol-\@fpage-\@pyear-supplement.pdf.

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Table 1. Chosen parameterizations for selected physical processes in WRF.

table

Process	Parameterization
Radiation	RRTMG short- and longwave
Cloud microphysics	Morrison double-moment scheme
Land surface	Noah Land Surface Model
Urban surface	Urban Canopy Model
Planetary boundary layer	Mellor-Yamada Nakanishi and Niino 2.5
Cumulus parameterization	Grell 3-D ensemble

Table 2. Henry's law constants H^* $(\mathrm{M\,atm^{-1}})$ for different volatility bins (C^* in $\mathrm{\mu g\,m^{-3}}$, at 298 K) as derived in Hodzic et al. (2014a). Shown are averaged values used for anthropogenic and biogenic semi-volatile mixtures. All water solubilities are used with a temperature dependence of 6014 $(-\mathrm{d}\ln(H^*)/\mathrm{d}(1/T))$.

	1	10	100	1000
anthropogenic	1.1×10^{8}	1.8×10^{7}	3.2×10^{6}	5.5×10^{5}
biogenic	5.3×10^{9}	7.0×10^{8}	9.3×10^{7}	1.2×10^{7}

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Table 3. Simulations conducted. DD/WD denotes if dry/wet deposition of SVOCs is considered, and H^* refers to the Henry's law constants used for SVOCs~~,~~. xVEGFRA states whether dry deposition velocities are scaled by the vegetation fraction of each grid cell (see text). kOH ~~to~~ denotes the aging rate constant ($\mathrm{SVOC} + \mathrm{OH}$) ~~,~~and f_0 to the reactivity parameter in the Wesely (1989) dry deposition scheme. kOH is reported as $\mathrm{cm^3\,molec^{-1}\,s^{-1}}$, H^* as $\mathrm{M\,atm^{-1}}$, the temperature dependence as $-\mathrm{d}\ln(H^*)/\mathrm{d}(1/T)$. Parameters varied compared to the REF simulation are shown in bold font.

case name	DD	WD	H^* (T dependence)	xVEGFRA	f_0	kOH
REF	x	x	Hodzic et al. (2014a)		0.0	1.0×10^{-11}
DRY	x		Hodzic et al. (2014a)		0.0	1.0×10^{-11}
WET		x	Hodzic et al. (2014a)		0.0	1.0×10^{-11}
NODEP			**no SVOC deposition**		0.0	1.0×10^{-11}
SOA volatility						
LOWVOL	x	x	Hodzic et al. (2014a)		0.0	**1×10^{-11}, 1×10^{-10} for $C^* = 1.0$**
LOWVOL_NODEP			**no SVOC deposition**		0.0	**1×10^{-11}, 1×10^{-10} for $C^* = 1.0$**
FAST_AGING	x	x	Hodzic et al. (2014a)		0.0	**4.0×10^{-11}**
FAST_AGING_NODEP			**no SVOC deposition**		0.0	**4.0×10^{-11}**
SVOC solubility						
H_ACETIC	x	x	**4.1×10^3 (6300)**		0.0	1.0×10^{-11}
H_HNO3	x	x	**2.6×10^6 (8700)**		0.0	1.0×10^{-11}
H_1E5	x	x	**1.0×10^5 (0)**		0.0	1.0×10^{-11}
H_1E8	x	x	**1.0×10^8 (0)**		0.0	1.0×10^{-11}
H_1E10	x	x	**1.0×10^{10} (0)**		0.0	1.0×10^{-11}
dry deposition scheme						
F_0.1	x	x	Hodzic et al. (2014a)		**0.1**	1.0×10^{-11}
F_1.0	x	x	Hodzic et al. (2014a)		**1.0**	1.0×10^{-11}
VEGFRA	x	x	Hodzic et al. (2014a)	**x**	0.0	1.0×10^{-11}
VEGFRA_NODEP			**no SVOC deposition**	**x**	0.0	1.0×10^{-11}

Table 4. Contributions of dry and wet deposition through the gas-/particle-phase as well as resulting change in surface level SOA concentrations over the continental US in June, July, and August for ~~the different VBS parameterizations considered~~selected sensitivity studies. Values in the two lowermost rows are percentual changes (%), all other rows are accumulated deposited mass in Gg.

		REF		LOWVOL		FAST_AGING		VEGFRA	
		anthro.	biog.	anthro.	biog.	anthro.	biog.	anthro.	biog.
	wet dep.	21.9	19.4	15.5	13.7	32.7	31.8	24.2	24.5
particle	dry dep.	1.8	1.6	1.1	1.1	2.6	2.6	1.0	1.0
	total	23.7	21	16.6	14.8	35.3	34.4	25.2	25.5
	wet dep.	12.0	17.4	6.5	9.6	6.3	10.8	12.7	20.3
gas	dry dep.	21.5	42.9	11.1	25.2	12.3	30.4	15.7	37.0
	total	33.5	60.3	17.6	34.8	18.6	41.2	28.4	57.3
mass fraction lost by gas-phase dep. (%)		59	74	51	70	35	54	53	69
avg. surface SOA conc. changes (%)		-41	-56	-32	-48	-23	-39	-31	-45

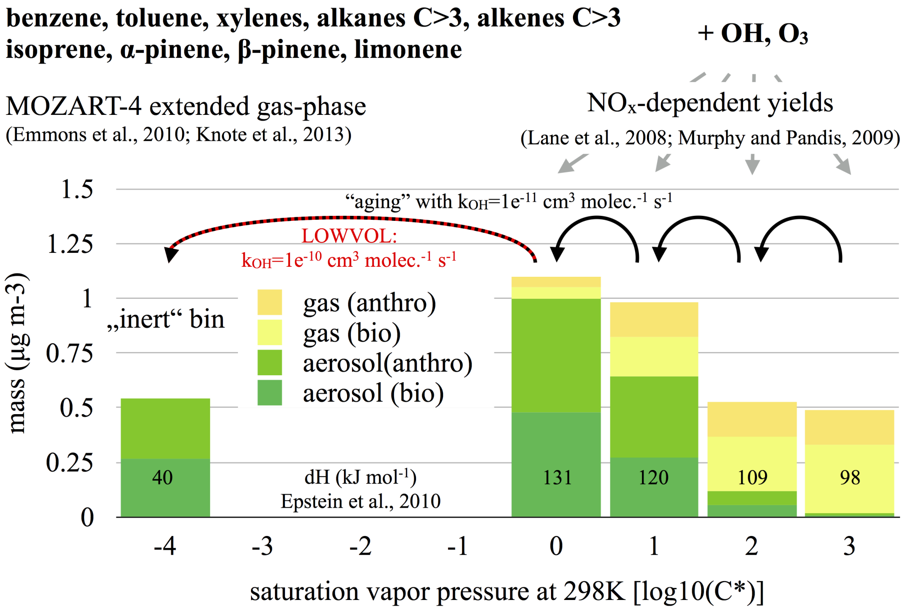

Fig. 1. Schematic overview of the Volatility Basis Set as implemented in WRF-Chem. SOA/SVOC values are surface level concentrations from the REF simulation averaged over the full year 2010 and the CONUS domain (land points only).

figure

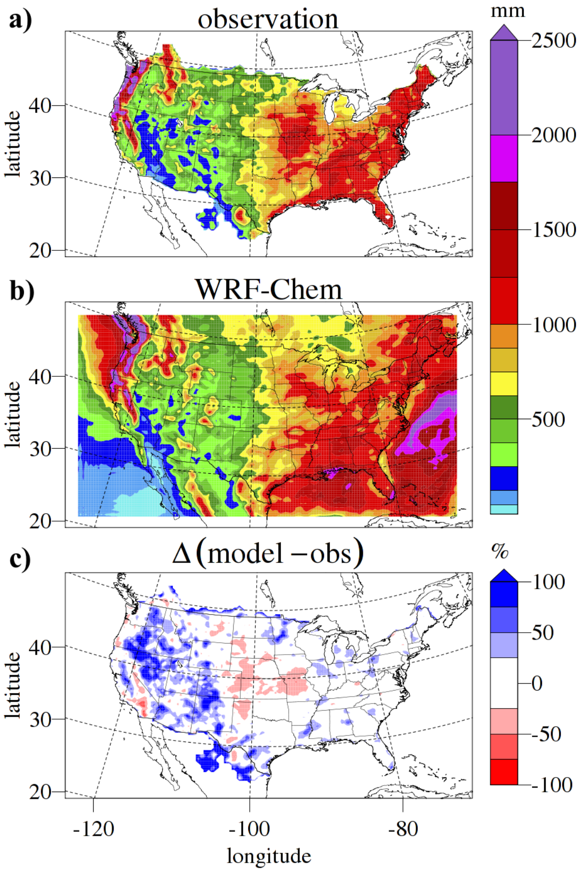

Fig. 2. Year 2010 accumulated precipitation. a) as observed by rain gauge/radar network~~(top left, “obs”)~~ ~~vs~~. b) WRF-Chem model results~~(top right, “mod”~~. c) ~~and~~ differences relative to ~~the~~ observations (~~bottom,~~ $\Delta(\text{model} - \text{obs}) = (\text{mod} - \text{obs})/\text{obs} \times 100$).

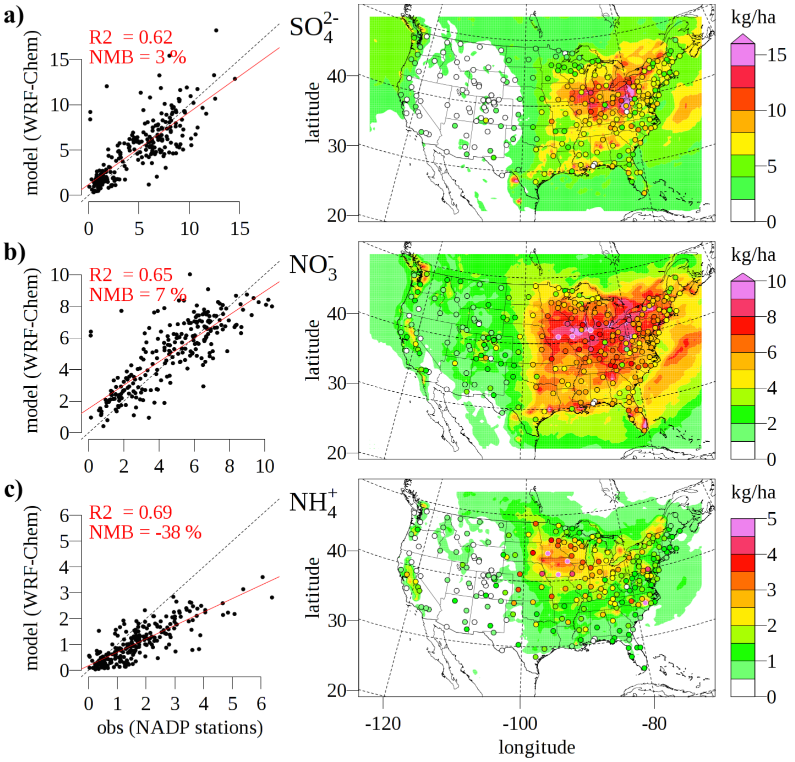

Fig. 3. Year 2010 accumulated wet deposition of inorganic ions ~~(~~a) SO_4^{2-}, b) NO_3^-, and c) NH_4^+ as measured by NADP stations (obs) and as predicted by WRF-Chem (model). As maps (right column), with stations as circles color-coded by measured amount, and as scatterplots (left column) with R^2 the squared Pearson correlation coefficient, and NMB the normalized mean bias ($\mathrm{NMB} = \Sigma(\mathrm{model} - \mathrm{obs})/\Sigma\mathrm{obs} \times 100$).

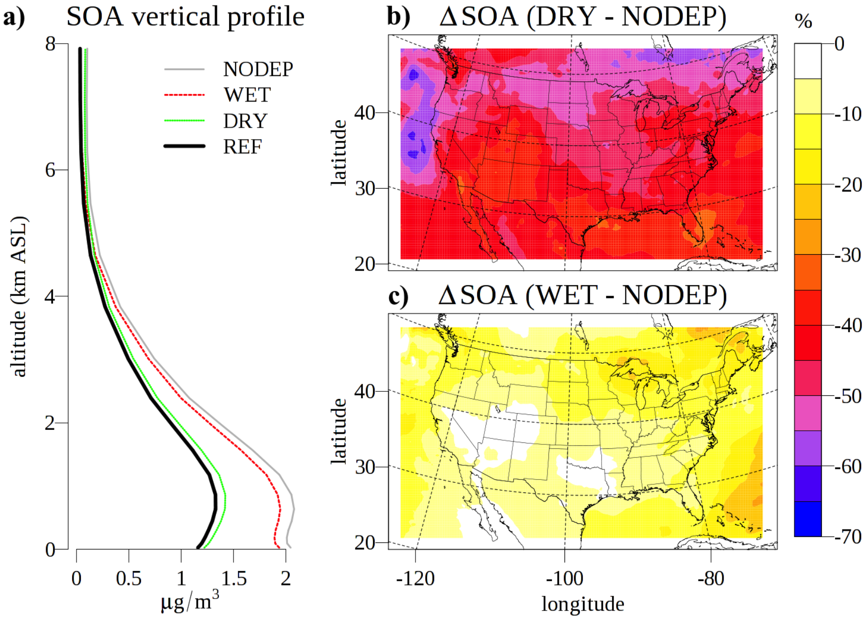

Fig. 4. Effects of dry and wet deposition of SVOCs on SOA concentrations. ~~Left plot:~~ a) vertical profiles of SOA concentrations as yearly average over land. ~~Right plots: changes~~ Changes in annual mean surface level SOA concentrations due to the consideration of b) dry (~~top,~~ DRY – NODEP) and c) wet deposition (~~bottom,~~ WET – NODEP) of SVOCs.

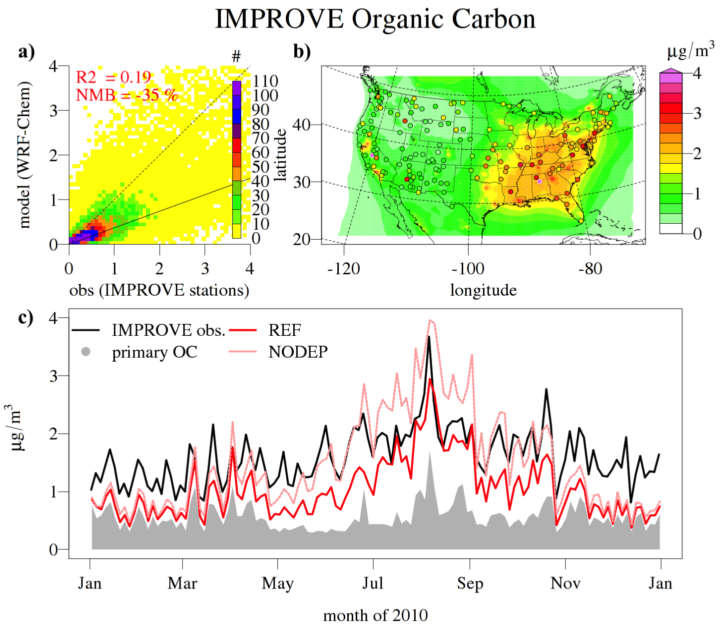

Fig. 5. Evaluation of ground level total organic carbon (OC) concentrations against IMPROVE measurements. ~~Top right: annual average OC surface level concentrations (REF simulation~~a) ~~. Filled circles represent measured concentrations. Top left:~~ density scatterplot of ~~annual~~ daily average concentrations at each IMPROVE station against modeled concentrations (R^2 and NMB as defined in Fig. ~~3~~3, again using the REF simulation). ~~Lower plots:~~ b) annual average OC surface level concentrations (REF simulation). Filled circles represent measured concentrations. c) time evolution of OC concentrations as average over all IMPROVE stations. Black solid line is measurement average. Grey area represents the POC contribution to total OC (from REF simulation). Light red ~~, red, green~~ and ~~violet~~ red lines are NODEP ~~, REF, LOWVOL~~ and ~~FASTSUBSCRIPTNBAGING~~ REF simulation averages of total OC respectively.~~The bottom plot shows only the summer period and adds sensitivity study results, but is otherwise identical to the middle plot.~~

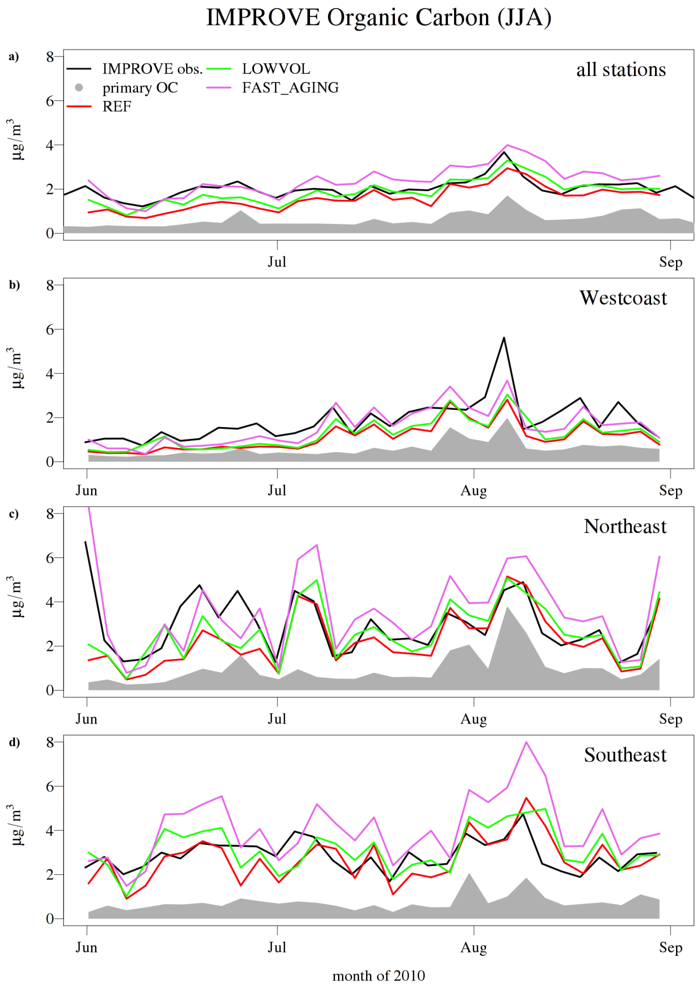

Fig. 6. Time lines of ground level total organic carbon (OC) concentrations against IMPROVE measurements like in Figure 5, but only for the summer period (June, July, August). Green and pink lines are for LOWVOL and FAST SUBSCRIPTNBAGING sensitivity studies, respectively. a) all stations. b) west coast: California, Oregon, Washington. c) Northeast: Connecticut, Maine, Massachusetts, New Hampshire, Vermont, New Jersey, New York, Pennsylvania, Maryland, District of Columbia, Illinois, Indiana, Michigan, Ohio. d) Southeast: Alabama, Florida, Kentucky, Georgia, North Carolina, South Carolina, Tennessee, West Virginia, Virginia.

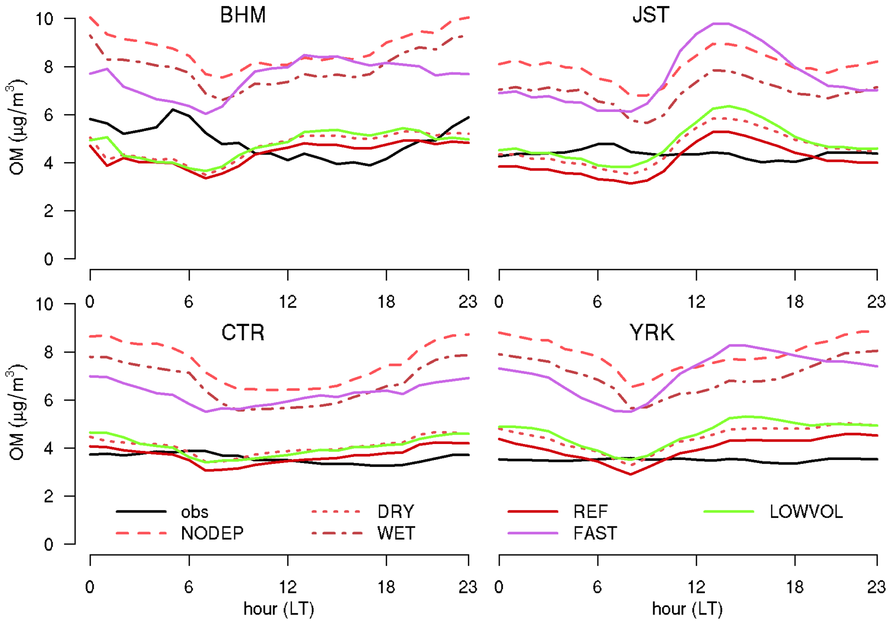

Fig. 7. JJA average diurnal cycles of organic matter (OM) concentrations at 4 field sites of the SEARCH network. Measurements assume an OM/OC ratio of 1.4 (Hansen et al., 2012), model results are scaled accordingly (see text).

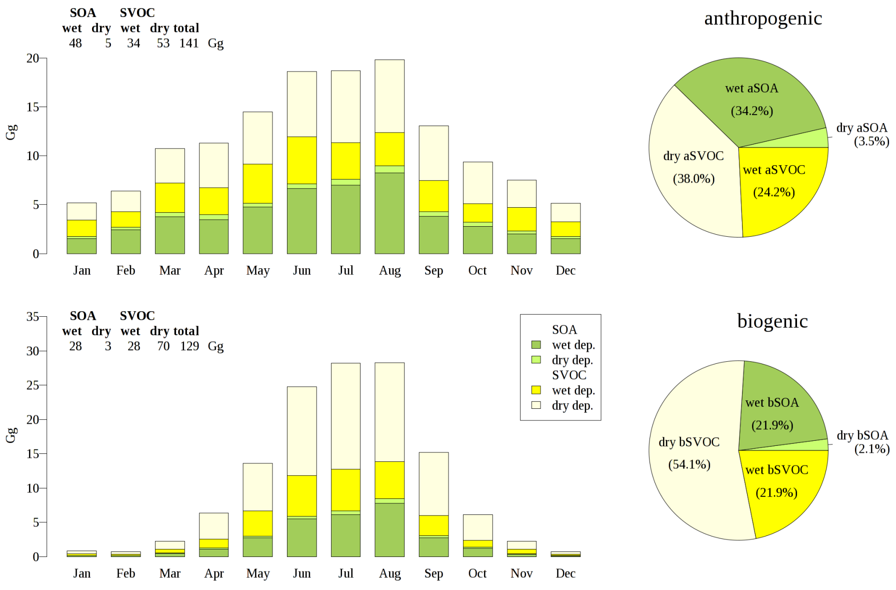

Fig. 8. Monthly (left) and yearly (right) accumulated deposited mass of anthropogenic (top) and biogenic (bottom) SVOC + SOA over the continental US split into the different pathways, and shown (on the left) for simulations assuming H^* of SVOCs according to GECKO-A results (REF simulation). Table on top-left shows total annual deposited mass.

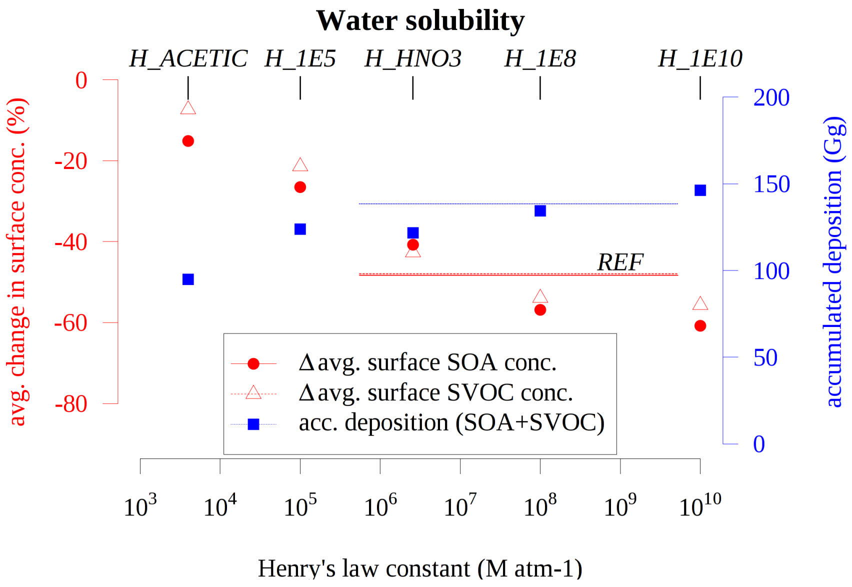

Fig. 9. Sensitivity to water solubility of SVOCs (H^*). Shown are continental US averages/totals of changes in surface level SOA (red dots)/SVOC (red triangles) concentrations and accumulated deposition of SOA + SVOCs (blue ~~dots~~rectangles). The results of the REF simulation using the range of H^* values derived in Hodzic et al. (2014a) are indicated as lines.

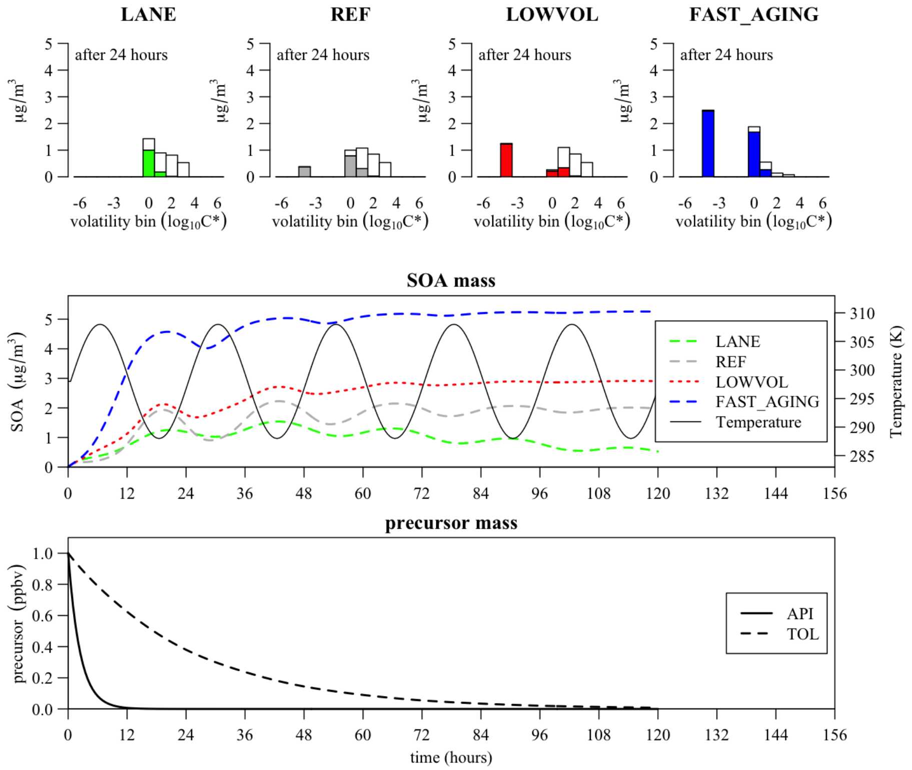

Fig. A1. Box-model simulations of the oxidation of 1 ppbv α-pinene and toluene. Top row: distribution of particulate (colored) and vapor mass (white) in the different volatility bins after 24 h. Second row: total particle mass of SOA formed, as well as temperature. Third row: time evolution of precursor concentration.

A1=1 figure

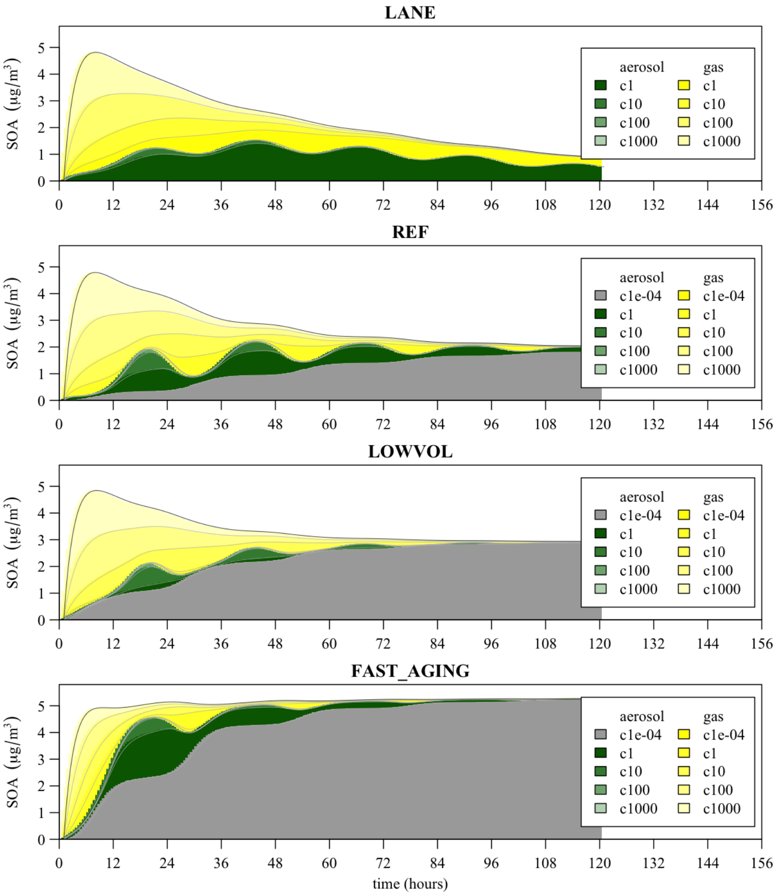

Fig. A2. Evolution of mass distribution in particle and vapor phase in the box model simulations for the different parameterizations.

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