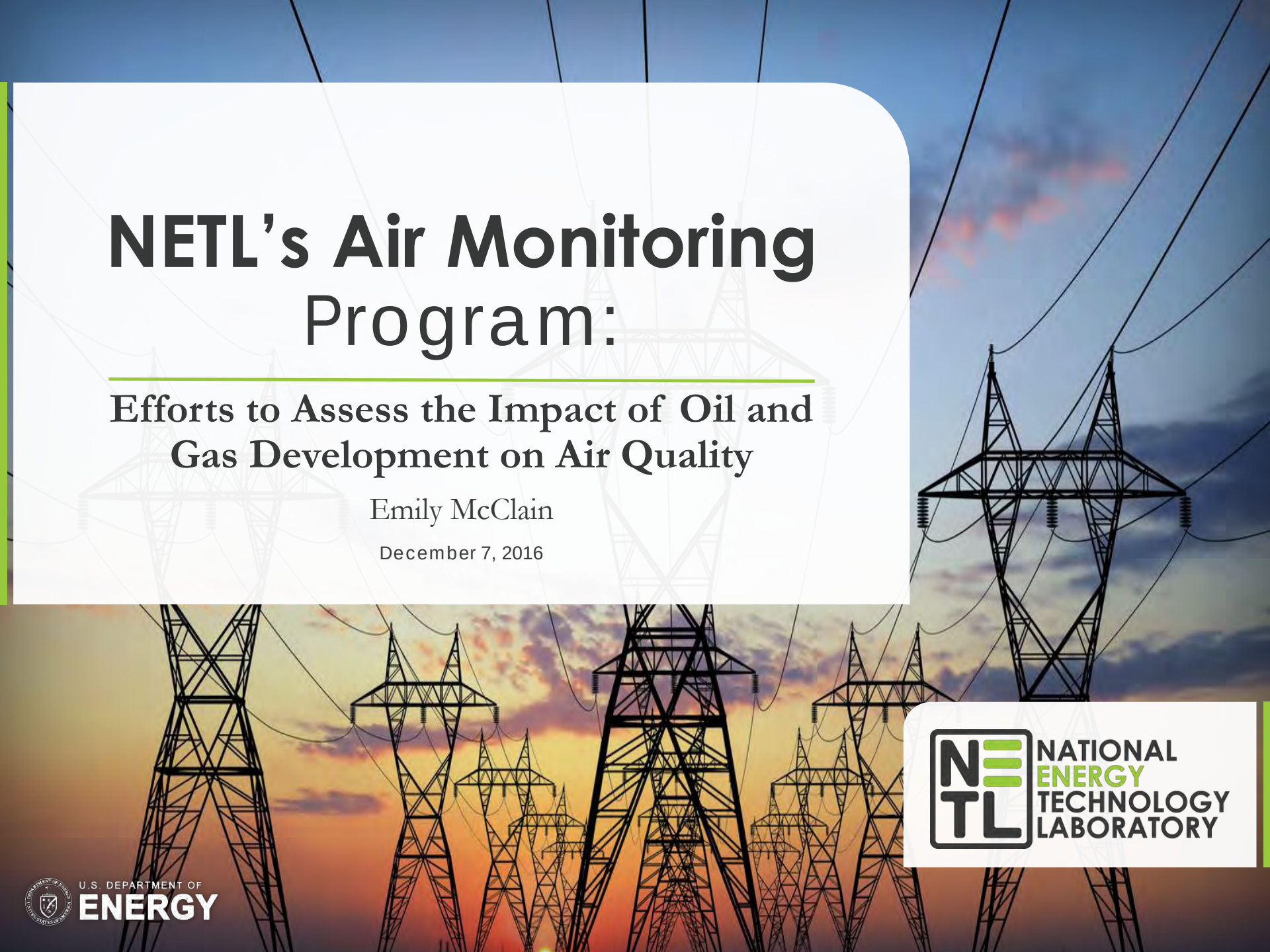
NETL's Air Monitoring Program:

Efforts to Assess the Impact of Oil and Gas Development on Air Quality

Emily McClain

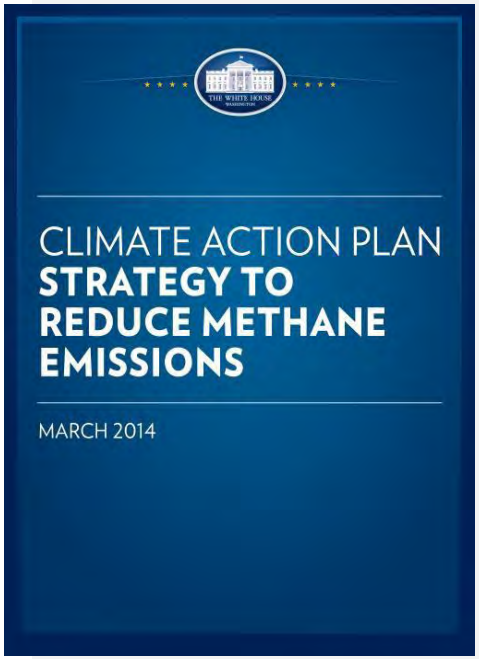
December 7, 2016



U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL's Natural Gas Midstream Research Mission



President **Obama's** Climate Action Plan

"Curbing emissions of methane is critical to our overall effort to address global climate change. … To achieve additional progress, the Administration will":

- Develop a comprehensive Interagency Methane Strategy (completed March 2014)
- Pursue a collaborative approach with state governments and the private sector and cover all methane emitting sectors
- Reduce CH_4 emissions from oil & gas sector 40-45% below 2012 levels by 2025

Interagency Methane Strategy – Three Pillars

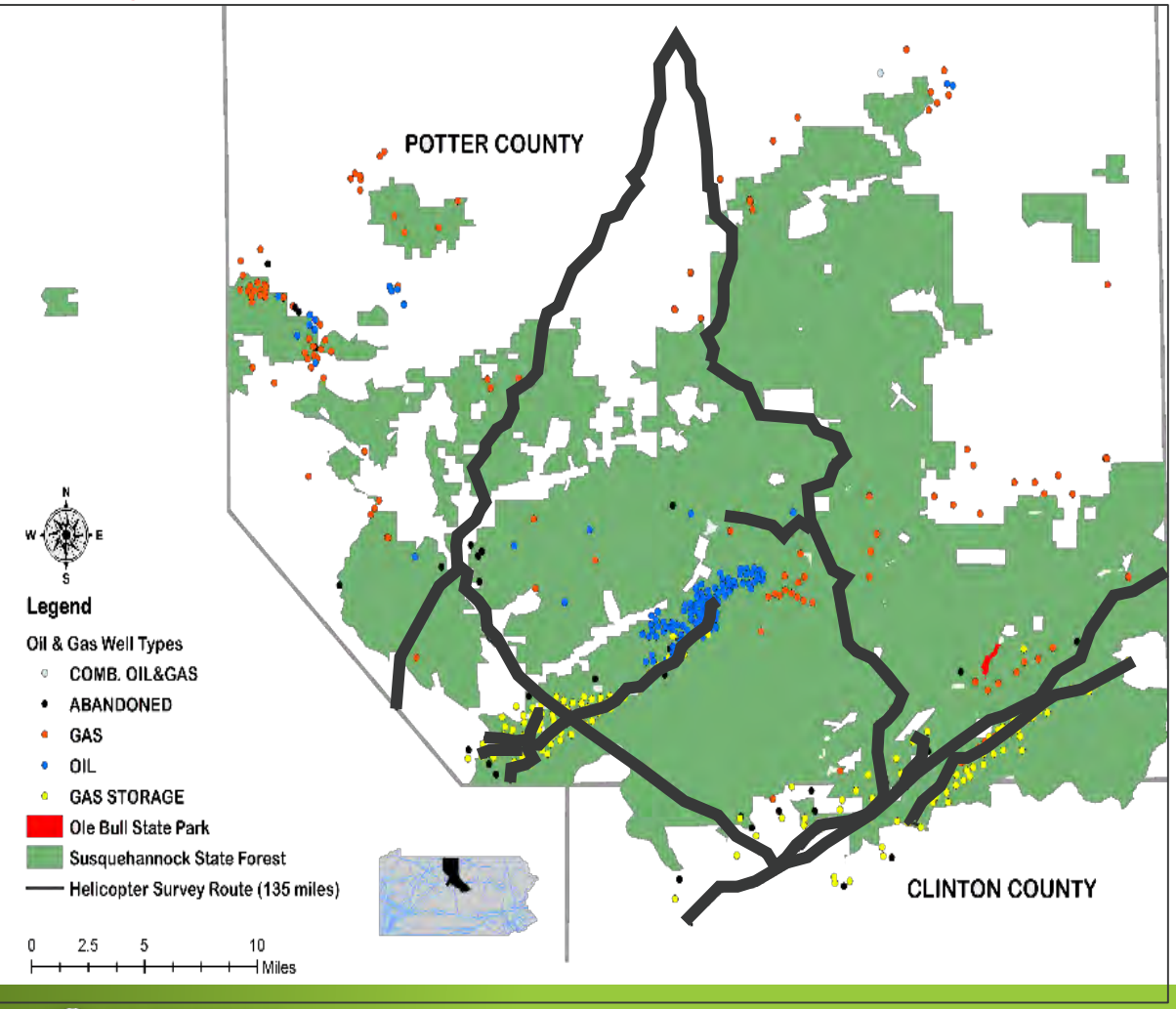
Assessing current emissions data and addressing data gaps	Identifying Technologies and Best Practices for Reducing Emissions	Identifying Existing Authorities and Incentive-based Opportunities for Reducing Emissions

NETL's Methane Emissions Quantification Program

- **OBJECTIVE**
  - By 2020: Emission quantification of natural gas infrastructure sufficient to update the EPA Greenhouse Gas Inventory (GHGI)
- **APPROACH**
  - Obtain a more detailed and comprehensive data set for selected components/facilities of the nation's natural gas midstream infrastructure.
  - Initial field efforts will concentrate on characterizing:
    1. Gathering system pipelines
    2. Abandoned and orphaned gas wells
    3. Legacy gas pipelines
- **NETL'S PARTNERS & THEIR ROLES**
  - Industry & Universities: R&D and field validation partners
  - National Labs: Partners in fundamental science R&D
  - NGOs: Independent quantification efforts funded with universities (e.g., EDF)
  - EPA: Identify GHGI needs and collaboration in field campaigns

1.) Susquehannock State Forest Field Campaign

Study Overview



AERIAL SURVEY

PHASE 1

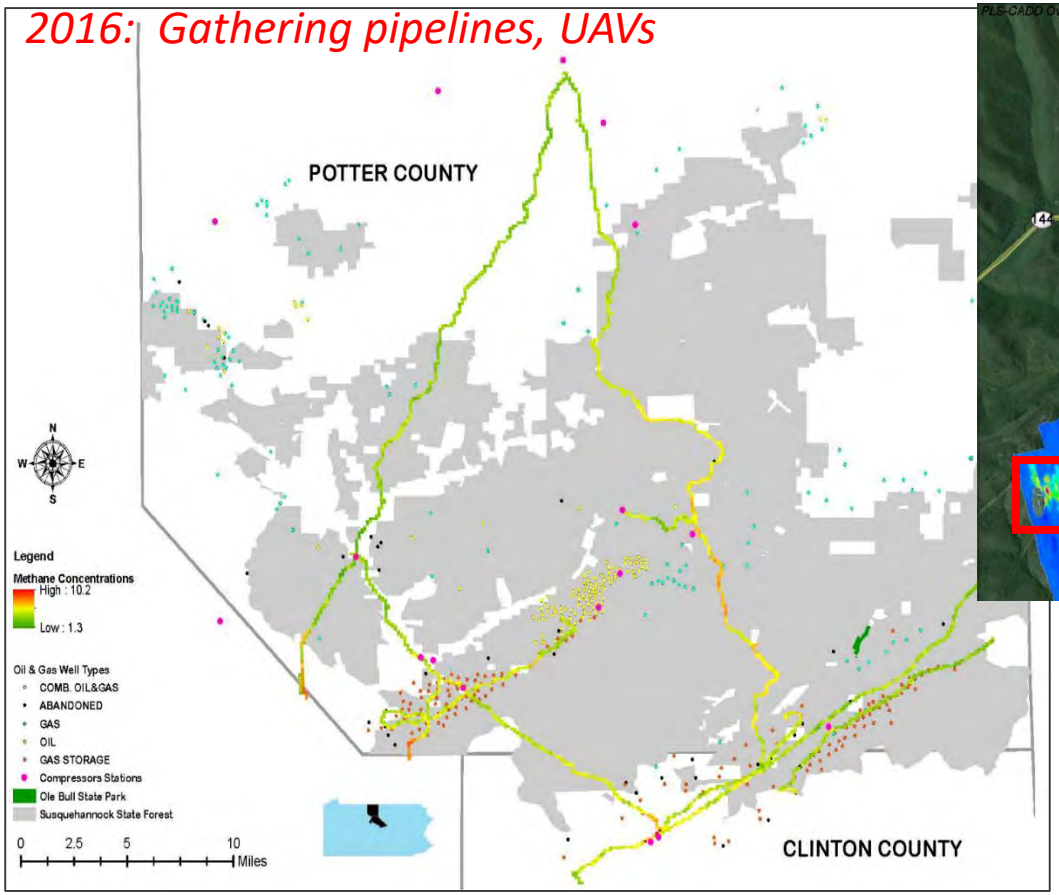
- Helicopter Based
- Downwind from pipeline right-of-way (ROW)
- 50m elevation, 50 mph
- 138 miles, single pass

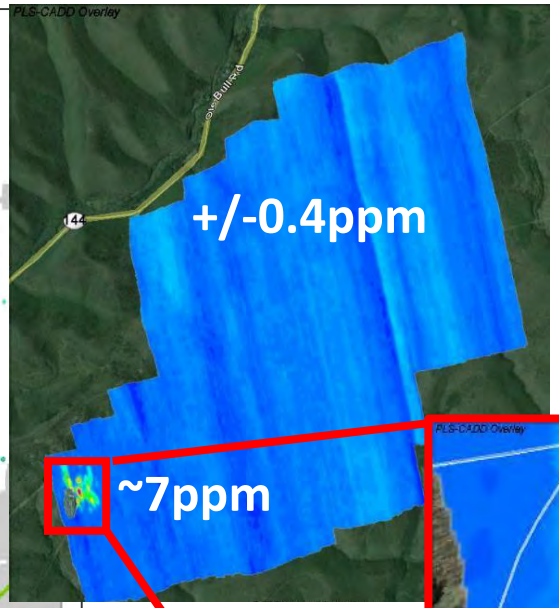
GROUND SURVEY

PHASE 2

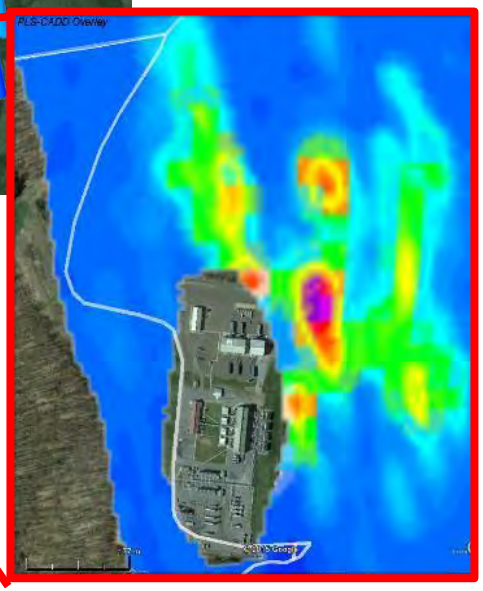
- Utility Terrain Vehicle (UTV) Based
- Along pipeline right-of-way (ROW)
- Survey speed of less than 5 mph
- Less than 138 miles to be surveyed due to terrain

Susquehannock State Forest Aerial Survey Results





Aerial Detection of Methane from a Compressor Station:



Equipment:

Picarro Methane Analyzer: ~3ppb detection limit, 2.5 second response time

Boreal GasFinder: ~0.5 ppm, 0.25 second

1) Susquehannock State Forest Ground-based Survey

Equipment	Function
Boreal Laser	Methane Analyzer
Anemometer	Meteorology
GPS	Location
Multiplexer	Data Coding
FLIR	Methane Imaging
PMD	Methane detector
VMD	Optical Methane Detector
SPAR300	Utility Locator

Susquehannock State Forest Ground-based Survey

Leak rate quantified: Blow-down valve

Susquehannock State Forest: Lessons Learned

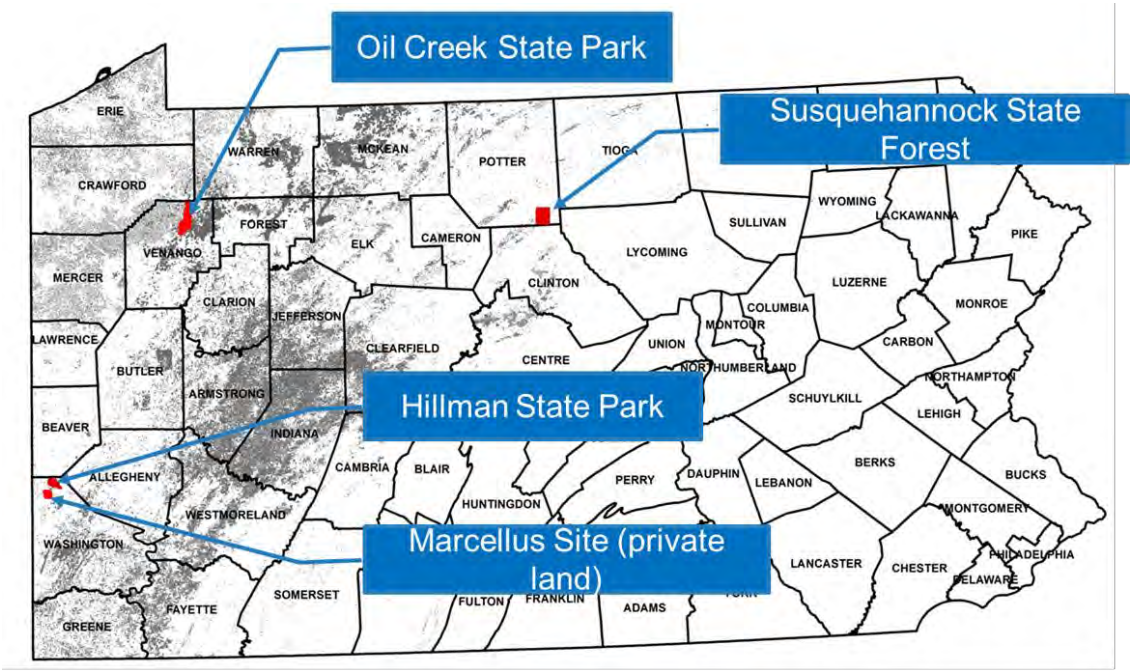
- **Proximal methane sources**
  - Includes natural sources (e.g. geological seepage)
- **Variables**
  - Leak Rate: require highly sensitive detectors
  - Wind speed and direction
  - Sensor Altitude -Low-level leaks not detected at high altitudes
  - Sample rate –high sampling rate required
  - Air pressure? Humidity?
  - Locating Pipeline and Rights-of-Ways

- **Looking forward: UAV-based surveys**
  - Line-of-sight requirement
  - Payload and sensitivity of detectors
  - Rapid growth of technology

2.) Legacy Well Methane Emissions

Study Overview

- Emission rate from abandoned wells uncertain; could contribute to "top-down" vs. "bottom-up" discrepancy
- Estimated 3-4 million abandoned wells in the US
- Possible high emitters could contribute to majority of emissions
- Not included in GHGI



NETL's Multifaceted Approach

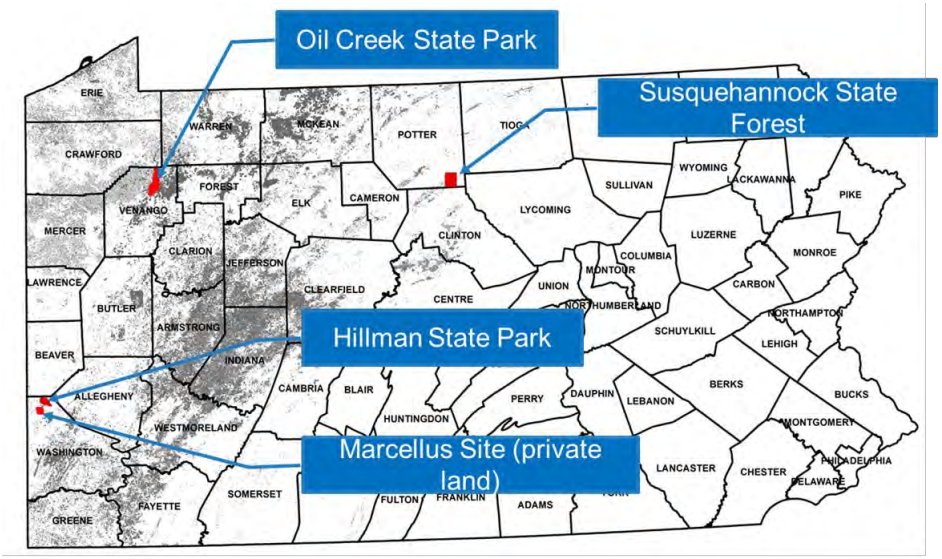
- NETL is making efforts to locate abandoned wells using airborne surveys and LiDAR New well locations will be added to PA state database
- Provides a more complete catalog inventory of abandoned wells
- Allows for monitoring of wells with varying attributes (exposed vs. buried)

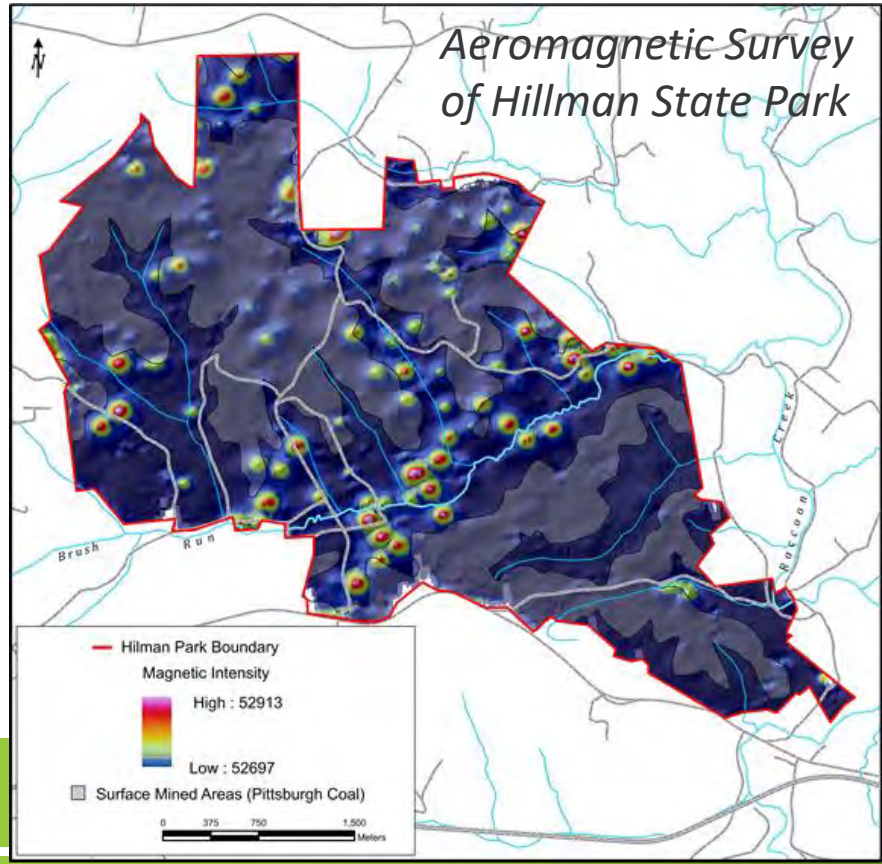
Locating Abandoned Wells

Measuring Air Emissions at Oil and Gas Operations

Locating Legacy Wells in Pennsylvania

Flight Area	Spud Dates	Recorded Wells	Found Wells
Marcellus Site	1900-1925	6	17
Hillman State Park	1880-1900	33	100 +
Susquehannock State Forest	Post-1950	38	39
Oil Creek State Park	1859-1990	323	767+





Legacy Well Methane Emissions

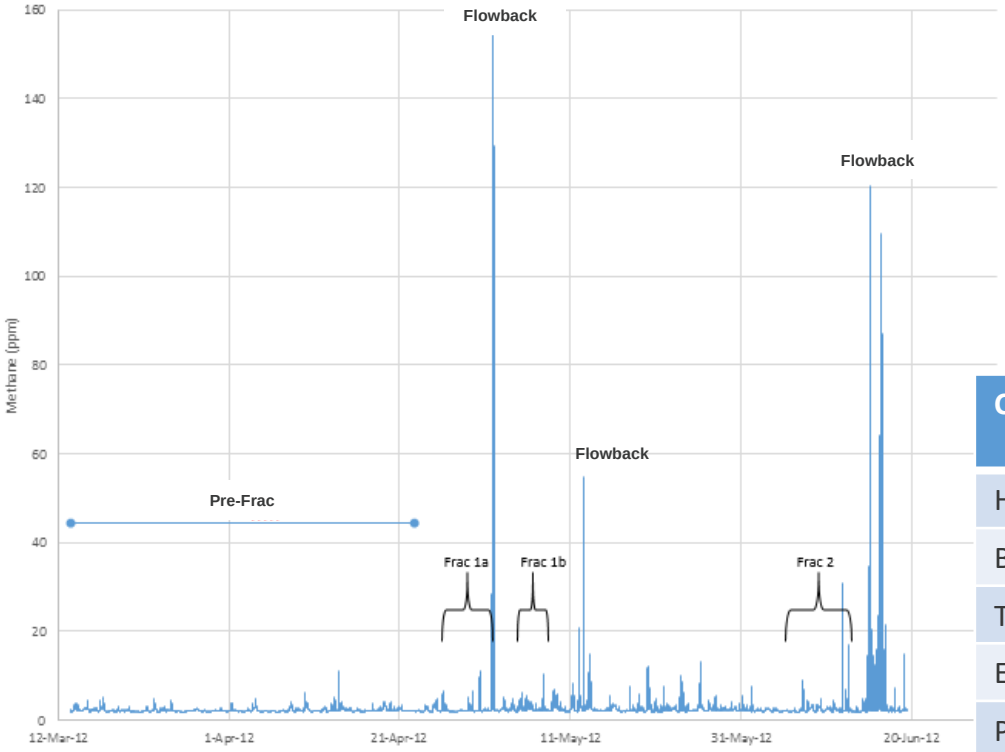
- **Methods development**
  - HiFlow sampler, flux chamber, field FID, bag sampling, infrared camera
  - Infrared camera provided qualitative information about where the leak points were located
- **Measured emission rate/flux from 31 wells in Hillman State Park**
  - Mean methane emission rate for wellheads 0.70 kg/well/day
  - Buried wells emission rate statistically not different from background

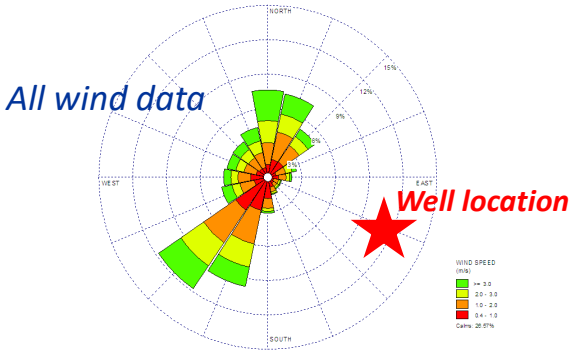
3.) Ambient Air Monitoring On a Marcellus Shale Well Pad in Greene County, PA

- VOCs
- NO_x, ozone
- CH_4 + $d^{13}C_{CH4}$
- CO_2 + $d^{13}C_{CO2}$
- PM_{10}, $PM_{2.5}$
- Meteorological Data

- Unattended, remote operation via satellite link
- Close proximity to source –on pad
- Use data in plume dispersion models to determine emission rate

Greene County Well Pad Methane Concentrations





Lakes Environmental WRPLOT

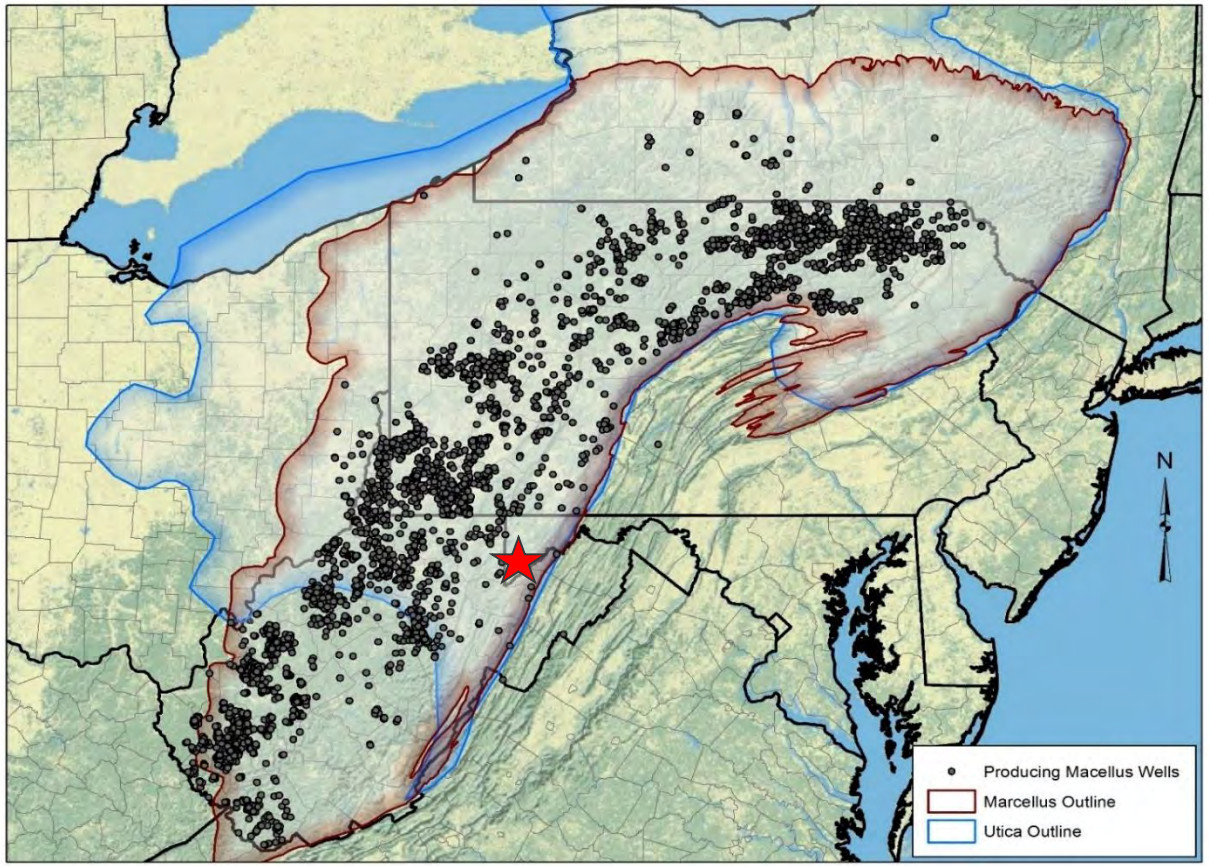
Compound*	Background (ppb)	First Frac Event (ppb)	Second Frac Event (ppb)
Hexane	0.3	0.6	0.4
Benzene	0.3	0.4	0.2
Toluene	0.7	1.3	2.3
Ethane	24.1	34.6	34.0
Propane	11.2	42.1	110.8
Isobutane	2.9	3.1	3.0
n-Butane	4.6	4.8	4.1
Isopentane	2.2	3.4	3.2
n-Pentane	1.8	2.2	1.8

*Compounds detected in at least 25% of the samples

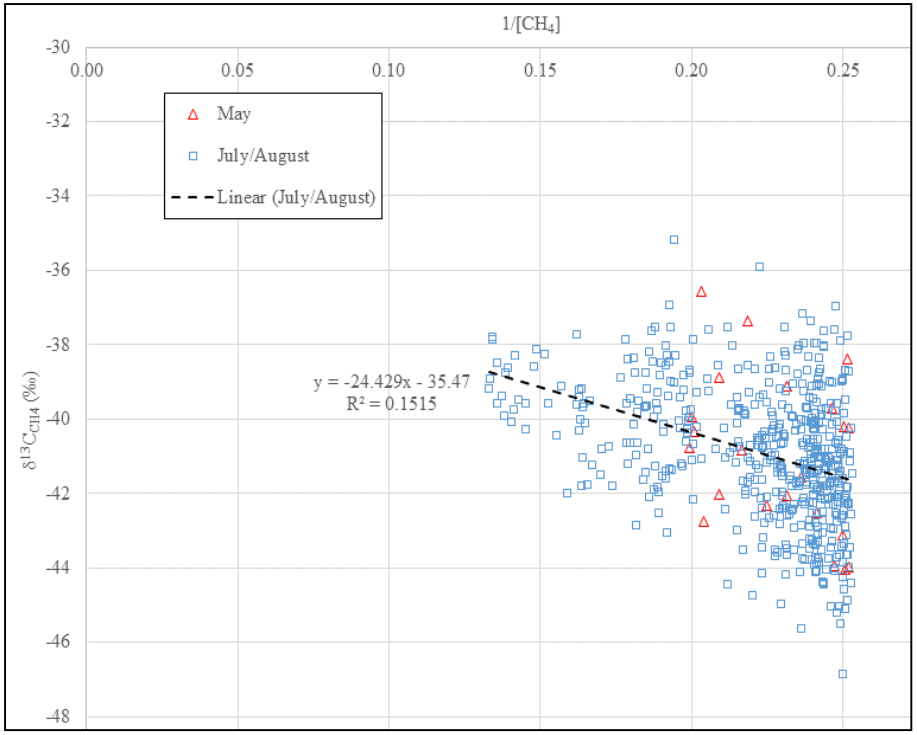
- Observed slight increase in all compounds over background, but low concentrations overall

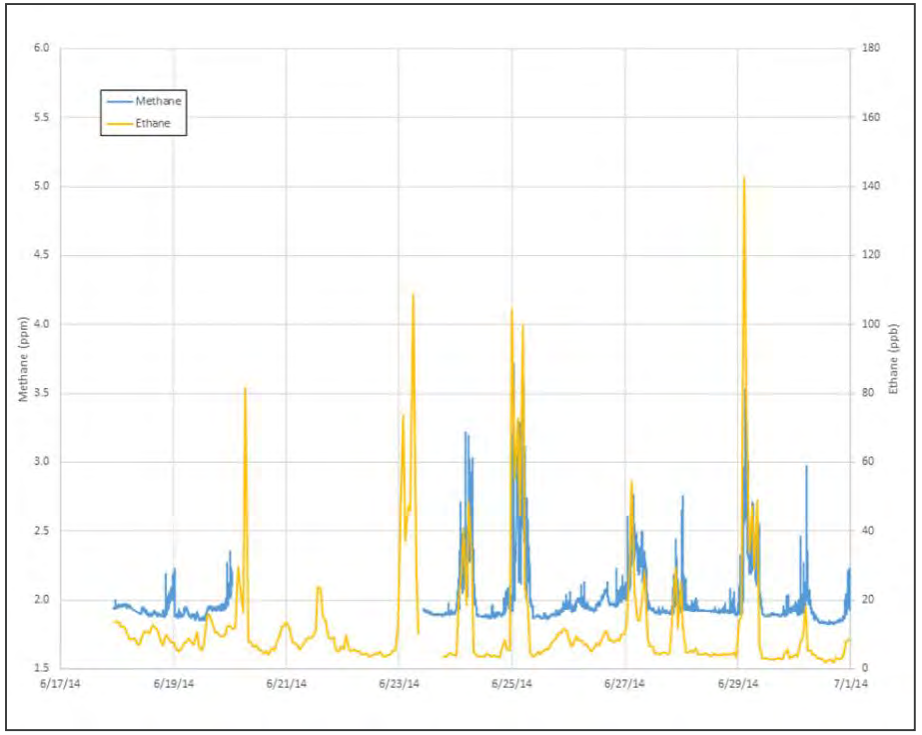
Status of Unconventional Oil and Gas Drilling in Maryland

- 2011: Maryland enacted moratorium on horizontal drilling and hydraulic fracturing citing concerns about human health and environmental impacts
- Agreement with Maryland Dept. of the Environment (MDE)
- Data collection in Oakland in Garrett County during two monitoring periods: May – August 2014 (spring/summer) and November 2014 through February 2015 (fall/winter)



Oakland, MD Data: Methane, Spring/Summer





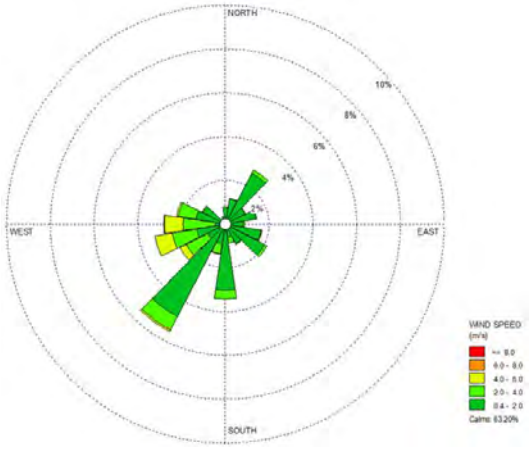
- When methane concentrations were elevated, corresponding isotopic signature indicated a thermogenic (geologic) origin
- Covariance of methane, ethane, and other alkanes suggests emission from a common natural gas source

	May		June		July/August	
	[CH_4]	**$\delta^{13}C$**	**[CH_4]**	**$\delta^{13}C$**	**[CH_4]**	**$\delta^{13}C$**
Average	2.0	-48.0	2.0	-47.8	2.0	-47.9
Std dev	0.2	3.8	0.2	3.7	0.2	3.5
Min	1.8	-66.2	1.8	-63.9	1.8	-65.8
Max	5.0	-30.2	3.7	-29.1	7.5	-31.1

*Results for the fall/winter monitoring period were very similar to the spring/summer period

Oakland, MD Data: Volatile Organic Compounds (VOCs)

Compound	Spring/ Summer Average	Spring/ Summer % Detection	Fall/Winter Average	Fall/Winter % Detection
Ethane	12	100	22	100
Propane	4	100	12	100
n-Butane	1	62	5	100
iso-Butane	0.4	24	3	99
n-Pentane	.5	33	2	92
iso-Pentane	.9	44	2	96



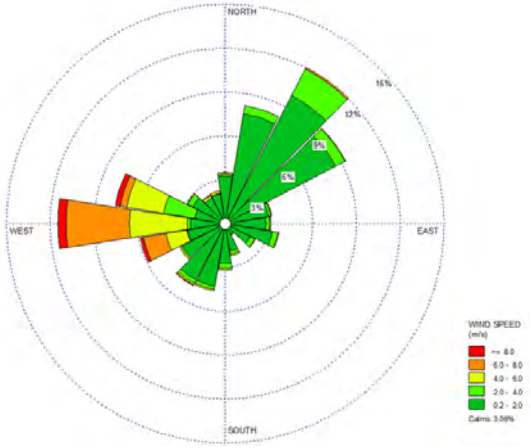
Wind rose for ethane concentrations >20 ppb during summer monitoring

Typical Natural Gas Composition (%):

Methane	Ethane	Propane	iso-Butane	n-Butane	iso-Pentane	n-Pentane
95.0	3.2	0.2	0.03	0.03	0.01	0.01

*From www.uniongas.com

- Combining the ethane concentration data with available wind direction data yielded potential source areas from the SW, S, and NE
- Second phase of ambient air monitoring at same location should moratorium be lifted



Wind rose for ethane concentrations >50 ppb during winter monitoring

Marcellus Shale Energy Environmental Laboratory (MSEEL)

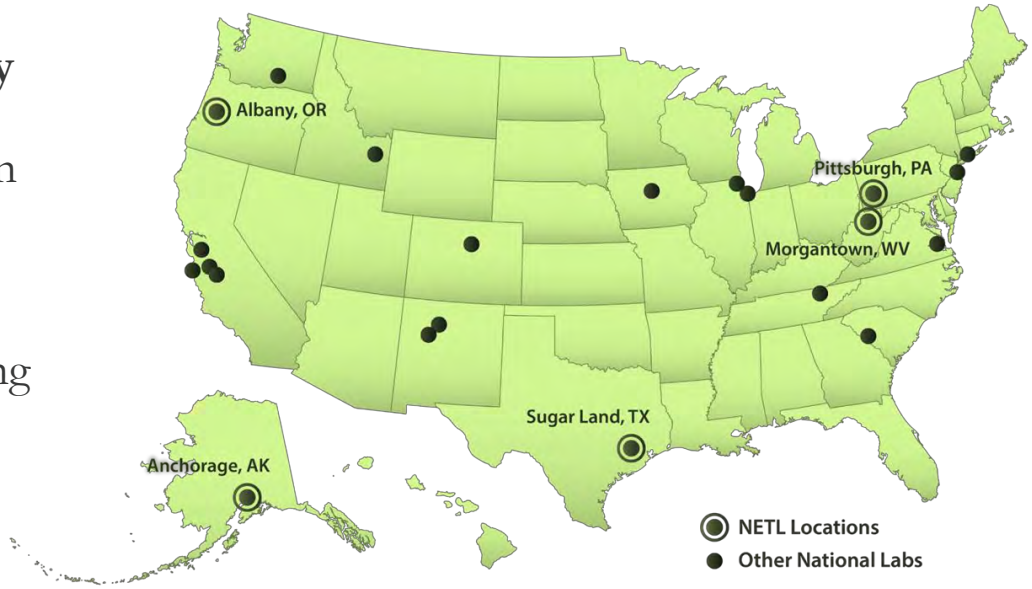
- **Air monitoring September 15, 2016 – January 31, 2016**
  - NETL's Mobile air monitoring laboratory
  - Passive sampling for N-containing compounds (Collaboration with Pitt)
  - WVU trace elements and PM sampling
- **Drilling, HF, flowback, production phases**
- **Preliminary results:**
  - NO_x and ozone followed typical diurnal patterns, no obvious correlation with activities occurring on the well pad
  - Methane concentrations elevated during HF, highest during flowback
  - Isotopic signature of methane shows thermogenic source during peak events

Thank you

NATIONAL ENERGY TECHNOLOGY LABORATORY

National Energy Technology Laboratory

- **Full-service DOE federal laboratory**
  - Program planning
  - Budget formulation and execution
  - Procurement
  - Project management
  - Legal
  - Financial management & reporting
  - Onsite research
  - Program performance & benefit analysis



- **Dedicated to energy R&D, domestic energy resources**
  - Fossil Energy
  - Support Offices of Electricity and Energy Efficiency

- **Fundamental science through technology demonstration**

- **Unique industry–academia–government collaborations**

NETL's Assessment of Shale Gas Development's Air Quality Impacts

Problem:

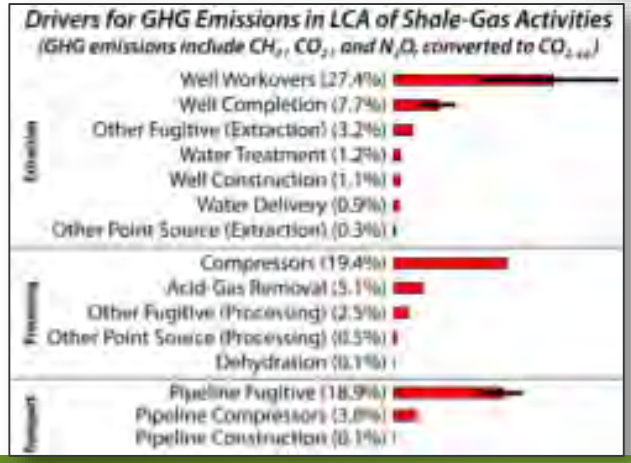
- Uncertain/inaccurate values for emission factors associated with large contributors to life-cycle emissions

Objectives:

- To collect field data of representative ambient and point source air emissions

Emissions of methane, volatile organic compounds, particulate matter, reactive nitrogen, carbon dioxide

NETL's Mobile Air Monitoring Laboratory



NETL's Use of Multiple Measurement Approaches:

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 Methane Emissions Quantification Program:

Gathering Pipelines Leak Rate Estimation

- **IMPORTANCE**
  - Current emission factor for natural gas pipelines is not discretized for type of pipeline (gathering, transmission, distribution), pipeline material, age, pressure
  - These distinctions likely contribute to significantly different leakage rates and therefore national estimates may be inaccurate
- **SCOPE**
  - Conduct surveys of natural gas gathering pipelines to estimate methane leakage rate; collect information about pipeline material, age, pressure, etc. that will allow more refined emissions characterization
  - Methods development
- **EXPECTED ACCOMPLISHMENTS**
  - 2017: Emission factor for natural gas gathering system in north-central PA
  - Beyond (2020): Continued surveys in other areas; investigate feasibility of UAV-based surveys; provide recommendation for gathering pipeline emission factor

NETL Facilities/Capabilities

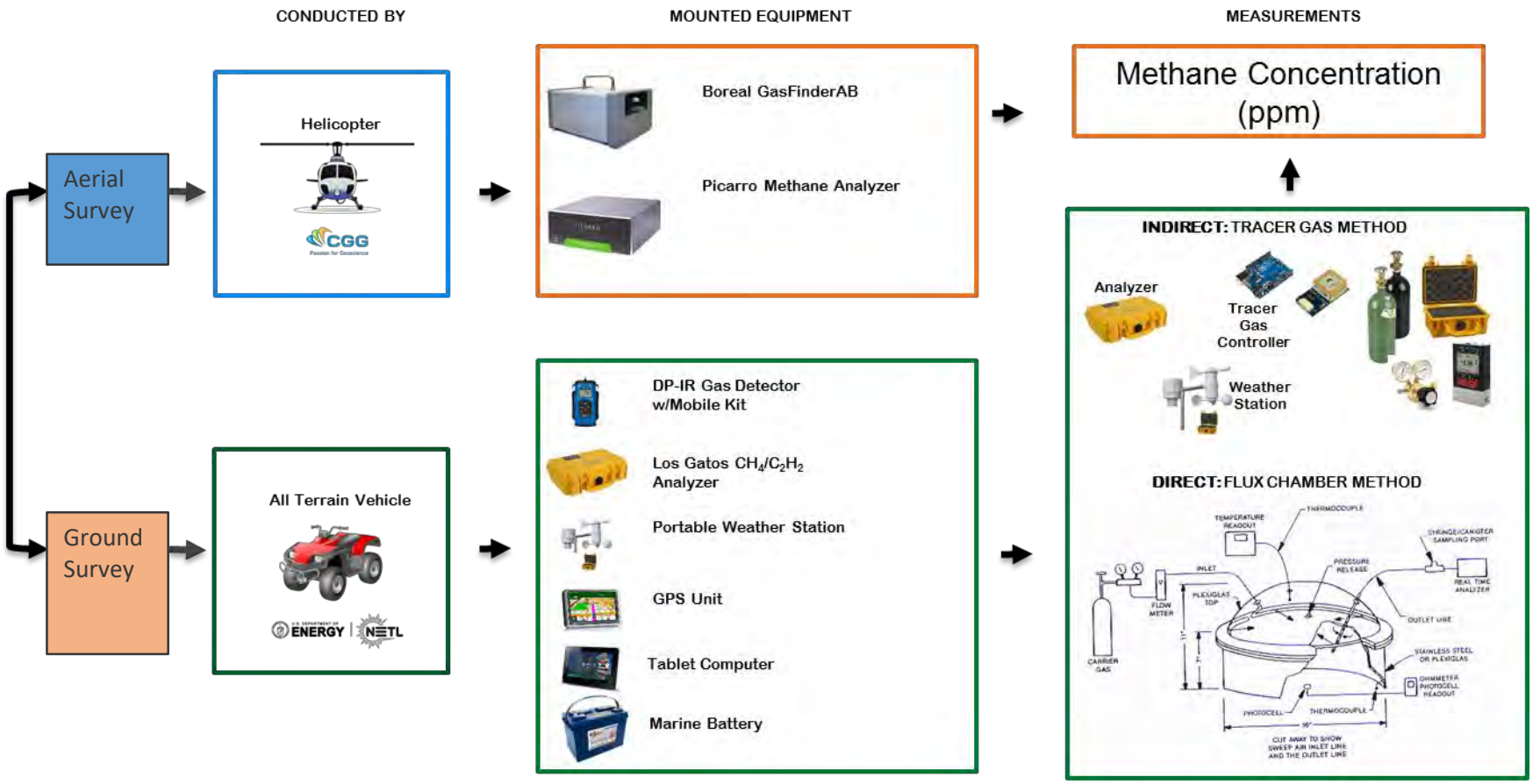
NETL's Mobile Air Monitoring Laboratory

VOCs, NO_x, ozone, CH_4 + $\delta^{13}C_{CH4}$, CO_2 + $\delta^{13}C_{CO2}$, PM_{10}, $PM_{2.5}$, Meteorological Data

Unattended, remote operation via satellite link

- Source Emissions Measurements: Hi-Flow Sampler, Dynamic Flux Chamber
- Tracer Release for Indirect Methane Emissions Measurements

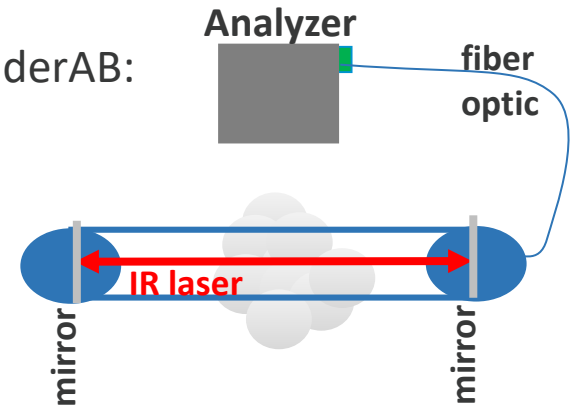
- **Pipeline Study Design**



Susquehannock State Forest: Aerial Survey Instrumentation

Picarro G2203 Methane Analyzer:

Boreal GasFinderAB:

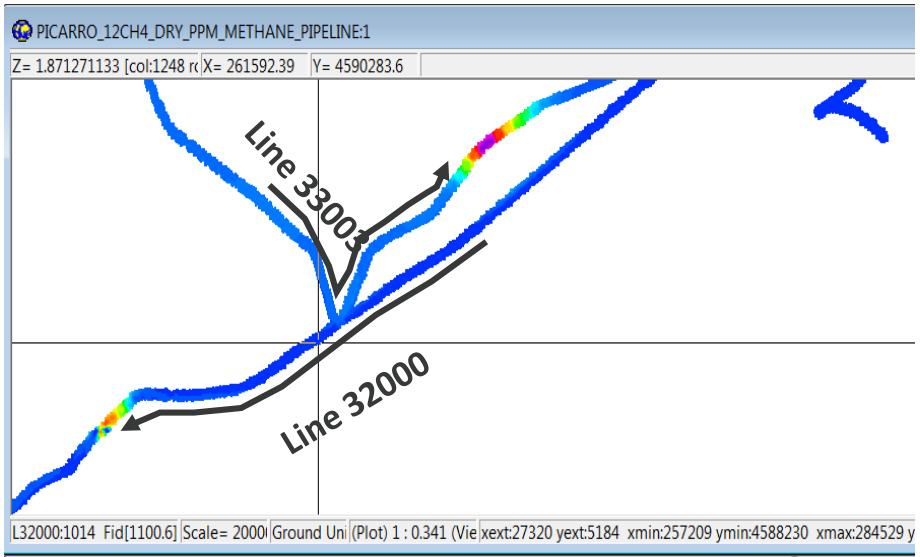


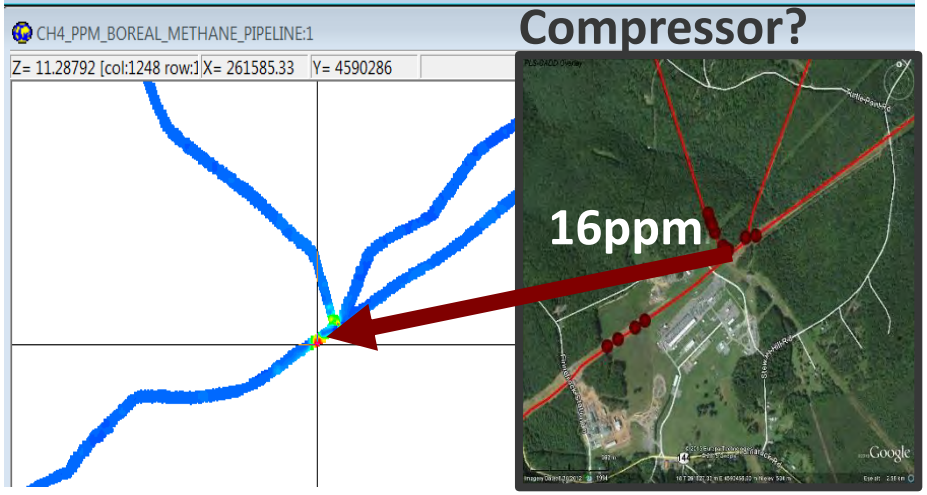
Ground-based Portable Meteorological Station:

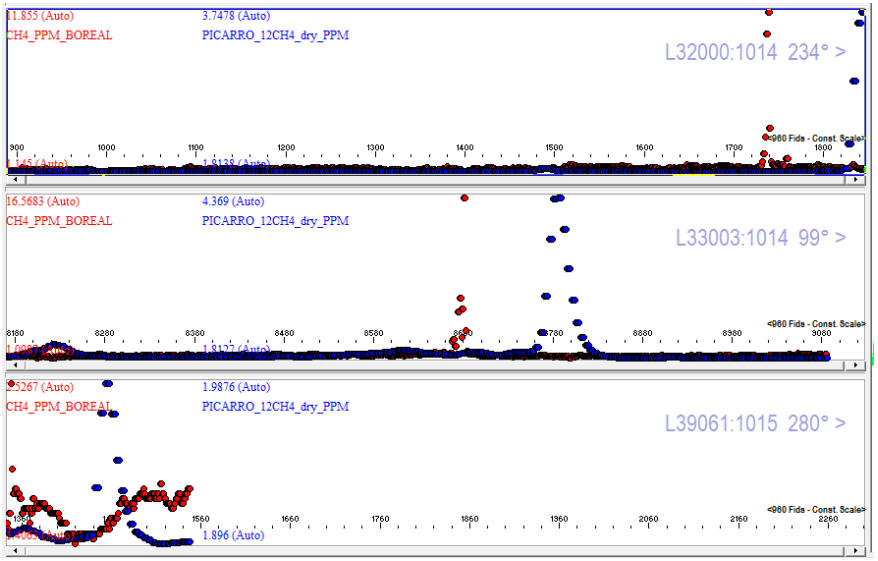
Top-Down Survey Challenges

- **Proximal methane sources**
  - Includes natural sources (e.g. geological seepage)
- **Variables**
  - Leak Rate
  - Wind speed and direction
  - Sensor Altitude
  - Sample rate
  - Air pressure? Humidity?
- **Plume modeling to optimize detection**

Susquehannock State Forest Aerial Survey Challenge: Analyzer Time Delay







Picarro delayed after Boreal by about 9-11 seconds

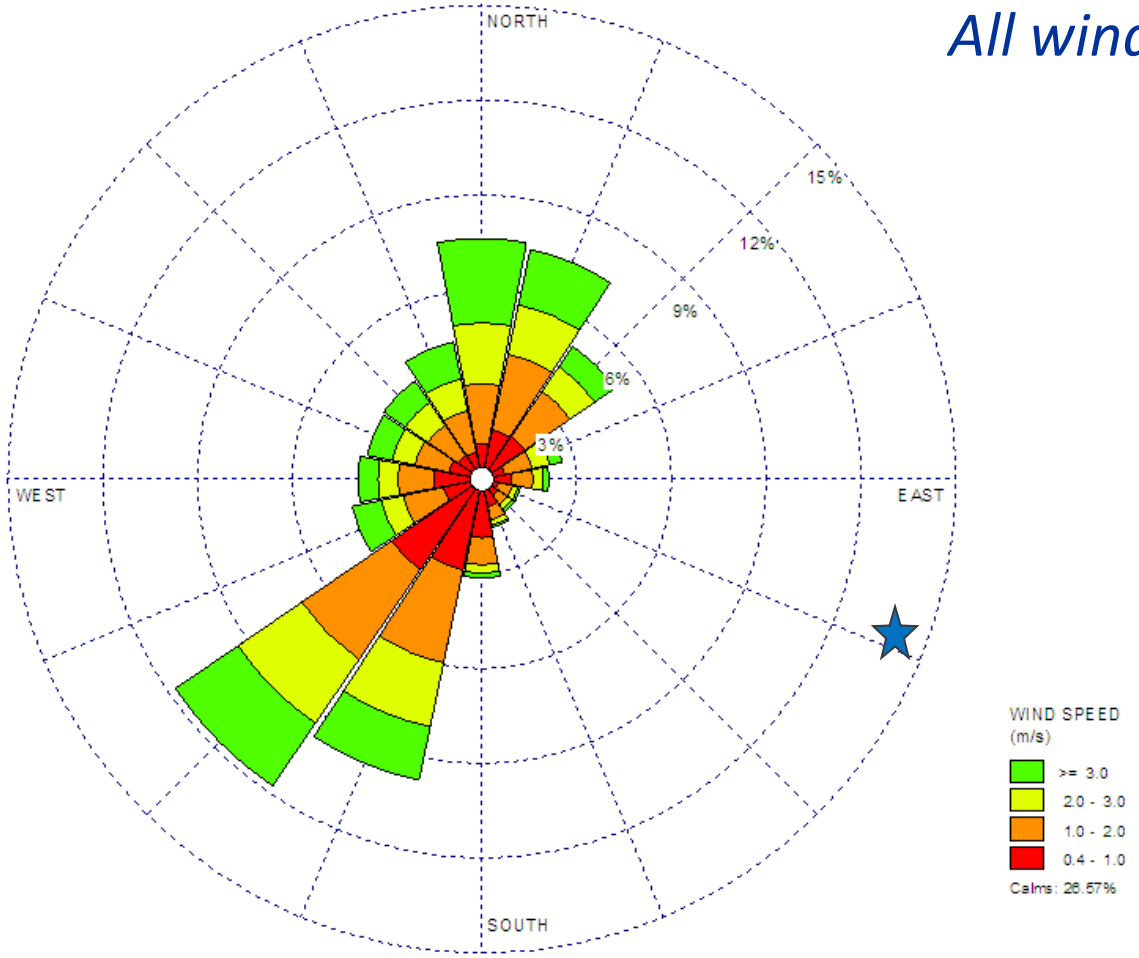
NETL's Mobile Air Monitoring Laboratory

- **Pollutants Measured:**
  - VOCs (Perkin Elmer Ozone Precursor Analyzer, GC-FID)
  - Ozone, NO_x (Teledyne-API Gas Analyzers)
  - Methane and Carbon Isotopes in Methane (Picarro CRDS)
  - CO_2 and Carbon Isotopes in CO_2 (Picarro CRDS)
  - PM_{10} and $PM_{2.5}$ (Thermo Fisher TEOM 1405DF)
  - Organic and Elemental Carbon in Aerosols (Sunset Labs NDIR)

- **Meteorological Station (Davis Vantage Pro2 Plus, R.M. Young Ultrasonic Anemometer)**
  - Wind Speed and Direction
  - Temperature
  - Relative Humidity
  - Barometric Pressure
  - Rainfall
  - Solar Intensity

Greene County Marcellus Shale Well Pad

All wind data

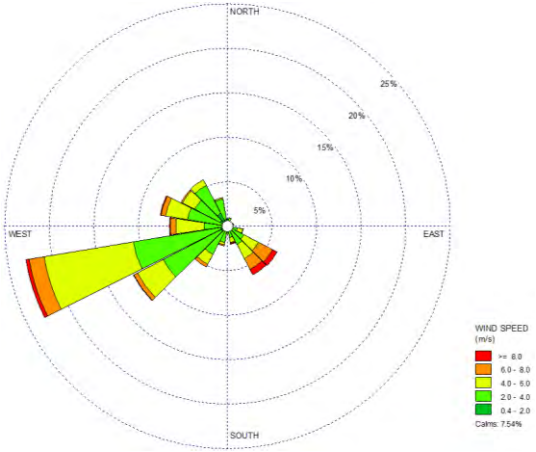


Lakes Environmental WRPLOT

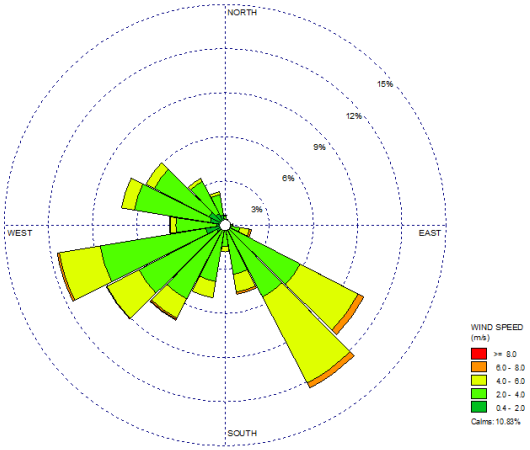
Wind Roses

Spring/Summer

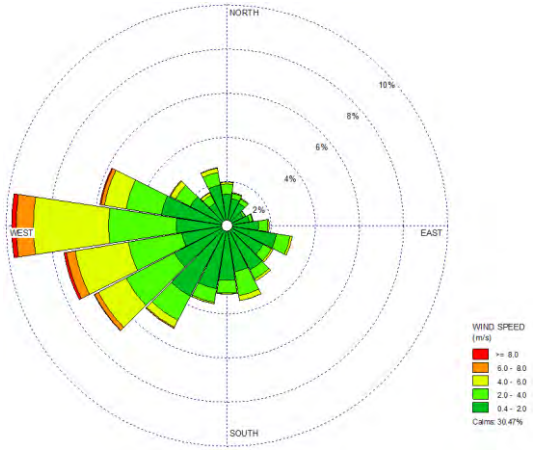
Average monthly wind speeds 1.5 – 3.4 m/s



May 2014



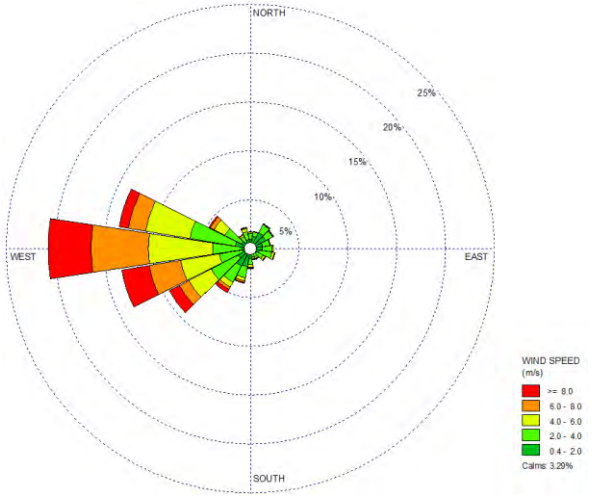
June - mid July 2014



Late July – August 2014

Fall/Winter

Average wind speed 5.4 m/s



Carbon Isotopes

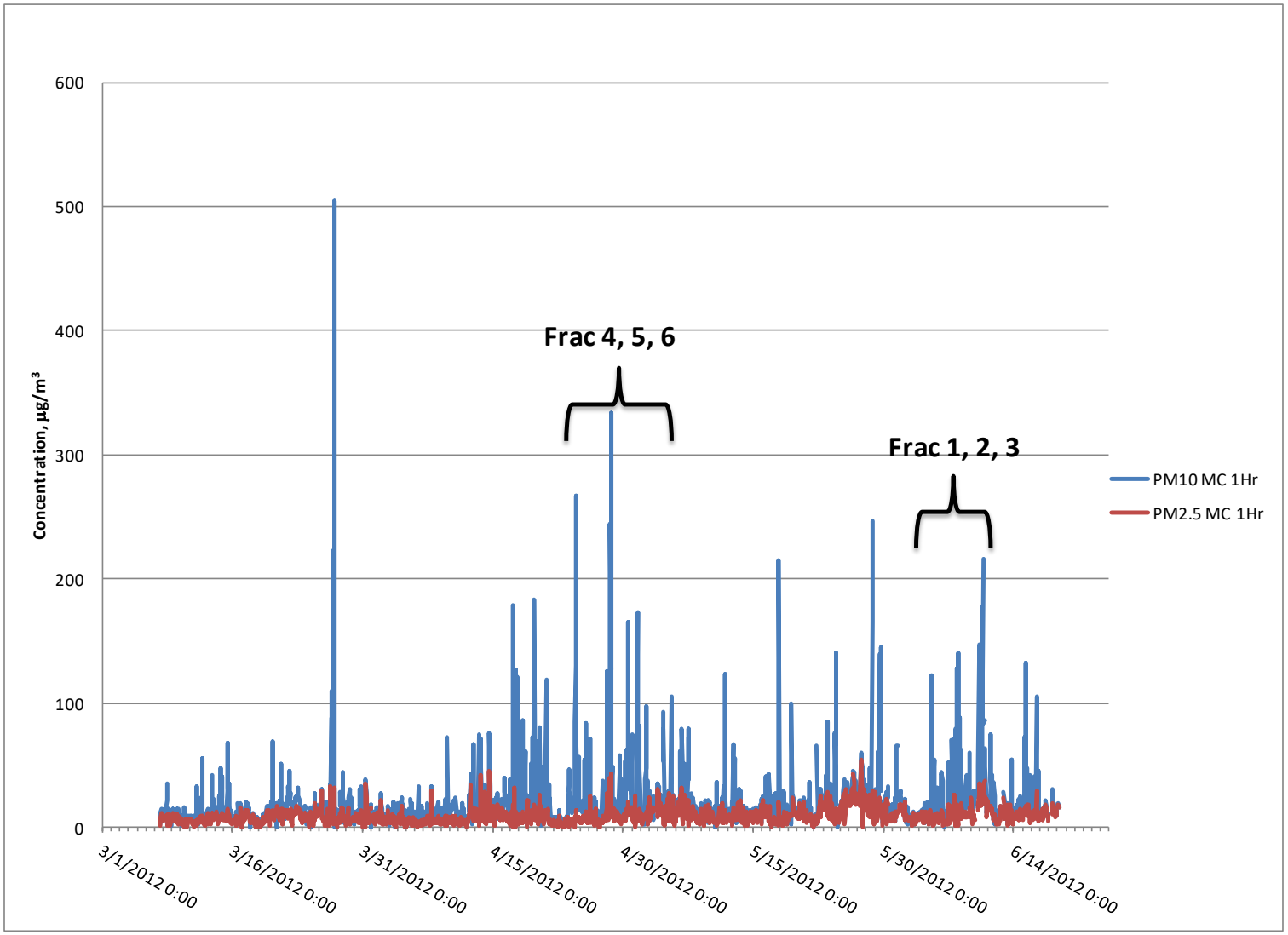
- **Marcellus gas is ~97% methane (CH_4)**
- **^{12}C (98.89%) ^{13}C (1.11%)**
- **$\delta^{13}C = \{(R_{sample} / R_{standard}) - 1\} * 1000$ ‰ R= $^{13}C/^{12}C$**

- **$\delta^{13}C_{CH4}$:**
  - Atmospheric ~-50‰
  - Biogenic -50 to -80‰
  - Thermogenic -25 to -40‰
- **$\delta^{13}C_{CO2}$:**
  - Atmospheric ~-10‰
  - Combustion -20 to -50‰

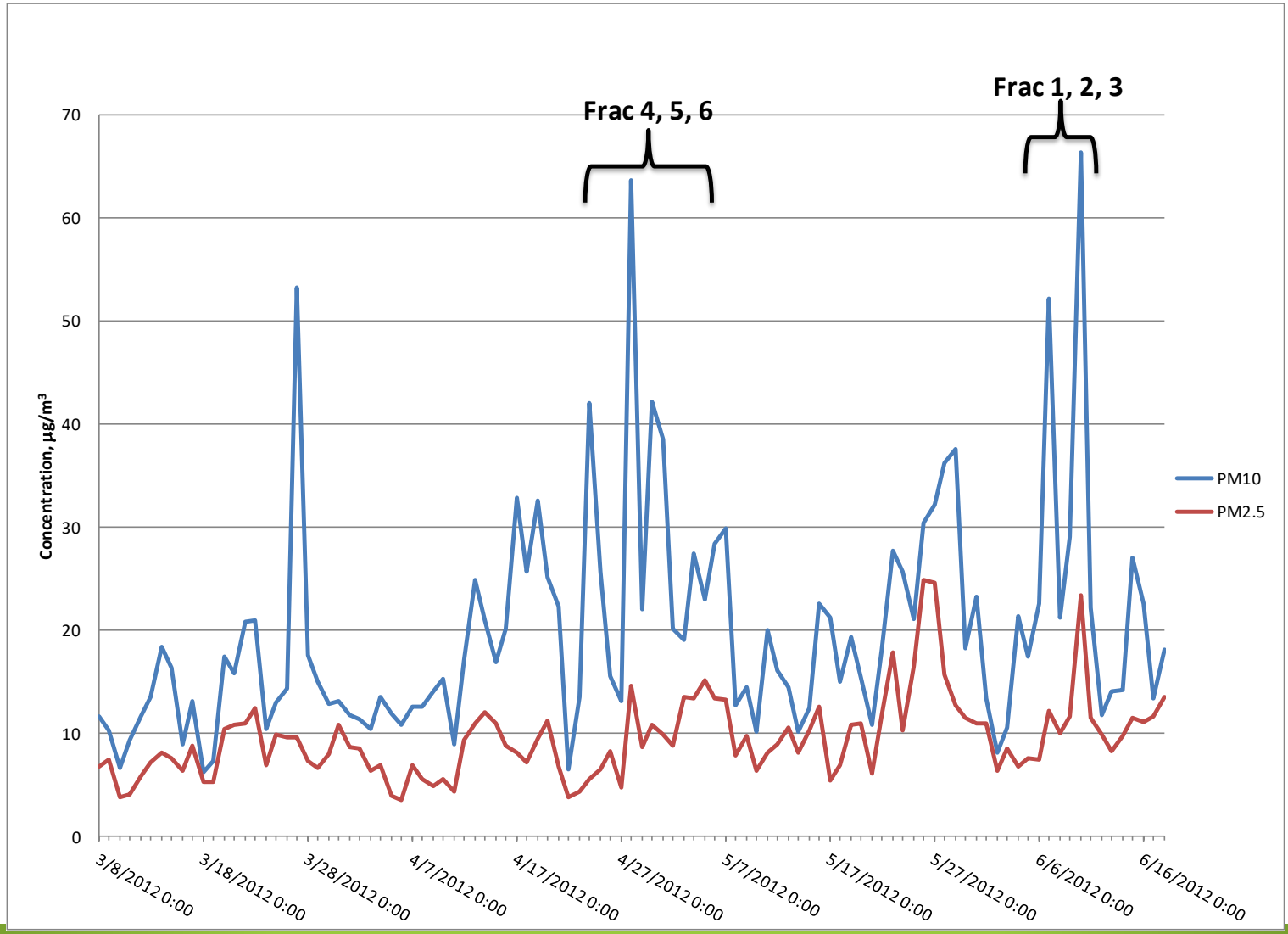
Volatile Organic Compounds (VOCs)

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)

Particulate Matter Concentrations: 1-Hour Average



Particulate Matter Concentrations: 24-Hour Average



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

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

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

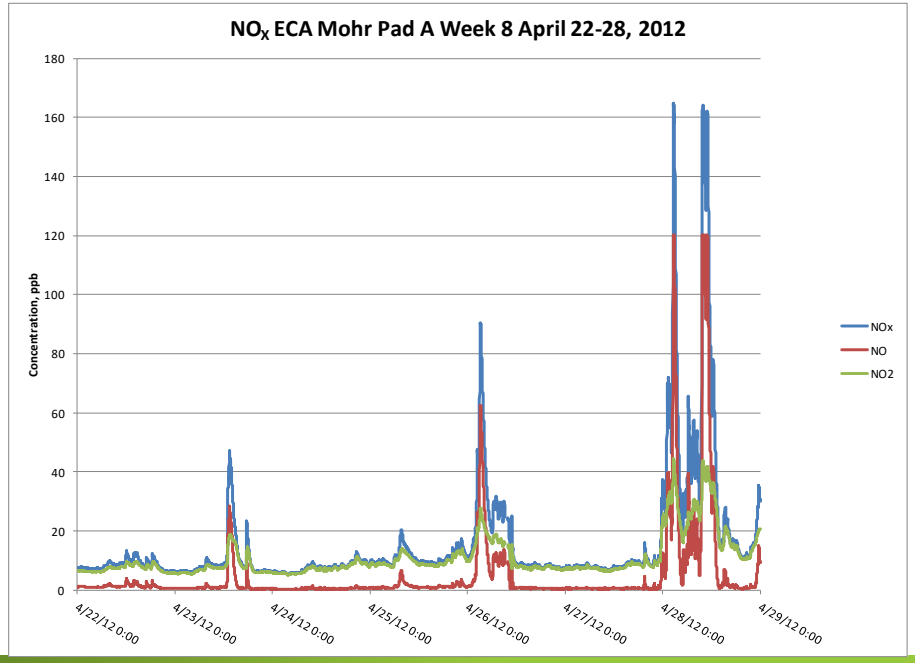
Maximum 1-hour average: 504 µg/m^3 (Not during frac)

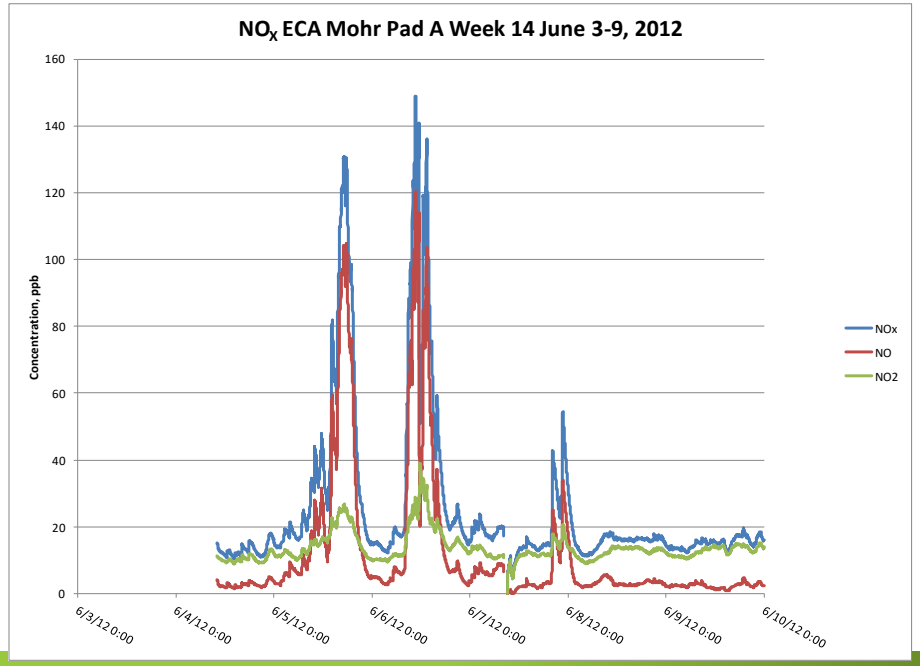
24-hour average $PM_{2.5}$ range of 4-25 µg/m^3

Maximum 1-hour average: 55 µg/m^3

NO_x Results

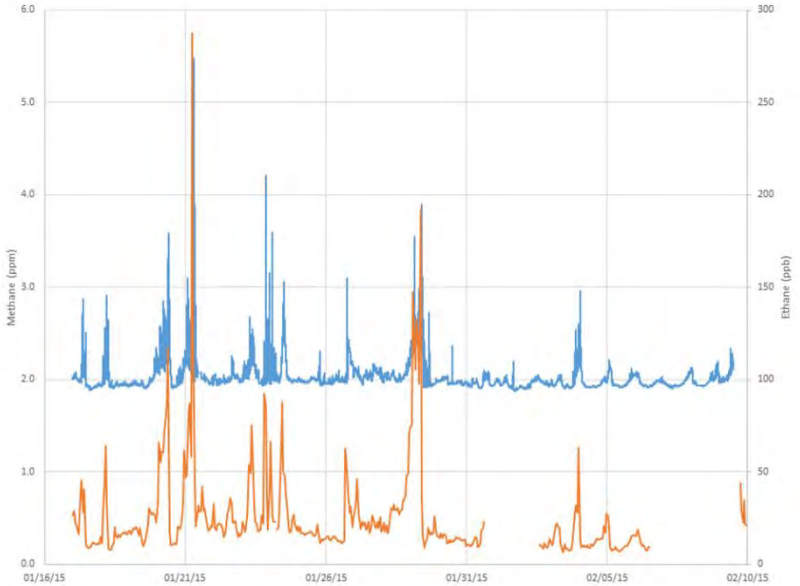
- NO_2 has an annual average standard of **53ppb,** 1-hour standard of **100ppb**
- Pre- and post-frac: overall average at ECA Mohr Pad A: **5-15ppb,** with peaks not exceeding **60ppb**
- During frac: peaks significantly greater

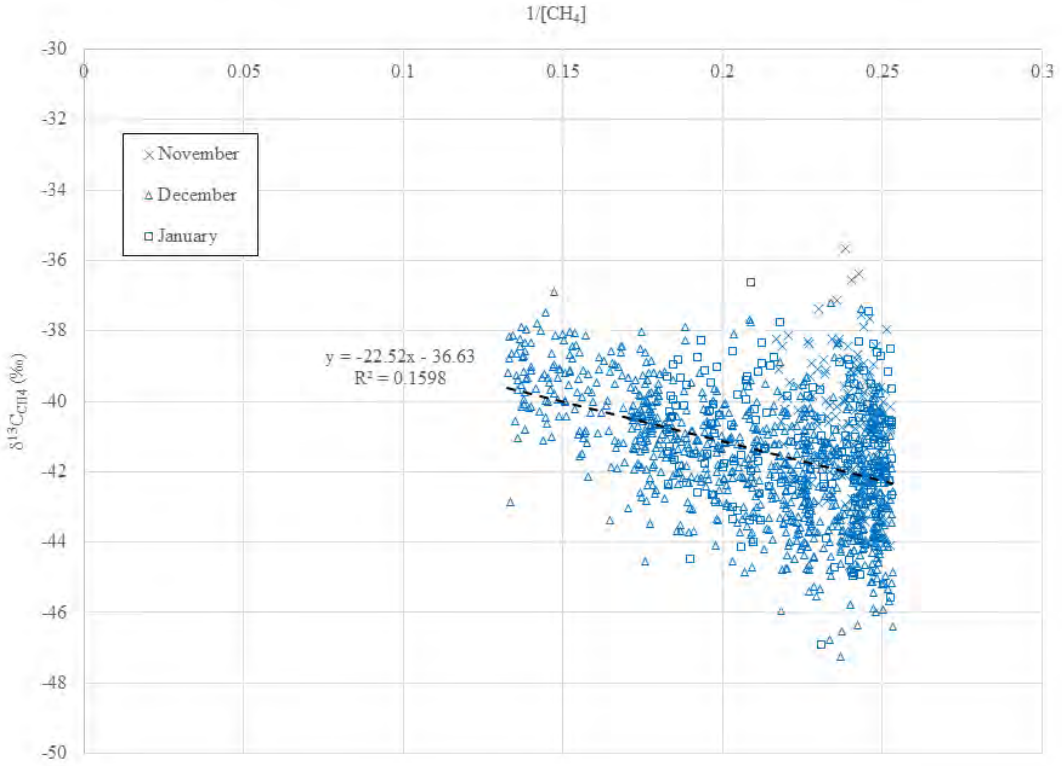




Methane, Fall/Winter

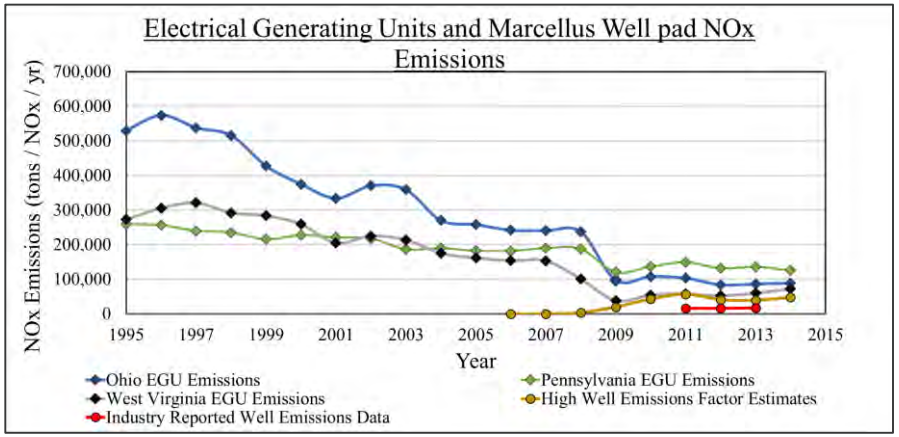
	November		December		January		February	
	$[CH_4]$	**$\delta^{13}C$**	**$[CH_4]$**	**$\delta^{13}C$**	**$[CH_4]$**	**$\delta^{13}C$**	**$[CH_4]$**	**$\delta^{13}C$**
Average	2.0	-46.5	2.0	-50.1	2.0	-48.2	2.0	-47.7
Std dev	0.2	3.9	0.2	3.5	0.2	4.2	0.1	3.9
Min	1.8	-64.2	1.9	-65.3	1.8	-66.5	1.9	-65.3
Max	4.6	-33.8	7.5	-32.6	5.5	-28.6	3.0	-30.7

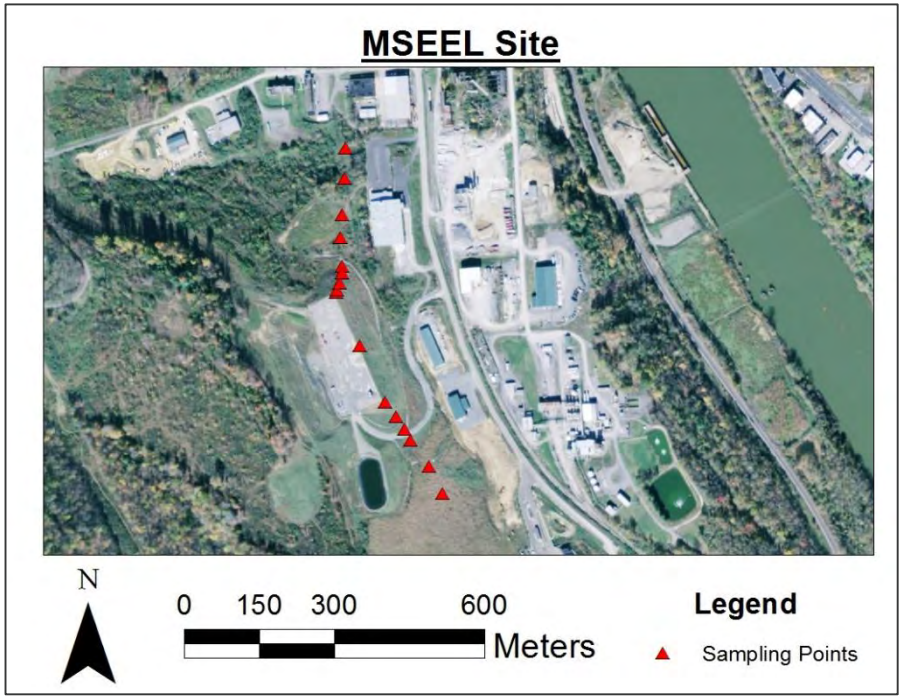




Fate and Transport of N-Containing Compounds

Measurement of ambient air concentrations and deposition fluctuations of nitrogen dioxide ($NO_{2)}$ and nitric acid ($HNO_{3)}$ along upwind and downwind transects adjacent to a Marcellus Shale unconventional well pad





- During periods of heightened activity, NO_2 concentration initially peaks near the well pad and decreases with distance upwind and downwind, returning to background levels ~300 m from the central site
- HNO_3 concentration peaks ~150 m away from the well pad during periods of heightened activity
- *Evidence of oxidation of NO_2 by O_3. Time-weighted ambient concentration of NO2 did not surpass the NAAQS*

Ongoing/Future Work

- Ground-base Surveys
- OCSP P&A Wells
- MSEEL/USEEL