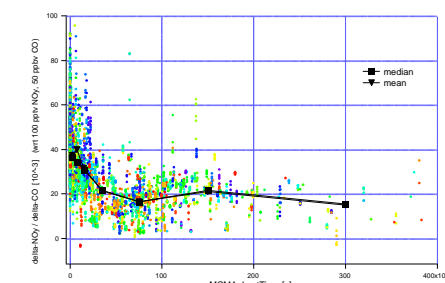
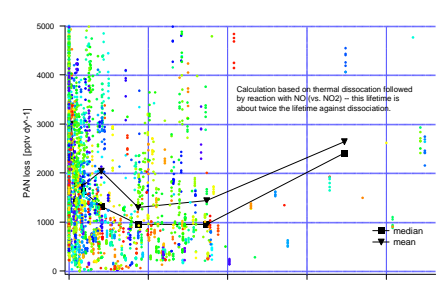
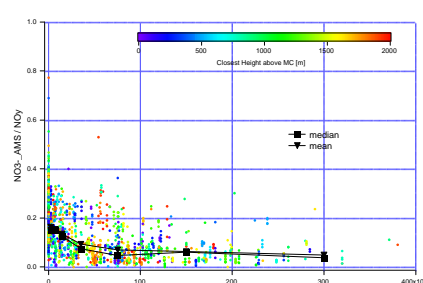
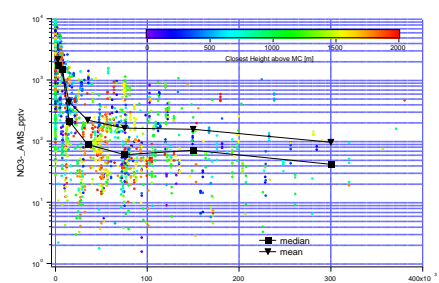
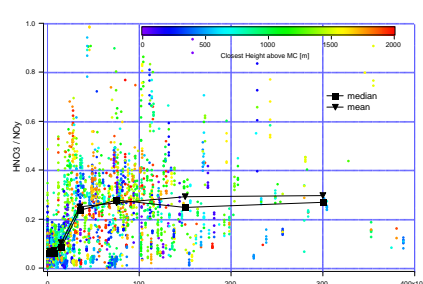
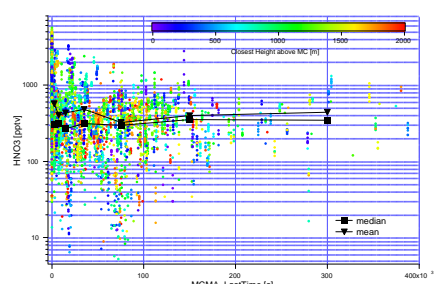
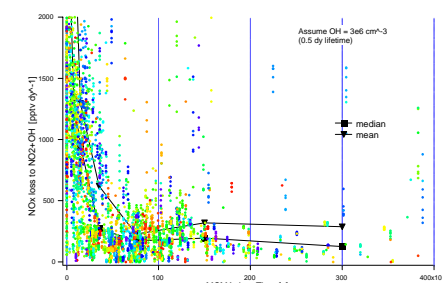
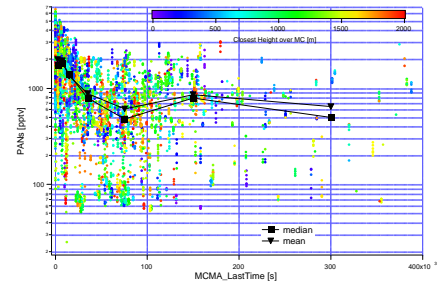
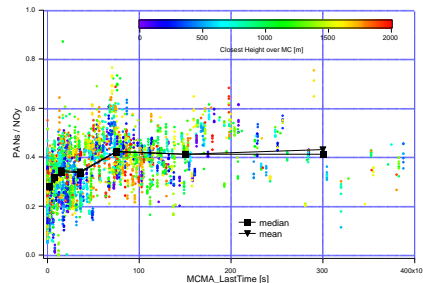
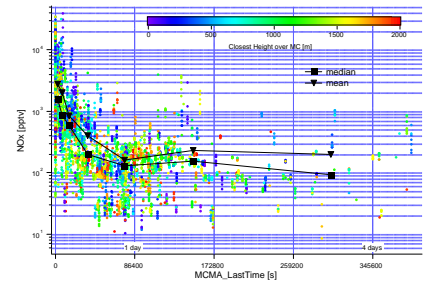
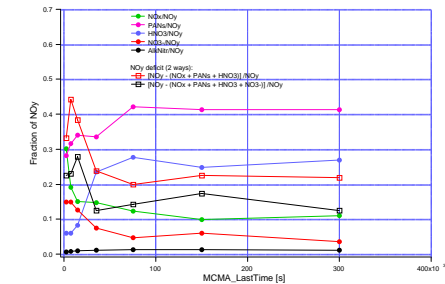
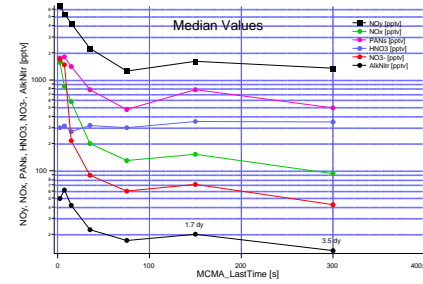
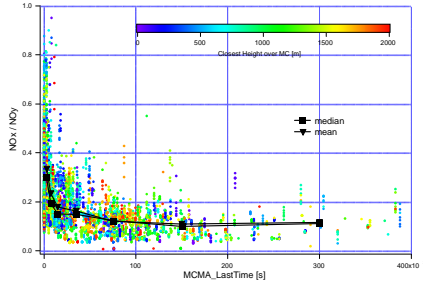
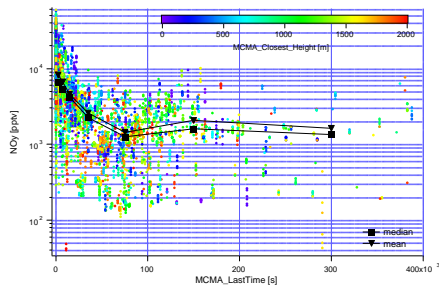


# NO<sub>y</sub> Partitioning, and its Evolution, Measured on the C130 during MIRAGE

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**General Approach:** The partitioning of NO<sub>y</sub> is examined as a function of the size (emission of pollutants) of air is determined using calculations of back-trajectories to trace the history of air parcels prior to sampling along the track of the C130. Measurements are included for those parcels which traveled over Mexico City at heights up to 2 km above the surface.

**Specifics:** The trajectories were calculated using FLEXPART-WRF with wind fields from WRF MIRAGE operational forecasts. C130 measurements from a 10-s merge are plotted versus "MCMA\_LastTime [s]", which, according to the trajectory calculations, was the last time (ago) that the C130-sampled air was over Mexico City (for all plots the x-axis extends to an age of  $4 \times 10^5$  s = 4.6 dy). The results are not very sensitive to the 2-km height value chosen to restrict the results to likely boundary layer traverses over Mexico City.



## Results:

After 24 hours, there is little reduction in the absolute magnitude of NO<sub>y</sub> (plot at upper left); NO<sub>y</sub> is somewhat conserved over days 1-3, with little loss (or dilution), at least in the mean/median. The lack of loss is corroborated by a plot (lower right) of delta-NO<sub>y</sub>/delta-CO (ratio of increments above "background"), which is relatively flat after day 1. However, a decrease during the first day indicates loss during that time relative to CO, which is conserved on this time scale.

NO<sub>x</sub> also shows little decline over days 1-3, both in absolute amount and as a fraction of NO<sub>y</sub>, after an initial drop during day 1. The calculated lifetime against loss via OH+NO<sub>2</sub> is only 0.5-1.0 dy, implying a source from PAN decomposition in order to maintain NO<sub>x</sub> at a near-constant 100-150 pptv (median) over days 1-3.

Total PANs also show little change after 1 day. The median calculated lifetime for PAN is about 1 day and implies a large source of NO<sub>x</sub> due to "irreversible" decomposition (plot at right), much larger than the loss of NO<sub>x</sub> via OH+NO<sub>2</sub> (also at right). However, much of this NO<sub>x</sub> may recycle back into new PAN formation, in view of the large amounts of acetaldehyde present (not shown), thereby maintaining the nearly constant PANs over days 1-3, even though the lifetime is much shorter than that. Significant O<sub>3</sub> formation is expected in conjunction but is not readily apparent using this approach (plot not shown, but median O<sub>3</sub> relatively flat over days 1-3 at 55-60 ppbv). A more complete understanding of the interplay of NO<sub>x</sub>, PAN, and O<sub>3</sub> awaits further analysis, especially using models and perhaps considering the evolution of individual air parcels rather than the means/medians of the dataset as a whole (scatter is large).

In the mean/median, HNO<sub>3</sub> is relatively constant at 300-400 pptv, and after the day-1 decrease in NO<sub>y</sub>, has an NO<sub>y</sub> fraction of a steady 25%.

Aerosol nitrates also decrease during day 1, but do so much more dramatically than other species, especially in the first 1/4 day (see plot of medians above), dropping to median values of 40-70 pptv over days 1-3.

The C<sub>1</sub>-C<sub>4</sub> alkyl nitrate fraction of NO<sub>y</sub> is small, at ~1% (median values shown above).

The NO<sub>y</sub> deficit is 15-20% after day 1 (top right), but it shows an interesting peak during the first half-day, suggesting the presence of short-lived contributors, not measured individually, and so not accounted for in the deficit calculation. The analysis of the NO<sub>y</sub> deficit of course awaits a detailed error analysis in order to determine its significance.