Airborne measurements of peroxyacetyl nitric anhydride (PAN) and peroxyacetic acid (PAA) over the Amazon rainforest: the role of isoprene and the fate of the peroxyacetyl-radical

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Supplementary information

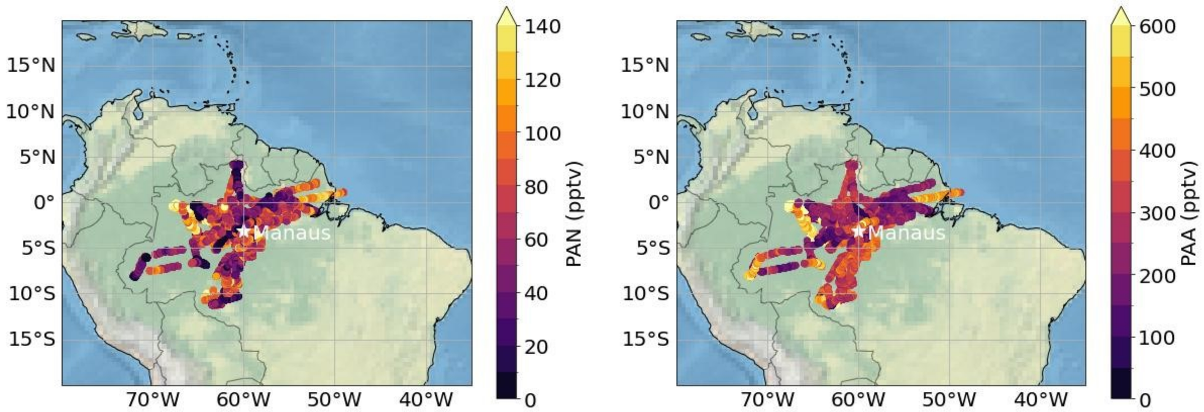


Figure S1: Mixing ratios of PAN (left panel) and PAA (right panel) along the flight tracks during the CAFE Brazil campaign.

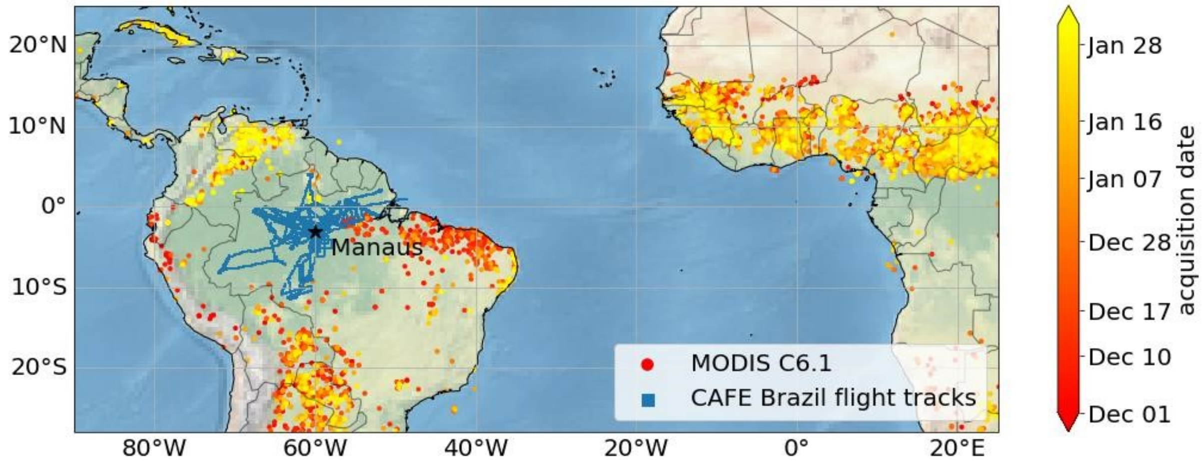


Figure S2: Open fires (MODIS satellite observations detected with >0.95 confidence) in Brazil and tropical Africa between December 2022 and January 2023, colour-coded by acquisition date (dots). The flight tracks during CAFE Brazil are marked in blue.

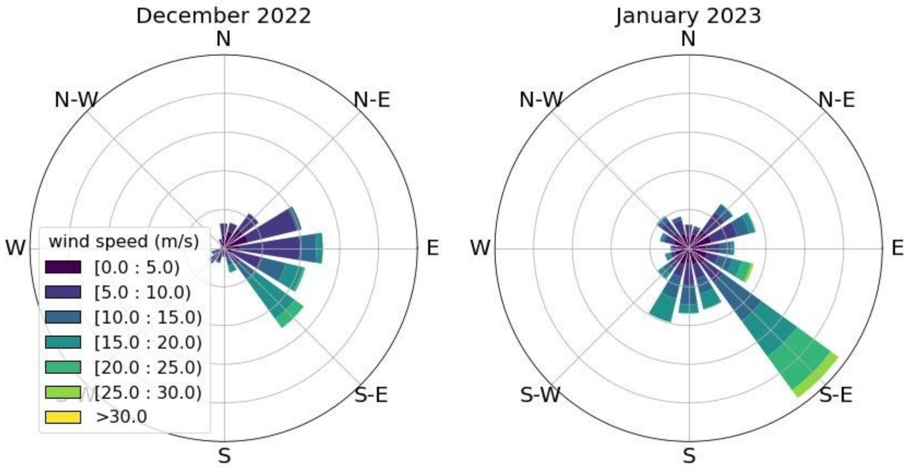


Figure S3: Frequency of wind directions and wind speeds measured with the BAHAMAS instrument aboard HALO in December 2022 (left) and January 2023 (right) during CAFE Brazil.

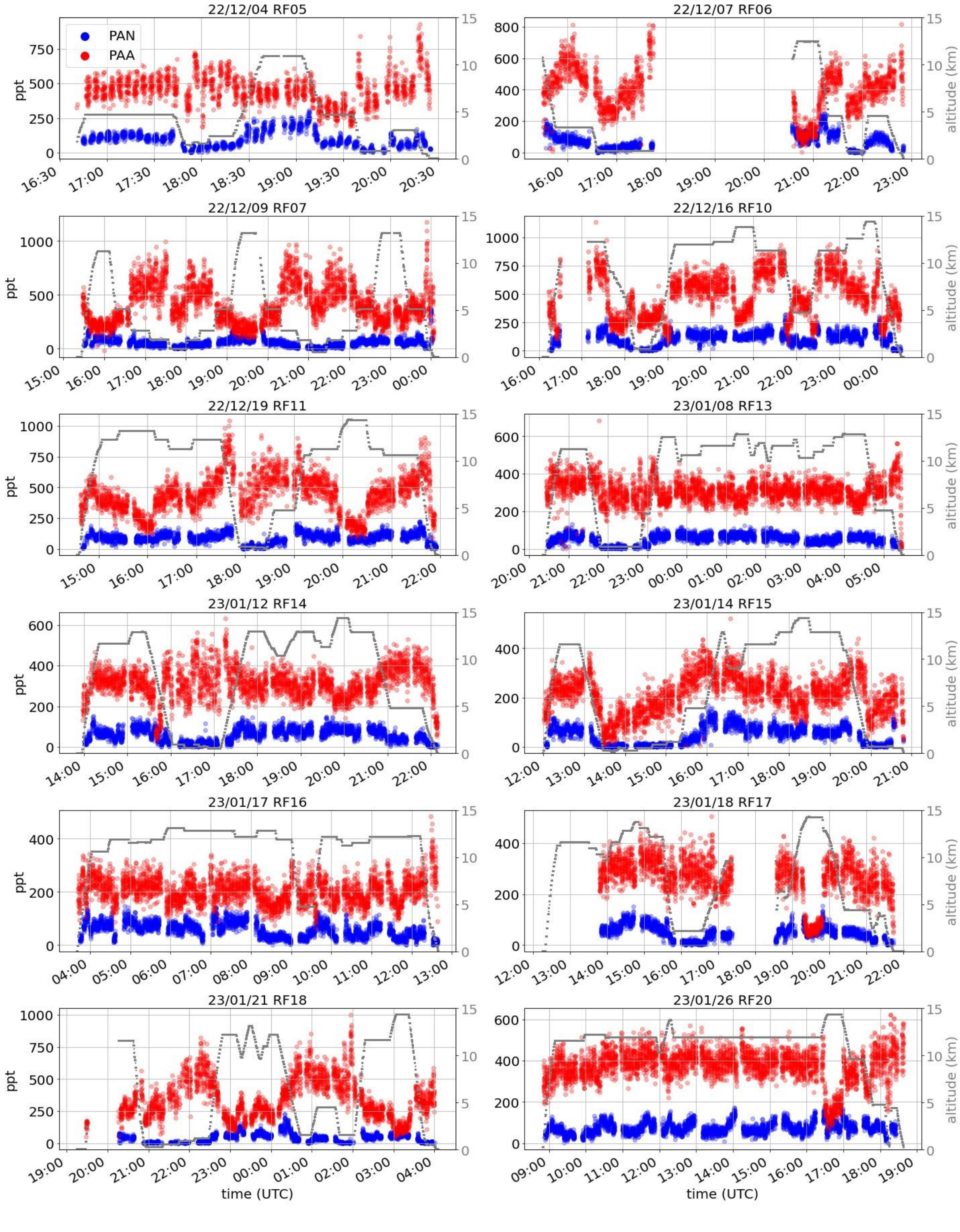


Figure S4: PAN (blue) and PAA (red) mixing ratios along the flight tracks for those flights analysed in this work.

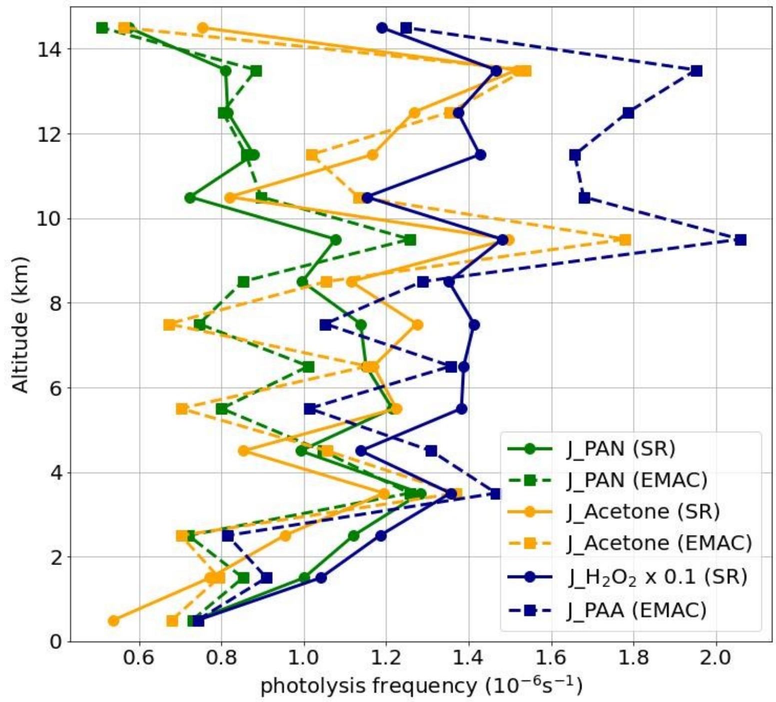


Figure S5: Median daytime values of measured (solid line with circles) and modelled (dashed lines with squares) photolysis frequencies for PAN (green), acetone (orange) and PAA (blue) for all daytime flights analysed in this work (where the modelled $J_i > 10^{-7}$ s^{-1}). Note that photolysis frequencies of PAA were not directly measured but approximated by the photolysis frequencies of H_2O_2 multiplied by a fixed factor of 0.1. This factor was derived as a typical daytime ratio between J_PAA/J_H_2O_2 above Manaus in January from the Tropospheric Ultraviolet and Visible Radiation Model (https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/).

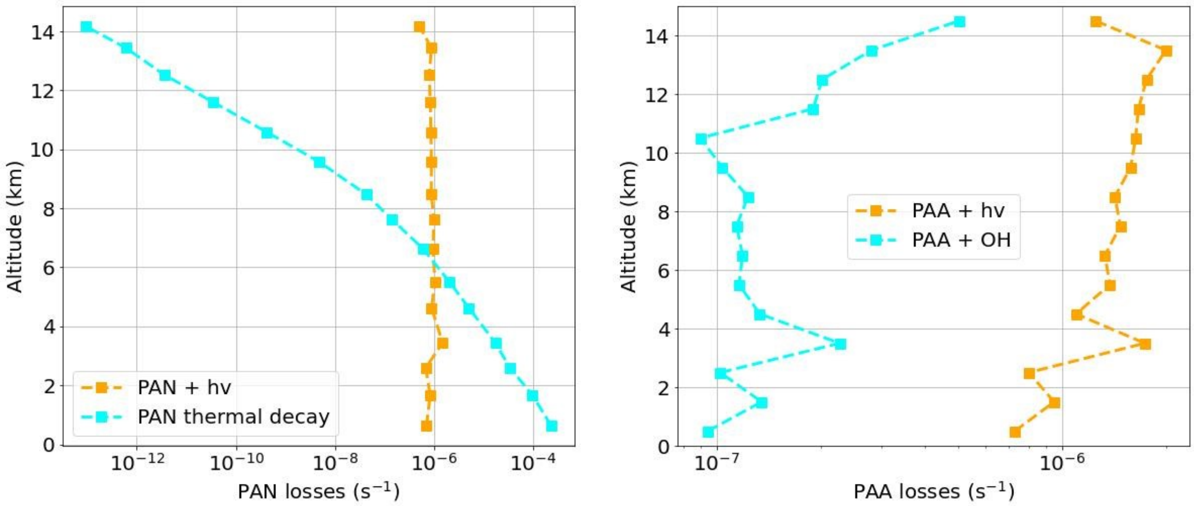


Figure S6: Left panel: Calculated loss terms for PAN using model photolysis frequencies (orange) and thermal decomposition (cyan). The thermal decompsoition rate coefficient has been corrected by the factor (1-*f*). Right panel: Calculated loss terms for PAA from model photolysis frequencies (orange) and oxidation with OH (cyan) using the latest IUPAC recommendation of the reaction rate coefficient for OH + PAA.

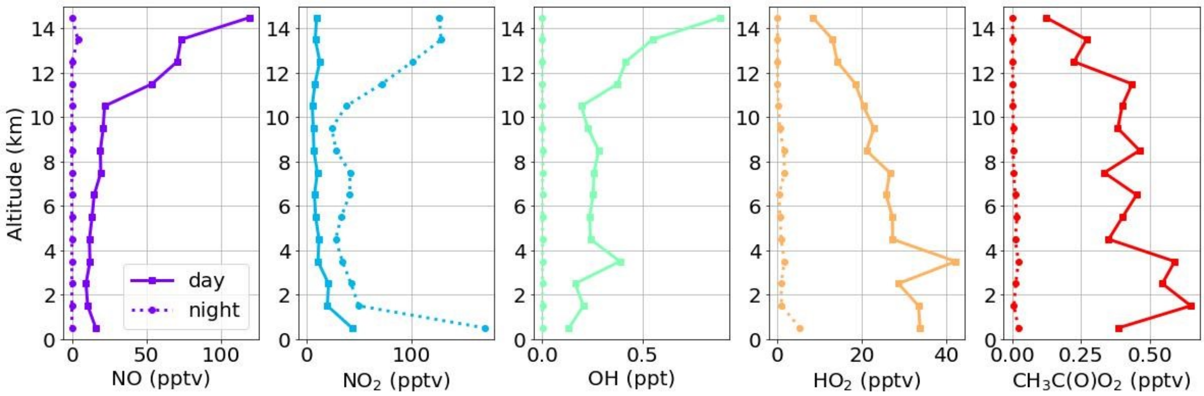


Figure S7: Median daytime (solid lines) and night time (dashed lines) vertical profiles of modelled mixing ratios of NO, NO_2, OH, HO_2 and $CH_3C(O)O_2$ along the flight tracks during the CAFE Brazil campaign.

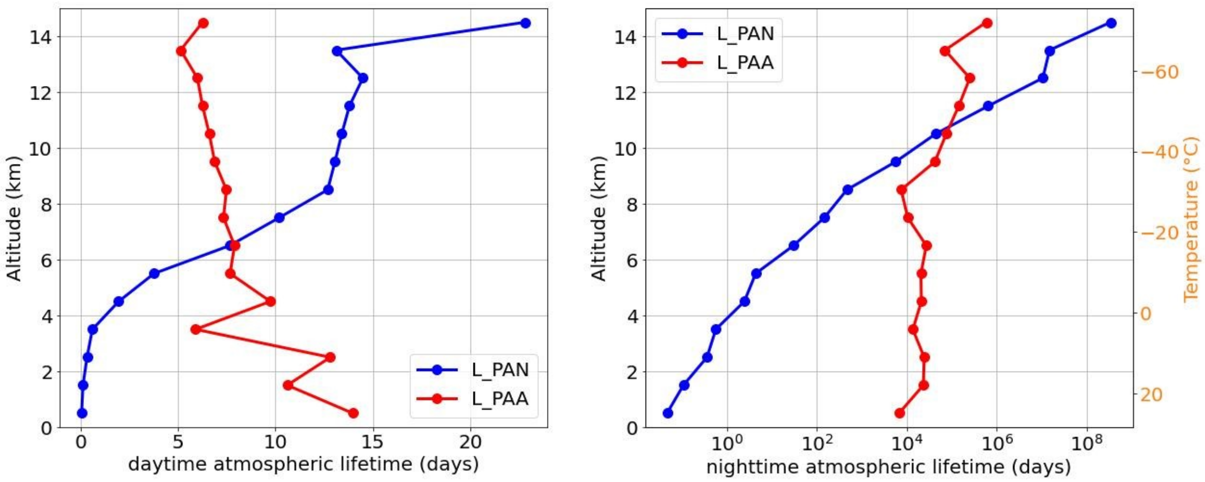
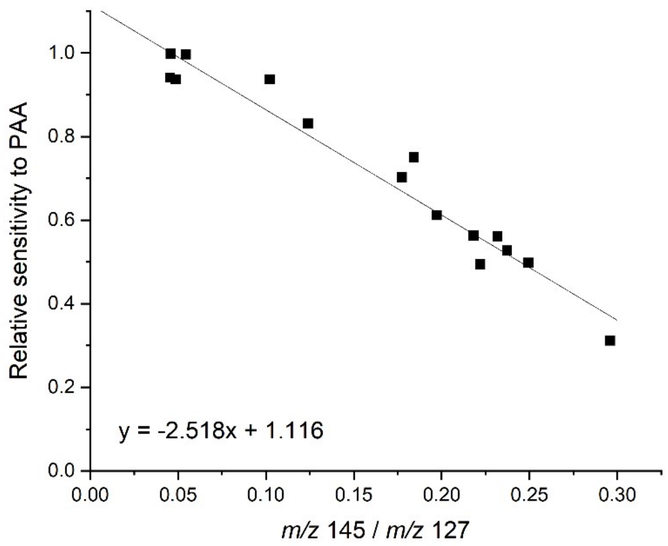


Figure S8: Median calculated atmospheric lifetime of PAN (blue) and PAA (red) during the daytime (left) and during the night time night time (right) according to Equations (5) and (6). PAN losses include the thermal and photolytic decay, PAA losses include photolytic decay and reaction with OH.

Total measurement uncertainty on PAN and PAA

The total measurement uncertainty for PAN measurements during CAFE Brazil is estimated as 30% and includes the variability of the instrument's sensitivity during a flight derived from the in-flight calibrations (4-12%), the uncertainty on the NO calibration gas standard (< 5%), the uncertainty on the conversion efficiency of NO to PAN (5%) and uncertainty on the potential losses of the $CH_3CO_2^-$ ion (*m/z* 59) during calibration owing to reactions with formic acid (6%) and other acids (not quantified) formed in the photochemical calibration source.

The major source of uncertainty for the PAA measurements is the instrument's sensitivity which was calibrated only once (under dry conditions) during the CAFE Brazil campaign. A further attempt to cross-calibrate was made in January but had to be rejected due to HYPHOP operational problems caused by intruded water. Eight out of the twelve flights analysed during CAFE Brazil took place in January and may therefore have a higher uncertainty for the PAA sensitivity.
In addition, the sensitivity of the CIMS for PAA depends strongly on the relative humidity, or more accurately, the concentration of H_2O in the IMR which modifies the relative concentrations of I^- and its water cluster (I^-H_2O). Corrections were made as described previously (Crowley et al.) by monitoring the ratio of signal attributed to I^- (*m/z* 127) and I^-H_2O (*m/z* 145) as shown below. The largest humidity dependent corrections during Cafe-Brasil were ~ factor 2.5 (when flying in the boundary layer).



Given the uncertainties on the HYPHOP instrument for measuring PAA as previously described in Crowley et al. 2025 (50%), and the fact that the relative-sensitivity of the CIMS to PAA and PAN varied 1) between campaigns and 2) when compared to laboratory calibrations by a factor of ~two (despite both molecules being measured at the same mass) we prefer to quote a conservative measurement uncertainty of 100% to the PAA measurements (plus the uncertainty associated with the humidity correction).