

We thank both reviewers for their constructive comments and suggestions. We have made changes in the revised manuscript accordingly. Specific responses to each of the comments are provided below (reviews' comments in blue and authors' responses in black).

Anonymous Referee #1

Summary: This study reports the concentration of water-soluble organic carbon (WSOC) and sulfate in 900 24-hr PM_{2.5} samples from 15 sites in the SE USA. The main conclusion is that these secondary aerosols are spatially homogeneous throughout the year, once samples with [levoglucosan] > 50 ng/m³ were removed. While these results are not surprising and represent only an incremental increase in our knowledge of secondary aerosols in the SE USA, the extensive size of the data set supports the main conclusion to a greater extent than a single field campaign could. The presentation is excellent and the topic is of interest to ACP readers. I recommend publication after the following comments are addressed.

Major points: P9623, L10-11: "suggesting the temperature effects were mainly on the photochemical processes" - Are you saying that faster photochemistry is more important than synoptic meteorology in causing the correlation between temperature and SOA? If so, I think this statement needs to be supported. I also think it is likely that the relationship between temperature and SOA is driven by temperature dependence of BVOC emissions as well as photochemistry, and no clear evidence has been presented to separate those two effects.

We agree with the reviewer that this statement may lead to some confusion and have tried to clarify our arguments. We do think temperature effects on observed WSOC concentrations was mainly a result of faster photochemistry and/or temperature changes related to changes in synoptic meteorology and had less to do with enhancements on biogenic VOC emissions possibly leading to higher SOA formation. Guenther et al. (1995) have shown an exponential dependence of biogenic hydrocarbon emissions on temperature, and an earlier study (Goldstein et al., 2009) interpreted an exponential relation between aerosol optical thickness and Temp. as proof of the influence of

biogenic emissions. However, what we found from our data set is that both WSOC and sulfate are exponentially correlated with temperature, although the correlation between WSOC and T ($r^2=0.54$) was slightly better than sulfate and T ($r^2=0.33$). Since sulfate formation is not linked to biogenic emissions, our conclusion was that the pronounced seasonality of WSOC (SOA) per se does not necessarily suggest a biogenic SOA origin.

To make our point clearer, the text has been modified in the revised manuscript and it now reads: “*Sulfate and WSOC both tracked ambient temperature throughout the year, suggesting the temperature effects were mainly linked to faster photochemistry and/or synoptic meteorology and less due to enhanced biogenic hydrocarbon emissions.*”

Goldstein, A. H., Koven, C. D., Heald, C. L. and Fung, I. Y.: Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States, P. Natl. Acad. Sci., 106, 8835-8840, doi:10.1073/PNAS.0904128106, 2009.

Guenther A, et al., A global model of natural volatile organic compound emissions. J. Geophys. Res., 100:8873–8892, 1995.

Minor points: P9627, L6-8: You mention that the CSN filters were not adjusted for sampling artifacts, but what about the FRM filters? As written, the implication is that the FRM filters were adjusted.

Measurement of ambient particulate organic carbon (OC) with quartz filters (i.e. the type of filters used at CSN sites) is prone to both positive and negative sampling artifacts. The sampling artifacts mentioned in the corresponding sentence were referring specifically to the positive sampling artifacts (i.e. absorption of volatile organic gases onto the quartz filter media) since no inline denuder was used in this sampling method. Without adjusting for these possible artifacts, the measured OC is likely to represent an upper estimate of the ambient OC. On the other hand, the FRM filters, due to the nature of Teflon filters, have minimum positive sampling artifacts. However, the FRM filters suffered from negative sampling artifacts that were explained in details in P9628, L3-13.

To clarify, the text (P9627, L6-8) has been changed to “*The OC measurements (TOT NIOSH method) obtained from the subset of EPA CSN sites were not adjusted for*

possible positive sampling artifacts and thus represented an upper estimate of ambient OC.”

P9628, L17: What was the time resolution of the PILS samples? Also, was a PM_{2.5} impactor used? How about a denuder?

The time resolution of the PILS samples was 10 min. A PM_{2.5} cyclone and a parallel plate carbon denuder were used. The following information about the PILS sampling has been added under Sect. 2.2 in the revised manuscript: *“The ambient fine particles were concentrated into a continuous liquid flow via a PILS with an upstream URG PM_{2.5} cyclone and a parallel plate carbon denuder (Eatough et al., 1993). Three background WSOC measurements were performed daily (at 3:00, 10:00 and 19:00 EST) throughout the study period by diverting the sampling flow through a Teflon filter (47 mm dia., 2.0 μm pore size, Pall Life Sciences). Ambient WSOC data were blank-corrected and reported at 10-min resolution. The limit of detection (LOD) for WSOC was approximately 0.1 μg C m⁻³ and the overall measurement uncertainty ~10%.”*

Section 3.2.1 - could be condensed to one paragraph (as written, both paragraphs have the same conclusion)

The two paragraphs in Sect 3.2.1 have been combined into one in the revised manuscript.

P9637, L1-3: What about other biogenic compounds (besides isoprene)? This comment applies to the manuscript in general - is the qualitative relationship shown for isoprene not seen, e.g., for monoterpenes? Do the authors believe that isoprene is the dominant WSOC SOA precursor throughout the region?

We believe that isoprene is the most important biogenic SOA precursor in the southeast. The contribution of monoterpenes to SOA (WSOC) formation compared to that from isoprene is minor. For example, Ding et al. (2008) found significant correlation between WSOC and isoprene oxidation products 2-methyltetrols ($r^2=0.68-0.88$) and no correlation between WSOC and pinene derived *cis*-pinonic acid at three inland SE sites during

summer of 2004, suggesting isoprene plays an important role in SOA formation in the southeast. Chan et al. (2010) and Lin et al. (2012) both found that isoprene-derived epoxydiols (IEPOX) contributed significantly to the observed organic carbon mass (~3% to 8%) from filter samples collected at JST and YRK sites. Monoterpenes could potentially be important biogenic SOA precursors during colder months when isoprene emissions are minimal, but it is not the focus of this manuscript.

Chan, M. N., Surratt, J. D., Claeys, M., Edgerton, E. S., Tanner, R. L., Shaw, S. L., Zheng, M., Knipping, E. M., Eddingsaas, N. C., Wennberg, P. O., and Seinfeld, J. H.: Characterization and quantification of isoprene-derived epoxydiols in ambient aerosol in the southeastern United States, *Environ. Sci. Technol.*, 44(12), 4590-4596, 2010.

Ding, X., Zheng, M., Yu, L. P., Zhang, X. L., Weber, R. J., Yan, B., Russell, A. G., Edgerton, E. S., and Wang, X. M.: Spatial and seasonal trends in biogenic secondary organic aerosol tracers and water-soluble organic carbon in the southeastern United States, *Environ. Sci. Technol.*, 42(14), 5171-5176, 2008.

Lin, Y.-H., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S. L., Knipping, E. M., Edgerton, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.: Isoprene epoxydiols as precursors to secondary organic aerosol formation: Acidcatalyzed reactive uptake studies with authentic compounds, *Environ. Sci. Technol.*, 46, 250-258, 2012.

P9639, L1-3: Could there be a possible artifact associated with the PILS? For example could there be gas-phase WSOC that is absorbed into droplets or other liquid water in the instrument?

We do not think the sampling artifact, especially the positive artifact mentioned by the reviewer, associated with the online PILS system is significant for two reasons. First, the possible positive artifacts of the PILS sampling due to absorption of organic gases were reduced by placing a parallel plate carbon denuder upstream of the PILS. Second, three background WSOC measurements were performed daily and any absorption of WSOC gases should be included in the blank measurement (i.e. the assumption is that SVOCs would pass through the blank Teflon filter). The reported PM_{2.5} WSOC data were blank-corrected by interpolation between these measurements and therefore the positive artifacts have been further reduced.

P9639, L7-17: This paragraph is a nice summary of previous work, but seems out of place in the results section of this manuscript. I would recommend omitting, or transferring to the introduction.

We feel this paragraph is well suited in the result section as it not only serves as a brief summary of the major findings by Zhang et al. (2011), but also provides important insights based on results from both Zhang et al. (2011) and the present study. Specifically, we observed that Atlanta urban WSOC was on average 31% higher than rural WSOC. It is curious whether this urban excess WSOC was contributed directly from the anthropogenic sources or through anthropogenic-biogenic interactions. Zhang et al. found that light-absorbing WSOC (i.e. brown carbon) is mainly from anthropogenic sources and therefore can be used as a rough measure of anthropogenic SOA. By comparing Atlanta WSOC light absorption with that in LA, it is concluded that about 1/4 of the observed Atlanta urban excess WSOC is from direct contribution of anthropogenic sources. Overall, we feel the findings by Zhang et al. (2011) are very consistent with the present study, and should be discussed here.

P9639, L19-21: Please give some details on the chemical composition used in the PMF analysis - if there are too many to list, at least mention the number of inorganic compounds and the type of organic analyses (OC, EC, WSOC, specific compounds, etc.).

Nine PM_{2.5} chemical species (WSOC, Na⁺, NH₄⁺, K⁺, Mg²⁺, SO₄²⁻, oxalate, xylose, and levoglucosan) and the light absorption data (b_{ap365}) were used in the PMF analysis. This information has been added in the revised manuscript.

Section 3.4 - was PMF factor 3 correlated to RH? This could be additional evidence that it arises from aqueous processing.

The reviewer has a valid point. Unfortunately, RH data are not available for this data set so no correlation can be made between RH and Factor 3 relative contribution. Even though RH data are available, it is doubtful if any meaningful correlation can be obtained between the highly averaged (daily) RH and PMF Factor 3, since RH changes drastically

within a daily cycle and the particle water content that is important for liquid-phase reactions is very sensitive to RH changes.

P9642, L2 - The use of the word “non-volatile” to describe the WSOC is confusing – it implies that the samples were subjected to heating and/or dilution. Please clarify.

The term “non-volatile WSOC” was used to refer to those water-soluble organic compounds that did not evaporate from the Teflon filter media during sampling and storage. To avoid confusion, “non-volatile WSOC” has been changed to “WSOC from the FRM filter samples” in the revised manuscript.

Figure 3 is unnecessary - and in a sense confusing because it is the spatial correlation (not the correlation to PM2.5) that I think is the most important contribution of this manuscript. I would omit, and shorten the discussion in the text.

We think Figure 3 is needed in the manuscript because it makes two important points. First, the large slopes of WSOC and sulfate vs. PM2.5 mass suggest that WSOC and sulfate are two major components of PM2.5 over the SE region, which has important implication on PM2.5 control strategy. Second, the tight correlation between WSOC (sulfate) and PM2.5 implies that the fractions of WSOC (sulfate) in the total PM2.5 at different urban and rural sites are very similar, which supports the main conclusion of this manuscript that WSOC (sulfate) is spatially uniform throughout the SE region.

I also find Figure 9 unnecessary - perhaps it could go in the SI, but it seems too minor a point to include in the main portion of the manuscript.

We agree with the reviewer that Figure 9 makes a minor point that is also shown in Figure 8 and 10. We have removed this figure and the related discussion in the revised manuscript.

Anonymous Referee #2

Summary and Overall Recommendation:

In this manuscript, the authors present detailed chemical data obtained from the analyses of FRM filters (which excludes biomass burning events based on measured amounts of levoglucosan) collected from 15 different sites in the southeastern U.S during the entire year of 2007. From the chemical analyses of these filters, the authors found that water-soluble organic carbon (WSOC) and inorganic sulfate contributed the largest mass fractions to the PM_{2.5} observed in this region. More importantly, they clearly found that WSOC and sulfate had a pronounced seasonality (peaking in summer) and spatial homogeneity. All of the chemical data, which included inorganics, WSOC, carbohydrates (sugars), and average bulk absorption (bap₃₆₅), obtained from these FRM filters served as inputs for positive matrix factorization (PMF) analyses. A total of 4 factors were found from PMF analysis, where two of these factors explained ~78% of the FRM WSOC variability. One of these two factors, which was called factor 3, explained ~ 50% of the FRM WSOC variability and was associated with oxalate and brown carbon (as measured by bap₃₆₅). Based on recently published studies, the authors suggested that factor 3 was a result of condensed-phase or aqueous-phase chemistry. The other factor, which was designated as factor 4, explained ~ 25% of the FRM WSOC variability and was associated with ammonium sulfate. It was suggested by the authors that factor 4 represents either a regional "aged" SOA or possibly an acid-catalyzed route. The authors were correct in suggesting that more work is needed to investigate the hypothesized sources of these PMF solutions. Although this uncertainty does not hinder the manuscript from being published in ACP, the present findings demonstrate promise for future work, especially if the authors consider coupling these results to molecular-level characterization of the WSOC fraction. Since it is implied throughout the manuscript that isoprene is likely a source of the WSOC (or SOA) in this region, it seems to me the authors need to strongly consider in future work to couple their analyses with those measuring isoprene SOA constituents (as well as other biogenic and anthropogenic SOA constituents) to gain further understanding of these two factors. Currently, I think that both factors 3 and 4 could both be associated with isoprene; however, more organic

speciation is needed in order to confirm this. The lack of detailed chemical characterization of the organic fraction is the main weakness of the study. It would be interesting to see how the mass concentrations of isoprene-derived SOA constituents, like those recently shown in Lin et al. (2012, ES&T), as well as other SOA constituents correlate to the PMF results found here.

In addition to the off-line chemical analyses of FRM filters, online measurements of WSOC were obtained from both a rural site in Yorkville, GA and from an urban site in Atlanta, GA during the AMIGAS campaign in 2008. From the online analyses, the authors found that the urban WSOC was ~31% higher than the rural WSOC. However, when using the FRM filters, it was only found that the urban WSOC was ~10% higher than the rural WSOC. The authors gave very reasonable explanations for this difference between the online and offline measurements. Specifically, it was suggested that this difference was either a result of temporal resolution or the loss of semi-volatiles.

Overall, this manuscript is already a major contribution to the field and will be of interest to many readers of ACP, especially to those planning to take part in the community-led Southern Oxidant & Aerosol Study (SOAS) in summer 2013. Thus, I recommend this paper be accepted once the authors address my minor comments below.

Minor/Specific Comments:

1.) Page 9632, Lines 10-12:

I would also include Lin et al. (2012, ES&T) in this citation, as they found that isoprene epoxydiol (IEPOX)-derived SOA contributed ~8% of the OC (or 10% of OM) at the Yorkville, GA site. I should point out that this % contribution to the total OC is based on only 6 compounds (or tracers) found in the aerosol phase produced from the heterogeneous chemistry of gaseous IEPOX on sulfate particles.

The reference information for Lin et al. (2012) is as follows:

Lin, Y.-H.; Zhang, Z.; Docherty, K. S.; Zhang, H.; Budisulistiorini, S. H.; Rubitschun, C. L.; Shaw, S. L.; Knipping, E. M.; Edgerton, E. S.; Kleindienst, T. E.; Gold, A.; Surratt, J. D. Isoprene epoxydiols as precursors to secondary organic aerosol formation:

Acidcatalyzed reactive uptake studies with authentic compounds. Environ. Sci. Technol. 46, 250-258, 2012.

Lin et al. (2012) is very relevant to the statement and has been cited in the revised manuscript.

2.) Page 9634, Lines 12-16:

The authors state: "An alternative explanation is that the formation of WSOCnb is not independent of sulfate (e.g., WSOC formed through acid-catalyzed reaction) so the uniform distribution of sulfate has some impact on SOA formation and thus the distribution of WSOCnb. However, no strong evidence has been presented for a widespread acid-catalyzed reaction in the southeastern US (Gao et al., 2006; Peltier et al., 2007)"

I'm not sure I completely agree with this statement. First, I should mention that the Gao et al. (2006, JGR) study did not measure or quantify any isoprene-derived SOA. Thus, they likely found no evidence for acid-catalyzed reactions in ambient aerosol. This is important to point out especially since isoprene SOA has been shown in the laboratory to be more enhanced by increasing aerosol acidity (i.e., Surratt et al., 2007, ES&T; Offenberg et al. 2009, ES&T) than compared to monoterpenes. Recent work by Lin et al. (2012) has shown that reactive uptake of synthesized gaseous IEPOX onto acidified sulfate aerosols yields the same aerosol constituents found in the S.E. USA. IEPOX is known to undergo acid-catalyzed ring-opening reactions, even at atmospherically relevant levels of aerosol acidity (Eddingsaas et al., 2010, JPCA; Cole-Filipiak et al., 2010, ES&T).

We thank the reviewer for providing additional information on this point. The statement "However, no strong evidence has been presented for a widespread acid-catalyzed reaction in the southeastern U.S. (Gao et al., 2006; Peltier et al., 2007)." is removed from the manuscript, and the following statements have been added in the revised manuscript: "Recent work by Lin et al. (2012) found that reactive uptake of gaseous isoprene-derived epoxydiols (IEPOX) onto acidic seed aerosols yielded the same aerosol constituents that have been observed in the ambient aerosols in rural southeast."

3.) Page 9637, Lines 3-4:

The authors state: "Higher WSOC is generally associated with much higher CO and NO_x levels, which frequently occurs at the urban site." The authors conclude that local anthropogenic emissions enhance WSOC since they are linked to CO and NO_x. I don't argue against this, but could JST WSOC be higher due to more NO_x allowing for much higher levels of OH to oxidize isoprene, and thus, produce more SOA from isoprene? What I mean is, the OH levels are likely higher in the urban atmosphere due to NO_x, and as a result, this could be important in getting isoprene oxidized to its critical later-generation oxidation products, such as IEPOX and MPAN (Surratt et al., 2010), that have been demonstrated previously to produce SOA from isoprene.

We think the hypothesis proposed by the reviewer is possible. As discussed in the end of Sect. 3.3.2, based on findings by Zhang et al. (2011), a large majority (~75%) of the observed urban excess WSOC in Atlanta is from biogenic SOA formed under anthropogenic influence. The text has been modified in the revised manuscript and it now reads: *"Higher JST WSOC is generally associated with much higher CO and NO_x levels and lower wind speeds at the urban site (not plotted), indicating local production of WSOC under anthropogenic influence."*

4.) Correlations to consider in the future for factors 3 and 4:

As I already stated in my overall/summary comment above, I think it is important to consider in future work to use known SOA tracers to correlate with your factors 3 and 4. This could possibly provide insights into the sources of your two factors. I would consider the IEPOX-derived SOA tracers (Lin et al., 2012), as well as the other known monoterpene, sesquiterpene, and aromatic tracers (Kleindienst et al., 2007, Atmos. Environ.). Have you tried estimating aerosol acidity from your IC data? If so, I wonder how this correlates with factor 4? In future field experiments, it would be interesting to compare your PMF output to high-resolution aerosol mass spectrometry (HR-AMS) data, especially since this could provide you the oxygen-to-carbon (O:C) atomic ratio. As the authors already know, the O:C ratios can give one a sense of the age of the aerosol. It would be interesting in future work to see how O:C ratios correlate to your factors.

Lastly, if VOC or SVOC data were available, it would be interesting to see how these might correlate to the PMF results.

We thank the reviewer for the recommendations for future work, and agree that combining the results of the present study with information on speciated SOA compounds (e.g., IEPOX and other tracers) as well as AMS and VOC/SVOC data would provide valuable insights on SOA sources and formation in the southeast region. The following statement has been added in the revised manuscript: “*A more comprehensive data set that includes speciated SOA tracer compounds (e.g., IEPOX and other known monoterpene, sesquiterpene, and aromatic tracers) as well as high-resolution aerosol mass spectrometry (HR-AMS) and VOC/SVOC data is needed to better resolve the causes for differences between F3 and F4.*”

Regarding the IC ion data and aerosol pH, we could not obtain an accurate estimate of the aerosol acidity from our data since the measurement uncertainties for many ions (e.g., NO_3^- , Cl^- , Ca^{2+} , Mg^{2+}) from the FRM filters are too large to perform such a calculation. The average molar ratio of NH_4^+ to SO_4^{2-} of 1.6 obtained from this data set seems to suggest that the sulfate in the southeast is not fully neutralized. However, no significant correlation was found between NH_4^+ to SO_4^{2-} molar ratio and the PMF factor F4 relative contribution.