HONO Sources to the Troposphere

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HONO measurements from the NOAA P3 during SENEX

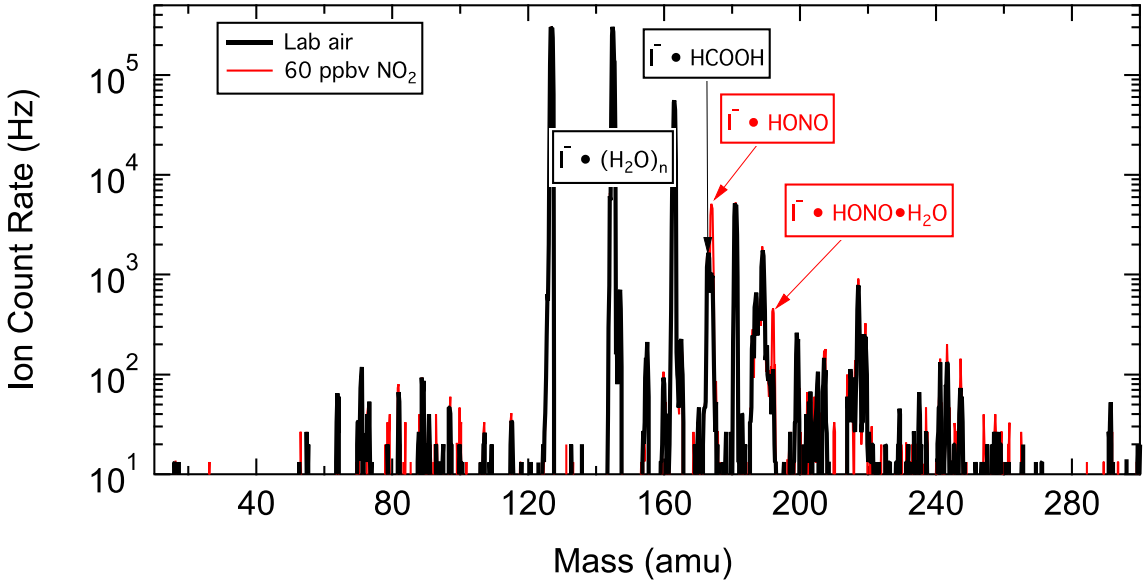
- Why
- How
- What

Why HONO in SENEX: by-product of effort to measure multiple organic acids

Goal: Modify Chemical Ionization Mass Spectrometer (CIMS) to detect organic acids

- Previously: $SiF_5^- + HNO_3 \rightarrow SiF_5^- \bullet HNO_3$ (VERY selective)
- Well known: $I^- + HNO_3 \rightarrow I^- \bullet HNO_3$

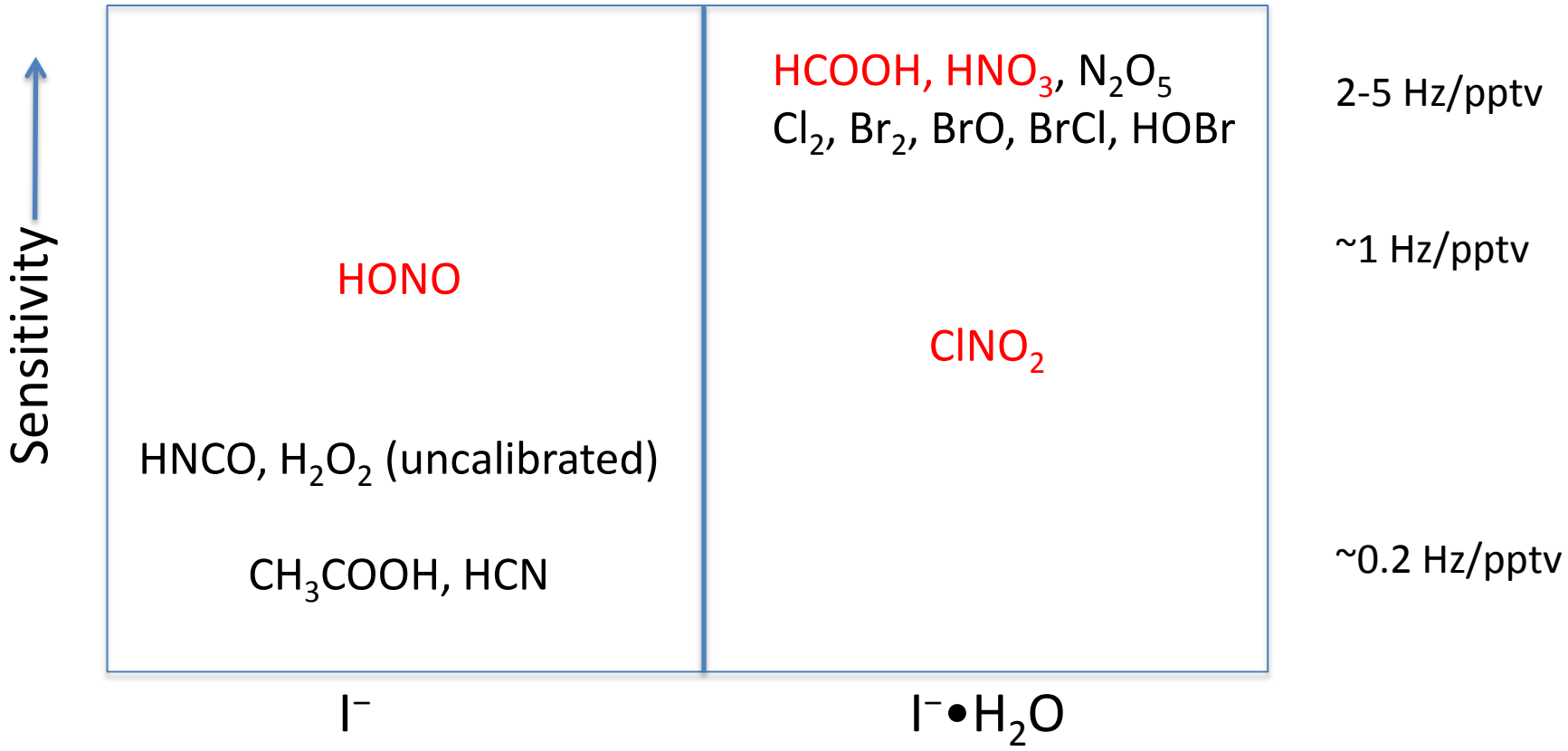
  $I^- + HCOOH \rightarrow I^- \bullet HCOOH$
- Interference test with NO_2 (same mass as HCOOH)



No interference from NO_2. HONO detected

Why: Because it worked (and others compounds didn't)

- Compounds with similar molecular weights can't be resolved by this mass spectrometer:
  butyric (88.11) and pyruvic acids (88.06); propionic (74.08) and glyoxylic acids (74.04); oxalic (90.03) and lactic acids (90.08)
- No sensitivity: acrylic & methacrylic acids, glycolic acid, alkyl nitrates, VOCs, NO_2, SO_2, glyoxal…



Control humidity in detector to maintain constant sensitivity

How: HONO detection limits

Sampling details

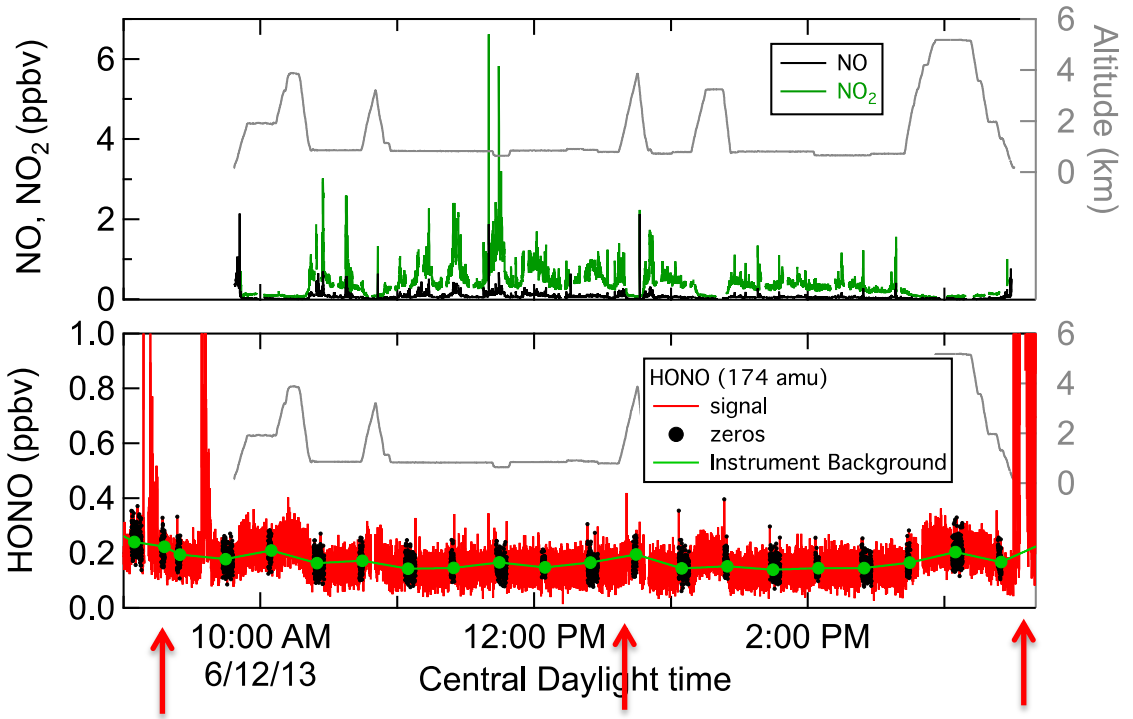
- HONO, HCOOH, and HNO_3 measured once per second
- Inlet: 70 cm long Teflon at 40 ˚C, 0.64 cm ID, residence time ≈ 170 ms
- Instrument background: sample through charcoal filter every ½ hour
- Calibrations: HNO_3 or HCOOH once per hour
  HONO from HCl + humidified $NaNO_2$ in laboratory
  HONO calibration accuracy ±40%, 1 s time response

- *Example of raw data:*
  June 12 flight, Atlanta

- *precision*
  25 pptv for 1 s data
  11 pptv for 10 s averages

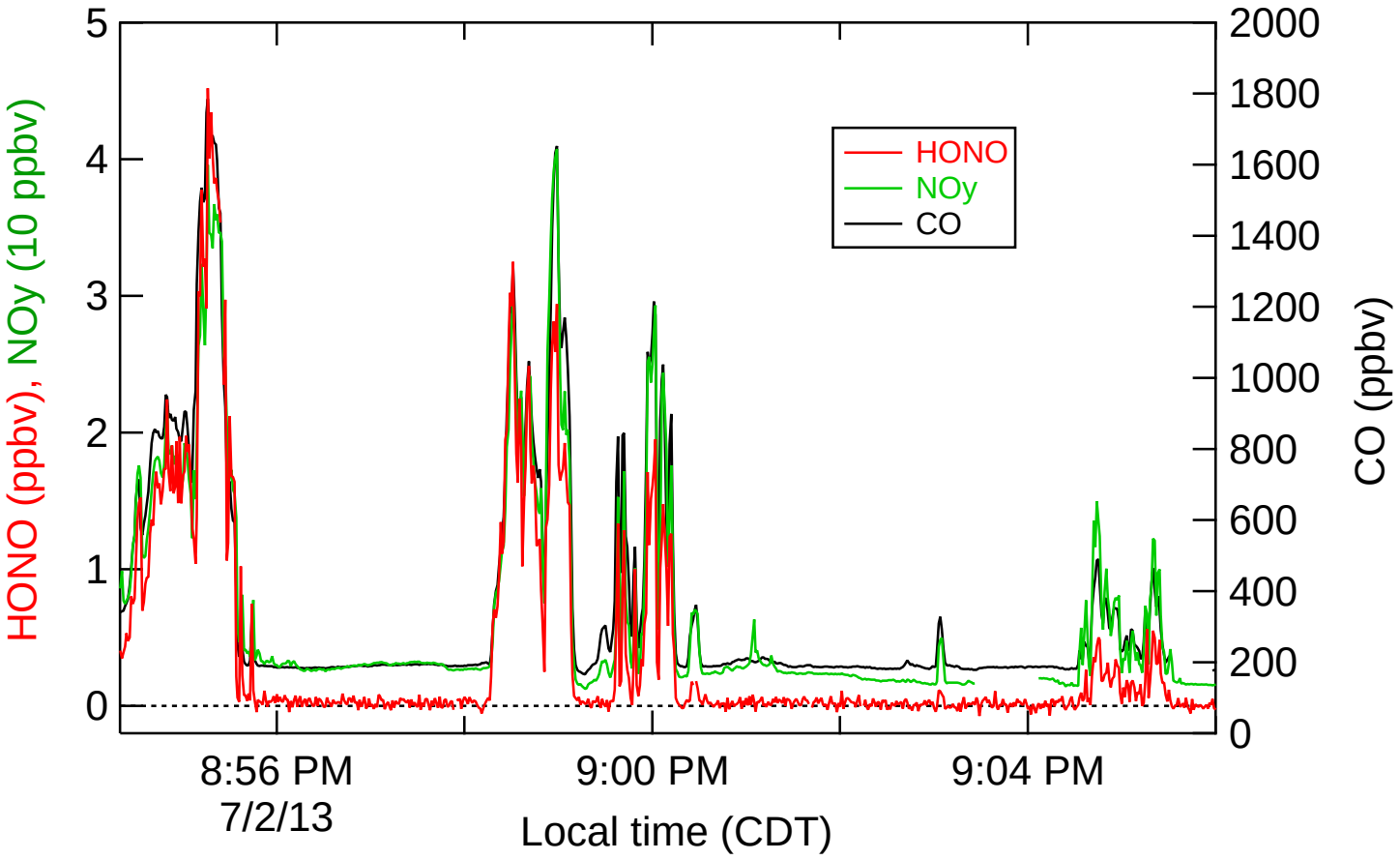
- *Instrument background*
  160 ± 30 pptv
  (Achilles heel)

- *detection limit:*
  40 pptv for 1s data
  30 pptv for 10 s averages



What: HONO in fire plumes

- *Nighttime*
- *Prescribed fires*
- *Western TN*
- *0.6–0.8 km AGL*
- *1 s data*

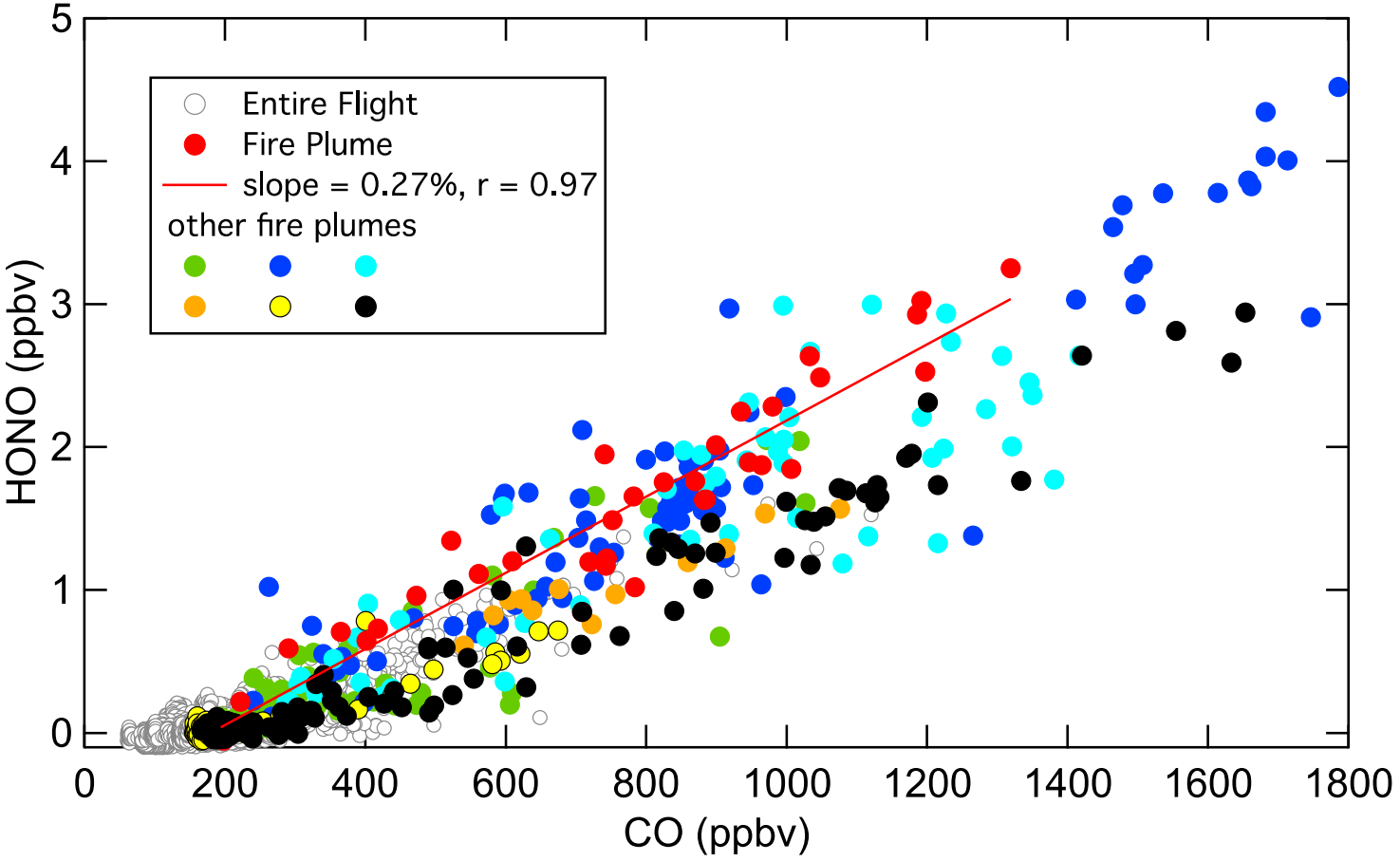


Fire plumes sampled day and night during SENEX:

- HONO > 4 ppbv, by far the largest mixing ratios observed
- HONO correlated with emitted CO and NOx

HONO to CO fire emission ratio

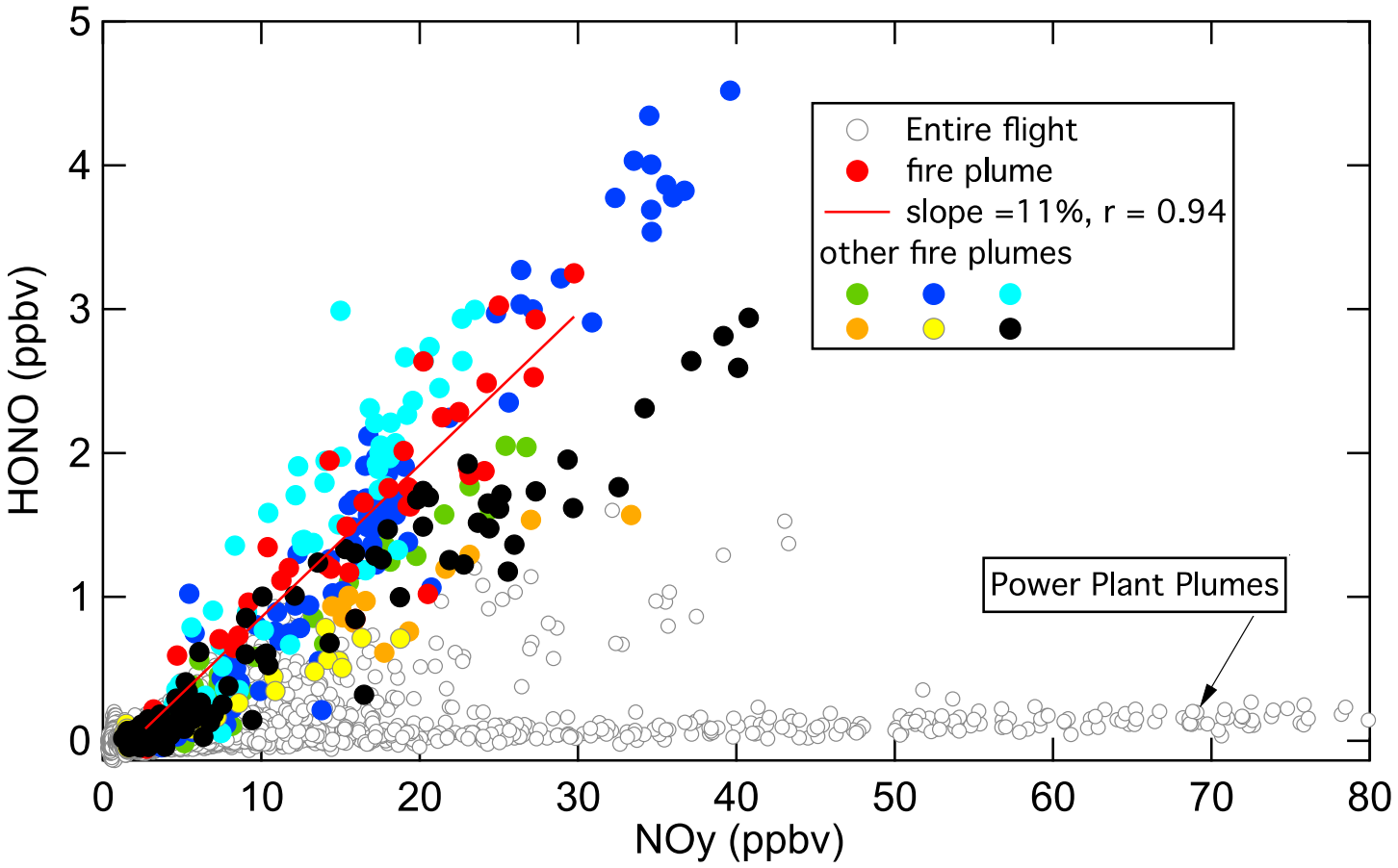
- *Nighttime*
- *Prescribed fires*
- *July 2, 2013*
- *Western TN*
- *0.6–0.8 km AGL*
- *1 s data*
- *>20 plumes*



- HONO to CO enhancement ratios varied from 0.13–0.52%
- Consistent with previous reports of 0.2–0.5%
  (Akagi, 2011; Burling, 2011; Veres, 2010; Yokelson, 2007)

HONO to NOy fire emission ratio

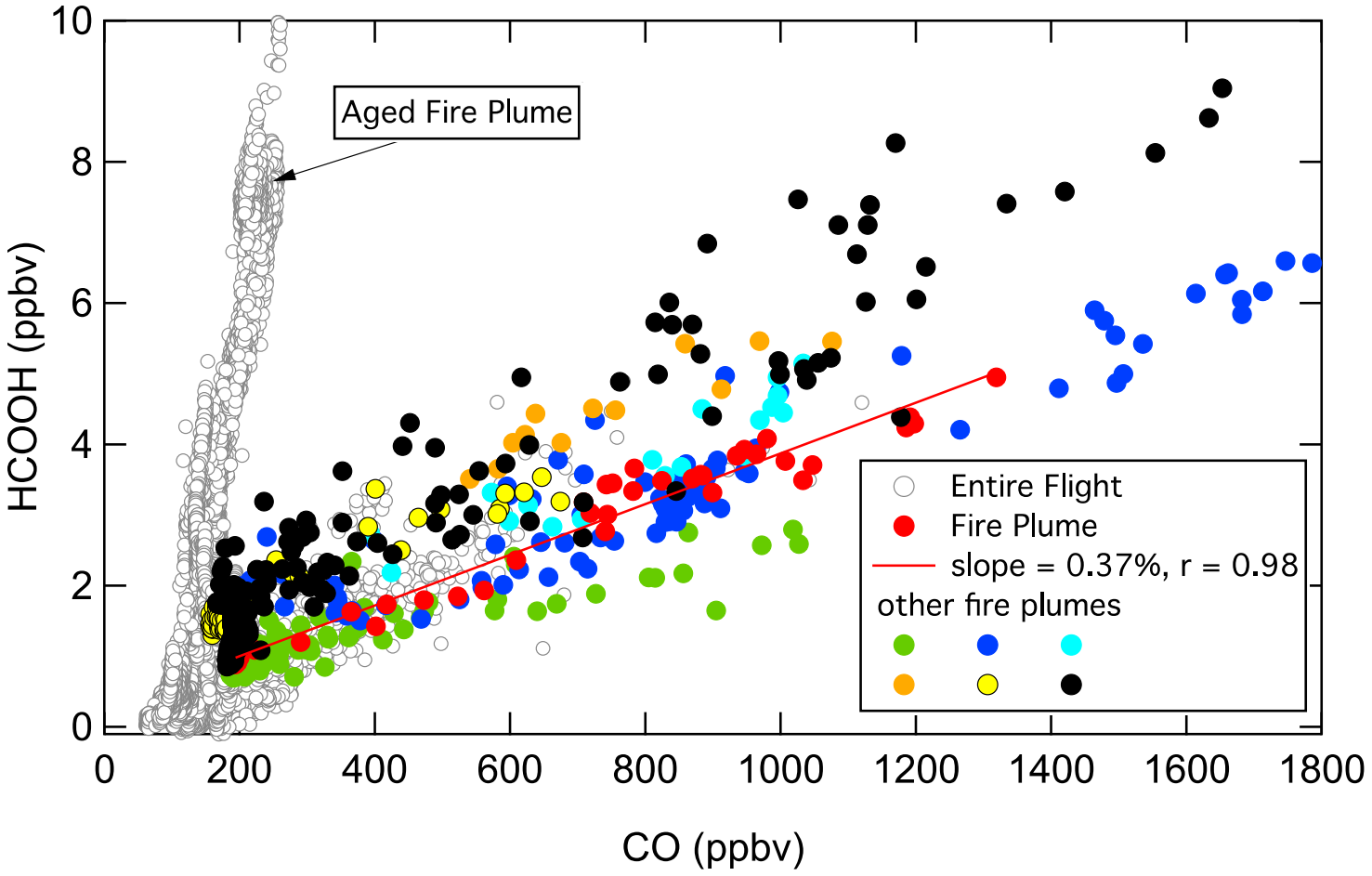
- *Nighttime*
- *Prescribed fires*
- *1 s data*
- *>20 plumes*



- HONO to NOy enhancement ratios varied from 2–14%
- Consistent with previous reports of 7.7–22%
  (e.g. Burling et al., 2011)

Digression: HCOOH fire emissions

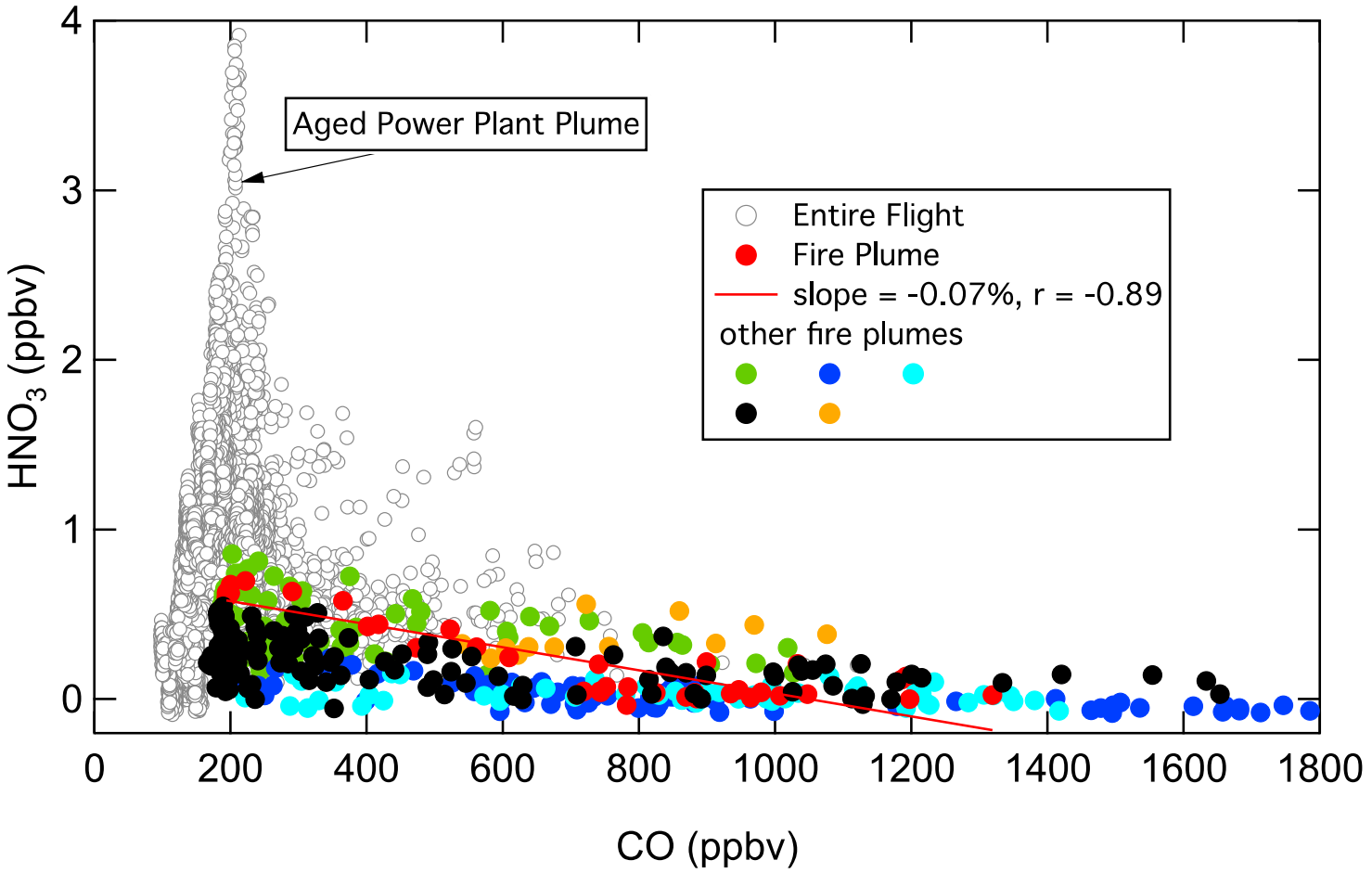
- *Nighttime*
- *Prescribed fires*
- *1 s data*
- *HCOOH from same CIMS*



- HCOOH to CO enhancement ratios varied from 0.2–0.5%
- Consistent with previous reports of ≈0.4% (e.g. Burling, Veres)
- Formic acid useful fire tracer

Digression: HNO_3 removal in fire plumes

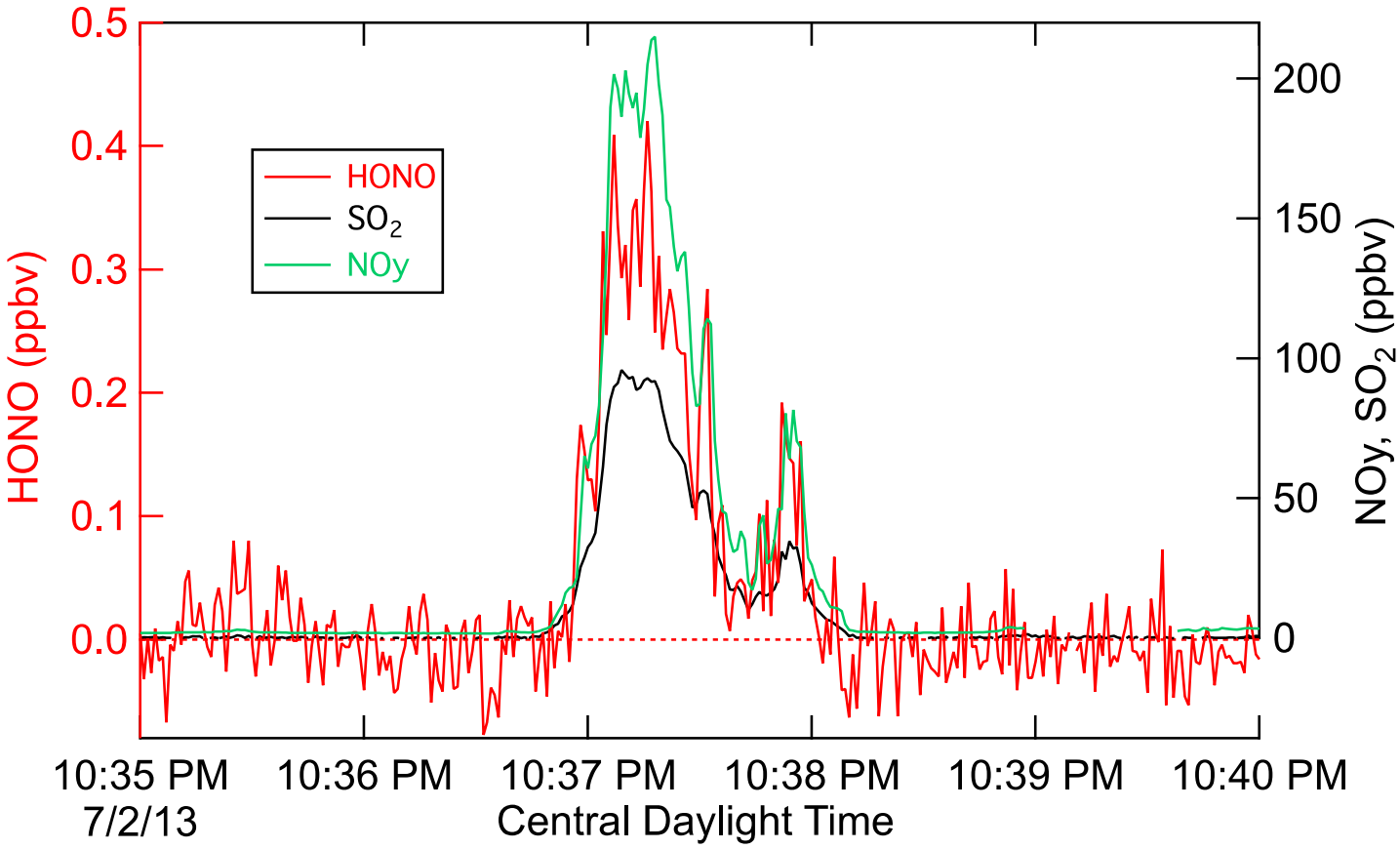
- *Nighttime*
- *Prescribed fires*
- *1 s data*
- *HNO_3 from same CIMS*



Gas phase HNO_3 removed in fired plumes

HONO emission from power plants

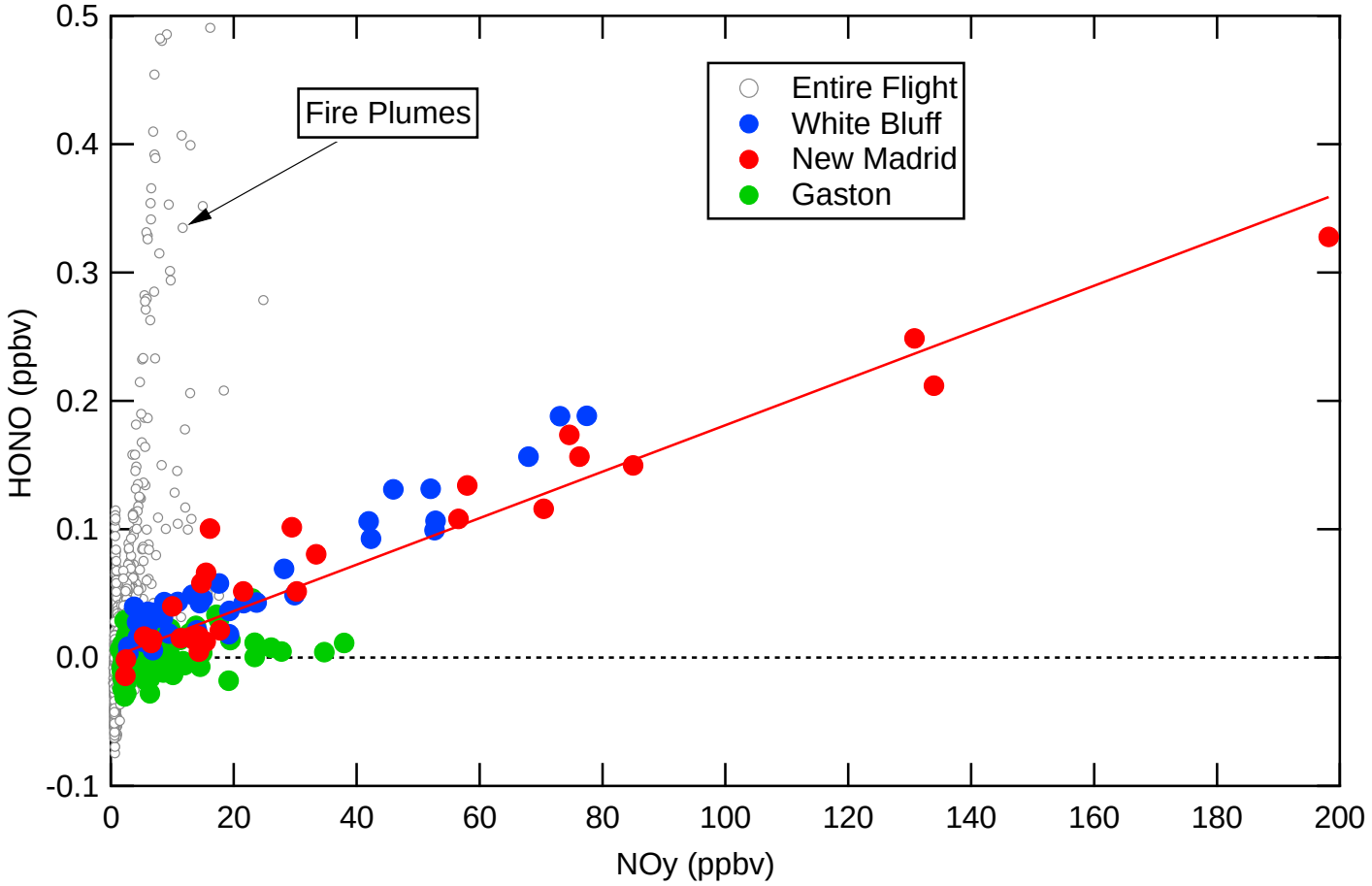
- *Nighttime*
- *New Madrid power plant plume 20 km downwind 0.6 km AGL*
- *1 s data*



HONO correlated with emitted SO_2 and NOy in power plant plumes

HONO to NOy power plant emission ratio

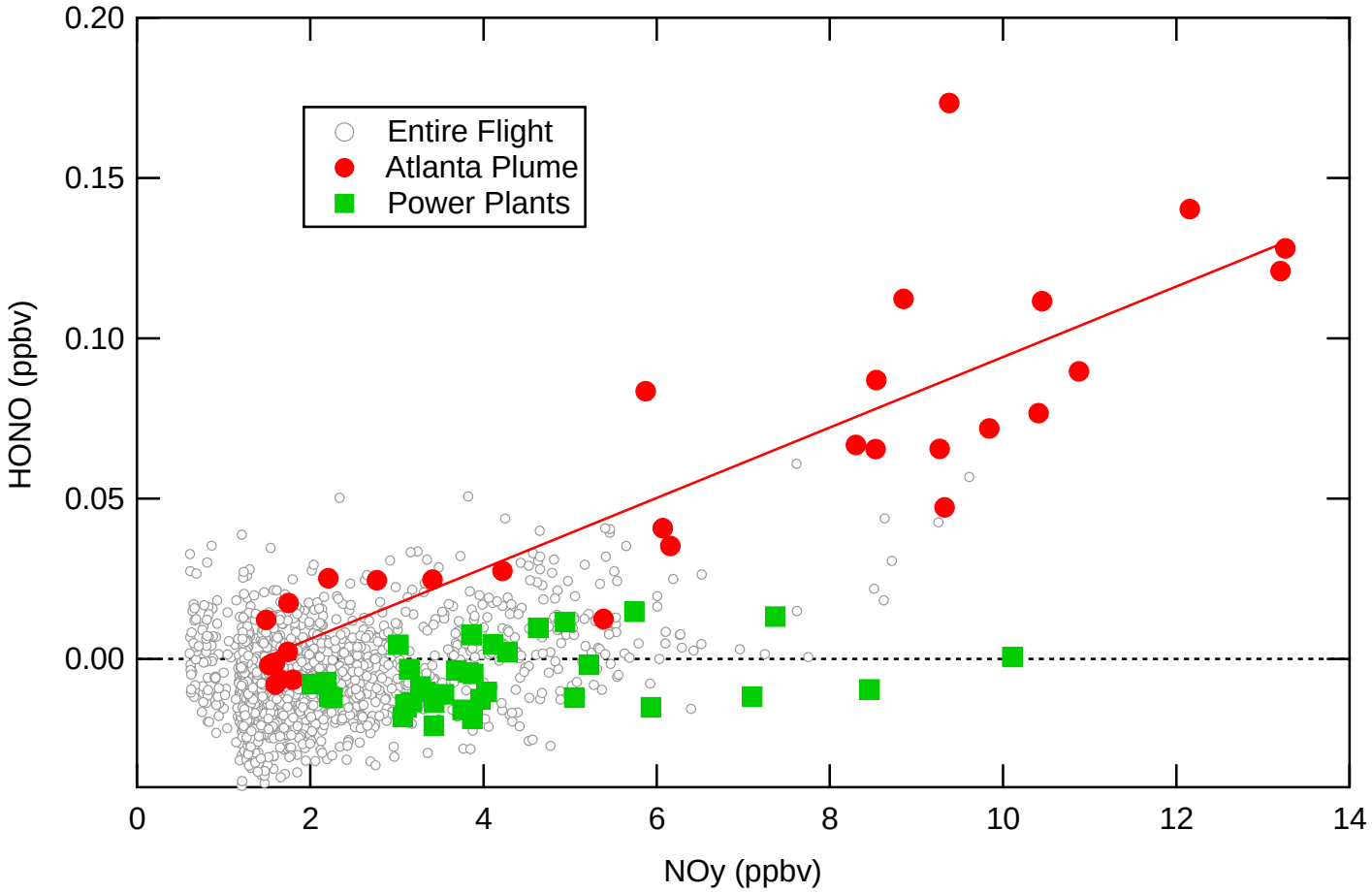
- *Nighttime*
- *10 s averages*
- *July 1-2 and 2-3*



- Fresh plumes from coal-fired power plants measured at night
- HONO:NOy ≈ 0.2% (less than cars, planes)
- Sometimes HONO emission ≈ 0

HONO in urban plumes at night

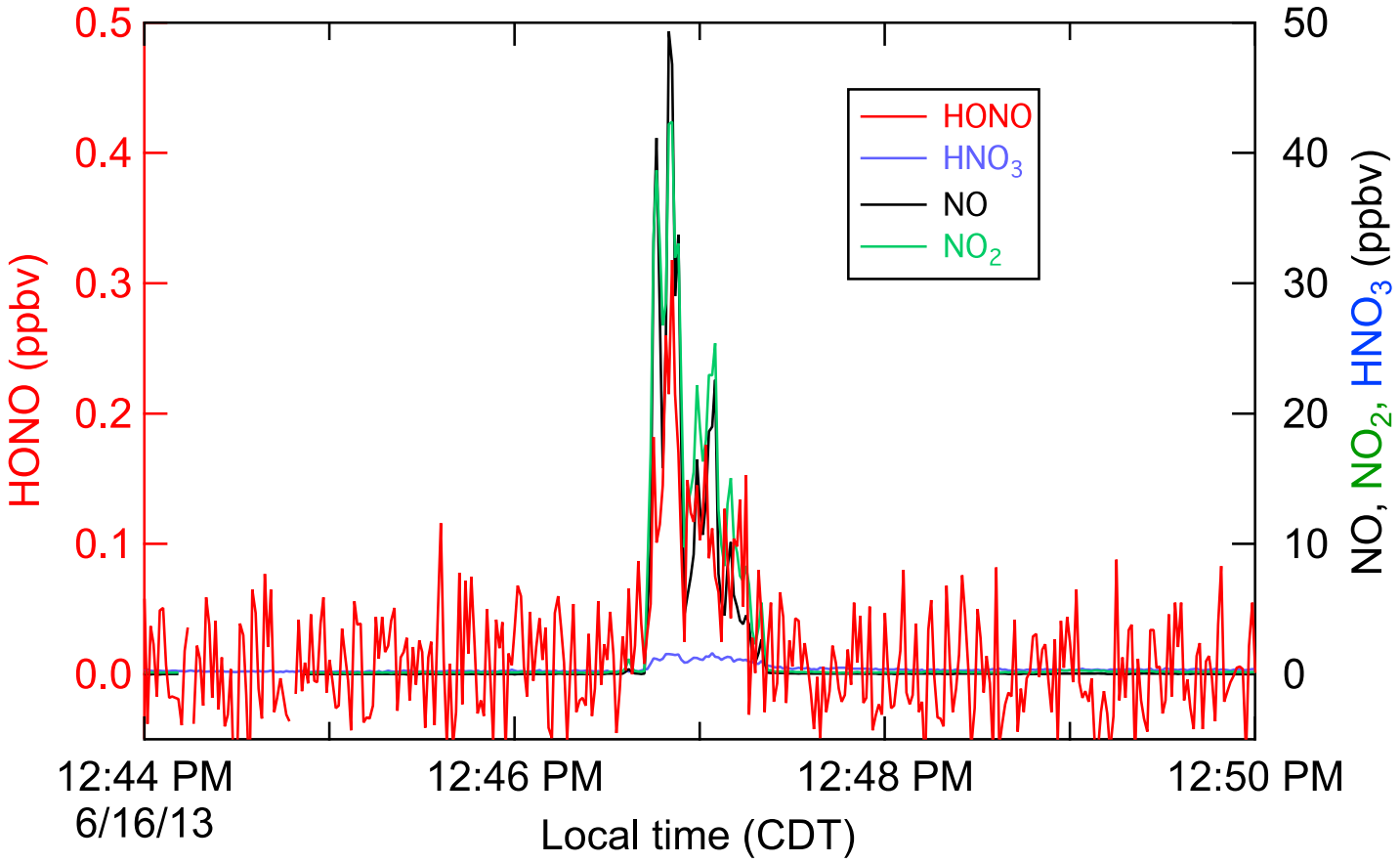
- *Nighttime, June 19*
- *Atlanta vicinity*
- *Atlanta plume*
  9:45 PM
  60 km downwind
  0.6 km AGL
- *10 s data*



- HONO ≈ 150 pptv in nighttime Atlanta plume
- HONO:NOy ≈ 0.9% in nighttime Atlanta plume
- Plumes transported at night may be decoupled from the surface

Daytime HONO: fresh power plant plumes

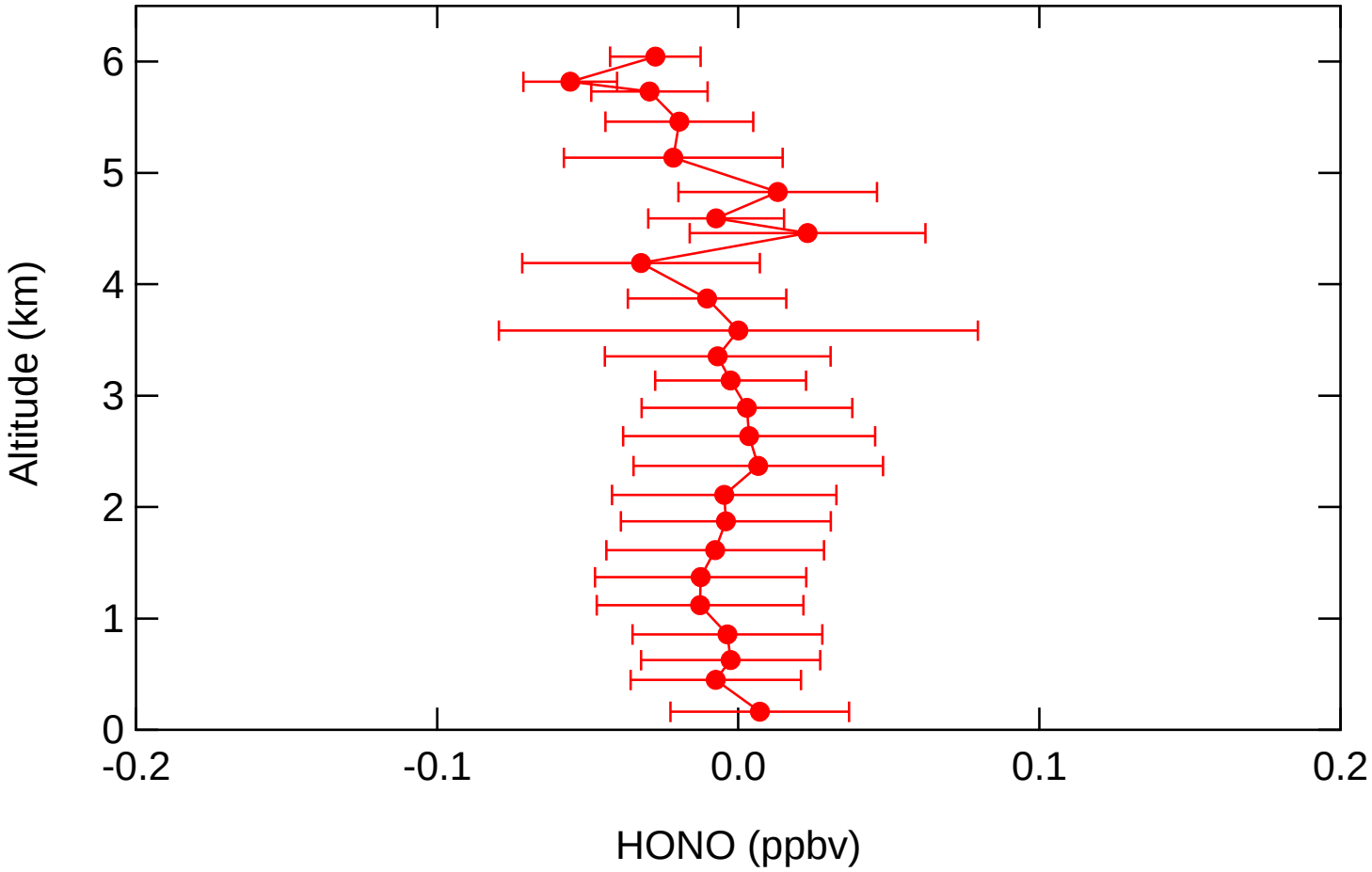
- *mid-day June 16*
- *8 km downwind from Branch power plant (120 km ESE of Atlanta)*
- *0.6 km AGL*
- *1 s data*
- *> 300 pptv HONO*



- Daytime HONO also in fresh plumes from paper mills, fires, aircraft
- Plume modeling could sort out HONO contributions from:
  - Emission
  - Formation (OH + NO)
  - Loss (photolysis)
  - Dilution

Daytime HONO altitude profile

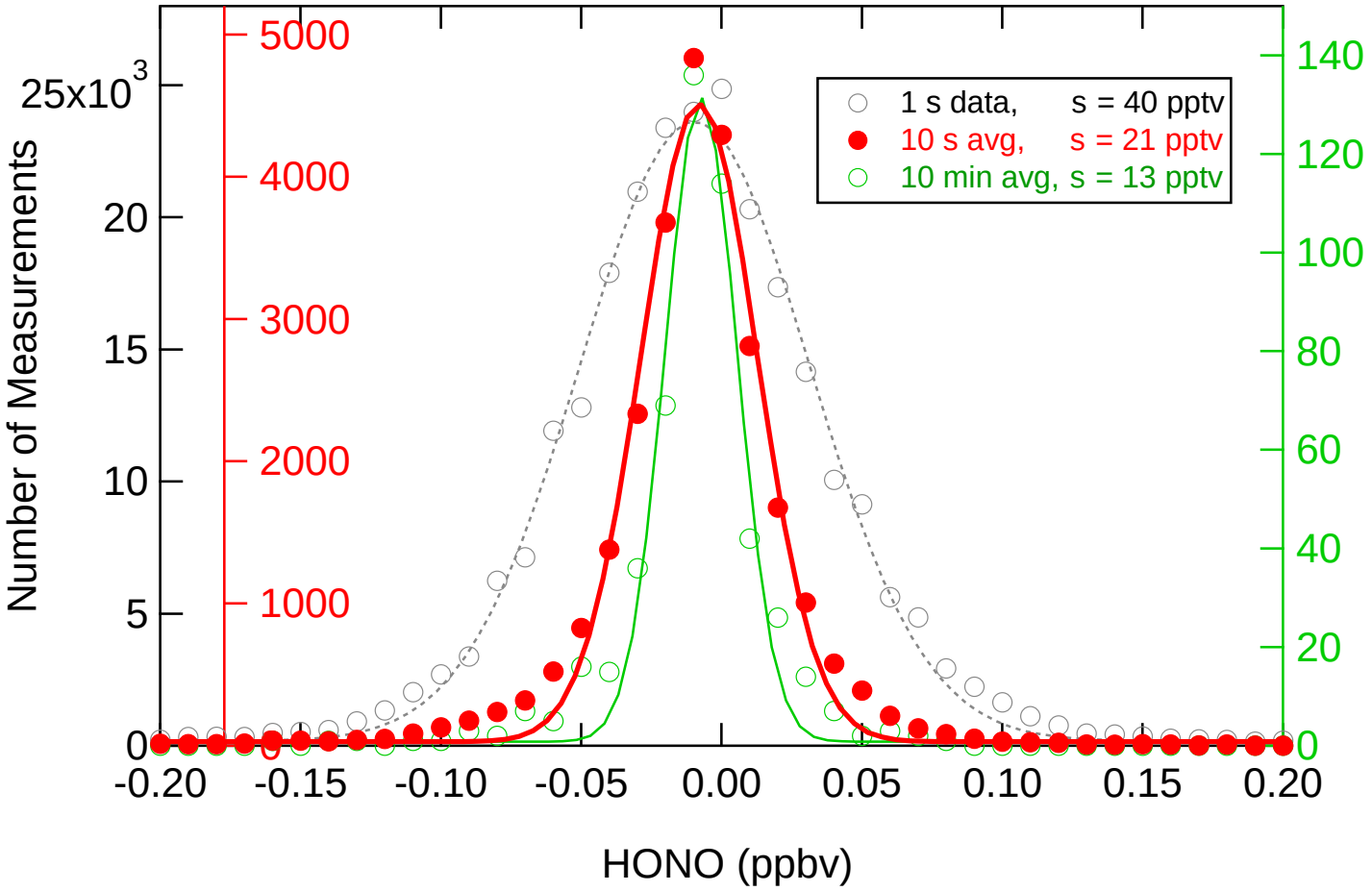
- *14 daytime SENEX flights*
- *10 s data*
- *most measurements <1 km AGL*
- *error bars: 1 std dev of mean, σ ≈ 30 pptv*



- No trend with altitude
- All daytime 10 s measurements: HONO = -5 ± 30 pptv
- Photostationary state (PSS): HONO ≈ 1 pptv (for NO ≈ 50 pptv)

Frequency distribution, daytime HONO measurements

- *14 daytime flights*
- *measurements 0.4–6 km AGL*
- *most <1 km AGL*
- *fit to normal distribution, width = σ*



- Centered about HONO = −7 pptv
  (imperfect background correction)
- Consistent with $HONO_{PSS}$ ≈ 1 pptv

Conclusions

- HONO measured once per second on 18 research flights
- Largest HONO mixing ratios in fresh fire plumes measured at night
- Fire HONO emissions consistent with past studies
- Power plant HONO emission ratio quantified
  HONO:NOy≈0.2%, though sometimes HONO:NOy≈0
- Daytime HONO > 30 pptv always from nearby combustion source
- Outside of fresh plumes, daytime HONO consistent with PSS

Acknowledgements

HNO_3, HCOOH, HONO: John Nowak
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$ClNO_2$ calibration: Steve Brown, Pete Edwards, Reed Wommack
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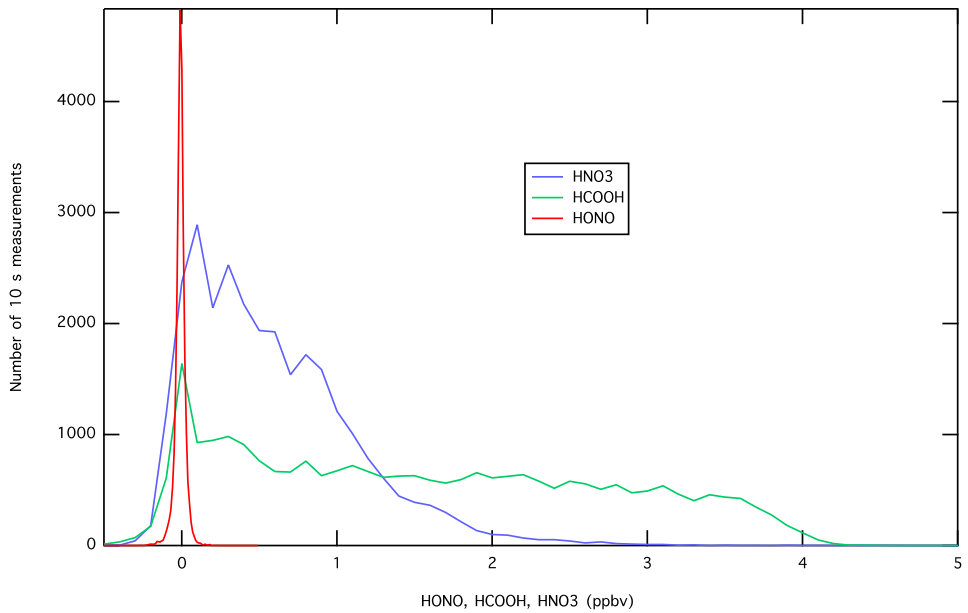
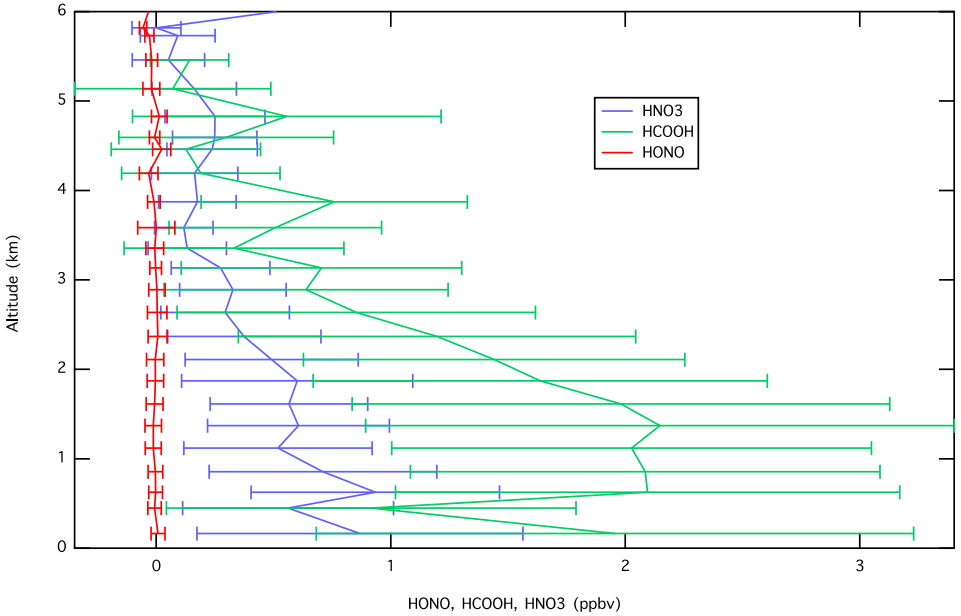
Extra


Number of 10 s measurements
4000
3000
2000
1000
0
HNO3
HCOOH
HONO
0
1
2
3
4
5
HONO, HCOOH, HNO3 (ppbv)


Altitude (km)
6
5
4
3
2
1
0
HNO3
HCOOH
HONO
0
1
2
3
HONO, HCOOH, HNO3 (ppbv)