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***Interactive comment on* “Spatial and seasonal variations of fine particle water-soluble organic carbon (WSOC) over the Southeastern United States: implications for secondary organic aerosol formation” by X. Zhang et al.**

Anonymous Referee #2

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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 sum-

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mer) 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 $\sim 78\%$ of the FRM WSOC variability. One of these two factors, which was called factor 3, explained $\sim 50\%$ 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 $\sim 25\%$ 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

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authors found that the urban WSOC was $\sim 31\%$ higher than the rural WSOC. However, when using the FRM filters, it was only found that the urban WSOC was $\sim 10\%$ 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 $\sim 8\%$ 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: Acid-catalyzed reactive uptake studies with authentic compounds. *Environ. Sci. Technol.* 46, 250-258, 2012.

2.) Page 9634, Lines 12-16:

The authors state: "An alternative explanation is that the formation of WSOC 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 distri-

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bution of WSOC. 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).

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.

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

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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 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 9621, 2012.

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