Short comment on "Aircraft-based observations of isoprene epoxydiol-derived secondary organic aerosol (IEPOX-SOA) in the tropical upper troposphere over the Amazon region" by Schulz et al.

(https://doi.org/10.5194/acp-2018-232)

On page 9, lines 11-16, the authors state:

"A first estimation of organic nitrates can be derived from the ratio of the nitrate-related ions at m/z 30 (NO⁺) and m/z 46 (NO₂⁺). The signal at m/z 30 is mostly from NO⁺, but also the organic ion CH₂O⁺ can contribute with a small amount (Allan et al., 2014). Such interferences at m/z 30 with CH₂O⁺ are corrected in the evaluation software by the fragmentation table (Allan et al., 2004), but it is not possible to distinguish unambiguously between the NO⁺ and the CH₂O⁺ ions with a C-ToF-AMS. The signal at m/z 46 is usually dominated by NO₂⁺ ions (Jimenez et al., 2003; Allan et al., 2004)."

Then the authors proceed to use the default AMS unit mass resolution fragmentation table as an estimate of the NO⁺ and NO₂⁺ ion abundances and their ratios to separate ammonium nitrate from organic nitrates. The default unit mass resolution (UMR) fragmentation table assumes only a small interference at m/z 30 from CH₂O⁺ ions (2.2% of OA at m/z 29); however, for biogenic SOA the interference can be much larger (of comparable magnitude to OA m/z 29). For example, see high-resolution (HR) spectra for biogenic precursor laboratory-generated SOA or ambient PMF OOA factors at the AMS spectral database and references thererin (http://cires1.colorado.edu/jimenez-group/HRAMSsd/) or discussions in the supplementary information of Fry et al. (ACPD 2018). Importantly, for strongly biogenically-influenced rural/remote sites where nitrate is small compared to OA (as in this study), the CH₂O⁺ ions at m/z 30 as well as the $CH_2O_2^+$ ions at m/z 46 are comparable or larger than the corresponding nitrate ions, and can lead to large errors in NO⁺, NO₂⁺, the NO₂⁺/NO ratio, and total nitrate concentrations if not carefully taken into account. To correct for these interferences in UMR data (also with a CToF-AMS) for measurements in the SE United States during summertime (strongly biogenically influenced), an analysis using HR data from a similar region/period was developed, applied and described in detail in Fry et al. (ACPD 2018). Corrections to NO⁺ and NO₂⁺ were on average -55% and -33%, respectively, and the reconstructed UMR-based NO_x + ion signals matched the HR signals very well. Thus, it is strongly recommended that the authors either conduct a similar analysis with available HR data collected in the Amazon (e.g., de Sá et al., ACPD, 2018) or the correction from Fry et al. (ACPD 2018) be applied. This correction will likely have large effects on both the inorganic/organic nitrate apportionment and the concentrations (of either type of nitrate and total nitrate).

On a separate but related topic, the paper states that the particles have insufficient amount of ammonium to neutralize the anions present. However, errors in pRONO₂ estimation may affect this. In addition, organosulfates (such as from IEPOX) may also be present which may affect this balance. These possibilities should be discussed.

Fry, J. L., Brown, S. S., Middlebrook, A. M., Edwards, P. M., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Allen, H. M., Ryerson, T. B., Pollack, I., Graus, M., Warneke, C., de Gouw, J. A., Brock, C. A., Gilman, J., Lerner, B. M., Dubé, W. P., Liao, J. and Welti, A.: is a manuscript under review for the journal Atmospheric Chemistry and Physics (ACP). Secondary Organic Aerosol (SOA) yields from NO3

radical + isoprene based on nighttime aircraft power plant plume transects, Atmos. Chem. Phys. Discuss., 1–36, doi:10.5194/acp-2018-255, 2018.

de Sá, S. S., Palm, B. B., Campuzano-Jost, P., Day, D. A., Hu, W., Isaacman-VanWertz, G., Yee, L. D., Brito, J., Carbone, S., Ribeiro, I. O., Cirino, G. G., Liu, Y. J., Thalman, R., Sedlacek, A., Funk, A., Schumacher, C., Shilling, J. E., Schneider, J., Artaxo, P., Goldstein, A. H., Souza, R. A. F., Wang, J., McKinney, K. A., Barbosa, H., Alexander, M. L., Jimenez, J. L. and Martin, S. T.: Urban influence on the concentration and composition of submicron particulate matter in central Amazonia, Atmos. Chem. Phys. Discuss., 1–56, doi:10.5194/acp-2018-172, 2018.

Sincerely, Doug Day