This study describes the characteristics of regional aerosol over the Southeast during the summer of 2013. Through comparisons with the GEOS-Chem model the paper aims to explain the distribution, speciation, and seasonality of PM and AOD in the region. The study provides some new insights into aerosol sources in the region and the August-October transition in concentrations. However, the text over-stretches in some interpretation, and leaves open some key questions. Here are some major issues that the authors should address/correct:

1. The GEOS-Chem model aerosol simulation used in this study is very different from previous published versions (meteorology, ML heights, resolution, emissions, injection heights, chemical mechanism especially with respect to sulfate and OA formation). In order to interpret the results, and particularly comparison with previous GEOS-Chem studies, this study should provide some context for how these changes impact the PM simulation, and where possible (e.g. the impact of changes to sulfate and SOA formation, as well as ML heights) some "before" and "after" comparisons. It's not clear from the manuscript whether the ability of the model to capture PM concentrations in the Southeast in 2013 is a result of the extensive model modifications and if so, which factor(s) are most important.

We have added quantification of the major changes and their impact on the PM simulation in Section 2.

2. Figure 10 and Section 6: The figure shows that the model substantially underestimates MODIS AOD (factor of 2?) in the summer in the SEUS (a seen in Figure 13). This bias should be quantified and discussed in the text, particularly in light of the closer agreement in surface PM and extinction discussed previously (i.e. closure is not achieved, statements on page 17675, line 21-23, page 17676, line 9-10 and all similar statements in the text should be removed). This comparison appears to be in line with the previous results of Goldstein et al., 2009 and Ford and Heald., 2013. The statistics in Figure 10 suggest that both MODIS and GEOS-Chem are both biased low (NMB = -16% vs NMB = -18%) compared to AERONET, whereas the top-left panel of Figure 10 MODIS appears biased high compared to AERONET, not low. This should be resolved. (In addition the sentence on page 17672, line 25-26 is not supported by this analysis).

The model underestimates MODIS AOD by 28% averaged over the Southeast US during August and September 2013 (Figure 10). This is shown below in the difference plot and the information has been added into the text.

GEOS-Chem Percent Low Bias Relative to MODIS AOD
August-September 2013
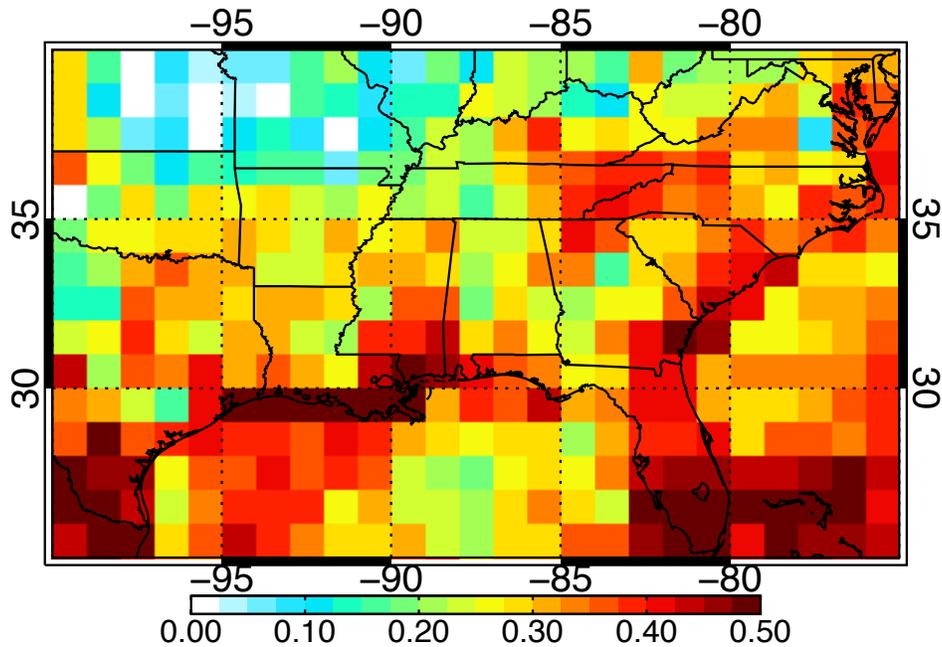
We have moderated our discussion on closure as suggested by the Reviewer. We have added text to explain the apparent discrepancy between the statistics shown inset on Figure 10 and the map. In particular, the statistics compared to AERONET are calculated only when there are collocated and corresponding data for both AERONET and MODIS, whereas the map shows the spatial average for all available data during the mission. This impact of sampling time and location on regional mean AOD is illustrated further in the figure below using GEOS-Chem. The red line shows pure GEOS-Chem output, the black and gray lines when sampling at the available MODIS and AERONET retrievals respectively.
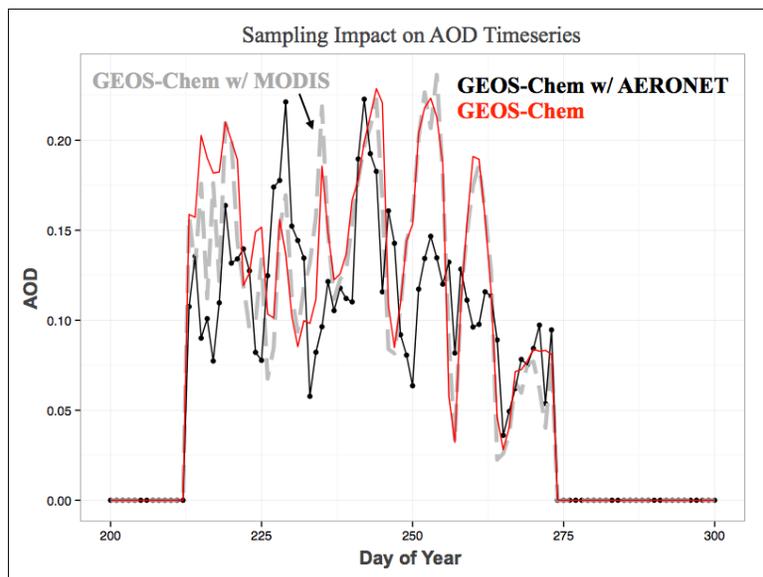
3. The plots and data do not support the conclusion that this model captures the seasonality in AOD in the Southeast. Figure 4 shows ~4-fold increase in observed AOD from winter to summer; whereas the model increase is at most a factor of 2. The text should be extensively revised accordingly, particularly in Section 7 and 8 and the abstract.

We have moderated the text and expanded on the discussion in Section 7 on the underestimate of the seasonal cycle. Our main point however is to focus on using the model to understand how there can be no seasonal cycle in surface PM, but a strong seasonal cycle in AOD.

4. It appears that a highly simplified/tuned non-volatile SOA simulation provides a more reliable simulation of observed OA concentrations and variability than has previously been achieved in field campaign comparisons. What are the implications of this? Does this study suggest that SOA is non-volatile, and models should eliminate the use of partitioning theory and NOx-dependent yields?

This is an excellent point – we have added commentary to the text as to the implications of the simplified OA parameterization, and added a sentence to the abstract.

Minor Comments

1. Two recent studies (Nguyen et al., ES&T, 2015; Xu et al., PNAS, 2015) have suggested important OA formation mechanisms for the SEUS. How do these relate to the current simulation (are these mechanism included in GEOS-Chem?).

These OA formation mechanisms are not explicitly considered in the GEOS-Chem simulations presented in this study. We now reference Marais et al. (2015) for a more mechanistic GEOS-Chem simulation of OA including consideration of the above references.

2. Page 17656, line 25-26: This sentence should be removed as the manuscript does not support the argument that variation in PBL height is responsible for the seasonality in AOD. (The analysis of Section 7 suggests that the variation in PBL height leads to the simulated seasonality but does not quantify this effect. Furthermore the simulated seasonality underestimates the observed seasonality by a factor of ~2).

Sentence has been removed.

3. Page 17660, lines 27-28: Please clarify - aren't "aqueous aerosols, or cloud processing" included in the sulfate simulation in GEOS-Chem?

We have removed this statement, which was indeed confusing.

4. Page 17661 line 19-page 17662 line 2: This paragraph is confounding. The authors discuss how SOA yields depend on the fate of RO2, but have assumed that the yield is constant under all conditions, despite their statement that both low-NOx and high-NOx

regimes being equally important in this region. This seems like a major limitation of the model simulation, but the implications are not discussed. What conditions do the fixed yields represent and does this represent a lower/upper limit for SOA formation in the region?

This is indeed a limitation of the work and we now refer to Marais et al. (2015) for a more mechanistic GEOS-Chem simulation including different SOA yields in the two regimes.

5. Page 17662, lines 17-18: How does the GEOS-FP meteorology compare with GEOS-5 or MERRA with regards to ML heights? What is the impact of the correction of the ML heights on AOD and PM2.5 simulated in the region?

This information has been added to the text in Section 2.

6. Page 17665, lines 17-19: Is the GEOS-Chem simulation compared to these observations in these studies? If not, please justify this statement.

The comparison numbers of the model to the observations from these studies have been added to the text.

7. Page 17665, lines 27-28: If the trend in OC is driven by a decrease in anthropogenic emissions, why is the downward trend only significant in summer in this analysis?

We don't speculate in the paper on the factors driving the OC trends in summer or winter because we don't feel that our OC simulation is sufficiently mechanistic for this purpose. Again we defer to Marais et al. (2015), which discusses the issue of OC response to long-term trends in SO_2 and NO_x emissions.

8. Page 17667, line 1-2: "these small inconsistent biases may not be significant." – a 20% bias does not seem all that small. Please remove or justify this statement.

Sentence has been removed.

9. Figures 5 and 6 seem inconsistent, particularly with respect to concentrations in the 2-4km altitudes. Figure 6 shows that the median model concentration of sulfate is ~2 times lower than observed aboard the SEAC4RS aircraft, whereas Figure 5 shows much better agreement for mean sulfate. Similarly, median model OA appears lower than observed. The authors should comment on the differences between means and medians and/or choose a consistent approach to their analysis. In light of Figure 6, the statement of page 17668 line 28 seems over-stated.

We thank the reviewer for pointing out the inconsistency for sulfate. Median values are shown in both Figures 5 and 6. However, in Figure 6 the observed vertical profile for sulfate shown is for the SAGA measurement, not the AMS measurement as stated in the text. The figure has been updated accordingly and there are no changes to the conclusions stated in the text (which has also been moderated in tone). The OA values are consistent between Figures 5 and 6.

10. Figure 8: The relationship shown with this cloud of points is not very convincing, and thus this analysis does not seem particularly useful. I recommend removing the figure and shortening the discussion.

The figure has been removed and the text has been revised accordingly – more detailed follow up work on this phenomenon will be explored in Silvern et al. (in prep).

11. Section 6: Why is CALIOP not included in this analysis? It may inform the differences between the CRDS and HSRL, and could provide context for comparing 2013 with previous years. This seems like a major gap in the analysis.

CALIOP data are sparse and interpretation is difficult. We chose not to use them.

12. Page 17673, lines 14-24: Clarify that this mechanism is not included in the current simulation (Figure 12 could be misleading).

Clarification added to the text.

Response to Reviewer #2

We thank the anonymous reviewer for their helpful comments – we have made changes to the manuscript in response to their suggestions outlined in red below.

This paper describes the aerosol characteristics as simulated by the GEOS-Chem model during the NASA SEAC4RS field campaign in 2013. The paper presents comparisons of the aerosol measurements acquired by the NASA DC-8 aircraft and compares the GEOS-Chem simulations with these measurements. Overall the paper provides a very good description of the GEOS-Chem simulations and these comparisons. However, there are a couple of major items the authors need to address before publication. I recommend the authors address these items before publication.

Major 1. The discussion regarding AOD comparisons is confusing. Looking at Figure 10, it looks like the model significantly underestimates AOD relative to MODIS. The MISR comparison looks better but the model still seems to underestimate AOD. The discussion seems to indicate that the GEOS-Chem AOD underestimate is consistent with the aerosol extinction estimate but Figure 9 does not seem to show the same underestimate in aerosol extinction as in AOD. What is the underestimate in extinction relative to both HSRL and the CRDS? Also, why not compare the GEOS-Chem model AOD with the AERONET measurements during the diurnal cycle in at least a few locations? If there is some question as to the ability of the model to represent AOD, it would be good to make some more detailed measurements of AOD with AERONET at various times of the day and a few locations. Also, the DC-8 also deployed the 4STAR instrument, which measured column AOD at many wavelengths; this may help provide additional data for layer AOD comparisons.

Please also see the response to Comment #2 from Reviewer #1. Additional quantification of the model low bias has been added into the text (a low bias of 14.7% relative to CRDS and 16.4% relative to HSRL; 8% low bias relative to MISR; 28% low bias relative to MODIS). Our ability to compare to the AERONET diurnal cycle (i.e. the AOD during the sunlit portion of the day) is limited by the lack of necessary output from the high-resolution simulation results. We will include the 4STAR comparisons, reproduced in the vertical profile shown below at 550 nm (the wavelength of the GEOS-Chem AOD output), in the Supplementary Material. These are the good retrievals (marked with quality flag = 0), which show the above plane AOD. The column low bias (19.1%), taken as the low bias in the lowest 1-km layer, is similar to the low biases discussed previously. The choice of scale truncates some very large observations.
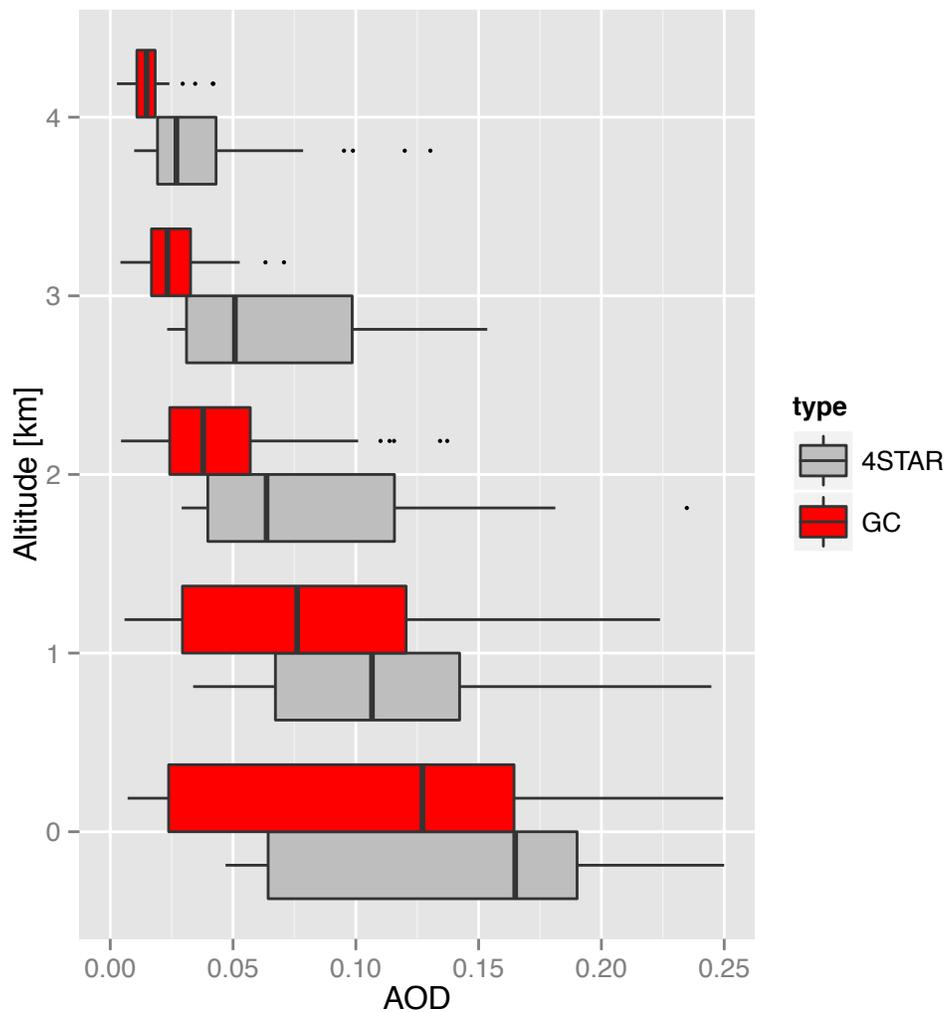
2. There should be more discussion regarding ML heights related to the model. How does the GEOS-Chem derive ML heights? From Richardson number? Aerosol gradients? If the mechanism is different from the lidar measurements, one may expect to see differences depending on location and time of day. Why were the GEOS-Chem heights 30-50% too high before adjustment? What was done to the model to reduce this bias? Does this imply that the model requires external information to constrain the PBL height to satisfactorily estimate PM2.5? How would the GEOS-Chem results been different if these external measurements of PBL height not been available?

Additional discussion of ML heights, how they are defined, and the impact of the ML height adjustment on $PM_{2.5}$ has been added to the text. GEOS-Chem does not directly derive ML height, it is provided from the parent meteorological fields (GEOS-FP) generated by the NASA Global Modeling and Assimilation Office. The ML high bias remains in a more direct comparison when GEOS-FP simulated backscatter profiles are fed into the same processing algorithm for the lidar measurements (Scarino et al., 2014b). The daytime ML height, which is read from the processed GEOS-FP file, was decreased by 40% to correct for this bias. This does imply that a good representation of ML height

is critical for CTM PM$_{2.5}$ applications, but does not necessarily imply that external information is necessary.

Minor

3. Abstract. Why does the model require a missing oxidant?

We elaborate on the need for a missing oxidant for sulfate in Section 2 and deleted that sentence from the abstract (it's not really a take-home message).

4. Abstract. There are statements that say GEOS-chem reproduces observed column aerosol mass with 6%, extinction within 16%, and space-based AOD within 21%. Is GEOS-chem biased higher or lower than these other measurements?

In all cases, the model is biased low – text has been adjusted to make this clearer.

5. Abstract. The abstract needs to mention the performance of GEOS-Chem related to PBL height and this impact on PM2.5.

We prefer not to. The ML bias has to do with the GEOS-FP meteorological fields, not GEOS-Chem proper. This seems like a technical issue to be covered in the text but does not rise to the level of the abstract as a take-home message for the reader.

6. Page 17659, Line 24. Should the Fischer et al., 2014 reference be 2015 instead? I would assume the Fischer reference should use SEAC4RS data.

Fischer et al. (2014) is a general reference about the need to account for fire plume buoyancy in GEOS-Chem.

7. Page 17659, line 29. Note that these are DC-8 flight tracks. It may be appropriate to note that these tracks also extend over other parts of the continental US as well as the Caribbean Sea.

Additional clarification has been added to the text.

8. Page 17662, line 19. The Scarino reference is not listed in the references.

Added to the text.

9. Page 17662, line 22. The Hair et al. reference does not indicate how the HSRL was used to derive ML heights.

See Scarino et al. (2014a), and references therein, which has been added to the reference list.

10. Page 17667, line 29. Since the model requires buoyant injection of forest fire smoke, does this mean the model requires external information to determine the height at which the smoke has been injected?

We now state in the text that we use generic injection heights for extratropical fires based on previous work.

Response to Reviewer #3

We thank the anonymous reviewer for their helpful comments – we have made changes to the manuscript in response to their suggestions outlined in red below.

This paper presents an observation-model integrated analysis of aerosol sources and seasonal variations in Southeast U.S. The high-resolution GEOS-Chem modeling is used as a platform to interpret a variety of aerosol observations from ground, aircraft, and satellite during the SEAC4RS campaign. Short-term trend of aerosol in the last decade is also discussed to some extent. The results from this study are a useful contribution to an improved understanding of aerosol sources and variability/trend in Southeast U.S. The paper is generally well written. I recommend the paper be published after authors adequately address following concerns.

My major concern is about their 40% downward correction of mixing layer (ML) height. First, what is definition of the ML? I thought it is defined as daytime maximum PBL height. However later they try to distinguish ML from PBL (p. 17668, line 26). Or do they define the mixing height just like that based on lidar profiling of aerosol? In any case they need define the ML in the first place and use it consistently throughout the paper.

Additional clarification has been added to the text. GEOS-Chem does not directly derive ML height, it is provided from the parent meteorological fields (GEOS-FP) generated by the NASA Global Modeling and Assimilation Office. The ML height from GEOS-FP is derived from the potential temperature gradient. The ML is not defined as the daytime maximum PBL height – here we define the PBL as the ML + CCL.

Second, it is argued that several studies (Scarino et al., 2015 – which is however not listed in the reference; Millet et al., 2015) have found GEOS-Chem simulated ML is too deep (e.g., 30-50% positive bias) across Southeast U.S. So they reduced the ML height by 40%. However it is not clear to me how they implemented this in the model. Did they adjust some tuning parameters to get the computed ML matching the observation? If they did this way, then they should document those tuning parameters so that other studies may take advantage of the outcome from this study. If not, what did they do exactly? Nevertheless it is important to document how they corrected the ML in the model.

Scarino et al. 2014ab have been added to the reference list. Additional information on how the ML was adjusted has been added to the text (a simple scaling of the variable read in from the offline GEOS-FP meteorological files during daytime hours).

Third, did they compare the GEOS-Chem ML height with some observations? For example, Seidel et al. (JGR, 117, D17106, doi:10.1029/2012JD018143, 2012) derived a climatology of PBL height over U.S. and Europe by using radiosonde observations. Is this PBL climatology useful for their study?

Evaluation of GEOS-FP ML heights against ceilometer measurements during SOAS is presented in Millet et al. (2015). Zhu et al. (in prep.) will present a more thorough comparison to lidar and climatological observations.

Fourth, the 40% downward correction was applied to the GEOS-Chem ML height throughout a year (Figure 13b). Here an inherent assumption is that the modeled ML has a positive bias of ~40% regardless of season. Is this assumption justified? How does this assumption affect their interpretation of the difference in the amplitude of the seasonal cycle between PM2.5 and AOD?

This is an excellent question. We make the assumption that the GEOS-FP ML bias applies year round because we lack highly resolved data such as from the lidar during SEAC^{4}RS. However, we do not expect this to change the interpretation of the difference in the seasonal cycle amplitude observed between $PM_{2.5}$ and AOD. As an endpoint scenario where there is a 40% reduction in ML height during summer and no reduction in ML height during winter, there is still a 40-50% enhancement (based on Figure 13b) in the ML height during the summer that leads to a difference in magnitude in the seasonal cycles.

Minor changes:

p.17653, l.10-11: "GEOS-Chem simulation of sulfate requires a missing oxidant, ..." I don't quite understand this sentence.

We deleted that sentence from the abstract.

p. 17655, l.1: Figure 1 shows both summertime and wintertime aerosol trend. But the winter trend is not discussed in main text at all.

We don't have much to say about the winter trend because it isn't the focus of our simulation.

p.17657, l.26: what does "FP" in GEOS-FP stand for?

The FP in GEOS-FP stands for "forward-processing." Added to the text.

p.17662, l.1-5: The description of AOD calculation is not right.

We don't understand the reviewer's concern. The description is correct. This is how AOD is operationally calculated in GEOS-Chem. Please see: http://www.atmos.colostate.edu/~heald/docs/GEOS_Chem_optics_description.pdf for more details.

p.17671, l.20: Why use Aqua/MODIS, but not Terra/MODIS?

In our previous work, we found little difference between MODIS AOD on Aqua and Terra and so we chose to focus on the afternoon MODIS data for this analysis.

1   **Manuscript with Tracked Changes**

2

3   **Sources, seasonality, and trends of Southeast US aerosol: an integrated analysis of surface,**

4   **aircraft, and satellite observations with the GEOS-Chem chemical transport model**

5

6   P. S. Kim[1], D. J. Jacob[1,2], J. A. Fisher[3], K. Travis[2], K. Yu[2], L. Zhu[2], R. M. Yantosca[2], M. P.

7   Sulprizio[2], J. L. Jimenez[4,5], P. Campuzano-Jost[4,5], K. D. Froyd[4,6], J. Liao[4,6], J. W. Hair[7], M. A.

8   Fenn[8], C. F. Butler[8], N. L. Wagner[4,6], T. D. Gordon[4,6], A. Welti[4,6,9], P. O. Wennberg[10,11], J. D.

9   Crounse[10], J. M. St. Clair[10,*,**], A. P. Teng[10], D. B. Millet[12], J. P. Schwarz[6], M. Z. Markovic[4,6,***],

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36

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38

39 **Abstract**

40

41   We use an ensemble of surface (EPA CSN, IMPROVE, SEARCH, AERONET), aircraft
42 (SEAC^{4}RS), and satellite (MODIS, MISR) observations over the Southeast US during the
43 summer-fall of 2013 to better understand aerosol sources in the region and the relationship
44 between surface particulate matter (PM) and aerosol optical depth (AOD). The GEOS-Chem
45 global chemical transport model (CTM) with 25 x 25 km^2 resolution over North America is used
46 as a common platform to interpret measurements of different aerosol variables made at different
47 times and locations. Sulfate and organic aerosol (OA) are the main contributors to surface PM$_{2.5}$
48 (mass concentration of PM finer than 2.5 μm aerodynamic diameter) and AOD over the Southeast
49 US. OA is simulated successfully with a simple parameterization assuming irreversible uptake of
50 low-volatility products of hydrocarbon oxidation. Biogenic isoprene and monoterpenes account
51 for 60% of OA, anthropogenic sources for 30%, and open fires for 10%. 60% of total aerosol
52 mass is in the mixed layer below 1.5 km, 25% in the cloud convective layer at 1.5-3 km, and 15%
53 in the free troposphere above 3 km. This vertical profile is well captured by GEOS-Chem,
54 arguing against a high-altitude source of OA. The extent of sulfate neutralization (f =
55 [NH$_4^+$]/(2[SO$_4^{2-}$] + [NO$_3^-$])) is only 0.5-0.7 mol mol^{-1} in the observations, despite an excess of
56 ammonia present, which could reflect suppression of ammonia uptake by OA. This would explain
57 the long-term decline of ammonium aerosol in the Southeast US, paralleling that of sulfate. The
58 vertical profile of aerosol extinction over the Southeast US follows closely that of aerosol mass.
59 GEOS-Chem reproduces observed total column aerosol mass over the Southeast US within 6%,
60 column aerosol extinction within 16%, and space-based AOD within 8-28% (consistently biased
61 low). The large AOD decline observed from summer to winter is driven by sharp declines in both
62 sulfate and OA from August to October. These declines are due to shutdowns in both biogenic
63 emissions and UV-driven photochemistry. Surface PM$_{2.5}$ shows far less summer-to-winter
64 decrease than AOD due to the offsetting effect of weaker boundary layer ventilation. The
65 SEAC4RS aircraft data demonstrate that AODs measured from space are consistent with surface
66 PM$_{2.5}$. This implies that satellites can be used reliably to infer surface PM$_{2.5}$ over monthly
67 timescales if a good CTM representation of the aerosol vertical profile is available.

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Margin comments:

Patrick 8/27/2015 11:44 AM
Deleted: GEOS-Chem simulation of sulfate requires a missing oxidant, taken here to be stabilized Criegee intermediates, but which could alternatively reflect an unaccounted for heterogeneous process.

Patrick 8/27/2015 11:44 AM
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Patrick 8/27/2015 11:44 AM
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Patrick 8/27/2015 11:44 AM
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1. Introduction

There is considerable interest in using satellite retrievals of aerosol optical depth (AOD) to map particulate matter concentrations (PM) in surface air and their impact on public health (Y. Liu et al., 2004; H. Zhang et al., 2009; van Donkelaar et al., 2010, 2015; X. Hu et al., 2014). The relationship between PM and AOD is a function of the vertical distribution and optical properties of the aerosol. It is generally derived from a global chemical transport model (CTM) simulating the different aerosol components over the depth of the atmospheric column (van Donkelaar et al., 2012, 2013; Boys et al., 2014). Sulfate and organic matter are the dominant submicron aerosol components worldwide (Murphy et al., 2006; Q. Zhang et al., 2007; Jimenez et al., 2009), thus it is important to evaluate the ability of CTMs to simulate their concentrations and vertical distributions. Here we use the GEOS-Chem CTM to interpret a large ensemble of aerosol chemical and optical observations from surface, aircraft, and satellite platforms during the NASA SEAC[4]RS campaign in the Southeast US in August-September 2013. Our objective is to better understand the relationship between PM and AOD, and the ability of CTMs to simulate it, with focus on the factors controlling sulfate and organic aerosol (OA).

The Southeast US is a region of particular interest for PM air quality and for aerosol radiative forcing of climate (Goldstein et al., 2009). $PM_{2.5}$ (the mass concentration of particulate matter finer than 2.5 μm aerodynamic diameter, of most concern for public health) is in exceedance of the current US air quality standard, 12 μg m^{-3} on an annual mean basis, in several counties (http://www.epa.gov/airquality/particlepollution/actions.html). Concentrations have been decreasing in response to regulation targeted at protecting public health (the Clean Air Act Amendments of 1990). Figure 1 shows the summertime (JJA) and wintertime (DJF) mean concentrations of aerosol components for 2003-2013 from surface monitoring stations in the Southeast US managed by the US Environmental Protection Agency (US EPA, 1999). Summertime sulfate concentrations decreased by 60% over the period while OA concentrations decreased by 40% (Hand et al., 2012b; Blanchard et al., 2013; Hidy et al., 2014). Trends in winter are much weaker. Decreasing aerosol has been linked to rapid warming in the Southeast US over the past two decades (Leibensperger et al., 2012ab).

The sulfate decrease is driven by the decline of sulfur dioxide (SO_2) emissions from coal combustion (Hand et al., 2012b), though the mechanisms responsible for oxidation of SO_2 to sulfate are not well quantified. Better understanding of the mechanisms is important because dry deposition competes with oxidation as a sink of SO_2, so that faster oxidation produces more sulfate (Chin and Jacob, 1996). Standard model mechanisms assume that SO_2 is oxidized to

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114   sulfate by the hydroxyl radical (OH) in the gas phase and by hydrogen peroxide (H_2O_2) and ozone

115   in clouds (aqueous phase). A model intercomparison by McKeen et al. (2007) for the Northeast

116   US revealed a general failure of models to reproduce observed sulfate concentrations, sometimes

117   by a factor of 2 or more. This could reflect errors in oxidation mechanisms, oxidant

118   concentrations, or frequency of cloud processing. Laboratory data suggest that stabilized Criegee

119   intermediates (SCIs) formed from alkene ozonolysis could be important SO_2 oxidants (Mauldin et

120   al., 2012; Welz et al., 2012), though their ability to produce sulfate may be limited by competing

121   reactions with water vapor (Chao et al., 2015; Millet et al., 2015).

122   The factors controlling OA are highly uncertain. OA originates from anthropogenic,

123   biogenic, and open fire sources (de Gouw and Jimenez, 2009). It is directly emitted as primary

124   OA (POA) and also produced in the atmosphere as secondary OA (SOA) from oxidation of

125   volatile organic compounds (VOCs). Current models cannot reproduce observed OA variability,

126   implying fundamental deficiencies in the model mechanisms (Heald et al., 2011; Spracklen et al.,

127   2011; Tsigaridis et al., 2014). A key uncertainty for air quality policy is the fraction of OA that

128   can be controlled (Carlton et al., 2010), as most of the carbon in SOA is thought to be biogenic in

129   origin. Gas/particle partitioning of organic material depends on the pre-existing aerosol

130   concentration (Pankow et al., 1994; Donahue et al., 2006), so that "biogenic" SOA may be

131   enhanced in the presence of anthropogenic POA and SOA (Weber et al., 2007). The SOA yield

132   from VOC oxidation also depends on the concentration of nitrogen oxide radicals ($NO_x \equiv NO +$

133   NO_2) (Kroll et al., 2005, 2006; A. Chan et al. 2010; Hoyle et al., 2011; Xu et al., 2014). NO_x in

134   the Southeast US is mostly from fossil fuel combustion and is in decline due to emission controls

135   (Russell et al., 2012), adding another complication in the relationship between OA concentrations

136   and anthropogenic sources. Oxidation of biogenic VOC by the NO_3 radical formed from

137   anthropogenic NO_x is also thought to be an important SOA source in the Southeast US (Pye et al.

138   2010). Reactions of organic molecules with sulfate to form organosulfates may also play a small

139   role (Surratt et al., 2007; Liao et al., 2015).

140   Long-term $PM_{2.5}$ records for the Southeast US are available from the EPA CSN,

141   IMPROVE, and SEARCH networks of surface sites (Malm et al., 1994; Edgerton et al., 2005;

142   Solomon et al., 2014). Satellite measurements of AOD from the MODIS and MISR instruments

143   have been operating continuously since 2000 (Diner et al., 2005; Remer et al., 2005; Levy et al.,

144   2013). Both surface and satellite observations show a strong aerosol seasonal cycle in the

145   Southeast US, with a maximum in summer and minimum in winter (Alston et al., 2012; Hand et

146   al., 2012a; Ford and Heald, 2013). Goldstein et al. (2009) observed that the amplitude of the

147   seasonal cycle of $PM_{2.5}$ measured at surface sites (maximum/minimum ratio of ~1.5; Hand et al.,

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148 2012a) is much smaller than the seasonal cycle of AOD measured from space (ratio of ~3-4;
149 Alston et al., 2012). They hypothesized that this could be due to a summertime source of biogenic
150 SOA aloft. Subsequent work by Ford and Heald (2013) supported that hypothesis on the basis of
151 spaceborne CALIOP lidar measurements of elevated light extinction above the planetary
152 boundary layer (PBL).

153   The NASA SEAC[4]RS aircraft campaign in August-September 2013 (Toon et al., 2015)
154 offers a powerful resource for better understanding the factors controlling aerosol concentrations
155 in the Southeast US and the relationship between surface PM and AOD measured from space.
156 The aircraft payload included measurements of aerosol composition, size distribution, and light
157 extinction along with a comprehensive suite of aerosol precursors and related chemical tracers.
158 Flights provided dense coverage of the Southeast US (Figure 2) including extensive PBL
159 mapping and vertical profiling. AERONET sun photometers deployed across the region provided
160 AOD measurements (Holben et al., 1998; http://aeronet.gsfc.nasa.gov/new_web/dragon.html).
161 Additional field campaigns focused on Southeast US air quality during the summer of 2013
162 included SENEX (aircraft) and NOMADSS (aircraft) based in Tennessee (Warneke et al., 2015;
163 http://www.eol.ucar.edu/field_projects/nomadss), DISCOVER-AQ (aircraft) based in Houston
164 (Crawford and Pickering, 2014), SOAS (surface) based in Alabama (http://soas2013.rutgers.edu),
165 and SLAQRS (surface) based in Greater St. Louis (Baasandorj et al., 2015). We use the GEOS-
166 Chem CTM with 0.25^{o} x 0.3125^{o} horizontal resolution as a platform to exploit this ensemble of
167 observational constraints by (1) determining the consistency between different measurements, (2)
168 interpreting the measurements in terms of their implications for the sources of sulfate and OA in
169 the Southeast US, (3) explaining the seasonal aerosol cycle in the satellite and surface data, and
170 (4) assessing the ability of CTMs to relate satellite measurements of AOD to surface PM.
171
172 **2. The GEOS-Chem CTM**
173
174   GEOS-Chem has been used extensively to simulate aerosol concentrations over the US
175 including comparisons to observations (Park et al., 2003, 2004, 2006; Drury et al., 2010; Heald et
176 al., 2011, 2012; Leibensperger et al., 2012a; Walker et al., 2012; L. Zhang et al., 2012; Ford and
177 Heald, 2013). Here we use GEOS-Chem version 9-02 (http://geos-chem.org) with detailed
178 oxidant-aerosol chemistry and the updates described below. Our SEAC[4]RS simulation for
179 August-October 2013 is driven by Goddard Earth Observing System – Forward Processing
180 (GEOS-FP) assimilated meteorological data from the NASA Global Modeling and Assimilation
181 Office (GMAO). The GEOS-FP meteorological data have a native horizontal resolution of 0.25°

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x 0.3125° (~25 x 25 km^2) with 72 vertical pressure levels and 3 h temporal frequency (1 h for surface variables and mixed layer depths). The mixed layer (ML) is defined in GEOS-FP as the unstable surface-based column diagnosed from the potential temperature gradient, with a vertical resolution of ~150 m. It is used in GEOS-Chem for surface-driven vertical mixing following Lin and McElroy (2010). The representation of clouds and their properties, such as liquid water content, are taken from the GEOS-FP assimilated meteorological fields. We use the native resolution in GEOS-Chem over North America and adjacent oceans [130° - 60° W, 9.75° - 60° N] to simulate the August 1 – October 31, 2013 period with a 5-minute transport time step. This is nested within a global simulation at 4° x 5° horizontal resolution to provide dynamic boundary conditions. The global simulation is initialized on June 1, 2012 with climatological model fields and spun up for 14 months, effectively removing the sensitivity to initial conditions.

GEOS-Chem simulates the mass concentrations of all major aerosol components including sulfate, nitrate, and ammonium (SNA; Park et al., 2006; L. Zhang et al., 2012), organic carbon (OC; Heald et al., 2006a, 2011; Fu et al., 2009), black carbon (BC; Q. Wang et al., 2014), dust in four size bins (Fairlie et al., 2007), and sea salt in two size bins (Jaegle et al., 2011). Aerosol chemistry is coupled to HO_x-NO_x-VOC-O_3-BrO_x tropospheric chemistry with recent updates to the isoprene oxidation mechanism as described by Mao et al. (2013). Gas/particle partitioning of SNA aerosol is computed with the ISORROPIA II thermodynamic module (Fontoukis and Nenes, 2007), as implemented in GEOS-Chem by Pye et al. (2009). Aerosol wet and dry deposition are described by H. Liu et al. (2001) and L. Zhang et al. (2001) respectively. OC is the carbon component of OA, and we infer simulated OA from OC by assuming OA/OC mass ratios for different OC sources as given by Canagaratna et al. (2015). Model results are presented below either as OC or OA depending on the measurement to which they are compared. Measurements from surface networks are as OC while the aircraft measurements are as OA.

Table 1 lists GEOS-Chem emissions in the continental United States (CONUS) for 2013. Values for the Southeast US in August-September are in parentheses. Emissions outside the CONUS are as in Kim et al. (2013) and are used in the global simulation to derive the boundary conditions for the nested grid. US anthropogenic emissions are from the EPA National Emissions Inventory for 2010 (NEI08v2). The NEI emissions are mapped over the 0.25° x 0.3125° GEOS-Chem grid and scaled to the year 2013 by the ratio of national annual totals (http://www.epa.gov/ttnchie1/trends/). For BC and SO_2 this implies 3% and 10% decreases from 2010 to 2013, but we prescribe instead a 30% decrease for both to better match observed BC concentrations and trends in sulfate wet deposition. Our SO_2 emission adjustment is more consistent with the latest version of the EPA inventory (NEI11v1), which indicates a 34% decline

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224 between 2010 and 2013, and with the observed trend in surface concentrations from the SEARCH
225 network, which indicates a ~50% decline in the Southeast US over the same years (Hidy et al.,
226 2014). The NEI08 NH_3 emissions are scaled to 2° x 2.5^o gridded monthly totals from the
227 MASAGE inventory, which provides a good simulation of ammonium wet deposition in the US
228 (Paulot et al., 2014).

229   Open fires have a pervasive influence on OA and BC over the US (Park et al., 2007).
230 During SEAC^{4}RS, the Southeast US was affected by both long-range transport of smoke from
231 wildfires in the West (Peterson et al., 2014; Saide et al., 2015) and local agricultural fires. We use
232 the Quick Fire Emissions Dataset (QFED2; Darmenov and da Silva, 2013), which provides daily
233 open fire emissions at 0.1^o x 0.1^o resolution. Diurnal scale factors, which vary by an order of
234 magnitude between midday and evening and peak at 10-19 local time, are applied to the QFED2
235 daily emissions following recommendations from the Western Regional Air Partnership (WRAP,
236 2005) as in Saide et al. (2015). Following previous results from Turquety et al. (2007) and
237 Fischer et al. (2014) for extratropical fires, we inject 35% of fire emissions above the boundary
238 layer between 680 and 450 hPa to account for plume buoyancy.

239   Biogenic VOC emissions are from the MEGAN2.1 inventory of Guenther et al. (2012)
240 implemented in GEOS-Chem as described by Hu et al. (2015). Isoprene emissions are decreased
241 by 15% to better match SEAC^{4}RS observations of isoprene and formaldehyde concentrations and
242 surface fluxes (Travis et al., 2015; Wolfe et al., 2015; Zhu et al., 2015). Figure 2 shows the
243 SEAC^{4}RS DC-8 flight tracks superimposed on the distribution of isoprene emissions. Total
244 emissions over the Southeast US (domain outlined in Figure 2) during the 2-month SEAC^{4}RS
245 period were 2.2 Tg C for isoprene and 0.5 Tg C for monoterpenes. Monoterpene emissions did
246 not exceed isoprene emission anywhere.

247   Sulfate was too low in our initial simulations of the SEAC^{4}RS observations. We
248 addressed this problem by including SCIs as additional SO_2 oxidants in the model as previously
249 implemented in GEOS-Chem by Pierce et al. (2013). This increased mean sulfate over the
250 Southeast US by 50% and improved simulation of the SO_2/sulfate ratio (Section 4). Oxidation of
251 isoprene and monoterpenes provides a large source of SCIs in the Southeast US in summer. Sipila
252 et al. (2014) estimated SCI molar yields from ozonolysis of 0.58 ± 0.26 from isoprene, $0.15 \pm$
253 0.07 from α–pinene, and 0.27 ± 0.12 from limonene. Sarwar et al. (2014) previously found that
254 simulation of sulfate with the CMAQ CTM compared better with summertime surface
255 observations in the Southeast US when SCI + SO_2 reactions were included in the chemical
256 mechanism. However, production of sulfate from SCI chemistry may be severely limited by
257 competition for SCIs between SO_2 and water vapor and depends on the respective reaction rate

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266   constants (Welz et al., 2012; J. Li et al., 2013; Newland et al., 2014; Sipila et al., 2014; Stone et
267   al., 2014). Here we use SCI chemistry from the Master Chemical Mechanism (MCMv3.2; Jenkins
268   et al., 1997; Saunders et al., 2003) with the SCI + SO_2 and SCI + H_2O rate constants from Stone
269   et al. (2014), using CH2OO as a proxy for all SCIs, such that the SCI + SO_2 pathway dominates.
270   This would not be the case using the standard SCI + H_2O and significantly slower (~1000x) SCI
271   + SO_2 rate constants in MCM (Millet et al., 2015) or if reaction with the water vapor dimer is
272   important (Chao et al., 2015). Given these crude approximations coupled with the uncertain SCI
273   kinetics, the simulated SCI contribution to SO_2 oxidation can be viewed as a proxy for missing
274   oxidant or insufficient cloud processing in GEOS-Chem.

275   A number of mechanisms of varying complexity have been proposed to model OA
276   chemistry (Donahue et al., 2006; Henze et al., 2006; Ervens et al., 2011; Spracklen et al., 2011;
277   Murphy et al., 2012; Barsanti et al., 2013; Hermansson et al., 2014). These mechanisms tend to
278   be computationally expensive and have little success in reproducing the observed variability of
279   OA concentrations (Tsigaridis et al., 2014). The standard semi-volatile partitioning treatment of
280   OA in GEOS-Chem v9.02 (Pye et al., 2010) underestimates SEAC[4]RS observations several-fold.
281   Here we use a simple linear approach to simulate five components of OA – anthropogenic POA
282   and SOA, open fire POA and SOA, and biogenic SOA. Anthropogenic and open fire POA
283   emissions are from the NEI08 and QFED2 inventories described above. For anthropogenic and
284   open fire SOA, we adopt the Hodzic and Jimenez (2011) empirical parameterization that assumes
285   irreversible condensation of the oxidation products of VOC precursor gases (AVOC and BBVOC
286   respectively). AVOCs and BBVOCs are emitted in proportion to CO, with an emission ratio of
287   0.069 g AVOC (g CO)$^{-1}$ (Hayes et al., 2014) and 0.013 g BBVOC (g CO)$^{-1}$ (Cubison et al., 2011).
288   They are both oxidized by OH in the model with a rate constant of 1.25×10^{-11} cm^3 molecule^{-1} s^{-1}
289   to generate SOA. This approach produces amounts of SOA and timescales of formation
290   consistent with field measurements at many locations (de Gouw and Jimenez, 2009; Hodzic and
291   Jimenez, 2010; Cubison et al., 2011; Jolleys et al., 2012; Hayes et al., 2014).

292   We assume biogenic SOA to be produced with a yield of 3% from isoprene and 5% from
293   monoterpenes, formed at the point of emission. Laboratory studies have shown that different
294   biogenic SOA formation mechanisms operate depending on the NO concentration, which
295   determines the fate of the organic peroxy radicals (RO_2) produced from VOC oxidation (Kroll et
296   al., 2005, 2006; A. Chan et al., 2010; Xu et al., 2014). In the high-NO pathway the RO_2 radicals
297   react with NO, while in the low-NO pathway they react with HO_2, other RO_2 radicals, or
298   isomerize. During SEAC[4]RS the two pathways were of comparable importance (Travis et al.,
299   2015). We use four separate tracers in the model to track SOA formed from isoprene and

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309 monoterpenes via the high- and low-NO pathways. This tracer separation is purely diagnostic as
310 the SOA yields are assumed here to be the same in both pathways. The SOA is apportioned to the
311 high- or low-NO tracer by the fraction of RO_2 reacting with NO at the point and time of emission.
312 A more mechanistic GEOS-Chem simulation of SOA in SEAC[4]RS including NO_x-dependent
313 yields and comparison to semi-volatile partitioning theory is reported by Marais et al. (2015).

314   GEOS-Chem computes the AOD for each aerosol component i by summing the optical
315 depths over all vertical model layers $L = [1,\ldots,n]$:

316

317 $$\text{AOD} = \sum_i \sum_{L=1}^{n} \alpha_i(L) M_i(L) \quad [1]$$

318

319 where $\alpha_i(L)$ and $M_i(L)$ are respectively the component mass extinction efficiency (m^2 g^{-1}) and
320 partial column mass (g m^{-2}) for level L. The α_i values are pre-calculated for selected wavelengths
321 using a standard Mie scattering algorithm. The algorithm assumes specified aerosol dry size
322 distributions and optical properties from the Global Aerosol Data Set (GADS; Koepke et al.,
323 1997), with updates by Drury et al. (2010) on the basis of summer observations from the ICARTT
324 aircraft campaign over the eastern US. The mass extinction efficiencies are then adjusted for
325 hygroscopic growth as a function of the local relative humidity (RH), following R. Martin et al.
326 (2003). The total AOD is reported here at 550 nm and is the sum of the contributions from all
327 aerosol components. Comparison of dry aerosol size distribution and hygroscopic growth show
328 good general agreement with observations similar to Drury et al. (2010) (Supplementary
329 Material).

330   Comparison of GEOS-FP ML heights with lidar and ceilometer data from SEAC[4]RS,
331 SOAS, and DISCOVER-AQ indicates a 30-50% positive bias across the Southeast US in daytime
332 (Scarino et al., 2014b; Millet et al., 2015). We decrease the daytime GEOS-FP ML heights by
333 40% in our simulation to correct for this bias. This increases simulated surface $PM_{2.5}$ by 15-25%.
334 During SEAC[4]RS, ML heights were measured by the NASA-Langley High Spectral Resolution
335 Lidar (HSRL; Hair et al., 2008, Scarino et al., 2014a) on the basis of aerosol gradients under
336 clear-sky conditions. After correction, the modeled ML height is typically within 10% of the
337 HSRL data along the SEAC[4]RS flight tracks, with a mean daytime value (± 1 standard deviation)
338 of 1690 ± 440 m in the HSRL data and 1530 ± 330 m in the model (Zhu et al., 2015). The
339 daytime ML was typically capped by a shallow cloud convective layer (CCL) extending up to
340 about 3 km, capped in turn by a subsidence inversion and the free troposphere above. When
341 giving column statistics we will refer to the ML as below 1.5 km and the CCL as between 1.5 and
342 3 km.

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345   Several companion papers apply the same GEOS-Chem model configuration as described
346   here to other analyses of the SEAC[4]RS data focused on gas-phase chemistry. These include
347   investigation of the factors controlling ozone in the Southeast US (Travis et al., 2015), isoprene
348   chemistry and the formation of organic nitrates (Fisher et al., 2015), validation of satellite HCHO
349   data as constraints on isoprene emissions (Zhu et al., 2015), and sensitivity of model
350   concentrations and processes to grid resolution (K. Yu et al., 2015). These studies include
351   extensive comparisons to the gas-phase observations in SEAC[4]RS. Our focus here will be on the
352   aerosol observations.
353
354   **3. Surface Aerosol Concentrations**
355
356   We begin by evaluating the simulation of $PM_{2.5}$ and its components against ground
357   observations. Total $PM_{2.5}$ is measured gravimetrically at 35% RH at a large number of EPA
358   monitoring sites (Figure 3). Filter-based measurements of $PM_{2.5}$ composition are taken every
359   three days at surface networks including the EPA CSN (25 sites in the study domain marked in
360   Figure 2, mostly in urban areas), IMPROVE (15 sites, mostly in rural areas), and SEARCH (5
361   sites, urban and suburban/rural). These three networks all provide 24-h average concentrations of
362   the major ions (SNA), carbon species (BC and OC), and dust, though there are differences in
363   protocols (Edgerton et al., 2005; Hidy et al., 2014; Solomon et al., 2014), in particular with
364   respect to OC artifact correction. The IMPROVE and SEARCH OC are both blank-corrected but
365   in different ways (Dillner et al., 2009; Chow et al., 2010), while CSN OC is uncorrected. We
366   apply a constant 0.3 $\mu g\ m^{-3}$ background correction to the CSN OC data as in Hand et al. (2012a).
367   The resulting CSN OC measurements are within 1% of SEARCH and 44% higher than
368   IMPROVE when averaged across the Southeast US. When necessary, OA is inferred from the OC
369   filter samples using an OA/OC mass ratio of 2.24 as measured in the boundary layer during
370   SEAC[4]RS by an aerosol mass spectrometer (AMS) onboard the DC-8 aircraft (Section 4). We do
371   not discuss sea-salt concentrations as they make a negligible contribution to $PM_{2.5}$ inland (< 0.1
372    $\mu g\ m^{-3}$ averaged across the EPA networks).
373   Figure 3 shows mean August-September 2013 $PM_{2.5}$ at the EPA sites and compares to
374   GEOS-Chem values. Concentrations peak over Arkansas, Louisiana, and Mississippi,
375   corresponding to the region of maximum isoprene emission in Figure 2. The spatial distribution
376   and composition of $PM_{2.5}$ is otherwise fairly homogeneous across the Southeast US, reflecting
377   coherent stagnation, mixing, and ventilation of the region (X. Zhang et al., 2012; Pfister et al.,
378   2015). Sulfate accounts on average for 25% of $PM_{2.5}$ while OA accounts for 55%. GEOS-Chem

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380 captures the broad features shown in the surface station PM$_{2.5}$ data with little bias (R = 0.65,
381 normalized mean bias or NMB = -1.4%). The model hotspot in southern Arkansas is due to OA
382 from a combination of biogenic emissions and agricultural fires. As discussed below, agricultural
383 fires make only a small contribution on a regional scale.

384   The spatial distributions of sulfate and OC concentrations are shown in Figure 4. The
385 observed and simulated sulfate maxima are shifted to the northeast relative to total PM$_{2.5}$ shown
386 in Figure 3. GEOS-Chem captures a larger fraction of the observed variability at rural sites (R =
387 0.78 for IMPROVE) than at urban/suburban sites (R = 0.71 for SEARCH, 0.62 for CSN) as
388 would be expected from the sub-grid scale of urban pollution. A scatterplot of the simulated daily
389 mean surface sulfate concentrations compared to the filter observations from all three networks in
390 August-September 2013 is shown in the Supplementary Material. The model bias (NMB) is +5%
391 relative to IMPROVE, +10% relative to SEARCH, and +9% relative to CSN. Over the Southeast
392 US domain defined in Figure 2, 42% of sulfate production is from in-cloud production by H$_2$O$_2$,
393 22% is from gas-phase oxidation by OH, and 36% is from gas-phase oxidation by SCIs. Previous
394 studies by Pierce et al. (2013) and Boy et al. (2013) found similarly large contributions of SCIs to
395 sulfate production over forested regions in summer. However, there is substantial uncertainty in
396 the SCI kinetics, as discussed above, and it is possible that other oxidants are responsible for the
397 missing sulfate (hence the "Other" label in Figure 4).

398   The observed OC distribution shows a decreasing gradient from southwest to northeast
399 that maps onto the distribution of isoprene emissions shown in Figure 2. The IMPROVE OC is
400 generally low compared to CSN and SEARCH, as has been noted previously (Ford and Heald,
401 2013; Attwood et al., 2014). GEOS-Chem reproduces the broad features of the observed OC
402 distribution with moderate skill in capturing the variability (R = 0.64 for IMPROVE, 0.62 for
403 SEARCH, 0.61 for CSN). Model OC is biased high with a NMB of +66% for IMPROVE, +29%
404 for SEARCH, and +14% for CSN. The range of NMBs for the different networks could reflect
405 differences in measurement protocols described above - IMPROVE OC is lower than SEARCH
406 by 27% for collocated measurements made at Birmingham, Alabama (Supplementary Material).
407 We discuss this further in the next section in the context of the aircraft data.

408   Source attribution of OC in the model (Figure 4) suggests a dominance of biogenic
409 sources. Isoprene alone contributes 42% of the regional OC burden. This is in contrast with
410 previous work by Barsanti et al. (2013), who fitted chamber observations to a model mechanism
411 and found monoterpenes to be as or more important than isoprene as a source of OC in the
412 Southeast US (particularly under low-NO conditions). SEAC[4]RS observations support a

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414 significant role of isoprene as a source of OA (W. Hu et al., 2015; Campuzano-Jost et al., 2015;
415 Liao et al., 2015).

416 Anthropogenic sources in the model contribute 28% to regional OC, roughly evenly
417 distributed across the region. Open fires contribute 11%, mainly from agricultural fires in
418 Arkansas and Missouri. Influence from western US fires is significant in the free troposphere (see
419 Section 4) but not at the surface.

420 When all of the components are taken together, we find that 81% of the surface OC in the
421 Southeast US is secondary in origin. This is well above the 30-69% range of previous literature
422 estimates for the region (Lim and Turpin, 2002; S. Yu et al., 2004; Kleindienst et al., 2007;
423 Blanchard et al., 2008) and likely reflects the decreasing trend in anthropogenic emissions (Figure
424 1) and possibly a low bias in some estimation methods (Docherty et al., 2008). Assuming fossil
425 fractions of 50% and 70% for anthropogenic primary and secondary OC respectively (Zotter et
426 al., 2014; Hayes et al. 2014), we estimate that 18% of the total OC burden is derived from fossil
427 fuel use. This is consistent with an 18% fossil fraction from radiocarbon measurements made on
428 filter samples collected in Alabama during SOAS (Edgerton et al., 2014).

429

430 **4. Aerosol Vertical Profile**

431

432 We now examine the aerosol vertical distribution measured by the NASA DC-8 aircraft
433 and simulated by GEOS-Chem along the flight tracks on 18 flights over the Southeast US (Figure
434 2). Aerosol mass composition was measured by a High-Resolution Aerodyne AMS for SNA and
435 OA (Canagaratna et al., 2007) and by the NOAA humidified dual single-particle soot photometer
436 for BC (HD-SP2; Schwarz et al., 2015). Dust concentrations were measured from filter samples
437 (Dibb et al., 2003), but the ML values are ~10× higher than measured by surface networks or
438 simulated in GEOS-Chem, as previously found by Drury et al. (2010) during ICARTT. Instead
439 we estimate dust concentrations from Particle Analysis by Laser Mass Spectrometer (PALMS)
440 measurements (Thomson et al., 2000; Murphy et al., 2006). The PALMS data provide the size-
441 resolved number fraction of dust-containing particles, which is multiplied by the measured
442 aerosol volume size distribution from the LAS instrument (Thornhill et al., 2008; Chen et al.,
443 2011) and an assumed density of 2.5 g cm^{-3}. The size distribution is truncated to PM$_{2.5}$ by
444 applying the transmission curve for the 2.5 μm aerosol impactor used by the ground networks.

445 Figure 5 shows the median sulfate, OA, and dust vertical profiles over the Southeast US.
446 Also shown are the median concentrations from the surface networks over the study domain
447 shown in Figure 2. The difference between the surface and aircraft data that can be attributed to

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454 differences in sampling (time and duration) is quantified by the difference in GEOS-Chem output
455 when the model is sampled with the surface data vs. when the model is sampled with the aircraft
456 data. For sulfate, the model underestimates the aircraft observations by 20% below 5 km but
457 overestimates the surface observations by 5-10% as discussed in Section 3. The general shape of
458 the vertical profile is well simulated (with a low bias from 3 to 4 km) and this applies also to SO_2
459 and to the SO_2/sulfate ratio (Supplementary Material). The sulfate concentrations are highest near
460 the surface and drop rapidly with altitude, but there is significant mass loading in the lower free
461 troposphere. 23% of the observed sulfate column mass lies in the free troposphere above 3 km
462 and this is well simulated by the model (23%). Analysis of SENEX and SEAC[4]RS vertical
463 profiles by Wagner et al. (2015) suggests that most of this free tropospheric sulfate is ventilated
464 from the PBL rather than being produced within the free troposphere from ventilated SO_2. GEOS-
465 Chem shows moderate skill in explaining the variability in the aircraft sulfate data (R = 0.81 for
466 all observations in the Southeast US, R = 0.68 below 3 km, R = 0.49 above 3 km).

467 Similarly to sulfate, OA measured from aircraft peaks at the surface and decreases rapidly
468 with height (Figure 5). The aircraft OA mass concentration below 1 km is 25-50% higher than
469 measured at the surface networks. IMPROVE is substantially lower than the other networks, as
470 has been noted above and in previous studies (Ford and Heald, 2013; Attwood et al., 2014), and
471 may be due to instrumental issues particular to that network. The discrepancy between the AMS
472 observations and CSN/SEARCH can largely be explained by differences in sampling, as shown
473 by the model. The GEOS-Chem simulation matches closely the aircraft observations. The vertical
474 distribution of OA is similar to that of sulfate, with 20% of the total column being above 3 km
475 both in the model and in the observations. The GEOS-Chem source attribution, also shown in
476 Figure 5, indicates that open fires contribute ~50% of OA in the free troposphere. This fire
477 influence is seen in the observations as occasional plumes of OA up to 6-7 km altitude (individual
478 gray dots in Figure 5). Fire plumes can be problematic for interpreting the AOD/PM relationship
479 for individual scenes but much less so in a temporal average as the mean influence on the column
480 is small. Simulating fire influence successfully in the model does require buoyant injection of
481 western US wildfire emissions in the free troposphere, as noted in previous studies (Turquety et
482 al., 2007; Fischer et al., 2014).

483 Comparison of GEOS-Chem to the individual OA observations along the aircraft flight
484 tracks shows good simulation of the variability (R = 0.82 for all observations, R = 0.74 below 3
485 km, R = 0.42 above 3 km). This is despite (or maybe because of) our use of a very simple
486 parameterization for the OA source. Further GEOS-Chem comparison to SEAC[4]RS and SOAS
487 observations is presented by Marais et al. (2015) using a more mechanistic analysis of SOA. The

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492 successful GEOS-Chem simulation of the OA vertical profile argues against a large CCL source
493 from aqueous-phase cloud processing. This is supported by the work of Wagner et al. (2015),
494 who found little OA enhancement in air masses processed by cumulus wet convection.

495   Dust made only a minor contribution to total aerosol mass in the Southeast US during
496 SEAC[4]RS, accounting for less than 10% of observed surface $PM_{2.5}$ (Figure 3). The PBL dust
497 concentrations measured by PALMS are roughly consistent with the surface data but the model is
498 much lower (Figure 5). This reflects a southward bias in the model transport of Saharan dust
499 (Fairlie et al., 2007), but is of little consequence for the simulation of $PM_{2.5}$ or the AOD/PM
500 relationship over the Southeast US. Figure 5 shows few free tropospheric plumes in the
501 SEAC[4]RS observations, consistent with the dust climatology compiled from CALIOP data by D.
502 Liu et al. (2008).

503   Figure 6 compiles the median observed and simulated vertical profiles of aerosol
504 concentrations and composition during SEAC[4]RS. OA and sulfate dominate at all altitudes.
505 Ammonium is associated with sulfate as discussed in the next Section. OA accounts for most of
506 $PM_{2.5}$ below 1 km, with a mass fraction F_{OA} = [OA]/[$PM_{2.5}$] of 0.62 g g^{-1} (0.65 in GEOS-Chem).
507 This is consistent with the surface SEARCH data (F_{OA} = 0.56 g g^{-1}). Figure 1 shows a lower F_{OA}
508 in the IMPROVE surface observations, increasing from 0.34 g g^{-1} in 2003 to 0.44 g g^{-1} in 2013,
509 reflecting instrumentation bias as discussed above. The aircraft data show that most of the aerosol
510 mass is OA at all altitudes. The aerosol column is mostly in the PBL (60% in the ML, ~25% in
511 the CCL), but ~15% is in the free troposphere with 10% above 5 km (Figure 6, right panel).
512 GEOS-Chem reproduces the observed shape of the vertical distribution of total aerosol mass, and
513 this is an important result for application of the model to derive the AOD/PM relationship.

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515 **5. Extent of Neutralization of Sulfate Aerosol**

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517   The extent of neutralization of sulfate aerosol by ammonia, computed from the fraction f
518 = [NH_4^+]/(2[SO_4^{2-}] + [NO_3^-]) where concentrations are molar, has important implications for the
519 aerosol phase and hygroscopicity, for the formation of aerosol nitrate (S. Martin et al., 2004; J.
520 Wang et al., 2008), and for the formation of SOA (Froyd et al., 2010; Eddingsaas, et al., 2012;
521 McNeill et al., 2012; Budisulistiorini et al., 2013; Liao et al., 2015). Figure 6 shows ammonium
522 to be the third most important aerosol component by mass in the Southeast US in summer after
523 OA and sulfate. Summertime particle-phase ammonium concentrations have declined at
524 approximately the same rate as sulfate from 2003 to 2013 (Figure 1 and Blanchard et al., 2013).
525 However, we find no significant trend over that time in ammonium wet deposition fluxes over the

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531 Southeast US (National Atmospheric Deposition Program, 2015), in contrast to a ~50% decline in
532 sulfate wet deposition. This implies that ammonia emissions have not decreased but the
533 partitioning into the aerosol has.

534 One would expect ammonium aerosol trends to follow those of sulfate if the aerosol is
535 fully neutralized ($f = 1$), so that partitioning of ammonia into the aerosol phase is limited by the
536 supply of sulfate. However, this is not the case in the observations. Figure 7 shows the extent of
537 neutralization in the observations and the model assuming that the SNA aerosol is externally
538 mixed from other ionic aerosol components such as dust. The model aerosol is fully neutralized
539 ($f = 1$) but the observed aerosol is not, with a median extent of neutralization of 0.55 mol mol^{-1} in
540 the CSN data and 0.68 mol mol^{-1} in the AMS data below 2 km. This is comparable to $f = 0.49$
541 mol mol^{-1} observed at the SOAS Centreville site earlier in the summer. The CSN data include full
542 ionic analysis and we examined whether internal mixing of SNA aerosol with other ions could
543 affect the extent of neutralization. The top right panel of Figure 7 shows that it does not,
544 reflecting the low concentrations of these other ions. The AMS reports total sulfate. While
545 organosulfates have a low pKa and would interact with ammonium as a single charged ion, they
546 were typically a small fraction of total sulfate (Liao et al., 2015).

547 A possible explanation is that ammonia uptake by aerosol with $f < 1$ may be inhibited by
548 organic particle material. This has been demonstrated in a laboratory study by Liggio et al.
549 (2011), who show that the time constant for ammonia to be taken up by sulfate aerosol with
550 incomplete extent of neutralization increases with the ratio of condensing organic gases to sulfate
551 and may be hours to days.

552 The complete extent of neutralization of sulfate aerosol in the model, in contrast to the
553 observations, leads to bias in the simulated aerosol phase and hygroscopicity for relating AOD to
554 PM. Calculations by J. Wang et al. (2008) for ammonium-sulfate particles of different
555 compositions show a 10-20% sensitivity of the mass extinction efficiency to the extent of
556 neutralization, with the effect changing sign depending on composition and RH. An additional
557 effect of $f = 1$ in the model would be to allow formation of ammonium nitrate aerosol, but nitrate
558 aerosol is negligibly small in the model as it is in the observations (Figure 6). At the high
559 temperatures over the Southeast US in the summer, we find in the model that the product of
560 HNO_3 and NH_3 partial pressures is generally below the equilibrium constant for formation of
561 nitrate aerosol. By contrast, surface network observations in winter show nitrate to be a large
562 component of surface $PM_{2.5}$ (Figure 1; Hand et al., 2012b; Ford and Heald, 2013), reflecting both
563 lower temperatures and the lower levels of sulfate.

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6. Aerosol Extinction and Optical Depth

We turn next to light extinction measurements onboard the DC-8 to better understand the relationship between the vertical profiles of aerosol mass (Section 4) and AOD. Aerosol extinction coefficients were measured on the SEAC[4]RS aircraft remotely above and below the aircraft by the NASA HSRL and at the altitude of the aircraft by the in situ NOAA cavity ringdown spectrometer (CRDS; Langridge et al., 2011). Figure 8 compares the two measurements, both at 532 nm, with GEOS-Chem. Though the two instruments sampled different regions of the atmosphere at any given time, the mission median profiles are similar. The exception is between 2 and 4 km where the HSRL extinction coefficient is lower. The shapes of the vertical extinction profiles are consistent with aerosol mass (Figure 6). The fraction of total column aerosol extinction below 3 km is 93% for the HSRL data (91% in GEOS-Chem when sampled at the observation times) and 85% for the CRDS data (85% in GEOS-Chem). Almost all of the column extinction is below 5 km (94% for the CRDS and 93% for GEOS-Chem). Integrated up to the ceiling of the DC-8 aircraft, the median AODs from HSRL and the CRDS are 0.14 and 0.17 respectively (0.12 and 0.15 for GEOS-Chem).

Figure 9 shows maps of the mean AOD over the Southeast US in August-September 2013 as measured by AERONET, MISR, MODIS on the Aqua satellite, and simulated by GEOS-Chem. The model is sampled at the local satellite overpass times (1030 for MISR and 1330 for MODIS). We use the Version 31 Level 3 product from MISR (gridded averages at 0.5° x 0.5° resolution) and the Collection 6 Level 3 product from MODIS (gridded averages at 1° x 1° resolution). We exclude MODIS observations with cloud fraction greater than 0.5 or AOD greater than 1.5 to account for cloud contamination and sensor saturation as in Ford and Heald (2013). We use the Level 2 cloud-filtered daytime average AERONET observations, which can be viewed as a reference measurement.

Comparison of daily collocated MODIS and MISR retrievals with AERONET observations shows high correlation and little bias (statistics inset in Figure 9). These statistics were calculated only when there are collocated and corresponding data for both AERONET and the satellite retrieval, whereas Figure 9 shows the spatial average of all available data during August-September 2013. MODIS shows a broad maximum over the Southeast US that corresponds well with observed $PM_{2.5}$ in Figure 3. There is greater heterogeneity in the MISR average due to sparse sampling. GEOS-Chem captures the spatial pattern of the regional AOD enhancement when sampled with the different retrievals and underestimates the magnitude by 16% (NMB relative to AERONET), consistent with the underestimate of the aircraft aerosol

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extinction data (including the NASA Ames 4STAR sun photometer, Supplementary Material). The model underestimates AOD (NMB) by 28% relative to MODIS and by 8% relative to MISR.

7. The Aerosol Seasonal Cycle

As pointed out in the introduction, there has been considerable interest in interpreting the aerosol seasonal cycle over the Southeast US and the difference in seasonal amplitude between AOD and surface $PM_{2.5}$ (Goldstein et al. 2009, Ford and Heald, 2013). Figure 10 shows MODIS monthly average AOD over the Southeast US for 2006-2013. The observed AOD in 2013 shows a seasonal cycle consistent with previous years. There has been a general decline in the seasonal amplitude over 2006-2013 driven by a negative summertime trend, with 2011 being anomalous due to high fire activity. The same long-term decrease and 2011 anomaly are seen in the surface $PM_{2.5}$ data (Figure 1). Examination of Figure 10 reveals that the entirety of the seasonal decrease from summer to winter takes place as a sharp transition in the August-October window, in all years.

We analyzed the causes of this August-October transition using the GEOS-Chem simulation of the SEAC[4]RS period. Figure 11 (panel A) shows the time series of daily median AOD from AERONET, GEOS-Chem sampled at the times and locations of the AERONET observations, and MODIS over the Southeast US. The difference between AERONET and MODIS can be explained by differences in sampling (they otherwise correspond well with each other, see Section 6). Observations through early September show large oscillations with a 7-10 day period driven by frontal passages. These are well reproduced by the model. The observed AODs then fall sharply in mid-September and again this is well reproduced by GEOS-Chem. The successful simulation of the August-October seasonal transition implies that we can use the model to understand the causes of this transition. Figure 11 also shows the sulfate and OA contributions to GEOS-Chem AOD. Sulfate aerosol contributes as much to column light extinction as OA, despite lower concentrations, due to its higher mass extinction efficiency. Both the sulfate and OA contributions to AOD fall during the seasonal transition.

We find that the sharp drops in sulfate and OA concentrations over August-October are due to two factors. The first is a decline in isoprene and monoterpene emissions due to cooler surface temperatures and leaf senescence (panel B of Figure 11). The second is a transition in the photochemical regime as UV radiation sharply declines (Kleinman, 1991; Jacob et al., 1995), depleting OH and H_2O_2 (panel C) and hence sulfate formation.

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657   The seasonal transition in photochemical regime also involves a shift from a low-NO to a
658 high-NO chemical regime (Kleinman, 1991; Jacob et al., 1995). This would affect the SOA yield
659 (Marais et al., 2015), though this is not represented in the current GEOS-Chem simulation. Panel
660 D of Figure 11 shows the ratio of isoprene hydroperoxides (ISOPOOH) to isoprene nitrate
661 (ISOPN) concentrations measured in the PBL during SEAC[4]RS by the Caltech CIMS (Crounse et
662 al., 2006; St. Clair et al., 2010) and simulated by GEOS-Chem. ISOPOOH is formed under low-
663 NO conditions, while ISOPN is formed under high-NO conditions. Both observations and the
664 model show a decline in the ISOPOOH/ISOPN concentration ratio over the course of SEAC[4]RS,
665 with the model showing extended decline into October. If the SOA yield is higher under low-NO
666 conditions (Kroll et al., 2005, 2006; Xu et al. 2014) then this would also contribute to the
667 seasonal decline in OA.

668   We have thus explained the seasonality of AOD as driven by aerosol sources. Previous
669 studies have pointed out that surface $PM_{2.5}$ in the Southeast US has much weaker seasonality than
670 AOD, and observed $PM_{2.5}$ in 2013 had no significant seasonality (Figure 12, top panel). This
671 difference in the amplitude of the seasonal cycle between $PM_{2.5}$ and AOD is also simulated by
672 GEOS-Chem, as shown in Figure 12. It is driven in GEOS-Chem by the seasonal variation in ML
673 height (middle panel of Figure 12), dampening the seasonal cycle of $PM_{2.5}$ by reducing
674 ventilation in winter. The AOD in GEOS-Chem is lower than observed in summer and higher in
675 winter, so that the seasonality is weaker than observed (a factor of 2 compared to an observed
676 factor of 3-4). The summer underestimate is consistent with the aircraft observations, as discussed
677 previously. The winter overestimate could reflect seasonal error in model aerosol sources or
678 optical properties.

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680 **8. Conclusions**

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682   We have used a large ensemble of surface, aircraft, and satellite observations during the
683 SEAC[4]RS field campaign over the Southeast US in August-September 2013 to better understand
684 (1) the sources of sulfate and organic aerosol (OA) in the region; (2) the relationship between the
685 aerosol optical depth (AOD) measured from space and the fine particulate matter concentration
686 ($PM_{2.5}$) measured at the surface; and (3) the seasonal aerosol cycle and the apparent inconsistency
687 between satellite and surface measurements. Our work used the GEOS-Chem global chemical
688 transport model (CTM) with 0.25^{o} x 0.3125^{o} (~25 x 25 km^{2}) horizontal resolution over North
689 America as an integrative platform to compare and interpret the ensemble of observations.

690        $PM_{2.5}$ surface observations are fairly homogenous across the Southeast US, reflecting

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697 regional coherence in stagnation, mixing, and ventilation. Sulfate and OA account for the bulk of

698 PM$_{2.5}$. GEOS-Chem simulates sulfate without bias but this requires uncertain consideration of

699 SO$_2$ oxidation by stabilized Criegee intermediates to account for 30% of sulfate production. The

700 OA simulation bias is +14% relative to CSN sites and +66% relative to IMPROVE sites but the

701 IMPROVE data may be too low. OA in the model originates from biogenic isoprene (40%) and

702 monoterpenes (20%), anthropogenic sources (30%) and open fires (10%).

703 Aircraft vertical profiles show that 60% of the aerosol column mass is in the mixed layer

704 (ML), 25% is in the convective cloud layer (CCL), and 15% is in the free troposphere (FT). This

705 is well reproduced in GEOS-Chem. OA accounts for 65% of the aerosol column mass in the

706 observations and in the model. The successful simulation of OA vertical profiles argues against a

707 large OA source in the free troposphere other than PBL ventilation. Occasional fire and dust

708 plumes were observed in the free troposphere but have little impact on temporal averages.

709 The extent of neutralization of sulfate aerosol over the Southeast US ($f = [NH_4^+]/(2[SO_4^{2-}]$

710 $+ [NO_3^-])$) is observed to be in the range 0.49-0.68 mol mol^{-1} for the different data sets, despite an

711 excess of ammonia being present. This is inconsistent with thermodynamic equilibrium and with

712 the observation of a 2003-2013 decline in ammonium aerosol concentrations paralleling that of

713 sulfate. We hypothesize that the departure from equilibrium is correlated with OA, as supported

714 by laboratory findings by Liggio et al. (2011) that organic particle material may impede ammonia

715 uptake by sulfate aerosol. This may have important implications for aerosol hygroscopicity and

716 chemistry.

717 The vertical profile of aerosol light extinction measured from the aircraft follows closely

718 that of aerosol mass. GEOS-Chem has a ~16% low bias in aerosol extinction compared to these

719 observations and simulates correctly the vertical profile. Sulfate accounts for as much of the

720 column light extinction as OA, despite lower mass concentrations. Evaluation of collocated

721 MODIS and MISR AOD retrievals with AERONET shows excellent agreement. GEOS-Chem is

722 16% too low compared to AERONET and 7-28% too low compared to MODIS and MISR,

723 consistent with its bias relative to the aircraft extinction data. We thus find reasonable agreement

724 between AODs measured from space and from the surface, aircraft aerosol extinction and mass

725 profiles, and surface PM$_{2.5}$ measurements, the largest discrepancy being between different

726 measurements of OA.

727 We find that the previously reported summer-to-winter decrease in MODIS AOD data

728 over the Southeast US is driven by a sharp August-to-October transition, in all years. This

729 seasonal transition is well captured by GEOS-Chem where it is caused by declines in both sulfate

730 and OA. Biogenic emissions of isoprene and monoterpenes shut down during this time period due

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740 to lower temperatures and leaf senescence, and rapidly declining UV radiation suppresses SO_2
741 oxidation by OH and H_2O_2. The seasonal decline of UV radiation also suppresses the low-NO
742 pathway of isoprene oxidation, which may be associated with larger OA yields than the high-NO
743 pathway.

744   Previous studies have pointed out an apparent inconsistency between the large seasonal
745 variation of AOD measured from space and the much weaker seasonal variation of $PM_{2.5}$
746 measured at the surface (Goldstein et al., 2009; Ford and Heald, 2013). We find that this can be
747 largely explained by the seasonal trend in boundary layer ventilation, offsetting the effect of
748 decreased wintertime PM sources on the surface concentrations. Overall our results show that
749 measured AODs from space are consistent with measurements of $PM_{2.5}$ air quality in the
750 Southeast US. This implies that satellite measurements can reliably be used to infer $PM_{2.5}$ if a
751 good CTM representation of PBL mixing and ventilation is available.
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1450 **Tables**

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1452 Table 1: Contiguous US (CONUS) Emissions for 2013[a]

Source	NO_x [Tg N]	CO [Tg]	SO_2 [Tg S]	NH_3 [Tg]	BC [Tg]	OC [Tg]	Isoprene[b] [Tg C]	Monoterpenes[b] [Tg C]
Anthropogenic[c]	2.7 (0.07)	29.8 (0.65)	2.8 (0.14)	3.5[d] (0.11)	0.26 (0.008)	0.58 (0.01)	-	-
Open Fires[e]	0.14 (0.004)	7.9 (0.21)	0.13 (0.002)	0.44 (0.008)	0.19 (0.003)	0.93 (0.01)	-	-
Soil[f]	0.69 (0.03)	-	-	-	-	-	-	-
Vegetation	-	-	-	0.17 (0.002)	-	-	12.2 (2.2)	4.1 (0.5)
Total	3.5 (0.11)	37.7 (0.85)	2.9 (0.14)	4.1 (0.12)	0.45 (0.01)	1.5 (0.02)	12.2 (2.2)	4.1 (0.5)

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1454 [a]Annual totals. Emissions in the Southeast US for the two-month SEAC[4]RS period (August-
1455 September) are shown in parentheses. The Southeast US domain is as defined in Figure 2.
1456 [b]Biogenic VOC emissions are from the MEGAN2.1 inventory (Guenther et al., 2012) with
1457 isoprene emissions decreased by 15% (see text).
1458 [c]Anthropogenic emissions are from the EPA National Emissions Inventory (NEI08v2) scaled
1459 nationally to 2013 and with additional adjustments described in the text.
1460 [d]Agricultural ammonia emissions are from the MASAGE inventory on a 2° x 2.5^o grid (Paulot et
1461 al., 2014), and are distributed on the 0.25^o x 0.3125^o grid following NEI08v2 as described in the
1462 text.
1463 [e]Open fire emissions are from the Quick Fire Emissions Dataset (Darmenov and da Silva, 2013),
1464 with adjustments described in the text.
1465 [f]Soil and fertilizer NO_x emissions are from the BDSNP algorithm (Hudman et al., 2012).
1466 Fertilizer emissions are included in the anthropogenic total.

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Figure Captions

Figure 1: Summertime and wintertime trends in mean surface $PM_{2.5}$ in the Southeast US for 2003-2013. Seasonal averages for each component are calculated by combining data from the EPA CSN and IMPROVE networks over the Southeast US domain defined in Figure 2. Ammonium is only measured by CSN. Organic aerosol (OA) and black carbon (BC) are only from IMPROVE because of change in the CSN measurement protocol over the 2003-2013 period and differences in the OA measurements between the two networks (see text for details). OA is inferred here from measured organic carbon (OC) using an OA/OC mass ratio of 2.24 as measured by the Aerodyne Aerosol Mass Spectrometer (AMS) in the boundary layer over the Southeast US. Note the different scales in different panels (sulfate and OA contribute most of $PM_{2.5}$). Trends are calculated using the Theil-Sen estimator (Theil, 1950) and are shown only if significant at the $\alpha =$ 0.05 level. Only the sulfate trend is significant in winter.

Figure 2: Flight tracks of the DC-8 aircraft during SEAC[4]RS superimposed on mean MEGAN2.1 isoprene emissions for August-September 2013. The thick black line delineates the Southeast US domain as defined in this paper [95° W – 81.5° W, 30.5° N – 39° N].

Figure 3: Mean $PM_{2.5}$ in the Southeast US in August-September 2013. EPA observations (circles) are compared to GEOS-Chem model values (background). Model values are calculated at 35% relative humidity as per the Federal Reference Method protocol. Observed mean $PM_{2.5}$ speciation by mass is shown in the pie charts for representative CSN sites. Organic aerosol (OA) mass concentrations are derived from measurements of organic carbon (OC) by assuming an OA/OC mass ratio of 2.24.

Figure 4: Mean sulfate (top) and OC (bottom) surface air concentrations in the Southeast US in August-September 2013. Network observations from CSN (circles), IMPROVE (squares), and SEARCH (triangles) are compared to GEOS-Chem model values (background). OC measurements are artifact-corrected as described in the text. Source attribution for sulfate and OC is shown at right as averages for the Southeast US domain defined in Figure 2. For sulfate, source attribution is by SO_2 oxidant. For OC, source attribution is primary or secondary, by source type, and by NO regime.

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1507   Figure 5: Median vertical profiles of aerosol concentrations over the Southeast US (Figure 2)
1508   during the SEAC⁴RS aircraft campaign (August-September 2013). Observed and simulated
1509   profiles of sulfate (left), OA (center), and dust (right) in 1-km bins are shown with the
1510   corresponding median surface network observations. OC from the surface networks is converted
1511   to OA using an OA/OC ratio of 2.24. The contributions of anthropogenic SOA, biogenic SOA,
1512   and open fire POA to total simulated OA are also shown. The individual observations are shown
1513   in gray and the horizontal bars denote the 25th and 75th percentiles of the observations.
1514   Concentrations are in μg m^{-3} converted to STP conditions for the aircraft data and under local
1515   conditions for the surface data. The choice of scale truncates some very large individual
1516   observations.

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1518   Figure 6: Median vertical profiles of aerosol composition over the Southeast US during
1519   SEAC⁴RS (August-September 2013). Observations from the DC-8 aircraft (left) are compared to
1520   GEOS-Chem values sampled at the aircraft times and locations (center). Also shown is the
1521   observed and simulated fraction of the total aerosol mass column below a given height (right).
1522   The Southeast US domain is as defined in Figure 2.

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1524   Figure 7: Extent of neutralization of sulfate aerosol in the Southeast US (August-September
1525   2013). The extent of neutralization for an external sulfate-nitrate-ammonium (SNA) mixture is
1526   given by the $f = [NH_4^+]/(2[SO_4^{2-}] + [NO_3^-])$ molar ratio, and this can be adjusted for an internal
1527   mixture by considering additional ions. The top panels show observations from the CSN network
1528   assuming an external (left) or internal (right) mixture; there is little difference between the two
1529   because the concentrations of additional ions are usually small. The bottom panels show the
1530   SEAC⁴RS aircraft observations below 2 km and corresponding GEOS-Chem values. Also shown
1531   are the lines corresponding to different extents of neutralization ($f = 0.5$ for ammonium bisulfate
1532   and $f = 1$ for ammonium sulfate).

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1534   Figure 8: Median vertical profiles of aerosol extinction coefficients (532 nm) over the Southeast
1535   US during SEAC⁴RS. The left panel shows independent observations from the NASA HSRL and
1536   NOAA CRDS instruments, with GEOS-Chem sampled at the times and locations of the available
1537   instrument data. The individual CRDS observations are shown in gray and the horizontal bars
1538   denote the 25th and 75th percentiles of the CRDS observations for each 1-km bin. The choice of
1539   scale truncates some very large individual observations. The right panel shows the observed

(CRDS) and simulated fraction of the total AOD below a given height. The Southeast US domain is as defined in Figure 2.

Figure 9: Mean aerosol optical depths (AODs) over the Southeast US during SEAC[4]RS (August-September 2013). AERONET data are shown as circles and are the same in all panels. The top panels show MODIS and MISR satellite observations with comparison statistics to AERONET (correlation coefficients, numerical mean biases or NMBs of collocated observations in time and space). The bottom panels show GEOS-Chem model values sampled at the same locations and times as the satellite retrievals. The noise in the MISR panels reflects infrequent sampling (9-day return time, compared to 1-day for MODIS). The negative NMB for the MODIS data reflects occasional retrievals of negative AOD.

Figure 10: Seasonal variation of MODIS AOD over the Southeast US for 2006-2013. The Southeast US domain is as defined in Figure 2.

Figure 11: Seasonal transition of aerosol optical depth (AOD) and related variables over the Southeast US in August-October 2013. (A) AODs measured by MODIS and AERONET, and GEOS-Chem values sampled at AERONET times and locations with simulated contributions from sulfate and OA. (B) 24-h average MEGAN2.1 isoprene emissions and GEOS-FP surface air temperatures. (C) H_2O_2 concentrations measured from the aircraft below 1 km altitude and simulated by GEOS-Chem sampled at the times and locations of the observations. Each data point represents the median value over the Southeast US for an individual flight. GEOS-Chem H_2O_2 concentrations averaged over the entire region (i.e. without sampling along the flight tracks) are shown separately and extend into October. (D) Same as (C) but for the molar ratio of isoprene peroxides (ISOPOOH) to isoprene nitrates (ISOPN). The Southeast US domain is as defined in Figure 2.

Figure 12: Seasonal aerosol cycle in the Southeast US in 2013. (Top) Daily mean EPA and GEOS-Chem $PM_{2.5}$. (Middle) Daily maximum mixed layer height from GEOS-FP with 40% downward correction applied year-round as in GEOS-Chem (see Section 2). (Bottom) Daily mean AOD from MODIS and GEOS-Chem. GEOS-Chem results in this figure are from the coarse-resolution (4° x 5°) global simulation for 2013. Smoothed curves are calculated using a low-pass filter. All values are averaged over the Southeast US as defined in Figure 2.

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