Summary

The manuscript by Glicker et al. entitled "Chemical composition of ultrafine particles in central Amazonia during the wet season" presents a chemical characterization of ultrafine aerosol particles using a Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) in the course of the GoAmazon field campaign in 2014 and 2015. The authors contrast the ultrafine particle conditions and properties during two different periods, which they call anthropogenic period and biogenic period. They suggest that the chemical results obtained can be regarded as characteristic for the Manaus metropolitan area influence on one hand and clean remote regions further north on the other hand. A certain number of specifically observed ions are discussed in relation to potential sources and processes.

Relevance

This study is clearly an important endeavor since the origin and properties of ultrafine particles in the Amazon are still largely unknown. Particularly, very sparse information is available on the chemical composition of the ultrafine particle fraction. The increasing number and visibility of recent studies on ultrafine Amazonian aerosols underline the relevance of this topic (Wang et al., 2016; Andreae et al., 2018; Fan et al., 2018; Rizzo et al., 2018).

Formal aspects

The paper is well structured and mostly clearly written. The lengths of the text and the number of figures generally seems appropriate although certain crucial aspects may deserve an additional dedicated figure for clarification (see below). The existing body of literature in the field of Amazonian atmospheric research is only partly covered and the study would profit from further literature synthesis.

Scientific assessment

I have a fundamental scientific concern relating to a discrepancy of what the study suggests and concludes vs. what it actually delivers and supports with data. The overarching aim of the work is reflected in the title, announcing a characterization of the "Chemical composition of ultrafine particles in central Amazonia during the wet season". Furthermore, the abstract suggests that the study helps to determine "the chemical species and mechanisms that may be responsible for new particle formation and growth in the region" (p. 1, l. 19-20). Here, the word "region" refers to "central Amazonia" (p. 1, l. 14). In its current state, the study has not convinced me of really being representative for conditions in the central Amazon (as promised by the title, abstract, and sections in the main text), because the plots and data indicated a persistent influence of the Manaus city plume, which seems particularly strong for the ultrafine particles. It seems that the general discrimination into an "anthropogenic period" and a "biogenic period" is oversimplified. I don't doubt that both periods cover distinct conditions and that certain pollutant concentrations were "as much as three times larger" (p.6, l. 200) during the anthropogenic relative to the biogenic period. However, this does not imply that the biogenic period is sufficiently free of anthropogenic pollutants to uncover biogenic processes. In fact, the data/plots did not convince me that the conditions during the "biogenic period" were anywhere close to "clean" (p. 4, l. 131), "natural" (p. 1, l. 15), or even "pristine" (p. 2, l. 69) and "pre-industrial" (p. 1, l. 15) conditions (Hamilton, 2015). The only text section where this is critically reflected can be found in the conclusions: Here the authors state that "influences from anthropogenic sources […] may continuously affect the composition of ultrafine particles observed at the T3 measurement site" (p. 14, l. 388-390). Speaking as the *Advocatus Diaboli*: 'Could it be that we are looking throughout the entire measurement period at ultrafine particles of anthropogenic origin, only at varying states of dilution and mostly swamping biogenic processes in the background?' If so, the title and argumentation have to be adjusted. This general uncertainty does not harmonize with many statements in the text, such as the very strong conclusion in the last sentence of the study, stating that

"anthropogenic emissions and processes have a unique role to play in ultrafine particle formation and growth in the Amazon basin".

My recommendation

In principle, the manuscript fits well into ACP in terms of topic, methods, and potential conclusions. However, in the light of my aforementioned concerns, I think that a careful revision and clarification of certain aspects is necessary prior to publication. I am optimistic that addressing the aforementioned points and a careful clarification of what this study specifically provides/means within the wider context of the Amazonian aerosol cycling will ultimately strengthen the points of this work.

Specific major comments

In relation to my aforementioned criticism, some main aspects are outlined in more detail below:

1) Comment relating to terminology: The manuscript frequently and vaguely refers to terms such as "background", "natural", "clean", and "pristine" conditions. It has to be clarified what these terms exactly mean in the context of the presented measurements, the measurement location, and the Amazonian season during which the results were obtained.

2) Comment relating to back trajectories: The back trajectory plot shown in Fig. 2 is (at least) misleading as it shows only a snapshot of the air mass circulation. However, the text and figure caption infer that these snapshot trajectories "show the difference between the types of air masses that travel to the T3 site during the anthropogenic period […] and biogenic period […]". I did a quick trajectory frequency run to visualize conditions over multiple days of the anthropogenic vs. biogenic periods (Fig. R1). Clearly, the trajectory paths of both periods are different: during the anthropogenic period the path is tighter and seems to have more 'contact' to Manaus, whereas during the biogenic period the path is broader and spans over a larger region including Manaus. However, Fig. R1 suggests that Manaus influenced both periods, though to a different extent. Moreover, I don't see evidence that the conditions during the "biogenic period" bring air masses from "clean, remote regions" (p. 4, l. 131). In fact, the trajectories during both periods pass over the Amazon River, which might be quite polluted due to ship traffic, settlements etc. **In summary:** I think a more systematic trajectory analysis is needed here and a more differentiated discussion of what this means for "biogenic" conditions.
   Further minor comments in the context: (i) The starting height of the trajectories is not specified. (ii) I could not reproduce the circulation for Mar 23 shown in Fig. 2 suggesting air masses straight from the north. Under which settings was this derived? (iii) In p. 7, l. 202 & 221, it is stated that "[…] during the background period, air masses arrived at the T3 site from the northeast to northwest ~70% of the time (Figure 2)." Where is the number "~70%" coming from? This is not transparently described.

“Anthropogenic period” (Mar 15 to 18) “Biogenic period” (Mar 20 to 25)

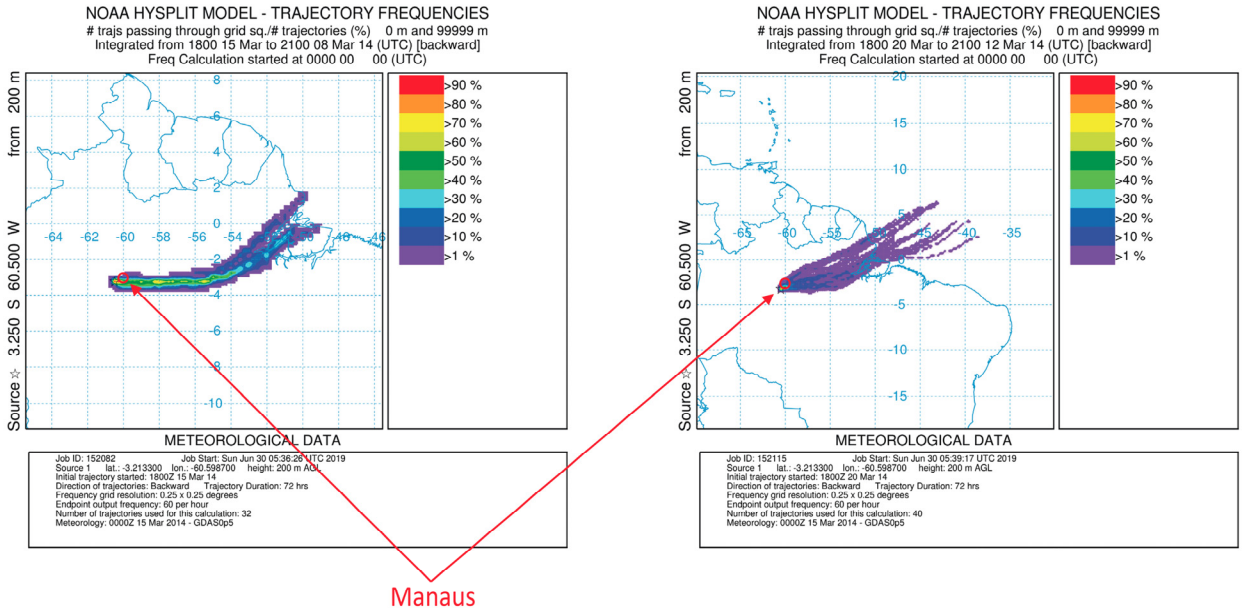

Fig. R1. Back trajectory frequency plots, contrasting “anthropogenic” vs. “biogenic periods”.

3) Comment relating to the ‘overview’ Figure 1: Figure 1 seems to be meant as an overview plot to illustrate the overall conditions during the measurement period. It puts a major focus on local meteorological parameter, which is of course helpful. However, it only provides very sparse aerosol context given that a broad range of aerosol data was measured during the GoAmazon campaign. Particularly, I feel that some basic time series such as on total particle concentration and black carbon (BC) concentration would be very helpful to illustrate the contrast between both periods. In particular, BC could help to identify periods without detectable anthropogenic aerosol influence. Moreover, a particle concentrations in the ultra-fine particle size range (i.e., <30 nm) would be very interesting/relevant as this is the focus of the whole study. Maybe also particle concentrations for the Aitken and accumulation mode ranges would be helpful, since the typical multimodal shape of the Amazonian aerosol distribution (Artaxo et al., 2013; Andreae et al., 2015) can hardly be seen in the SMPS contour plot in Fig. 1.

4) Comment on aerosol size distributions: The focus of this study is the analysis of ultrafine particles, which generally have a rather low abundance in the Amazon. Actually, the low abundance (though not absence) is a main reason why ultrafine particle studies in the Amazon are so exciting/relevant. For illustration, I compiled some size distribution plots from previous studies in Fig. R2 – all of them show the characteristic multimodal shape without a clearly resolved nucleation mode. How does this relate to Fig. 1 in the present study? How representative are the size distributions in Fig. 1 for the Amazon region? All episodes with the very high abundance of ultrafine particles in Fig. 1 (also during the “biogenic period”) differ substantially from the distributions in Fig. R2, suggesting an impact of Manaus or even more local pollution. What about the ‘as clean as it gets’ conditions in Fig. 1 – do they resemble the plots in Fig. R2? What is missing in the text is a dedicated comparison of the observed size distributions in Fig. 1 with the existing literature (e.g., those in Fig. R2). Ideally, the authors could add a plot with dN/dlogD distributions

that directly compares the condition during their measurement period(s) with characteristic distributions from previous publications. **In summary:** The study aims at "determining the chemical species and mechanisms that may be responsible for new particle formation and growth in the region" (p. 1, l. 19/20). I think that it is not convincingly shown (yet) that the aerosol size distributions, which underlie the TDCIMS analysis, resemble the previously published size distributions that are typical for the Amazon region. It could well be that certain episodes in the measurement period resemble those characteristic conditions, however, it is very hard to see from Fig. 1. Putting the conditions of the present study into a broader literature context will likely strengthen the case of this work substantially.

Further minor comment in the context: The color scale in Fig. 1 is confusing since most of the shown concentration range is red. What is the purpose for doing it like that?

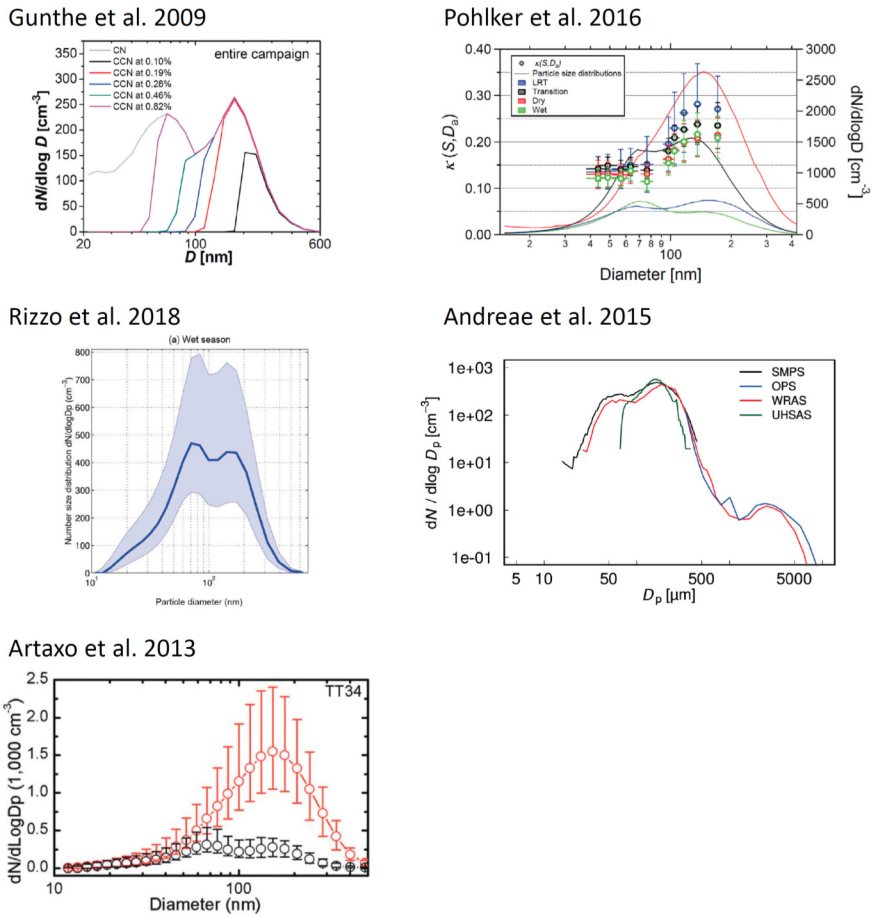

Fig. R2. Previously reported aerosol size distributions from the Amazon region (Gunthe et al., 2009; Artaxo et al., 2013; Andreae et al., 2015; Pohlker et al., 2016; Rizzo et al., 2018).

References

Andreae, M. O., Acevedo, O. C., Araùjo, A., Artaxo, P., Barbosa, C. G. G., Barbosa, H. M. J., Brito, J., Carbone, S., Chi, X., Cintra, B. B. L., da Silva, N. F., Dias, N. L., Dias-Júnior, C. Q., Ditas, F., Ditz, R., Godoi, A. F. L., Godoi, R. H. M., Heimann, M., Hoffmann, T., Kesselmeier, J., Konemann, T., Kruger, M. L., Lavric, J. V., Manzi, A. O., Moran-Zuloaga, D., Nolscher, A. C., Santos Nogueira, D., Piedade, M. T. F., Pohlker, C., Poschl, U., Rizzo, L. V., Ro, C. U., Ruckteschler, N., Sá, L. D. A., Sá, M. D. O., Sales, C. B., Santos, R. M. N. D., Saturno, J., Schongart, J., Sorgel, M., de Souza, C. M., de Souza, R. A. F., Su, H., Targhetta, N., Tóta, J., Trebs, I., Trumbore, S., van Eijck, A., Walter, D., Wang, Z., Weber, B., Williams, J., Winderlich, J., Wittmann, F., Wolff, S., and Yáñez-Serrano, A. M.: The Amazon Tall Tower Observatory (ATTO): overview of pilot measurements on ecosystem ecology, meteorology, trace gases, and aerosols, Atmos. Chem. Phys., 15, 10723-10776, 10.5194/acp-15-10723-2015, 2015.

Andreae, M. O., Afchine, A., Albrecht, R., Holanda, B. A., Artaxo, P., Barbosa, H. M. J., Borrmann, S., Cecchini, M. A., Costa, A., Dollner, M., Futterer, D., Jarvinen, E., Jurkat, T., Klimach, T., Konemann, T., Knote, C., Kramer, M., Krisna, T., Machado, L. A. T., Mertes, S., Minikin, A., Pohlker, C., Pohlker, M. L., Poschl, U., Rosenfeld, D., Sauer, D., Schlager, H., Schnaiter, M., Schneider, J., Schulz, C., Spanu, A., Sperling, V. B., Voigt, C., Walser, A., Wang, J., Weinzierl, B., Wendisch, M., and Ziereis, H.: Aerosol characteristics and particle production in the upper troposphere over the Amazon Basin, Atmos. Chem. Phys., 18, 921-961, 10.5194/acp-18-921-2018, 2018.

Artaxo, P., Rizzo, L. V., Brito, J. F., Barbosa, H. M. J., Arana, A., Sena, E. T., Cirino, G. G., Bastos, W., Martin, S. T., and Andreae, M. O.: Atmospheric aerosols in Amazonia and land use change: from natural biogenic to biomass burning conditions, Faraday Discuss., 165, 203-235, 10.1039/c3fd00052d, 2013.

Fan, J., Rosenfeld, D., Zhang, Y., Giangrande, S. E., Li, Z., Machado, L. A. T., Martin, S. T., Yang, Y., Wang, J., Artaxo, P., Barbosa, H. M. J., Braga, R. C., Comstock, J. M., Feng, Z., Gao, W., Gomes, H. B., Mei, F., Pohlker, C., Pohlker, M. L., Poschl, U., and de Souza, R. A. F.: Substantial convection and precipitation enhancements by ultrafine aerosol particles, Science, 359, 411-418, 10.1126/science.aan8461, 2018.

Gunthe, S. S., King, S. M., Rose, D., Chen, Q., Roldin, P., Farmer, D. K., Jimenez, J. L., Artaxo, P., Andreae, M. O., Martin, S. T., and Poschl, U.: Cloud condensation nuclei in pristine tropical rainforest air of Amazonia: size-resolved measurements and modeling of atmospheric aerosol composition and CCN activity, Atmospheric Chemistry and Physics, 9, 7551-7575, 2009.

Hamilton, D. S., Lee, L. A., Pringle, K. J., Reddington, C. L., Spracklen, D. V., and Carslaw, K. S.: Occurrence of pristine aerosol environments on a polluted planet, Proceedings of the National Academy of Sciences of the United States of America, 111, 18466-18471, 10.1073/pnas.1415440111, 2014.

Pohlker, M. L., Pohlker, C., Klimach, T., Hrabe de Angelis, I., Barbosa, H. M. J., Brito, J., Carbone, S., Cheng, Y., Chi, X., Ditas, F., Ditz, R., Gunthe, S. S., Kesselmeier, J., Konemann, T., Lavrič, J. V., Martin, S. T., Moran-Zuloaga, D., Rose, D., Saturno, J., Su, H., Thalman, R., Walter, D., Wang, J., Wolff, S., Artaxo, P., Andreae, M. O., and Poschl, U.: Long-term observations of cloud condensation nuclei in the Amazon rain forest – Part 1: Aerosol size distribution, hygroscopicity, and new model parameterizations for CCN prediction, Atmos. Chem. Phys., 16, 15709-15740, 10.5194/acp-2016-519, 2016.

Rizzo, L. V., Roldin, P., Brito, J., Backman, J., Swietlicki, E., Krejci, R., Tunved, P., Petaja, T., Kulmala, M., and Artaxo, P.: Multi-year statistical and modeling analysis of submicrometer aerosol number size distributions at a rain forest site in Amazonia, Atmospheric Chemistry and Physics, 18, 10255-10274, 10.5194/acp-18-10255-2018, 2018.

Wang, J., Krejci, R., Giangrande, S., Kuang, C., Barbosa, H. M. J., Brito, J., Carbone, S., Chi, X., Comstock, J., Ditas, F., Lavric, J., Manninen, H. E., Mei, F., Moran-Zuloaga, D., Pohlker, C., Pohlker, M. L., Saturno, J., Schmid, B., Souza, R. A. F., Springston, S. R., Tomlinson, J. M., Toto, T., Walter, D., Wimmer, D., Smith, J. N., Kulmala, M., Machado, L. A. T., Artaxo, P., Andreae, M. O., Petaja, T., and Martin, S. T.: Amazon boundary layer aerosol concentration sustained by vertical transport during rainfall, Nature, 539, 416-419, 10.1038/nature19819, 2016.