Peroxy acetyl nitric anhydride (PAN) and peroxy acetic acid (PAA) over the Atlantic west of Africa during CAFE-Africa and the influence of biomass-burning

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Supplementary Information



Figure S1. *Upper Left:* Flight tracks during the HALO mission "CAFE-Africa". The flights took place in 2018 on the 10.08 (Fl04), 12.08 (Fl05), 15.08 (Fl06), 17.08 (Fl07), 19.08 (Fl08), 22.08 (Fl09), 24.08 (Fl10), 26.08 (Fl11), 29.08 (Fl12), 31.08 (Fl13), 02.09 (Fl14), 04.09 (Fl15). The flight tracks are colour-coded by the aircraft altitude. *Upper-right:* Tracks of the four CAFE-Africa flights in which the HALO aircraft intercepted air masses impacted by biomass burning as evidenced by elevated mixing ratios of CO (shown as the colour scale). *Lower-left* and *lower-right:* As for upper-right, but colour-coded by black-carbon and CH₃CN, respectively.



Figure S2. Time series of the biomass burning markers BCn (black carbon particle concentration), CO and CH₃CN as well as PAN and PAA for flights F04, F10, F12, and F13.



Figure S3. Correlation between CH₃CN and black carbon (BC). The indicative trend lines have slopes of BC/CH₃CN = 1800 (upper) and 180 cm⁻³ ppbv⁻¹ (lower).



Figure S4. Calculated percentage of CO, PAA and PAN remaining after transport from the biomassburning region to the point of interception during flights 04, 10, 12 and 13. The losses of CO, PAN and PAA were calculated from modelled (EMAC) temperatures, pressures, photolysis frequencies and OH-fields along the back-trajectories using rate expressions described in the text. The PAN loss frequency via its thermal decomposition or photolysis (to reform $CH_3C(O)O_2$) was modified to take its reformation through $CH_3C(O)O_2 + NO_2$ into account (i.e. the rate coefficient or photolysis frequency of the channel leading to $CH_3C(O)O_2$ is multiplied by (1-f)).



Figure S5. Details of the loss processes for PAA and PAN during transport (using Hysplit backtrajectories) for flights FL04, FL10, FL12 and FL13. R-OH+PAA was calculated from the model OH concentration and the temperature dependent expression for the OH + CH₃C(O)OOH rate coefficient. J-PAA, J-PAN1 and J-PAN2 are photolysis frequencies for PAA or PAN. k-PAN is the pressure and temperature dependent thermal decomposition rate coefficient for PAN, corrected for its reformation via recombination of CH₃C(O)O₂ and NO₂. The percentage loss of both PAA and PAN (black dashed line) is the same as in Fig. S4.



Figure S6. See Figure 2 of manuscript in which single, Hysplit-back-trajectories were shown during a biomass-burning impacted period of flights 04, 10, 12 and 13. Here these are reproduced (solid black lines) with back-trajectories for the previous and following 5 minutes (covering > 100 km in distance) which are shown as magenta lines.



Figure S7. Correlation between PAA and PAN for biomass-burning impacted periods. The two datapoints (red-squares) labelled BB4a were not included in the fit.