Review of "Chemical composition of ultrafine aerosol particles in central Amazonia during the wet season" by Glicker et al.

General Comments:

This manuscript reports the composition of ultrafine particles during the wet season in central Amazonia as measured by a Thermal Desorption Chemical Ionization Mass Spectrometer (TD-CIMS). The top five abundant ions by signal from each of negative and positive ion modes are reported for a ten-day period representing anthropogenically-influenced and background conditions. The authors find that particulate bisulfate is elevated during the anthropogenic period, though omnipresent, and that organic nitrogen is characteristic of background airmasses. 3-methylfuran (ascribed to IEPOX chemistry) is the dominant component in positive ion mode and interpreted to contribute to new particle growth and formation processes. Finally, the authors find using principal component analysis that ultrafine particle composition can be divided into two clusters, one mostly comprised of organics, and the other comprised of inorganic ions, both distinct from a third cluster with most AMS PM1 measured constituents, indicating unique sources/chemistry for ultrafine and PM1 particles. Overall, this work provides novel measurement of ultrafine particle composition in central Amazonia and would be appropriate for publication in ACP after the following comments are addressed. It is generally written clearly, but lacks some depth in providing additional insight from the measurements. For example, the discussion on PCA analysis could provide more insight into the observed correlations between species/clusters, and as written tends to just reiterate earlier descriptions of the ascribed sources for TDCIMS ion assignments.

Specific Comments:

1) Line 60: In addition to Alves et al., 2016, consider adding citation to the following:
    a. Jardine, K. J., Yañez Serrano, a., Arneth, a., Abrell, L., Jardine, A. B., Van Haren, J., Artaxo, P., Rizzo, L. V., Ishida, F. Y., Karl, T., Kesselmeier, J., Saleska, S. and Huxman, T.: Within-canopy sesquiterpene ozonolysis in Amazonia, J. Geophys. Res. Atmos., 116(19), 1–10, doi:10.1029/2011JD016243, 2011.
    b. Jardine, A. B., Jardine, K. J., Fuentes, J. D., Martin, S. T., Martins, G., Durgante, F., Carneiro, V., Higuchi, N., Manzi, A. O. and Chambers, J. Q.: Highly reactive light-dependent monoterpenes in the Amazon, Geophys. Res. Lett., 42(5), 1576–1583, doi:10.1002/2014GL062573, 2015.
    c. Shrivastava, M. K., Andreae, M. O., Artaxo, P., Barbosa, H. M. J., Berg, L. K., Brito, J., Ching, J., Easter, R. C., Fan, J., Fast, J. D., Feng, Z., Fuentes, J. D., Glasius, M., Goldstein, A. H., Alves, E. G., Gomes, H., Gu, D., Guenther, A., Jathar, S. H., Kim, S., Liu, Y., Lou, S., Martin, S. T., McNeill, V. F., Medeiros, A., de Sá, S. S., Shilling, J. E., Springston, S. R., Souza, R. A. F., Thornton, J. A., Isaacman-VanWertz, G., Yee, L. D., Ynoue, R., Zaveri, R. A., Zelenyuk, A. and Zhao, C.: Urban pollution greatly enhances formation of natural aerosols over the Amazon rainforest, Nat. Commun., 10(1), 1046, doi:10.1038/s41467-019-08909-4, 2019.
    d. Yáñez-Serrano, A. M., Nölscher, A. C., Williams, J., Wolff, S., Alves, E. G., Martins, G. A., Bourtsoukidis, E., Brito, J. F., Jardine, K. J., Artaxo, P. and Kesselmeier, J.: Diel and

seasonal changes of biogenic volatile organic compounds within and above an Amazonian rainforest, Atmos. Chem. Phys, 15, 3359–3378, doi:10.5194/acp-15-3359-2015, 2015.

e. Yee, L. D., Isaacman-Vanwertz, G., Wernis, R. A., Meng, M., Rivera, V., Kreisberg, N. M., Hering, S. V, Bering, M. S., Glasius, M., Upshur, M. A., Bé, A. G., Thomson, R. J., Geiger, F. M., Offenberg, J. H., Lewandowski, M., Kourtchev, I., Kalberer, M., de Sá, S. S., Martin, S. T., Alexander, M. L., Palm, B. B., Hu, W., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Liu, Y. J., Mckinney, K. A., Artaxo, P., Viegas, J., Manzi, A., Oliveira, M. B., De Souza, R., Machado, L. A. T., Longo, K. and Goldstein, A. H.: Observations of sesquiterpenes and their oxidation products in central Amazonia during the wet and dry seasons, Atmos. Chem. Phys, 18, 10433–10457, doi:10.5194/acp-18-10433-2018, 2018.

2) Lines 73-78: It might be worthwhile to define “ultrafine”, “Aitken”, “accumulation”, and “coarse mode” particles for readers less familiar with these distinctions in Dp ranges.
3) Line 101: Please rephrase “…can have an oversized impact…” as it is not very scientifically clear wording.
4) Line 156: Can the authors also include the MS for positive ion mode? Why was m/z 75 not selected for regular measurement considering its ion intensity is relatively large?
5) Line 160: Please provide additional information in Smith, 2016 under references to make it easier to find.
6) Line 161: Can you specify the threshold for “low concentrations” of ultrafine particles?
7) Figure 1: For size distribution plot, why are the units of intensity for dN/dlogdP in molec/cm^3 rather than #/cm^3 considering that particle concentrations have been discussed earlier in manuscript as #/cm^3?
8) Lines 224-238: This is very interesting analysis. Would the authors be able to infer from this an average % increase in loading on top of “background” conditions that is attributable to anthropogenic influence, assuming that the “background” composition from the March 15-March 19 period is approximately same for the March 20-25 period?
9) Figure S3: Please include figure legends for the ions shown in these diurnal profiles and specify that this is negative ion mode in caption.
10) Lines 264-269: Can the authors clarify if bisulfate ion as indicator of particulate sulfate can also include natural/background sources of sulfate? Since it has been previously established that there are a lot of natural sources of sulfate (e.g. DMS) (Andreae et al., 1990; Andreae and Andreae, 1988) as well as background levels (long-range transport including anthropogenic) (de Sá et al., 2017), would the authors anticipate these sources to be contributing to the majority of the bisulfate anion signal during 19 Mar to 26 Mar 2014?
11) Line 293: Please specify basis of 55-95% of PM as mass basis, etc.
12) Lines 305-306: Based on the diurnal profile of m/z 83 assigned as 3-methylfuran, the authors could better support the claim for IEPOX as a proposed source by comparing with diurnal profiles of gas-phase isoprene oxidation products by PTR-MS (Liu et al., 2016, 2018), particle-phase isoprene oxidation products by SV-TAG Figure 1c, d ((Isaacman-VanWertz et al., 2016), and AMS IEPOX-SOA PMF factor Figure 4b (de Sá et al., 2018) ? Does it make sense for Isoprene + OH → IEPOX to occur 8:00-10:00 UTC and peak, followed by minimum 14:00-16:00 UTC, and then build again?

13) Figure 4: Can the chemical assignments be added after the TDCIMS measured m/z's for ease of chemical interpretation just looking at figure, (e.g. m/z 89 hydrogen oxalate, m/z 59 acetate, etc.)
14) Lines 371-373: Move this explanation of natural bisulfate sources up in manuscript based on Specific Comment regarding Lines 264-269) above.
15) Section 3.3. Authors should include more analysis and interpretation of Figure 3. Can any of these questions below be answered with the PCA analysis:
    a. What do the authors make of the fact that AMS chloride and TDCIMS m/z 35 chloride are in the same cluster despite different size distribution ranges of the two measurement techniques?
    b. Why does TDCIMS measured m/z 42 (organic nitrogen) negatively correlate with AMS nitrate? What implications does this have in terms of sources of organic nitrogen between ultrafine and PM1?
    c. Lines 375-379: Why was AMS-measured K+ not included in the PCA analysis to see if it is distinct/similar to TDCIMS across size distributions?
16) Lines 379-381: Repetitive with lines 365-367.

Technical Corrections:

1) Line 56: Delete "is."
2) Line 124: Change "process" to "processes."
3) Lines 131: Change "mass" to "masses."
4) Lines 174-181: Reorder references to ARM, 2018a-d so they appear in alpha order.
5) Line 353: Delete "and" at start of line.
6) Line 395: No need to capitalize "Area."
7) Line 396: Change "underscore" to "underscores"

References:

Andreae, M. O. and Andreae, T. W.: The Cycle of Biogenic Sulfur Compounds Over the Amazon Basin 1. Dry Season, J. Geophys. Res., 93(D2), 1487–1497, doi:10.1029/JD093iD02p01487, 1988.

Andreae, M. O., Berresheim, H., Bingemer, H., Jacob, D. J., Lewis, B. L., Li, S.-M. and Talbot, R. W.: The atmospheric sulfur cycle over the Amazon Basin: 2. Wet season, J. Geophys. Res., 95(D10), 16813, doi:10.1029/JD095iD10p16813, 1990.

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Liu, Y. J., Brito, J., Dorris, M. R., Rivera-Rios, J. C., Seco, R., Bates, K. H., Artaxo, P., Duvoisin, S., Keutsch, F. N., Kim, S., Goldstein, A. H., Guenther, A. B., Manzi, A. O., Souza, R. A. F., Springston, S. R., Watson, T. B., McKinney, K. A. and Martin, S. T.: Isoprene photochemistry over the Amazon rainforest, Proc. Natl. Acad. Sci., 113(22), 6125–6130, doi:10.1073/pnas.1524136113, 2016.

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B., Artaxo, P., Souza, R. A. F., McKinney, K. A. and Martin, S. T.: Isoprene photo-oxidation products quantify the effect of pollution on hydroxyl radicals over Amazonia, Sci. Adv., 4(4), eaar2547, doi:10.1126/sciadv.aar2547, 2018.

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