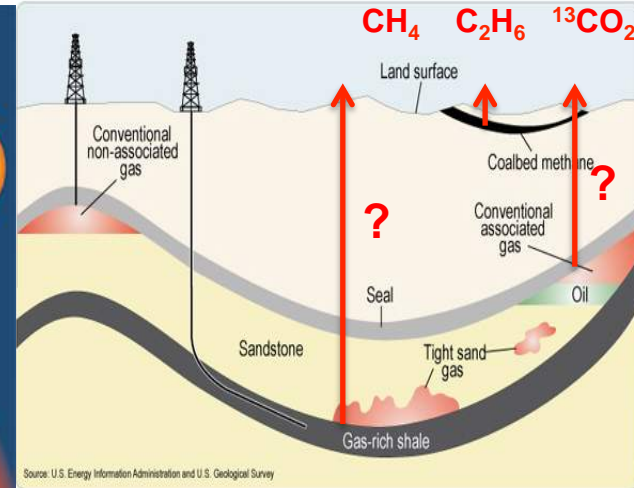
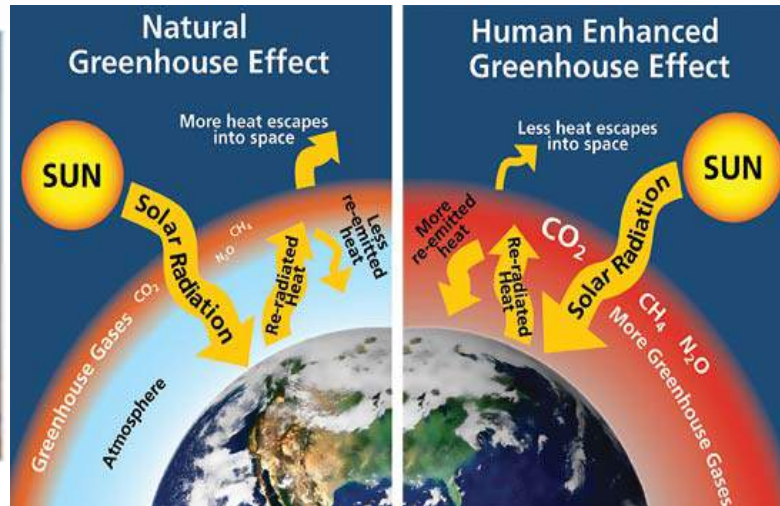


# CO<sub>2</sub> & CH<sub>4</sub> Emission Verification by High Frequency Mesoscale Atmospheric Observations

San Juan Power Plant



**Manvendra K. Dubey**  
EES-14 & IGPPS, LANL

[dubey@lanl.gov](mailto:dubey@lanl.gov)

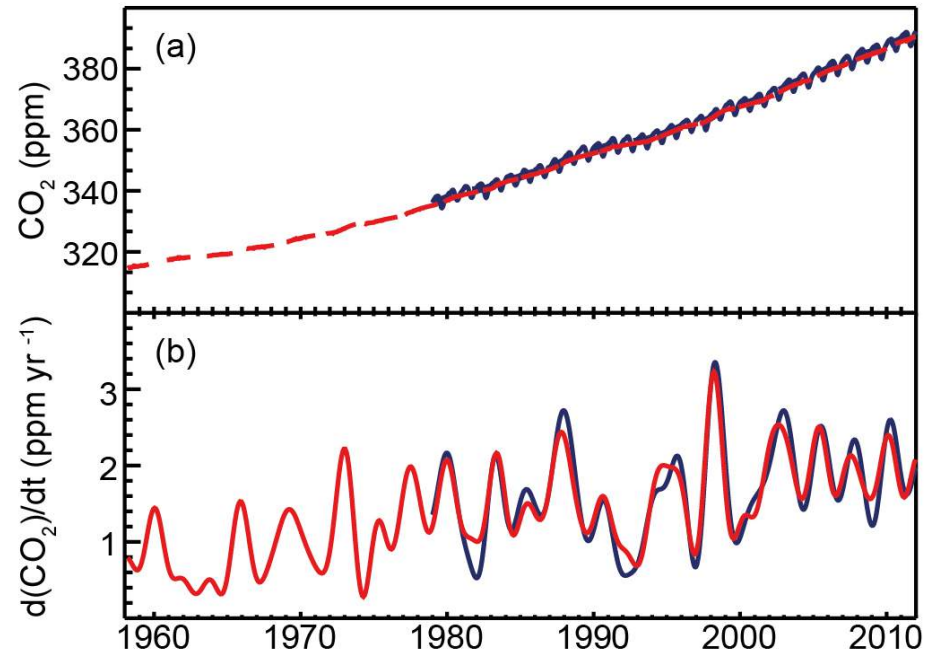
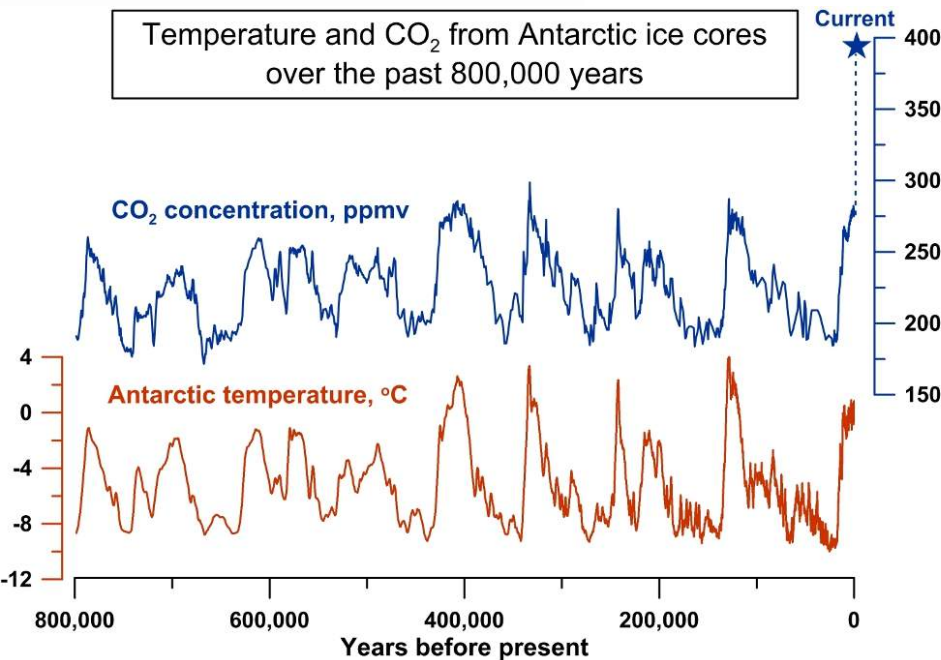
# Outline: Tackle the Emission Verification Challenge

- Can we verify CO<sub>2</sub> emissions for trading or a treaty?
  - Four Corners power plant emission attribution & verification.
- Can we quantify CH<sub>4</sub> leaks from fossil fuel infrastructure
- Fugitive CH<sub>4</sub> leaks from hydraulic fracturing are a hot issue.
- Current Measurement Challenges
  - Large Meteorological variability (in situ)
  - Low frequency sampling (satellite)
- Solar absorption spectroscopy (e.g. TCCON, Pandora)
  - Mean Mesoscale ( $\gamma$ ) 10km Column CO<sub>2</sub>, CH<sub>4</sub> & NO<sub>2</sub> Observations
- Model and Empirical Analysis
  - High Resolution Forward Modeling with inventory (CEMS, EDGAR)
  - Empirical tracer-trace relations for emission factor verification

# Atmospheric CO<sub>2</sub> Paleo-climatic Variations and Rapid Growth in The Anthropocene

## Ice core data from analysis of trapped bubbles

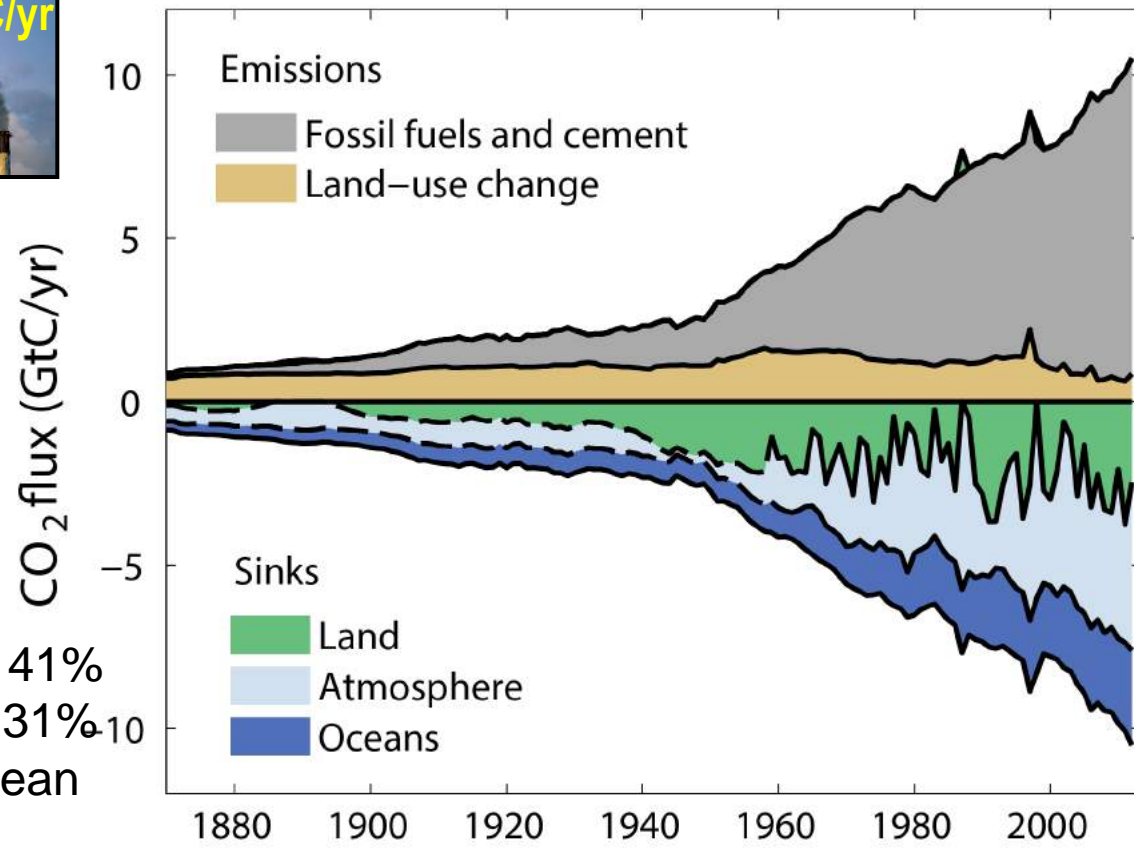
## Real time *in situ* data from global networks



- CO<sub>2</sub> > 400ppm, 43% increase since 1750, highest in 0.8 million years
- Greenhouse gas that traps terrestrial IR to warm the earth
- Acidifies oceans and suppresses calcite precipitation (coral growth)

# Global CO<sub>2</sub> Cycle: Currently ~55% of human emissions soaked up by the biosphere & oceans

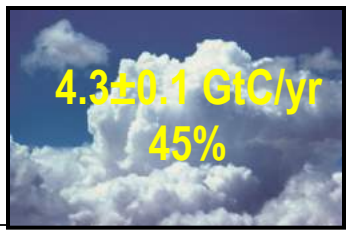
CO<sub>2</sub> Emissions = Atmospheric rise + land uptake + oceanic sink



**Will nature's CO<sub>2</sub> buffering as climate change intensifies?**

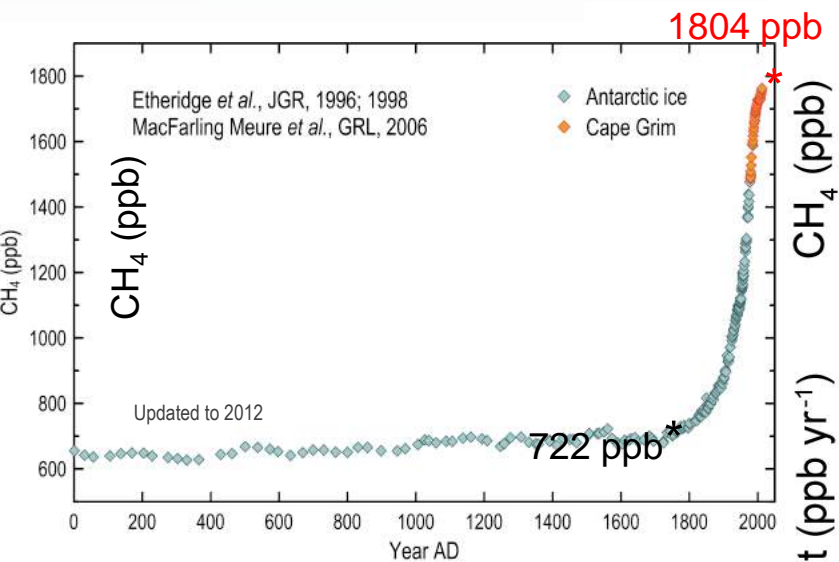
- Forest dieback!
- Release from thawing tundra!
- Ocean outgassing!
- Slow calcification!

\*Since 1870: 41% atmosphere, 31% land, 28% ocean



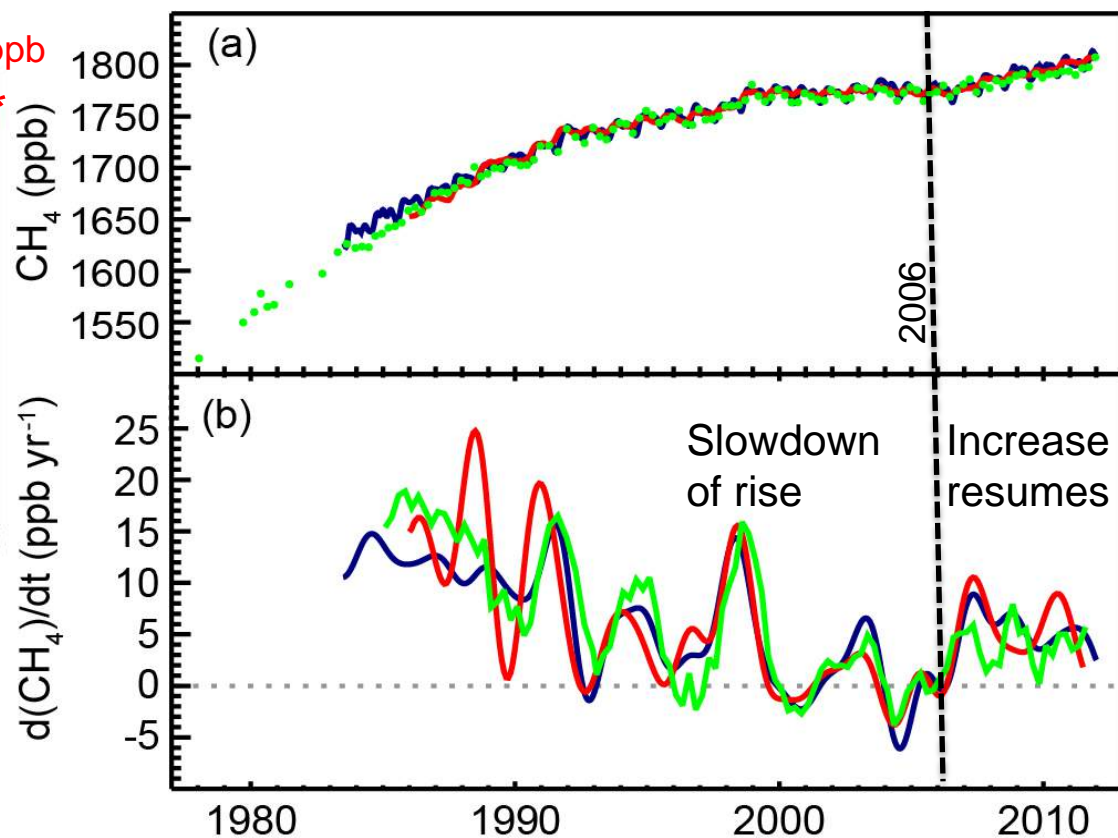
# Atmospheric CH<sub>4</sub>: Rising again

## Ice core data from analysis of trapped bubbles

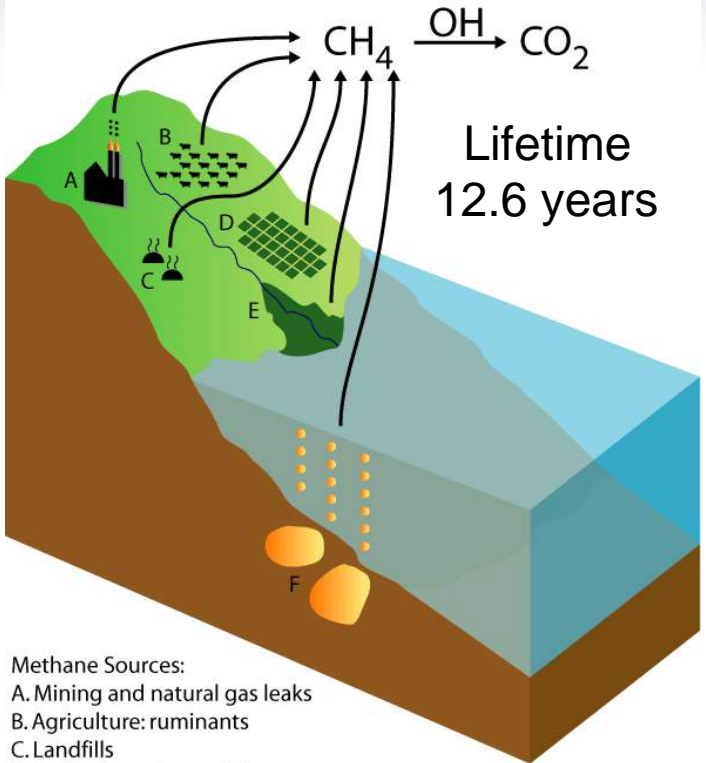


- 150% increase since 1750
- Greenhouse gas
- Source of stratospheric H<sub>2</sub>O
- \* Produces tropospheric O<sub>3</sub>

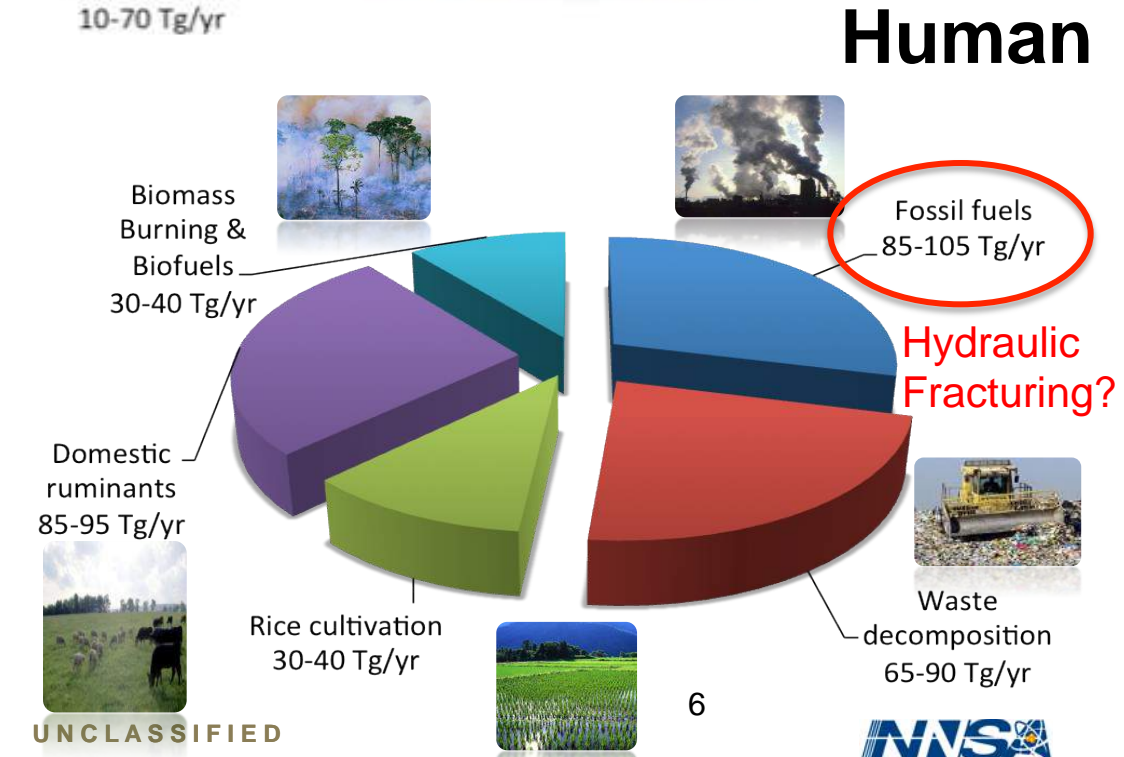
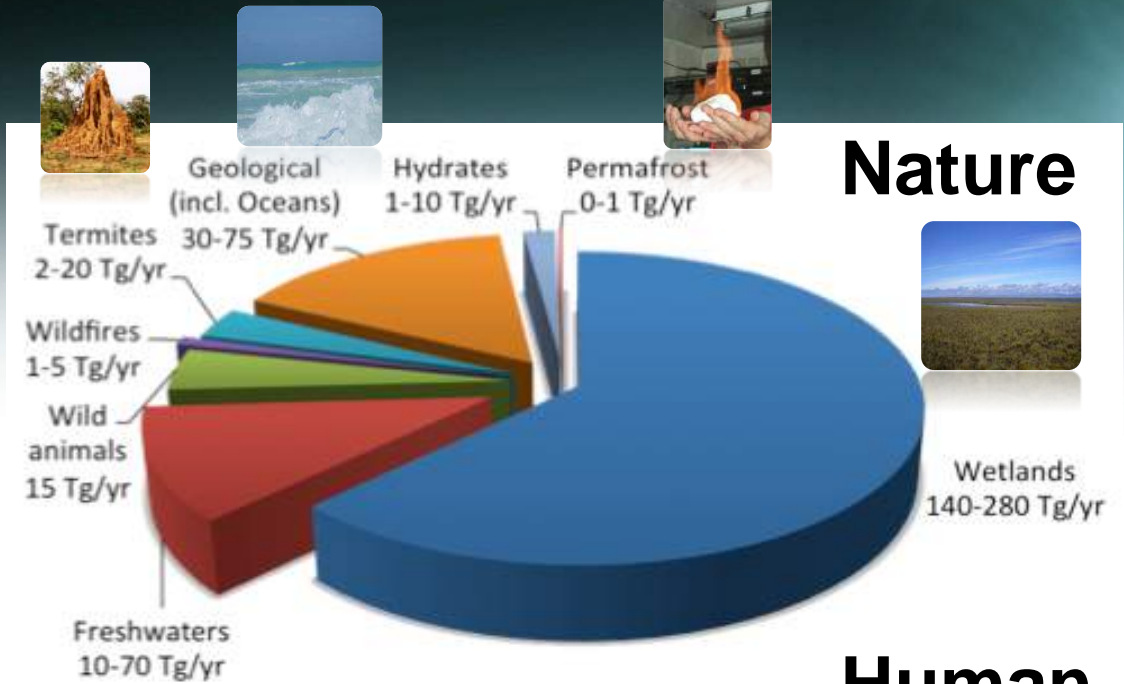
## Real time in situ data from global networks



# Methane: lifetime ~ 10 yrs, Complex source mix



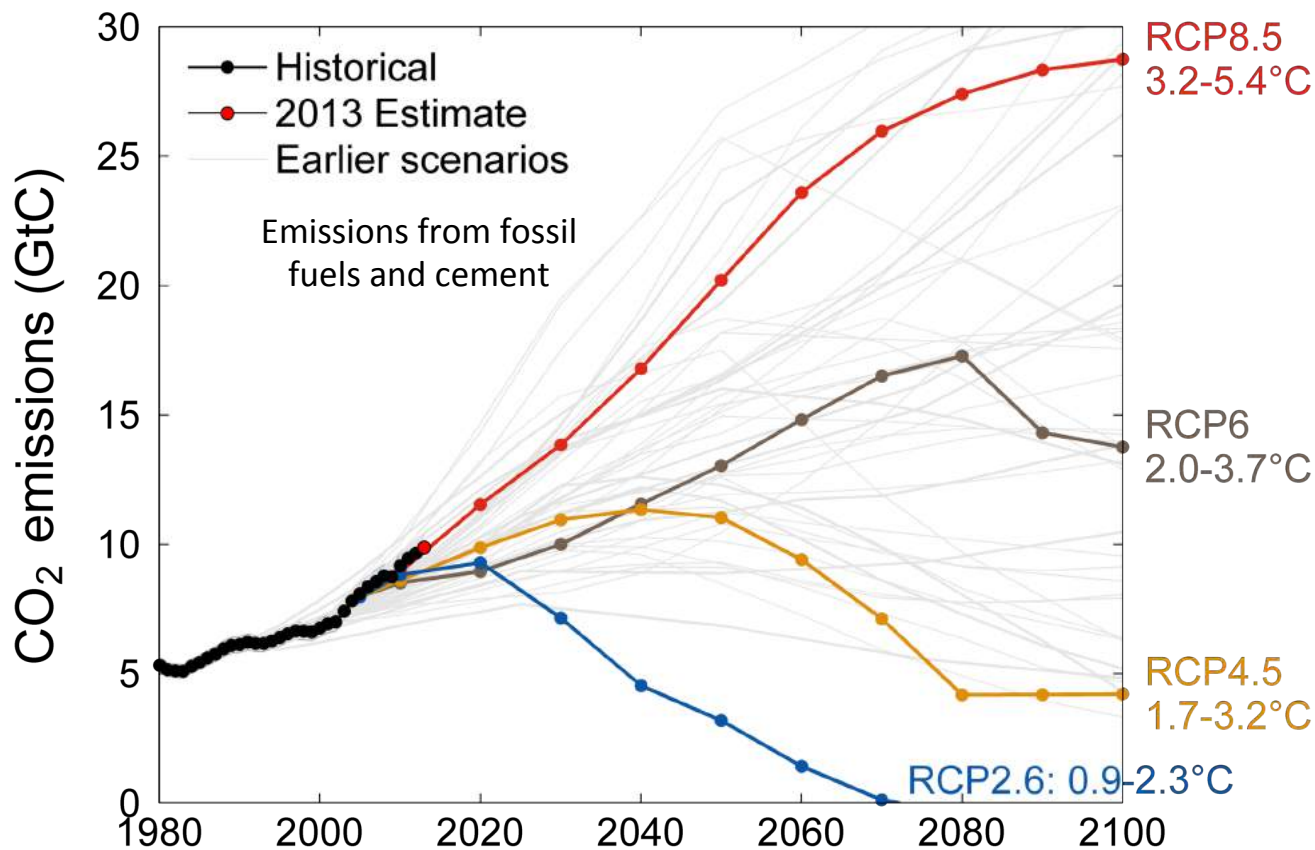
- Methane Sources:
- A. Mining and natural gas leaks
  - B. Agriculture: ruminants
  - C. Landfills
  - D. Agriculture: rice paddies
  - E. Natural wetlands
  - F. Hydrates



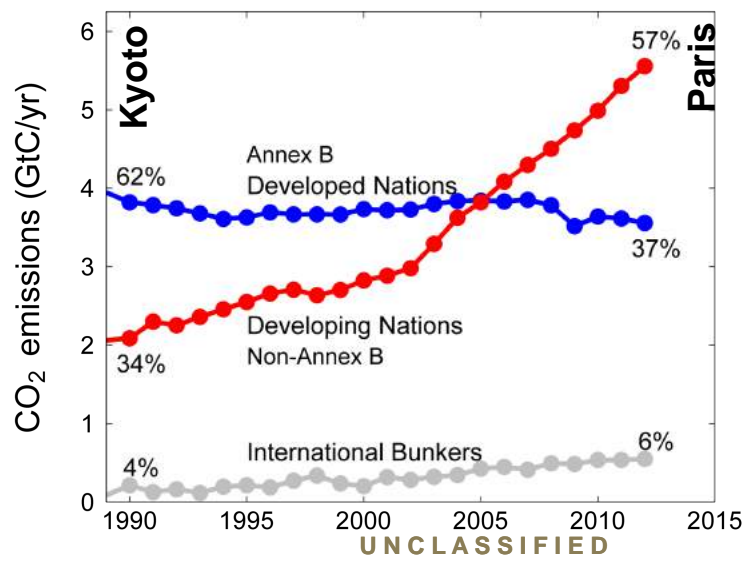
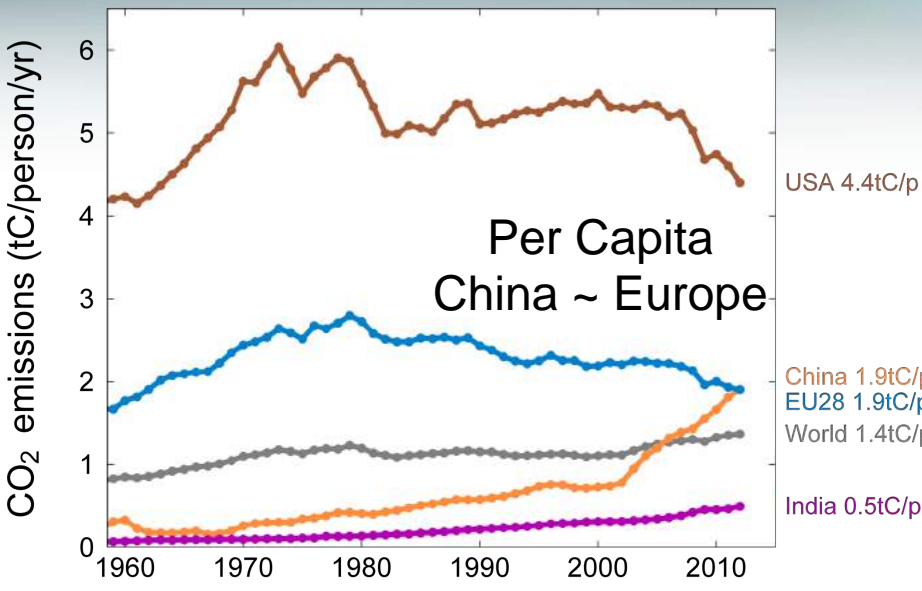
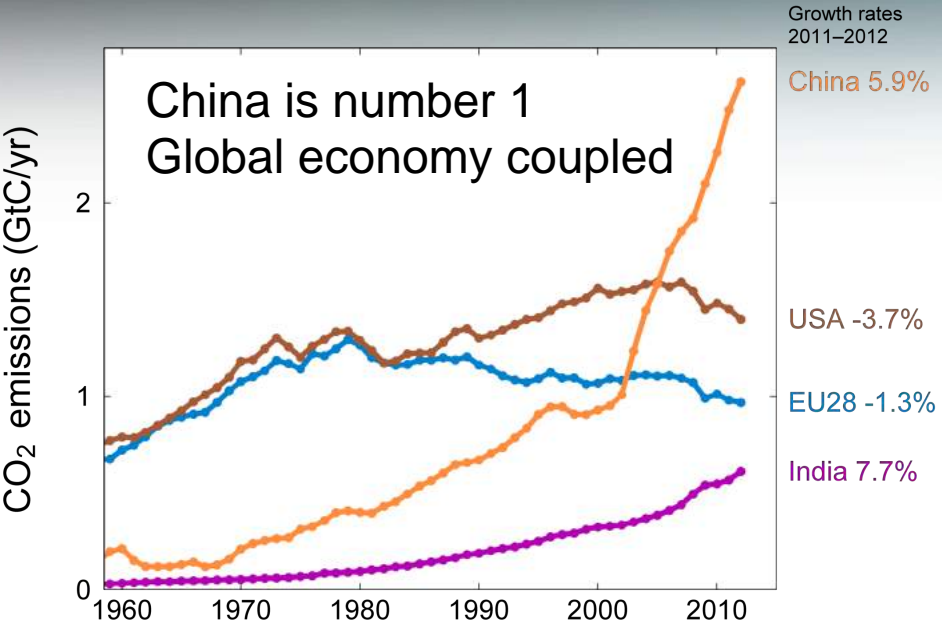
# The need for a climate treaty or trading: Observed emissions at high end hedged to 3-5C

Emissions on high end of past projections and are on track for 3.2–5.4°C  
“likely” increase in temperature above pre-industrial

Large and sustained mitigation is required to keep below 2°C



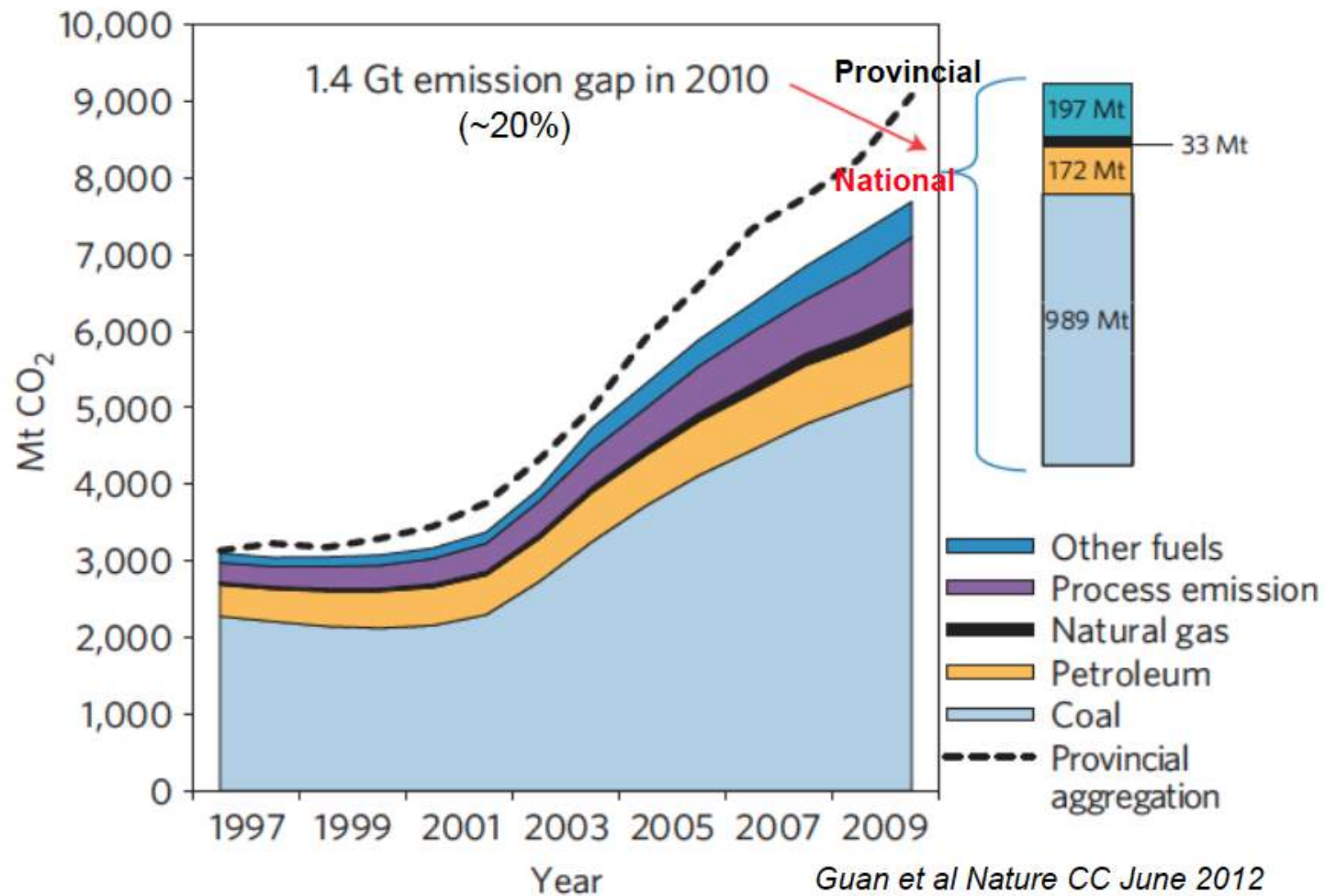
# Changed Emission Patterns: Need to update treaty framework (verify both sinks to sources)



- Kyoto targeted forestation
- Copenhagen grappled with verification, unsuccessfully
- Paris needs to develop an effective framework



# The need for verification: China's CO<sub>2</sub> Provincial & National Inventories Diverge by 1.4Gt



# The US Verification Science Challenge: Need and Opportunity

Detect and infer emissions from small human CO<sub>2</sub> signal (<1ppm) over large and variable natural background (390 ppm) in complex flows from afar without spatio-temporally resolved inventories.

National Academies Report  
March 19, 2010



VERIFYING GREENHOUSE GAS  
EMISSIONS: METHODS TO  
SUPPORT INTERNATIONAL  
CLIMATE AGREEMENTS

Global Greenhouse Gas  
Information



MULTILAB NNSA-JPL STUDY  
January 2012

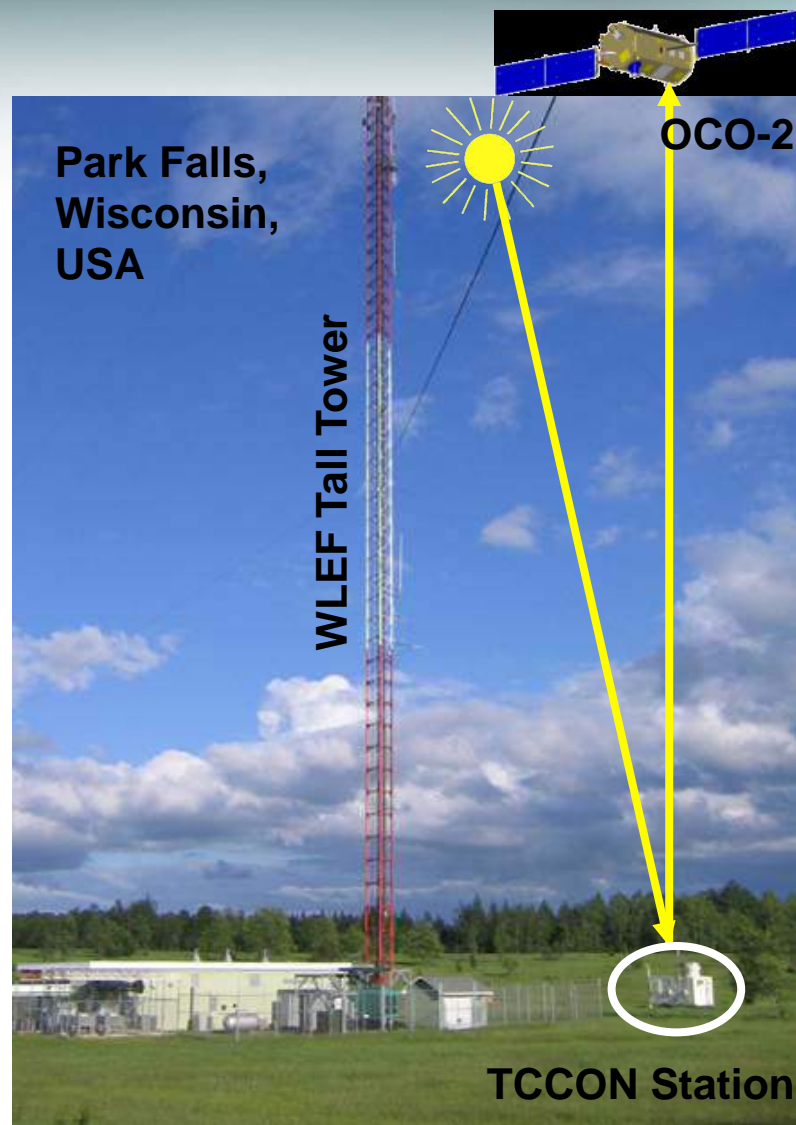
JAPAN's GOSAT &  
NASA's OCO2 satellites



LANL (DOE-OBBER)  
sole validation target  
from ground in  
Amazon (<0.3ppm)

# TCCON Science Objectives

- Constrain global fluxes of carbon and improve our understanding of the carbon cycle
- Provide the primary validation (ground-truth) dataset for satellite instruments
  - GOSAT
  - OCO-2
  - SCIAMACHY
  - ASCENDS
  - AIRS
  - TES
  - CARBONSAT
- Provide a transfer standard between the satellite measurements and the ground-based *in situ* network



# TCCON Instruments

- Ground-based Fourier transform spectrometers
- Remote sensing of total columns of CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO, H<sub>2</sub>O, HDO, O<sub>2</sub> via solar absorption
- Divide trace gas columns by O<sub>2</sub> column to get dry-air mole fractions: X<sub>CO<sub>2</sub></sub>, X<sub>CH<sub>4</sub></sub>, X<sub>N<sub>2</sub>O</sub>, X<sub>CO</sub>, X<sub>H<sub>2</sub>O</sub>, X<sub>HDO</sub>

Molecule	Precision	Accuracy
----------	-----------	----------

CO <sub>2</sub>	~0.8 ppm	~0.8 ppm
-----------------	----------	----------

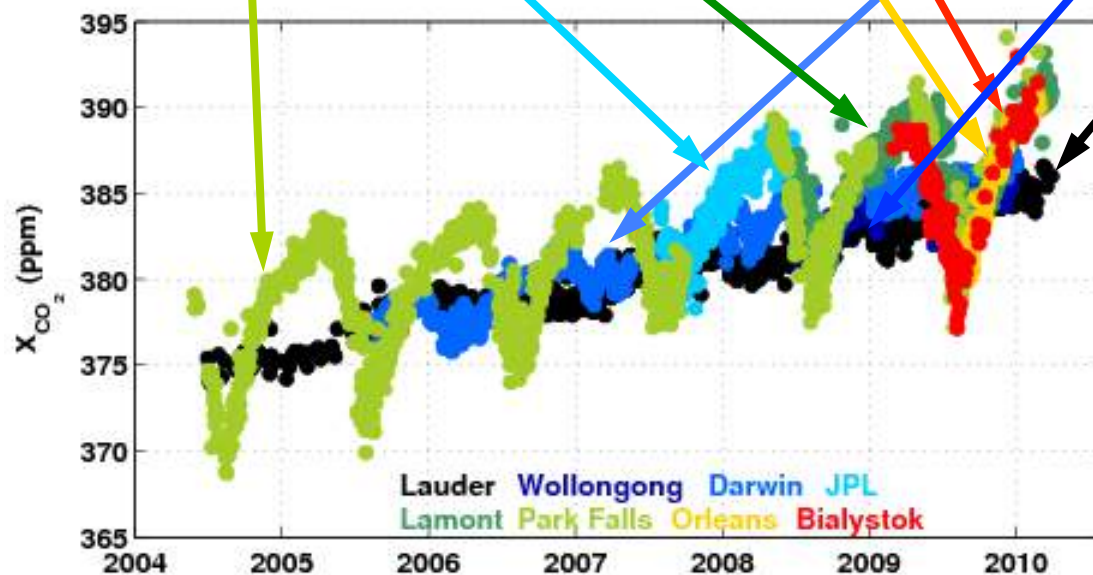
CH <sub>4</sub>	~5 ppb	~7 ppb
-----------------	--------	--------

N <sub>2</sub> O	~1.5 ppb	~3 ppb
------------------	----------	--------

CO	~0.5 ppb	~4 ppb
----	----------	--------



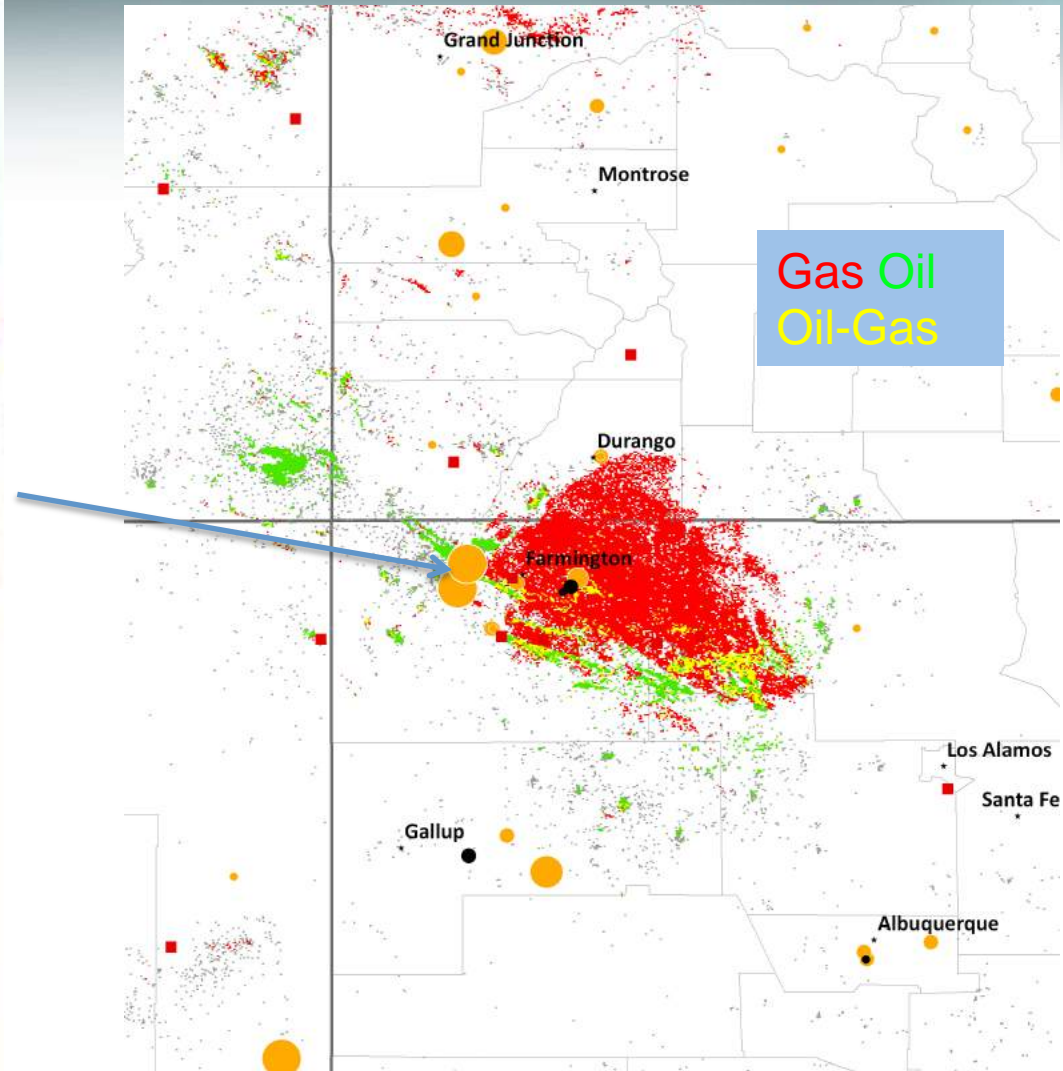
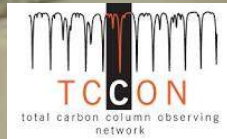
# TCCON Measurements



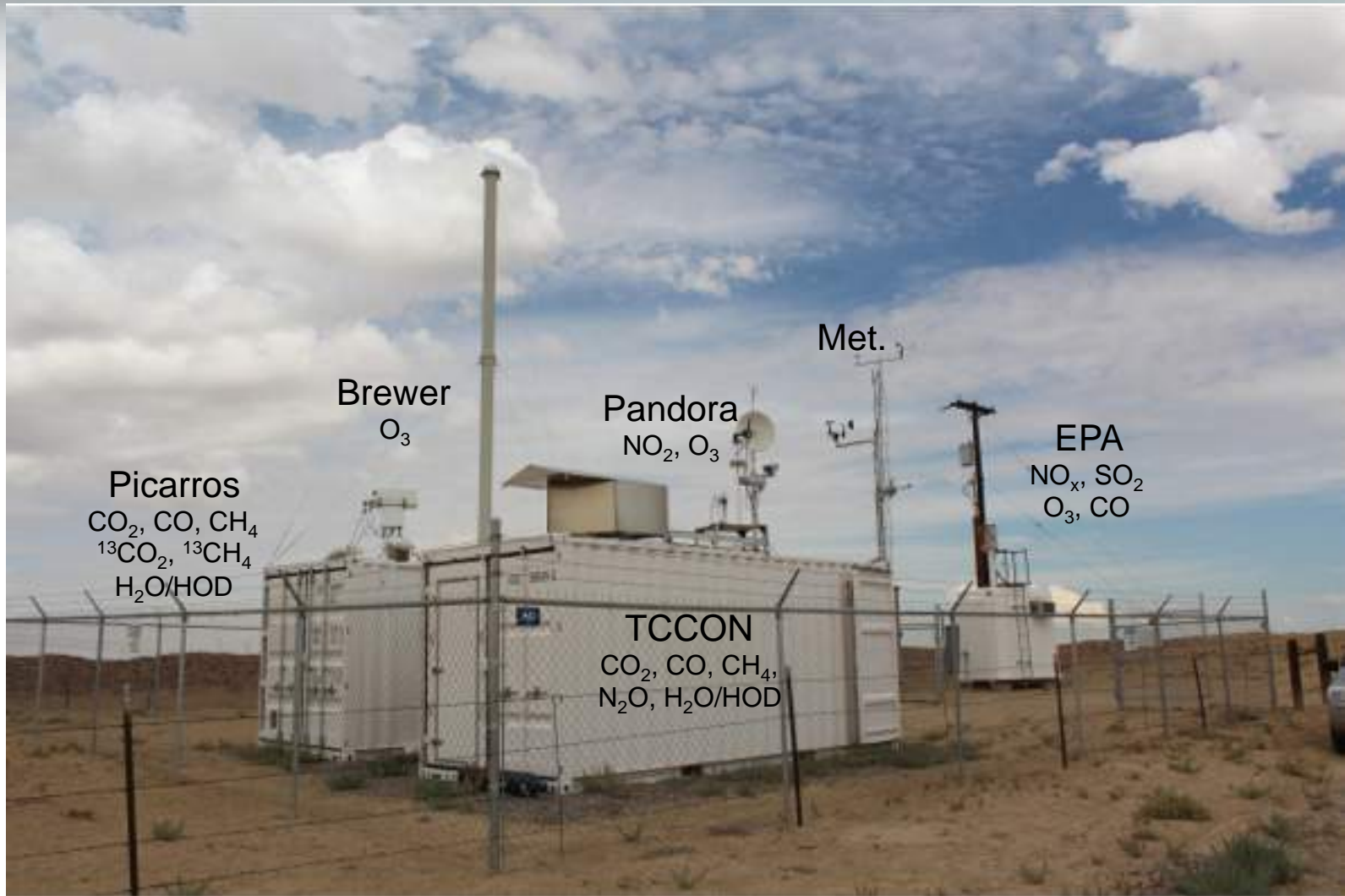
# 4-Corners Site: In between San Juan & 4Corners Power Plants E/SE of Coal, Gas & Oil Mining Region

Regional (~10km) Scale Solar Fourier Transform Spectrometer Observations of Column Concentrations of Trace Gases

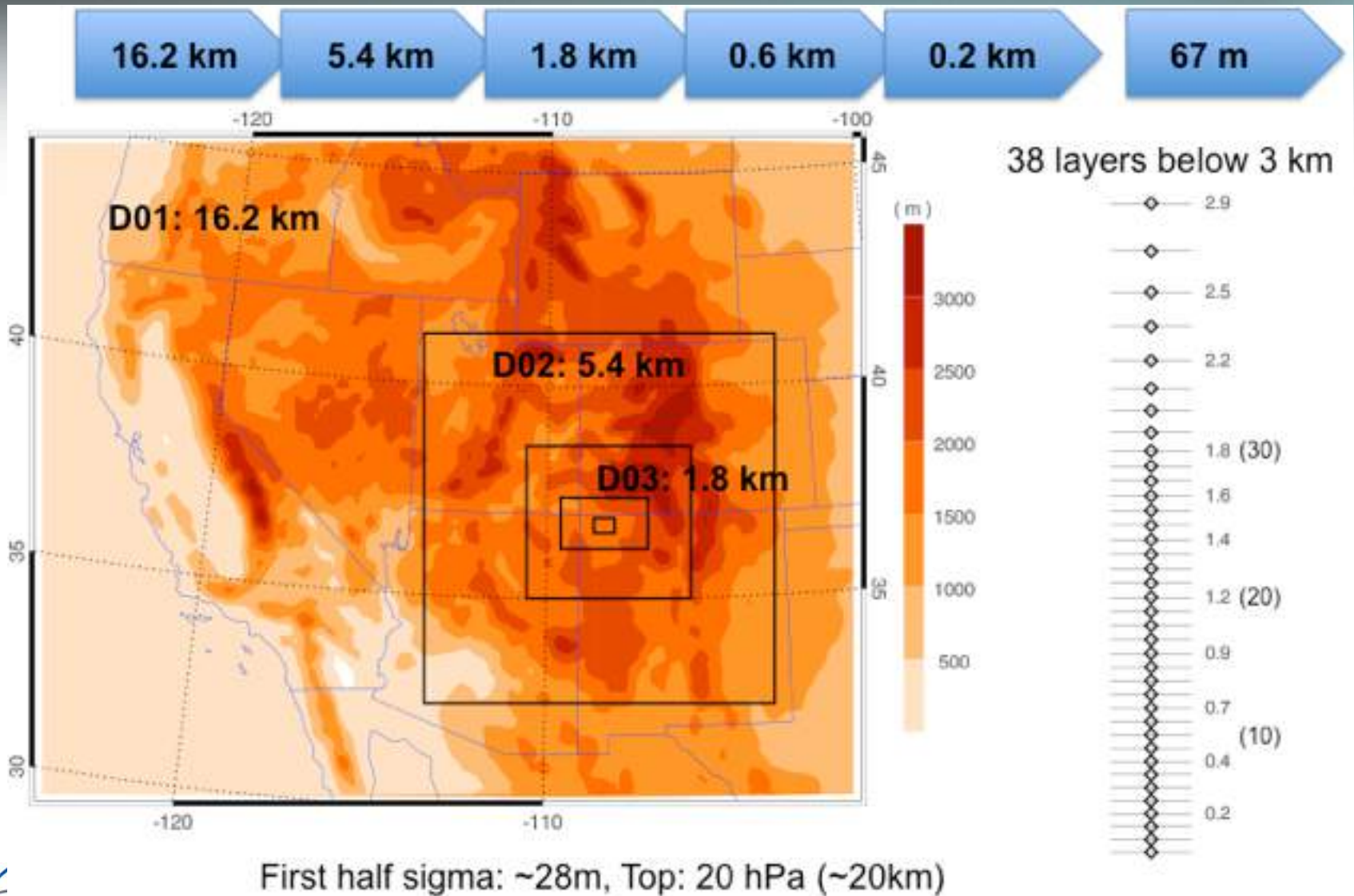
CO<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O, H<sub>2</sub>O  
every 2 minutes during day



# Four Corners GHG and Pollution Monitoring



# Nested WRF Chem Model of 4Corners (NCEP) with real time CEMS power plant emissions + NEI urban inventory

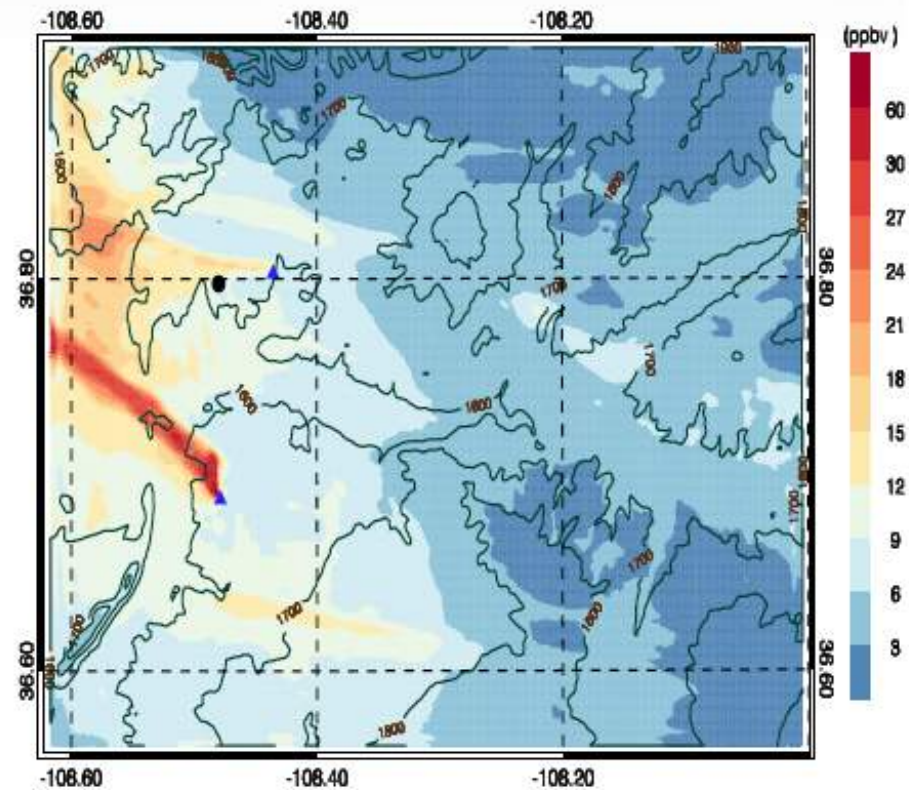
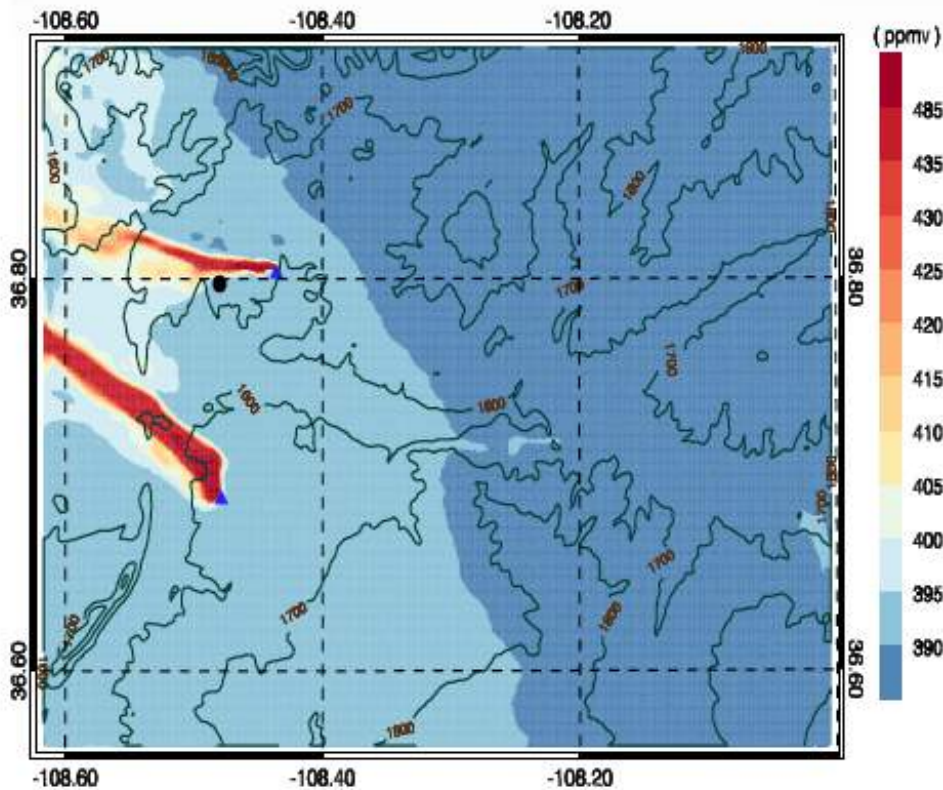




# WRF Chem Plume Simulation (200m res.)

16 UTC 03/15/2011: XCO2 (Max=2540.8 ppmv)

16 UTC 03/15/2011: XNO2 (Max= 105.6 ppbv)

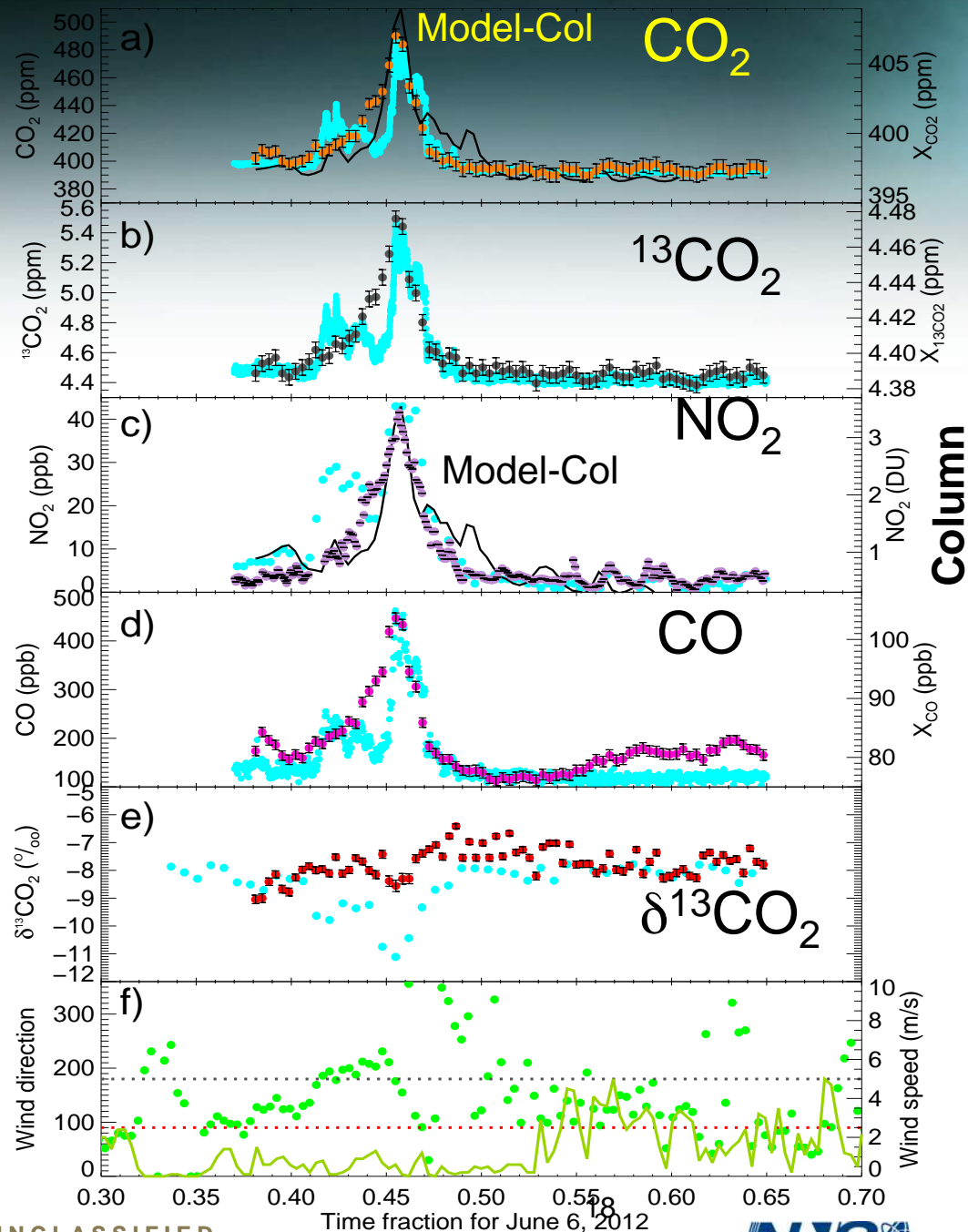


# Power Plant Plume Composition

Traced in exquisite detail at multiple scales by remote (column) and *in situ* (point) surface sensors.

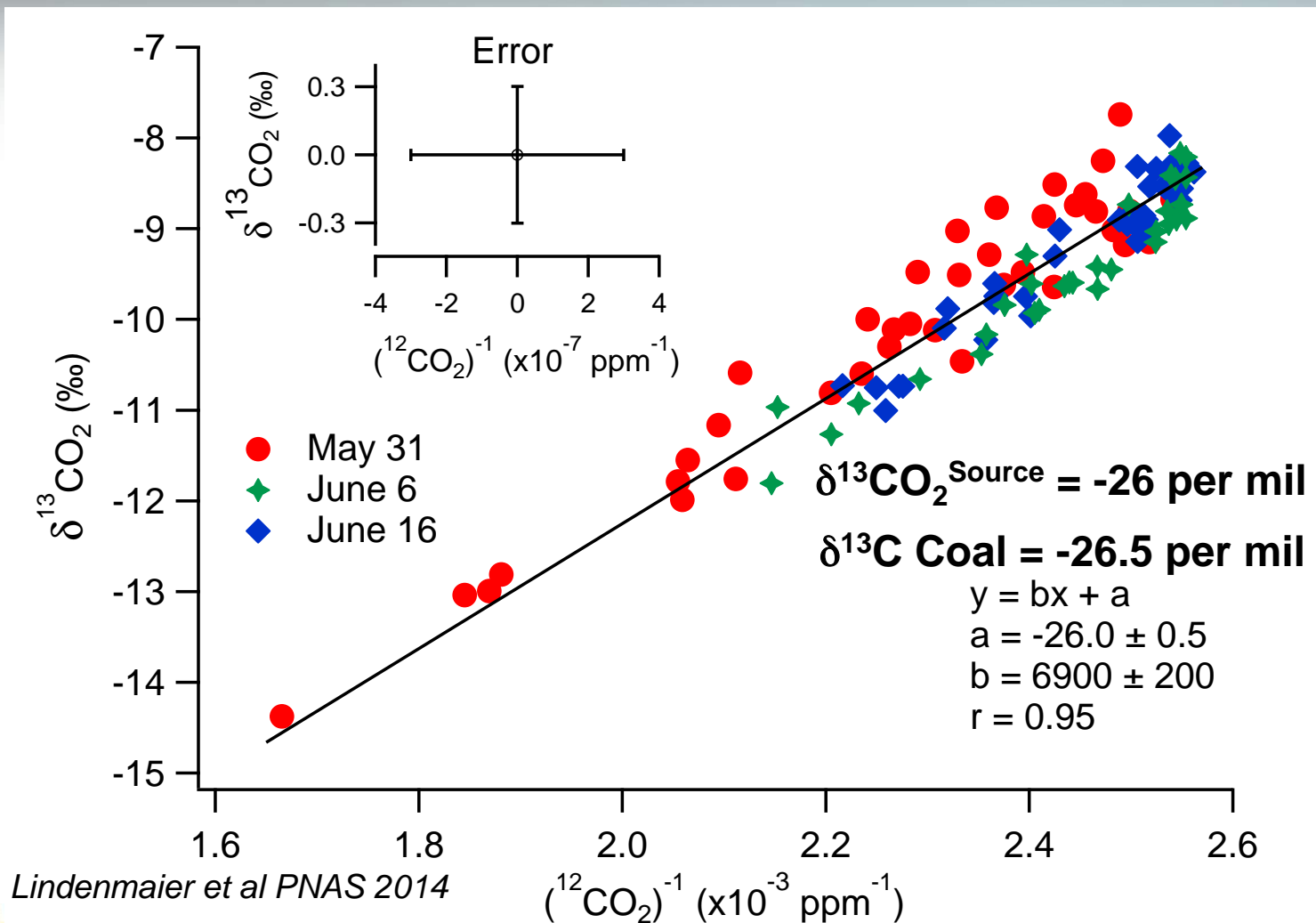
Forward WRF-Chem simulations with CEMS reproduce the column  $\text{CO}_2$  and  $\text{NO}_2$  plume signals.

Surface *in situ*



Lindenmaier et al PNAS 2014

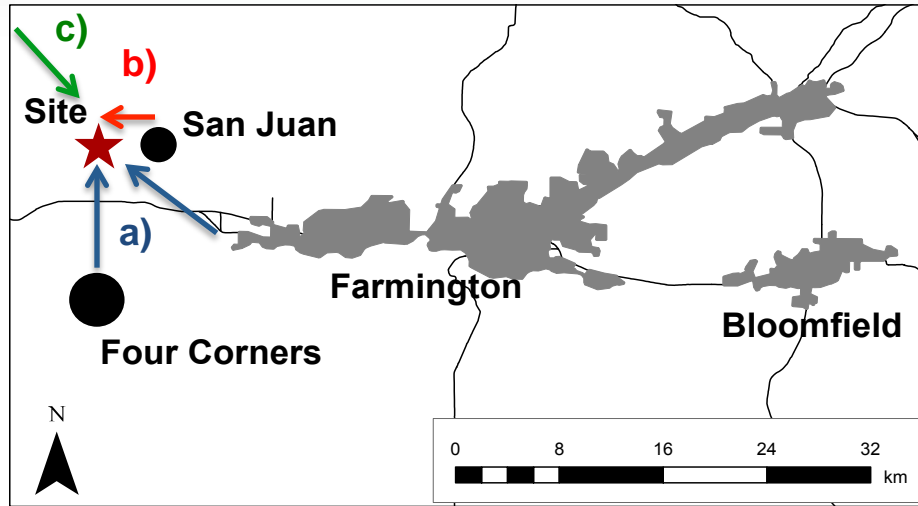
# Source Attribution with *in situ* $^{13}\text{C}$ Keeling Plot



Lindenmaier et al PNAS 2014

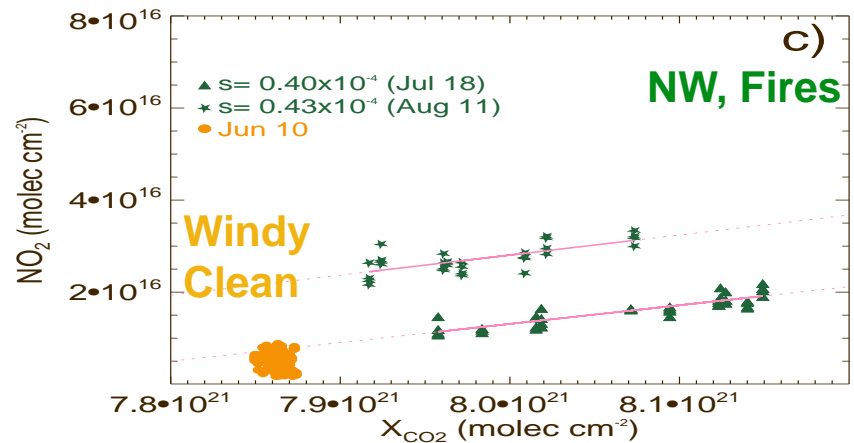
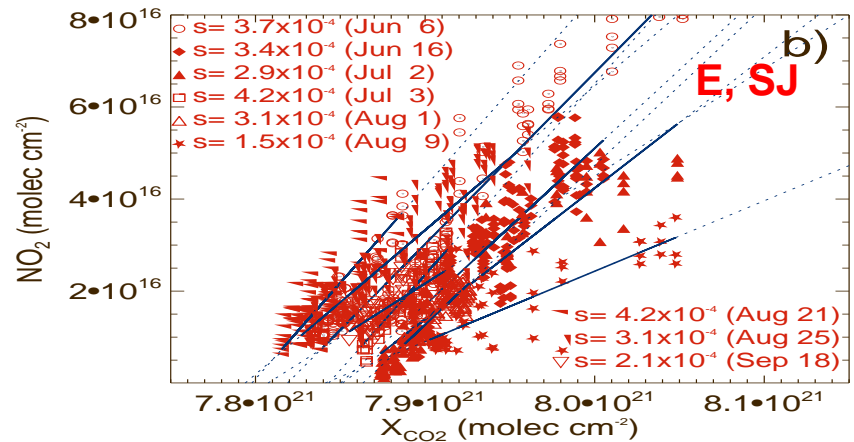
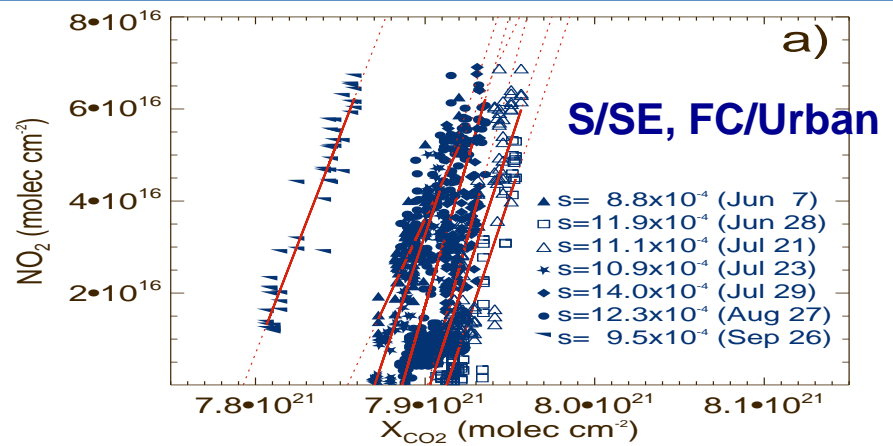
# Column $\text{NO}_2/\text{CO}_2$ : Source Attribution (123 plumes)

Fire

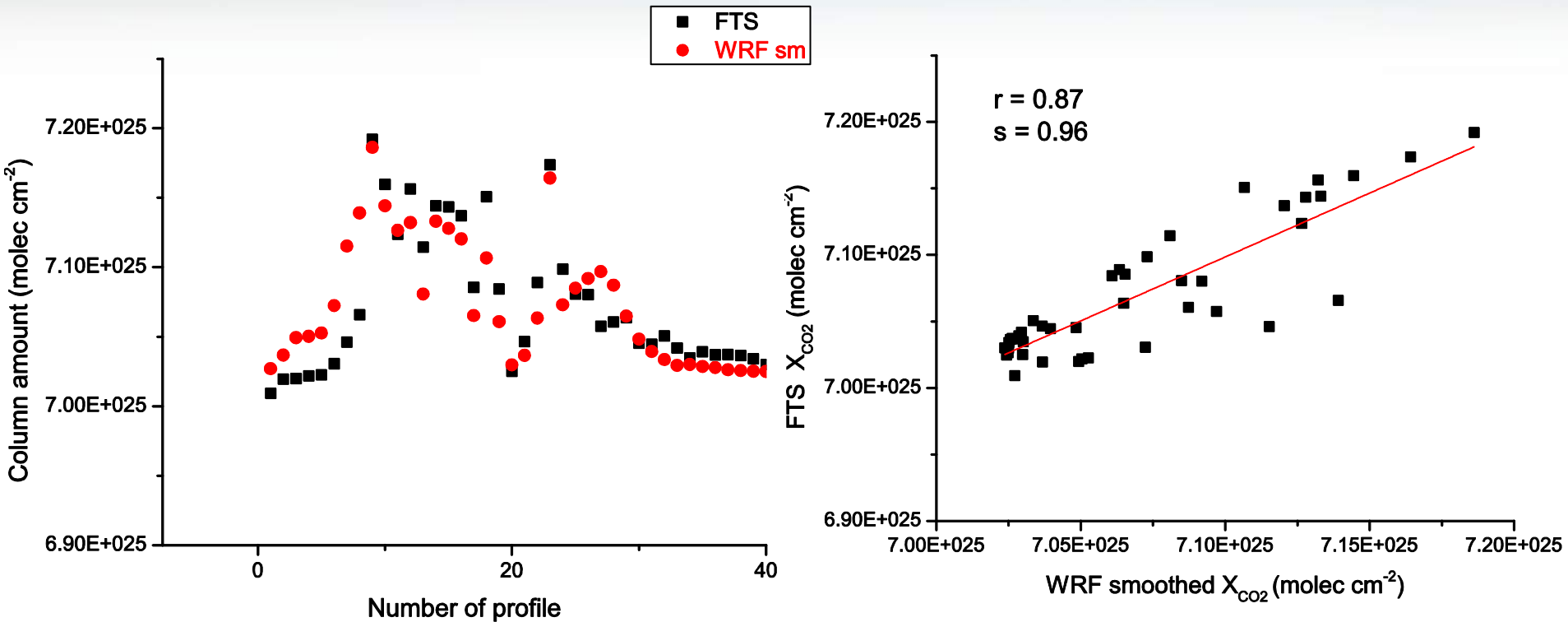


75% of atmosphere sampled  
by FTS is polluted  
Discriminate Sources

Lindenmaier et al PNAS 2014



# WRF columns vs. FTS columns March 15 2011

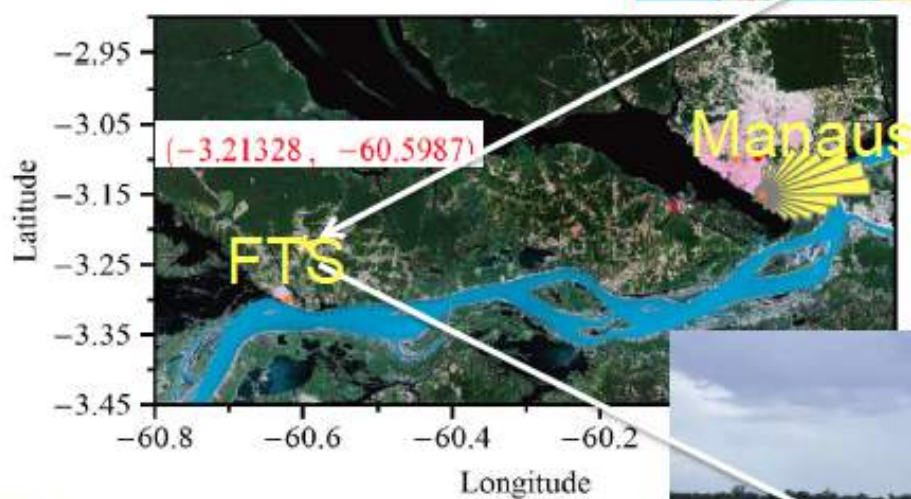
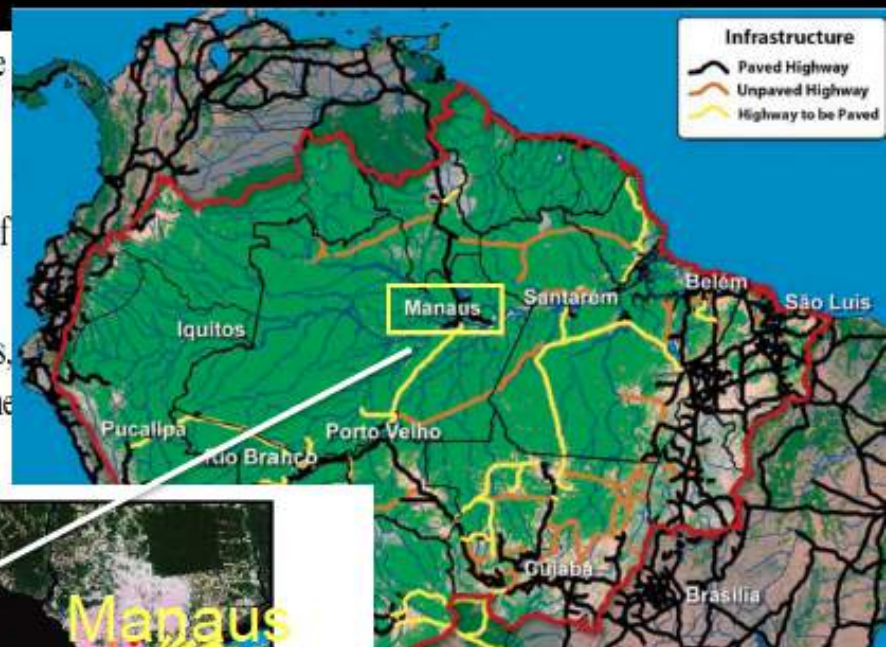


**CEMS verified to 4% accuracy by  
FTS column data in SJPP plume**

# DOE-OBER GoAmazon Manaus, Brazil 2014 (TES, ARM)

**Carbon Cycle** - improve Community Earth System Model (CESM) for land-atmosphere processes in the Amazon Basin, including aerosol-cloud-precipitation connections

- Objective - Reduce uncertainties in our knowledge of feedbacks between vegetation-hydrology that underlie the Amazon forest dieback hypothesis. The uncertain range of feedbacks at present leads to large differences in ESM predictions.
- Objective - Response of photosynthesis and transpiration, including BVOC emissions, to changes in the direct and diffuse components of incoming solar radiation, i.e., in the context of current and future scenarios of aerosols and clouds in the Amazon Basin.

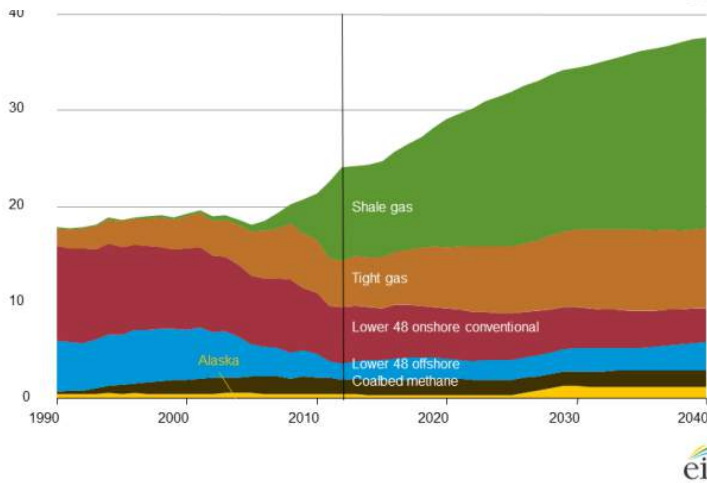
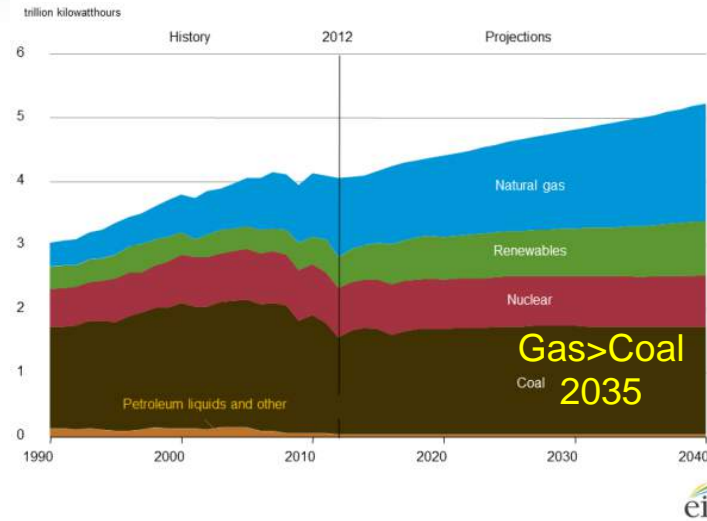


UNCLASSIFIED

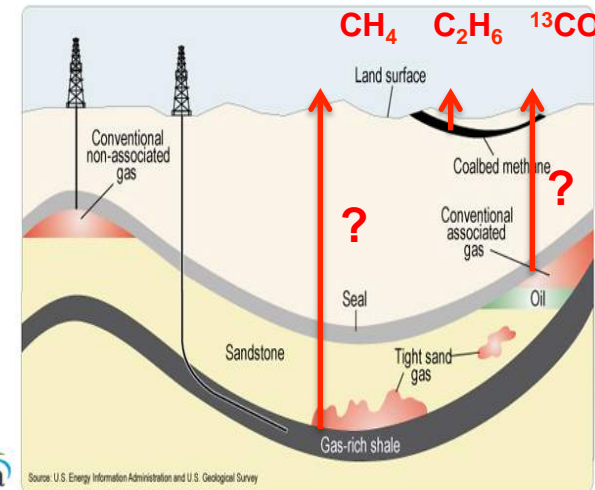
# Natural Gas Opportunities & Challenges for Climate

## Growing Methane Supply from Hydraulic Fracturing

Figure MT-30. Electricity generation by fuel in the Reference case, 1990-2040

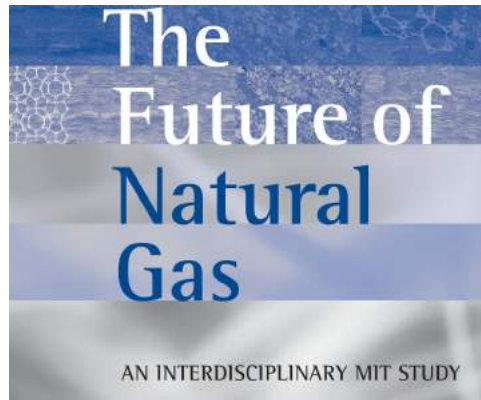


## Fugitive Leaks?



**Need to baseline leaks from conventional mining as we quantify those from unconventional methods.**

## Moniz Report



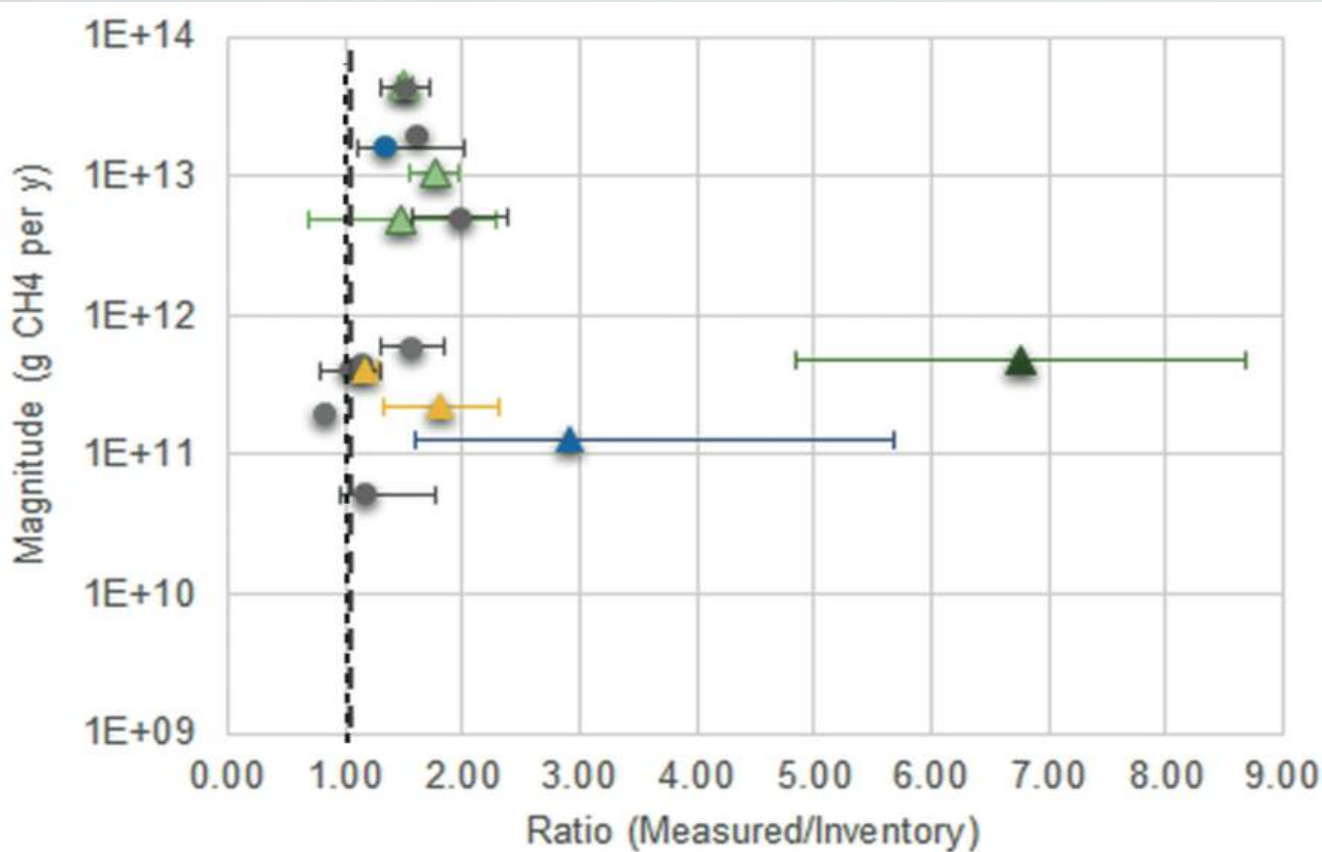
EPA & DOE should review & update CH<sub>4</sub> emissions from gas production and distribution. CH<sub>4</sub> leaks at the levels indicated by the new EPA estimates, could prompt efforts to capture them for environmental & business...

# Shale Gas is Clean and Abundant Domestic Fuel that is being Mined Profitably by Hydraulic Fracturing to Supplant Coal and Oil to help US achieve Energy Independence

- *Clean Air*: No particulates or SO<sub>x</sub> and less NO<sub>x</sub> making a desirable transportation and energy fuel\*
- *Climate Friendlier*: CH<sub>4</sub> produces half as much CO<sub>2</sub> per unit energy produced as coal?
- **Fugitive CH<sub>4</sub> leaks highly uncertain and a sensitive issue!**
- CH<sub>4</sub> 25 times more potent a GHG than CO<sub>2</sub> (100yr)\*
- CH<sub>4</sub> leaks < 3% needed for smaller climate impact than coal?
- HC leaks and Rig & Infrastructure emissions pollute local air\*
- 6-11% leaks from top-down data > x 3 EPA inventories
- *Moniz Study*: “the environmental impacts of shale development are challenging but manageable”



# Inventories & emissions factors (bottom up) underestimate actual measured CH<sub>4</sub> emissions (top down) across scales



Brandt,  
Science  
2014

Ensure CH<sub>4</sub> leaks <3% keep it climate friendlier than coal & make it a bridge to carbon neutrality  
Area of national need that DOE has prioritized & LANL is harnessing its SoS capability to assess

# Satellite: SCIAMACHY 2003-2009 CH<sub>4</sub> Hotspots

25-50 ppb excess over background above O&G regions

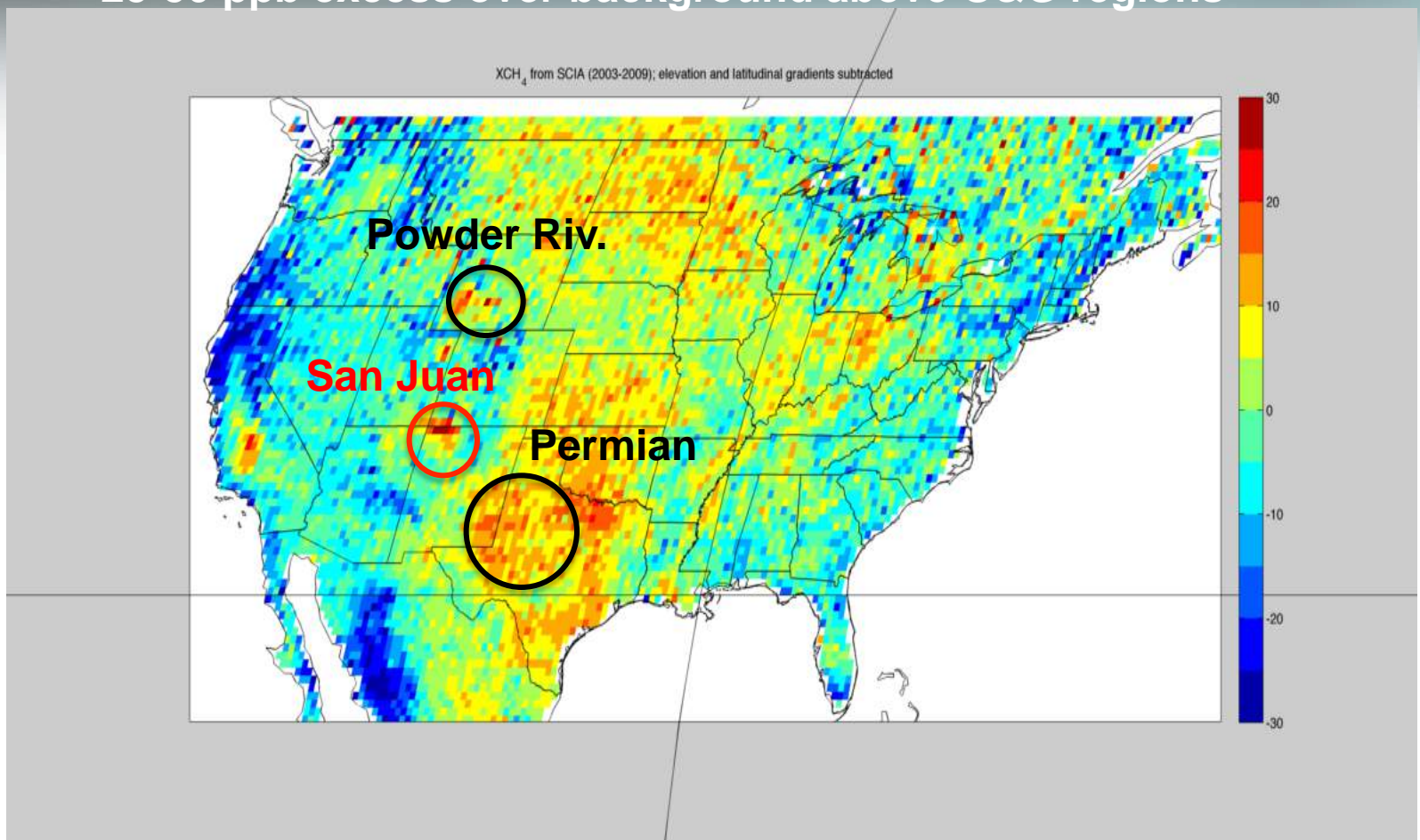


Figure 1: Average methane anomaly as seen by SCIAMACHY from 2003-2009. The four-corners region exhibits the largest regional enhancement in the conterminous US.

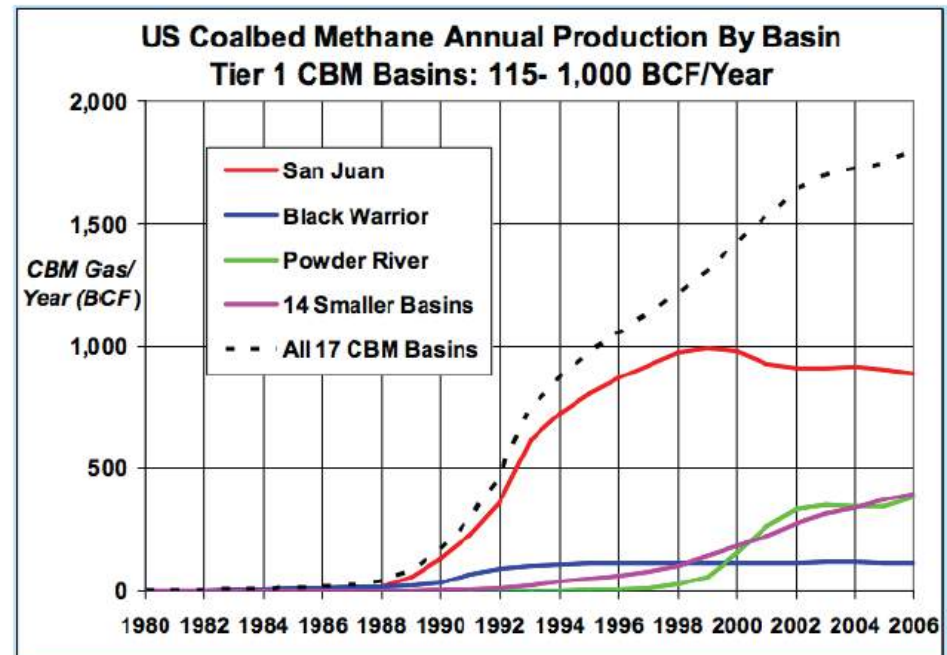
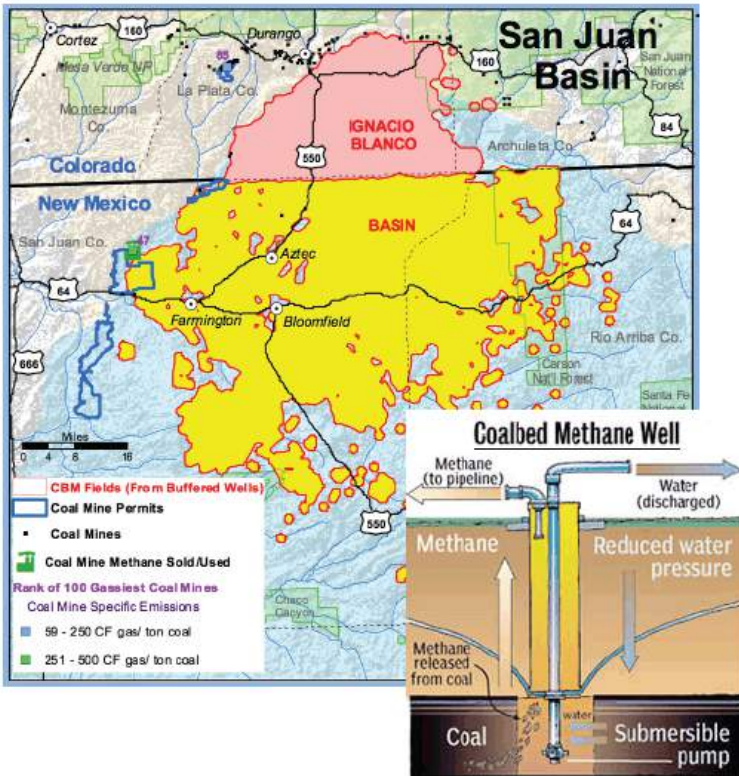
Also a gas hub!

# 4-Corners: What is going on?

Largest Coalbed methane production area in the US

Production of 1.32 trillion cubic feet per year in 2007  
corresponds to about 27 Tg/yr

What part of the emissions is related to production vs. natural seepage? Hard to say...



# Satellite see CH<sub>4</sub> hot spot at 4-Corners: Edgar inventory has sources at right locale

Satellite

Kort et al GRL 2014

Edgar-Inventory

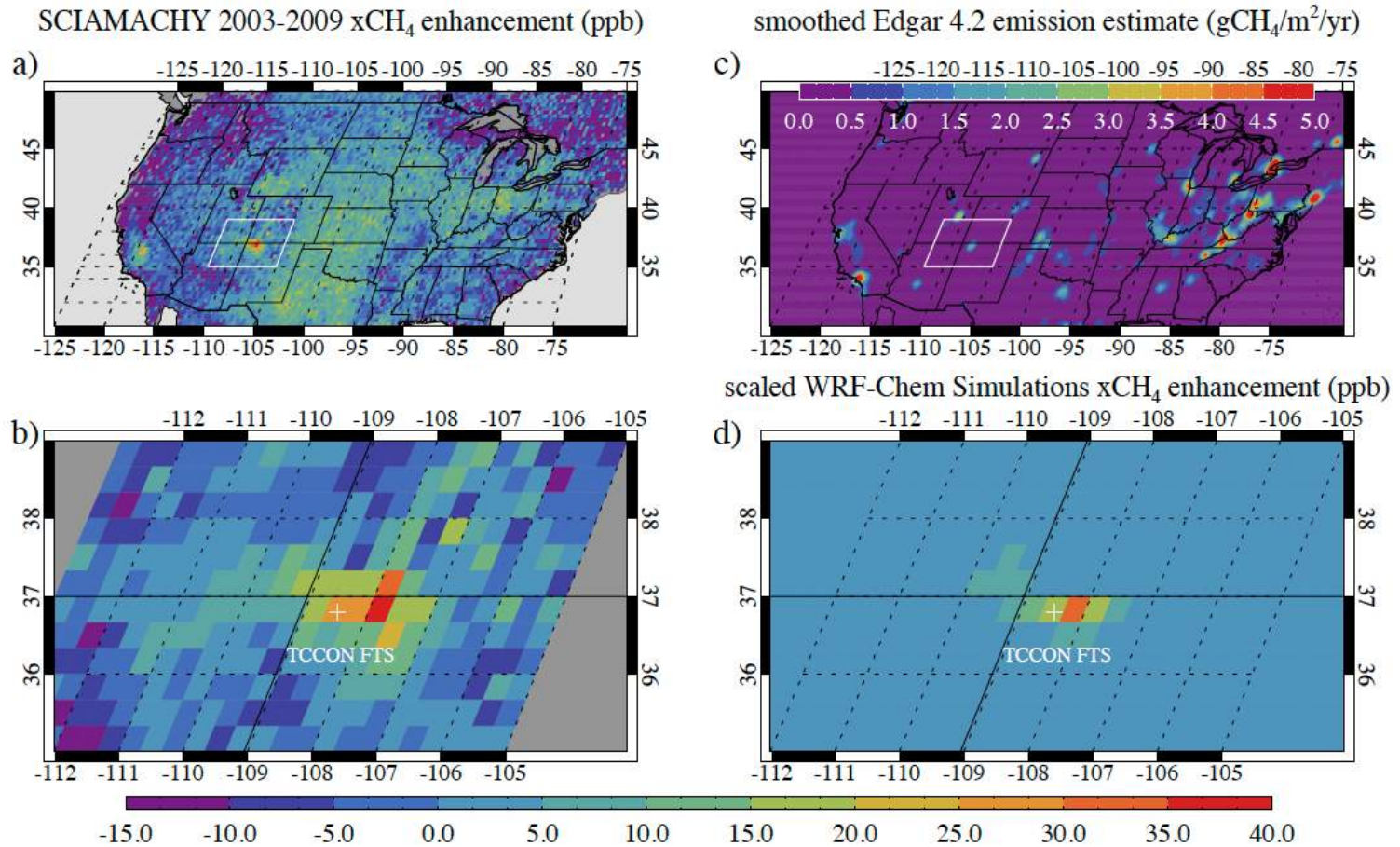
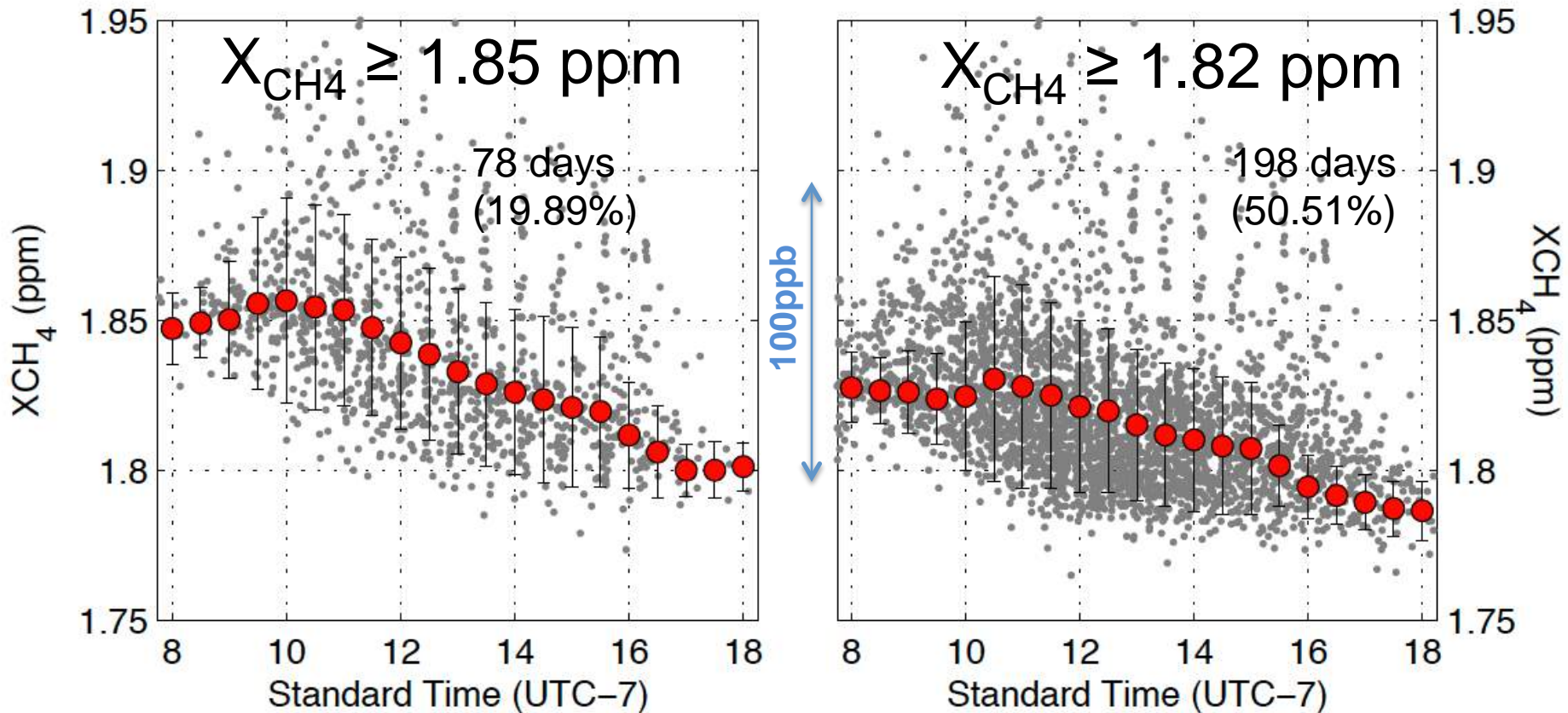


Figure 1: Column methane anomalies and emissions over the conterminous US

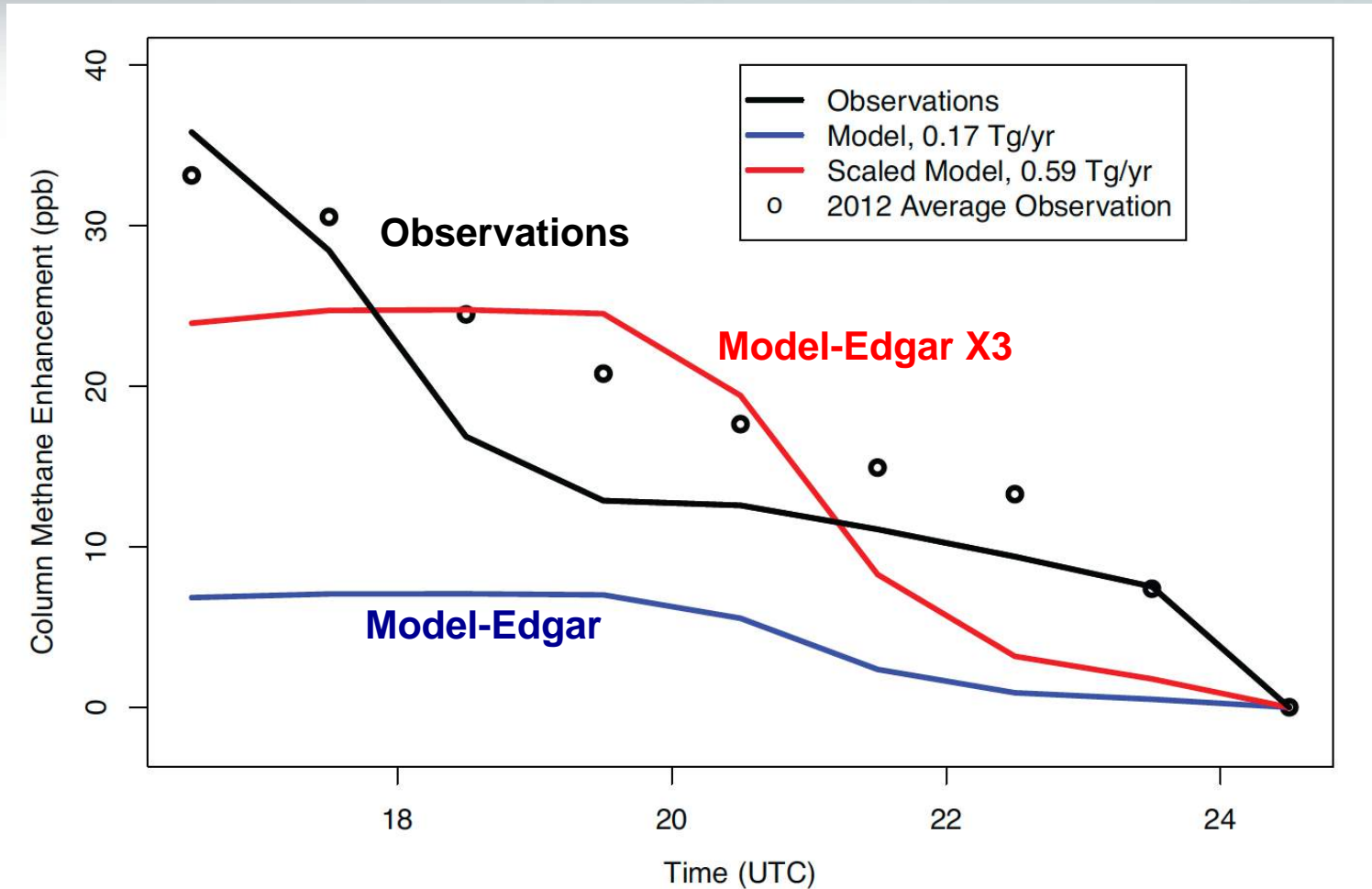
# High regional CH<sub>4</sub> plumes observed routinely with when winds are low and from SE

Total measurement days 2011+2012 =392



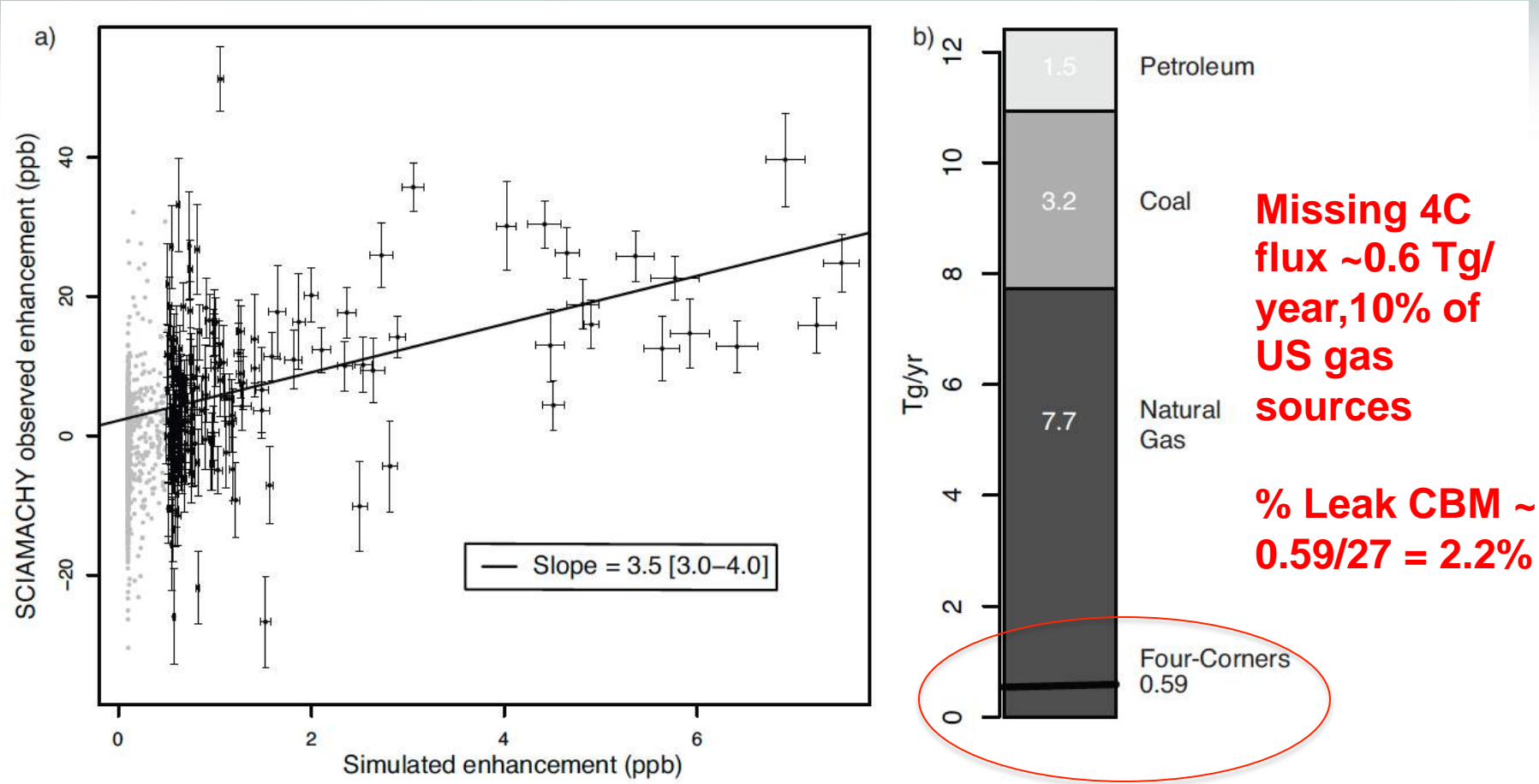
(X<sub>CH<sub>4</sub></sub> ≥ 1.85 ppm means that at least one value that day reached 1.85 ppm)

# Edgar emissions have to be scaled by x 3 in WRF model to match 4-Corners FTS data



Kort et al in review Nature Geosciences 2014

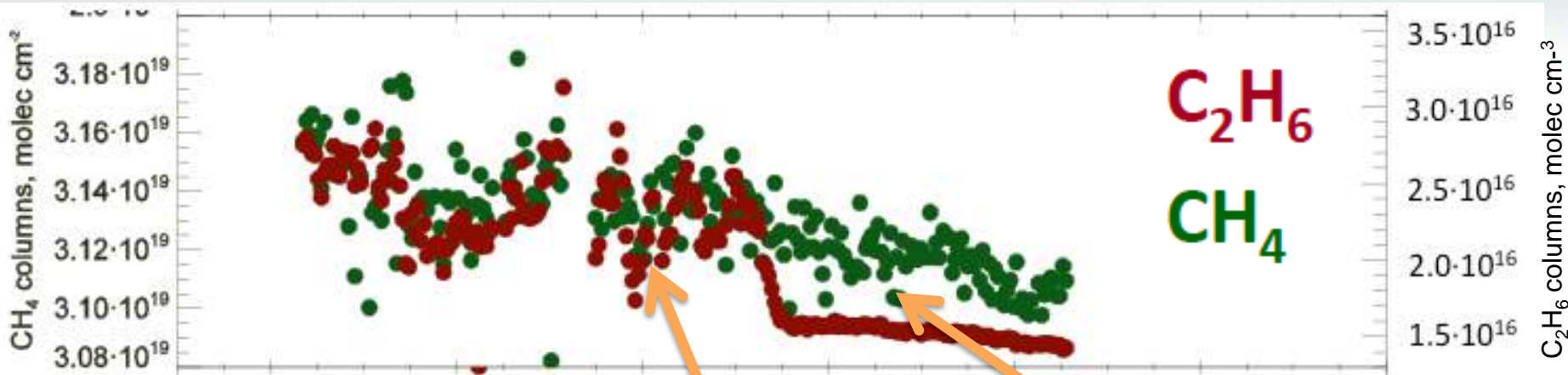
# Satellite data confirm 4-Corners “missing” emission in inventory is double of value in current Edgar inventory



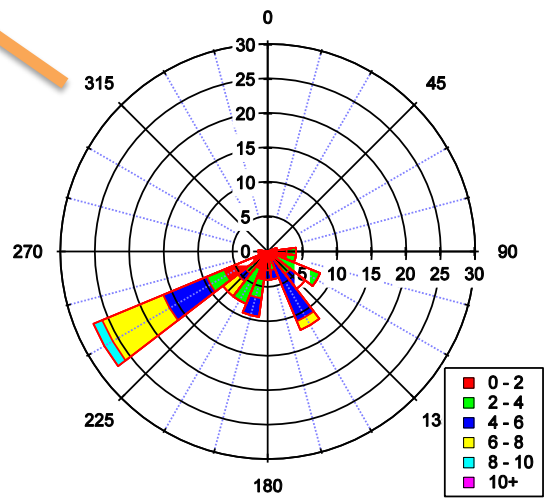
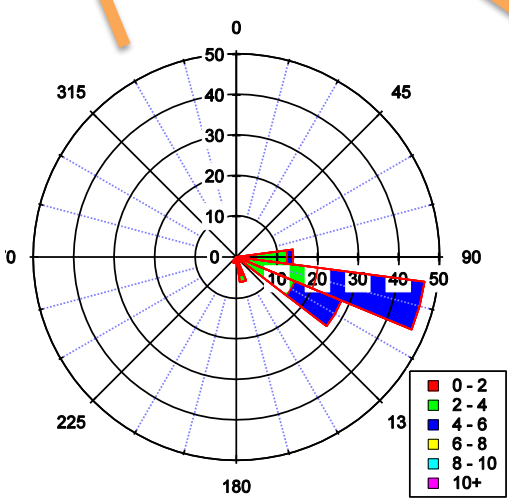
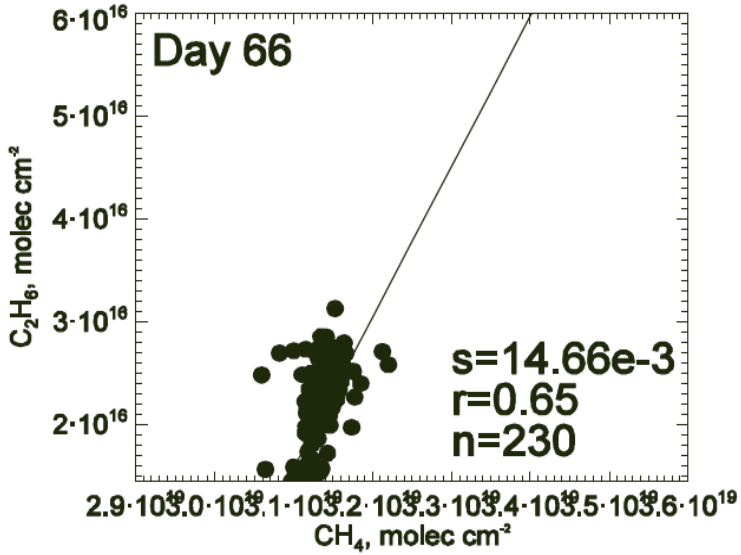
**Figure 2: Methane enhancement for Four Corners region & US EPA inventory estimates.**

Consistent with US wide study *Miller PNAS '13*. But had no data for 4Corners and showed Edgar emissions were too high. Turner et al 2015 inversions correct for this with our data.

# Attribution of Fugitive Sources: Regional solar FTS (Mid-IR, InSb) retrievals of column $C_2H_6$ & $CH_4$



$C_2H_6/CH_4 = 1.5\%$

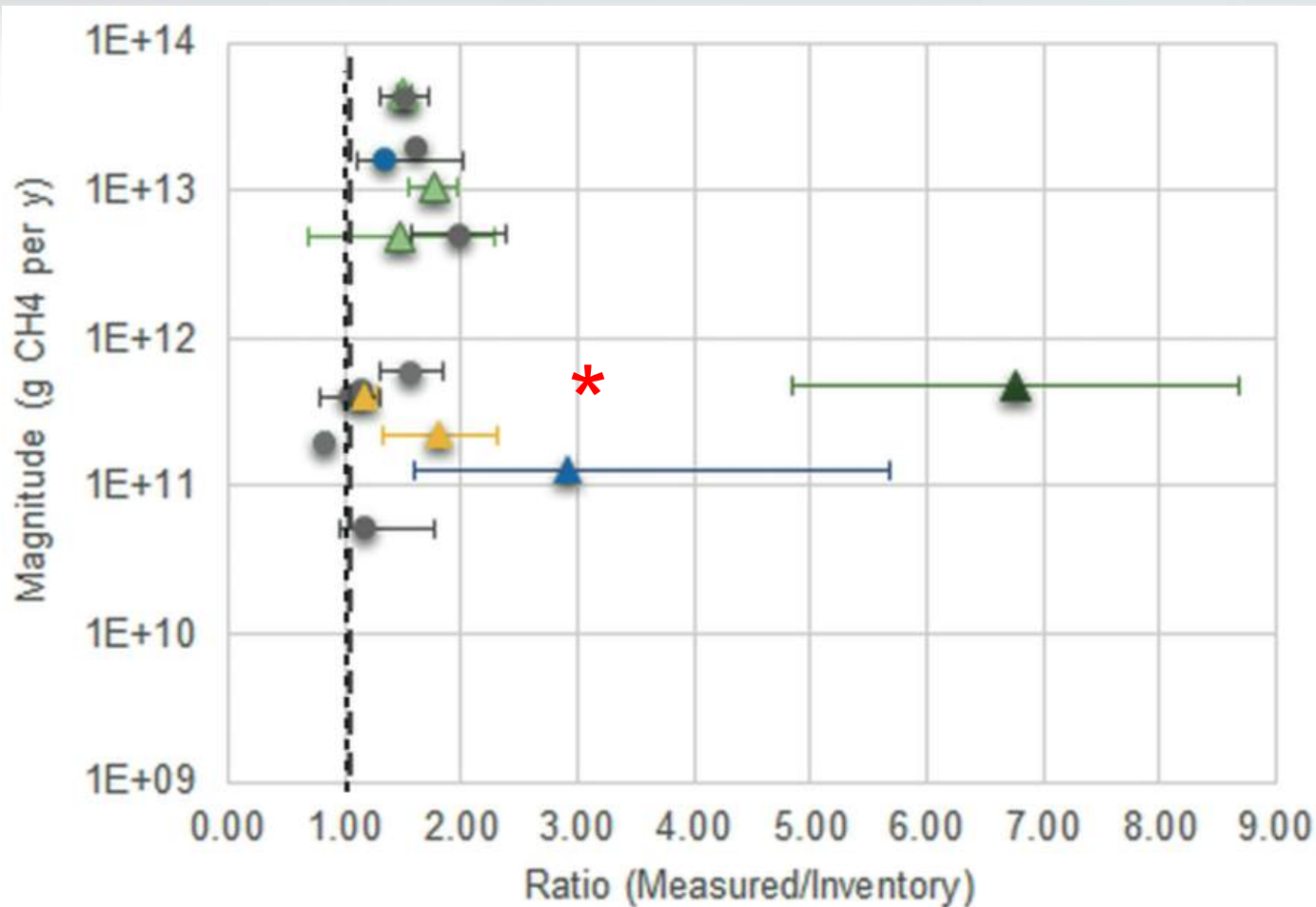


UNCLASSIFIED





# Inventories & emissions factors (bottom up) underestimate actual measured CH<sub>4</sub> emissions (top down) across scales



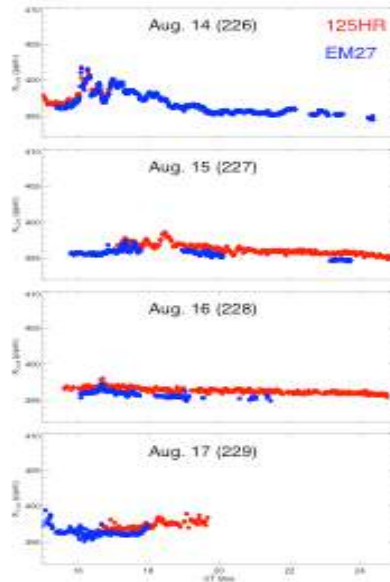
Brandt,  
Science  
2014

\*4Corners

**\*4Corners** Attributed to conventional coal bed methane production (pre hydraulic fracturing)

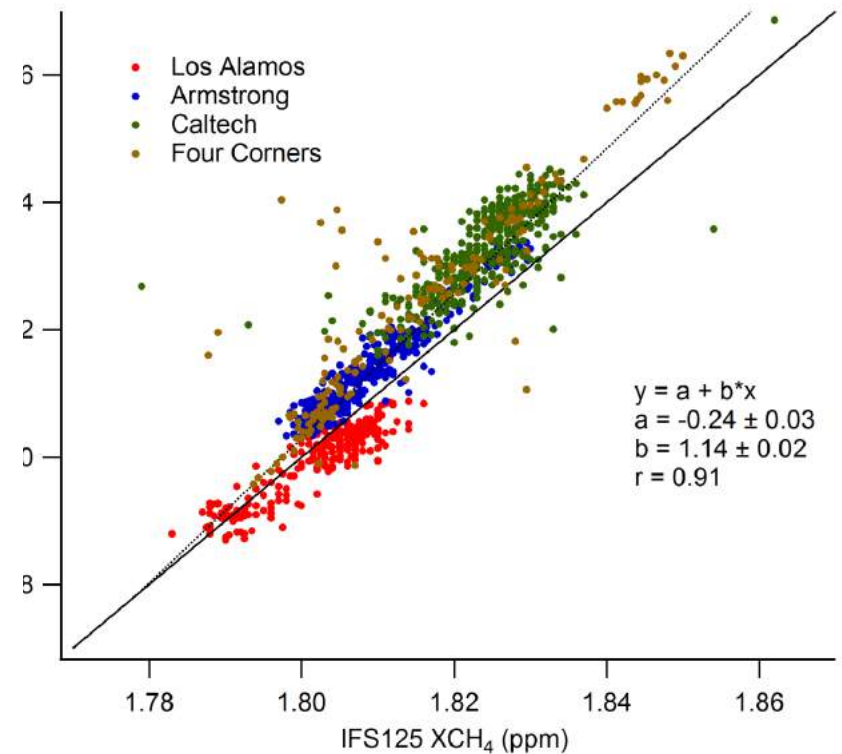
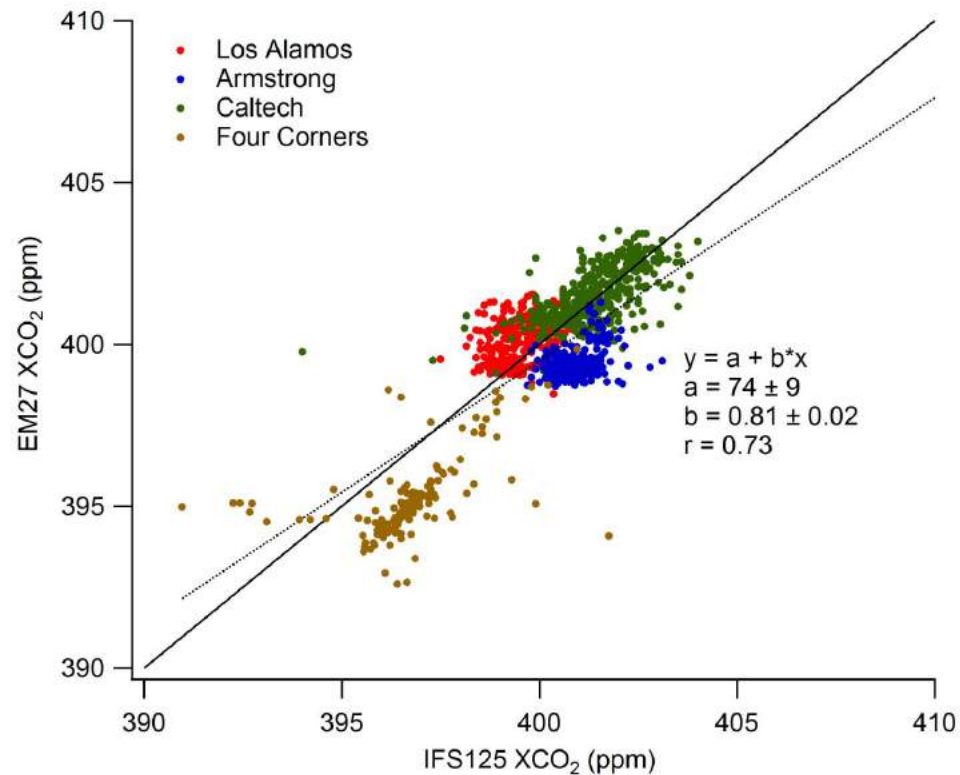
# Portable mini-mobile FTS compared with TCCON at 4-Corners, Los Alamos, Armstrong & Caltech

Developing a **portable** and **robust** instrument Without compromising **Accuracy** and **long term** stability! EM27/SUN validated with TCCON: Promising results.

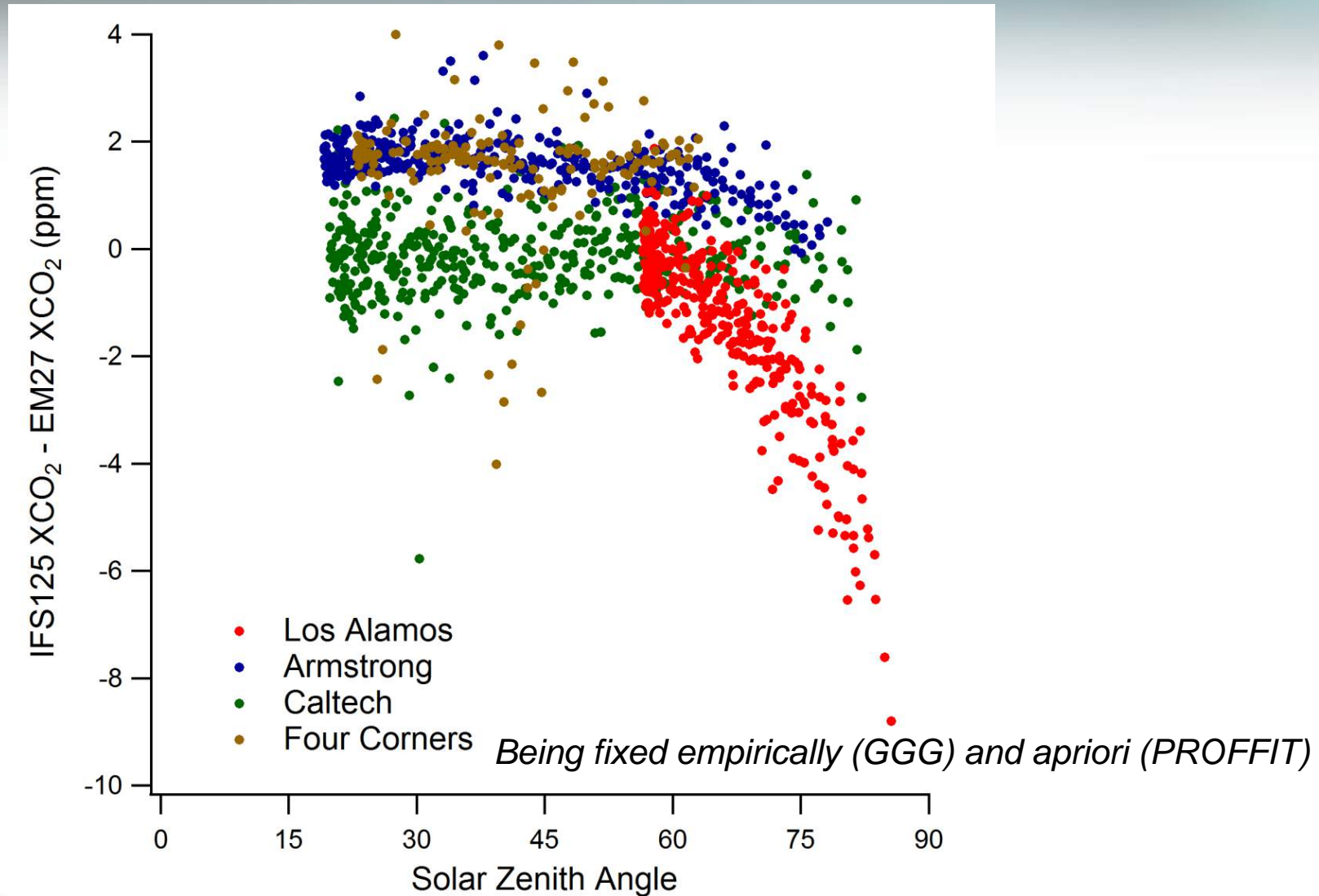


- Pendulum FTIR
- Resolution: 0.5 cm<sup>-1</sup>
- 470 x 630 x 350 cm
- ~25 kg incl. tracker

# TCCON-EM27SUN Comparisons



# Low CO<sub>2</sub> Bias at High Solar Zenith



# Mesoscale Atmospheric Emission Verification

- Remote  $\text{NO}_2$  and  $\text{CO}_2$  verification of power plant emissions.
- WRF simulations with CEMS agree well with FTS column, with less scatter from met. variability than *in situ* network (McKain 12)
- Satellite  $\text{CH}_4$  hot spots at 4-Corners attributed to coal bed  $\text{CH}_4$
- Modeling of data shows current  $\text{CH}_4$  inventory low by factor of 3.
- Remote  $\text{C}_2\text{H}_6$  signatures used to attribute  $\text{CH}_4$  sources
- Compact mobile FTS expands observational opportunities
- Amazon rainforest monitoring in Brazil with  $\text{OCO}_2$  validation
- Mini FTS-TCCON comparisons are promising

