

Dear Editor,

Manuscript number: acp-2020-1100

Title: Aerosol characteristics at the Southern Great Plains site during the HI-SCALE campaign

We thank the editor and reviewers for the valuable comments and suggestions. We respond to each of the reviewers' comments and suggestions below. We feel we have thoroughly addressed all comments. Reviewers' comments are in black, our response is in blue, and changes to the text follow in italics.

Reviewer 1

This research work presents the general aerosol characteristics at a rural site of north-central Oklahoma during HI-SCALE campaign. Generally, the results of this work was based aerosol mass spectrometer measurement. The chemical composition and OA PMF factor analysis during spring and summer intensive campaign were shown. The characterization of PMF factors: BBOA, isoprene-derived SOA, HOA and other OOA were demonstrated and compared with previous studies.

This paper is well written and organized. I do not have many scientific and technical questions. The only thing is that I did not found very novel scientific finding in this paper. It is more like a report for the AMS measurement at north-central Oklahoma observation site, although the aerosol composition and source apportionment at this site has been reported previously as well. Some of the conclusions, which are based on deduction, are ambiguous. If this paper shall be published in ACP, I suggest it might be better to publish as a measurement report.

Our response: We thank the reviewer for the comments and have carefully considered publishing this as a measurement report. We feel that there is enough new science to justify publishing this as a regular manuscript. To our knowledge, there is only one other paper describing real-time aerosol chemical composition measurements at the ARM SGP site (Parworth et al 2015). The SGP site is the most heavily instrumented and longest-running of the three DOE-ARM supersites in the world and it represents an important rural continental environment. Understanding aerosol sources and properties at this type

of site is important for improving the representation of aerosols in earth system models. The main scientific findings of this paper are:

- 1) We evaluate sources of organic aerosol at the DOE ARM site and quantify HOA, OOA, BBOA, and IEPOX-SOA contributions to the total organic aerosol. We use backtrajectory analysis and real-time VOC measurements to understand the origin of these sources.
- 2) We report, for the first time, observations of VOC concentrations and their seasonal differences at the SGP site, which is important for modeling SOA formation.
- 3) We find that the OA composition observed at the SGP site was highly oxygenated, which helps to identify the chemical mechanisms contributing to SOA formation and aging at the site, such as the role of autooxidation generating HOMs. These observations will help improve representation of SOA at rural, continental sites.

In addition, we highlight the following differences from the Parworth 2015 paper, which is the only previous paper focusing on aerosol chemical composition at ARM's SGP site.

- 1) We observe different seasonal trends in aerosol composition than Parworth 2015.
- 2) The Parworth study did not have supporting VOC measurements, which characterizes the SOA source gases at the site and provides additional information on air mass origin.
- 3) We deployed an HR-ToF AMS at the site while Parworth deployed a quadrupole ACSM. The HR-ToF AMS allow us to better characterize the aerosol oxidation state and allowed us to identify additional PMF factors that were unresolved by Parworth.
- 4) OA in the Parworth study was somewhat more aged on average, whereas the use of HR-ToF AMS allowed us to distinguish the seasonal variation of OA oxidation states.
- 5) We separate and quantify the contribution of HOA and IEPOX-SOA PMF factors to the OA chemical composition at the SGP site. These important aerosol sources were not identified in the Parworth study.

We believe this paper worth a publication on ACP as a research article.

Other comments:

Line 177: It is hard to conclude the more acidic aerosol is another explanation for lower nitrate concentration since the acidity and ammonium nitrate partitioning influence each other. The author can give more accurate calculation on pH influenced on nitrate partitioning as done in Guo et al. (Guo et al., 2016;Guo et al., 2017)

Our response: We are unsure of exactly what the reviewer is suggesting in this comment. The thermodynamics of sulfate/nitrate/ammonium mixtures are well understood and show that lower pH results in less nitrate partitioning into the condensed phase when other factors are held constant. We used ISORROPIA II to estimate the aerosol acidity and found that pH averaged 1.33 ± 0.54 during the summer IOP and 2.28 ± 0.78 during the spring IOP (the information has been added into the main text, please see Lines 178-180). The AMS-measured concentrations of anions and cations are used in these calculations and we do not have all measurements needed for fully understanding pH of aerosol (i.e., many gas phase measurements are missing). Nevertheless, the calculated pH supports our statement that aerosols are more acidic in summer. As shown in Figure R1, nitrate partitioning to the aerosol phase will be less favored at lower pH and aerosol was more acidic in summer than in spring.

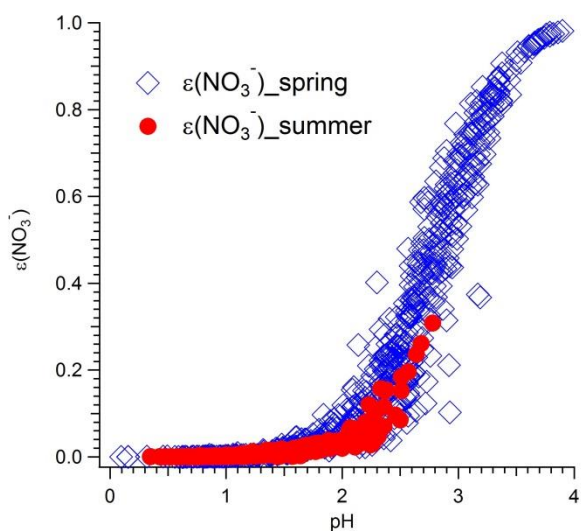


Figure R1. The “S curve”, showing the relationship between $\epsilon(\text{NO}_3^-)$ and pH calculated by ISORROPIA II for both spring and summer IOPs, in which $\epsilon(\text{NO}_3^-)$ represents the particle-phase mass fractions of total nitrate (i.e., gas phase plus particle phase).

Because of limitations in input data, the calculation was done in an “iteration” way. We use the measured aerosol-phase data as initial input, run ISORROPIA in the “forward” mode to predict gas-phase concentrations of NH_3 , HNO_3 and HCl , and use the sum of predicted gas-phase and measured aerosol-phase concentrations as the input for next round. After ~ 20 rounds of iteration, the differences of predicted gas-phase concentrations from adjacent rounds and differences between predicted and measured aerosol-phase concentrations, were within 10%, i.e., comparable with measurement uncertainties. The results were further constrained with the NH_3 levels from nearby sites in the AMON network (Atmospheric Ammonia Network, <http://nadp.slh.wisc.edu/amon/>). The limited data input will of course bring in some uncertainties, but we believe the statement on more acidic aerosols in summer and the consequent influences on nitrate partitioning are valid.

Line 179: I do not quite get this statement. The higher ammonium than that required to fully balance AMS-measured anions usually suggests potential presence of amine in aerosol phase (Docherty et al., 2011). And the anionic species in seasalt aerosols cannot be detected separately. Usually, they were detected as NaCl in AMS under high RH (Ovadnevaite et al., 2012).

Our response: We agree that the presence of amines may be a possible explanation for our observations. We have added this into the discussion: “*This may be due to the potential presence of amines in the particle phase, as amines may contribute to fragments nominally assigned to NH_4 (Docherty et al., 2011)*” (Lines 186-187).

We also now recognize that our statement about seasalt aerosol was in error and have removed it from the text.

Line 270: In addition to biogenic emission dominated areas, the m/z 91 was also found enhanced in the urban areas based on the spectrum of HOA (Ng et al., 2011) or from oxidation of aromatics. Since there were also strong anthropogenic emission influences in this site. The contribution from anthropogenic influences to m/z 91 is also one of the probabilities.

Our response: We agree that in some literature studies, the m/z 91 was attributed to anthropogenic influence. In our PMF results f_{91} was enhanced (~13%) in the HOA spectrum. This is mostly attributed to the $C_7H_7^+$ fragment. As the reviewer stated, $C_7H_7^+$ can arise from biogenic SOA but can also arise from fragmentation of aromatic compounds; therefore, we introduced another fragment, $C_3H_7O_3^+$, a tracer of isoprene photooxidation. Both $C_7H_7^+$ and $C_3H_7O_3^+$ correlated with LO-OOA (Figure 6), supporting that the LO-OOA factor is associated with isoprene photooxidation chemistry. In addition, we found no correlation between m/z 91 and other anthropogenic tracers such as benzene and toluene. Thus for our discussion on LO-OOA here, we believe the influence of anthropogenic emissions to m/z 91 is minimal.

We have included it into our discussion (Lines 284-288).

Line 398-403 What makes the IEPOX-SOA being through more oxidation process in spring than in summer? I just do not understand why the oxidation of methyltetrol tend to happen in spring compared to summer. Have the authors considered the impact of PMF analysis uncertainty to this factor analysis.

Our response: Indeed, the PMF analysis might bring some uncertainties. However, the IEPOX factors in the spring and summer displayed significantly different mean carbon oxidation state in spring (1.61 ± 0.003) than in summer (-0.10 ± 0.005). These differences are large and unlikely to be due to irregularities in the PMF analysis. We note that we identify both an HOA and multiple OOA factors in both spring and summer, so it is relatively unlikely that the IEPOX-SOA factor is contaminated with unresolved HOA or OOA.

While we cannot definitively explain the reason for these differences, we explore several possible explanations in the manuscript. Seasonal changes in biogenic emissions show that the both isoprene and monoterpenes levels were lower in spring. This may allow some isoprene oxidation products to undergo further oxidation/aging process due to the relatively abundant oxidants during spring. Some recent studies, such as Chen et al. (2020), have proposed relevant mechanisms producing more oxygenated/functionalized

organosulfates from IEPOX products. Since most studies on IEPOX SOA were previously conducted during summer season, we believe this unique observation at SGP site during spring season provided a new perspective on SOA chemistry, especially in rural environment with limited emissions.

Line 443 Coggon et al. (Coggon et al., 2016) has reported that the emissions of nitrogen-containing VOCs (NVOCs) strongly depend on the fuel nitrogen content. They found markedly lower concentrations of acetonitrile for residential wood Burning. The authors can check if this is one of the reasons for low acetonitrile observed here.

Our response: We thank the reviewer for pointing this out and have included this as a possible reason for our observations.

We have adjusted the statements as: *“A second possibility is that the biomass burning did not emit significant amounts of acetonitrile. Acetonitrile emissions were reported to be significantly different among various biomass burning sources, with lower nitrogen containing biomass emitting less acetonitrile (Coggon et al., 2016). Thus it is possible that the fuel had lower nitrogen content.”* (Lines 468-471)

Reference:

Coggon, M. M., et al.: Emissions of nitrogen-containing organic compounds from the burning of herbaceous and arboraceous biomass: Fuel composition dependence and the variability of commonly used nitrile tracers, *Geophys Res Lett*, 2016, 43, 9903-9912.

Docherty, K. S., et al.: The 2005 Study of Organic Aerosols at Riverside (SOAR-1): instrumental intercomparisons and fine particle composition, *Atmos. Chem. Phys.*, 2011, 11, 12387-12420.

Guo, H., et al.: Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States, *Journal of Geophysical Research: Atmospheres*, 2016, 121, 10,355-310,376.

Guo, H., et al.: Fine particle pH and gas–particle phase partitioning of inorganic species in Pasadena, California, during the 2010 CalNex campaign, *Atmos. Chem. Phys.*, 2017, 17, 5703-5719.

Ng, N. L., et al.: Real-Time Methods for Estimating Organic Component Mass Concentrations from Aerosol Mass Spectrometer Data, *Environ Sci Technol*, 2011, 45, 910-916.

Ovadnevaite, J., et al.: On the effect of wind speed on submicron sea salt mass concentrations and source fluxes, *Journal of Geophysical Research: Atmospheres*, 2012, 117