
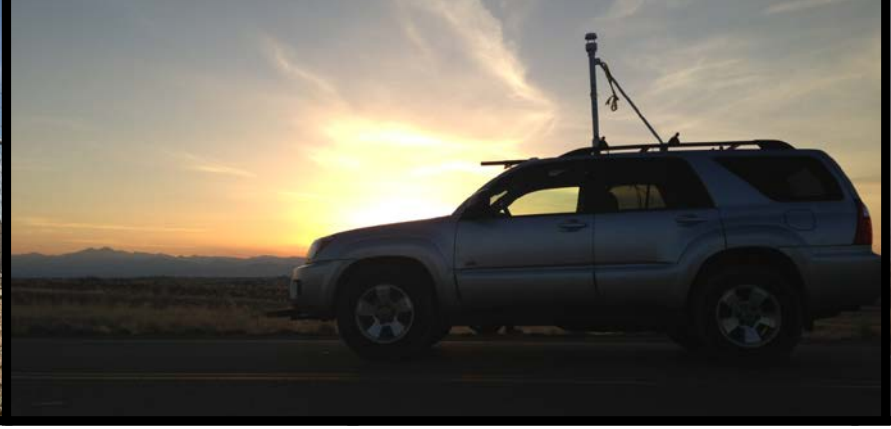


# Quantifying the relative contribution of natural gas fugitive emissions to total methane emissions in Colorado, Utah, and Texas using mobile $\delta^{13}CH_4$ analysis

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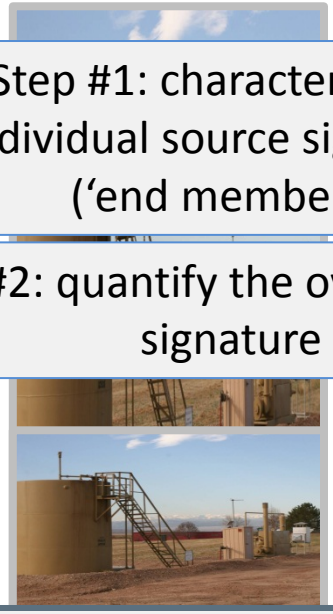
*Thanks to: Scott Herndon, Tara Yacovitch, Eric Kort, Amy Townsend-Small, David Lyon, Ramon Alvarez, Bob Harriss, Steve Conley, Sonja Wolter, and many more!*

# Using Stable Isotopes to Identify Sources

$$\delta^{13}CH_4(‰) = 1000\left[\frac{{}^{13}CH_4/\,{}^{12}CH_4}{r_{VPDB}} - 1\right]$$

$$\delta_{tot} \approx \frac{E_{O\&G}\delta_{O\&G} + E_{cow}\delta_{cow} + E_{land}\delta_{land}}{E_{O\&G} + E_{cow} + E_{land}}$$



Step #1: characterize the individual source signatures ('end members')

Step #2: quantify the overall source signature

-60 -55 -50 -45 -40 -35 -30

$\delta_{tot}$ Overall Source Signature

Source: Quay et al. (1988) "isotopic composition of methane release from wetlands: implications for the increase in atmospheric methane" Glob. Biogeochem. Cycl. v2, 385-397.

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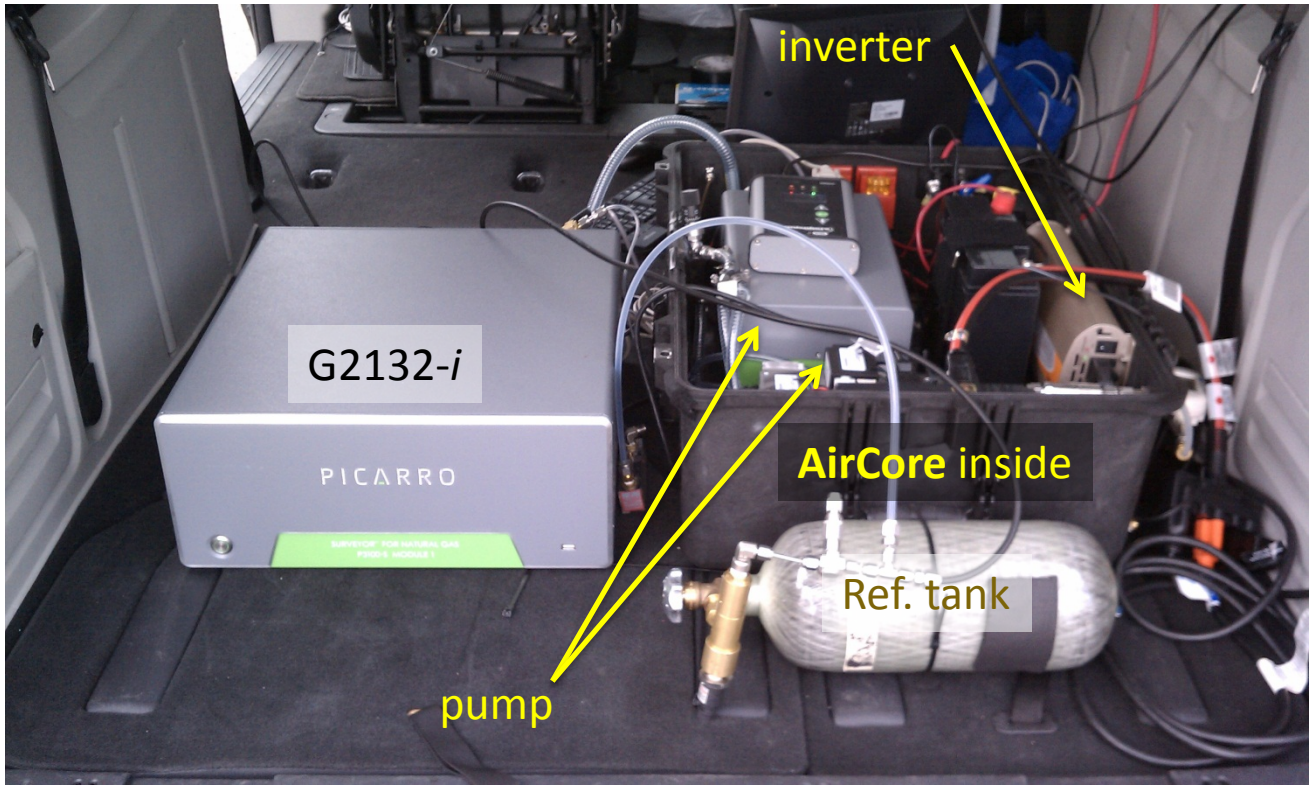
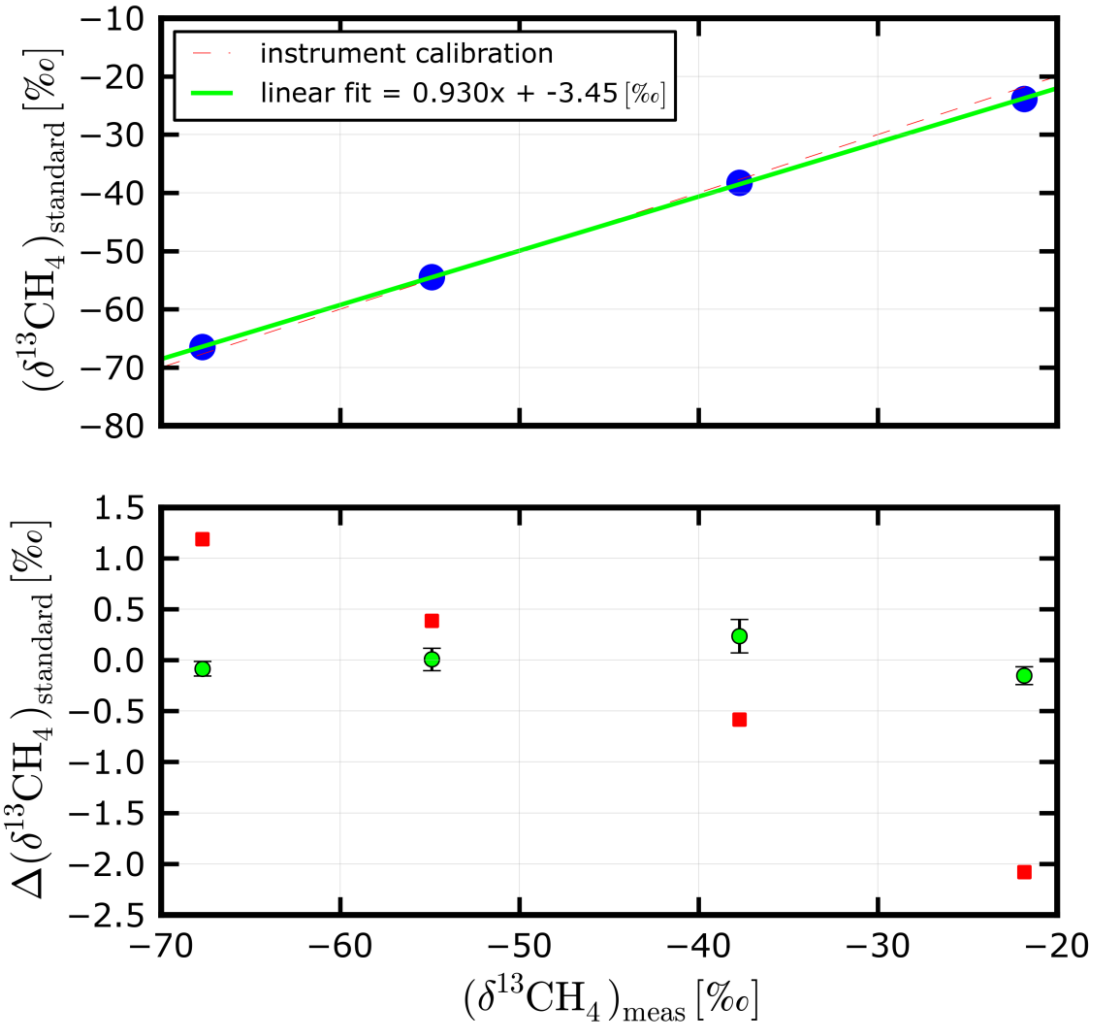
# Mobile $\delta^{13}CH_4$ Laboratory





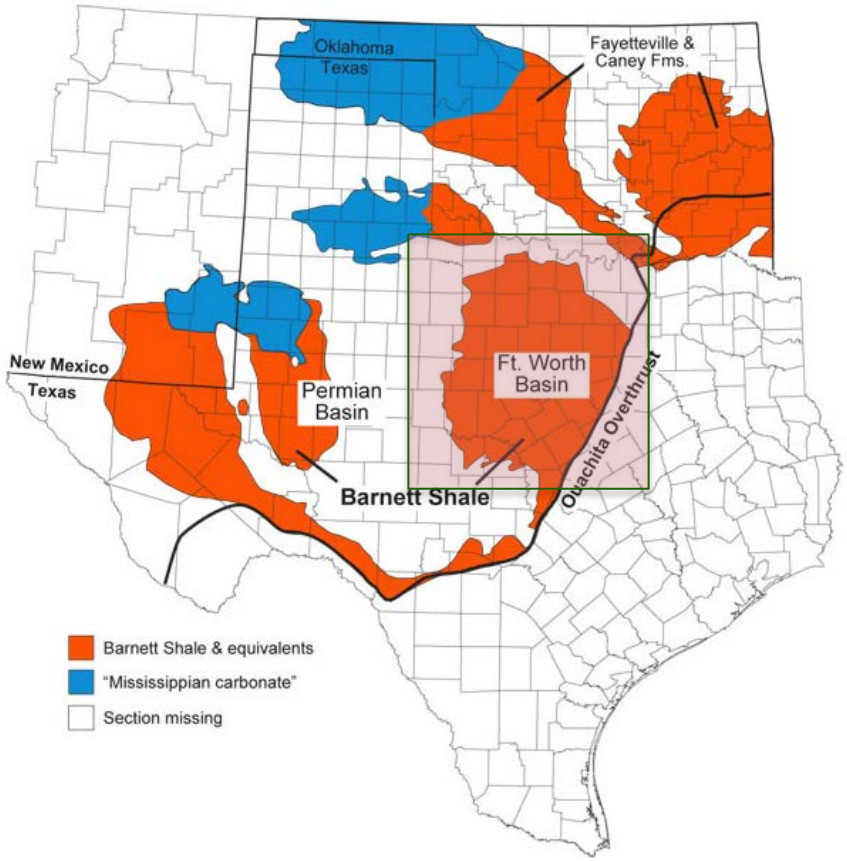

| | |
|---|---|
| Precision, $\delta^{13}C$ in $CH_4$ (1-σ , 1 hr window) | < 0.8 ‰ guaranteed precision at > 1.8 ppm 5 min. average<br>< 0.5 ‰ guaranteed precision at > 1.8 ppm, 15 minute average |

# Instrument $\delta^{13}CH_4$ Calibration




- Calibration using four standards from Isometric Instruments (http://www.isometricinstruments.com/)
- ~ 1-2 permil error in factory calibration
- Residuals <0.3 permil

# Barnett Shale (Ft. Worth Basin) – 6.8% of US prod.




- EDF Barnett Coordinated Campaign
  - Airborne measurements: U. Colorado / NOAA / Scientific Aviation / Purdue / Sander Geophysics / U. Michigan / Aerodyne, Princeton
  - Ground measurements: U. Houston, Picarro, Duke, Aerodyne, U. Cincinnati, UC Irvine, WVU, UT Dallas
  - Meteorology: Penn State



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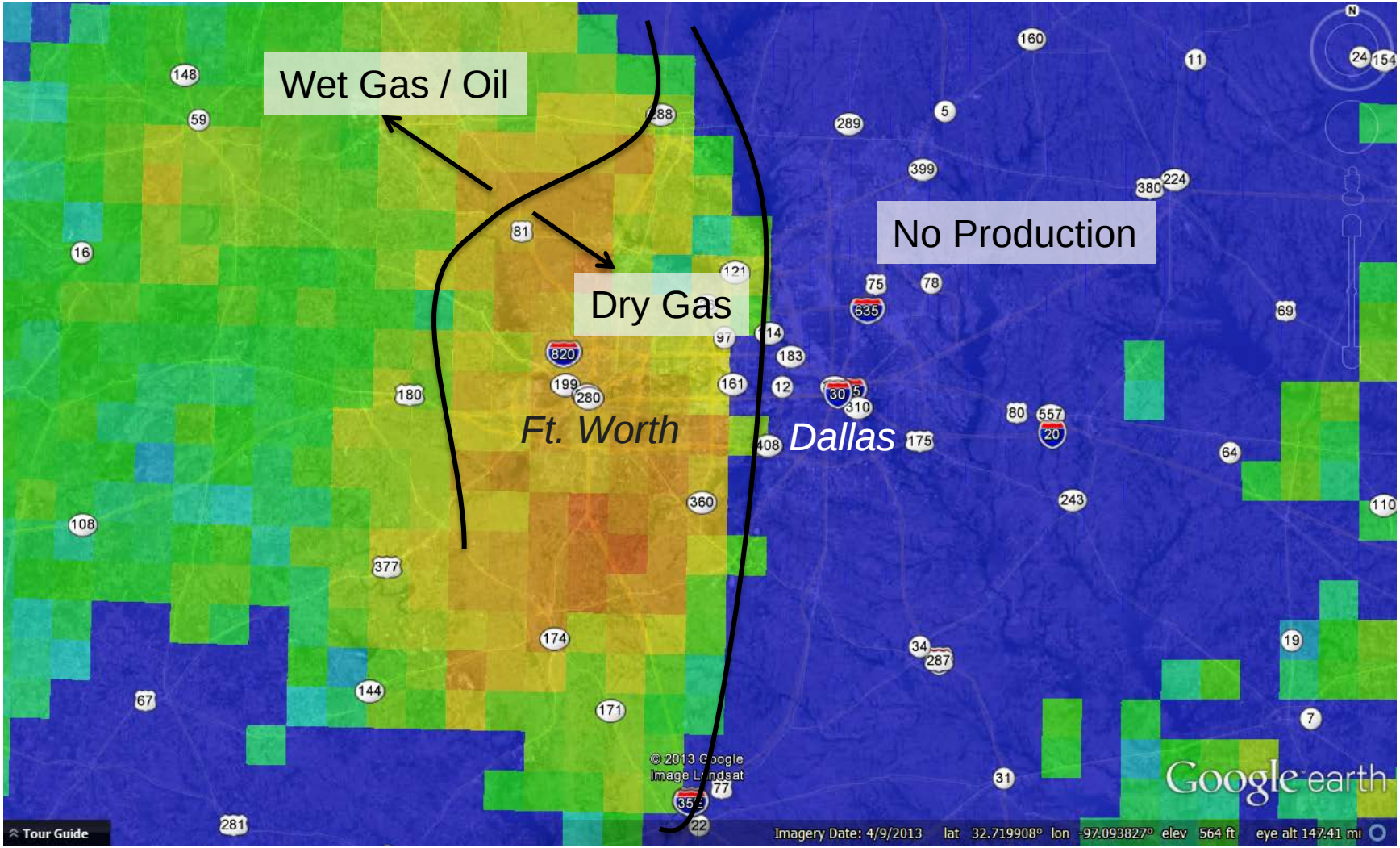
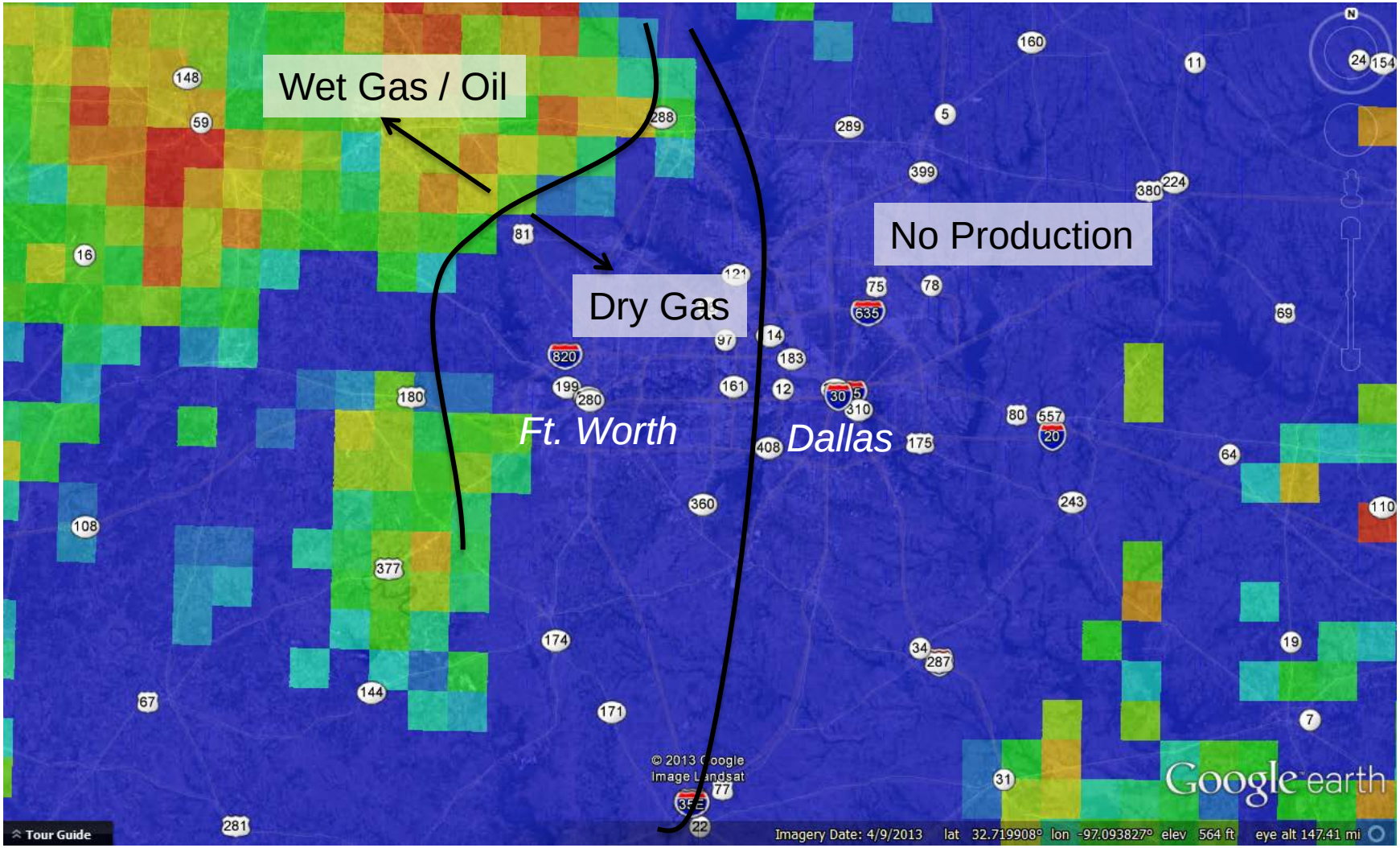
# Barnett Shale – Gas Production




"Wet gas" = high $C_{2+}$ content

# Barnett Shale – Oil Production



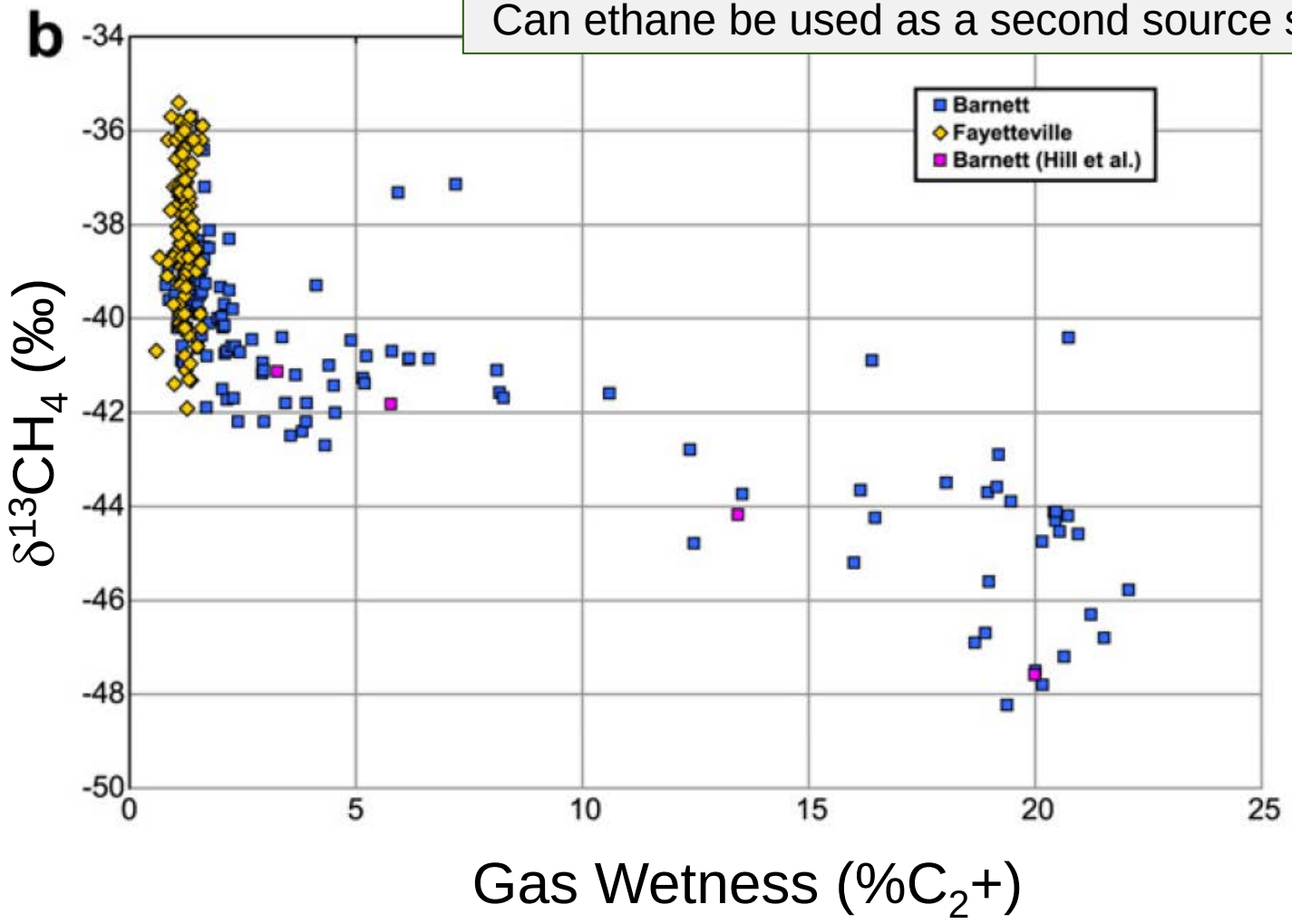

"Wet gas" = high $C_{2+}/C_1$ ratio

# Methane Isotopes At All Length Scales

- Methane in the ground (from literature)
- Driving by methane plumes during the day
  - Single source ~ 0.01 $km^2$
- MegaCore measurements in the nocturnal boundary layer
  - Dozens of sources: ~1 $km^2$
- Flights in the daytime PBL
  - 100s and 1000s of sources, >100 $km^2$

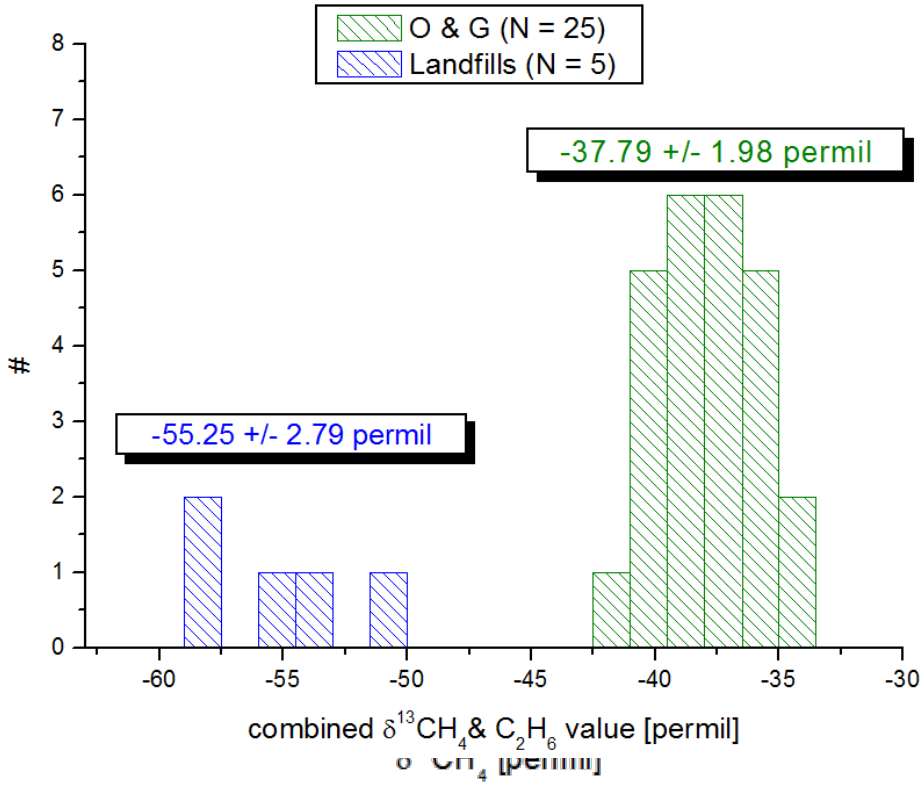
# Wet Gas Has a Lighter $\delta^{13}CH_4$ Signature in the Barnett

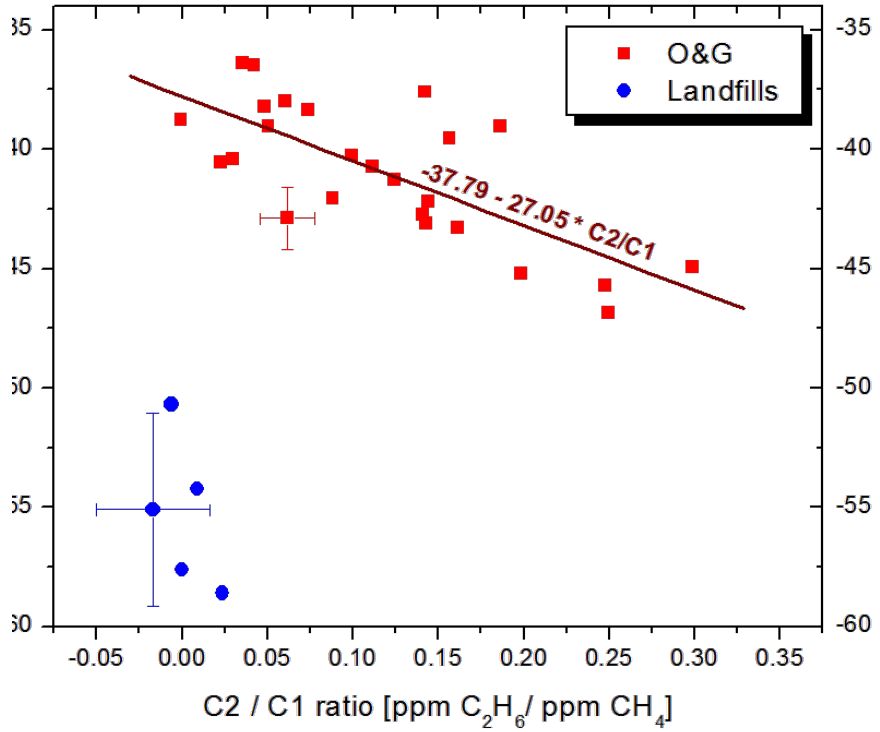
Can ethane be used as a second source signature?




Reproduced from *J. Zumberge, K. Fernwon, and S. Brown, (2012): "Isotopic reversal ('rollover') in shale gases produced from the Mississippian Barnett and Fayetteville formations," Marine and Petroleum Geology 31, p 43-52.*

# Observed Atmospheric Signal: Isotopes and ethane / methane ratios

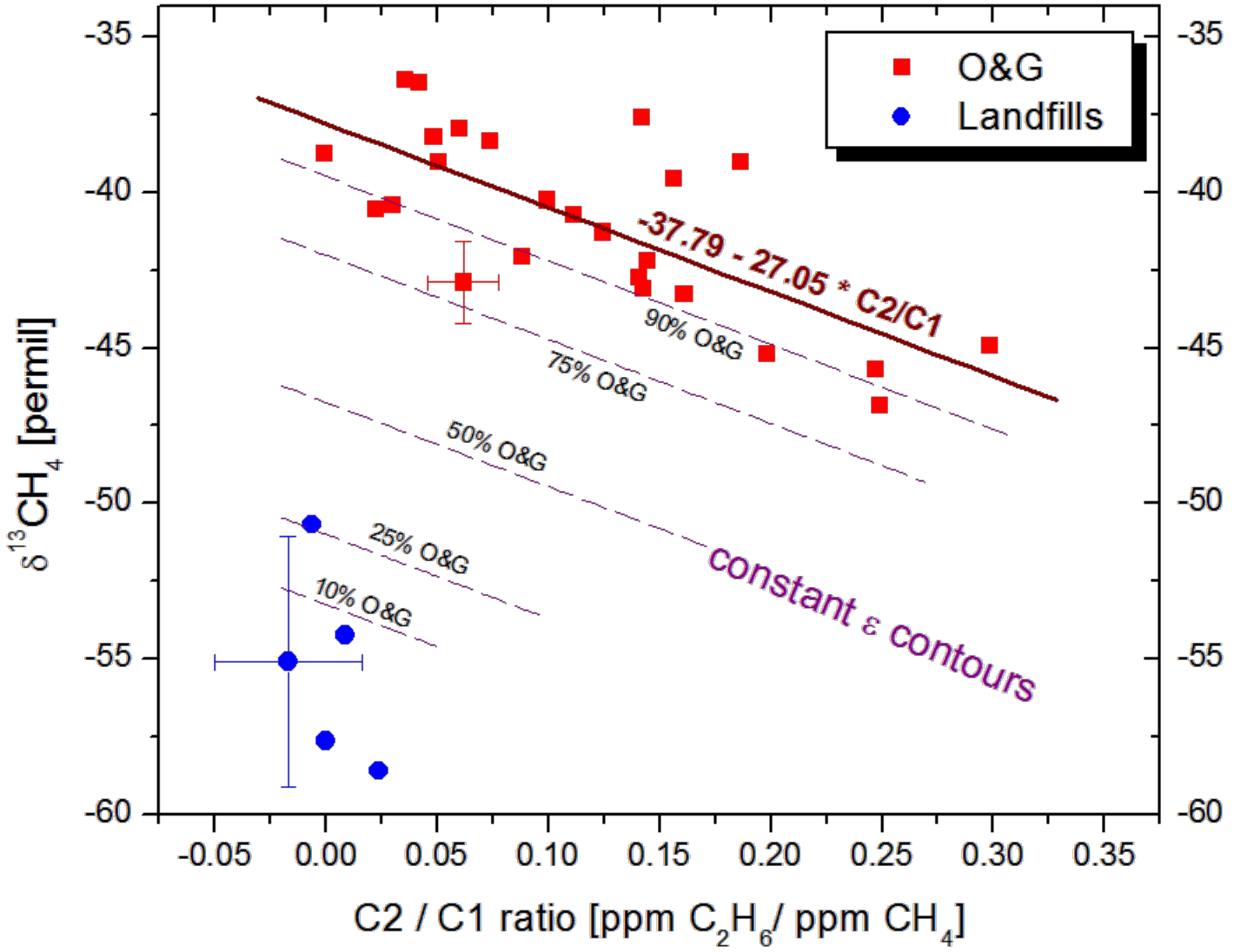



$$\varepsilon = \delta^{13}CH_4 + 27.05 \times C_2H_6 / CH_4$$

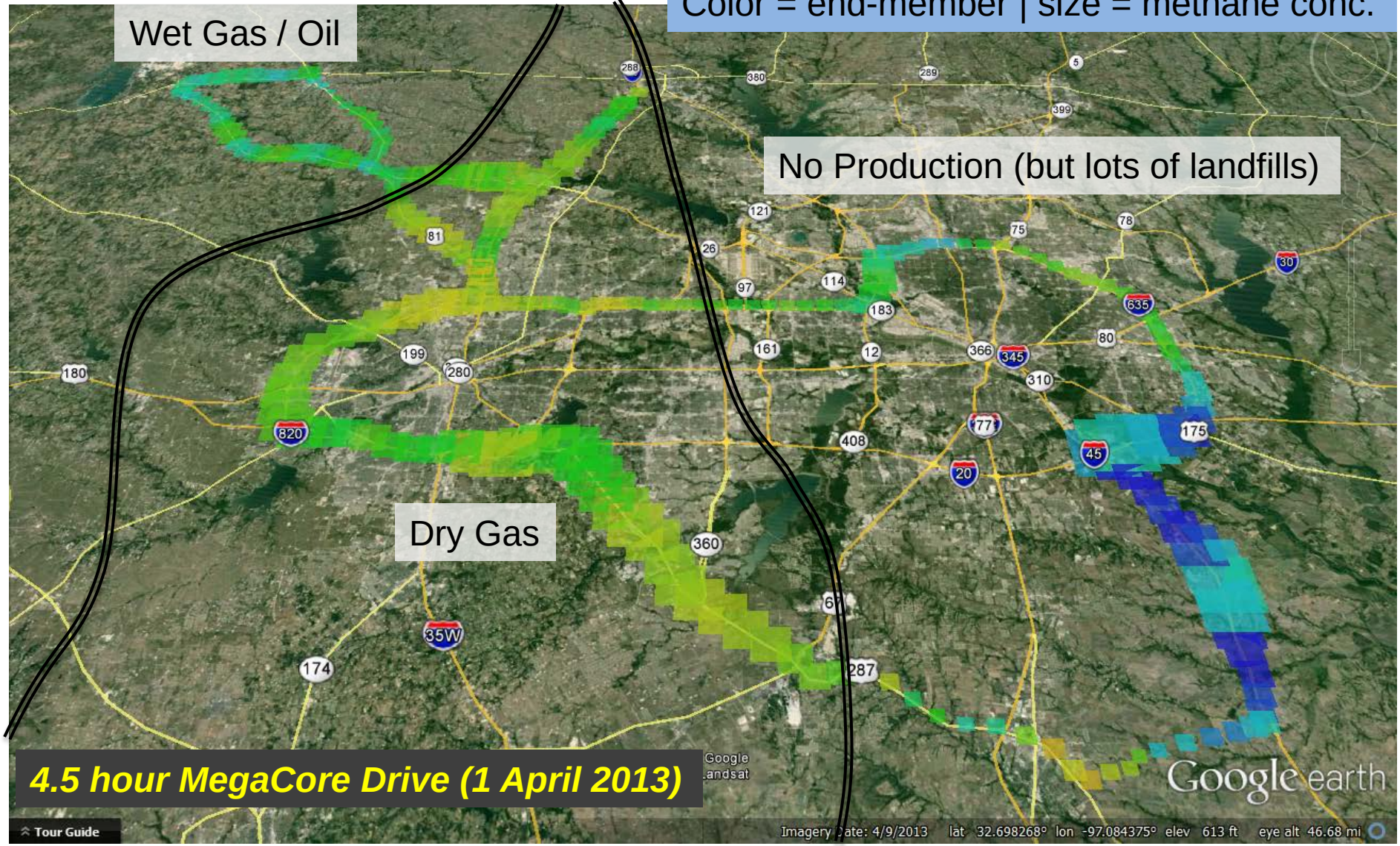
- Use the combined parameter ε to partition emissions

# Partitioning emissions using ε



# Results: Regional $\delta^{13}CH_4$ and ethane via MegaCore measurements

# 20130401: Observing the Local $\delta^{13}CH_4$ Source Signature



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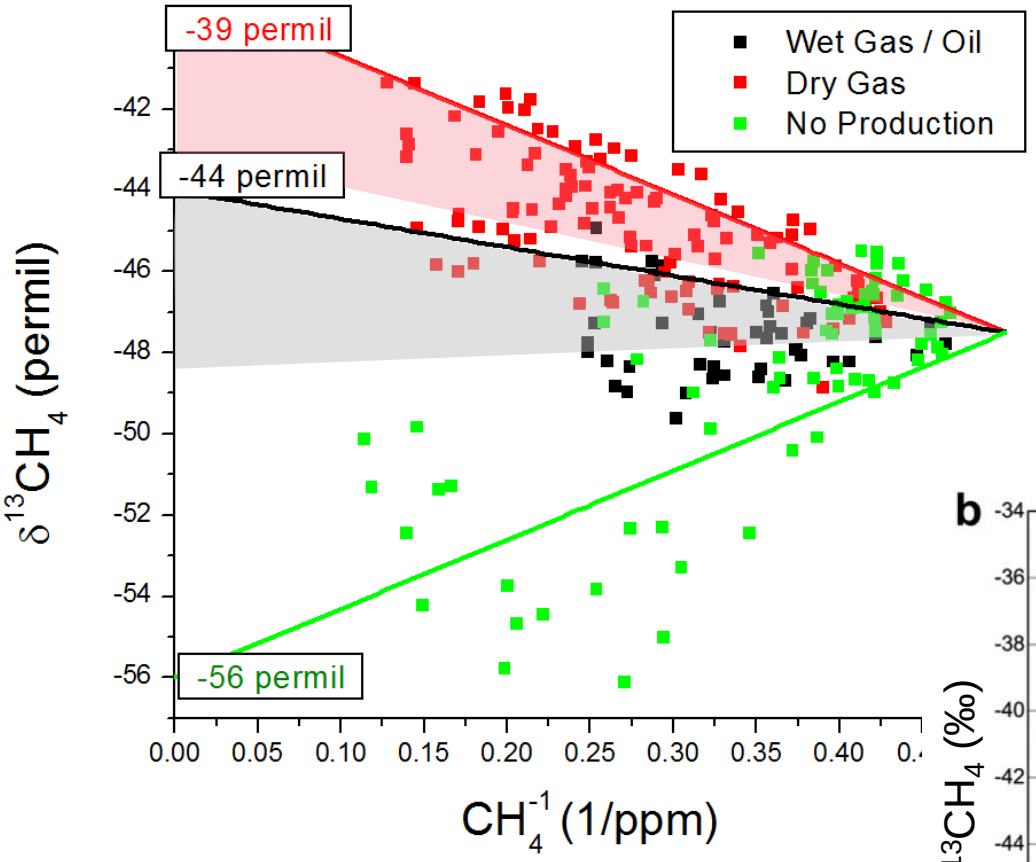
# 20130401: Isotopic Signature and $C_2/C_1$ Ratio in Different Regions

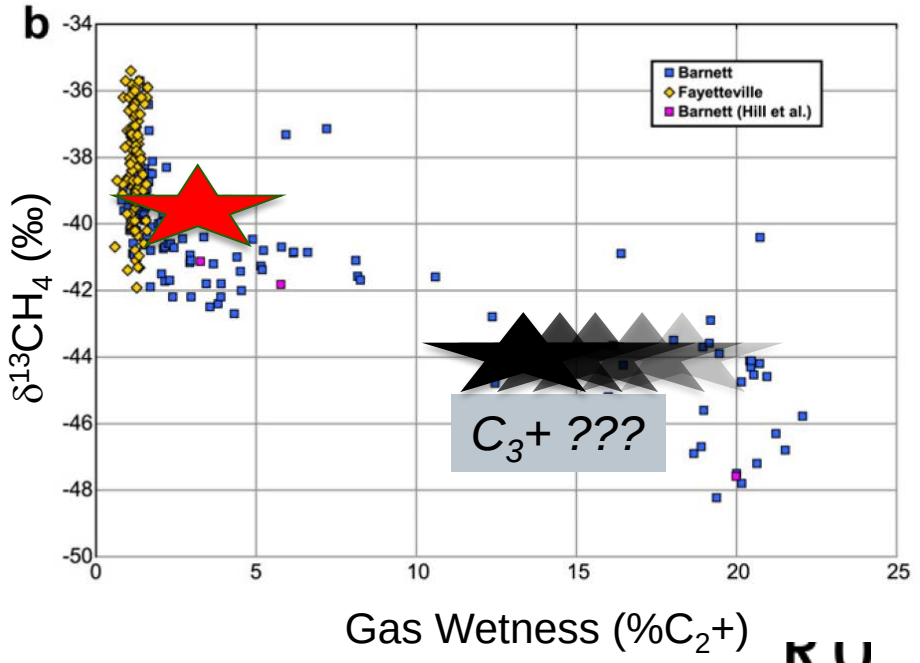



***Observed Ethane / methane ratios:***

Wet Gas / Oil = 15 ± 3%

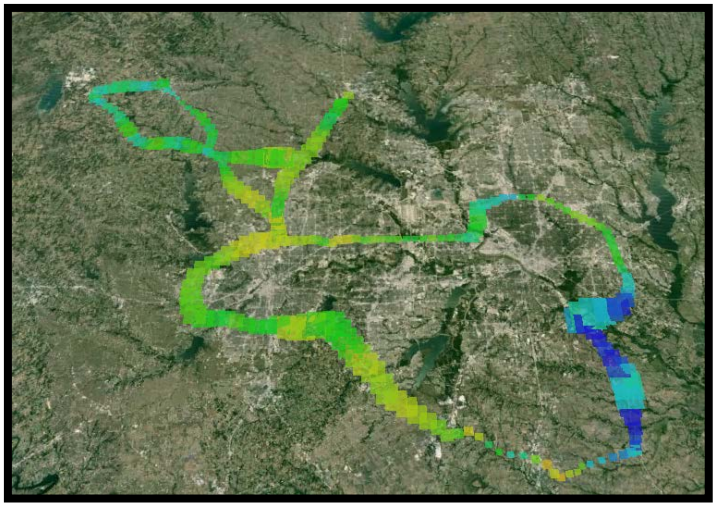
Dry Gas = 4 ± 3%

No Production = - 1 ± 3%

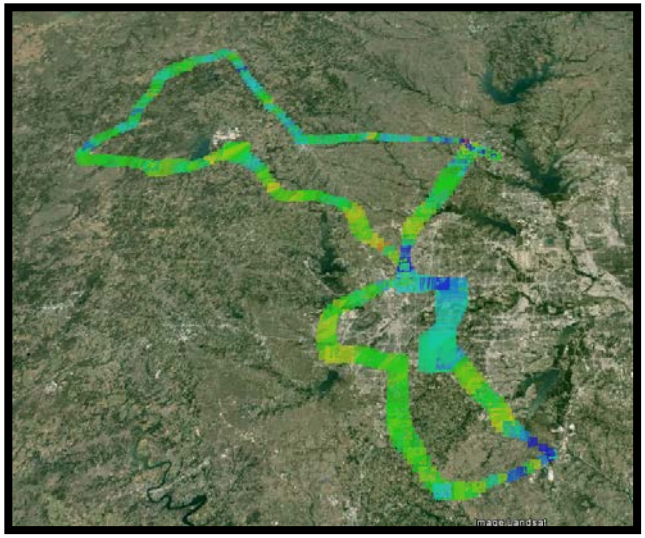


# Weighted Sum of Observed O&G Fraction

- 2013 0401 – includes Dallas, Ft. Worth, and O&G production areas (primarily dry gas)
  - Entire drive: O&G is **63%** of total observed emissions
  - In production areas only: **79%** of observed emissions
  - wet only: **67%** O&G
  - dry only: **82%** O&G
  - no production: **16%** O&G



- 2013 1027 – Ft. Worth and O&G production areas (more wet gas areas than for 20130401)
  - Entire drive: O&G is **62%** of total observed emissions
  - Excluding non-production area east of Ft. Worth: O&G is **69%** of total emissions
  - Just the area east of Ft. Worth: O&G is **28%** of total emissions



Estimated Error ~ +/-10%

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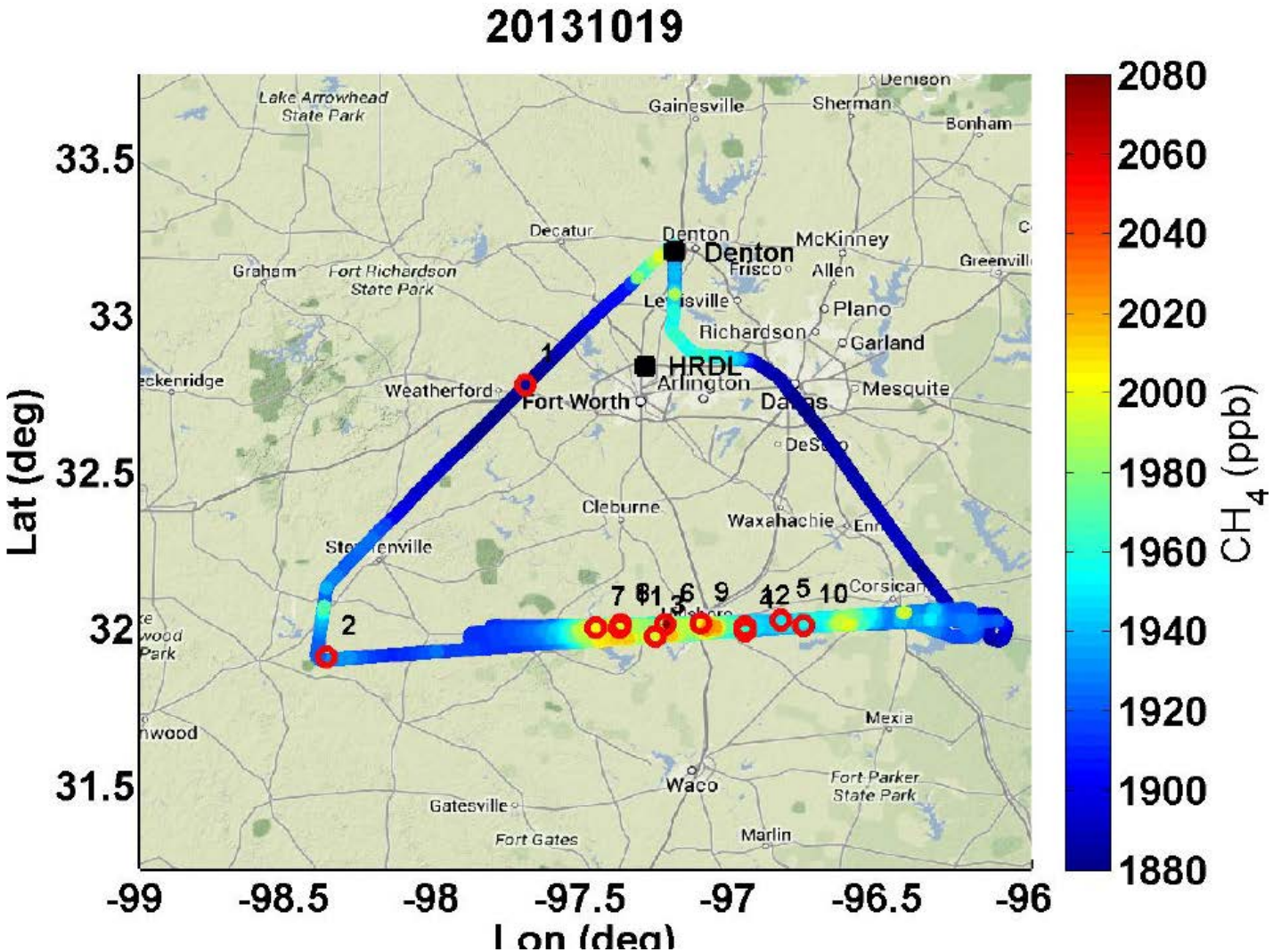
# Flight 20131019 – clear downwind plume

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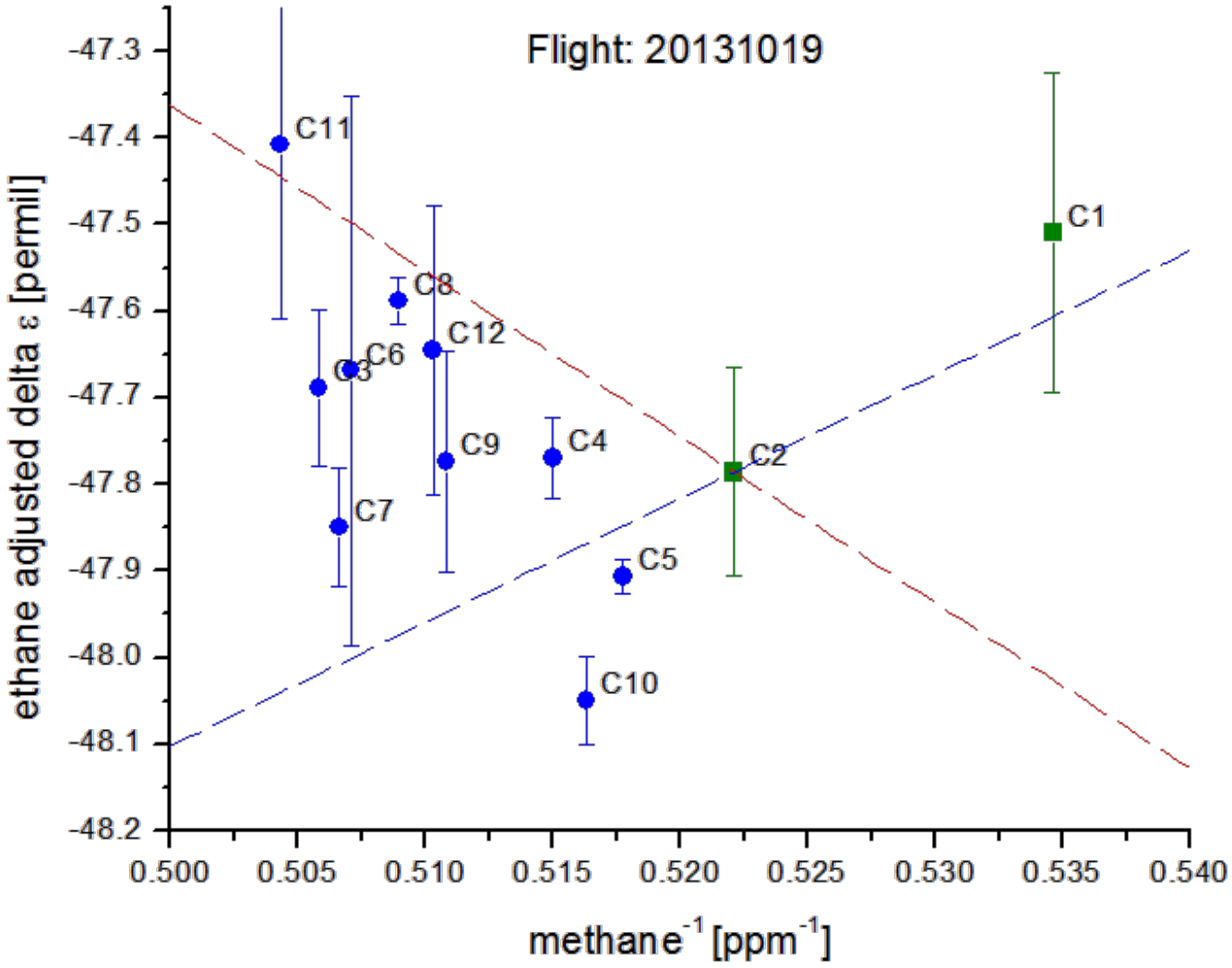
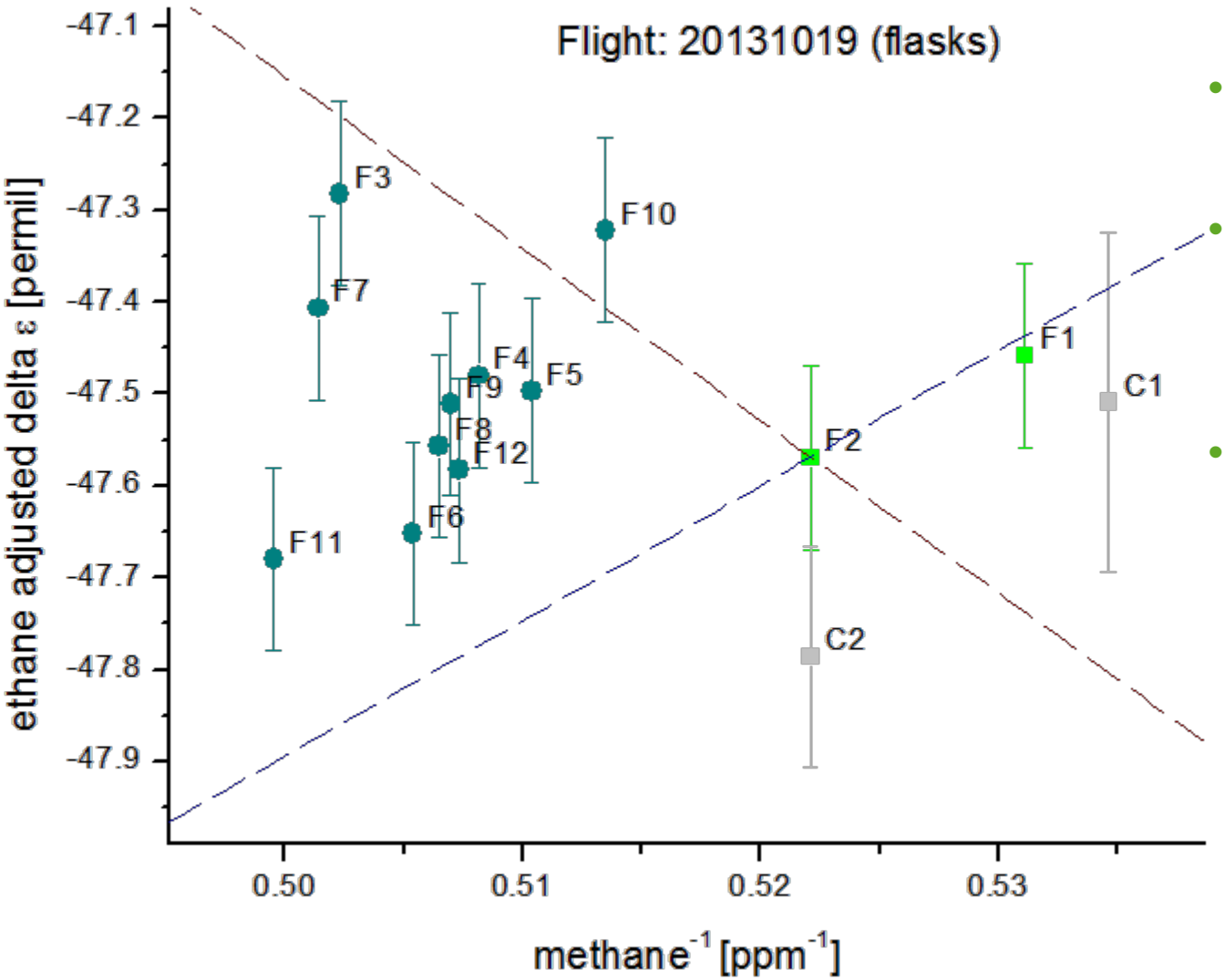
# Bag Samples C01 – C12




- Using a similar analysis as the MegaCore emissions fraction estimate (using E. Kort's ethane measurement to calculate the combined isotope – ethane parameter ε), we find:

**O&G = 67%**

# NOAA flask Samples




- Measured by IRMS at INSTAAR
- Using F2 as background,

O&G = 67%

- About 0.2 ‰ offset between CRDS and IRMS measurements

# Flight Partitioning Summary

- Summary of three flights
  - Note: ‘B’ flight was not a mass balance day
- 61 – 75% O&G emissions, consistent with MegaCore measurements (62-63%)

| Flight | Bag CRDS Analysis | NOAA flask IRMS analysis |
|---|---|---|
| A: 20131016 | 75 ± 15% (A1 background) | |
| B: 20131017 | 61 ± 9% (C2 background)<br>72 ± 13% (A1 background) | |
| C: 20131019 | 67± 15%(C2 background) | 67 ± 17% (F1 background) |

*uncertainty given by uncertainty in background delta (about ±0.1‰)*


**Conclusion: $\delta^{13}CH_4$ and Ethane are better together for emissions partitioning O&G producing regions**

**Thank You!!**

*This work was funded in part by the Environmental Defense Fund

# Analysis of MegaCore Regional Emissions

First we define the combined $d^{13}CH_4$ & ethane parameter $\varepsilon$ :

$$\varepsilon = \delta^{13}\mathrm{CH}_4 + 27.05 C_2/C_1$$

We then define the local fraction $f(s) = \frac{[\varepsilon(s) - \varepsilon_{landfill}]}{[\varepsilon_{O\&G} - \varepsilon_{landfill}]}$ at position $s$. In this expression, $\varepsilon(s)$ is the intercept of a Keeling plot (using each MegaCore data point, along with a representative background data point, to interpolate the intercept), and $\varepsilon_{landfill}$ and $\varepsilon_{O\&G}$ are the two key end members for landfills and oil and gas, respectively.

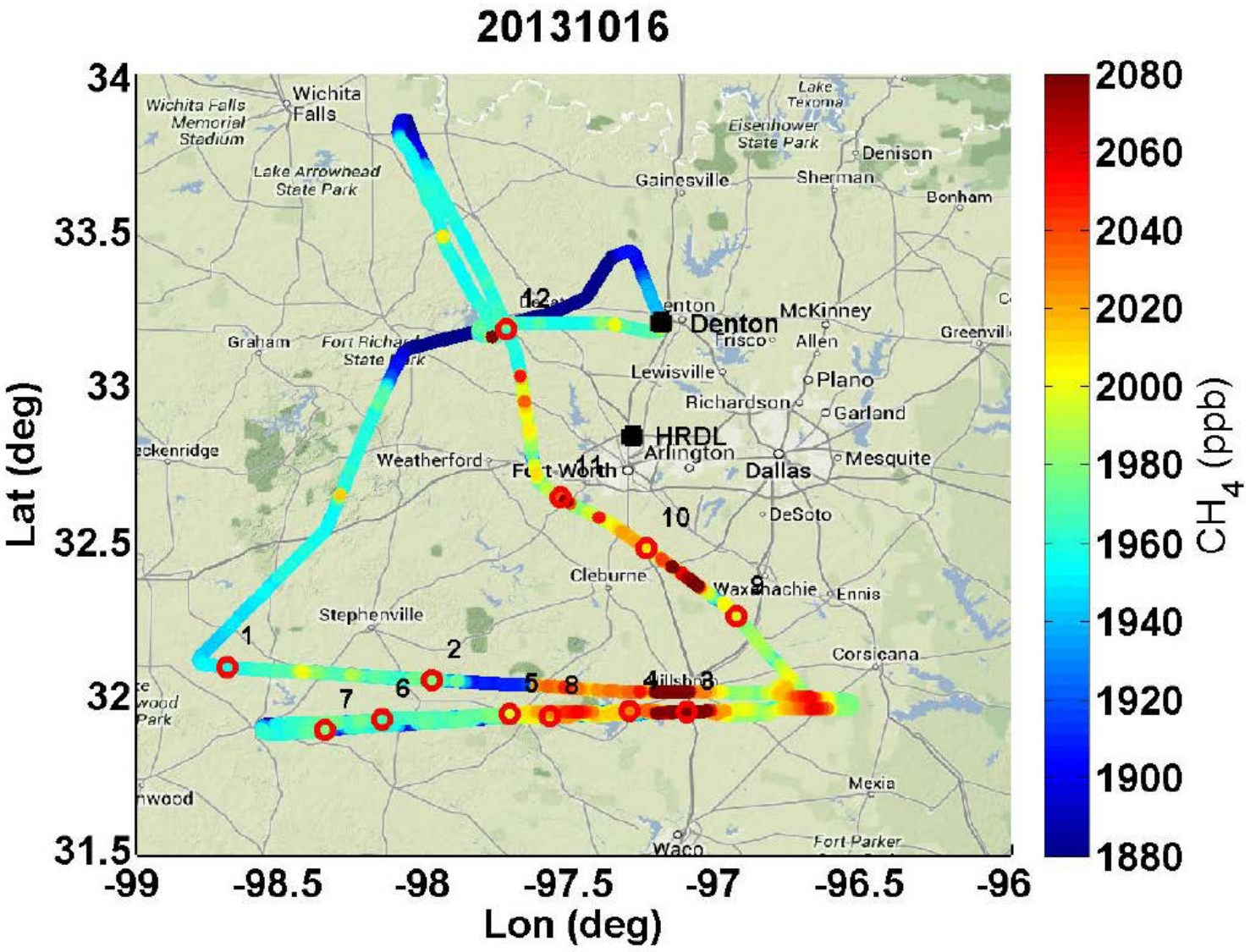
We then calculate the overall fraction of the observed emissions from O&G from each MegaCore measurement using the following integral, where the observed regional ratio is weighted by the excess methane observed in that area:

$$F_{O\&G} = \frac{\int^{drive\ path} [C(s) - C_{background}] f(s) ds}{\int^{drive\ path} [C(s) - C_{background}] ds},$$

where $C(s)$ is the spatially dependent methane concentration and $f(s)$ is the local O&G fraction.

# Isotope Analysis of 20131016 flight "A Series"

# Flight 20131016

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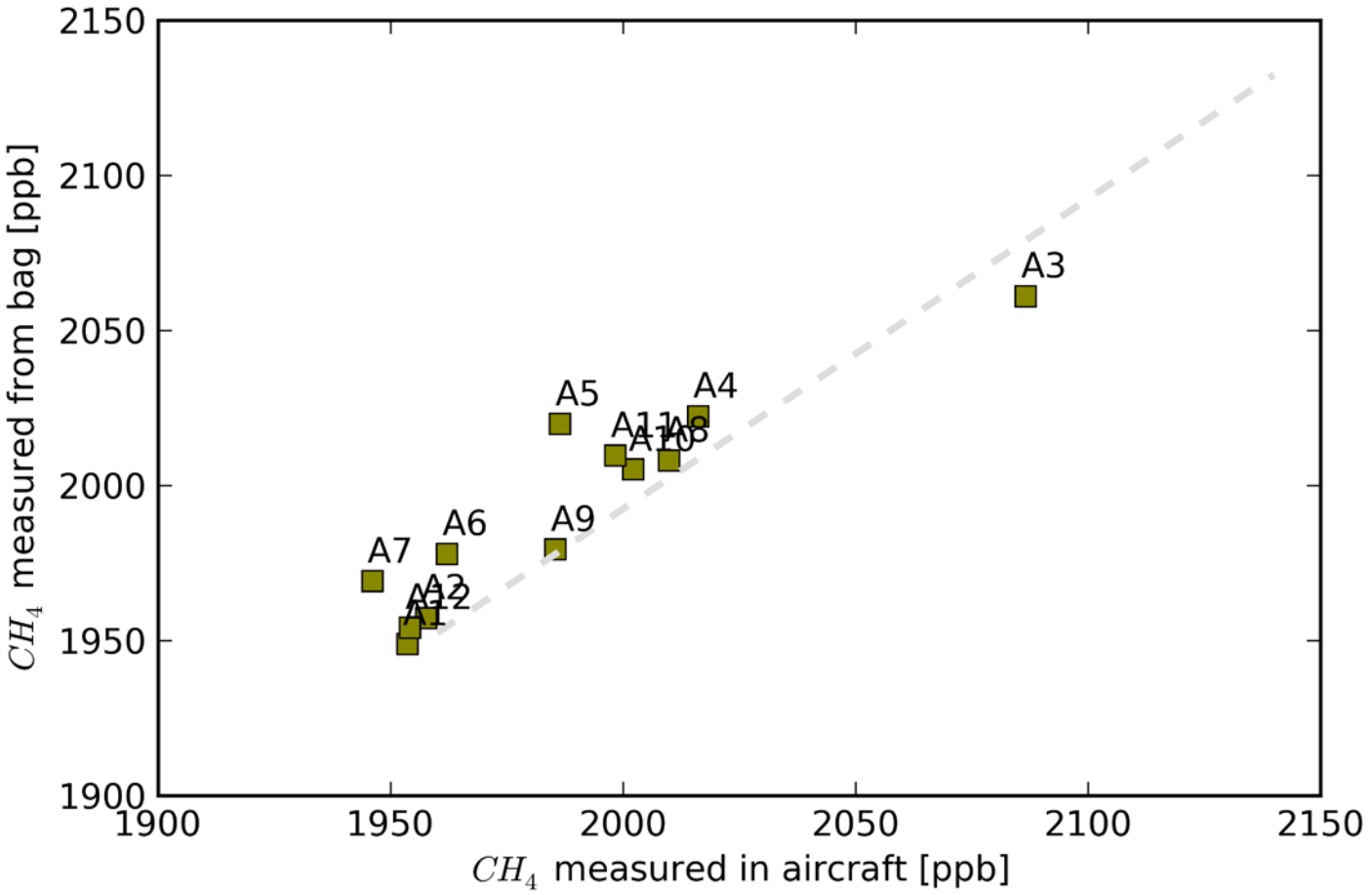
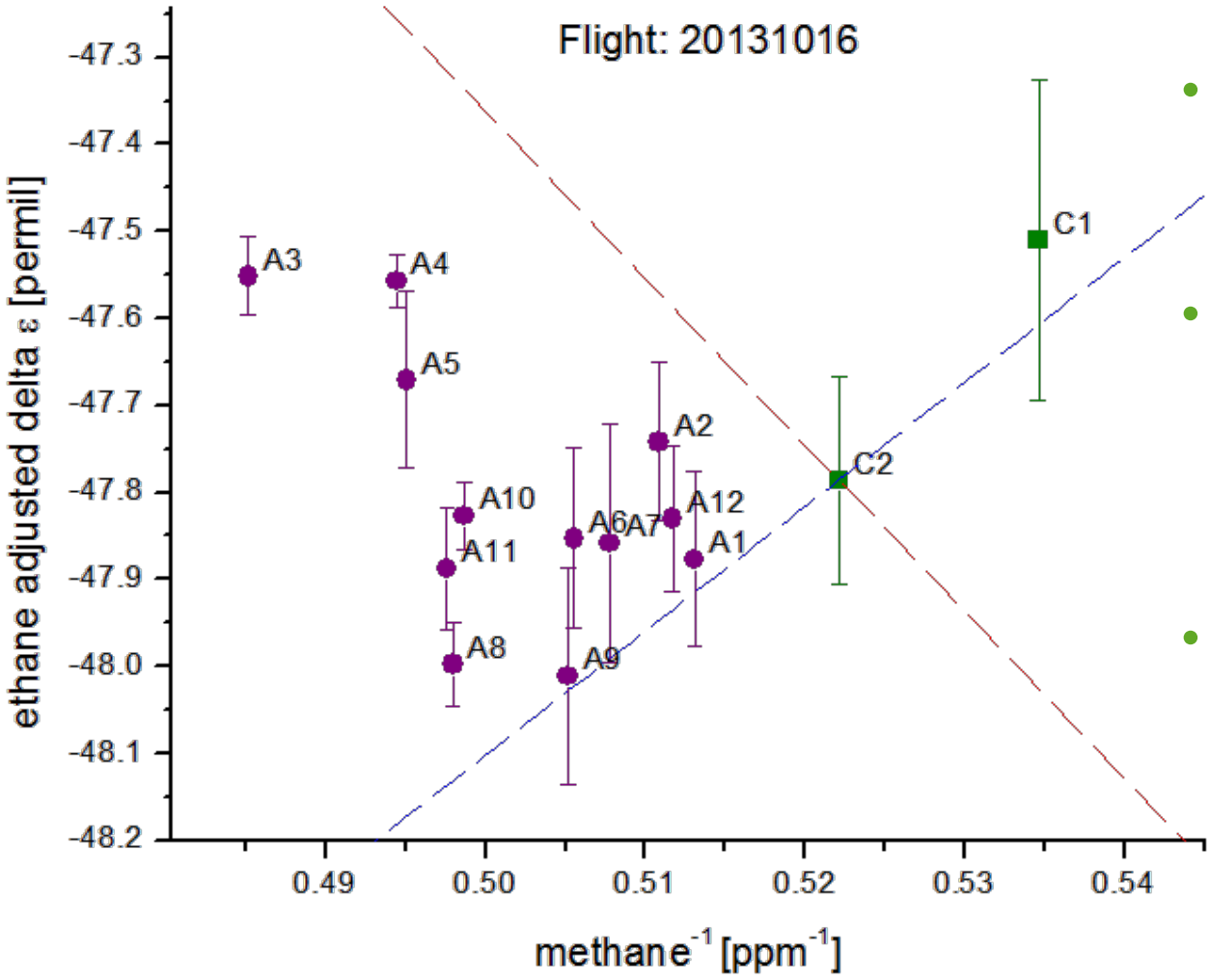
# Concentrations



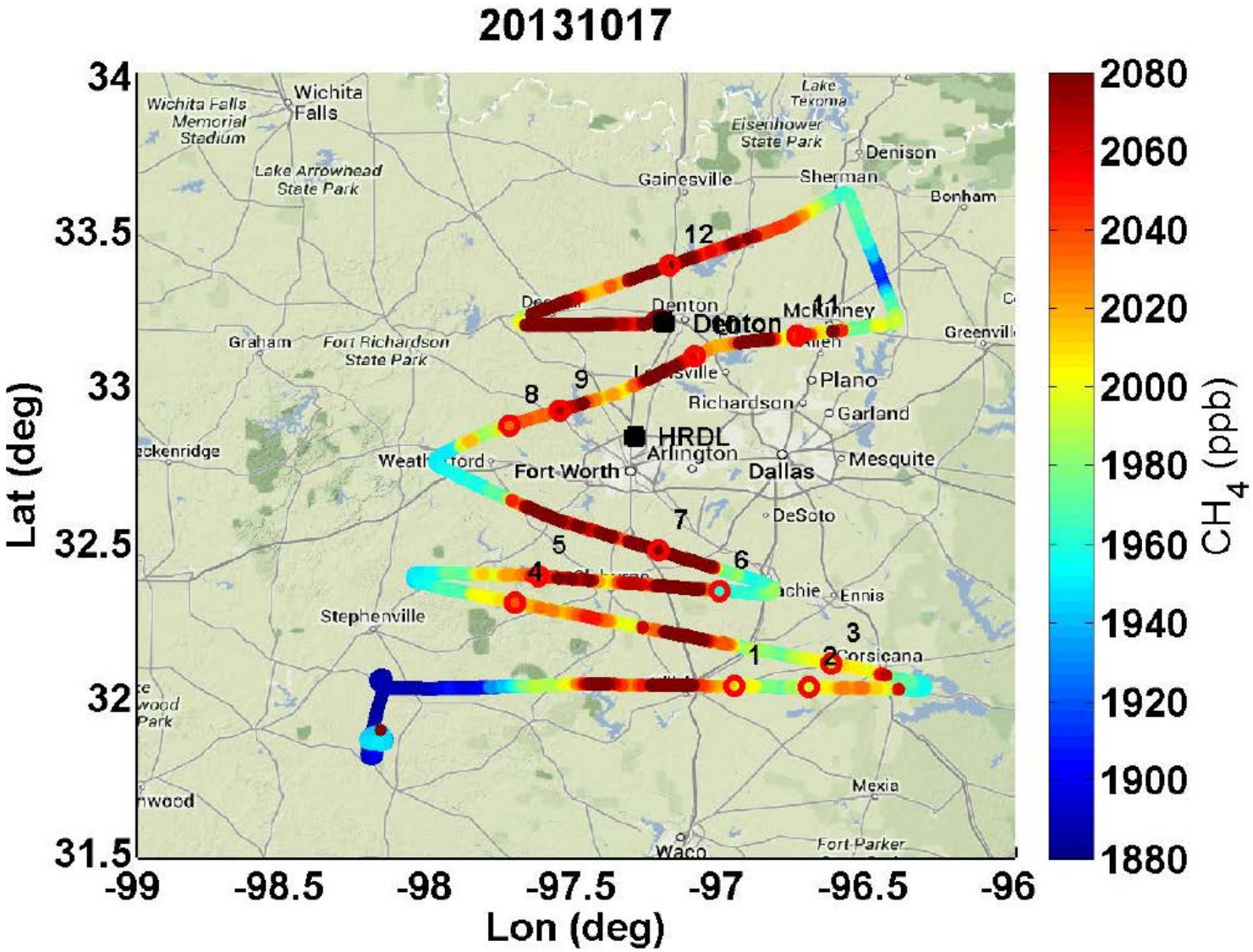
# Isotopes (Keeling Plot)




- Using C2 as a background: O&G = 55% of emissions
- **Using A1 as a background: O&G = 75%**
- excluding mid-plume bags A9-A12

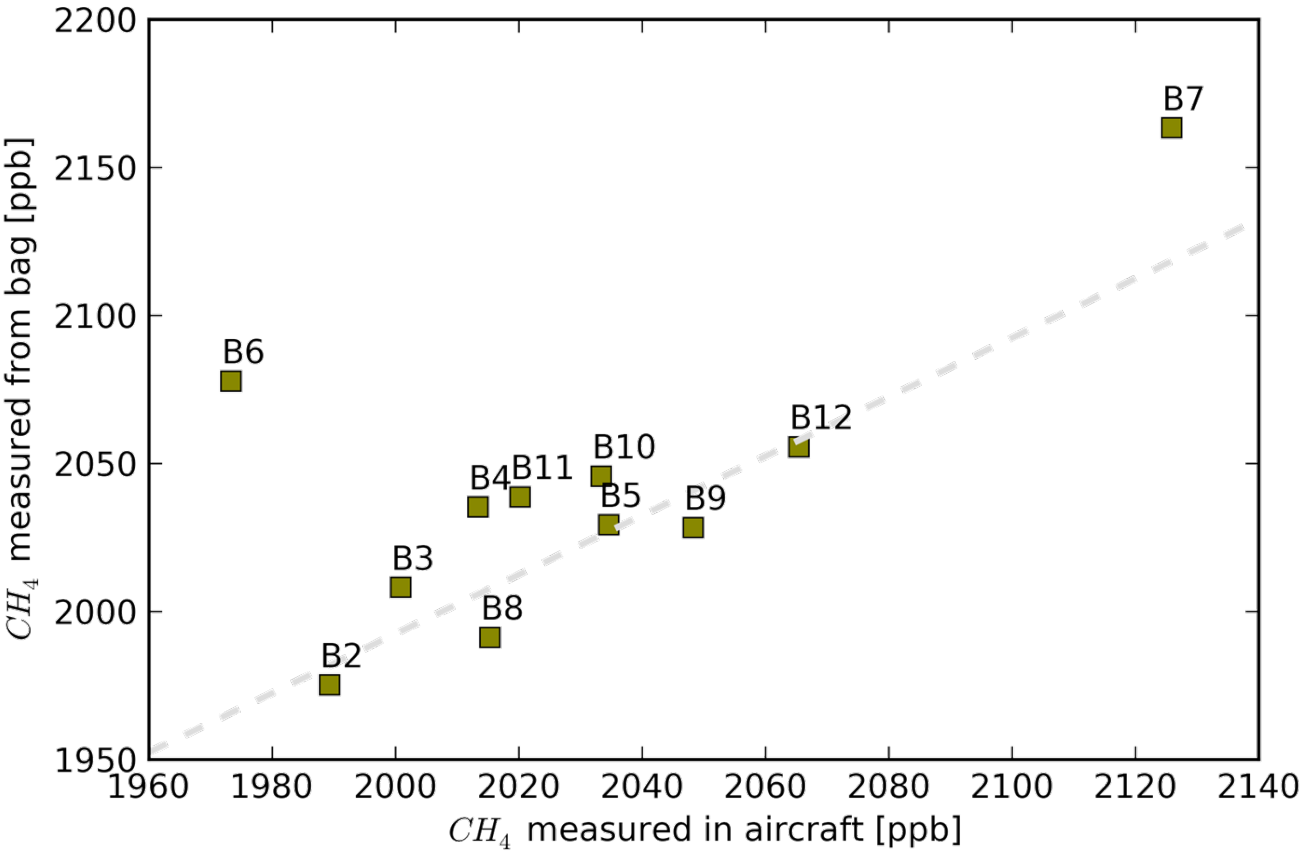
# Isotope Analysis of 20131017 flight "B Series"

# Flight 20131017 – low wind conditions



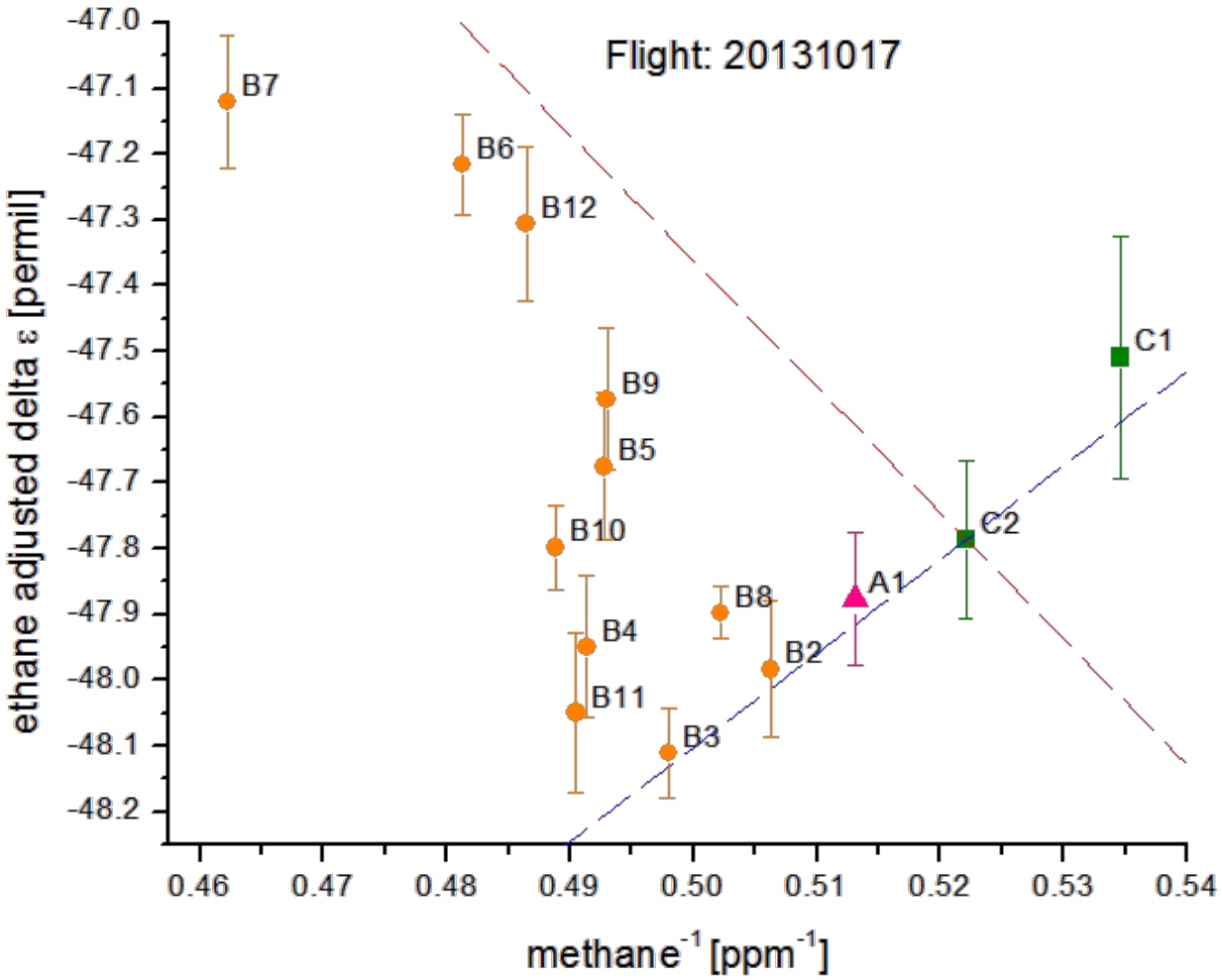

*Note: sample bag B01 was missing*

# Concentration analysis




- Poor correlation
- Contamination? Then it would tend to be above the line
- Timing on the aircraft data?

# Isotope analysis

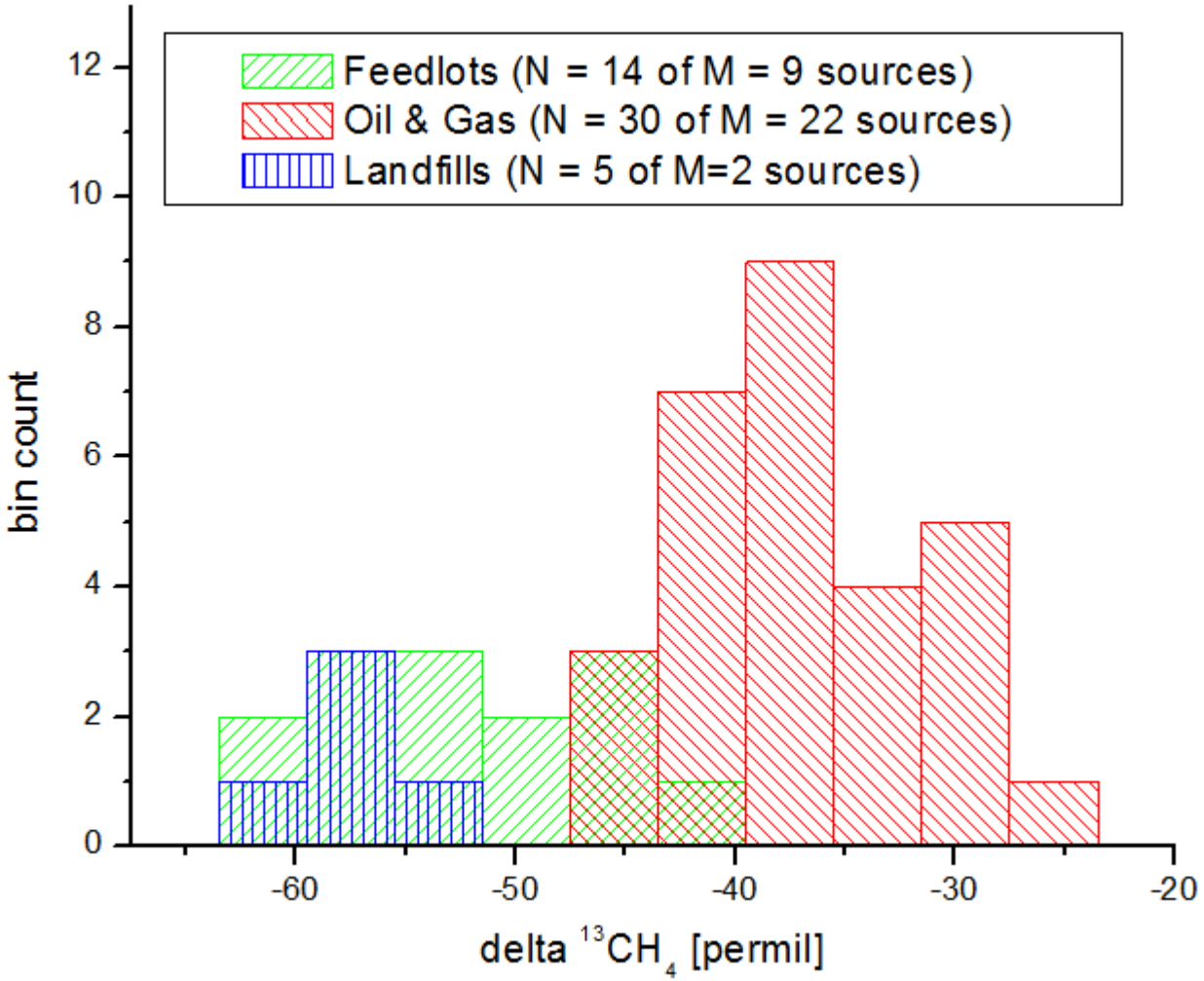



- Using C2 as a background: O&G = 61% of emissions
- Using A1 as a background: O&G = 72% of emissions

- After calibration to bottles
- LO tank, injected into a tedlar bag on position #1, retrieved 1.784 ppm (+1.5 ppb above tank value) and -42.28 +/- 0.07 permil (0.02 permil above assigned value)

# Isotope Analysis of 20131019 flight "C Series"

# Individual End Members (33 sources total)



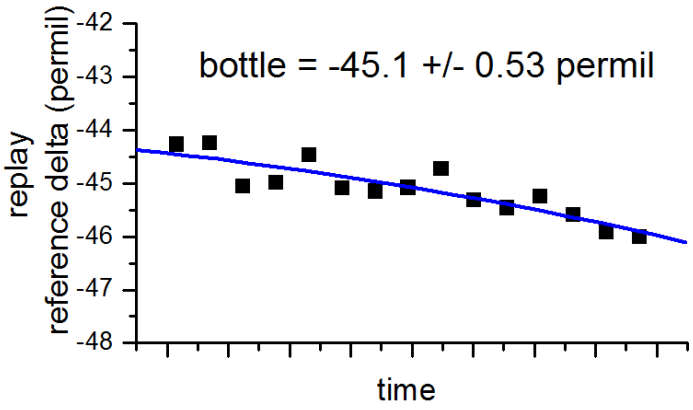

| | |
|---|---|
| $\delta_{cow}$ | – 45 to – 55 (C4 diet) |
| $\delta_{O\&G}$ | – 30 to – 60 |
| $\delta_{land}$ | – 48 to – 56 |

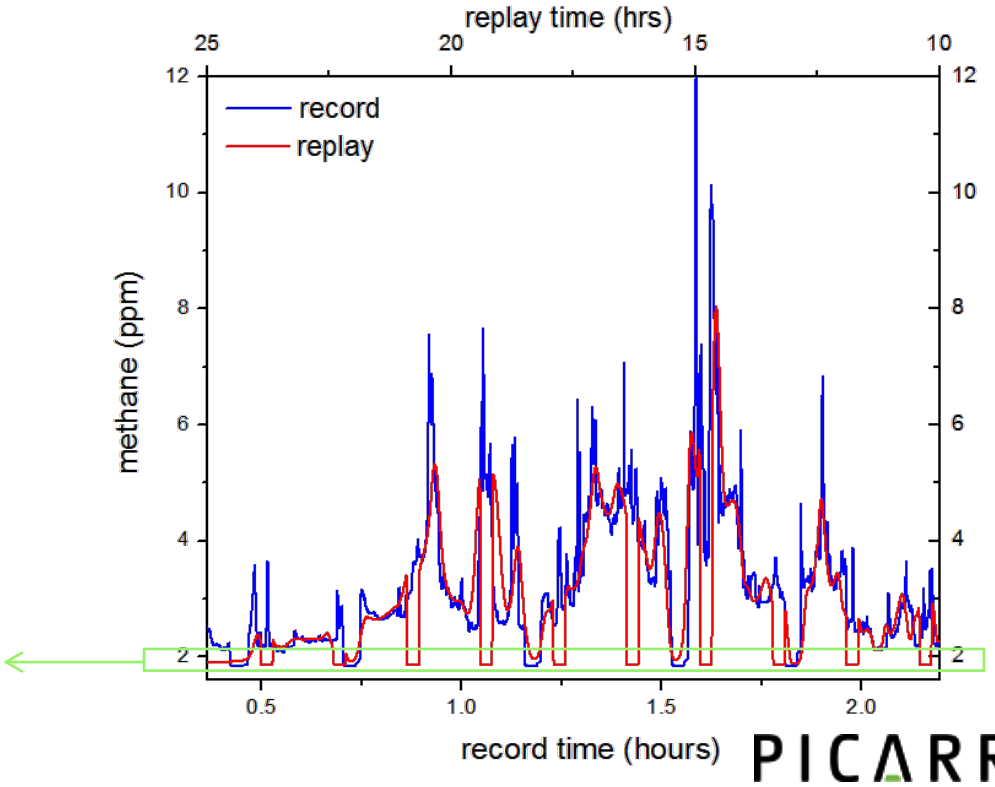
Quay et al. (1988)

(10-15 minutes of analysis / sample)

# MegaCore: A Really Big Air Core

- 1500’ ft of 3/8” O.D. synflex tubing
- Sample ambient air during ~2 – 5 hour drive
- Playback sample into *i*CH4 analyzer for 15 - 30 hours in the laboratory

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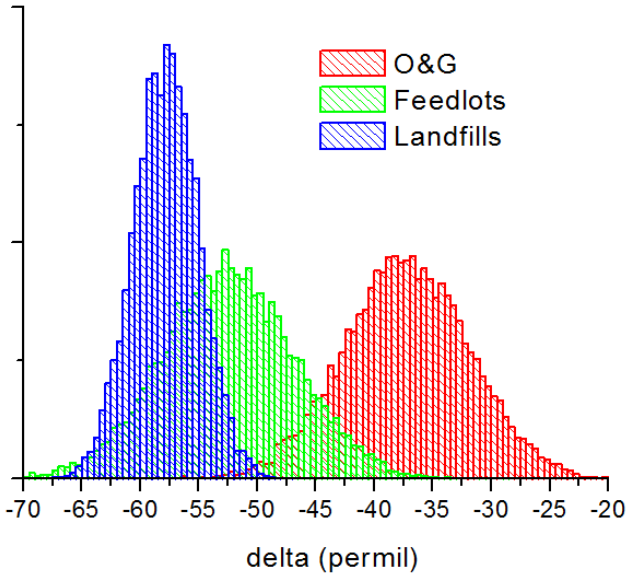
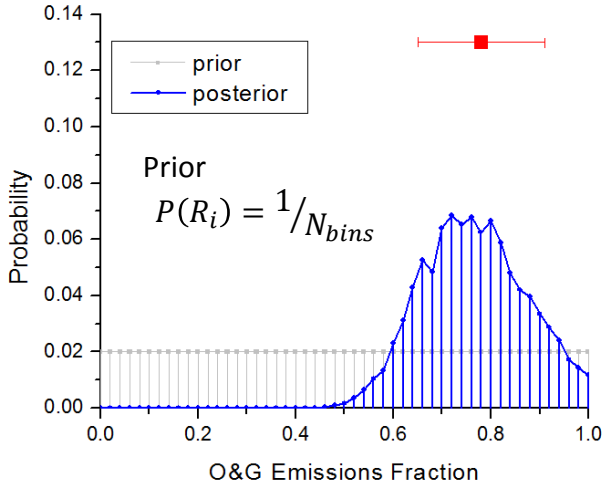
# Emissions & Isotopes Model

$$\delta_{tot} = R_{O\&G}\delta_{O\&G} + (1 - R_{O\&G})\delta_{C\&L}$$



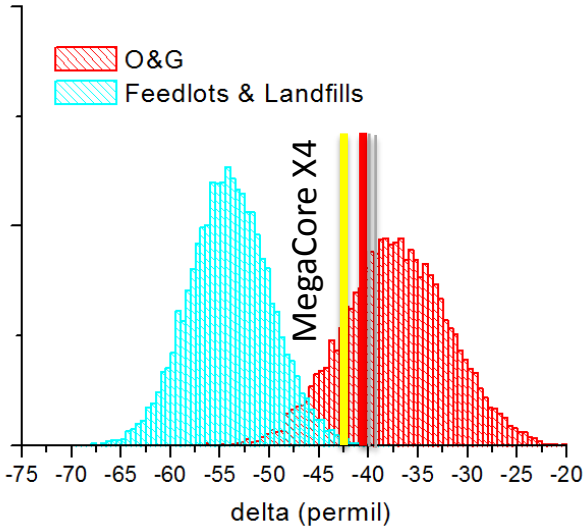

Bayesian analysis of O&G Emissions Fraction (hypothesis) given the MegaCore data (evidence)




$$P(R_i|\delta_{obs}) = \frac{P(\delta_{obs}|R_i)P(R_i)}{\sum_{R_j=0-1} P(\delta_{obs}|R_j)P(R_j)}$$

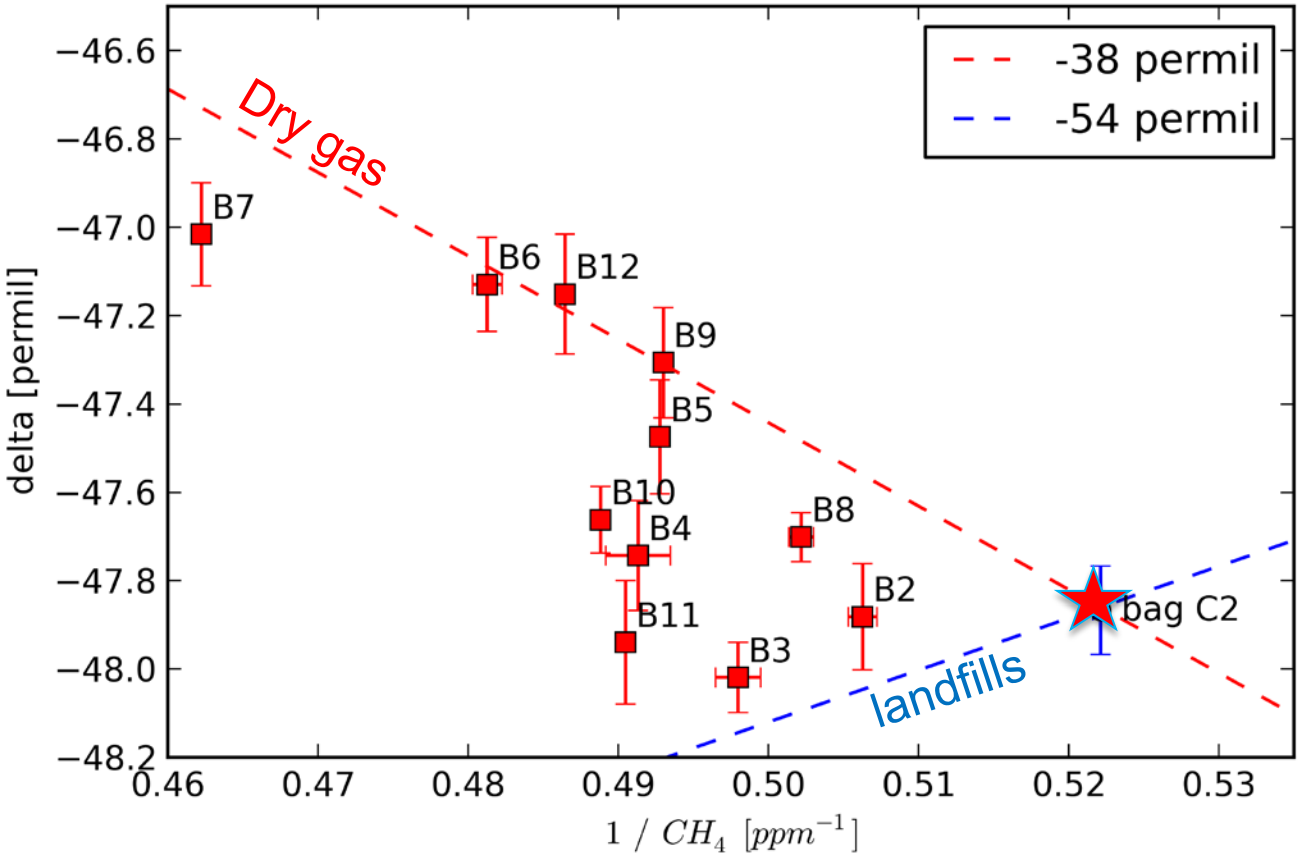
Monte Carlo simulation of feedlot and landfill emissions and isotope signatures to generate combined feedlot & landfill source profile

$$\delta_{C\&L} = \frac{E_{cow}\delta_{cow} + E_{land}\delta_{land}}{E_{cow} + E_{land}}$$




- O&G is **78 ± 13%** of total emissions in the Denver – Julesberg Basin

# Isotope Analysis of Sample Bags




- 16 port selector valve (4 ports for calibration, 1 port for known sample in bag, 4 replicates / bag) ; instrument air dried (Nafion)
- LO tank, injected into a tedlar bag on position #1, retrieved 1.784 ppm (+1.5 ppb above tank value) and -42.28 +/- **0.07** permil (0.02 permil above assigned value)

# 1000 km of MegaCore Sampling in the Barnett

# Isotope Measurements in “Lab 322”