# Long-term variability and source signature of gases emitted from O&NG and feedlot operations in the Colorado front range

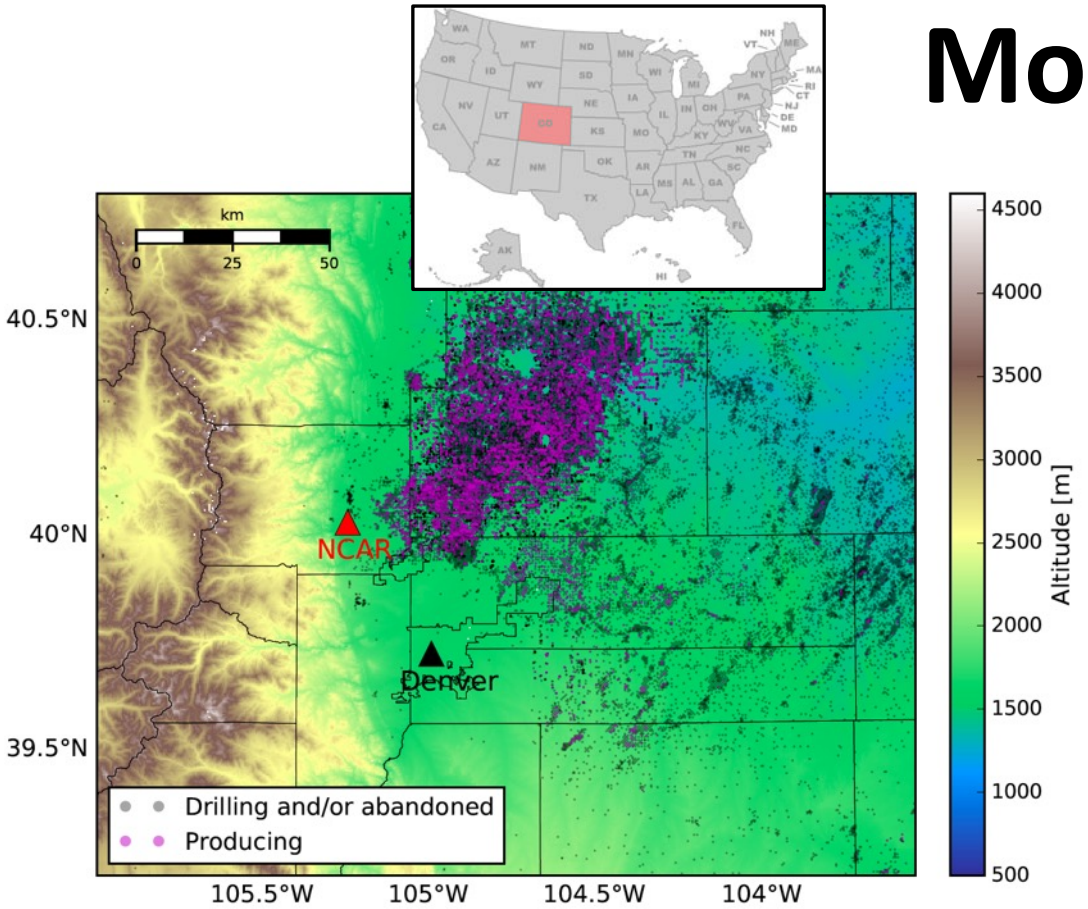
Ivan Ortega

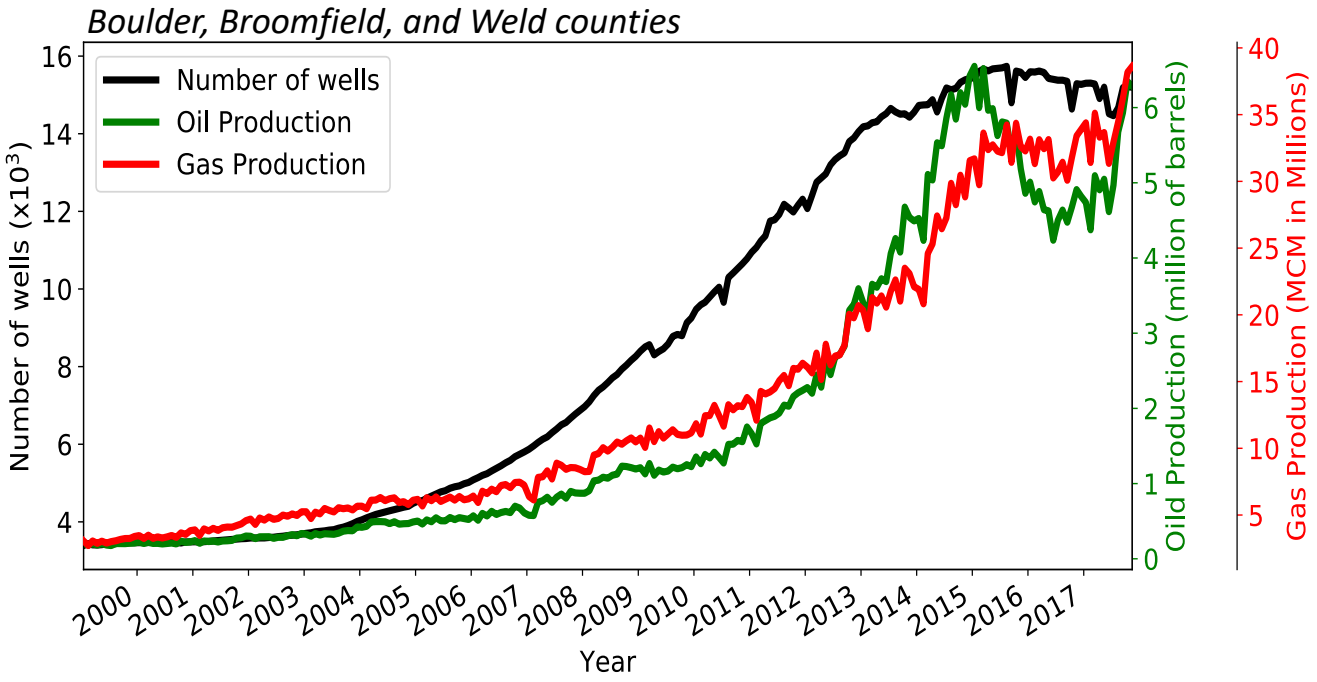
Jim Hannigan & Rebecca Buchholz

*Colorado panorama from the NOAA ozone and water vapor group*

Atmospheric Chemistry Observations & Modeling (ACOM)
National Center for Atmospheric Research (NCAR)

# Motivation

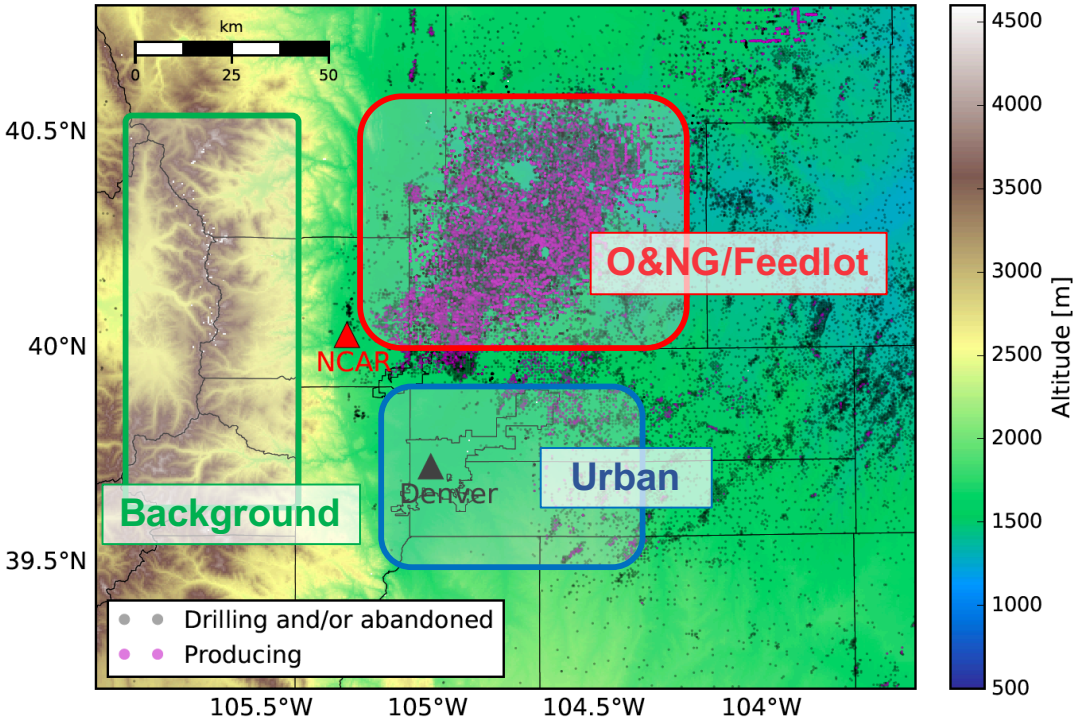


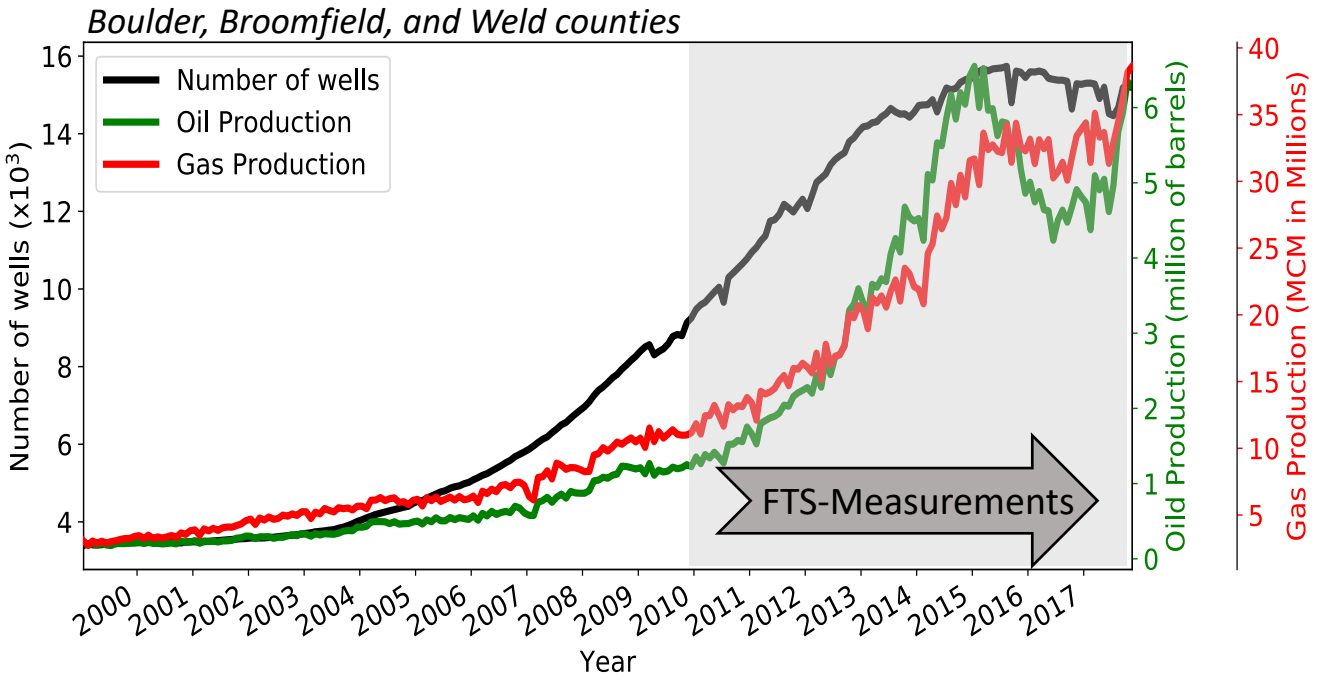




- Over the past decade oil and natural gas (O&NG) related activities have increased in the northern Colorado Front Range.

- Typically, observations are part of intensive short field deployments, e.g, FRAPPE, DISCOVER-AQ.

# Motivation




- Over the past decade oil and natural gas (O&NG) related activities have increased tremendously in the northern Colorado Front Range.

- Typically, observations are part of intensive short field deployments, e.g, FRAPPE, DISCOVER-AQ.

# Goals

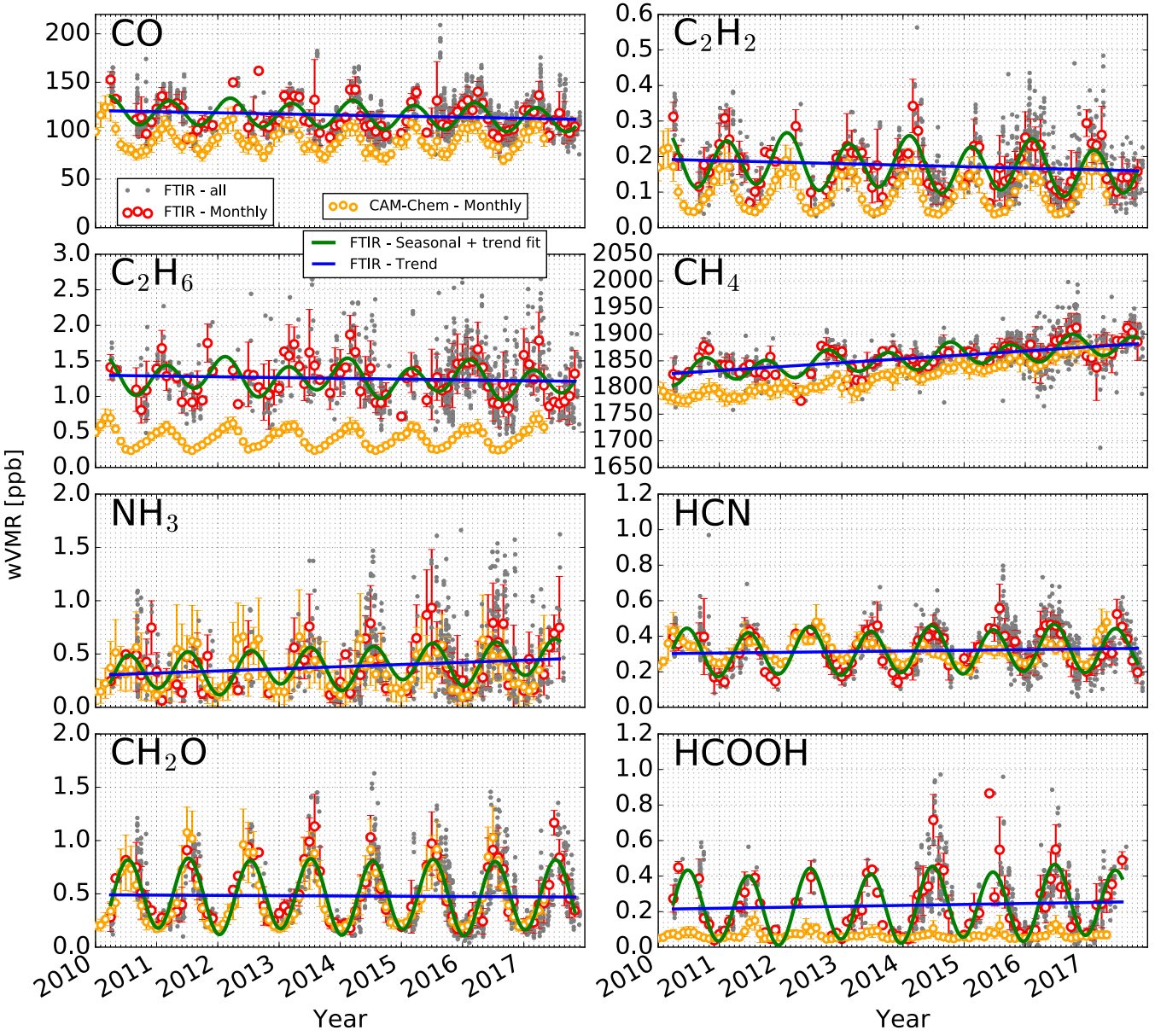
(1) Study trends of 7+ years of atmospheric gases related to:

- O&NG activities ($C_2H_6$ , $CH_4$ )
- Cattle feedlot operations ($NH_3$)
- Urban emissions (CO, $C_2H_2$),
- VOCs related to photochemistry and $O_3$ production ($H_2CO$, HCOOH).

(2) Assess the current state of chemistry transport models, in this case NCAR/CAM-Chem.

(3) Determine enhancements related to nearby O&NG and concentrated animal feeding operations with aim to determine enhancement ratios relative to CO of co-emitted species and estimate emission factors. Airborne observations are used to complement the FTIR observations

## Time series of mean weighted tropospheric VMR of gases derived from the FTIR in Boulder




Long-term trend and the seasonal modulation

$$f(t) = a_0 + a_1(t - t_0) + \sum_{n=1}^{N} b_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{N} c_n \sin\left(\frac{n\pi x}{L}\right)$$

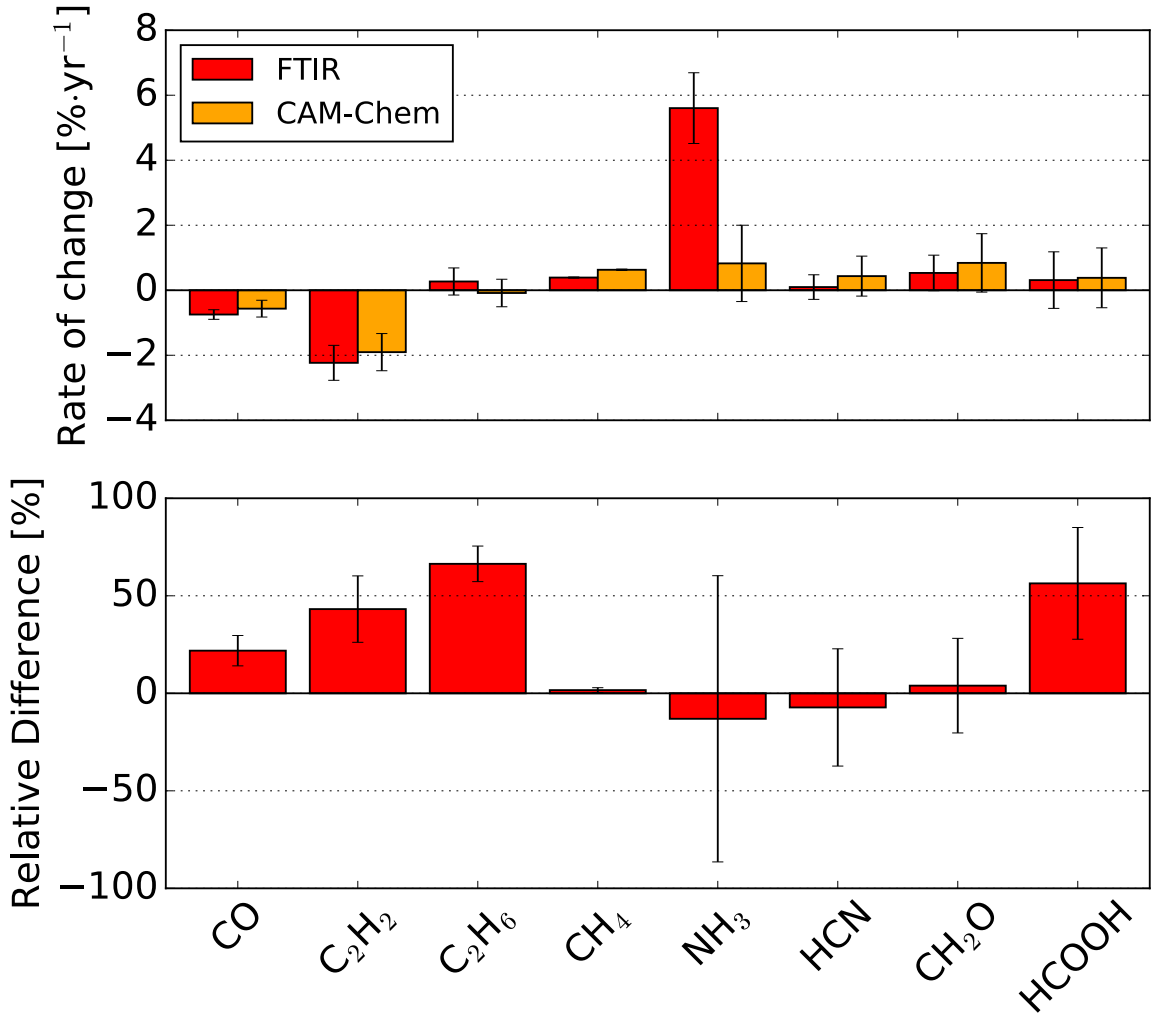
Linear component

Fourier series

## Full chemistry CAM6-chem simulations

| | |
|---|---|
| Resolution: | 1.25 longitude x 1.0 latitude, 56 levels (40 km model top) |
| Years Run: | 2010-2017, spin-up in year 2009 |
| Meteorology: | Nudged to NASA MERRA2 reanalysis product |
| Emissions: | Biomass burning → FINN (QFED was tested) |
| | Anthropogenic and Ocean → based on CMIP6 |
| | Biogenic → online MEGAN. |
| Chemistry: | 170 species, with over 400 reactions |

## Rate of change (FTIR & CAM-Chem)
## Relative difference between FTIR & CAM-Chem




## Some remarks

- Warner et al. (2017) identified an increase trend of $NH_3$ over the U.S. (2.61% $yr^{-1}$) using the Atmospheric Infrared Sounder (AIRS) aboard NASA's Aqua satellite - likely due to a combination of decreased chemical loss and increased soil temperaturas.
- Franco et al. (2016) showed a trend of $C_2H_6$ of 5.0 ± 4.5% $yr^{-1}$ from 2010-2014.
- Combustion tracers (CO) are declining in agreement with other measurements.
- Emissions of CO and $C_2H_6$ in CAM-Chem are underestimated.
- CAM-Chem represents well $H_2CO$ but work is needed to understand HCOOH

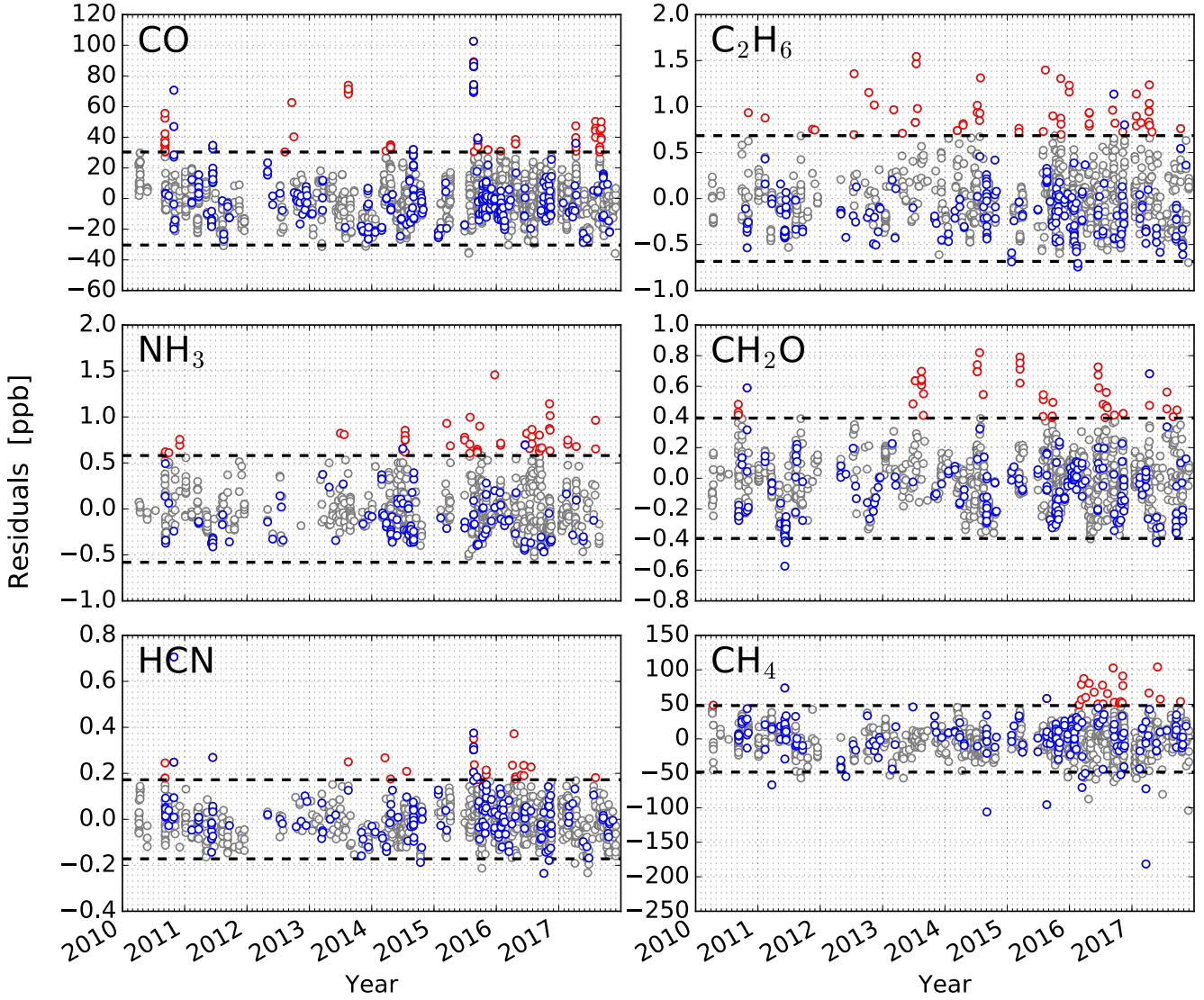
# Source attribution: O&NG and feedlot operations

(1) Calculate residuals:

$$\boldsymbol{Residuals} = \boldsymbol{wVMR_{FTIR}} - \boldsymbol{f(t)}$$

(2) Identify enhancements, in this case we found that measurements greater than 1-sigma standard deviation indicate possible enhancements.

(3) Distinguish air masses from background conditions using co-located wind measurements.



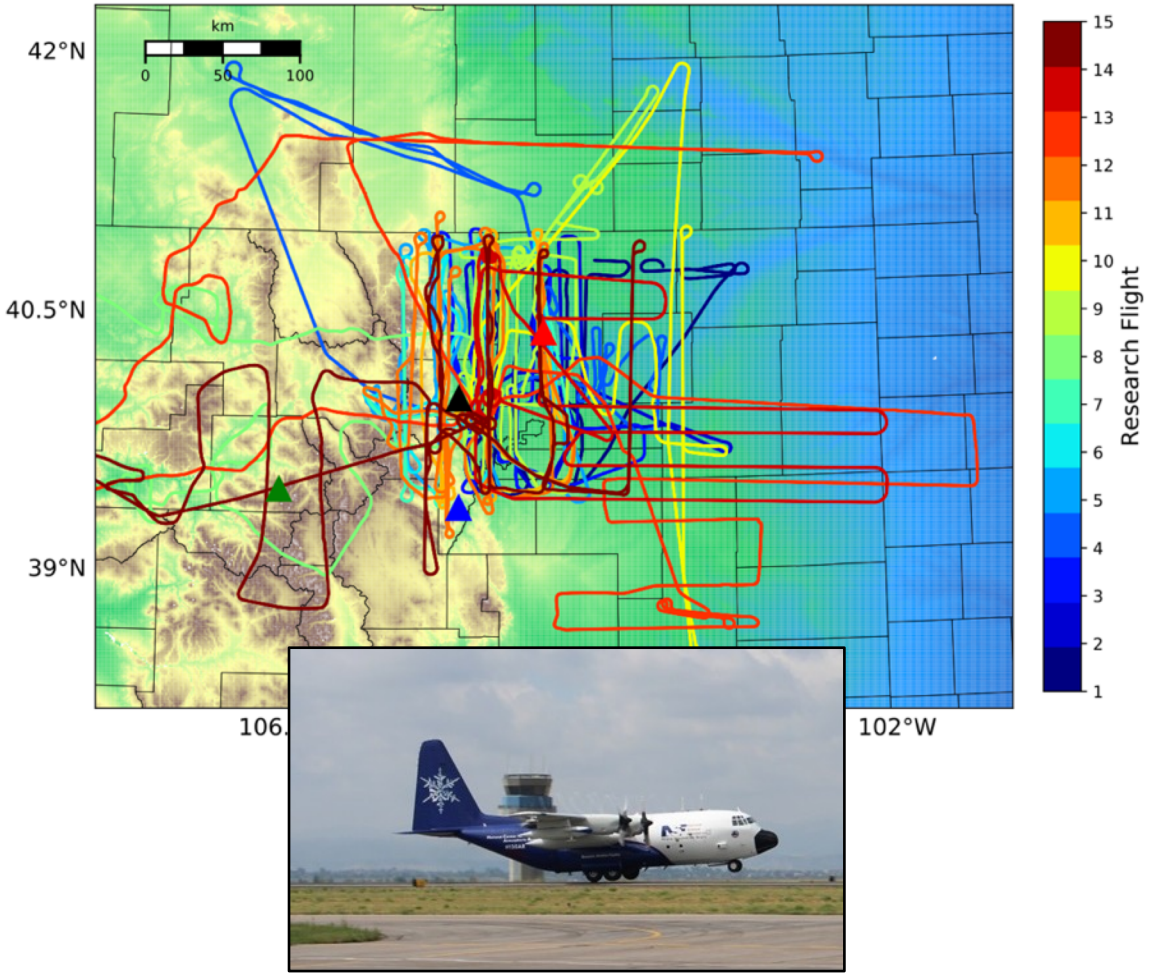

Gray - all data; Blue – background (west); Red - enhancements

# Airborne observations during FRAPPE

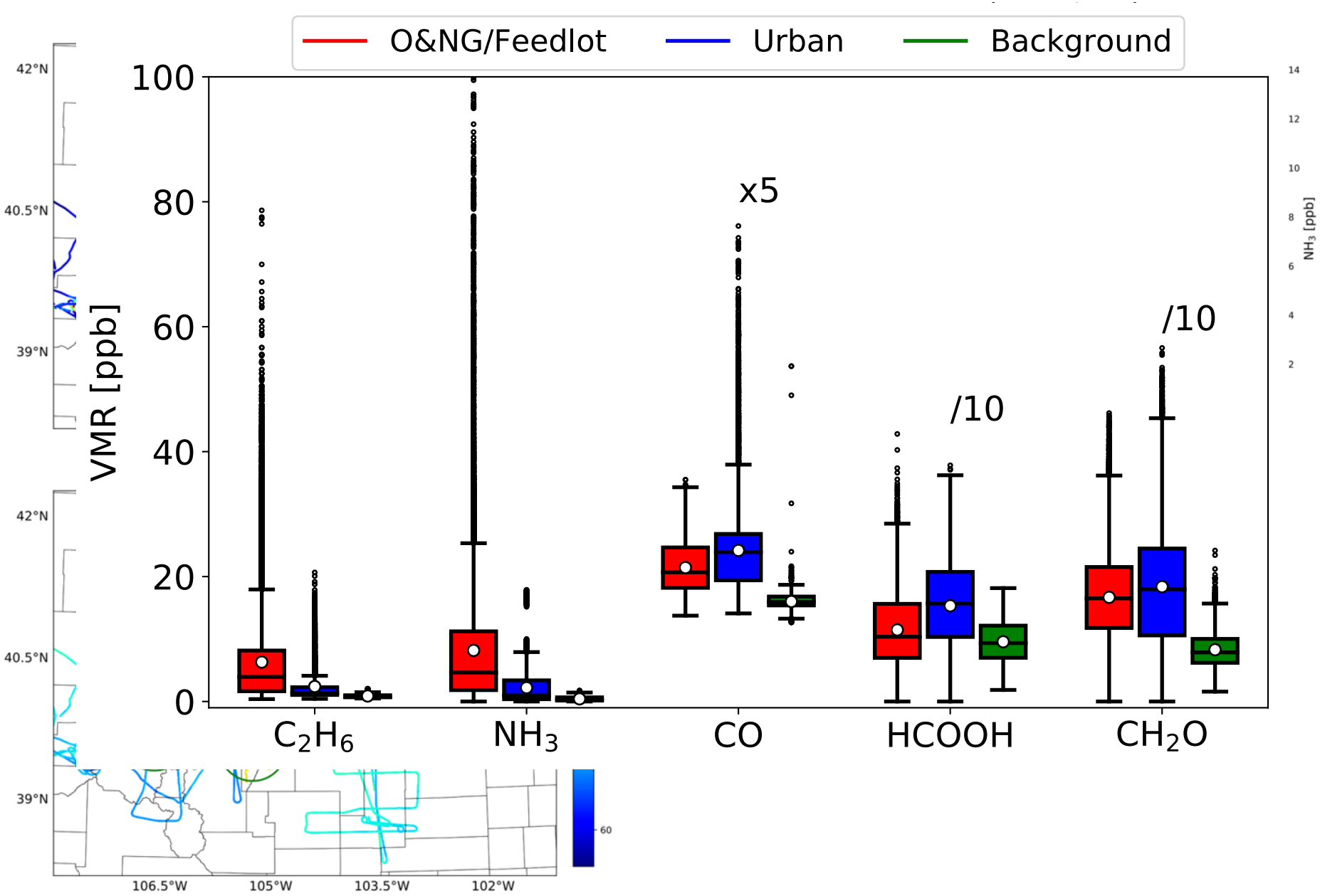
In the summer of 2014 the Front Range Air Pollution and Photochemistry Éxperiment (FRAPPÉ) was conducted with aim to study summertime ozone pollution - National Science Foundation (NSF)/National Center for Atmospheric Research (NCAR) and State of Colorado.

| Gas | Instrument |
|---|---|
| CO | ACOM/NCAR analyzer |
| $C_2H_6$ | CU Boulder – INSTAAR , Compact Atmospheric Multi-species Spectrometer (CAMS) |
| HCHO | |
| $NH_3$ | Dual $NH_3$/$HNO_3$ QCL Instrument, Aerodyne |
| HCOOH | USNA PCIMS in-situ measurements |

Research Flights (C-130)

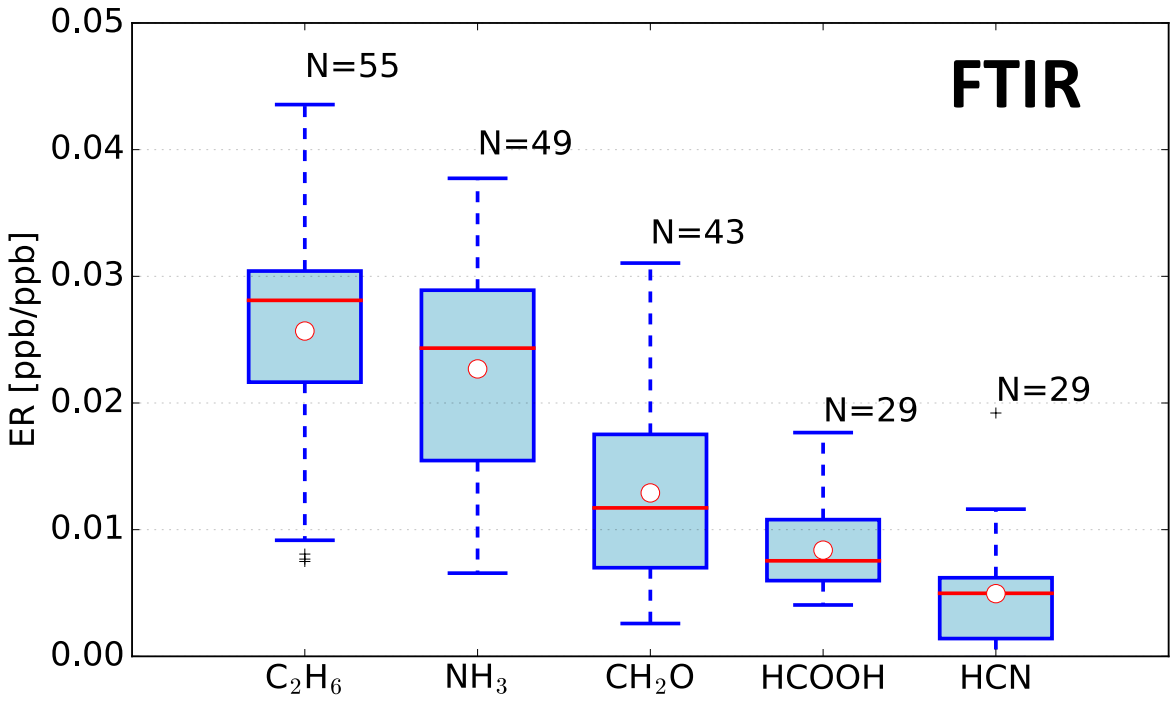


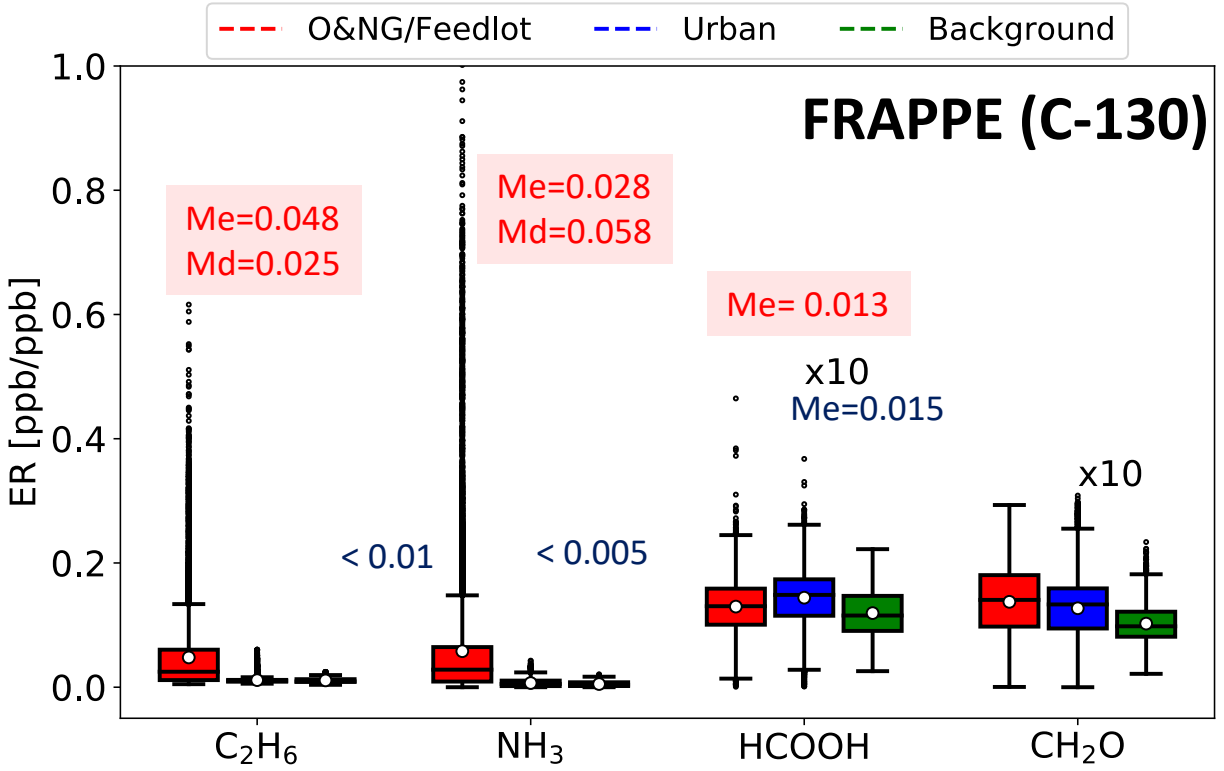
# Source attribution/characterization during FRAPPE



# Enhancement ratios (ER)

- Once enhancements likely due to O&NG and feedlots operations are identified enhancement ratios (ER) of $C_2H_6$ and $NH_3$ vs CO are calculated. Then emission factors are estimated for $C_2H_6$.
- For the FTIR the enhancement ratio (ER) is defined as the ratio between ΔX relative to ΔCO, where ΔX and ΔCO are the excess weighted VMR identified in the positive anomalies minus the weighted VMR from background conditions



# $C_2H_6$ Emission factors (EF) - Preliminary

$$EF_X = ER_X \frac{M_X}{M_{CO}} EF_{CO}$$

$EF_X$ = Emission Factor of gas X
$EF_{CO}$ = Emission Factor of CO in the sources of interest previously characterized (e.g., O&NG and biomass burning plumes)
$ER_{(X/CO)}$ = Emission Ratio of X to CO
$M$ = Molecular weight of X and CO

$EF_{CO}$ = 59.91 Tons/Day (O&NG Sources) EPA 2014 and validated during FRAPPE (60.42 Tons/Day)

| Gas | Emission Ratio | Emission Factor This work (Tons/day) | Emission Factor Kille et al., 2016 (Tons/day) |
|---|---|---|---|
| $C_2H_6$ | 0.026 | 1.67 | 1.52 |

# Summary & Outlook

- Seven years of FTIR measurements indicate: decline of combustion sources (CO); still increase of $C_2H_6$; increase of $NH_3$ (causes?).
- CAM-Chem captures the seasonal cycle and trends for most species, however underestimates others, e.g., $C_2H_6$ and HCOOH likely due to poor emissions and VOC oxidation sources, respectively.
- Enhancement ratios of O&NG and feedlot operations have been identified.
- Airborne observations during FRAPPE have been used to characterize source local regions.
- Top down emission factors of $C_2H_6$ have been estimated.
- Updated FTS 120/5 will be used to characterize diurnal cycles, weekends, etc

# Acknowledgment


- The measurements and analysis are performed with support from NASA. NCAR is supported by the National Science Foundation.

- We acknowledgment contributions from many people within ACOM (Mike Coffey, Eric Nussbaumer) and the FRAPPE Science team. In particular, Gabi Pfister from ACOM.


## Thanks!