The authors sincerely thank the reviewers for their thoughtful and thorough reviews. Responses to the *reviewer comments* (in italics) appear below.

Reviewer #1

General: *This paper details the development and implementation of an updated SOA parameterization into CMAQ. The update consists of fitting an Odum-2P parameterization to predictions based on recent VBS parameterizations for several traditional SOA precursors. The benefits of this update are two-fold:(1) no computational expense is added because the update still uses only two products per parent hydrocarbon, and (2) the accuracy of the VBS at lower OA loadings is captured. The paper is well written and the results represent a much needed update for CMAQ's SOA module. That being said, the paper has some serious shortcomings that must be addressed prior to a final decision on publication.*

Detailed Comments:

1. Measurement comparison

My main problem with the paper in its current form is that it spends a considerable amount of time discussing why the updated parameters are the best available, and virtually no time discussing the impact of these updates. This imbalance results in very few conclusions being drawn. The authors basically state that changing the SOA parameters will change the spatial and temporal distributions of SOA predictions, which may affect the accuracy of the predictions. I think a more balanced approach should be taken and a comparison to surface measurements is absolutely necessary. For instance, given CMAQ's documented history of underpredicting SOA concentrations nationwide, I was very surprised to read that CMAQ predictions in areas that are dominated by anthropogenic SOA decreased by 20% as a result of these updates (first paragraph of section 3.3). More surprising is that this finding was given only two sentences of discussion and no figures. I do not agree with the authors statement in the Conclusions section,"Recognizing the importance of processes not currently treated in the CMAQ SOA model (e.g., gas-phase aging beyond that typically captured in chamber studies and partitioning of POA), CTM predictions were not compared with ambient measurements." Any update significant enough to merit publication is significant enough to merit comparison with available measurements, even if the update worsens an existing discrepancy. For instance, how many regional CTM modeling papers have hypothesized that using an Odum-2P model as opposed to a VBS is a possible explanation. Therefore, I encourage the authors to include surface measurements as well as additional discussion regarding how their recent updates to both biogenic and anthropogenic SOA compare to those measurements and to previous studies. Once this is done, the conclusions section should be considerably stronger.

At the advice of this reviewer, we have now included a figure and discussion comparing modeled secondary organic carbon (SOC) mass concentrations for the three cases (base case, best available-high NOx, best available-low NOx) with measured SOC* from 155 IMPROVE sites, grouped into 6 regions (West Pacific, West, Central, Midwest, Northeast, Southeast).

For all three cases, the model- and measurement-based trends in predicted SOC mass concentration follow a similar pattern from region to region, except for the Midwest. For all regions, predicted SOC mass concentrations were in better agreement with measurement-based SOC using the best available parameters derived in this work, particularly for the low-NOx case.

Averaged over all sites, the percent bias improved from -63% to -15% from the base case to the best available-low NOx case. Perhaps not coincidentally, most of the IMPROVE measurement sites (115 out of the 155 included) are in locations where ≥50% of RO_2 is predicted to react with HO_2 (i.e., low-NOx pathway; see Fig. 9). SOC mass still was significantly underpredicted in the Midwest, Central and Northeast regions, where the percent bias is -43%, -23% and -21% respectively, for the best available low-NOx case, suggesting “missing” anthropogenic source(s) and/or other pathway(s).

*Semi-empirical estimates of SOC are calculated from observed OC and EC according to Yu et al. (2007) as follows:

$$\mathrm{OC}_{\mathrm{sec}} = \mathrm{OC}_{\mathrm{obs}} - \left[\min\left(\mathrm{OC}_{\mathrm{obs}}, \left(\frac{\mathrm{OC}}{\mathrm{EC}}\right)_{\mathrm{pri}} \times \mathrm{EC}_{\mathrm{obs}}\right)\right]$$

$(\mathrm{OC}/\mathrm{EC})_{\mathrm{pri}}$ is a ratio calculated from CMAQ outputs of primary OC and EC, reflecting the mixture of primary sources impacting a given site at the time when each sample was collected.

2. Chamber data vs Odum-2P vs VBS

The authors mention that the VBS parameters may be better able to represent SOA formation at low Mo, even when limited data exist. It should be mentioned that this is because the VBS is designed to weight each VBS C equally, regardless of the number of data points available at, or near a given loading. For instance, if a hypothetical data-set contained 100 yields measurements all taken near* $M_o = 100\ \mu g\ m^{-3}$ *and 1 data point taken near* $M_o = 1\ \mu g\ m^{-3}$*, the VBS parameters (*$C^* = 1{,}100\ \mu g\ m^{-3}$ *in this hypothetical) would capture the yield behavior at both loadings, and since the Odum-2P C* parameters are not fixed, they would be biased towards 100 100* $\mu g\ m^{-3}$*. With the authors' approach, the VBS is used to generate 99 additional synthetic data points near 1* $\mu g\ m^{-3}$*, thereby giving yields at* $C^* = 1$ *and* $C^* = 100$ *equal weighting when fitting the Odum-2P parameters. However, the yield predictions from either the VBS or the 2P-VBS will still only be as accurate as the single measured data point at* $M_o = 1\ \mu g\ m^{-3}$*. This is important because yield measurements at atmospherically relevant conditions (e.g.* $\leq 10\ \mu g\ m^{-3}$*) are more susceptible to things like high signal-to-noise ratios, gas-phase and particle-phase wall loss, etc. Therefore, any apparent improvements in agreement between predictions and observations may be somewhat fortuitous and/or incorrect. This is true for the VBS and the 2P-VBS. At least some additional discussion regarding this point should be added to the manuscript.*

We agree with the reviewer that the accuracy of predictions from either the 2p or VBS approaches (and by extension 2p-VBS) will still only be as accurate as the data available at low M_o. Fitting of both the 2p and VBS parameters is achieved using the method of least-squares, so it isn’t exactly true that each C^* is weighted equally if there are a greater number of data points at higher values of M_o and a lesser number of data points at lower values of M_o. For example, a 20% error in SOA yield at $M_o = 100\ \mu g\ m^{-3}$ has a greater absolute value than a 20% error at $M_o = 1\ \mu g\ m^{-3}$, thus in a simple least-squares fitting approach the data at higher M_o are implicitly weighted more. However, by fixing the C^* that is constrained by the data at the lowest M_o value (C^* value within an order of magnitude of that M_o, see Presto and Donahue, 2006), the observed yield at that M_o value is captured with the VBS approach. As described in the introduction and described/demonstrated in Section 2.1 of our paper (Fig. 1), this does not happen with the 2p approach unless there are sufficient data points at low M_o (or C^* values are intentionally constrained as part of the fitting algorithm, i.e., a hybrid VBS/2p method).

Regarding accuracy, we did note in the manuscript (Section 2.1) that the 2p-VBS parameters represent SOA formation with the same degree of uncertainty as the VBS parameters. Much effort was made (Sections 3.1 and 3.2) to evaluate widely-used 2p and VBS parameters, as well as the newly developed 2p-VBS parameters, to determine the "best-available" parameters based on comparisons with chamber data (note: this effort was not just to support the use of the newly developed parameters as suggested by this reviewer, but to evaluate all widely used parameters). In the revised manuscript, we have made a greater effort to differentiate between the theoretical underpinnings of the 2p-VBS approach and the 2p-VBS parameters, as the latter are impacted by the data and VBS fits reported in Tsimpidi et al. (2010). In agreement with this reviewer, we did not advocate the use of only the data at low M_o (in the few cases for which such data are available) to develop parameterizations for the reasons listed, as well as the limited ability at this time to validate such data (please see below).

The better agreement between the modeled SOC and measurement-based SOC was achieved in this work by better representing SOA formation by lower volatility monoterpene products, including by addition of a low-NOx pathway, with the 2p-VBS parameters. There are sufficient chamber data, at least for α-pinene, to support this result. Though the better agreement in SOC was not fortuitous, further work would be required to predict product structures and the associated properties (e.g., O/C ratios) that could be compared with measurements

I am also not convinced that chamber data at atmospherically irrelevant conditions should even be used at all in the development of these parameterizations. For instance, instead of fitting a VBS to all chamber data, and then fitting the Odum-2P parameters to the VBS, I wonder why the authors do not just refit the Odum-2P parameters using only chamber data at atmospherically relevant Mo (say $\leq 40\ \mu g\ m^{-3}$*). I understand the chamber yields at high loadings would not be constrained, but I wouldn't be surprised if the SOA yields from the traditional parent HCs could be represented with a 1-product model if only atmospherically relevant range of Mo were considered. This would further reduce the computational burden of CMAQ.*

The relevance of chamber experiments to the ambient atmosphere is critically important to understand in developing robust parameterizations for chemical transport models. Reacted HC concentrations and SOA mass loadings, discussed in this work, are two important considerations but there are many others. As more recent studies have shown (e.g., Henry et al., 2012; Eddingsaas et al., 2012), the relative concentrations of gas-phase species (e.g., oxidants, such as O_3, OH and NOx) also are important in determining SOA mass concentrations and physicochemical properties. Discarding data would be difficult to justify at this time because: 1) the difficulty of assigning atmospherically relevant ranges (e.g., NO/NO_2 ratios, SOA mass loadings) and thus difficulty determining which data are truly atmospherically relevant; and 2) the lack of data in the approximate range (as discussed in this manuscript for M_o, which for the continental US is $<< 40\ \mu g\ m^{-3}$). Regarding 2, the quality of the data at higher SOA mass loadings has been validated to some extent by comparisons between experiments, including between facilities, and with ambient data, and has led to considerable advances in our understanding of ambient SOA formation. As noted by this reviewer, experiments at low mass loadings are more difficult. There is the complication that gas-phase compounds may partition considerably to chamber walls, and that this partitioning is enhanced under low mass loadings (Matsunaga and Ziemann, 2010), making the push to more atmospherically relevant levels of reactants/products potentially problematic (not to mention the increased difficulty of making accurate measurements at low loadings). It is for the above reasons that we do not: 1) definitively identify atmospherically relevant/irrelevant studies, and 2) discard data from high reacted HC/SOA mass experiments. In the revised manuscript, we have elaborated on the above points in the supplemental section describing the 2p-VBS fits.

3. Instantaneous Reversible Equilibrium

In light of the growing body of evidence [Shrivastava et al.(2013), Saukko et al.(2012), Perraud et al.(2012), Kuwata and Martin(2012), Abramson et al.(2013), Zelenyuk et al.(2012), Cappa and Wilson(2011), Vaden et al.(2011), Vaden et al.(2010), Virtanen et al.(2010)] suggesting that the SOA in most of the chamber experiments used in this study may have been a highly viscous liquid or semi-solid, the authors need to defend the assumption of reversible equilibrium in CMAQ. The fact that experimental yields can be fit to the G/P partitioning framework of [Pankow (1994a), Pankow(1994b)] does not prove that instantaneous reversibility is an appropriate assumption. For instance, [Cappa and Wilson(2011)] showed that experimental SOA yield curves from α-pinene ozonolysis can be reproduced by the sequential partitioning model which does not assume reversible equilibrium.

We recognize that equilibrium timescales will change with particle properties and ambient conditions, potentially resulting in circumstances for which “instantaneous” equilibrium should not be assumed. As pointed out by this reviewer and Reviewer #3, there has been excellent research published to show this. At the same time, research also has been published suggesting that the assumption of equilibrium in CTMs is appropriate (Saleh et al. 2013). Saleh et al. (2013) and Wilson and Cappa (2011) pointed out that particle-phase diffusion limitations can be misinterpretations of deviations between modeled and measured partitioning behavior (e.g., evaporation) when the existence of very low volatility compounds (e.g., accretion products/oligomers) is not accounted for. Ambient (e.g., Williams et al., 2010; Yatavelli et al., 2013) and laboratory (Jang and Kamens, 2001) measurements of compounds in the gas and particle phases have shown that some compounds follow predicted partitioning behavior (assuming equilibrium) while other do not, supporting the suggestion that the assumption of equilibrium is appropriate (though may not always be).

Understanding phase state and particle diffusion limitations, and modifying existing models to better reflect this understanding, are clearly timely and important areas of research. However, we do not think that the level of understanding is sufficient to allow the development of robust parameterizations. The need to “defend” the assumption of irreversible equilibrium, in both the 2p and VBS models, seems premature at this time. However, given the importance of these recent findings (as expressed by this comment and those of Reviewer #3), in the revised manuscript we have added the following:

> "It is also important to note that the default implementation of the 2p and VBS approaches in these CTMs assumes instantaneous G/P equilibrium is achieved. Recent work suggests that this assumption is appropriate in CTMs (Saleh et al., 2013), though there have been several studies published (Virtanen et al., 2010; Cappa and Wilson, 2011; Vaden et al., 2011; Perraud et al., 2012; Shiraiwa and Seinfeld, 2012) suggesting that this assumption may not be appropriate under all conditions; changes in the physicochemical properties of particles due to changes in ambient conditions and/or condensed-phase chemistry may lead to circumstances where partitioning kinetics are controlled by particle-phase diffusion and instantaneous equilibrium cannot be assumed. The default assumption of instantaneous equilibrium is maintained in this work."

[Shrivastava et al.(2013)] implemented this methodology into WRF-Chem and used observations during the MILAGRO campaign to show that SOA predictions are higher throughout their entire domain. CMAQ predictions would be significantly different than what is shown in Figure 7-9 if this methodology, which is also consistent with chamber data and which would be very straightforward to implement into CMAQ, were to be adopted.

As a "first order approximation", Shrivastava et al. (2013) implemented a condensed-phase processing scheme to transform semi-volatile ("traditional") SOA into non-volatile SOA, to represent the formation of semi-solid/glassy particles. With this approach, complete conversion of semi-volatile SOA to non-volatile SOA occurred with a timescale of 5 minutes (effectively "instantaneous" conversion of all semi-volatile SOA to non-volatile SOA). This is in contrast to the 20 hour conversion timescale currently implemented in the CMAQ model. As noted by the reviewer, this modification increased SOA mass predictions (expectedly) throughout the domain. However, Shrivatava et al. (2013) noted that the aggressive conversion scheme ignored the findings of Vaden et al. (2011), the study which motivated the Shrivastava work, that 15% of the SOA formed evaporated in a few hours. (Evaporation of chamber-derived SOA also has been reported by Grieshop et al., 2007.) Shrivastava et al. (2013) concluded that their results were dependent on unconstrained parameterizations and that further data and understanding were necessary to facilitate getting "the right answers for the right reasons". The work of Shrivastava et al. (2013) will be important for future efforts of representing non-equilibrium partitioning in CTMs and we don't mean to suggest that process-level understanding needs to be perfect before parameterizations of important processes be included in such models. However, based on published literature, advocating the implementation of a parameterization that effectively assumes all SOA is non-volatile would be difficult to justify.

Minor Comments:

4. *Introduction: "α-pinene ozonolysis experiments by Yu et al. (1999) essentially all of the SOA mass formed was attributed to identified oxidation products that are relatively volatile". In Table 1 of Yu et al. (1999), the M_o ranges from 11.2 to 65.1 $\mu g\ m^{-3}$. The majority of the mass associated with oxidation products with K_p values on the order of 10^{-6} to 10^{-1} $m^3\ \mu g^{-1}$ will not be in the particle phase under these conditions.*

While the M_o range was ~11-65 $\mu g\ m^{-3}$ for all VOCs studied by Yu et al. (1999), the range was 39-65 $\mu g\ m^{-3}$ for the α-pinene experiments. Nevertheless, it is true that the total measured SOA mass cannot be predicted assuming equilibrium condensation of the products identified by Yu et al. (1999). In Pankow et al. (2001), it was assumed that products "A13" and "A14" were non-volatile (and thus having different structures than proposed by Yu et al., 1999) in order to achieve better measurement/model agreement. In addition to the possibility of misidentified products, some of the identified products had higher yields in the particle phase than would be predicted based on theory, which could be due to measurement errors (also discussed in Pankow et al., 2001)) or an indicator of accretion chemistry. While Yu et al. (1999) did attribute ~100% of the SOA mass to the identified products, we have modified (changes in bold) the sentence to read: "**~55-95%** of the SOA mass formed **can be** attributed to identified **and hypothesized** oxidation products that are relatively volatile".

5. *Introduction: "only ~50% would be expected in the condensed phase." I think the authors meant 33%. At equilibrium,* $G = A \times C^*/M_o \rightarrow G/A = C^*/M_o = 10/5 \rightarrow G = 2 \times A$. *Therefore, 2/3 of the material is in the gas phase and one third is in the particle phase.*

Thank you for catching this error. We originally had an "atmospherically relevant" M_o of 10 μg m^{-3}. ~50% has now been changed to ~30%.

6. *Section 2.1: "...retaining source attribution in CTMs is computationally cost prohibitive for many applications." One of the primary motivations of this work is to exploit the advantages of the VBS while maintaining the computational efficiency of the Odum-2P framework. It would be helpful if the authors added a couple sentences discussing the computational burdens associated with CMAQ modeling. For instance, how many tracers are in the unmodified version of CMAQv4.7.1 using SAPRC07, and how many tracers would be added if the authors were to use a standard VBS for each traditional SOA precursor as opposed to a 2P-VBS?*

In CMAQv4.7.1, with the SAPRC99 gas-phase chemistry and AE5 aerosol modules, there are 123 advected chemical species, including 20 semi-volatile lumped species to simulate SOA from the six classes of precursors listed in Table 3; this is the same for both 2p and 2p-VBS parameterizations. A 4-bin VBS implementation for the same six VOC precursors, retaining precursor information, would require an additional 16 advected semi-volatile species (in the gas and particle phases), increasing the total number advected species from 123 to 139 and computational time by ~28% (computational time is proportional to the number of advected species squared). The relative computational cost will be higher if more precursors are modeled explicitly and if additional volatility bins are needed to capture aging. We note that in this study we used a modified version of CMAQv4.7.1, that incorporates recent advances in isoprene chemistry into SAPRC07 (Xie et al., 2013), which increases the number of advected species, and slightly decreases the relative increase in computational time (to ~22%). We have added the following sentence to the revised manuscript: "Implementing precursor-specific VBS parameters for the traditional SOA precursors would increase computation time by ~25% not considering aging."

7. *Section 3.1.1: "In contrast, the low-NOx VBS parameterization was extrapolated from the high-NOx VBS parameterization as follows:" I do not understand why the low-NOx VBS parameterization was extrapolated from the high-NOx parameterization. In Table 1 of the Lane et al. 2008a paper, separate isoprene VBS parameterizations are given for high-NOx and low-NOx conditions.*

No extrapolations of VBS parameters were performed in this work. Section 3.1.1 details the extrapolation used to obtain the Table 1 parameters in Lane et al. (2008a). To make this clearer, the clause "as described in Lane et al. (2008)" has been moved; the sentence now reads: "In contrast, Lane et al. (2008a) extrapolated the low-NOx VBS parameterization from the high-NOx VBS parameterization as follows: ...".

8. *Last paragraph of section 3.2.3: "Pye and Pouliot (2012) recently reported on the explicit treatment of C6-C19 alkanes and PAHs, represented by naphthalene, in CMAQv.5.0. They concluded that C6-C19 alkanes and PAHs could represent 20-30% of SOA formation". Please mention that although Pye and Pouliot (2012) estimated alkanes and PAHs would contribute 20-30% of the predicted SOA, they predicted average SOA concentrations from alkanes and PAHs would be very small (30 ng m^{-3}).*

The sentence has been modified as follows: "…could represent 20-30% of SOA formation (< 50 ng m^{-3}) with highest contributions…".

References:

Eddingsaas et al., *Atmospheric Chemistry & Physics Discussions,* 12: 7413-7427, 2012

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Jang and Kamens, *Environmental Science & Technology,* 35: 4758-4766, 2001

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Matsunaga and Ziemann, *Aerosol Science & Technology,* 44: 881-892, 2010

Pankow et al., *Environmental Science & Technology,* 35: 1164-1172, 2001

Saleh et al., *Environmental Science & Technology,* 47: 5588-5594, 2013

Williams et al., *Proceedings of the National Academy of Sciences,* 107: 6676-6681, 2010

Yatavelli et al., *Atmospheric Chemistry & Physics Discussions,* 13: 17253-17297, 2013

Yu et al., *Environmental Science & Technology,* 41: 4690-4697, 2007