Measurement of Air Quality Impacts During Hydraulic Fracturing on a Marcellus Shale Well Pad in Greene County, Pennsylvania*

Natalie Pekney[1], Garret Veloski[2], Matthew Reeder[2], Joseph Tamilia[2], J. Rodney Diehl[2], and Richard W. Hammack[2]

Search and Discovery Article #80357 (2014)**
Posted February 11, 2014

*Adapted from oral presentation presented at AAPG Annual Convention and Exhibition, Pittsburgh, Pennsylvania, May 19-22, 2013

[1]U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA (Natalie.Pekney@netl.doe.gov)
[2]U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA

Abstract

NETL's mobile air monitoring laboratory was deployed to a Marcellus Shale well pad in Greene County, Pennsylvania to collect measurements of pollutant concentrations before and during hydraulic fracturing. A comparison of background ambient concentrations of pollutants associated with natural gas operations with concentrations of the pollutants measured during the various phases of hydrofracturing operations enabled an evaluation of the impact the activities had on local air quality. Instruments in the laboratory measured the ambient concentrations of methane, carbon dioxide, carbon isotopes in methane and carbon dioxide, volatile organic compounds, nitrogen oxides, ozone, particulate matter, sulfur dioxide, ammonia, organic and elemental carbon aerosols, as well as several meteorological parameters. Monitoring commenced on March 8, 2012 and ended on June 19, 2012. During this time, there were periods of no well pad activity that could be compared to periods of hydraulic fracturing activities. Three of six horizontal wells were hydraulically fractured from April 24 to May 7, and the other three wells where hydraulically fractured from June 4-11. During periods of low or no activity on the well pad, measured pollutants registered typical atmospheric background values with few exceptions. However, significant increases in concentrations of methane, NOx, PM10, and several VOCs were observed during the two hydraulic fracturing operations. Methane concentration and isotope data were used to distinguish between biogenic and thermogenic methane. This technique provides a fingerprint of fugitive methane emissions from the wells. During the fracturing of the first three wells, peaks in methane concentration correlated with changes in the methane isotopic signature to reflect influence of thermogenic methane. A similar pattern was observed during the fracturing of the second three wells, although the most significant evidence of thermogenic methane occurred afterward during flowback. Preliminary results from this project suggest that although measurements did not at any time exceed applicable exposure limits or air quality standards, there were discernible differences in measurements collected during the various phases of operation at the well pad. A complete evaluation of all the collected data will be presented, with estimates of well pad emissions distinguished from background conditions.

Website

U.S. Department of Energy: NETL, Energy Analysis, Website accessed January 27, 2013. http://www.netl.doe.gov/energy-analyses/pubs/NG-GHG-LCI.pdf

NATIONAL ENERGY TECHNOLOGY LABORATORY

MEASUREMENT OF AIR QUALITY IMPACTS DURING HYDRAULIC FRACTURING ON A MARCELLUS SHALE WELL PAD IN GREENE COUNTY, PENNSYLVANIA

AAPG ACE May 20, 2013

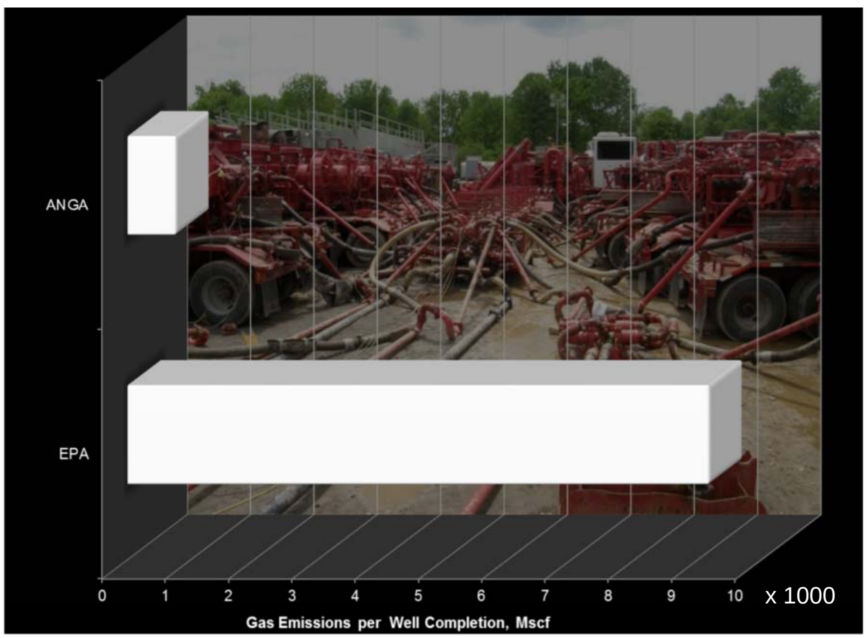
Natalie Pekney, Garret Veloski, Matthew Reeder, Joseph Tamilia, J. Rodney Diehl, Richard Hammack

U.S. Dept. of Energy National Energy Technology Laboratory

DOE efforts focus on improving fugitive emissions factor calculations and field emissions data for natural gas

Leads to improved ability to model long-term GHG effects

- First primary data analysis at the natural gas pad by an independent source
- Improved methodology for emissions factor
  - *increased statistical rigor and lowering estimate uncertainty*
- Fugitive emissions field data for natural gas extraction focused on decreasing modeling uncertainties
  - *application of rigorous methods across multiple operators, sites*



<u>Marcellus Shale Natural Gas Extraction and Transport</u>

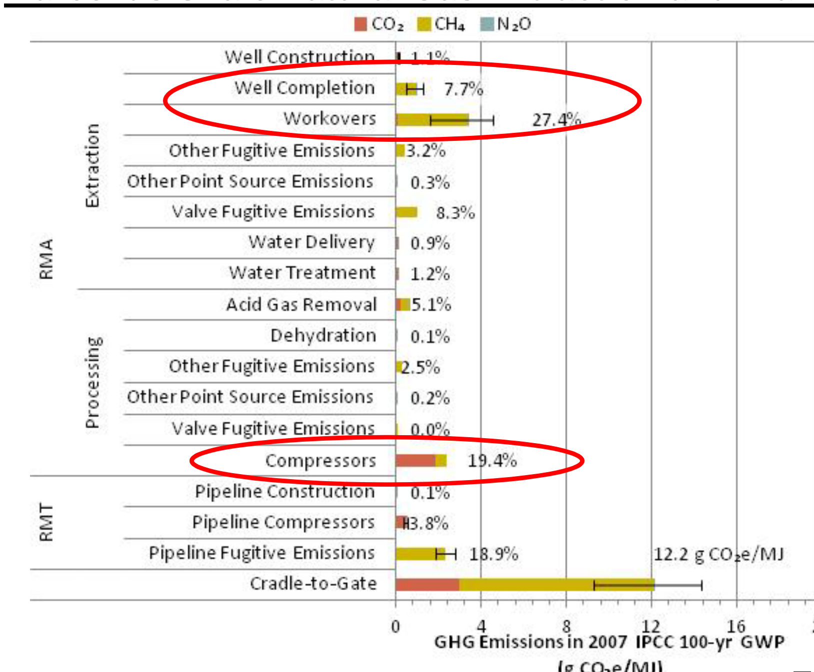


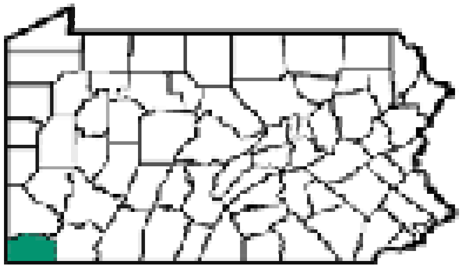
Figure from T. Skone, NETL

Problem: Limited number of high-quality field data sets representative of shale gas operations

- **Solution: Field measurements for representing ambient (regional effects) and point source (specific component) air emissions**
  - High level of rigor to evaluate regional versus activity-specific effects (e.g., operation stage; specific equipment)
- **Atmospheric chemistry and transport modeling for the Western Appalachian Basin**
  - Evaluate regional air quality impacts, changes in attainment status for ozone, particulate matter

Ambient	Point-Source
Values integrated over an area	Values for a specific location and/or operation
Plume interception dependent on local meteorology	Determination of background concentrations not necessary
Continuous measurements capture variations in operator/equipment activity	Provides a "snapshot" or short-term measurement

NETL's Mobile Air Monitoring Laboratory

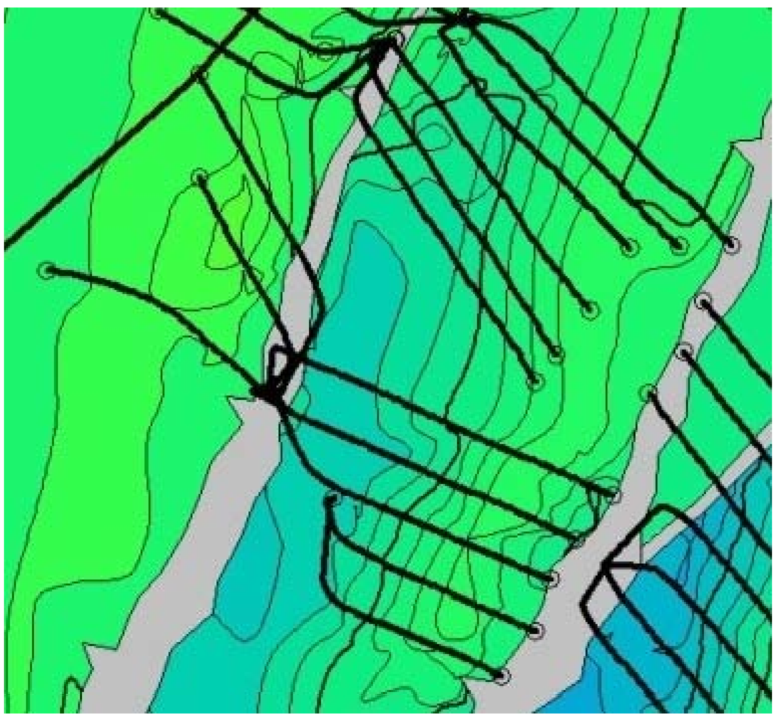


Greene County, Pennsylvania

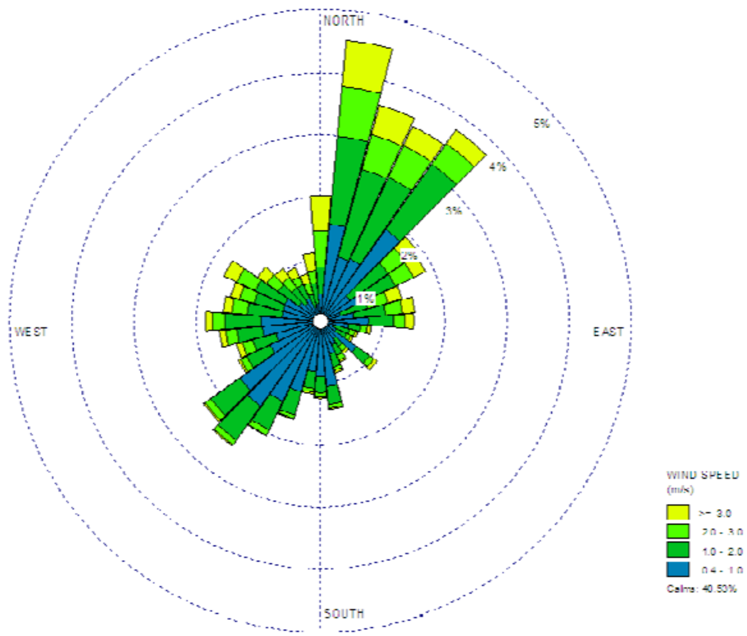
Collected Measurements Spring and Summer 2012 (~14 weeks)

Greene County Marcellus Shale Well Pad

- **Late April/early May: Frac 3 of the 6 wells**
- **Early June: Frac remaining 3 wells**
- **Mobile Air Monitoring Laboratory was on the SW corner of the well pad**



Wind Direction during monitoring

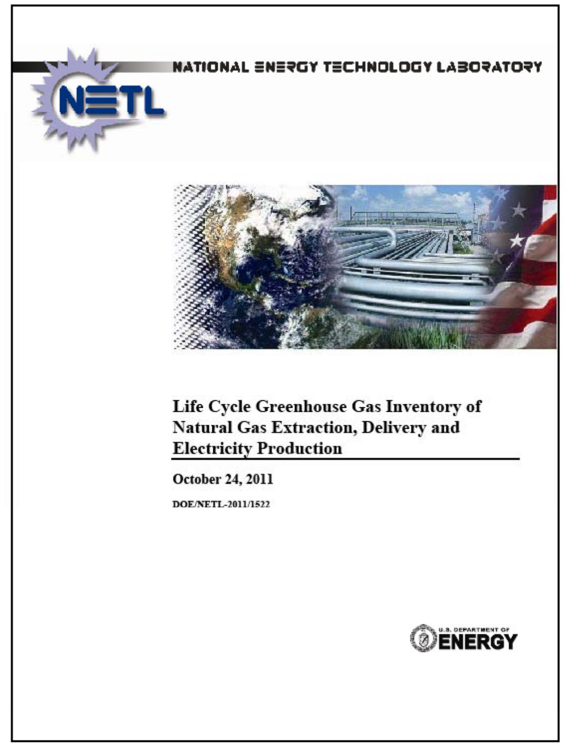


NETL's Mobile Air Monitoring Laboratory

- **Pollutants Measured:**
  - VOCs (Perkin Elmer Ozone Precursor Analyzer, GC-FID)
  - Ozone, NO_x, SO_2 (Teledyne-API Gas Analyzers)
  - Methane and Carbon Isotopes in Methane (Picarro CR-DS)
  - CO_2 and Carbon Isotopes in CO_2 (Picarro CR-DS)
  - PM_{10} and $PM_{2.5}$ (Thermo Fisher TEOM 1405DF)
  - Organic and Elemental Carbon in Aerosols (Sunset Labs NDIR)
  - Ammonia (Picarro CR-DS)
- **Meteorological Station (Davis Vantage Pro2 Plus)**
  - Wind Speed and Direction
  - Temperature
  - Relative Humidity
  - Barometric Pressure
  - Rainfall
  - Solar Intensity

Methane and Carbon Isotopes

- Natural gas is ~97% methane (CH_4)
  - CH_4 is a potent greenhouse gas, 8-72 times as potent as carbon dioxide
- NETL's Final LCA Report: http://www.netl.doe.gov/energy-analyses/pubs/NG-GHG-LCI.pdf
- **^{12}C (98.89%) ^{13}C (1.11%)**
- **$\delta^{13}C = \{(R_{sample} / R_{standard}) - 1\} * 1000$ ‰**
- **$R = {}^{13}C/{}^{12}C$**
- **$\delta^{13}C_{CH4}$:**
  - Atmospheric ~-50‰
  - Biogenic -50 to -80‰
  - Thermogenic -25 to -40‰


NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL

Life Cycle Greenhouse Gas Inventory of Natural Gas Extraction, Delivery and Electricity Production

October 24, 2011

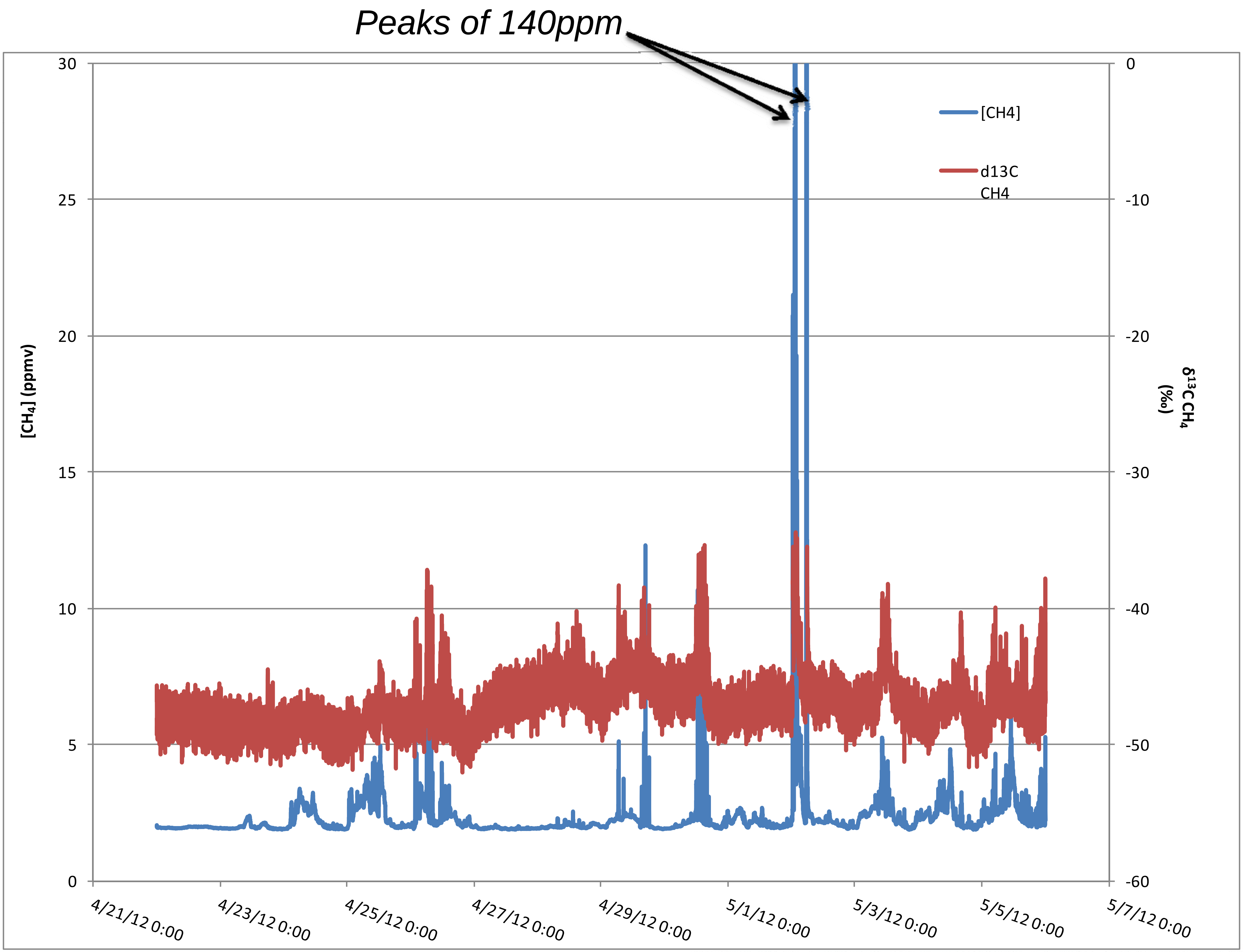
DOE/NETL-2011/1522

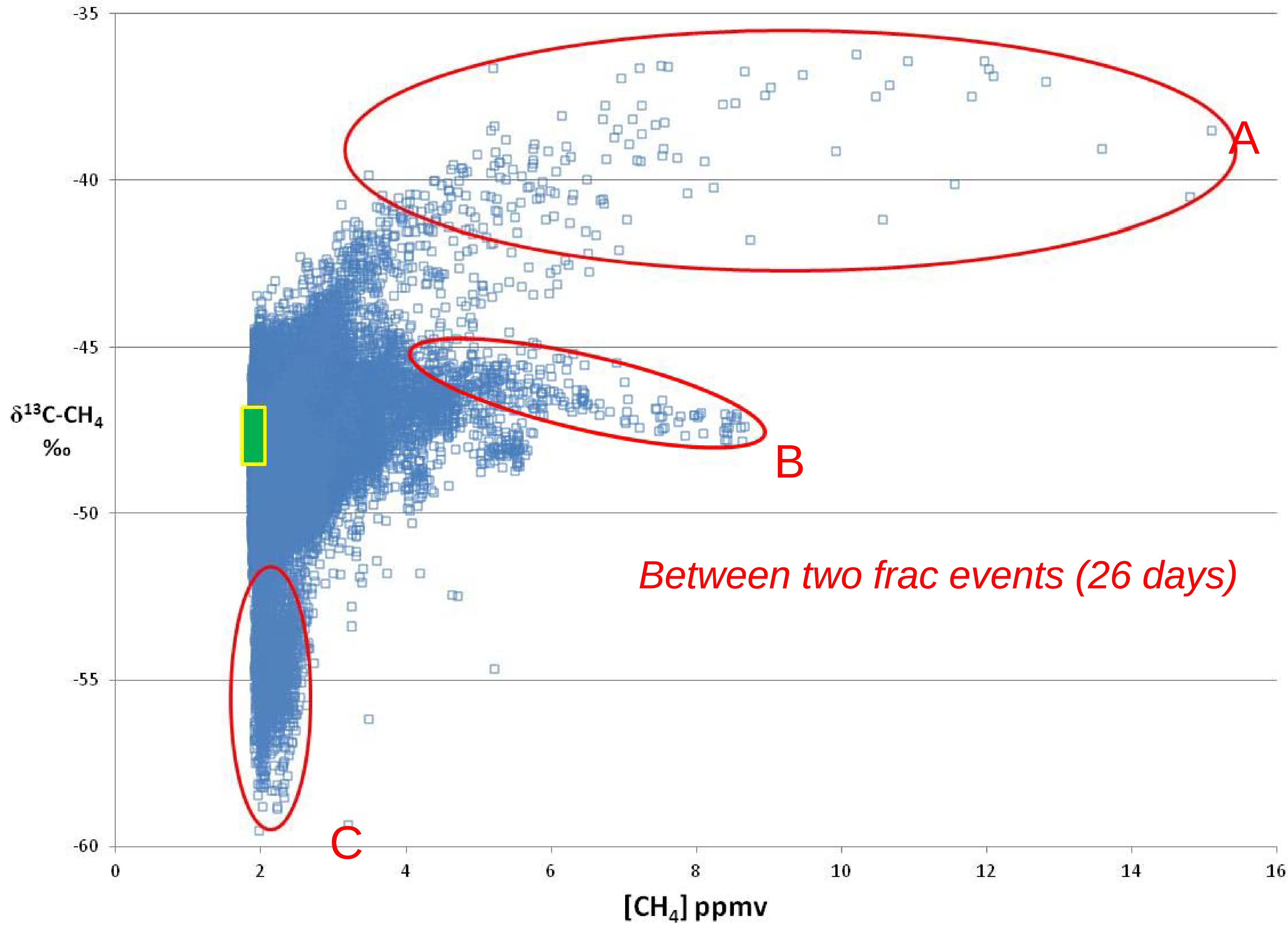
U.S. DEPARTMENT OF ENERGY

Methane and $\delta^{13}C_{CH4}$

- **Prior to first frac:**
  - Ambient Concentrations ranged 2-5ppm
  - No evidence of thermogenic methane; $\delta^{13}C_{CH4}$ ~-45‰
    - One exception: peak of 15ppm with $\delta^{13}C_{CH4}$ ~ -38‰ (thermogenic)
- **During first frac:**
  - Highest measured methane concentration of 140ppm
  - Episodic evidence of thermogenic methane

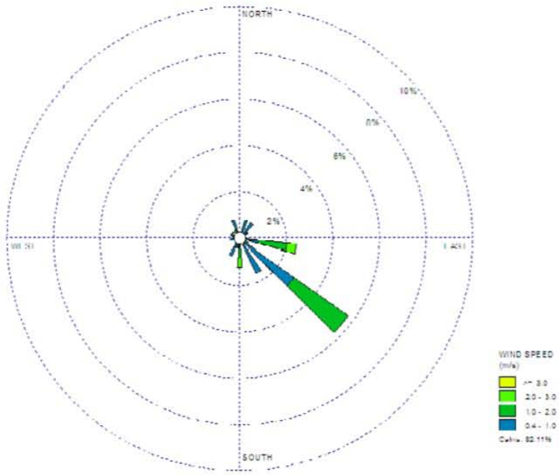
Presenter's notes: Looking out the windows of the frac van at the cows in pasture (biogenic!)


Peaks of 140ppm
30
25
20
15
10
5
0
0
-10
-20
-30
-40
-50
-60
[CH4]
d13C CH4
[CH4] (ppmv)
δ13C CH4 (‰)
4/21/12 0:00
4/23/12 0:00
4/25/12 0:00
4/27/12 0:00
4/29/12 0:00
5/1/12 0:00
5/3/12 0:00
5/5/12 0:00
5/7/12 0:00

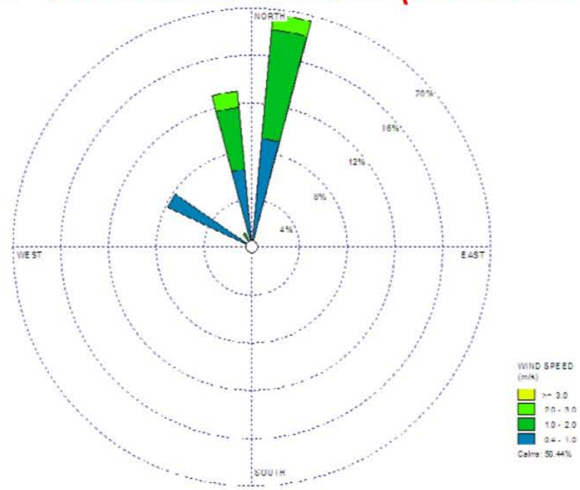


-35
-40
-45
-50
-55
-60
δ13C-CH4
‰
0
2
4
6
8
10
12
14
16
[CH4] ppmv
A
B
C
Between two frac events (26 days)

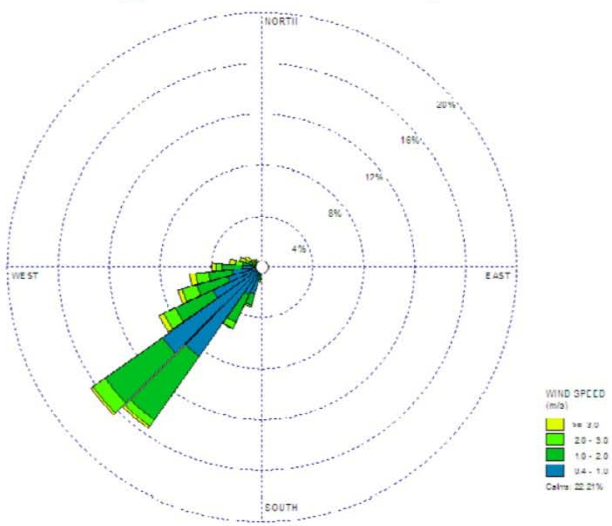
A: Thermogenic Source



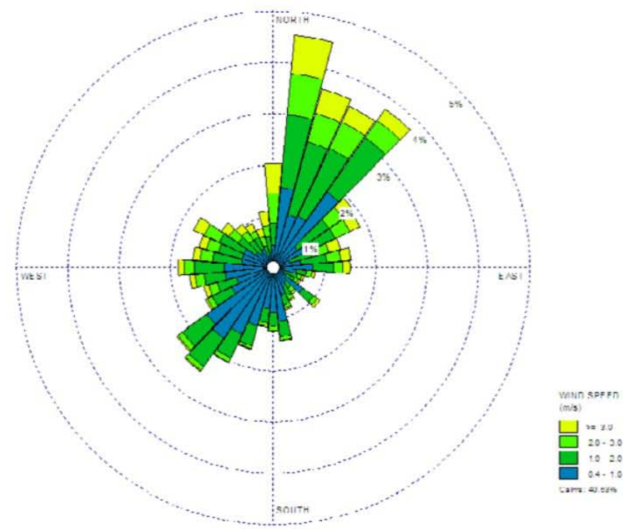
B: Vehicle Exhaust (isolated event)



C: Biogenic Source (isolated event)

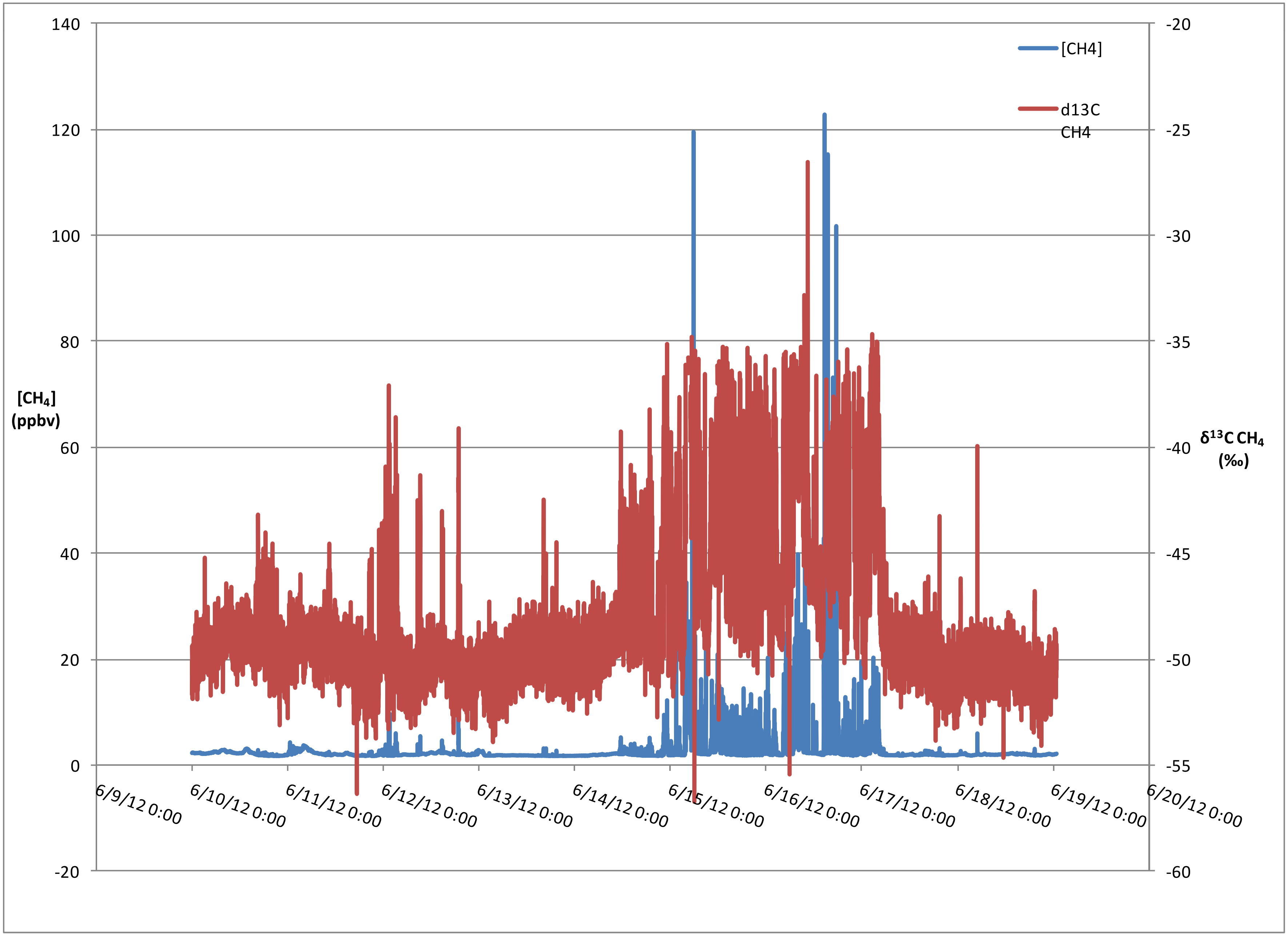


All Data, 26 days



Presenter's notes: Well is more NE of well pad than SE (location of thermogenic source?). N points to pad, SW, points to woods and not pasture.

Frac of Remaining 3 Wells (early June): Greater Production



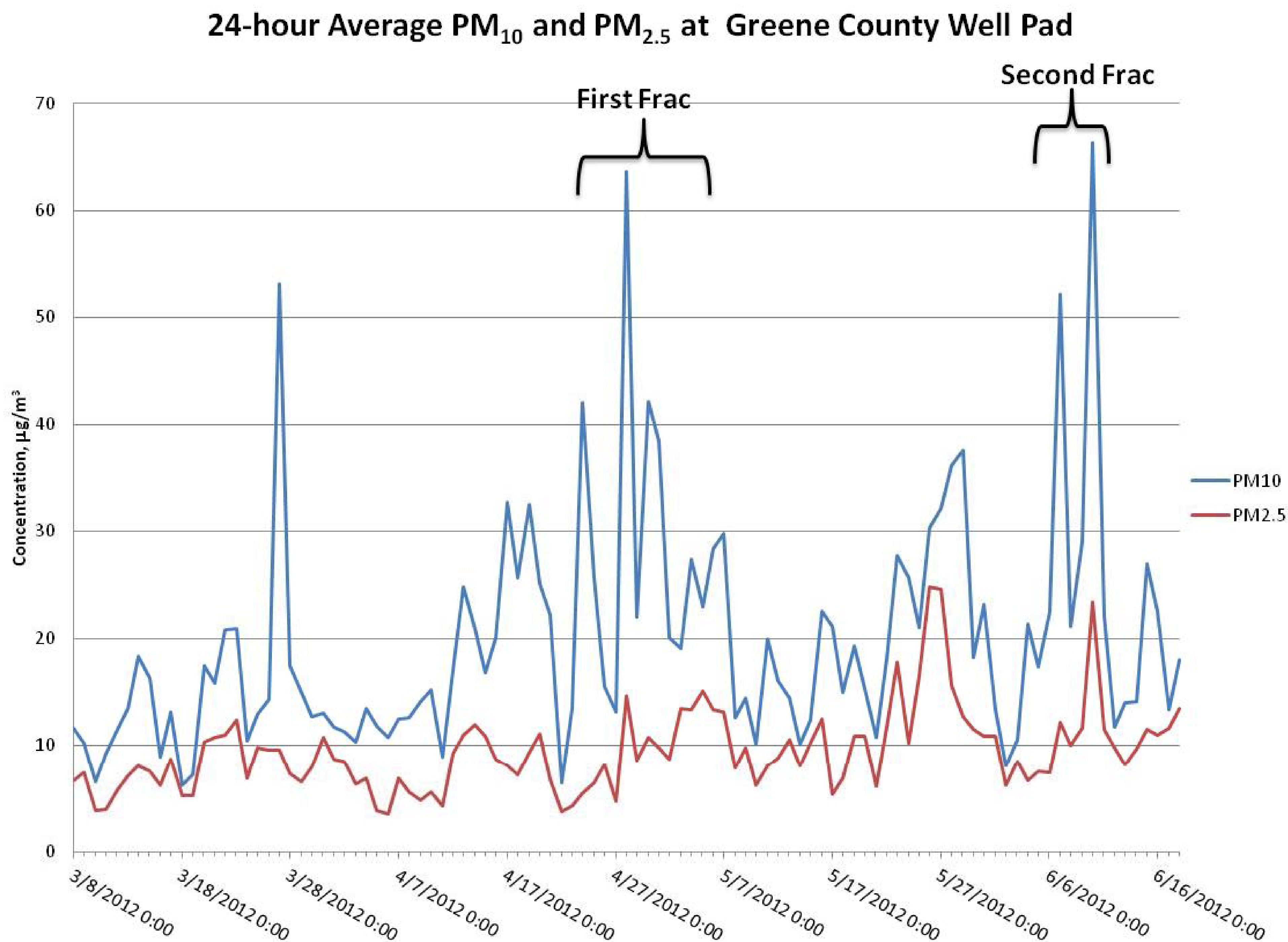
Volatile Organic Compounds (VOCs)

Acetylene
n-Butane
1-Butene
cis-2-Butene
trans-2-Butene
Cyclopentane
2,2-Dimethylbutane
2,3-Dimethylbutane
Ethane
Ethylene
1-Hexene
Isobutane
Isopentane
Isoprene
n-Pentane
1-Pentene
2-Methylpentane
3-Methylpentane
cis-2-Pentene
trans-2-Pentene
Propane
Propylene
Benzene
Cyclohexane
n-Decane
m-Diethylbenzene
p-Diethylbenzene
2,3-Dimethylpentane
2,4-Dimethylpentane
n-Dodecane
Ethyl Benzene
o-Ethyltoluene
m-Ethyltoluene
p-Ethyltoluene
n-Heptane
n-Hexane
Isopropylbenzene
n-Octane
Methylcyclohexane
Methylcyclopentane
2-Methylheptane
3-Methylheptane
2-Methylhexane
3-Methylhexane
n-Nonane
n-Propylbenzene
Styrene
Toluene
1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
2,2,4-Trimethylpentane
2,3,4-Trimethylpentane
n-Undecane
o-Xylene
m/p-Xylene (combined)

Greene County Well Pad Average VOCs

Compound*	Background (ppb)	Frac of first 3 wells (ppb)	Frac of remaining 3 wells (ppb)
Hexane	0.3	0.6	0.4
Benzene	0.3	0.4	0.2
Toluene	0.7	1.3	2.3
Ethane	24.1	34.6	34.0
Propane**	11.2	42.1	110.8
Isobutane	2.9	3.1	3.0
n-Butane	4.6	4.8	4.1
Isopentane	2.2	3.4	3.2
n-Pentane	1.8	2.2	1.8

**Compounds detected in at least 25% of the samples*
***On-site food station near the mobile air monitoring laboratory used propane for cooking*



24-hour Average PM10 and PM2.5 at Greene County Well Pad
First Frac
Second Frac
Concentration, µg/m3
0
10
20
30
40
50
60
70
3/8/2012 0:00
3/18/2012 0:00
3/28/2012 0:00
4/7/2012 0:00
4/17/2012 0:00
4/27/2012 0:00
5/7/2012 0:00
5/17/2012 0:00
5/27/2012 0:00
6/6/2012 0:00
6/16/2012 0:00
PM10
PM2.5

Greene County Well Pad PM_{10} and $PM_{2.5}$ Results

PM_{10} 24-hour standard is 150 μg/m^3

$PM_{2.5}$ annual average standard is 15 μg/m^3, 24-hour standard is 35 μg/m^3

<u>Greene County Well Pad</u>:

24-hour average PM_{10} range of 6-66 μg/m^3

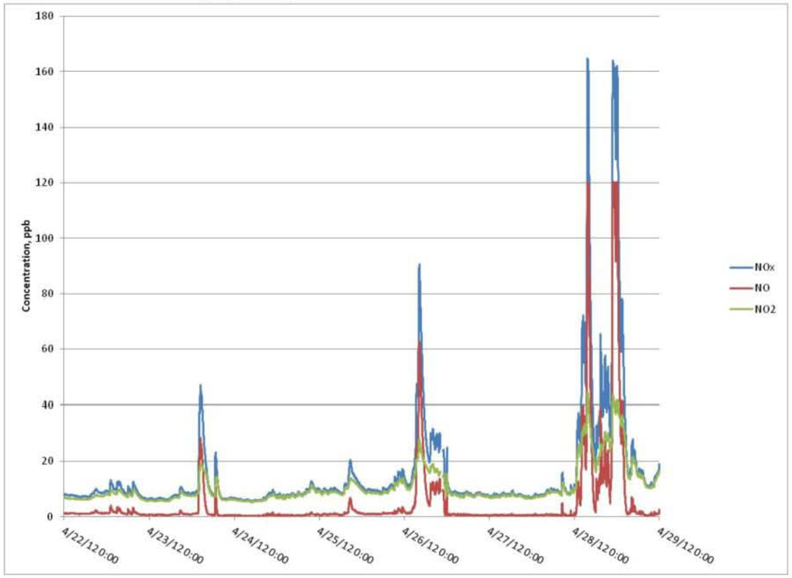
Maximum 1-hour average: 504 μg/m^3 (Not during frac)

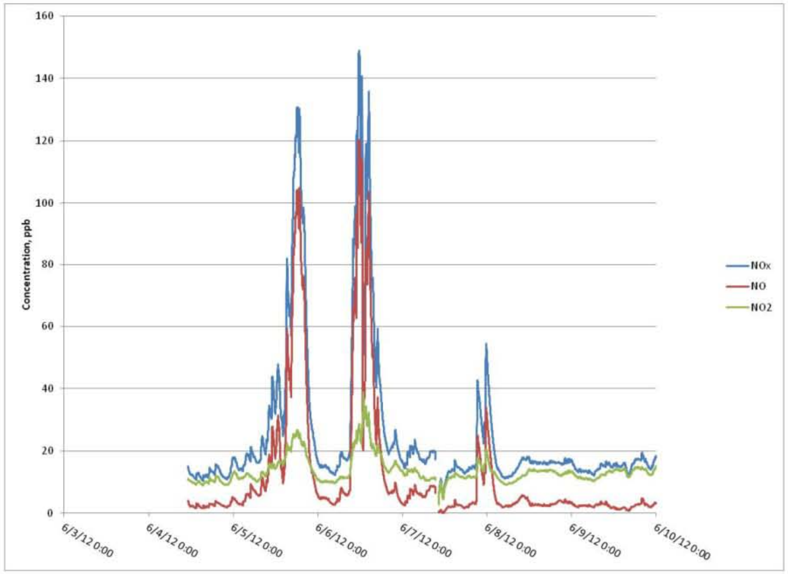
24-hour average $PM_{2.5}$ range of 4-25 μg/m^3

Maximum 1-hour average: 55 μg/m^3

NO_x Results

- NO_2 has an annual average standard of **53ppb,** 1-hour standard of **100ppb**
- Pre- and post-frac: overall average at Greene County well pad: **5-15ppb,** with peaks not exceeding **60ppb**
- During frac: short-term peaks significantly greater (**140-160ppb**)





Presenter's notes: NO2 short term exposure: adverse respiratory effects (inflammation, asthma). NOx reacts with ammonia to create particles, with VOCs to create ozone.

Summary and Conclusions

- **Methane: Peaks in concentration can be identified as thermogenic by evaluating corresponding $\delta^{13}C_{CH4}$**
- **Methane concentrations highest during flowback**
- **VOCs: Only modest concentration increase during frac as compared to "background"**
- **PM, NO_x: Highest concentrations during frac**

Future Work:

- **Analysis of data with wind direction**
  - Source "fingerprints"
  - Background vs. emissions from well pad
- **Calculate mass of methane emitted per well completion for comparison with emission factor currently used in emission inventories/LCA**

Manuscript draft anticipated July 2013