

We thank Douglas Day for his short comment that helped to improve the manuscript. Our response is formatted as follows:

### Short comment

Author's reply

### Changes to the manuscript

All page, line, section and figure numbers in bold refer to the original manuscript, all others to the revised version.

**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 ( $\text{NO}^+$ ) and  $m/z$  46 ( $\text{NO}_2^+$ ). The signal at  $m/z$  30 is mostly from  $\text{NO}^+$ , but also the organic ion  $\text{CH}_2\text{O}^+$  can contribute with a small amount (Allan et al., 2014). Such interferences at  $m/z$  30 with  $\text{CH}_2\text{O}^+$  are corrected in the evaluation software by the fragmentation table (Allan et al., 2004), but it is not possible to distinguish unambiguously between the  $\text{NO}^+$  and the  $\text{CH}_2\text{O}^+$  ions with a C-ToF-AMS. The signal at  $m/z$  46 is usually dominated by  $\text{NO}_2^+$  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  $\text{NO}^+$  and  $\text{NO}_2^+$  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  $\text{CH}_2\text{O}^+$  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 therein (<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  $\text{CH}_2\text{O}^+$  ions at  $m/z$  30 as well as the  $\text{CH}_2\text{O}_2^+$  ions at  $m/z$  46 are comparable or larger than the corresponding nitrate ions, and can lead to large errors in  $\text{NO}^+$ ,  $\text{NO}_2^+$ , the  $\text{NO}_2^+/\text{NO}^+$  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  $\text{NO}^+$  and  $\text{NO}_2^+$  were on average -55% and -33%, respectively, and the reconstructed UMR-based  $\text{NO}_x^+$  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).**

We corrected our data according to Fry et al., 2018. For the correction of  $m/z$  30 and 46 the organic signal at  $m/z$  29 and 45 were used, respectively. The correction of the nitrate mass concentration resulted in a reduction of about 39 % (on average) of the initial nitrate mass

concentration. However, there is no change of the general shape of the vertical profile, such that the finding of a nitrate increase in the UT remains unchanged.

We added the following to the manuscript in **Sect. 3.4 p. 9, line 16** (p. 10, line 9):

As organic interferences on the mass spectral signals at  $m/z$  30 (interference from  $\text{CH}_2\text{O}^+$ ) and  $m/z$  46 (interference from  $\text{CH}_2\text{O}_2^+$ ) can occur in environments with high biogenic contribution and/or small nitrate concentrations, a correction according to Fry et al. (2018) was applied. The correction of both signals at  $m/z$  30 and 46 is achieved by using correlated organic signals at  $m/z$  29, 42, 43, and/or 45 derived by high resolution measurements. The organic signals at  $m/z$  29 ( $\text{CHO}^+$ ) and  $m/z$  45 ( $\text{CHO}_2^+$ ) are closest to those affected by the interference and used for the correction here. Equations 4 and 5 give the individual correction for the nitrate signal at  $m/z$  30 and 46, respectively. The correction for  $\text{NO}^+$  includes the total signal at  $m/z$  30, the default fragmentation correction from the air signal (Allan et al., 2004), and a correction coefficient that depends on the  $m/z$  used for the correction ( $A_i$ ). As for  $m/z$  30 the correlated organic signal at  $m/z$  29 is used here, the organic signal at  $m/z$  29 (Org29) needs to be taken into account as well as the contribution of the isotopes of organic CO. For the correction of the nitrate fraction at  $m/z$  46 a term which includes a correlation coefficient  $B_i$  and the organic signal at  $m/z$  45 is subtracted from the signal at  $m/z$  46. The correction coefficient  $A_i$  is in this case 0.215,  $B_i$  is 0.127 (see supplement to Fry et al., 2018). In the organic signal at  $m/z$  28, 29, 30 and 45 the relative ionization efficiency ( $\text{RIE}_{\text{Org}}$ ) is already applied and needs to be reversed for the correction of the nitrate signal.

Nitrate fraction at  $m/z$  30:

$$\text{NO}^+ = m/z\ 30 - 0.0000136 * m/z\ 28 - A_i * (\text{Org29} - 0.011 * \text{Org28}) * \text{RIE}_{\text{Org}} - \text{Org30} * \text{RIE}_{\text{Org}} \quad (4)$$

Nitrate fraction at  $m/z$  46:

$$\text{NO}_2^+ = m/z\ 46 - B_i * \text{Org45} * \text{RIE}_{\text{Org}} \quad (5)$$

The total nitrate signal is then calculated by adding both fractions. The final nitrate mass concentrations were reduced by  $0.045\ \mu\text{g}\ \text{m}^{-3}$  (STP) on average corresponding to an averaged reduction of 39 % of the initial nitrate mass concentrations. A comparison of the initial and finalized nitrate mass concentrations can be found in the Supplement (see Fig. S2).

Furthermore, we added the following to the paragraph in **Sect. 4.5 p. 19, line 2** (p. 21, line 16):

Figure 10 shows the scatter plot of the corrected  $\text{NO}^+$  and  $\text{NO}_2^+$  for the LT (dark blue) and the UT (light blue). The linear fit curves for the LT and UT have an intercept of 0, proving that the applied correction is essential. Nevertheless, it has to be noted that the correction is based on correlations between different  $m/z$  signals derived from measurements at low altitudes (Fry et al., 2018), thus the application to UT data bears uncertainties, because the conditions (especially temperature) are different. However, high resolution AMS measurements at these altitudes are currently not available.

The linear fit for the LT data shows a higher slope than that derived from calibrations with ammonium nitrate. The linear fit for the UT shows also a higher slope and some data points are significantly above the fitted ratio between  $\text{NO}^+$  and  $\text{NO}_2^+$ . This can be seen as a first hint that organic nitrates might be observed, especially in the UT.

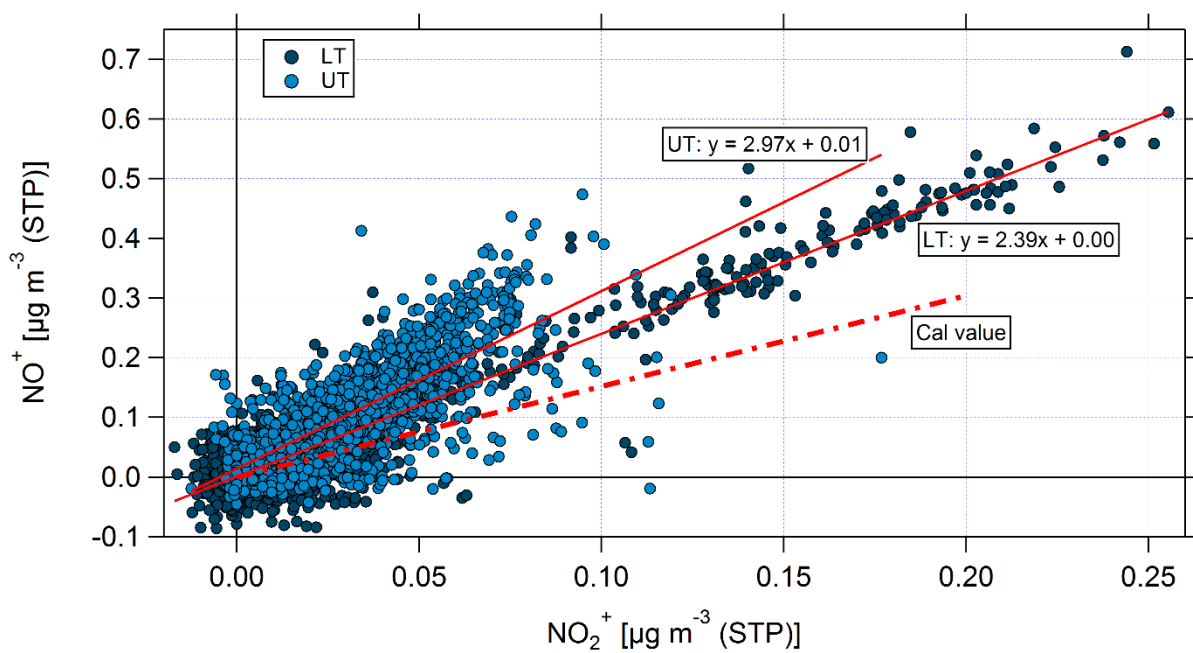


Figure 10. Scatter plot of  $\text{NO}^+$  and  $\text{NO}_2^+$  for the lower troposphere (LT, dark blue) and the upper troposphere (UT, light blue). The nitrate signals have been corrected for organic interference according to Fry et al., 2018. Linear fit curves are shown in red, the ratio of  $\text{NO}^+$  and  $\text{NO}_2^+$  derived from calibrations with ammonium nitrate is presented by the red dashed line.

We added the following to the supplement:

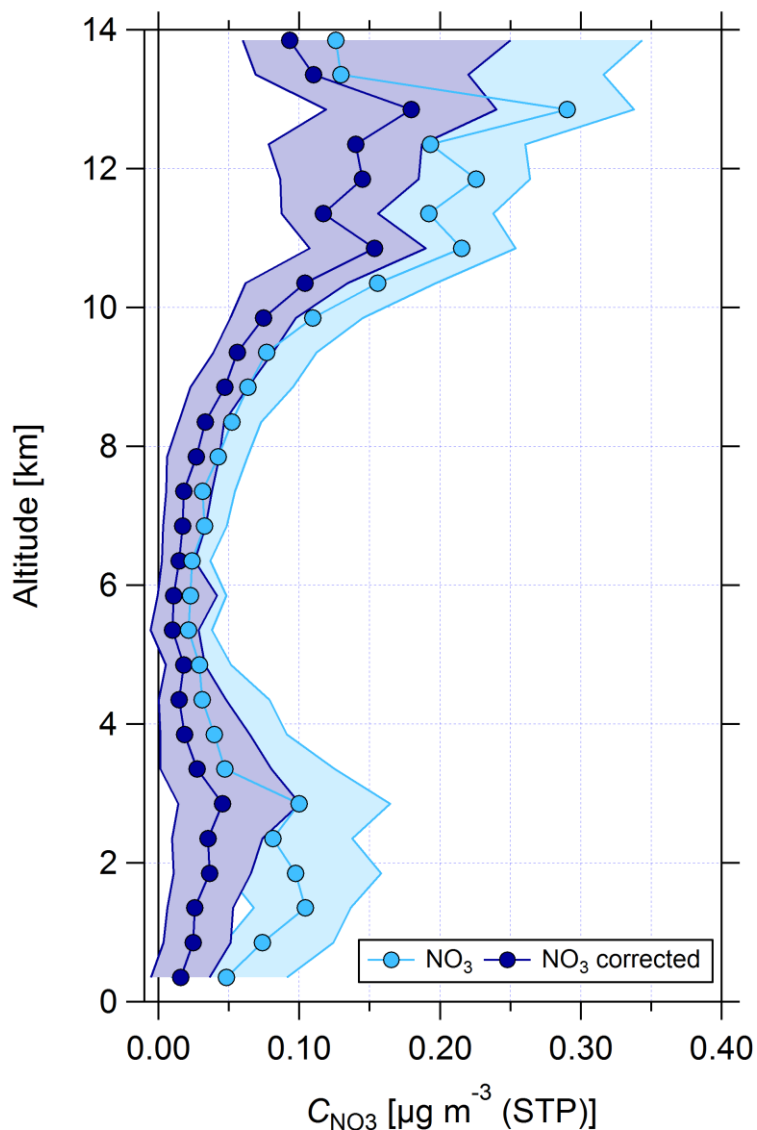


Figure S2. Vertical profile of median nitrate mass concentrations and interquartile ranges before (light blue) and after (dark blue) corrections according to Fry et al., 2018 and supplement to Fry et al., 2018.

**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  $pRONO_2$  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.**

We updated the neutralization calculation and the corresponding figure (**Fig. S3** (Fig. S6)). The aerosol is mainly neutralized although there seems to be a tendency of acidic aerosol at altitudes above 10 km. We changed the corresponding paragraph to the following in **Sect. 4.4 p. 17, line 2** (p. 20, line 8):

Although the correlation between IEPOX-SOA and nitrate is weak, it may indicate that not only sulfate, but also nitrate can provide the acidic conditions for the partitioning of IEPOX to IEPOX-SOA. For our data, taking only the inorganic species (nitrate and sulfate) into account

for acidity calculations, the aerosol is mainly neutralized (see Fig. S6). Although there is a tendency in the UT above 10 km that the measured ammonium is not sufficient to neutralize the inorganic species, a quantitative statement cannot be made as the values fall below or close by the DL. The presence of organosulfates and -nitrates could also affect the acidity calculations. As for the organonitrates the data are already corrected, for organosulfates such a similar correction is not possible with data from a C-ToF-AMS as there are no different fragmentation patterns between inorganic and organic sulfates (Farmer et al., 2010).

## References:

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.*, <https://doi.org/10.5194/acp-2018-172>, in review, 2018.

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.: Secondary Organic Aerosol (SOA) yields from NO<sub>3</sub> radical + isoprene based on nighttime aircraft power plant plume transects, *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-255>, in review, 2018.