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

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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

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*
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

<table>
<thead>
<tr>
<th>Ambient</th>
<th>Point-Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values integrated over an area</td>
<td>Values for a specific location and/or operation</td>
</tr>
<tr>
<td>Plume interception dependent on local meteorology</td>
<td>Determination of background concentrations not necessary</td>
</tr>
<tr>
<td>Continuous measurements capture variations in operator/equipment activity</td>
<td>Provides a &quot;snapshot&quot; or short-term measurement</td>
</tr>
</tbody>
</table>
NETL’s Mobile Air Monitoring Laboratory

Collected Measurements
Spring and Summer 2012
(~14 weeks)

Greene County,
Pennsylvania
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, **NOₓ**, SO₂ (Teledyne-API Gas Analyzers)
  - **Methane and Carbon Isotopes in Methane** (Picarro CR-DS)
  - CO₂ and Carbon Isotopes in CO₂ (Picarro CR-DS)
  - **PM₁₀ and PM₂.5** (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 (CH₄)
  – CH₄ 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 = \{($R_{\text{sample}} / R_{\text{standard}}$) -1\} *1000 ‰

• $R = \frac{^{13}\text{C}}{^{12}\text{C}}$

• $\delta^{13}$C$_{\text{CH}_4}$:
  – Atmospheric ~-50‰
  – Biogenic -50 to -80‰
  – Thermogenic -25 to -40‰
Methane and $\delta^{13}C_{CH4}$

- **Prior to first frac:**
  - Ambient Concentrations ranged 2-5ppm
  - No evidence of thermogenic methane; $\delta^{13}C_{CH4} \sim -45\%$
    - One exception: peak of 15ppm with $\delta^{13}C_{CH4} \sim -38\%$ (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
Between two frac events (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

![Graph showing [CH₄] (ppbv) and δ¹³C CH₄ (%) over time from June 9 to June 20.]
## Volatile Organic Compounds (VOCs)

<table>
<thead>
<tr>
<th>Acetylene</th>
<th>trans-2-Pentene</th>
<th>Methylocyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>n-Butane</strong></td>
<td><strong>Propane</strong></td>
<td><strong>Methylcyclopentane</strong></td>
</tr>
<tr>
<td>1-Butene</td>
<td><strong>Propylene</strong></td>
<td>2-Methylheptane</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td><strong>Benzene</strong></td>
<td>3-Methylheptane</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>Cyclohexane</td>
<td>2-Methylhexane</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>n-Decane</td>
<td>3-Methylhexane</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>m-Diethylbenzene</td>
<td>n-Nonane</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>p-Diethylbenzene</td>
<td>n-Propylbenzene</td>
</tr>
<tr>
<td><strong>Ethane</strong></td>
<td>2,3-Dimethylpentane</td>
<td>Styrene</td>
</tr>
<tr>
<td>Ethylene</td>
<td>2,4-Dimethylpentane</td>
<td><strong>Toluene</strong></td>
</tr>
<tr>
<td>1-Hexene</td>
<td>n-Dodecane</td>
<td>1,2,3-Trimethylbenzene</td>
</tr>
<tr>
<td><strong>Isobutane</strong></td>
<td>Ethyl Benzene</td>
<td>1,2,4-Trimethylbenzene</td>
</tr>
<tr>
<td><strong>Isopentane</strong></td>
<td>o-Ethyltoluene</td>
<td>1,3,5-Trimethylbenzene</td>
</tr>
<tr>
<td>Isoprene</td>
<td>m-Ethyltoluene</td>
<td>2,2,4-Trimethylpentane</td>
</tr>
<tr>
<td><strong>n-Pentane</strong></td>
<td>p-Ethyltoluene</td>
<td>2,3,4-Trimethylpentane</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>n-Heptane</td>
<td>n-Undecane</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td><strong>n-Hexane</strong></td>
<td>o-Xylene</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>Isopropylbenzene</td>
<td>m/p-Xylene (combined)</td>
</tr>
<tr>
<td>cis-2-Pentene</td>
<td>n-Octane</td>
<td></td>
</tr>
</tbody>
</table>
# Greene County Well Pad Average VOCs

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

*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 PM$\textsubscript{10}$ and PM$\textsubscript{2.5}$ at Greene County Well Pad

First Frac

Second Frac

Concentration, µg/m$^3$

PM$\textsubscript{10}$

PM$\textsubscript{2.5}$
Greene County Well Pad PM$_{10}$ and PM$_{2.5}$ Results

PM$_{10}$ 24-hour standard is 150µg/m$^3$
PM$_{2.5}$ annual average standard is 15µg/m$^3$, 24-hour standard is 35µg/m$^3$

Greene County Well Pad:
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\textsubscript{x} Results**

- \( \text{NO}_2 \) 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: NO\textsubscript{2} short term exposure: adverse respiratory effects (inflammation, asthma). NO\textsubscript{x} 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