



Supplement of

Measurement report: Sources, sinks, and lifetime of NO_x in a suburban temperate forest at night

Simone T. Andersen et al.

Correspondence to: Simone T. Andersen (simone.andersen@mpic.de) and John N. Crowley (john.crowley@mpic.de)

The copyright of individual parts of the supplement might differ from the article licence.

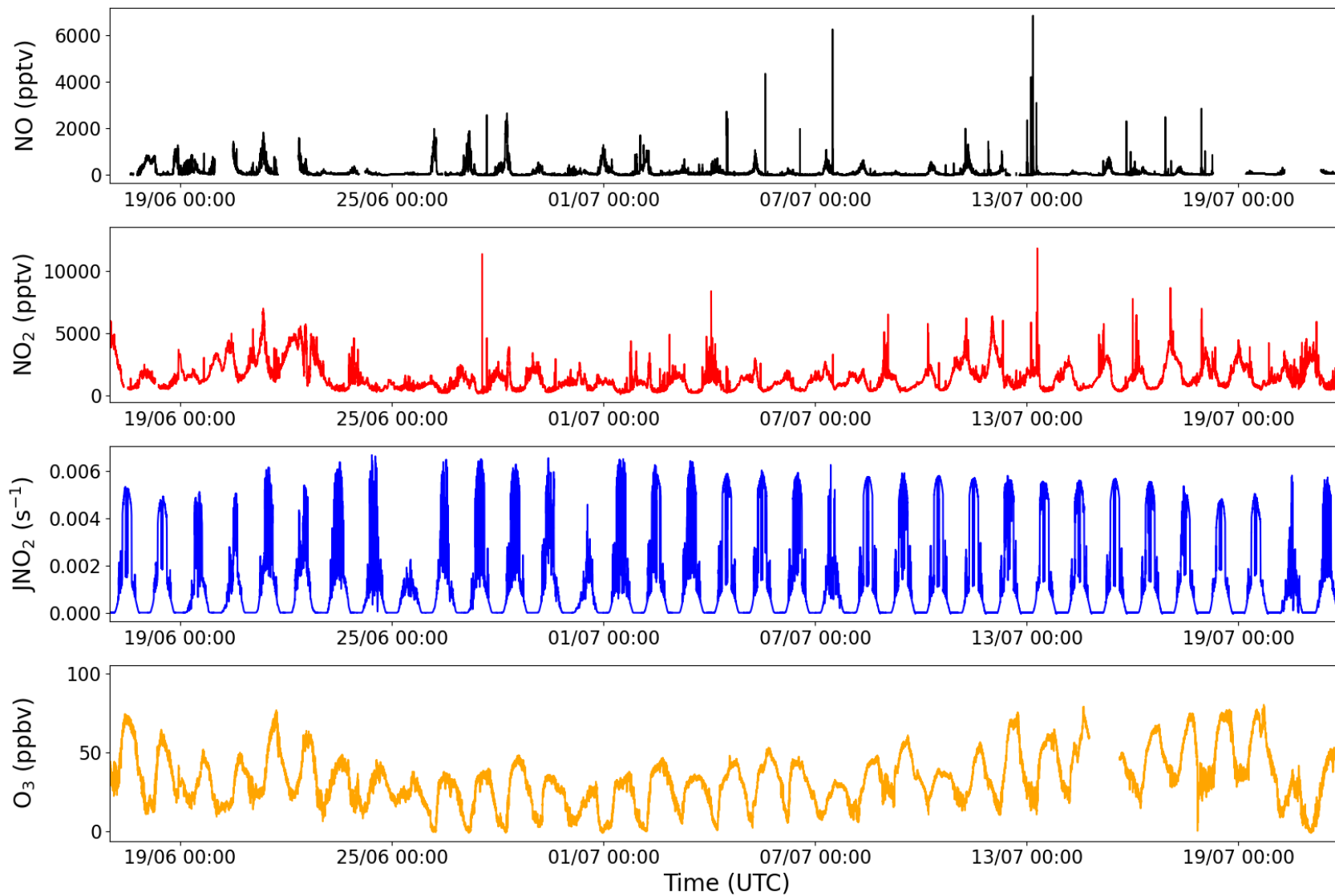


Figure S1: Time series of NO, NO₂, JNO₂, and O₃ between June 17th 2022 and July 22nd 2022 measured at 3-6 m above ground at the Rambouillet supersite during ACROSS.

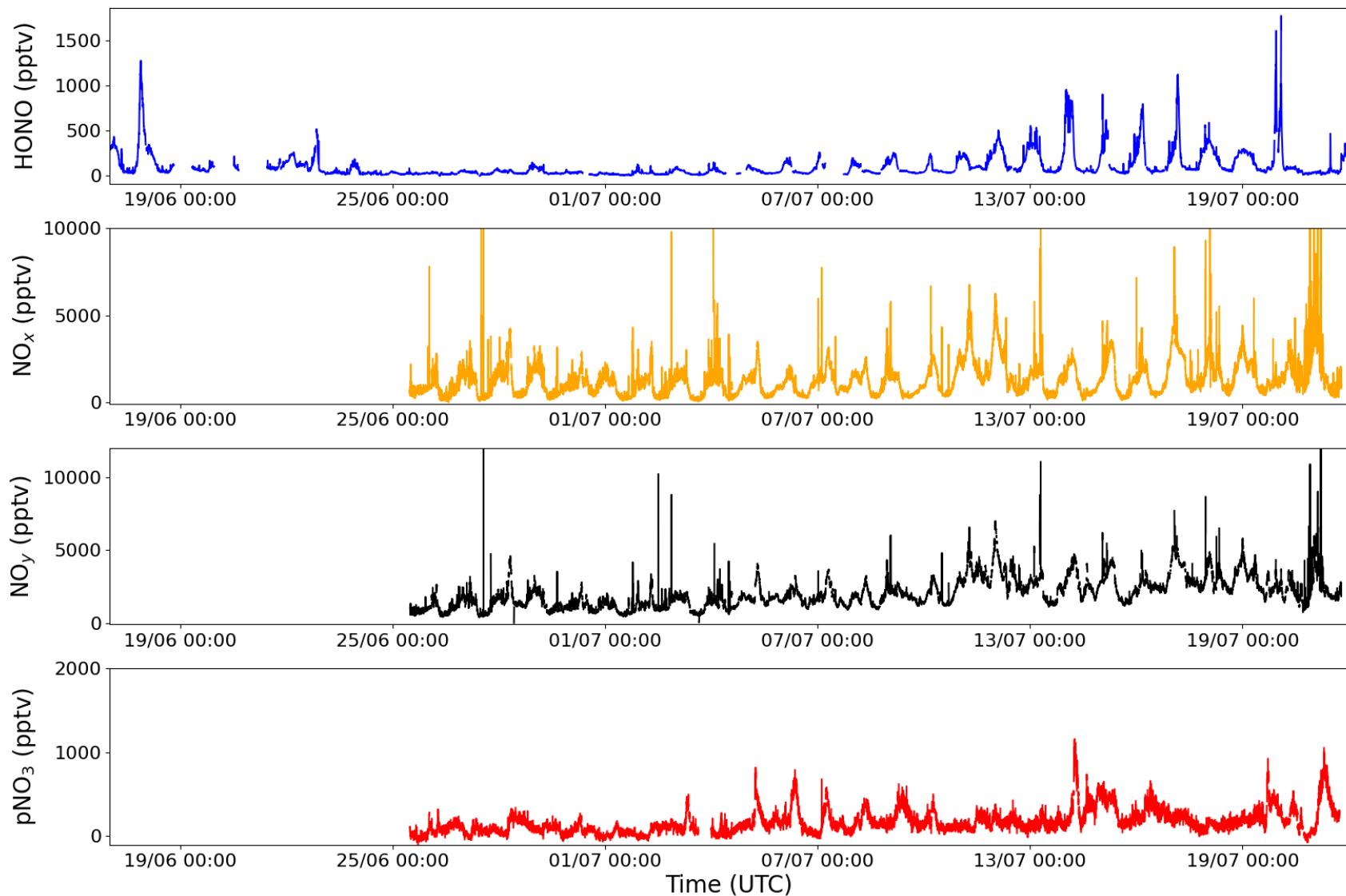


Figure S2: Time series of HONO, total NO_x, NO_y, and particulate nitrate (pNO₃) between June 17th 2022 and July 22nd 2022 measured at 2-6 m above ground at the Rambouillet supersite during ACROSS.

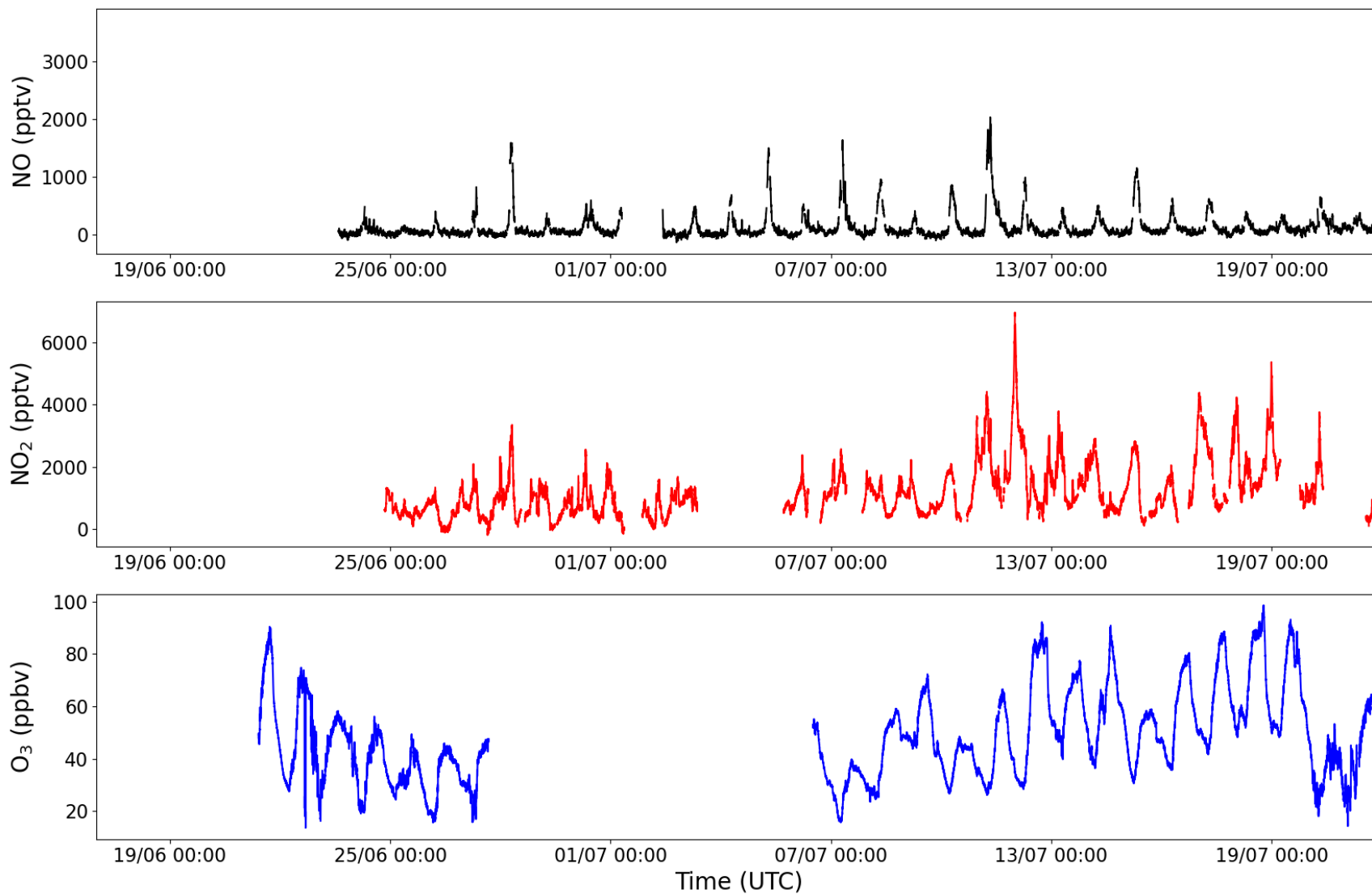


Figure S3: Time series of NO, NO₂, and O₃ between June 17th 2022 and July 22nd 2022 measured at 41 m above ground at the Rambouillet supersite during ACROSS.

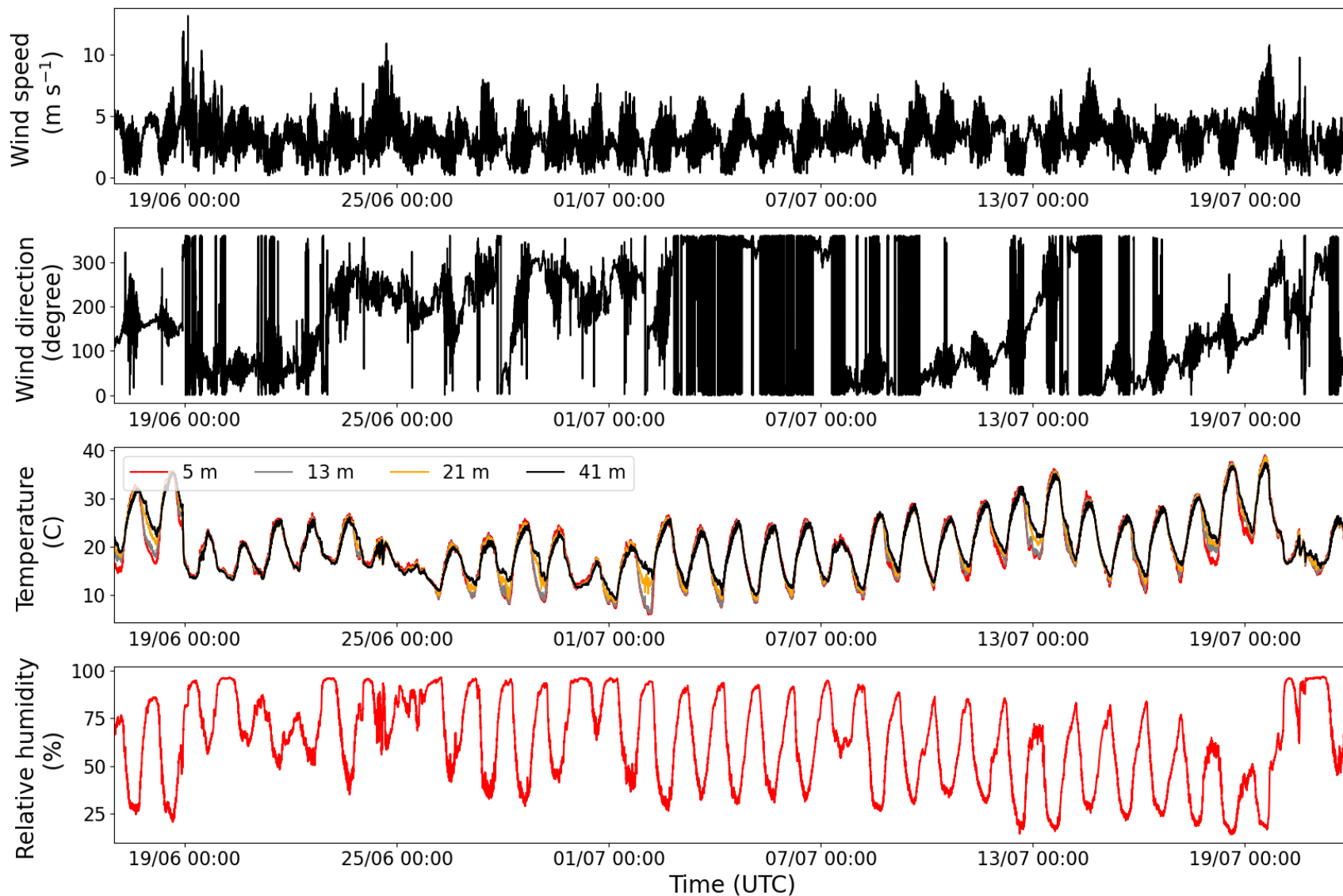


Figure S4: Time series of wind speed and direction, temperature, and relative humidity between June 17th 2022 and July 22nd 2022 measured at 5 m (red), 13 m (grey), 21 m (orange), and 41 m (black) above ground at the Rambouillet supersite during ACROSS.

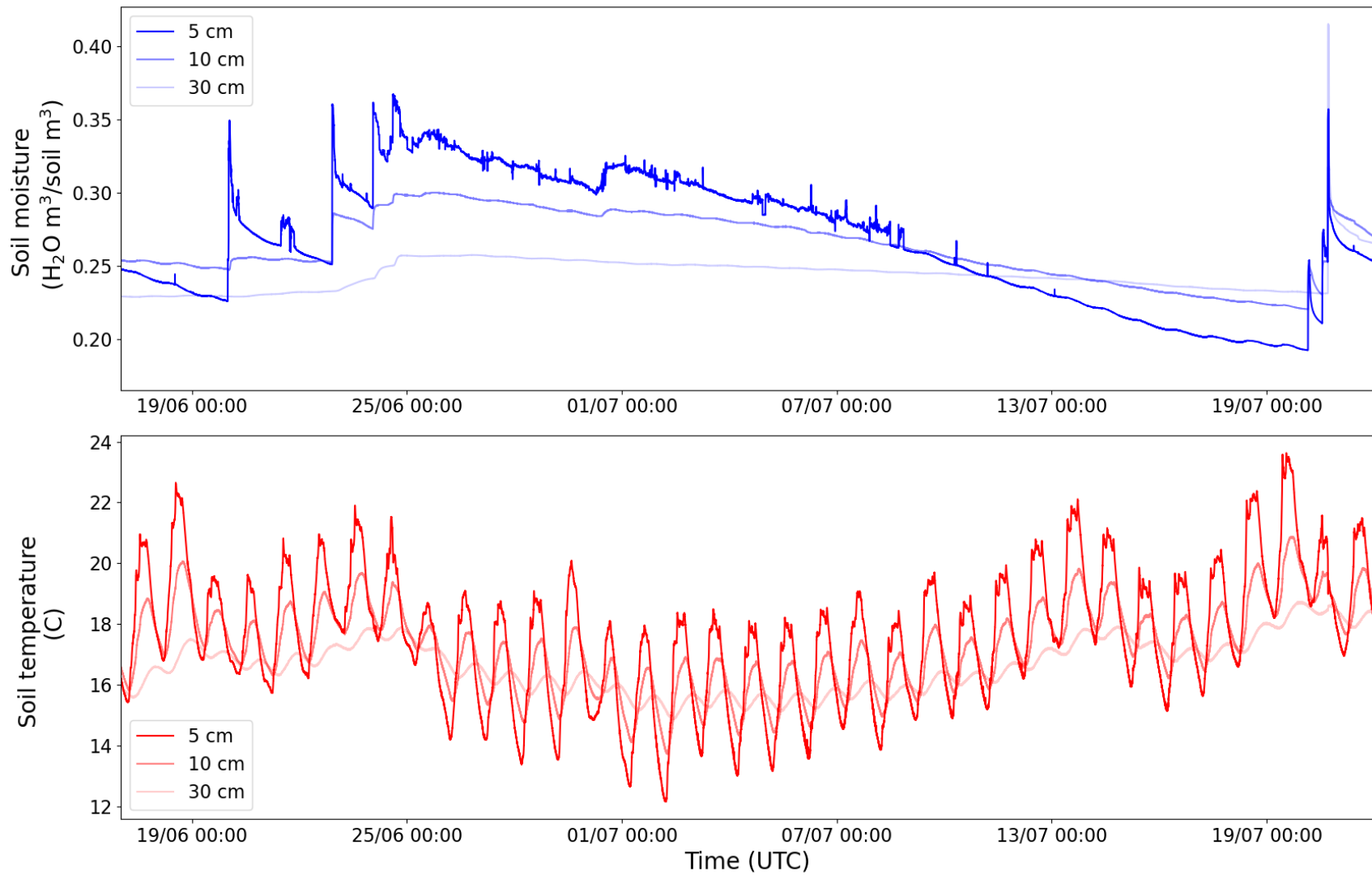


Figure S5: Time series of soil moisture and temperature between June 17th 2022 and July 22nd 2022 measured at 5, 10 and 30 cm below ground at the Rambouillet supersite during ACROSS.

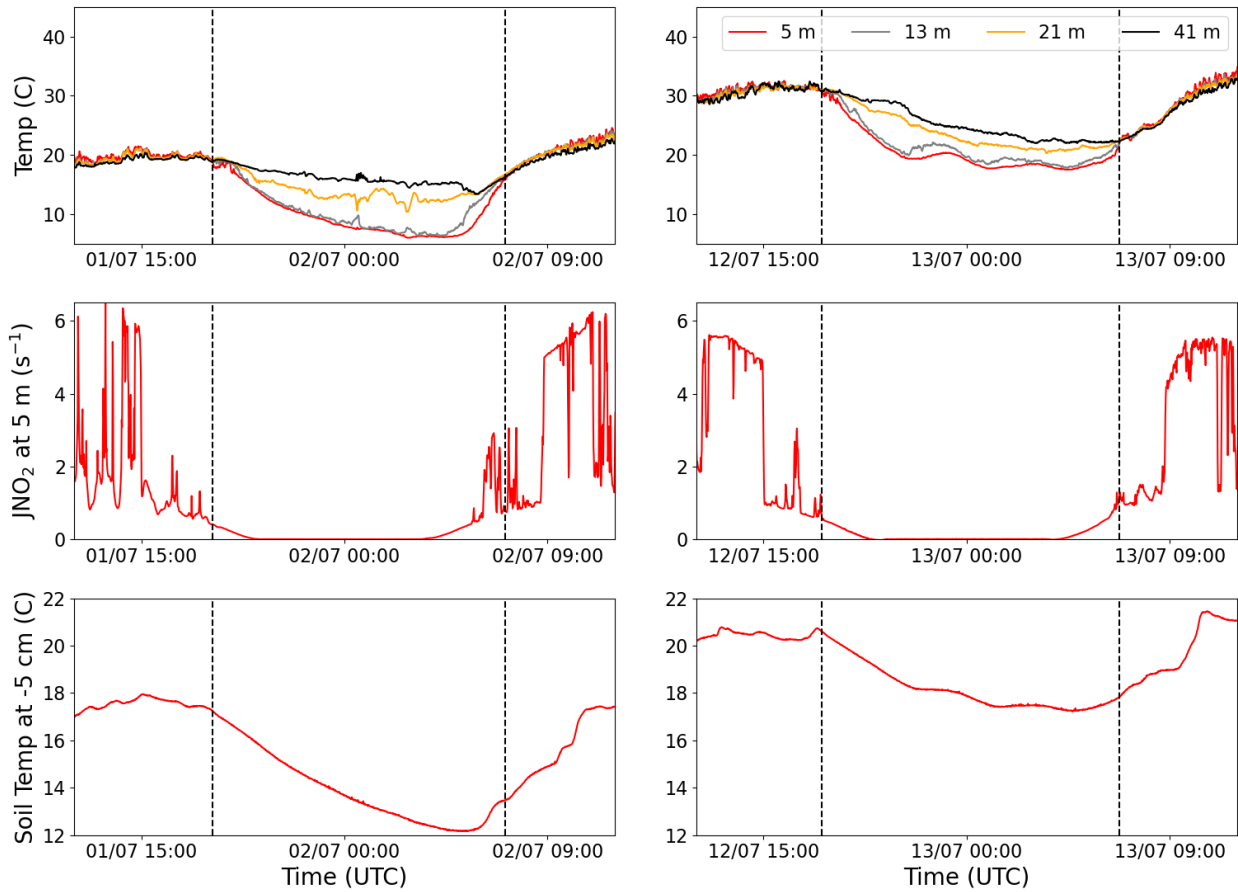


Figure S6: Temperature at 5 m (red), 13 m (grey), 21 m (orange), and 41 m (black), NO₂ photolysis rates (JNO₂) at 5 m, and soil temperature 5 cm below the surface plotted for two nights during ACROSS with large temperature inversions (beginning and end marked with dashed black lines). The temperature inversions begin on both nights when the soil temperature begins to decrease.

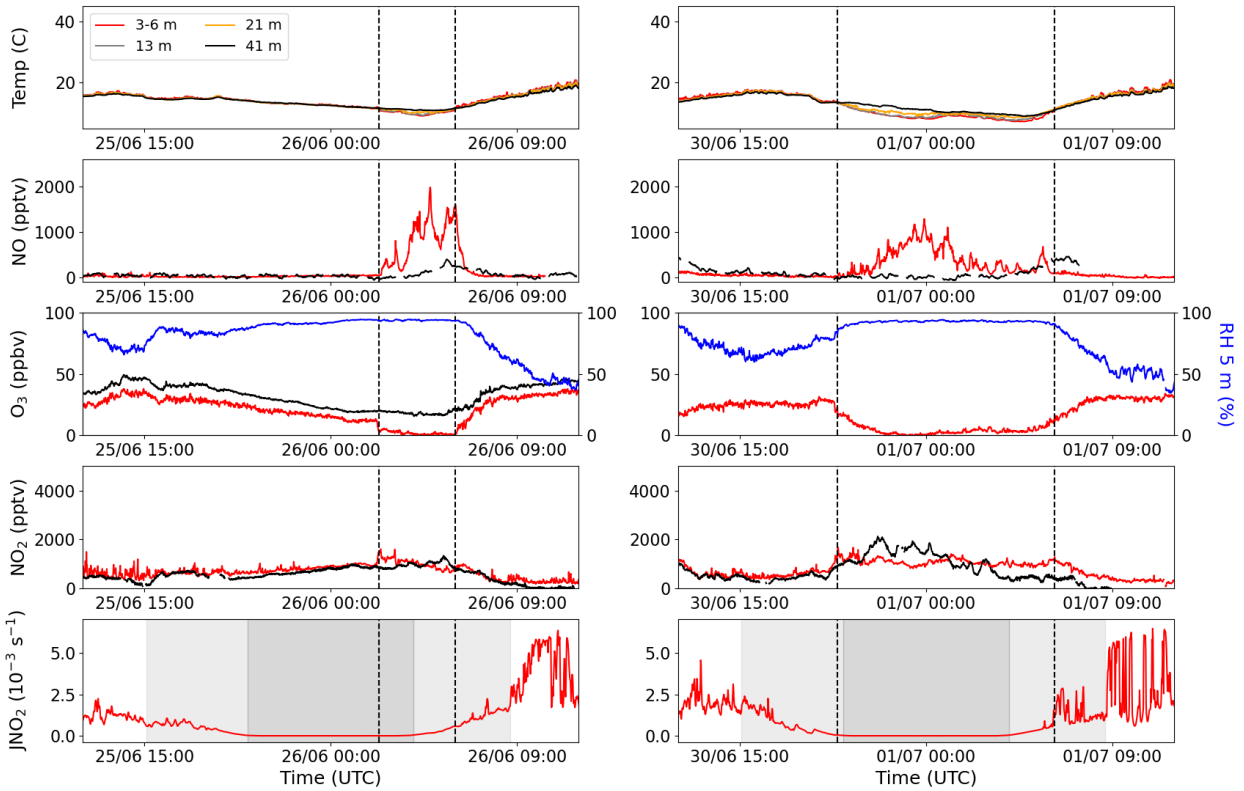


Figure S7: Measurements of temperature, NO, O₃, RH, NO₂, and JNO₂ for two different nights during the Atlantic part of the campaign. The different colours symbolize four different heights; red = 3-6 m, grey = 13 m, orange = 21 m, and black = 41 m, and the blue shows the RH at 5 m. The grey shaded areas in the JNO₂ plots shows the time the MPIC container was in shade during the afternoon and morning (light grey) and nighttime (dark grey). The vertical black dashed lines indicate the beginning and end of the observed temperature inversions in the top panels.

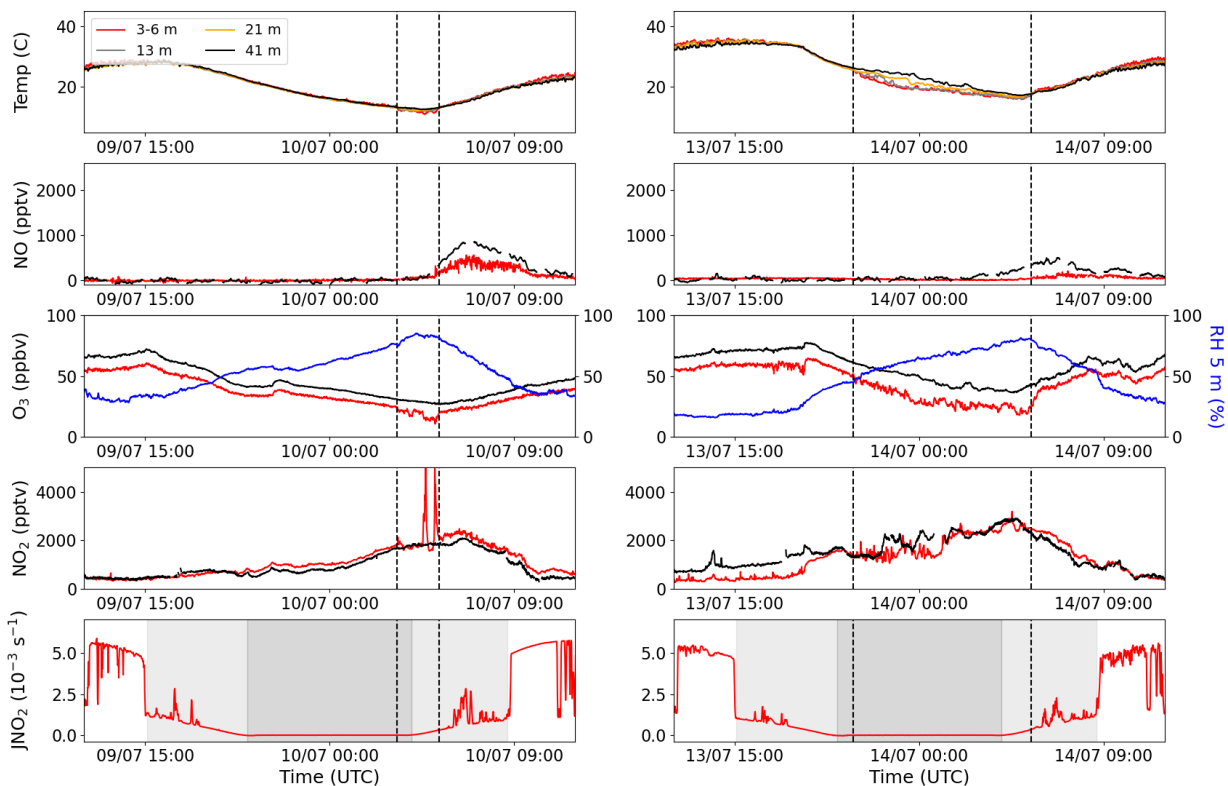


Figure S8: Measurements of temperature, NO, O₃, RH, NO₂, and JNO₂ for two different nights during the Continental part of the campaign. The different colours symbolize four different heights; red = 3-6 m, grey = 13 m, orange = 21 m, and black = 41 m, and the blue shows the RH at 5 m. The grey shaded areas in the JNO₂ plots shows the time the MPIC container was in shade during the afternoon and morning (light grey) and nighttime (dark grey). The vertical black dashed lines indicate the beginning and end of the observed temperature inversions in the top panels.

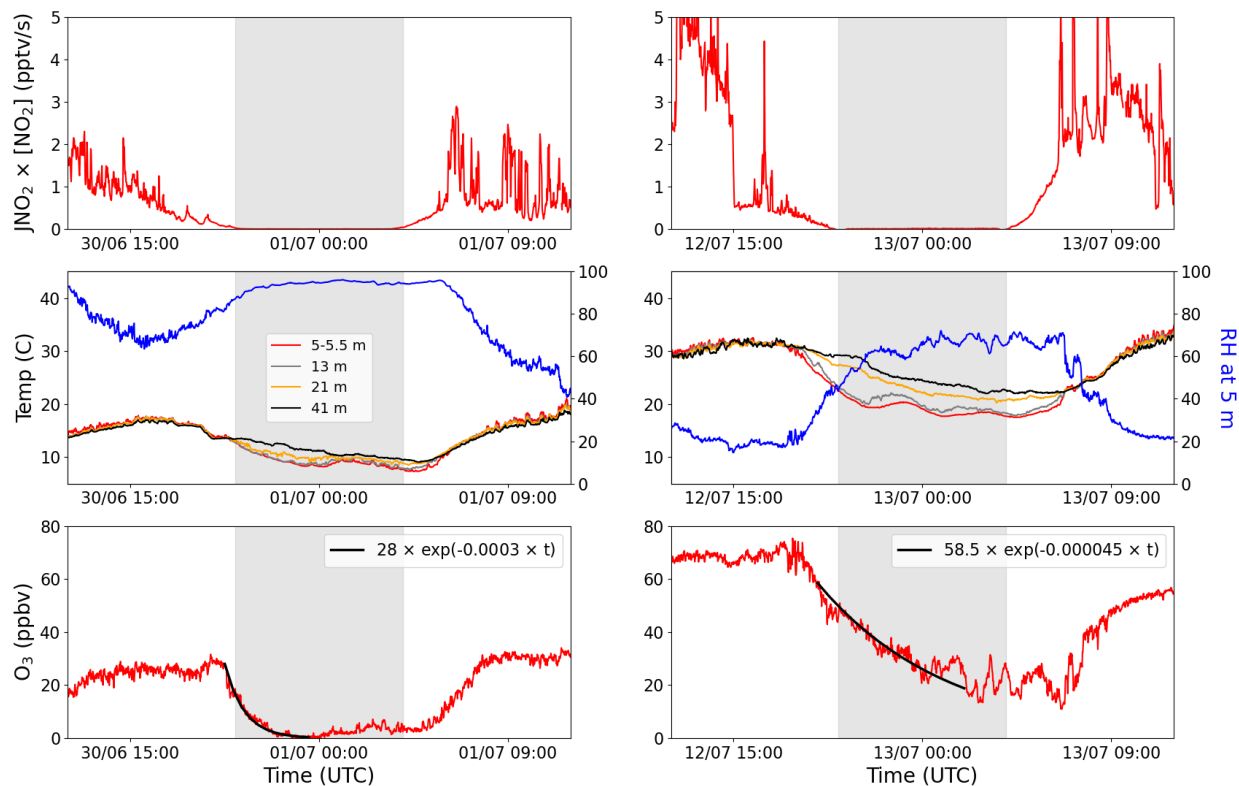


Figure S9: The production of O_3 ($JNO_2 \times [NO_2]$), temperature, RH, and O_3 plotted for two nights with observed temperature inversions; one high RH (left panels) and one with lower RH (right panels). The different colours symbolize four different heights; red = 5-5.5 m, grey = 13 m, orange = 21 m, and black = 41 m, and the blue shows the RH at 5 m. The net nighttime O_3 loss is fitted with an exponential decay curve in the bottom plots. The grey shaded areas show the nighttime, where no sunlight is present.

Corrections applied to the CLD NO-dataset

As indicated in the main text, a chemiluminescence device (CLD) was used for measurement of NO. The basic operational principal is the optical detection of fluorescence from NO₂* (electronically excited NO₂) following its formation in the reaction of NO with a large excess of O₃. The fractional conversion of NO to NO₂* and thus the sensitivity of the CLD depends on the reaction time and the concentration of O₃. O₃ is formed via O₂ photolysis using the 184.95 nm line of a low-pressure Hg-lamp. In normal operation, the amount of O₃ is maximised by using pure O₂ instead of air as the photolyte. During the ACROSS campaign the supply of O₂ was interrupted for several days (02.07.2022 at ~ 15:00 to 12.07.2022 at ~ 09:30) in which time an air flow was used instead. As calibrations of the CLD were not carried out during the campaign, the loss of sensitivity in this period was established by comparing CLD-NO measurements with those calculated from NO_x – NO₂, both measured using cavity-ring-down-spectroscopy, CRDS during the three phases (times are UTC) defined as:

- Phase 1 CLD operation with O₂ (until 02.07.2022, 15:00)
- Phase 2 CLD operation with air (02.07.2022, 15:00 to 12.07.2022, 09:30)
- Phase 3 CLD operation with O₂ (12.07.2022, 09:30 until end of campaign)

On order to do this as accurately as possible, we used only time periods in which features in the the CRDS-(NO_x-NO₂) were well above detection limit for prolonged periods.

Correlation plots of NO (CLD) versus NO_x-NO₂ (CRDS) are shown below for distinct NO features during each campaign phase. In each case, correction factors were applied to the NO (CLD) dataset to generate a slope of unity. The correction factors thus derived are 0.77 (Phase 1), 2.21 (Phase 2) and 0.91 (Phase 3). As expected, a large correction factor was required to align the data in phase 2, when the CLD was operated with air instead of O₂. The ratio of CLD sensitivity to NO when using O₂ compared to air is 2.6 ± 0.2 .

A correction procedure was also applied to the NO (CLD) dataset to account for differences in the back-ground signal during each of the phases described above. In order to do this, we make the assumption that the most frequent NO mixing ratio at nighttime is zero, as evidenced by periods of very low variability (in contrast to NO₂). Apparent NO mixing ratios well above zero (up to 100 pptv) on some nights which displayed little or no variability are unlikely to be real but related to too-infrequent zeroing of the instrument, which was carried out only a few times during the campaign. The maximum in the frequency distribution of the NO mixing ratio was observed in bins centered at 50, 10 and 110 ppt for phases 1, 2 and 3, respectively. These values were thus subtracted from the NO (CLD) measurements.

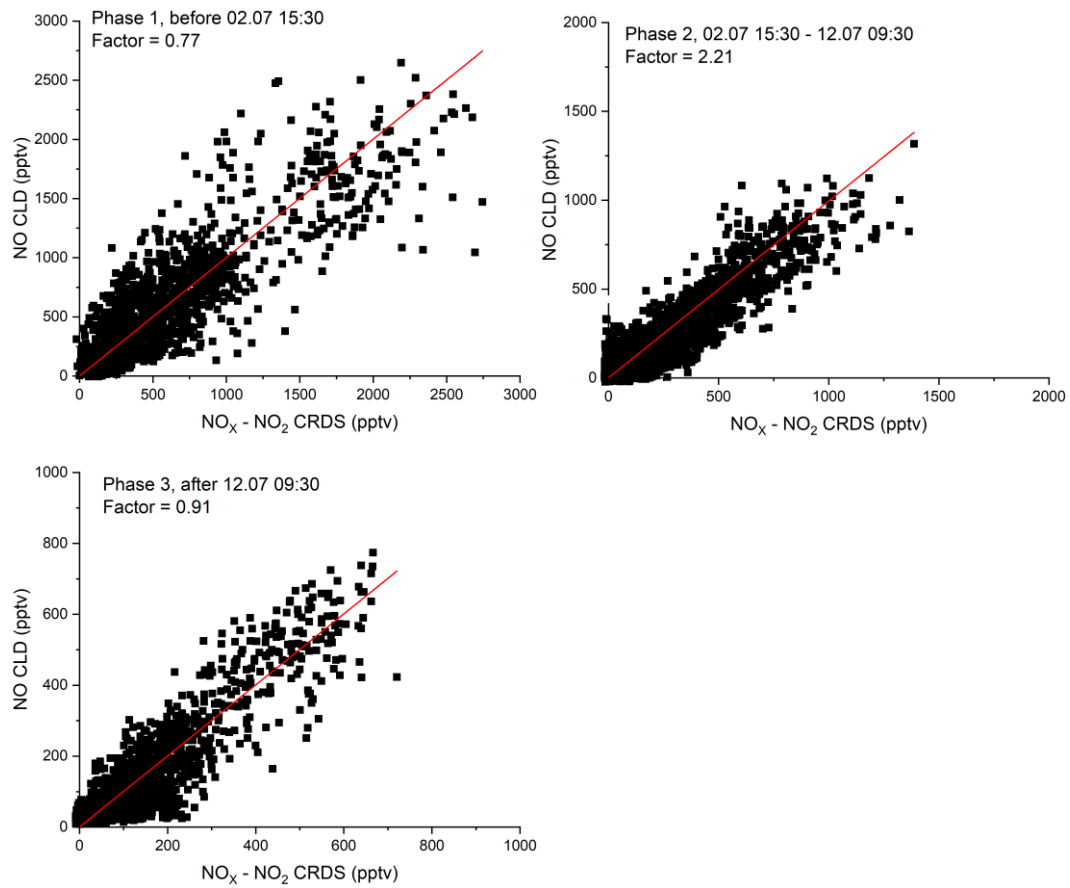


Figure S10. Plot of NO (measured by the CLD) versus $\text{NO}_x - \text{NO}_2$ (measured by CRDS) during three campaign phases. In each case, the factor in the legend has been applied to the NO (CLD) dataset to generate a slope of 1.

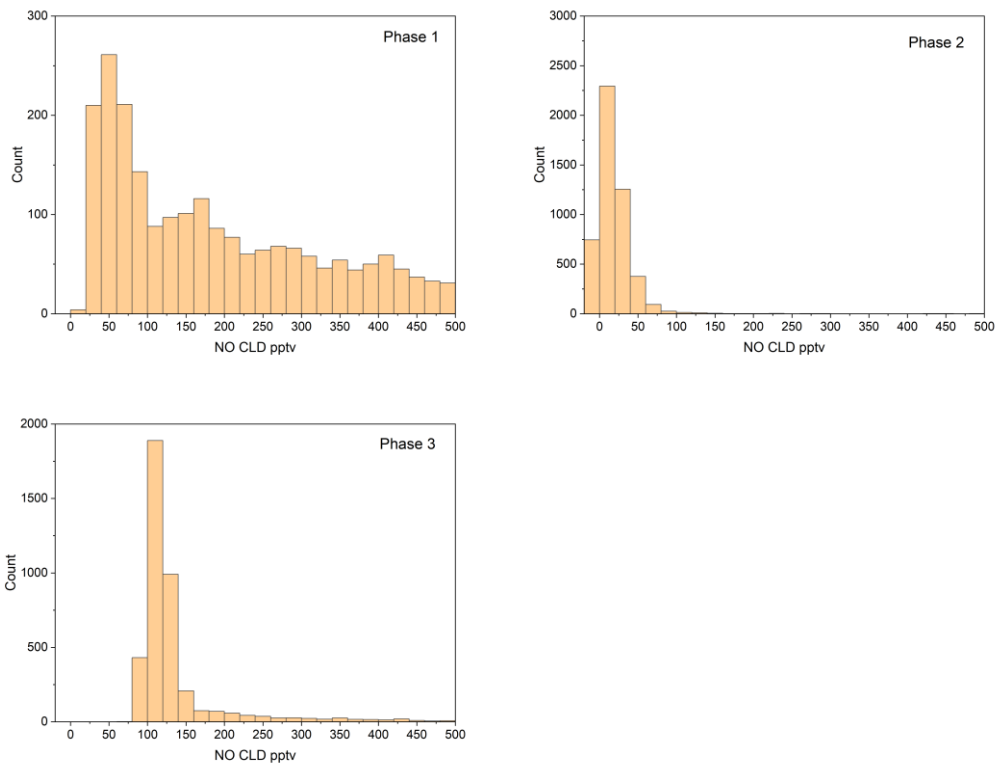


Figure S11. Frequency distribution of NO (CLD) measurements at nighttime during ACROSS. The Phases are the same time periods as described above and in Fig. S10. The NO mixing-ratio in the bin centered at the peak of the distribution was subtracted from the NO-dataset.