Airborne Measurements of Ammonia and Implications for Ammonium Nitrate Formation in the Central Valley and the South Coast Air Basin of California

- P-3 NH_3 Observations
- SoCAB NH_3 : Cars and Cows
- Central Valley Dairy NH_3 Flux
- NH_4NO_3 in Central Valley - NH_3 or HNO_3?

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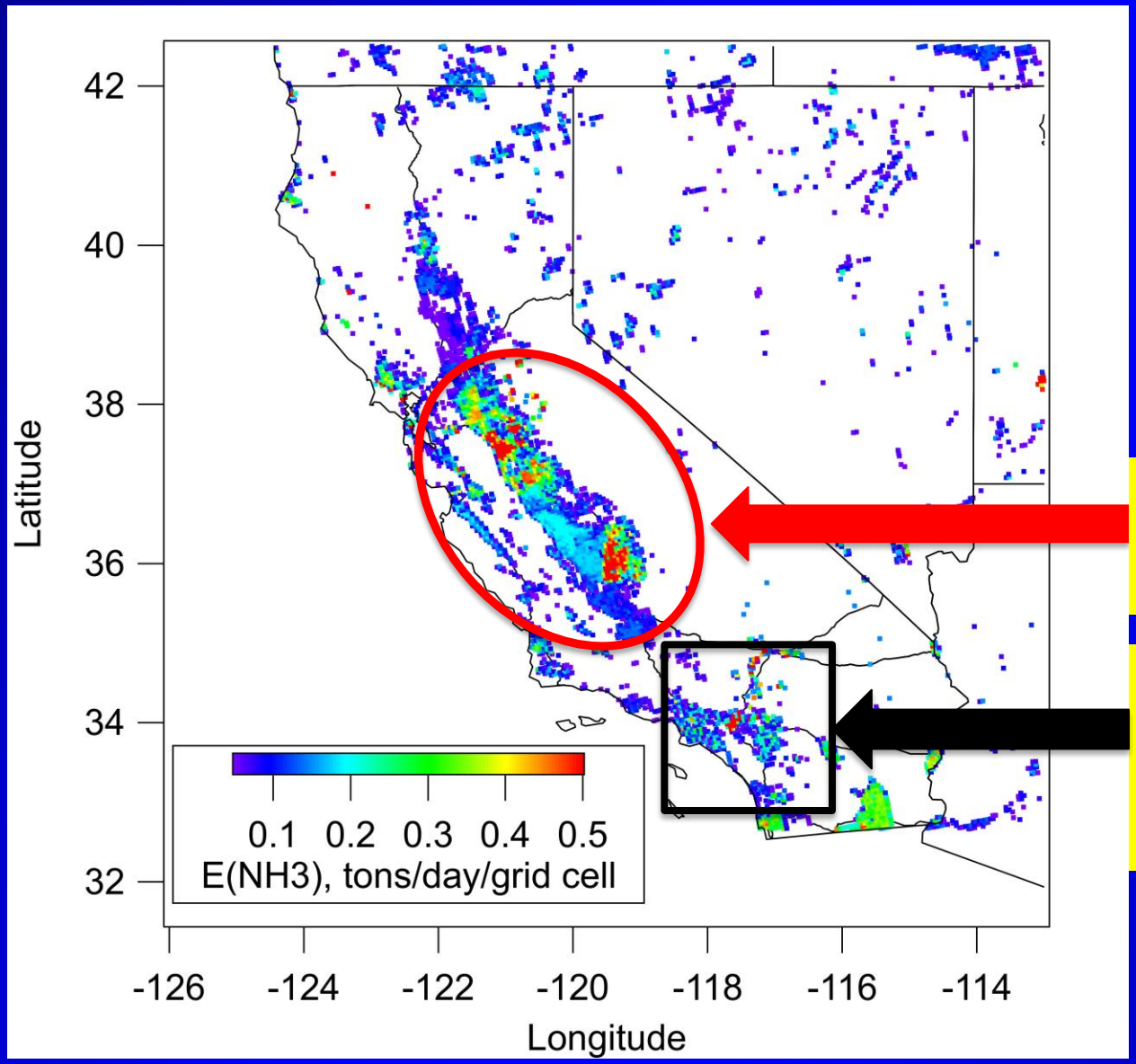
California NH_3 Area Emissions

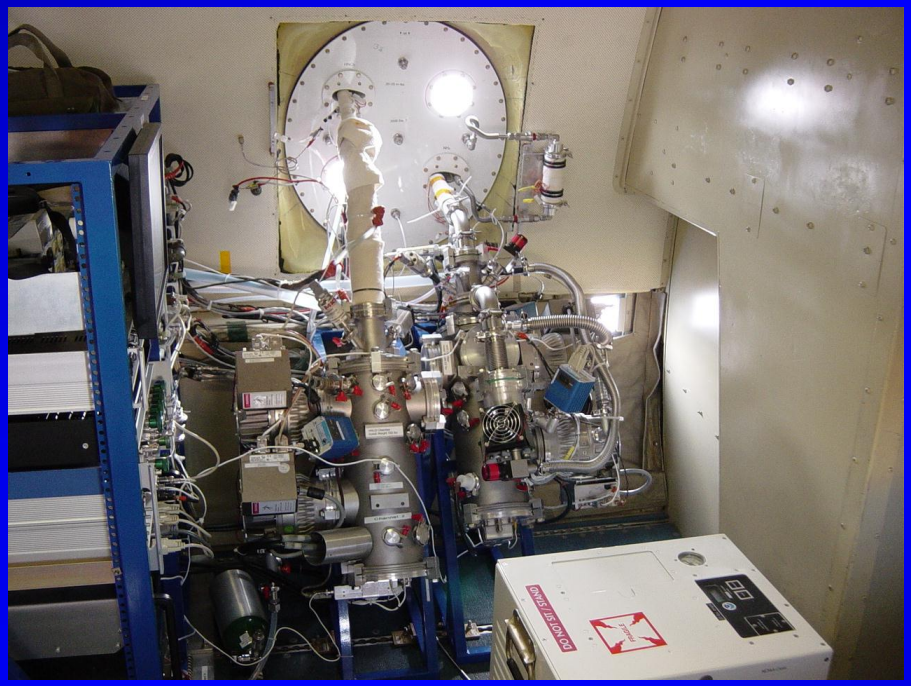


- EPA NEI 1999v3 (Frost et al., *JGR* 2006)
- All area sources
- Point sources excluded
- 4 km resolution
- Grid emissions < 0.05 tons/day not shown

Central Valley
- Agriculture

SoCAB
- Agriculture
- Cars

P-3 NH_3 CIMS Instrument

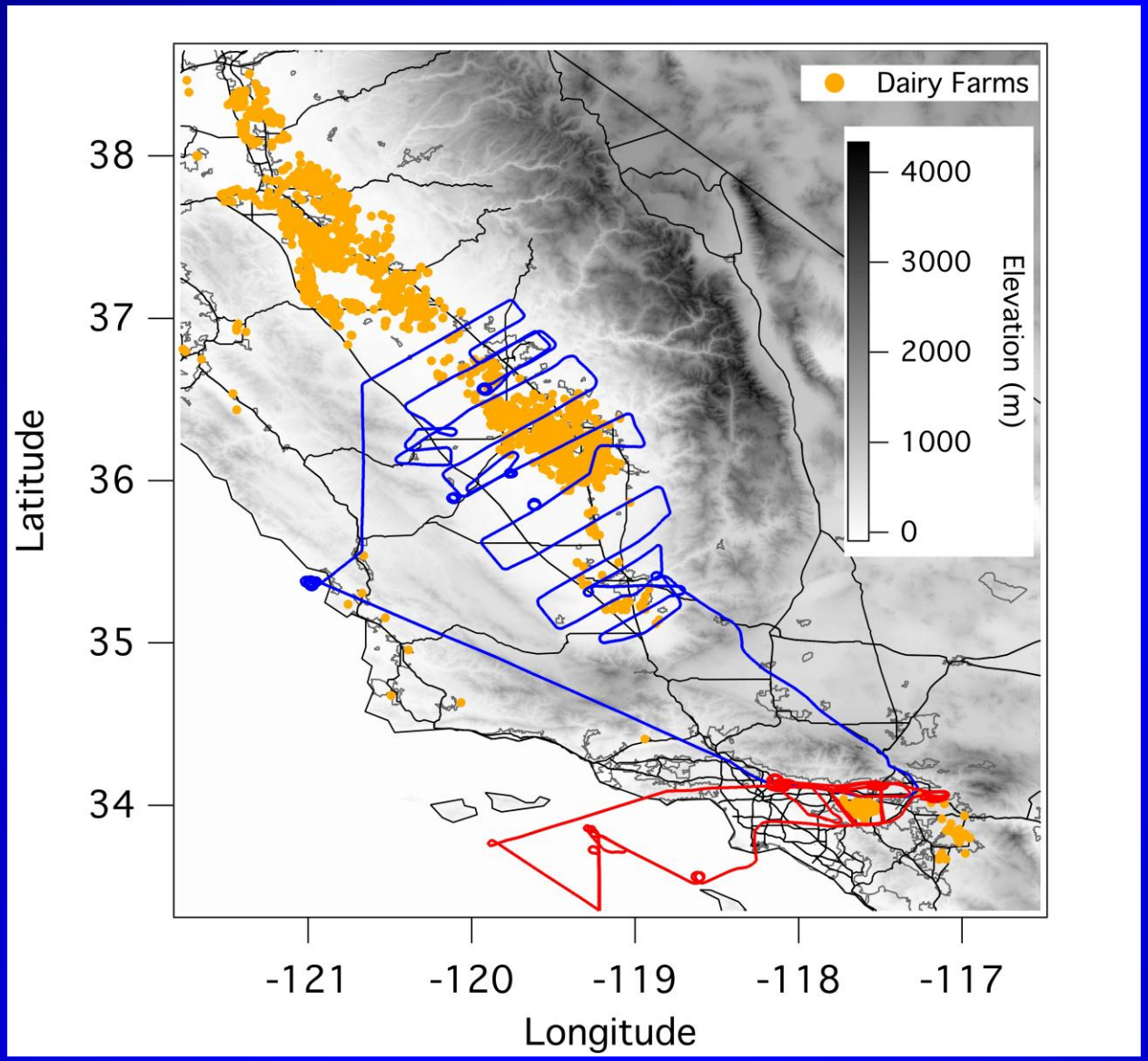


- Chemical Ionization Mass Spectrometry (CIMS) uses ion-molecule reactions to selectively react gas-phase species of interest to an easily detectable product ion. (Nowak et al., *JGR*, 2007, 2010)

$$(C_3H_6O)_2H^+ + NH_3 \rightarrow (C_3H_6O)_2H^+ \bullet NH_3$$

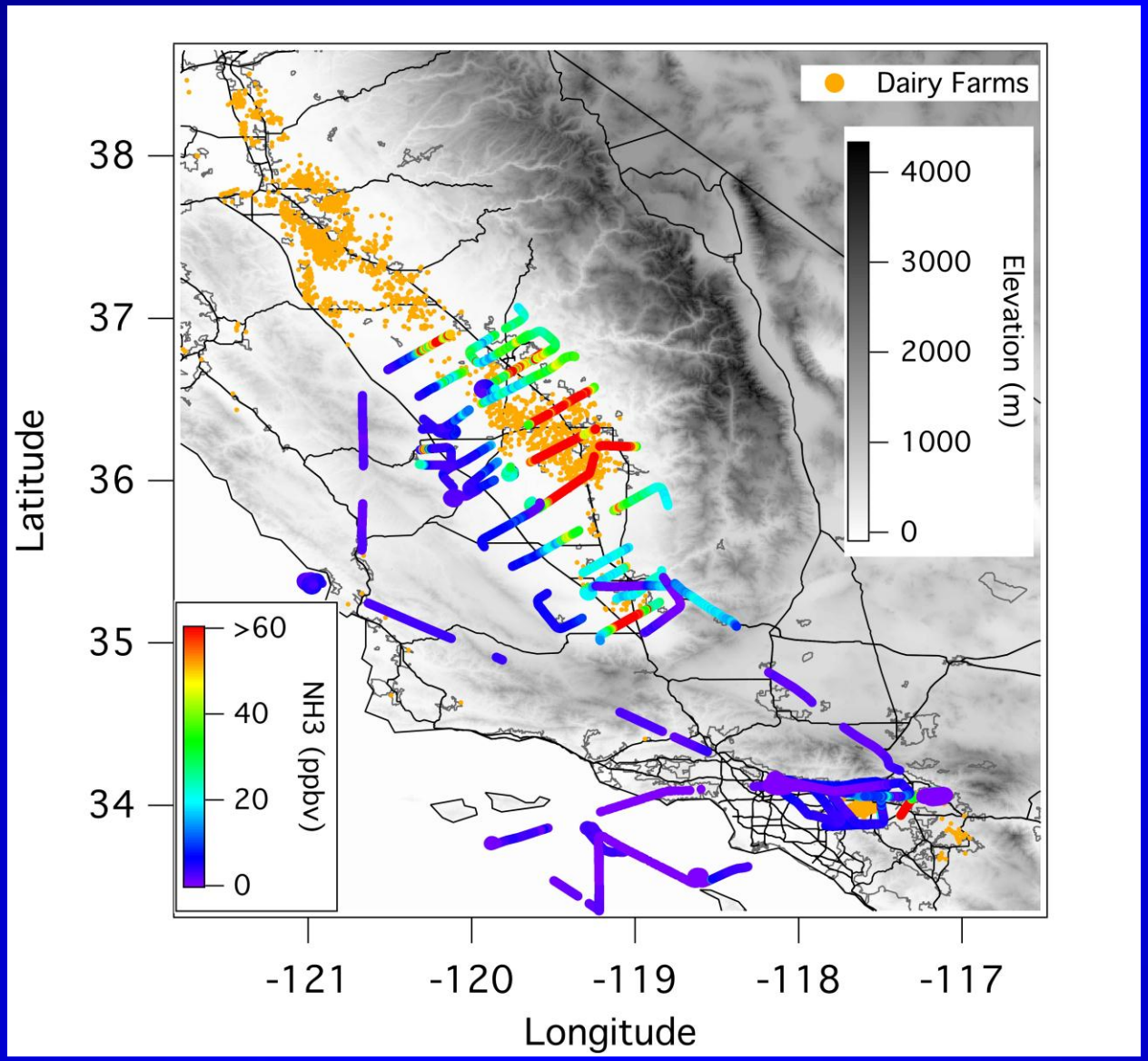
- Sensitivity ~ 1 ± 0.5 Hz/pptv (for 1 MHz reagent ion)
- Background ~ 0.2 to 1 ppbv (varied flight-to-flight)
- Time Response ~ 1 s
- Uncertainty ~ ± (30% + (0.100 to 0.200) ppbv)

P-3 NH_3 Sampling Strategy



- Dairy locations from Salas et al., PIER Report, 2008
- Flight tracks
  - May 7 – SJV
  - May 14 – LA
- 6 flights in the Central Valley
- 7 flights through the SoCAB

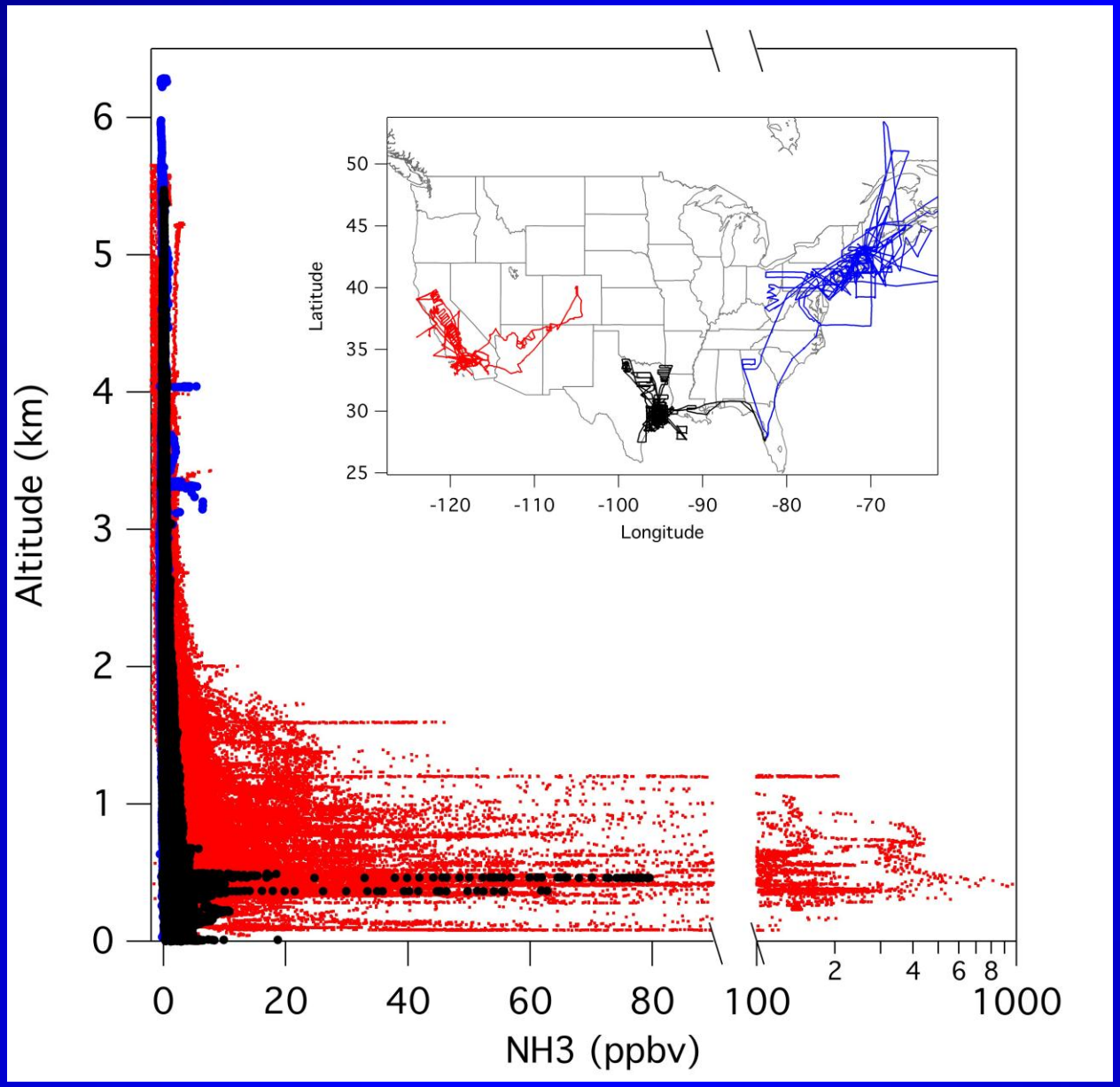
High NH_3 Mixing Ratios



Peak Mixing Ratios

- May 7 - 963 ppbv
- May 14 - 140 ppbv

CalNex NH_3 Altitude Profile



- 100 pptv – ~ 1 ppmv
- Highest near surface
- First in-situ profiles concurrent with satellite observations

NEAQS 2004

- BL mixing ratios up to 3 ppbv
- Biomass burning layers at altitude

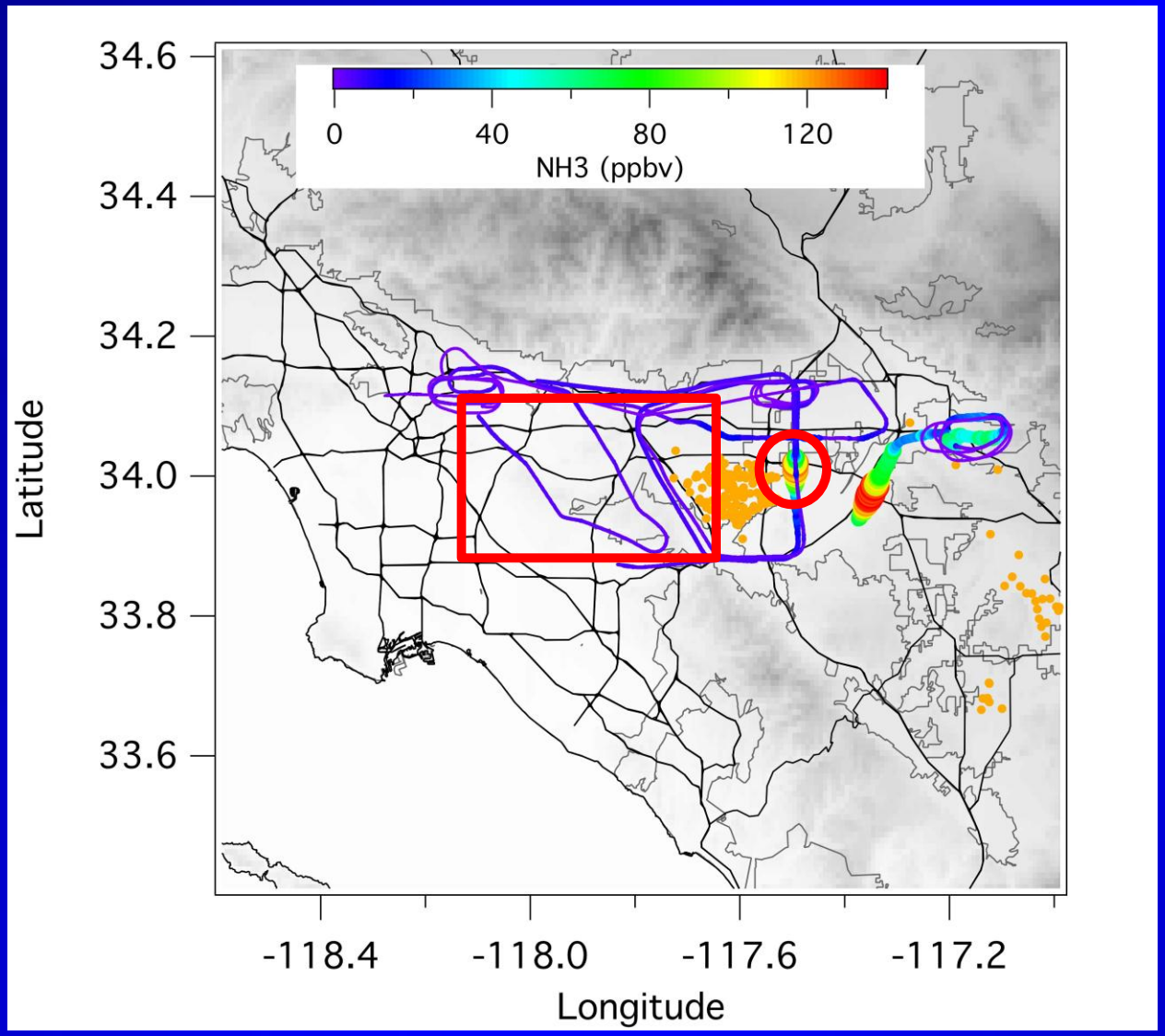
(Nowak et al., *JGR* 2007)

TexAQS 2006

- BL mixing ratios up to 8 ppbv
- BL plumes from industrial accident

(Nowak et al., *JGR* 2010)

South Coast Air Basin NH_3 Sources



- May 14 flight track colored and sized by NH_3 mixing ratio
- Automobiles
- Dairy farms

Why do automobiles emit NH_3?

Unregulated byproduct of three-way catalytic converters

- Resulting from over-reduction of NO on the catalyst surface
- Emissions mode dependent (i.e., acceleration events)

Emissions dominated by 'middle-aged' vehicles

- Older vehicles - no converter or deactivated catalyst
- Newer vehicles - better process control technology

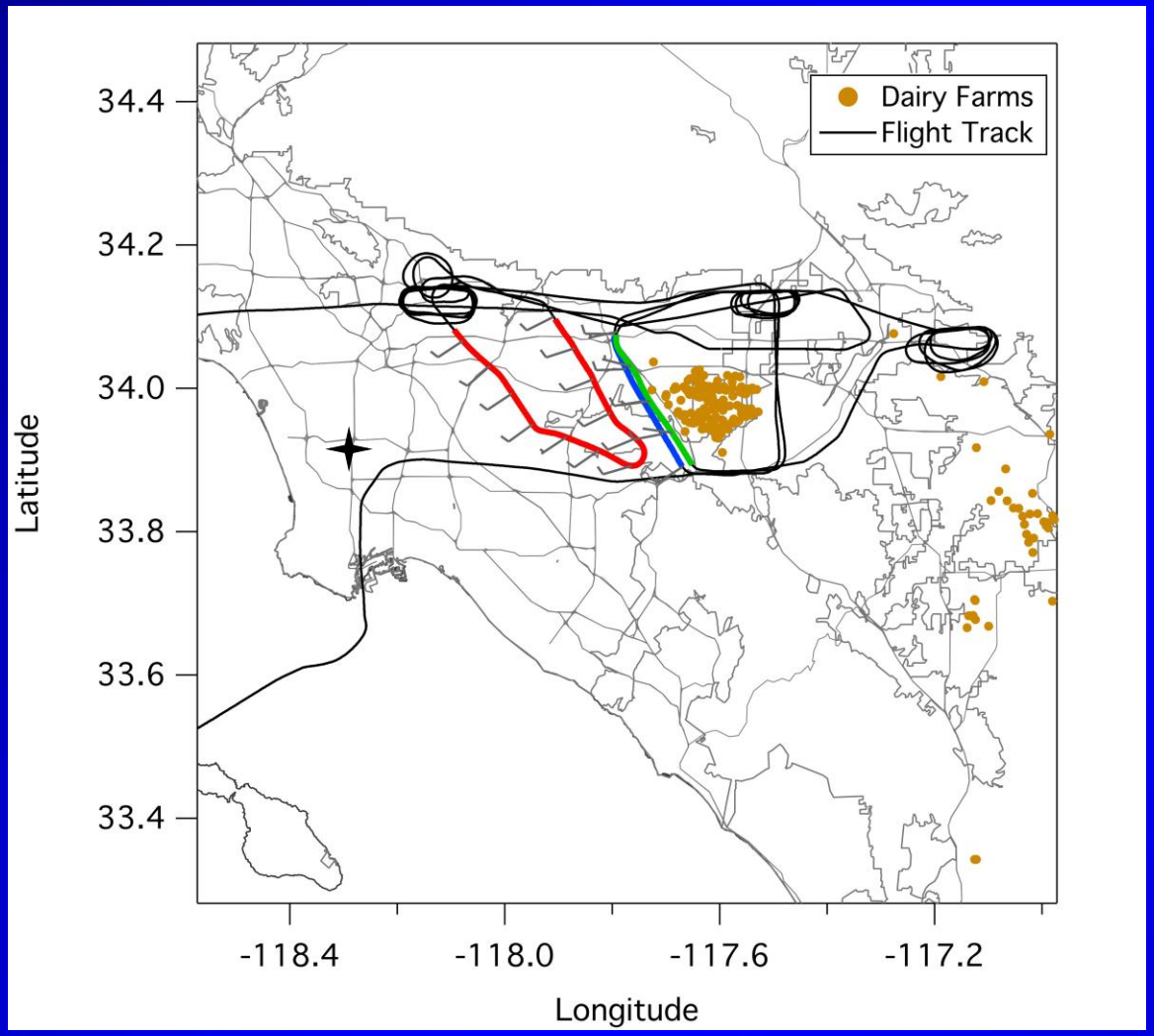
Now

Mainly light-duty vehicles

Future/Now

SCRs using urea
in heavy-duty vehicles ?

NH_3 Automobile Source – Data Selection



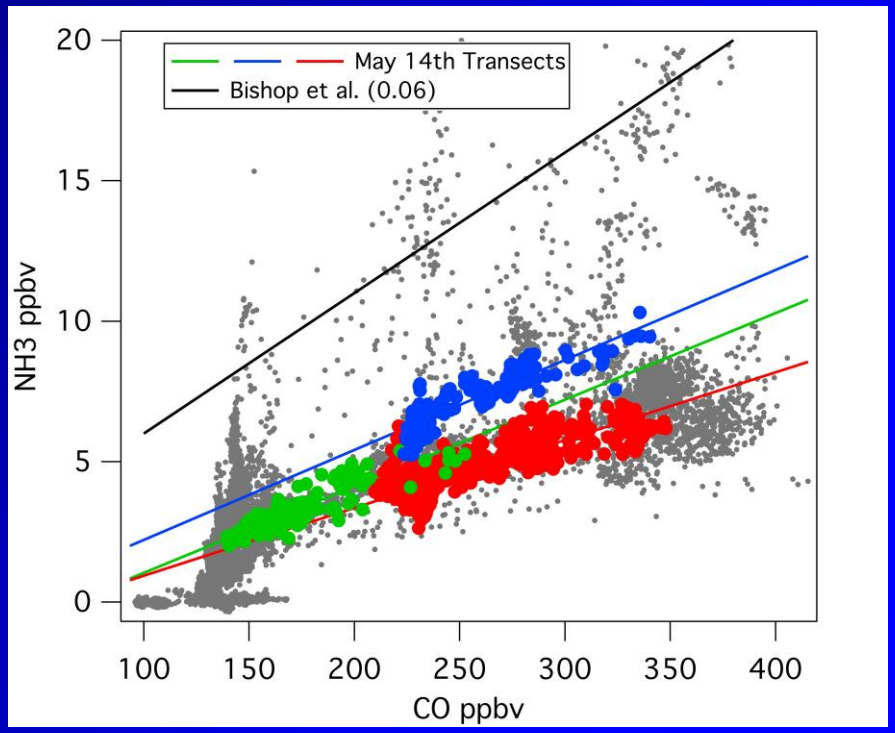
- May 14
- NH_3:CO
- NH_x (NH_3 + NH_4^+):CO
- May 8, 14, 16, 19, and June 20

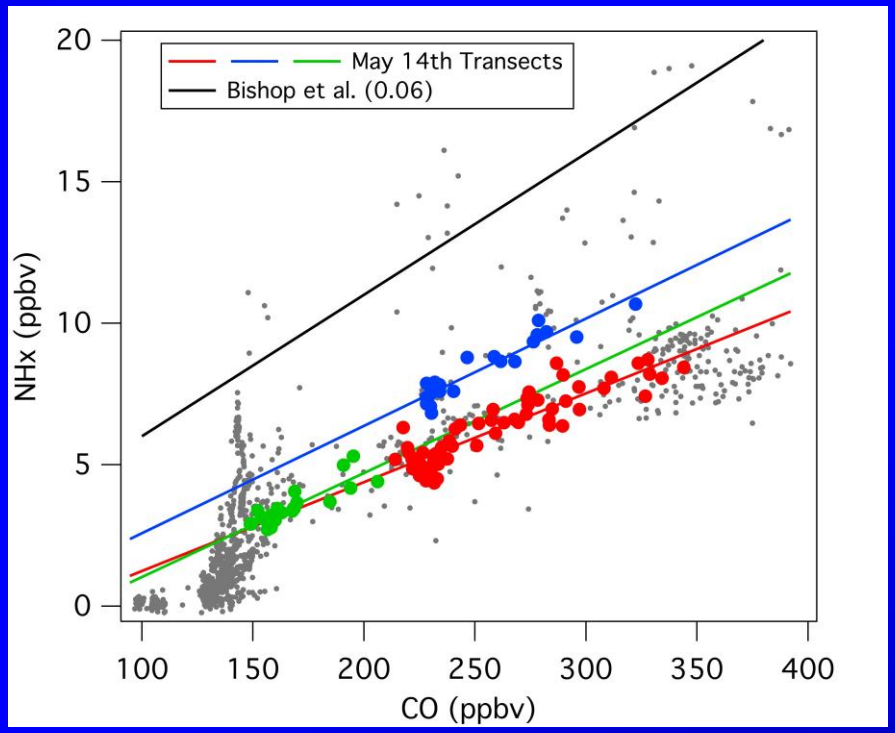
2008

- Fuel-based NH_3:CO
  - West LA ~ 0.060
  - Fresno ~ 0.040
  - San Jose ~ 0.048

Bishop et al., *ES&T 2010*

NH_3 Automobile Source

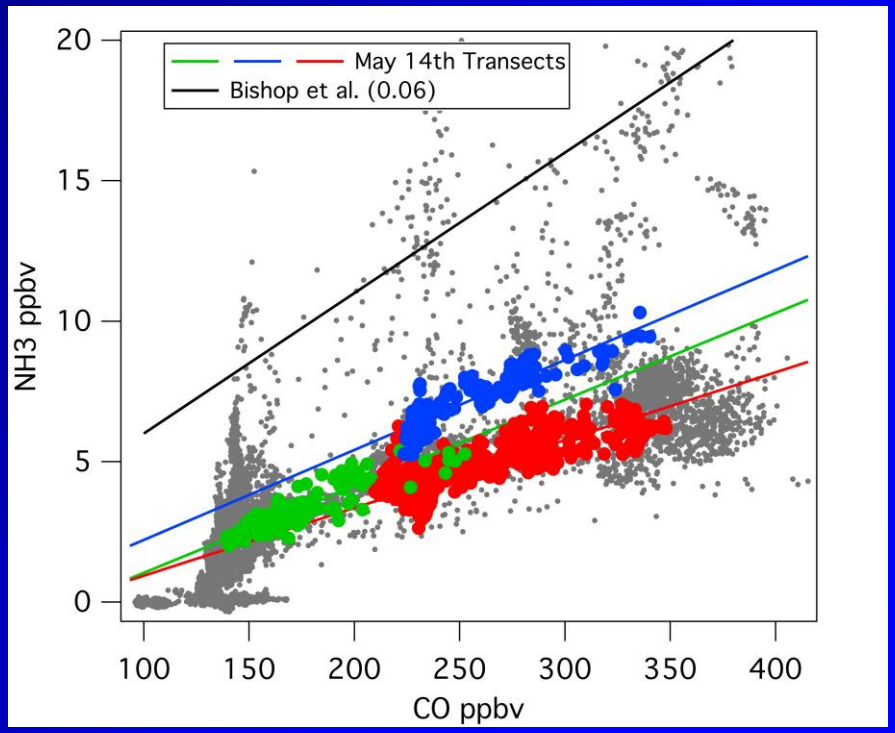


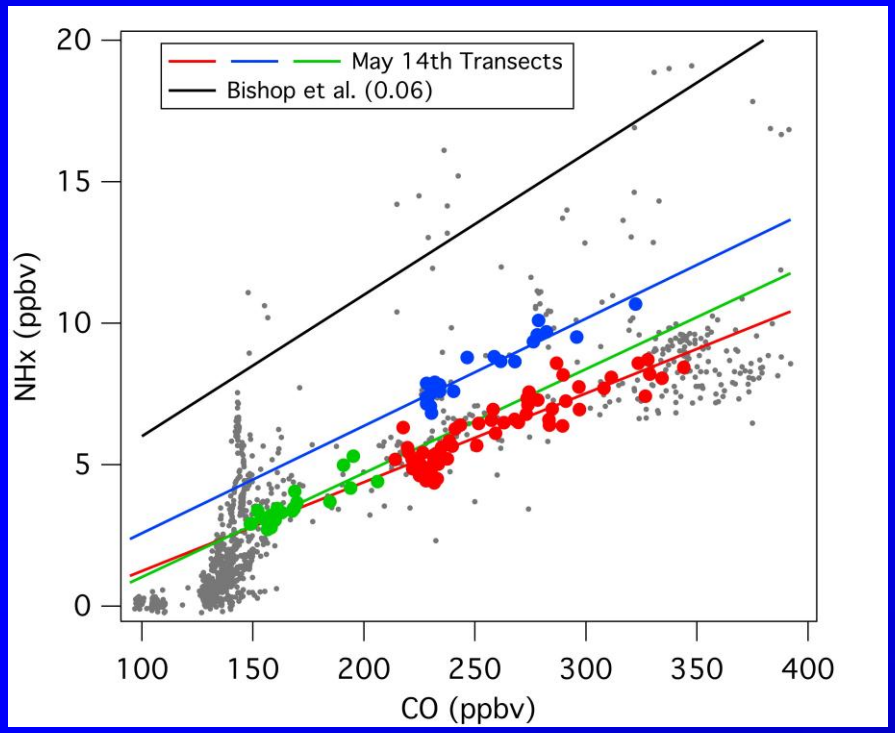


Summary of May 14 NH_3:CO and NH_x:CO Ratios

Transect	NH_3:CO	NH_x:CO
Red	$s = 0.024$, $r^2 = 0.72$	$s = 0.031$, $r^2 = 0.81$
Blue	$s = 0.032$, $r^2 = 0.82$	$s = 0.038$, $r^2 = 0.89$
Green	$s = 0.031$, $r^2 = 0.80$	$s = 0.037$, $r^2 = 0.75$

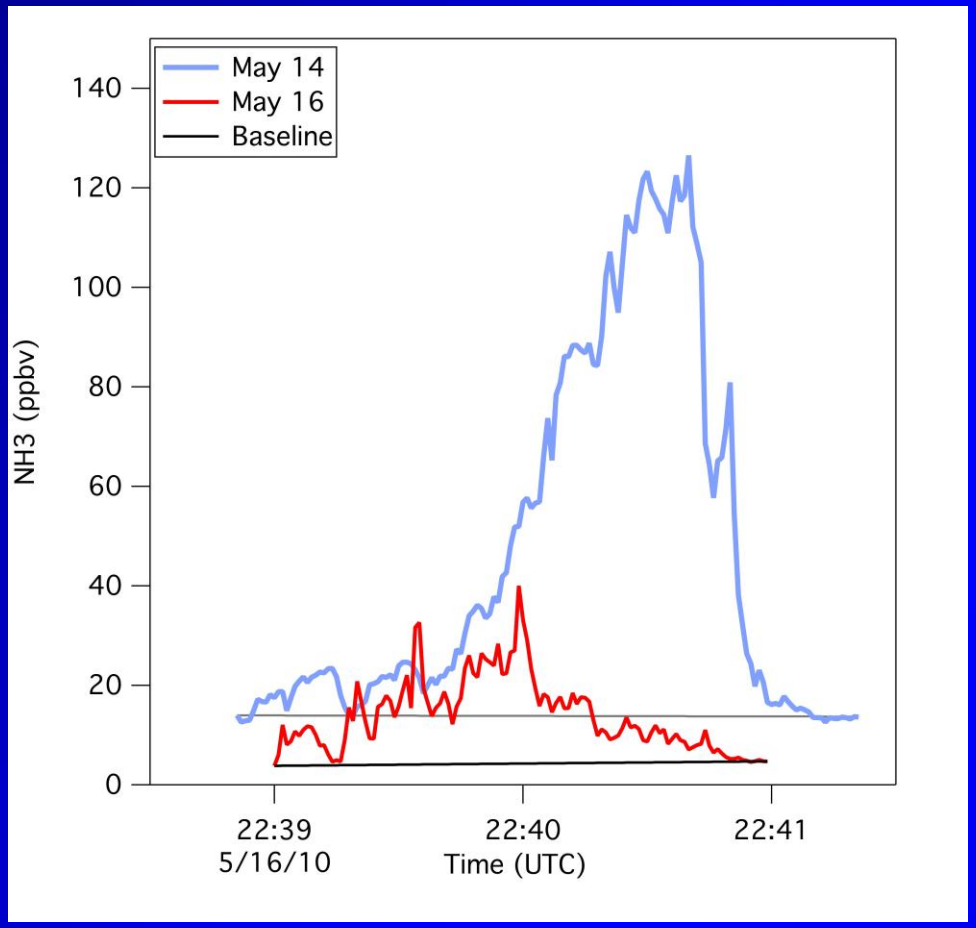
NH_3 Automobile Source





- NH_x:CO within factor of two of Bishop, 2010
- 2010 estimated SoCAB CO emissions ~ 2.68 x 10^9 g/day
  (www.arb.ca.gov/app/emsinv/emssumcat.php)
- For May 14, 83 – 101 metric tons/day
- All CalNex, 67 – 101 metric tons/day
- Compare to NH_3 flux from SoCAB dairy farms

Dairy Farm NH_3 Mass Flux Calculation



$$flux_m = v \cdot \cos(\alpha) \cdot \int n(z)dz \cdot \int X_m(y)dy$$

- Standard method, White et al., *Science*, 1976
- Wind speed
- Aircraft track correction
- Atmospheric number density over the boundary layer height
- Integral of the observed plume
- Factor of 2 uncertainty
- Two crosswind transects

- May 14
  - Dairy farm flux ~ 115 metric tons/day (± 50%)
- May 16
  - Dairy farm flux ~ 33 metric tons/day (± 50%)

SoCAB NH_3 Sources

May 14 ~ 83 – 101 (metric tons/day) ~ 115 (metric tons/day)

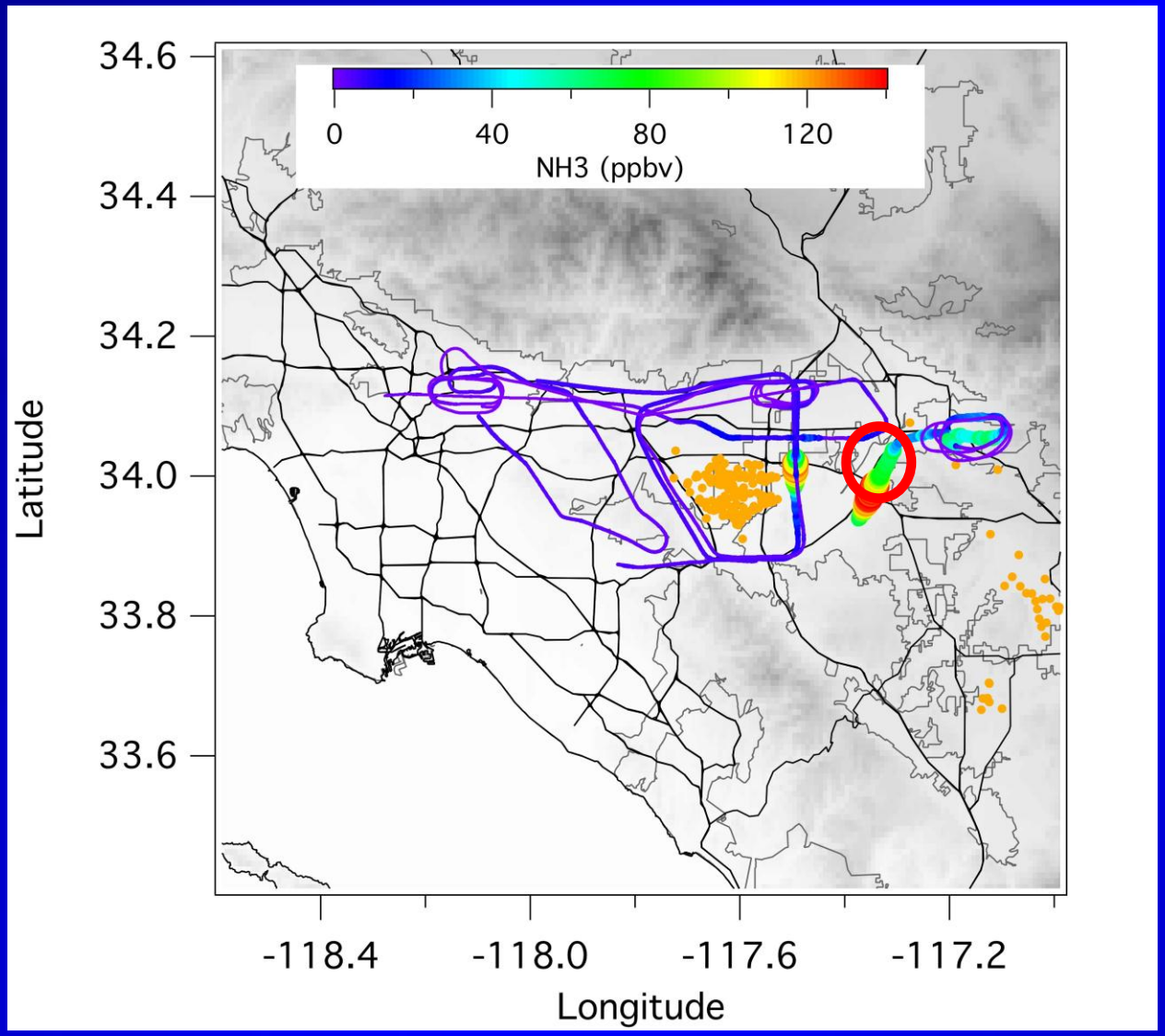
May 16 ~ 61 – 65 (metric tons/day) ~ 33 (metric tons/day)

Cars ≅ Cows

(within factor 2)

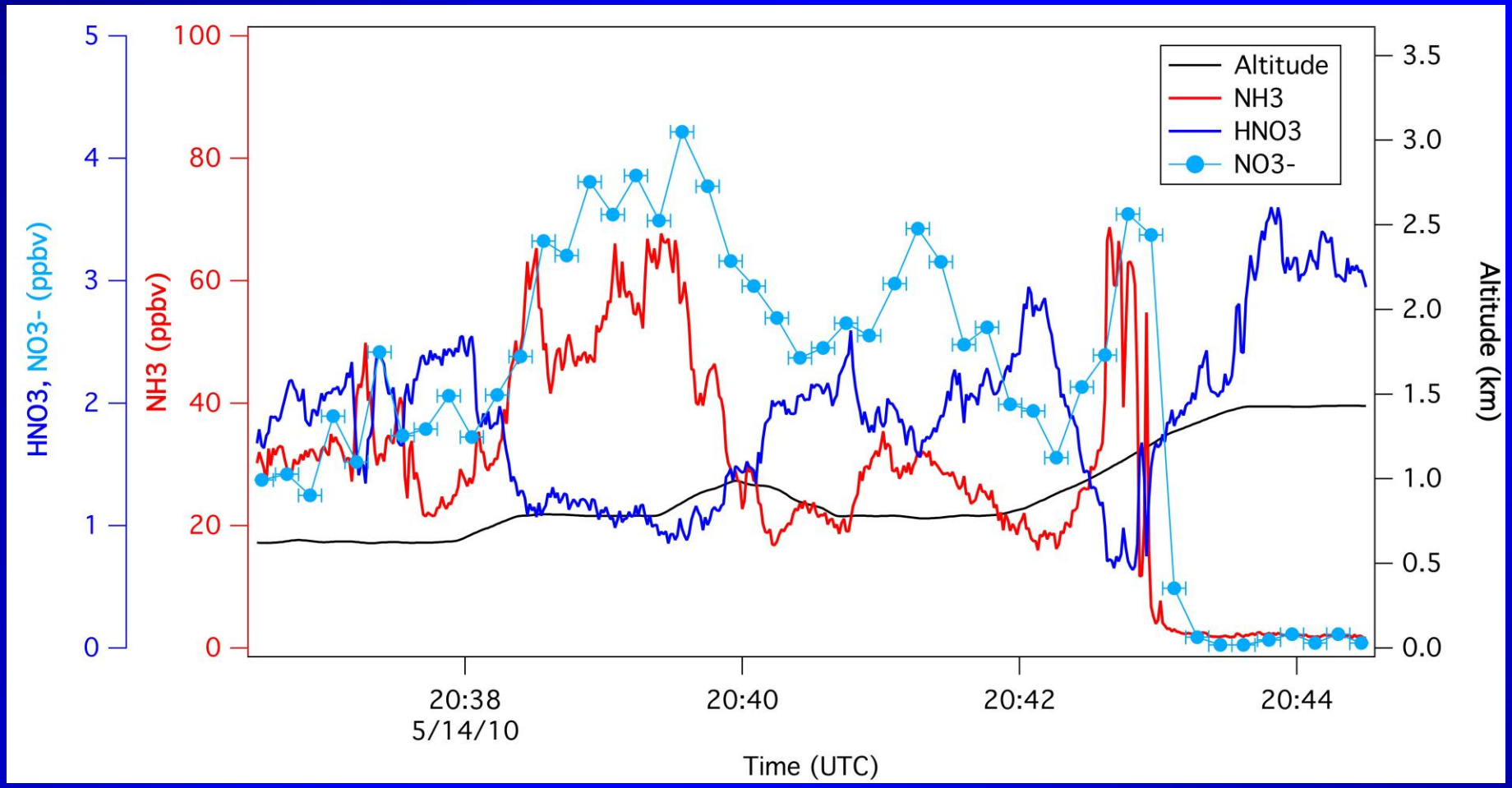
Cows geographically concentrated ➡ higher mixing ratios

Consequence of NH_3 emissions - NH_4NO_3



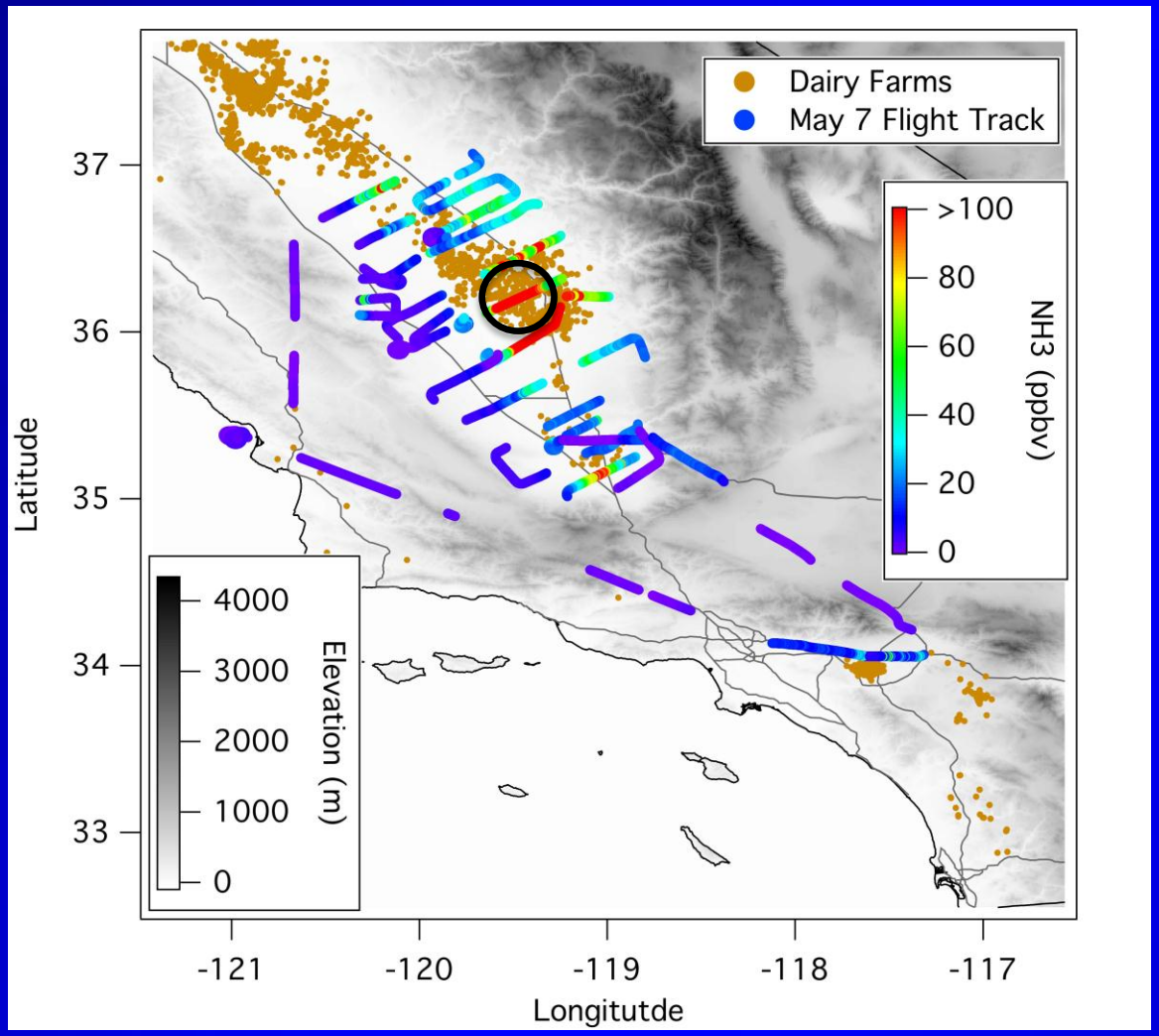
- NH_4NO_3 Formation

Consequence of NH_3 emissions - NH_4NO_3



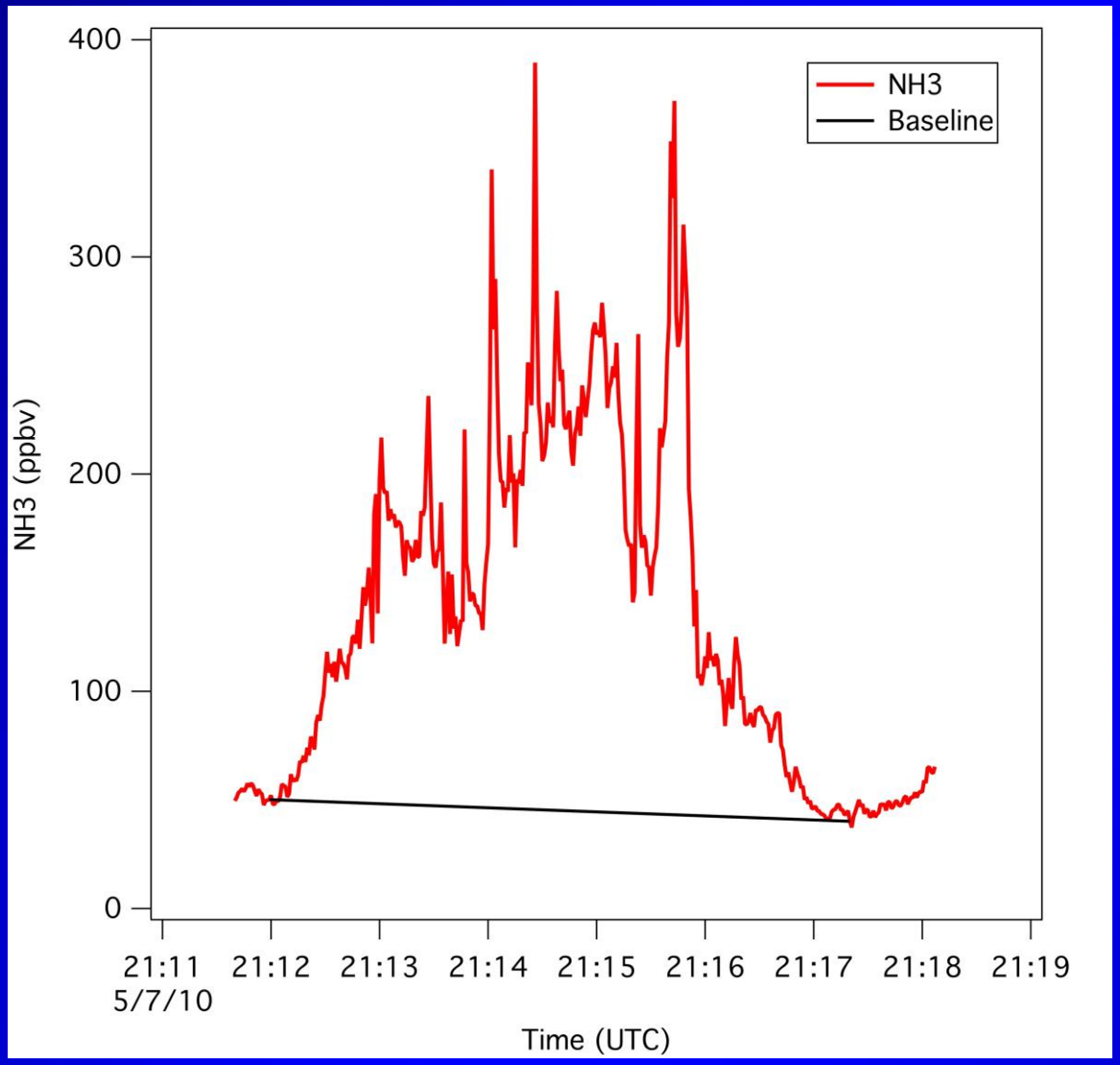
- NH_3 and HNO_3 anti-correlated
- NO_3^- increased indicating NH_4NO_3 formed
- ~10x more NO_3^- than in car transects

Central Valley NH_3 Dairy Farm Flux



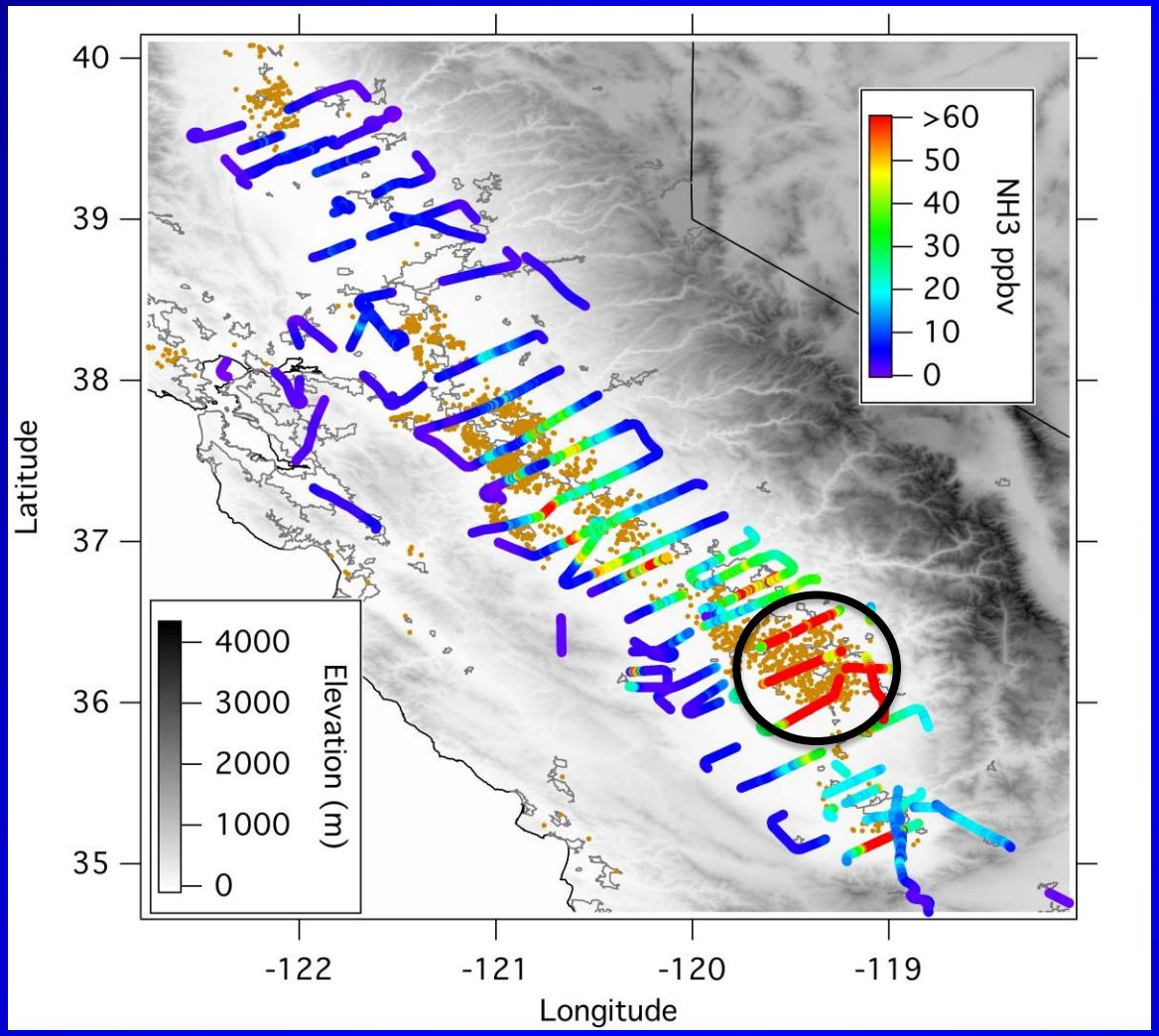
- Estimate flux from dairy farms

Central Valley NH_3 Dairy Farm Flux



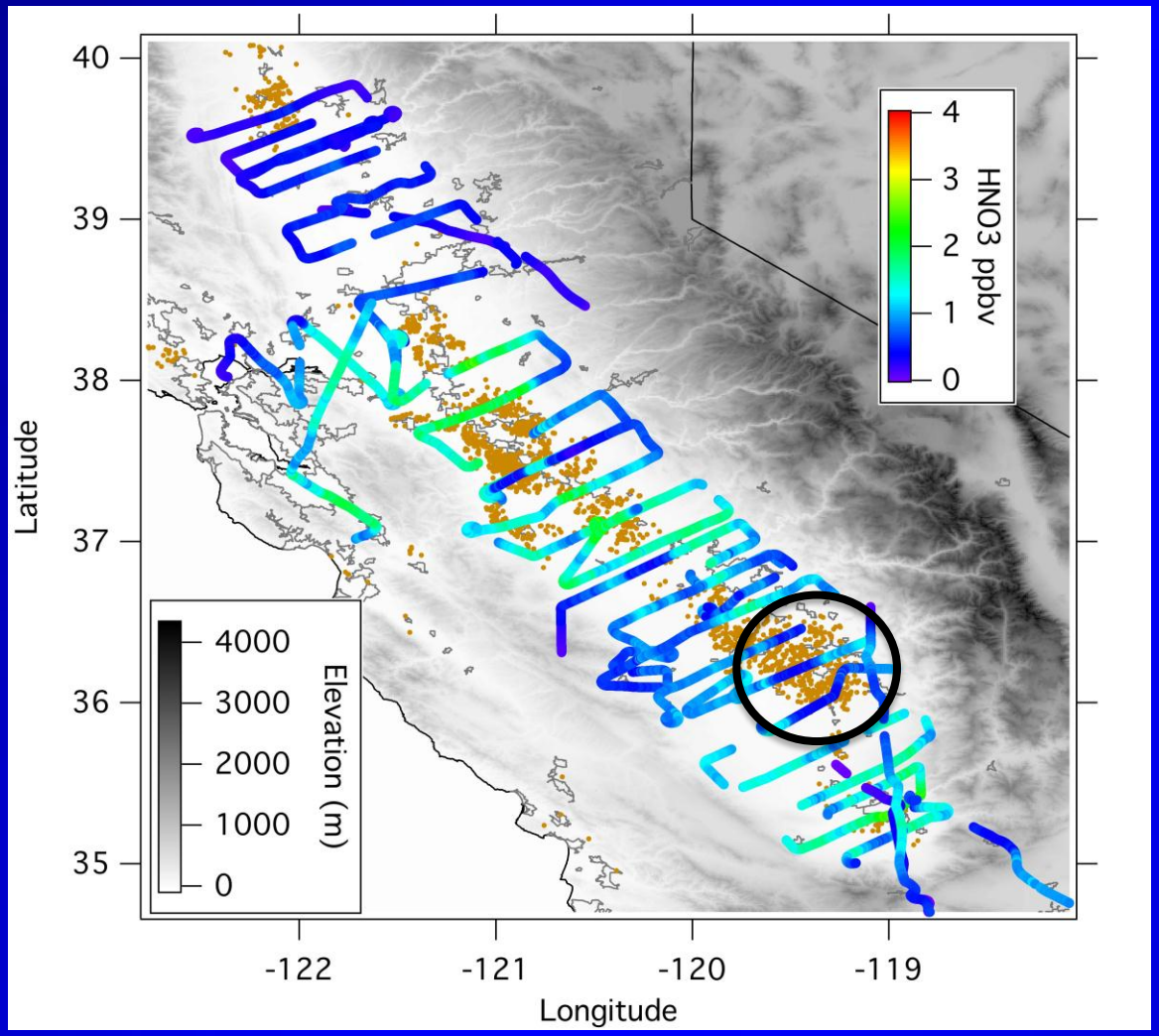
- Same flux calculation
- 636 metric tons/day
- ~6-20 times greater than SoCAB dairies
- Higher density of cows

Central Valley NH_3 Observations



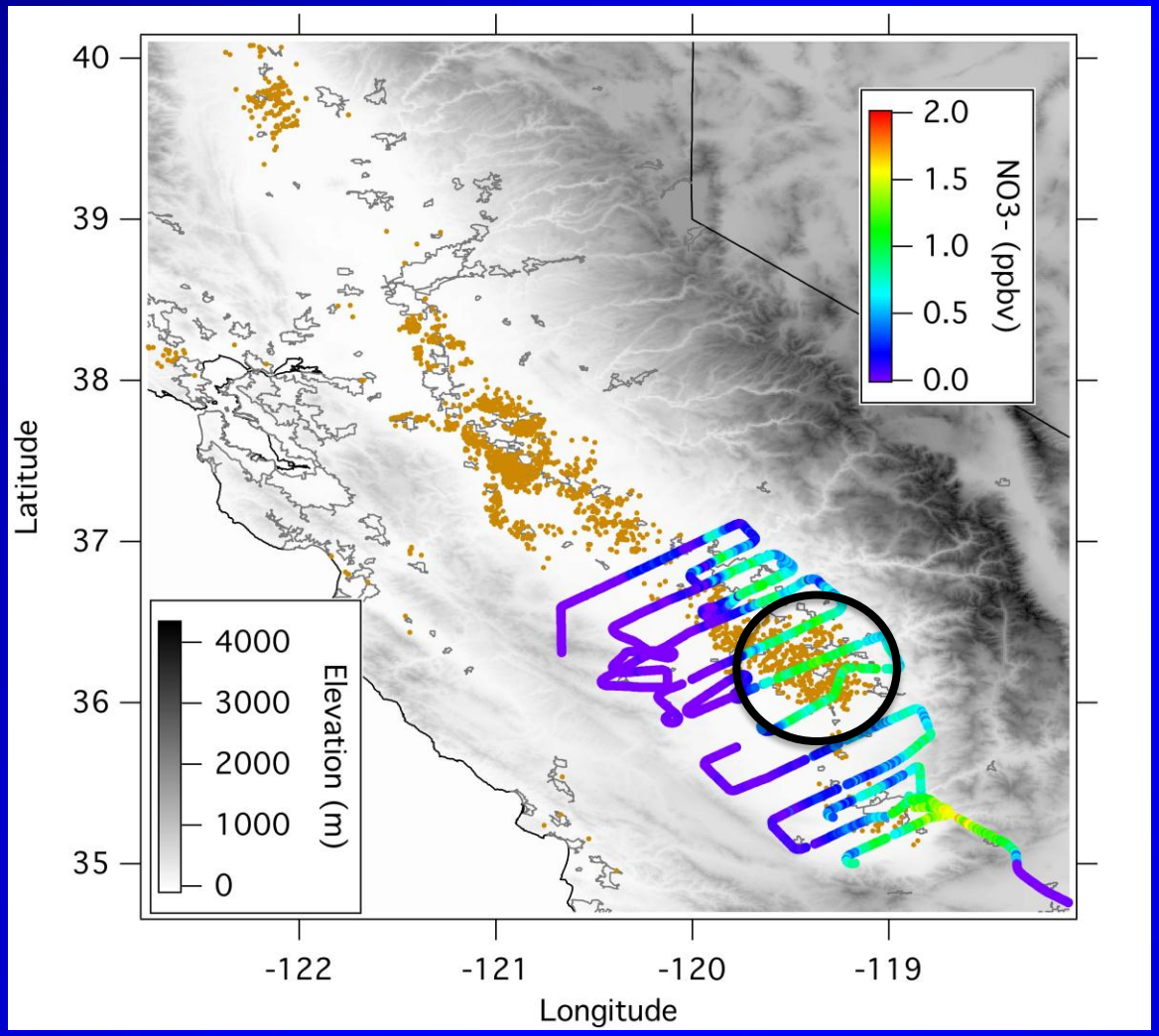
- May 7, 11, 12
- NH_3 peaks at 963 ppbv

Central Valley HNO_3 Observations



- May 7, 11, 12
- HNO_3 peaks at 3 ppbv

Central Valley NO_3^- Observations



- May 7
- NO_3^- peaks at <2 ppbv

- Despite abundance of NH_3, NO_3^- loading relatively small due to lack of HNO_3

Summary

- NH_3 mixing ratios high frequently over 10 ppbv, plumes up to 963 ppbv
- Estimated SoCAB automobile source 67 to 101 metric tons/day
- Estimated SoCAB dairy farm flux ~ 33 to 115 metric tons/day
- In South Coast Air Basin:

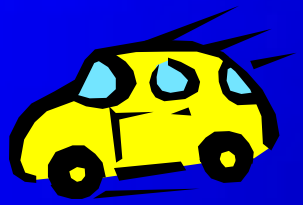
  Automobile ≈ Dairy farm (within factor of 2)
- Central Valley dairy farm flux up to 636 metric tons/day
- Despite abundance of NH_3 in the Central Valley, observed NO_3^- levels are low due to the lack of HNO_3

Sources of Ammonia

Animal Husbandry

Fertilizer Application

Biomass Burning, Soil Emissions



Cars, Industry

Measurement Techniques

- NH_3 - Chemical Ionization Mass Spectrometry (CIMS)
- HNO_3 - Chemical Ionization Mass Spectrometry (CIMS)
- Aerosol Composition - Compact Time of Flight Aerosol Mass Spectrometer (C-ToF-AMS)
- Aerosol Size Distributions -

  5-Channel Condensation Particle Counter (CPC)

  Ultra-High Sensitivity Aerosol Spectrometer (UHSAS)

  White Light Optical Particle Counter (White Light-OPC)
- CO - Vacuum UV Resonance Fluorescence

http://www.esrl.noaa.gov/csd/calnex/

Importance of Ammonia in the Atmosphere

- NH_3 typically most abundant atmospheric gas-phase base
- Water soluble and readily absorbed to surfaces, i.e., vegetation and soil
- Often major component of tropospheric aerosol as NH_4^+

$NH_3 + HNO_3 \leftrightarrow NH_4NO_3$	Ammonium Nitrate
$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$	Ammonium Sulfate
$NH_3 + HCl \rightarrow NH_4Cl$	Ammonium Chloride