NATIONAL ENERGY TECHNOLOGY LABORATORY

Data Report for Monitoring at Six West Virginia Marcellus Shale Development Sites using NETL's Mobile Air Monitoring Laboratory (July–November 2012)

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Cover Illustration: NETL's Mobile Air Monitoring Laboratory situated near a Marcellus shale gas well pad in Wetzel County, West Virginia. Flaring of the natural gas can be seen in the background.

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Data Report for Monitoring at Six West Virginia Marcellus Shale Development Sites using NETL's Mobile Air Monitoring Laboratory (July–November 2012)

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Acronyms, Abbreviations, and Symbols

Term	Description
CH_4	Methane
CO_2	Carbon dioxide
EC	Elemental carbon
EPA	U.S. Environmental Protection Agency
GC-FID	Gas chromatagraph with flame ionization detection
NAAQS	National Ambient Air Quality Standards
NETL	National Energy Technology Laboratory
NO_x	Oxides of nitrogen
NO_2	Nitrogen dioxide
OC	Organic carbon
OSHA	U.S. Occupational Safety and Health Administration
PAMS	Photochemical Assessment Monitoring Station
PEL	Permissible Exposure Limit
$PM_{2.5}$	Fine particulate matter
PM_{10}	Coarse particulate matter
SO_2	Sulfer dioxide
TEOM	Tapered Element Oscillating Microbalance
VOC	Volatile organic compounds
VPDB	Vienna Pee Dee Belemnite
WV	West Virginia
WVDNR	West Virginia Division of Natural Resources
WVU	West Virginia University

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EXECUTIVE SUMMARY

The West Virginia Department of Environmental Protection's Office of Oil and Gas was directed according to the Natural Gas Horizontal Well Control Act of December 14, 2011 (West Virginia Code §22-6A) to conduct studies of horizontal well drilling activities related to air quality. The planned study, "Noise, Light, Dust, Volatile Organic Compounds Related to Well Location Restrictions," required determination of the effectiveness of a 625 ft minimum set-back from the center of the pad of a horizontal well drilling site to the nearest occupied dwelling. An investigation was conducted at seven drilling sites by West Virginia University (WVU) and the National Energy Technology Laboratory (NETL) to collect data on dust, hydrocarbon compounds and on noise, radiation, and light levels. NETL's role in this study was to collect measurements of ambient pollutant concentrations at six of the seven selected sites using NETL's Mobile Air Monitoring Laboratory. The trailer-based laboratory was situated a distance of 492–1,312 ft from each well pad, on which activities included well pad construction, vertical drilling, horizontal drilling, hydraulic fracturing, and flaring, with the objective of evaluating the air quality impact of each activity for 1–4 weeks per site. Measured pollutants included volatile organic compounds (VOCs), coarse and fine particulate matter (PM_{10} and $PM_{2.5}$, respectively), ozone, methane (CH_4), carbon dioxide (CO_2), carbon isotopes of CH_4 and CO_2, organic carbon (OC), elemental carbon (EC), oxides of nitrogen (NO_x), and sulfur dioxide (SO_2). Major observations include:

- While it was desirable to locate the Mobile Air Monitoring Laboratory downwind of the well pad, challenges with terrain frequently prevented optimal siting. The well pads were located in mountainous, forested areas with access typically restricted to the lease roads. At two sites, the Donna and Weekley pads, the laboratory was located in the residents' yards. Given the short duration of the study and the difficulty in siting the laboratory downwind of the well pad, wind direction was favorable for direct well pad plume interception at only two of the six monitoring locations (Donna and Maury well pads).
- Operator activity was typically sporadic in nature. Monitoring was short-term, with 1–4 weeks at each site. A 3-year monitoring period is required for determining compliance with the National Ambient Air Quality Standards (NAAQS). However, when results for ozone, particulate matter, and nitrogen dioxide are compared to the NAAQS, no instances of exceedances were observed with the exception of one 8-hour period at the Weekley well pad site during which average ozone concentration was 78 ppb, 3 ppb above the NAAQS.
- Hydrocarbons present in natural gas (ethane, propane, butane, and pentane) were detected in almost all samples at every site. However, these compounds are typically present at trace levels in background air. Complex statistical analysis would be required to distinguish between background concentrations and contribution from the well pad activity, an effort that is beyond the scope of this project.
- Of the BTEX (i.e. organic chemicals Benzene, Toluene, Ethylbenzene and Xylenes) compounds, only toluene was consistently found at all sites. These compounds come from diesel or gasoline engine emissions, either from equipment used on the well pad or from traffic on local roads.

- Evaluating the isotopic signature of ambient CH_4 reveals the nature of the source (e.g., biogenic or thermogenic). At three of the sites (Donna, Weekley, and Maury well pads), elevated CH_4 concentrations were sometimes observed that corresponded to a change in isotopic signature that was indicative of thermogenic CH_4 and can therefore be attributed to the activity at the well pad. These events were short-lived, ranging from 1 hour to 1 day. Due to the sporadic nature of CH_4 emissions, it is recommended that any evaluation of well pad CH_4 emissions include adequate temporal coverage such that the evaluation is representative and episodic emissions do not over- or under-influence the estimation. Continuous monitoring during the entire course of the activity to be evaluated is recommended.

A final report of both NETL's and WVU's results are available at:

http://www.dep.wv.gov/oil-and-gas/Horizontal-Permits/legislativestudies/Documents/WVU%20Final%20Air%20Noise%20Light%20Report.pdf

This report summarizes data collected by NETL and does not include data collected by WVU.

1. NETL'S MOBILE AIR MONITORING LABORATORY

The National Energy Technology Laboratory (NETL) Mobile Air Monitoring Laboratory consists of an 18 ft temperature-controlled trailer housing several air pollution monitoring devices with samples of ambient air being drawn from inlets on the trailer roof (Figure 1). The laboratory was designed to operate unattended with continuous, automatic collection of data. Measured pollutants included volatile organic compounds (VOCs), coarse and fine particulate matter (PM_{10} and $PM_{2.5}$, respectively), ozone, methane (CH_4), carbon dioxide (CO_2), carbon isotopes of CH_4 and CO_2, organic carbon (OC), elemental carbon (EC), oxides of nitrogen (NO_x),and sulfur dioxide (SO_2). A satellite link provided the capability to remotely download data and control some instruments. Instrumentation included:

- Perkin Elmer Ozone Precursor Analyzer System, a gas chromatogram with flame ionization detection (GC-FID) with thermal desorption for measurement of hourly averaged concentrations of 56 VOCs listed in Appendix A
- Teledyne API ozone analyzer (1-minute concentrations)
- Teledyne API NO_x analyzer (1-minute concentrations of NO, NO_2, and $NO+NO_2=NO_x$)
- Teledyne API SO_2 analyzer (1-minute concentrations)
- Thermo Fisher Tapered Element Oscillating Microbalance (TEOM) for measurement of hourly averaged concentrations of PM_{10} and $PM_{2.5}$
- Sunset Laboratory OC and EC in Aerosols field analyzer for 2-hour averaged concentrations of OC and EC
- Picarro CH_4/CO_2 and CH_4/CO_2 isotopes analyzer (sub-minute concentrations and isotope ratios)
- Davis Instruments Vantage Pro2 Plus meteorological station for 1-minute measurement of temperature, relative humidity, wind speed and direction, rainfall, barometric pressure, and solar intensity

Figure 1: NETL's mobile air monitoring laboratory.

2. MEASUREMENTS

2.1 VOLATILE ORGANIC COMPOUNDS

VOCs were measured using a Perkin Elmer Ozone Precursor analyzer, a GC-FID with thermal desorption on the sample introduction that yields 1-hour average concentrations. The U.S. Environmental Protection Agency (EPA) Photochemical Assessment Monitoring Station (PAMS) standard was used to calibrate the analyzer at the start of monitoring at each site, and once per week subsequently. Measured compounds are listed in Appendix A along with the U.S. Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs). Because most of the compounds were very rarely or never detected, results are given in the following sections only for compounds that were detected in at least 10% of the samples. Tables 2–7 list for each monitoring site the average concentration, standard deviation, minimum and maximum concentrations, and frequency of detection for compounds that were detected in at least 10% of the samples. Ethane was the compound that was consistently detected in the highest concentrations, and because there are few sources of atmospheric ethane other than those related to natural gas, it can be used as a tracer for natural gas operations.

2.2 OZONE

The ozone analyzer used was a Teledyne-API 400A, which uses UV adsorption to yield 1-minute average concentrations. A two-point calibration on the analyzer was performed at the start and end of the monitoring period at each of the six locations, as well as during weekly site visits. At all sites ozone concentrations were observed to follow the typical photochemically-driven diurnal pattern of high concentrations during the day and lower concentrations at night. Because it is produced photochemically and is a secondary pollutant, ozone pollution tends to be regional in nature. Ozone is formed by chemical reactions of NO_x, CO, and VOCs in the presence of sunlight. These ozone precursors are all emitted by equipment used in natural gas drilling and production as well as many other sources. Ozone is a criteria pollutant, with an 8-hour standard of 75 ppb (EPA, 2012).

2.3 NITROUS OXIDE AND NITROGEN DIOXIDE (NO_X)

The NO_x analyzer used was a Teledyne-API 200AU, which uses chemiluminescence to yield 1-minute average concentrations of NO, NO_2, and their sum, NO_x. A two-point calibration on the analyzer was performed at the start and end of the monitoring period at each of the six locations, as well as during weekly site visits. NO_x can be formed by incomplete combustion of fuels, such as gas and diesel fuel for trucks, drill rigs, pumps and compressors used for natural gas drilling and production. Nitrogen dioxide, the indicator for NO_x, is a criteria pollutant with an annual average standard of 53 ppb and a 1-hour primary standard of 100 ppb (EPA, 2012).

2.4 METHANE AND ISOTOPIC METHANE, CARBON DIOXIDE AND ISOTOPIC CARBON DIOXIDE (CH_4/ISOTOPIC CH_4 AND CO_2/ISOTOPIC CO_2)

CH_4, the primary component of natural gas, is a principal greenhouse gas that is typically found at low concentrations at the earth's surface. CO_2, also a naturally occurring greenhouse gas, comes primarily from the combustion of fossil fuels and to a much lesser extent from volcanic eruptions. CH_4/isotopic CH_4 and CO_2/isotopic CO_2 data were measured using a Picarro G2201-i cavity ring-down spectrometer. This instrument simultaneously yields sub-1-minute CO_2 and

CH_4 concentrations as well as the isotopic composition of each. Isotope values are reported using delta notation:

$$\delta^{13}C_{sample} = \{(R_{sample}/R_{standard}) -1\} *1000$$

where R_{sample} is the ratio of $^{13}C/^{12}C$ in the sample, $R_{standard}$ is the ratio of $^{13}C/^{12}C$ in an international standard (in this case the Vienna Pee Dee Belemnite, VPDB) and the units are parts per thousand or "permil" (‰). For CH_4, various sources of the gas have distinguishable $\delta^{13}C$ values that can be used to potentially identify sources of the gas at the site. Sources are classified as either thermogenic (-30‰ to -40‰), generated deep underground from heating hydrocarbons, and biogenic (-50‰ to -70‰), generated by bacterial activity at the surface including from landfills, wetlands, livestock, and rice cultivation. The typical ambient CH_4 concentration is approximately 2 ppm with a $\delta^{13}C$ value near -50‰.

Atmospheric CO_2 is predominantly generated from the combustion of various hydrocarbon materials and as such the isotopic signature is heavily dependent on the $\delta^{13}C$ value of original material. For CO_2 generated from diesel or gasoline combustion, for example, the carbon isotopic signature is typically near -30‰, whereas CO_2 from CH_4 combustion has a $\delta^{13}C$ value near -50‰. The background atmospheric values of CO_2 concentration and isotopic composition are 389 ppm (±13) and -10.7‰ (±0.9‰), respectively.

2.5 PARTICULATE MATTER (PM_{10} AND $PM_{2.5}$)

One-hour average concentrations of PM_{10} and $PM_{2.5}$ were measured using a Thermo Fisher Tapered Element Oscillating Microbalance (TEOM) 1405-DF. PM can be emitted directly from oil and natural gas development sources like suspension of road dust from heavy truck traffic, or it can originate from chemical reactions of gases emitted in the atmosphere from vehicles, compressor stations, venting, flaring, etc. Generally, larger particles (PM_{10}) are associated with mechanical processes like erosion resulting in wind-blown dust and road dust, while finer particles ($PM_{2.5}$) are associated with chemical processes like combustion and aerosol formation. PM_{10} has a 24-hour standard of 150 $\mu g/m^3$ and $PM_{2.5}$ has an annual average standard of 15 $\mu g/m^3$ as well as a 24-hour standard of 35 $\mu g/m^3$ (EPA, 2012). Table 1 summarizes the PM_{10} and $PM_{2.5}$ data collected at each site by 24-hour averages for comparison with the NAAQS. More site specific information, including time series graphs, are included in Section 3.

Table 1: 24-hour average PM_{10} and $PM_{2.5}$ concentrations measured at each site

		PM_{10} (µg/m^3)	$PM_{2.5}$ (µg/m^3)
NAAQS 24-hour Standard		**150**	**35**
Range of 24-hour averages measured at each site	Donna Pad	12-29	6-15
	Weekley Pad	9-32	5-20
	Mills-Wetzel Pad	9-54	6-17
	Maury Pad	9-90	5-24
	Lemons Pad	5-24	3-13
	WVDNR Pad	2-50	1-13

2.6 SULFUR DIOXIDE (SO_2)

The SO_2 analyzer used was a Teledyne-API 100A, which uses a fluorescence technique to yield 1-minute average concentrations. A two-point calibration on the analyzer was performed at the start and end of the monitoring period at each of the six locations, as well as during weekly site visits. SO_2 can be formed by combustion of sulfur-containing fuels, such as petroleum and coal. SO_2 is a criteria pollutant with a 1-hour primary standard of 75 ppb and a secondary 3-hour standard of 0.5 ppm (EPA, 2012).

2.7 ORGANIC AND ELEMENTAL CARBON (OC AND EC)

Two-hour average OC and EC concentrations were obtained using the Sunset Laboratories Aerosol Carbon Field Analyzer. The analyzer had a $PM_{2.5}$ size-selective inlet, so reported concentrations are of OC and EC in $PM_{2.5}$. The analyzer uses a quartz oven and non-dispersive infrared detection. Blank sample analysis was automatically conducted daily at midnight, and a calibration check was conducted at the start and end of the monitoring period at each of the six locations, as well as during weekly site visits. EC is formed by combustion of organic material, such as fossil fuels, and is solely a primary pollutant. OC can be a primary or secondary pollutant. Primary sources can be anthropogenic or biogenic, and secondary sources are atmospheric oxidation processes. Both OC and EC can be emitted from the same source. With respect to natural gas operations, the VOCs emitted by gasoline- and diesel-powered engines and the natural gas itself can contribute to OC and diesel exhaust is a source of EC. The OC/EC analyzer experienced multiple problems related to leaks and software during monitoring at the six sites. OC and EC data are only available for the Maury pad and the Lemons pad (Section 3).

3. MONITORING LOCATIONS AND RESULTS

3.1 DONNA PAD

The NETL Mobile Air Monitoring Laboratory was deployed to the Donna pad in northern Marion County, WV on July 19, 2012. The operator was engaged in well stimulation activities from July 23–26, 2012. The laboratory was located approximately 400 m southeast of the well pad in the yard of a nearby resident with coordinates of 39°34'20.44"N, 80°17'26.22"W. The resident's electric service was used to power the laboratory, so the impact of diesel generator emissions does not need to be considered for this location. After unpacking, installing, and calibrating, all instruments were fully operational and collecting data on July 20. Monitoring at this site ended on August 1, 2012. During this period, wind typically came from the southeast or northwest; winds from the northwest were considered optimal for carrying plumes from the well pad toward the monitoring laboratory. Figure 2 shows a wind rose and histogram for the wind direction and speed during monitoring at the Donna pad location. Figures for other measured meteorological parameters (temperature, relative humidity, rainfall, and solar intensity) are included in Appendix B.

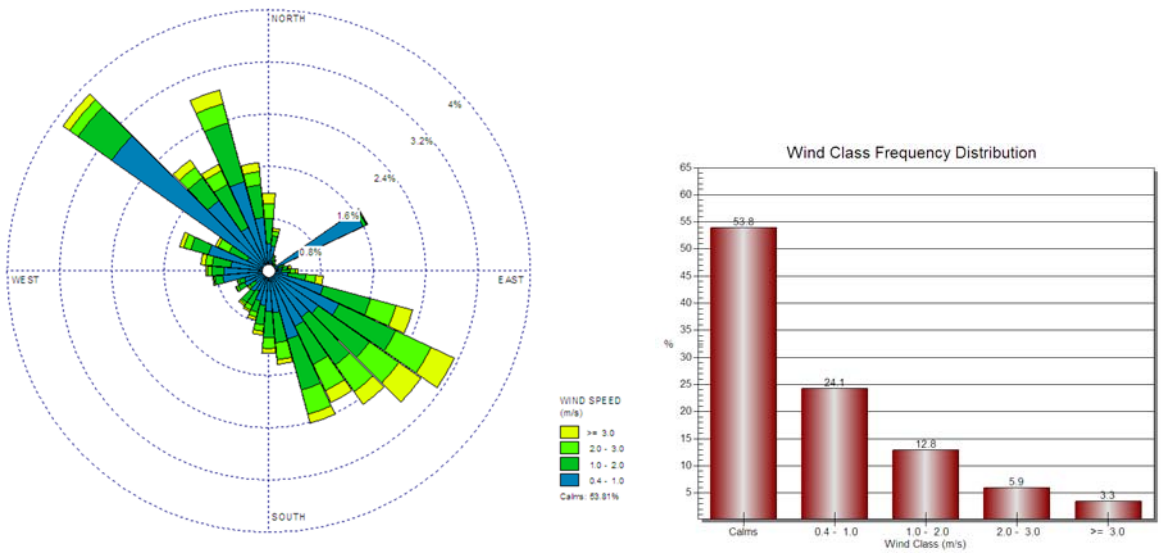

Figure 2: Wind rose and histogram for wind direction and speed during monitoring at the Donna pad location. For the wind rose, radial axis is percent of the time that the wind was coming from a particular direction.

VOCs. VOCs data were collected over the entire duration of the Donna pad monitoring campaign, July 20–August 1, for a total of 226 samples. Table 2 lists the average concentration, standard deviation, minimum and maximum concentrations, and frequency of detection for compounds that were detected in at least 10% of the samples. Alkanes such as ethane, propane, butane, and pentane, which are present in trace amounts in natural gas, were detected in 100% of the samples.

Table 2: VOCs concentrations for the Donna pad

Compound	Average (ppb)	Standard Deviation (ppb)	Minimum (ppb)	Maximum (ppb)	Frequency of Detection (%)
Hexane	1.2	2	0	10.3	42
n-heptane	0.4	1.0	0	5.1	19
Methylcyclohexane	0.4	1.0	0	5.2	19
Toluene	1.4	0.9	0	4.1	84
Ethane	59.4	108.3	9.2	837.5	100
Ethylene	0.6	0.8	0	3.5	37
Propane	22.2	20.8	3.4	175.9	100
Isobutane	5.3	3.9	0.7	31.4	100
n-butane	8.9	7.0	1.5	52.3	100
Isopentane	4.9	3.3	0.7	21.6	100
n-pentane	3.7	2.6	0.3	18.4	100
2-methylpentane	1.3	1.5	0	6.9	60
3-methylpentane	0.9	1.2	0	6.5	50
Isoprene	5.5	4.5	0	25.4	94

Ozone. Although the instrument was operating on July 20, ozone data are only available from July 24 through August 1 (Figure 3). There was a delay in obtaining data from the analyzer due to a faulty wiring connection. The average ozone concentration using 1-minute data at the Donna pad was 33 ppb, and the maximum hourly average concentration was 65 ppb. Day-to-night variations were as high as 50 ppb. Calculating 8-hour averages to more directly compare to the National Ambient Air Quality Standards (NAAQS) results in a range of 8-hour averages of 9–56 ppb.

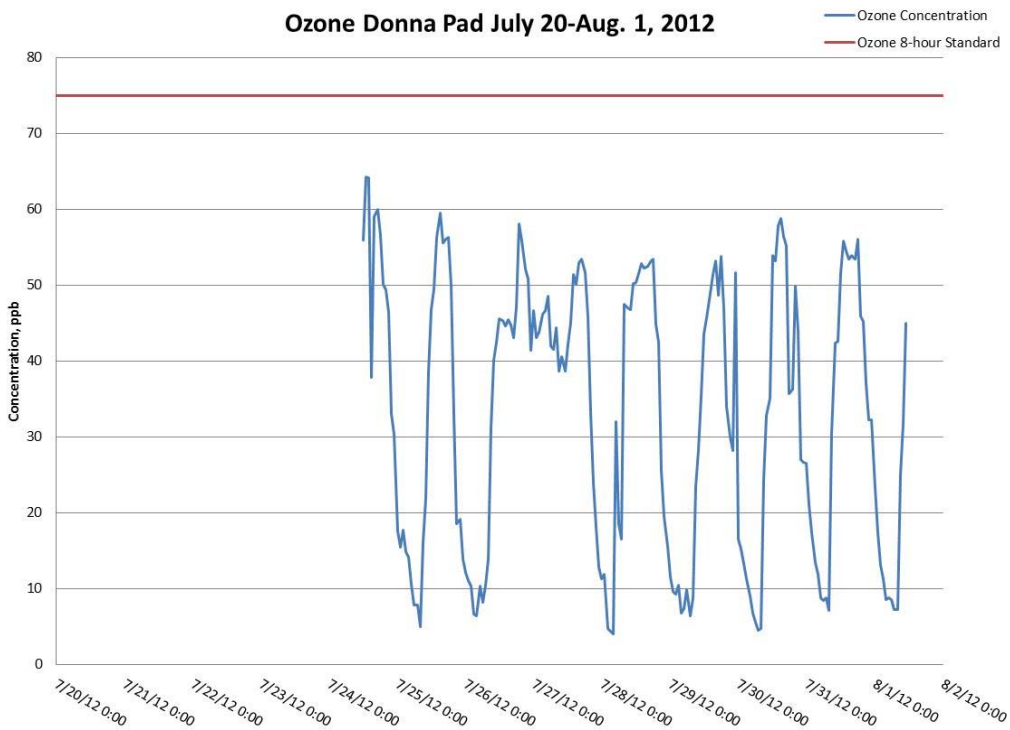

Figure 3: 1-minute average ozone concentrations at the Donna pad.

***NO_x*.** Data for NO_x are available for July 21–24 and July 27–August 1 (Figure 4). The gap between July 24 and 27 was due to an instrument malfunction that occurred during the calibration on July 24. The instrument was brought back to NETL in Pittsburgh for repairs and then returned to the Donna pad location. Unfortunately there are limited data for the time period that well stimulation activities occurred (July 23–26). The average concentration of NO_x at the Donna pad was 1.3 ppb, with peaks not exceeding 30 ppb. Calculating 1-hour averages from the 1-minute data for a more direct comparison with the NAAQS for NO_2 results in a range of 1-hour averages of 0.13–6.4 ppb.

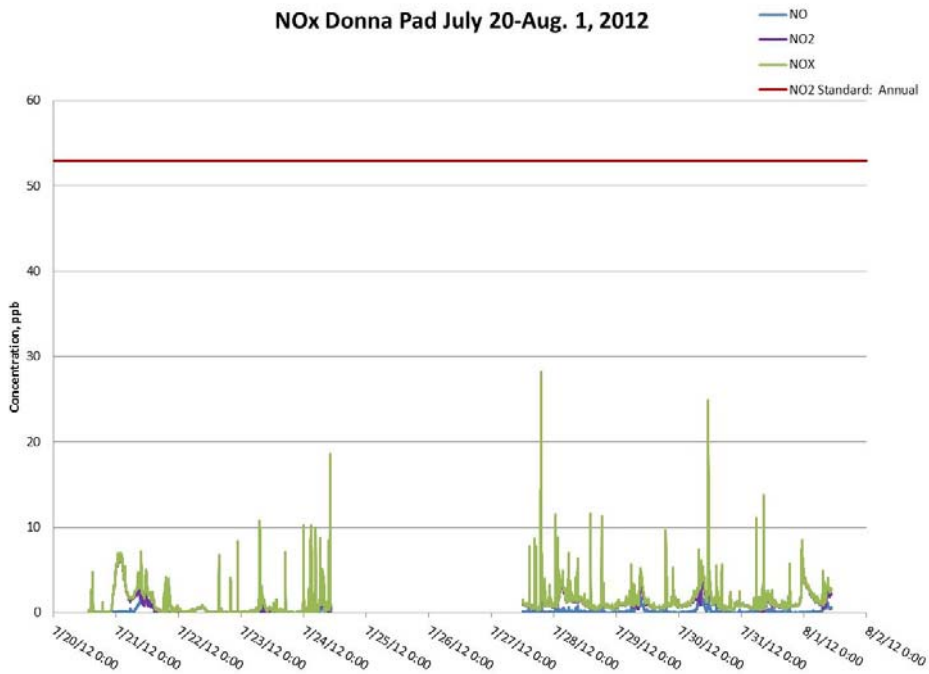

Figure 4: 1-minute average NO_x concentrations at the Donna pad.

CH_4 and CO_2. The ambient CH_4 concentration at the Donna Pad averaged 2.1 ppm (±0.1) with an average isotopic composition of -49.3‰ (±1.3‰), which are typical background atmospheric values (Figures 5–6). With the exception of a few short-term peaks, the only time the concentration exceeded 4 ppm occurred between the evening of July 28 through mid-day on July 29. During this time the average concentration of CH_4 was 8.1 ppm with a maximum concentration of 36.2 ppm. The average $\delta^{13}C$ for this time frame increased to -40.8‰ with a maximum value of -35.8‰, indicating a significant contribution from a thermogenic CH_4 source during this time. The operator was engaged in well stimulation activities from July 23–26, so it is likely that the well was in flowback on July 28–29. The source of the thermogenic CH_4 was not natural gas-powered equipment as all hydraulic fracturing equipment was diesel-powered.

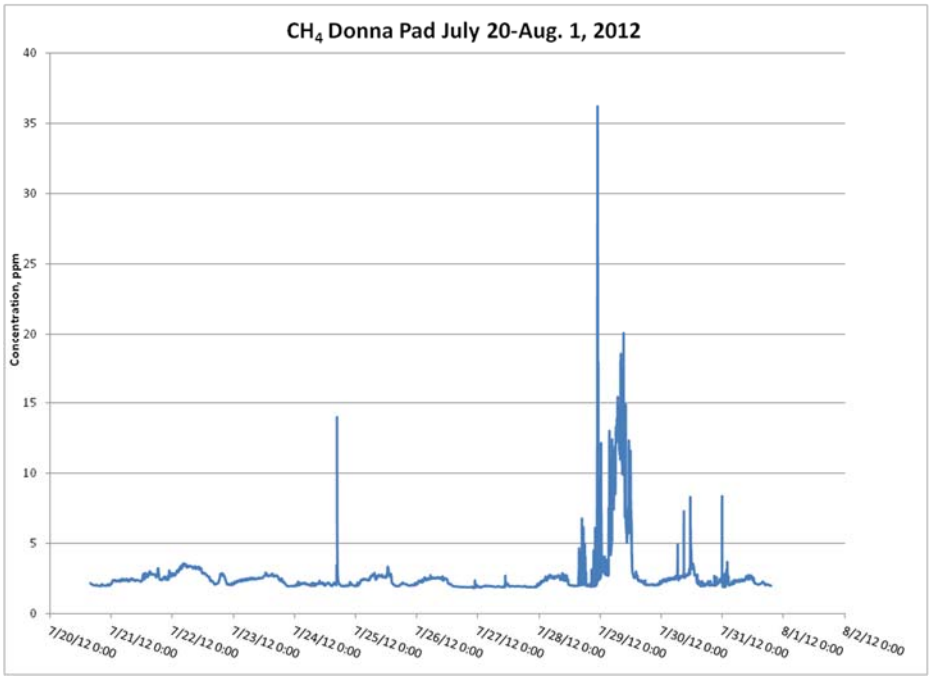

Figure 5: 1-minute average CH_4 concentrations at the Donna pad.

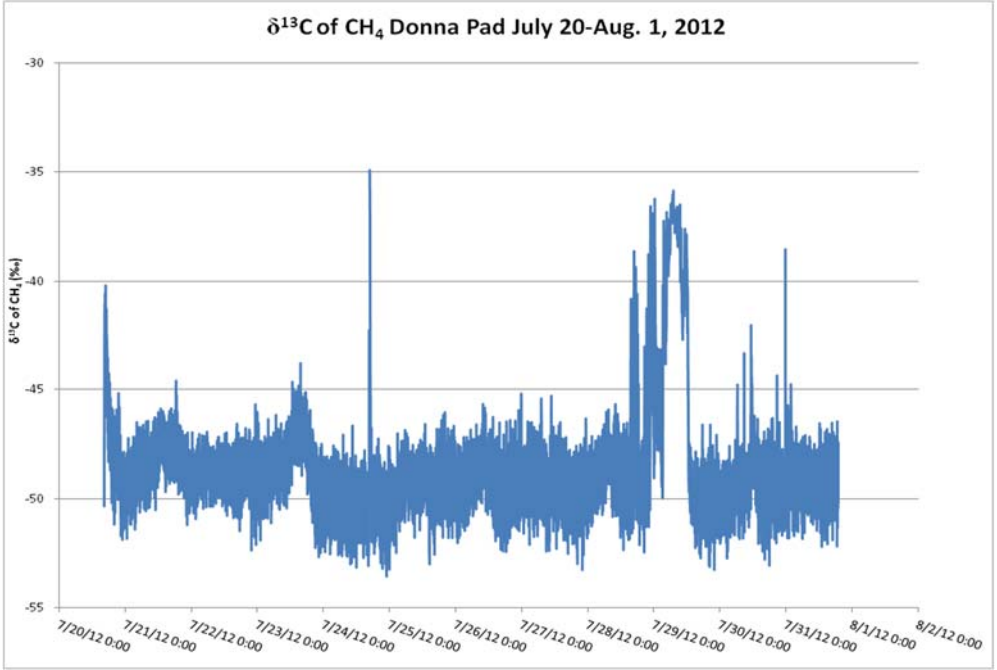

Figure 6: 1-minute average $\delta^{13}C$ of CH_4 at the Donna pad.

Over the 2 weeks of monitoring at the Donna pad, the CO_2 concentration averaged 425 ppm (±49) with $\delta^{13}C$ averaging -12.3‰ (±2.1‰) (Figure 7). As expected, the CO_2 concentrations and $\delta^{13}C$ values at the site cycle daily. Starting at approximately 8 p.m., the CO_2 concentration increased sharply to values typically greater than 450 ppm and occasionally greater than 500 ppm, before dropping back to near ambient levels by 7 a.m. During these times, the corresponding $\delta^{13}C$ values become more depleted, dropping to less than -14‰. The maximum CO_2 concentration at the site was 594 ppm with a corresponding $\delta^{13}C$ value of -16.0‰.

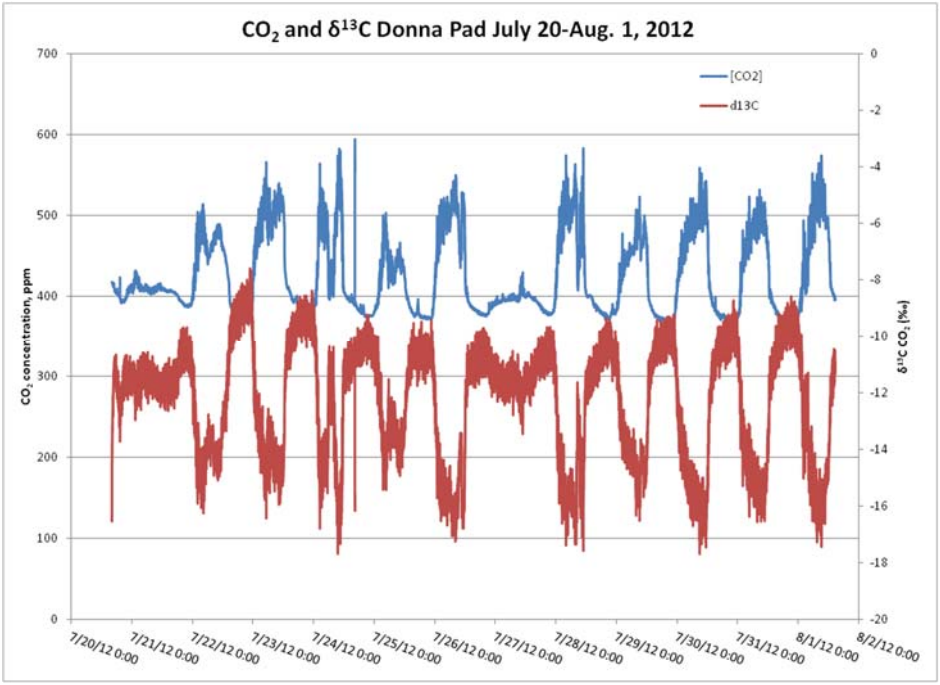

Figure 7: 1-minute average CO_2 concentrations and $\delta^{13}C$ of CO_2 at the Donna pad.

PM_{10} and $PM_{2.5}$. Data are available for July 20–August 1 (Figure 8). At the Donna pad, average PM_{10} concentration was 19 μg/m^3 and average $PM_{2.5}$ concentration was 11 μg/m^3. Maximum 1-hour average concentrations of PM_{10} and $PM_{2.5}$ were 76 μg/m^3 and 38 μg/m^3, respectively.

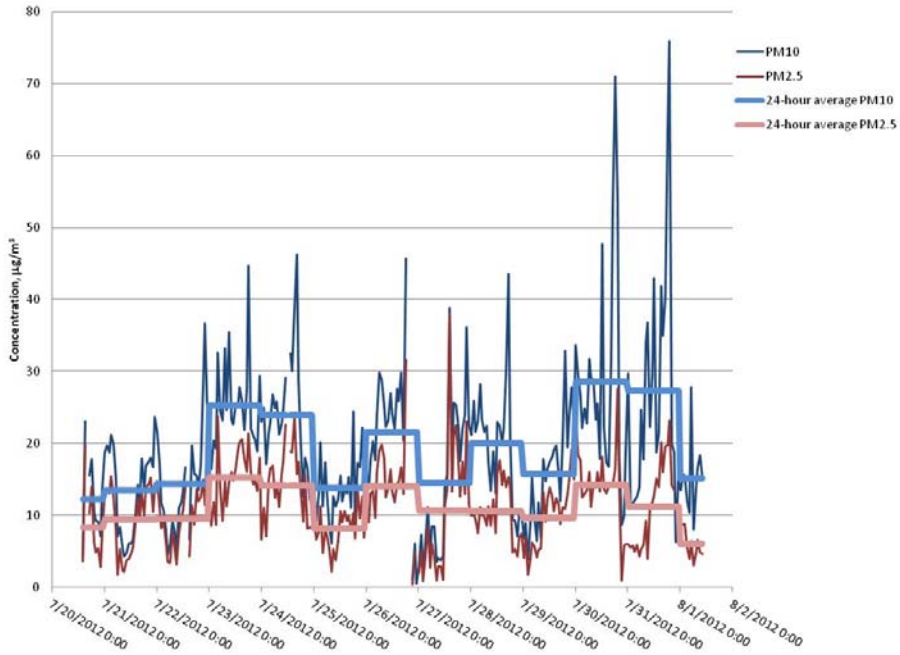

Figure 8: PM_{10} and $PM_{2.5}$ concentrations at the Donna pad.

SO_2. Data for SO_2 are available for the entire monitoring period, July 21–August 1 (Figure 9). The average concentration of SO_2 at the Donna pad was 3.3 ppb, with peaks not exceeding 23 ppb. Calculating 1-hour averages from the 1-minute data for a more direct comparison with the NAAQS for SO_2 results in a range of 1-hour averages of 1.4–11.5 ppb. Similarly, calculating 3-hour averages from the 1-minute data results in a range of 1.9–10.4 ppb.

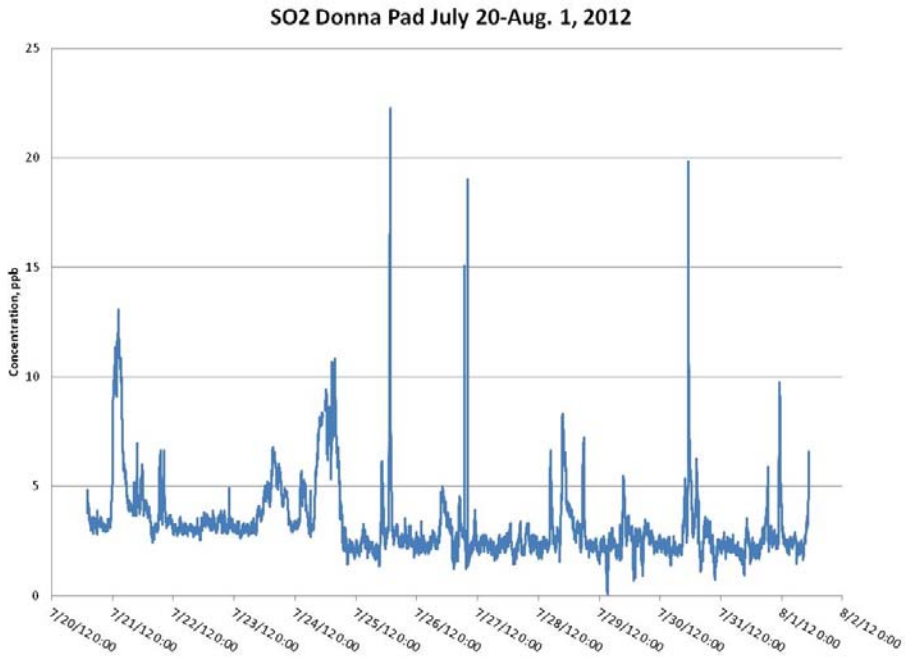

Figure 9: 1-minute average SO_2 concentrations for the Donna pad.

Site Summary. The CH_4 peak that occurred on July 28–29 corresponded to a peak in ethane concentration that averaged approximately 500 ppb, an order of magnitude greater than the average ethane concentration. During this time the wind was coming from the northwest, from the direction of the well pad. The high concentrations of CH_4 and ethane, the isotopic signature of thermogenic CH_4, and the wind direction provide clear evidence of interception of a plume of natural gas from the well pad during flowback. During well stimulation activities on July 23–26, there were no noticeable sustained elevated concentrations of ozone, VOCs, PM, CO_2, CH_4, or SO_2. Unfortunately NO_x concentrations were not measured during much of this time period. Concentrations for criteria pollutants measured were below NAAQS and VOCs were below PELs for the entire duration of monitoring at this site.

3.2 WEEKLEY PAD

The laboratory was moved from the Donna pad site to the Weekley pad site near New Martinsville, WV in western Wetzel County on August 2, 2012. The laboratory was located approximately 150 m southwest of the well pad in the yard of a nearby resident with coordinates of 39°35'24.94"N, 80°46'44.41"W. The resident's electric service was used to power the laboratory, so the impact of diesel generator emissions does not need to be considered for this location. After unpacking, installing, and calibrating, all instruments were fully operational and collecting data on August 3. Monitoring at this site ended on August 16, 2012. The wells at this site were being flowed back (flared) from August 3–18. Figure 10 shows a wind rose and histogram for the wind direction and speed during monitoring at the Weekley pad location. Wind speed was typically very low, with calm conditions 82% of the time. When there was wind, it was most frequently blowing from the southwest. At almost all times the laboratory was either monitoring during stagnant conditions or was upwind of the well pad. Figures for other measured meteorological parameters (temperature, relative humidity, rainfall, and solar intensity) are included in Appendix B.

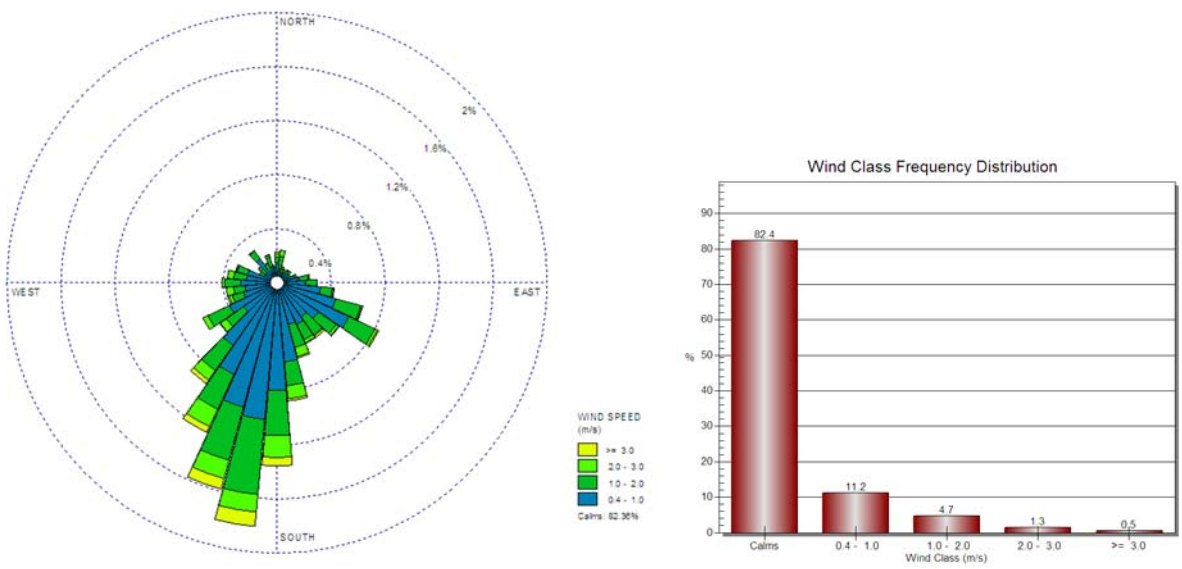

Figure 10: Wind rose and histogram for wind direction and speed during monitoring at the Weekley pad location. For the wind rose, radial axis is percent of the time that the wind was coming from a particular direction.

VOCs. At the Weekley pad site, there were a total of 274 samples. The analyzer ran continuously from August 3–16, with a break in the data for several hours on August 9 for a scheduled preventative maintenance check by a Perkin Elmer technician. Table 3 lists the average concentration, standard deviation, minimum and maximum concentrations, and frequency of detection for compounds that were detected in at least 10% of the samples. Alkanes were detected in 97–100% of the samples with maximums for some compounds as high as 3 ppm.

Table 3: VOCs concentrations for the Weekley pad

Compound	Average (ppb)	Standard Deviation (ppb)	Minimum (ppb)	Maximum (ppb)	Frequency of Detection (%)
Hexane	6.2	23.9	0.0	375.8	54
Methylcyclopentane	0.4	1.8	0.0	28.1	15
Cyclohexane	0.6	2.5	0.0	36.3	23
2-methylhexane	1.1	4.5	0.0	65.7	23
3-methylhexane	1.1	4.4	0.0	62.1	24
n-heptane	2.3	7.4	0.0	97.9	30
Methylcyclohexane	1.4	4.0	0.0	52.1	30
Toluene	0.7	1.3	0.0	12.1	32
2-methylheptane	0.4	1.5	0.0	15.5	16
3-methylheptane	0.5	1.9	0.0	19.9	17
n-octane	1.0	3.0	0.0	27.6	22
Nonane	0.4	1.4	0.0	11.5	12
Ethane	75.9	199.9	3.3	3,169	100
Propane	71.9	285.1	2.1	4.639	100
Isobutane	20.8	73.3	0.0	1,158	97
n-butane	44.5	199.9	1.0	3,249	100
Isopentane	17.0	24.0	0.0	186	100
n-pentane	19.2	75.6	0.0	1,212	99
2,3-dimethylbutane	0.4	2.3	0.0	35.3	11
2-methylpentane	4.7	15.2	0.0	240	76
3-methylpentane	3.0	9.7	0.0	151	67
Isoprene	6.6	5.2	0.0	23.8	90

Ozone. Ozone data are available for the entire monitoring period at this site, August 3–16 (Figure 11). The average ozone concentration using 1-minute data at the Weekley pad was 30 ppb, and the maximum hourly average concentration was 91 ppb. Day-to-night variations ranged from 20–85 ppb. The 8-hour average ranged from 4–78 ppb.

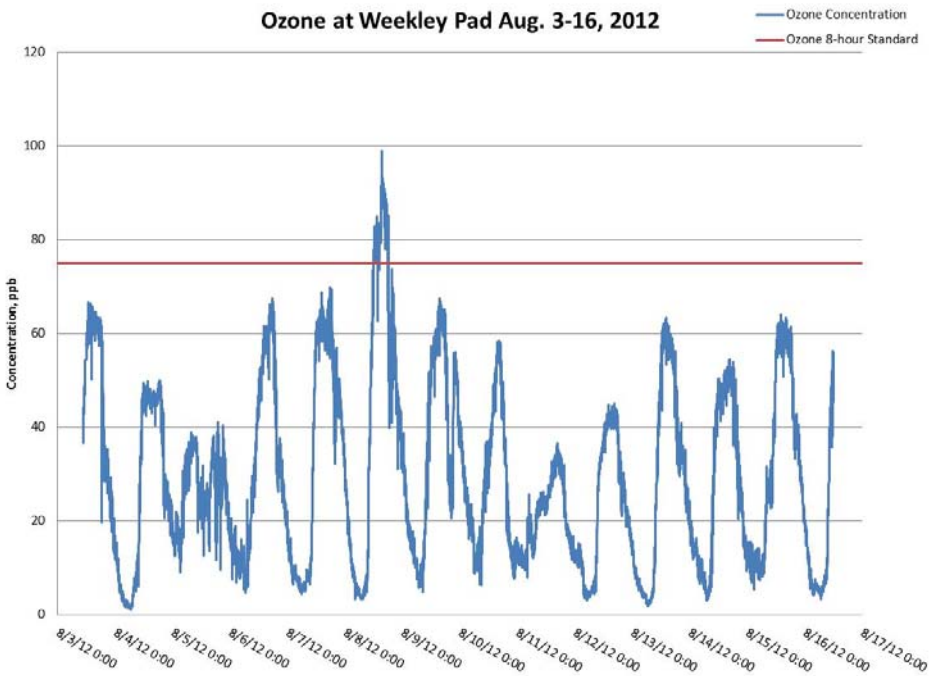

Figure 11: 1-minute average ozone concentrations at the Weekley pad.

***NO_x*.** Data for NO_x are available for the entire monitoring period at the Weekley pad site, August 3–16 (Figure 12). The average of the 1-minute NO_x concentration measurements was 3.4 ppb, with an hourly average maximum of 12 ppb. The 1-hour average for NO_2 ranged from 0.62–9.0 ppb.

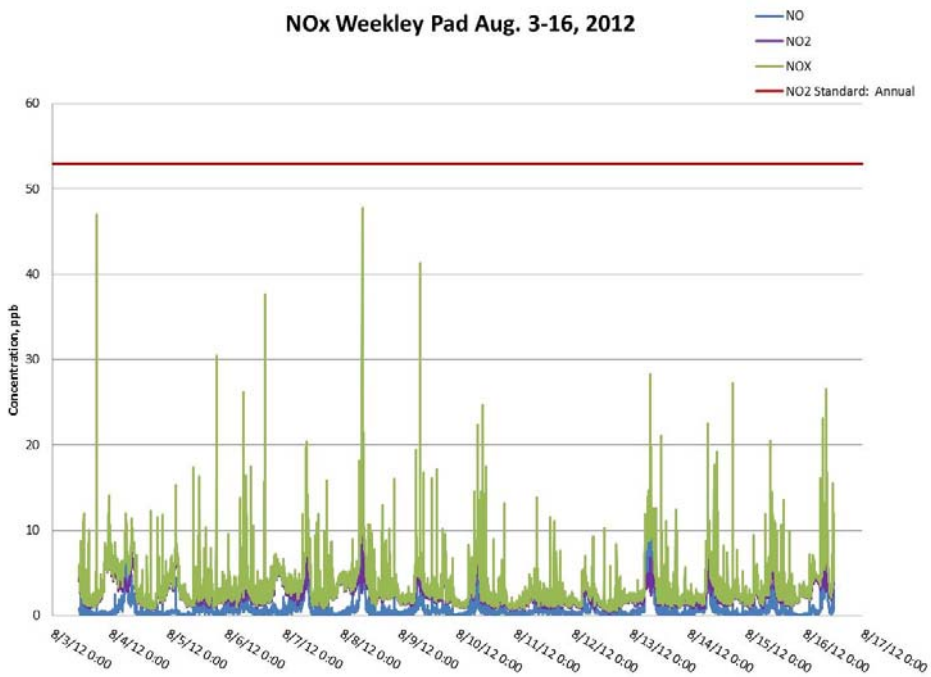

Figure 12: 1-minute average NO_x concentrations at the Weekley pad.

CH_4 and CO_2. The ambient CH_4 concentration at the Weekley pad averaged 2.0 ppm (±0.1 ppm) with an average isotopic composition of -51.1‰ (±1.3‰), which are typical background atmospheric values (Figures 13–14). During a period beginning at approximately August 3 at 1:30 a.m. to approximately 8:30 a.m. the CH_4 concentration averaged 9.7 ppm with an average $\delta^{13}C$ value of -39.2‰. The maximum concentration and most depleted isotopic signature were observed during this time (82.6 ppm and -36.9‰, respectively). The elevated CH_4 concentrations together with more enriched $\delta^{13}C$ values indicate a significant contribution from a thermogenic CH_4 source during this time. The wells were being flowed back (flared) from August 3–18. During the time that thermogenic CH_4 was detected, the conditions were particularly stagnant with wind speeds less than 1 m/s. Therefore, what was observed may not have been plume interception but a buildup of CH_4 from the well pad with slow dispersion due to the stagnant conditions. For the remainder of the monitoring period at this site, the CH_4 concentration was near ambient levels, exceeding 5 ppm on only two occasions.

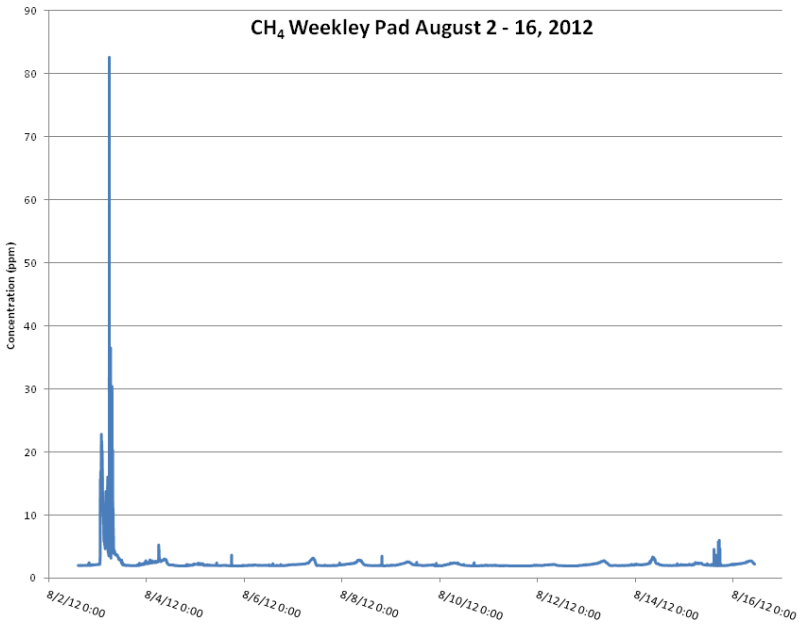

Figure 13: 1-minute average CH_4 concentrations at the Weekley pad.

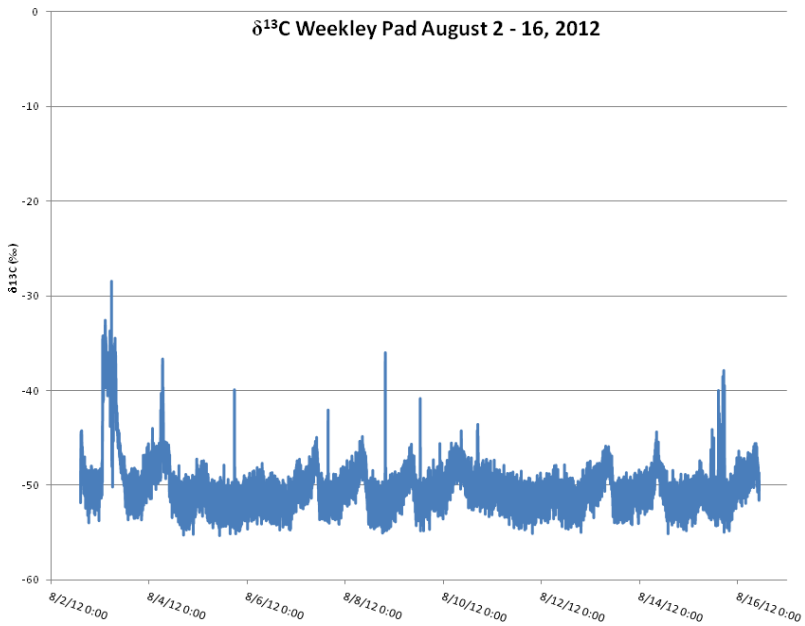

Figure 14: 1-minute average $\delta^{13}C$ of CH_4 at the Weekley pad.

Over the 2 weeks of monitoring at the Weekley pad site, the CO_2 concentration averaged 405 ppm (±27 ppm) with $\delta^{13}C$ averaging -12.1‰ (±1.4‰) (Figure 15). The maximum CO_2 concentration at the site was 478 ppm with a corresponding $\delta^{13}C$ value of -13.9‰. The CO_2 concentrations and $\delta^{13}C$ values at the site cycled daily. Starting at approximately 8 p.m., the CO_2 concentration increased sharply to values occasionally greater than 450 ppm before dropping back to near ambient levels by 7 a.m. During these times, the corresponding $\delta^{13}C$ values become more depleted, approaching -14‰.

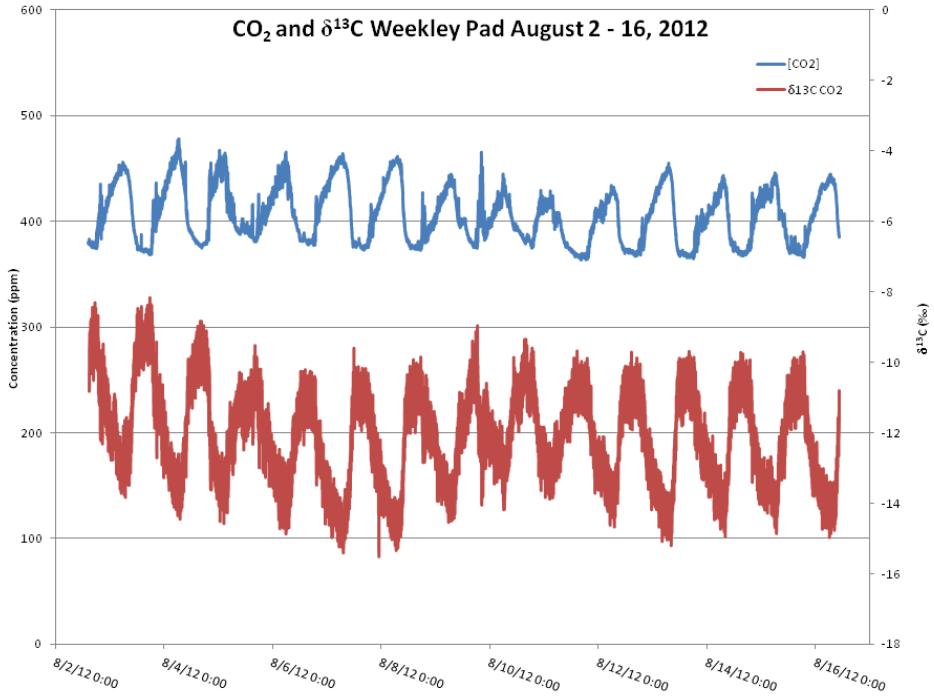

Figure 15: 1-minute average CO_2 concentrations and $\delta^{13}C$ of CO_2 at the Weekley pad.

PM_{10} and $PM_{2.5}$. Data are available for August 2–16 (Figure 16). At the Weekley pad, average PM_{10} concentration was 18 μg/m^3 and average $PM_{2.5}$ concentration was 12 μg/m^3. Maximum 1-hour average concentrations of PM_{10} and $PM_{2.5}$ were 109 μg/m^3 and 31 μg/m^3, respectively.

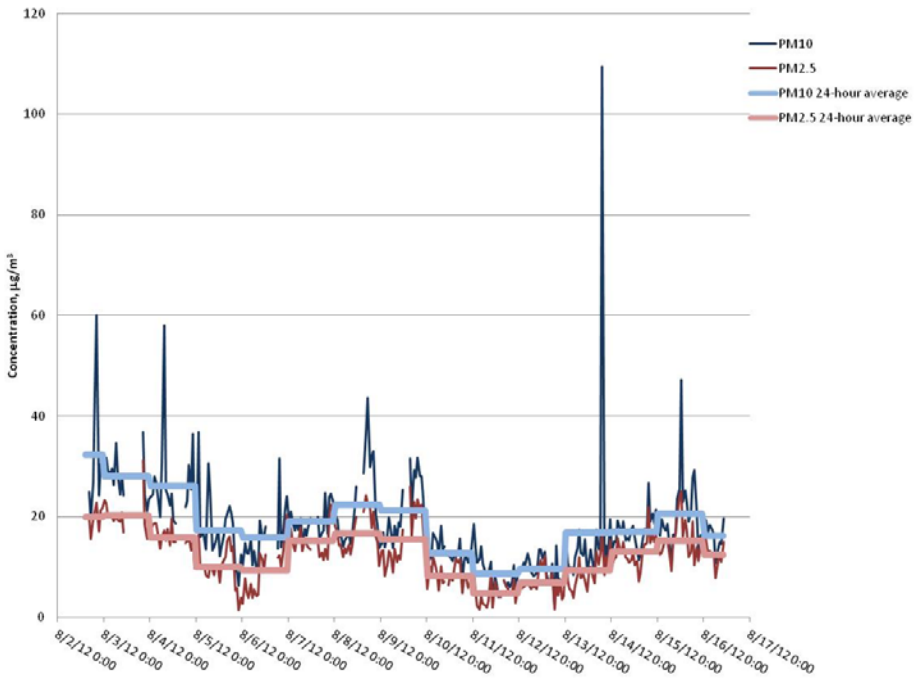

Figure 16: PM_{10} and $PM_{2.5}$ concentrations at the Weekley pad.

SO_2. Data for SO_2 are available for the entire monitoring period, August 3–16 (Figure 17). The average concentration of SO_2 at the Weekley pad was 2.7 ppb, with peaks not exceeding 27 ppb. One-hour averages ranged from 0.7–16.4 ppb. Similarly, calculating 3-hour averages from the 1-minute data results in a range of 1.1–12.4 ppb.

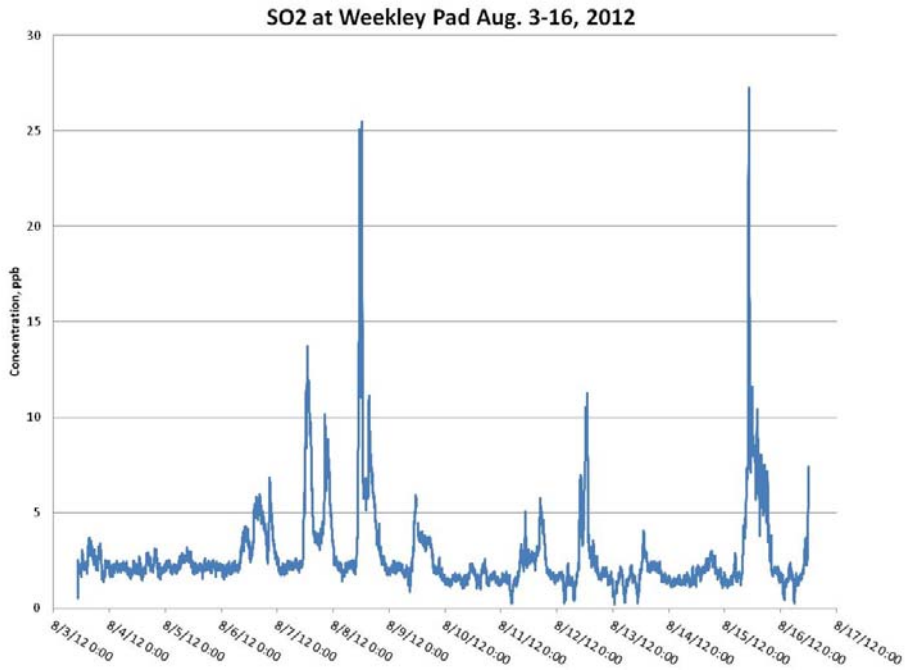

Figure 17: 1-minute average SO_2 concentrations for the Weekley pad.

Site Summary. At this site, there was one incidence of detection of thermogenic CH_4. Due to particularly stagnant conditions, what was likely observed was a buildup of CH_4 from the well pad with slow dispersion. The ethane concentration during this time was only slightly elevated; about 100 ppb compared to an average of 75 ppb. With one exception, concentrations for criteria pollutants measured were below NAAQS and VOCs were below PELs for the entire duration of monitoring at this site. There was one instance on August 8 where the 8-hour average ozone concentration was 78 ppb, 3 ppb higher than the national standard. On this date the air quality index in the region was classified as either moderate or unhealthy for sensitive groups, so the elevated ozone concentration measured at the site was reflective of regionally high ozone levels and not from the activity at the site (AIRNow, 2014). Due to the unfavorable wind speed and direction for the 2 weeks of monitoring at this site, it was not feasible to adequately evaluate the impact of the flowback/flaring that occurred.

3.3 MILLS WETZEL PAD #2

The mobile air monitoring laboratory was moved to the Mills Wetzel pad #2 site in southern Wetzel County on August 16, 2012. The laboratory was located approximately 190 m southwest of the well pad on the side of a gravel well pad access road with coordinates of 39°31'16.34"N, 80°39'24.82"W. As there was no available electric service at this site, the laboratory was operated using a diesel fuel-powered generator provided by Stone Energy. The generator was approximately 21 m from the laboratory in the approximate direction of the well pad and therefore, its emissions may have mixed with emissions coming from the well pad, as measured by the monitoring equipment. Also, earth-moving equipment was in use for pipeline construction less than 100 m from the laboratory. After unpacking, installing, and calibrating, all instruments were fully operational and collecting data on August 17. Monitoring at this site ended on August 24, 2012. The operator was engaged in well stimulation activities during this time. Figure 18 shows a wind rose and histogram for the wind direction and speed during monitoring at the Mills-Wetzel pad #2 location. Wind speed was typically very low, with calm conditions 77% of the time. When there was wind, it was most frequently blowing from the north and sometimes from directly west. At almost all times the laboratory was either monitoring during stagnant conditions or was not directly downwind of the well pad. Figures for other measured meteorological parameters (temperature, relative humidity, rainfall, and solar intensity) are included in Appendix B.

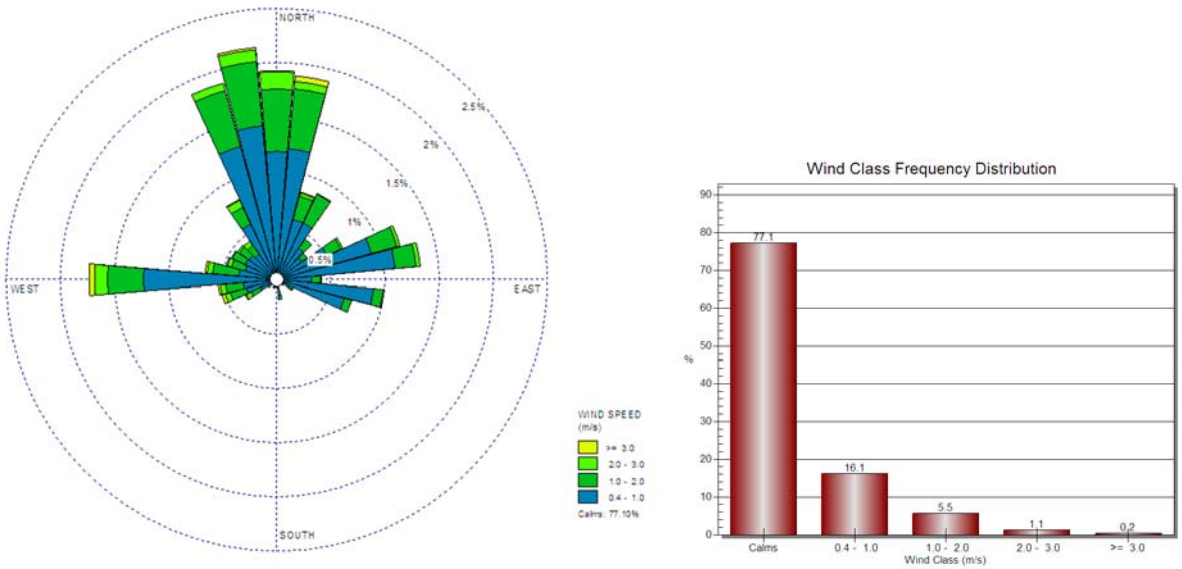

Figure 18: Wind rose and histogram for wind direction and speed during monitoring at the Mills-Wetzel pad #2 location. For the wind rose, radial axis is percent of the time that the wind was coming from a particular direction.

VOCs. At this site the analyzer ran continuously for the entire monitoring period from August 17–24 for a total of 144 samples. Table 4 lists the average concentration, standard deviation, minimum and maximum concentrations, and frequency of detection for compounds that were detected in at least 10% of the samples. Alkanes were detected in 100% of the samples with other compounds being detected less frequently.

Table 4: VOCs concentrations for the Mills-Wetzel pad #2

Compound	Average (ppb)	Standard Deviation (ppb)	Minimum (ppb)	Maximum (ppb)	Frequency of Detection (%)
Hexane	1.8	2.6	0.0	13.0	56
n-heptane	0.4	0.9	0.0	5.4	22
Methylcyclohexane	0.5	1.0	0.0	5.8	24
Toluene	1.0	1.6	0.0	10.7	44
Ethane	56.2	43.1	7.8	271.7	100
Ethylene	0.6	1.1	0	6.1	34
Propane	33.4	27.0	6.3	168.8	100
Isobutane	9.0	6.9	1.1	40.7	100
n-butane	16.3	13.1	3.9	79.5	100
Isopentane	10.9	10.1	2.1	68.7	100
n-pentane	7.6	6.7	0.7	40.3	100
2-methylpentane	2.2	2.4	0.0	13.1	69
3-methylpentane	1.2	1.8	0.0	9.2	46
Isoprene	5.2	4.7	0.0	21.4	68

Ozone. Ozone data are available for the entire monitoring period at this site, August 17–24 (Figure 19). The average ozone concentration using 1-minute data at the Mills-Wetzel pad #2 was 46 ppb, and the maximum hourly average concentration was 71 ppb. Day-to-night variations were as high as 60 ppb. The 8-hour average ranged from 20–67 ppb.

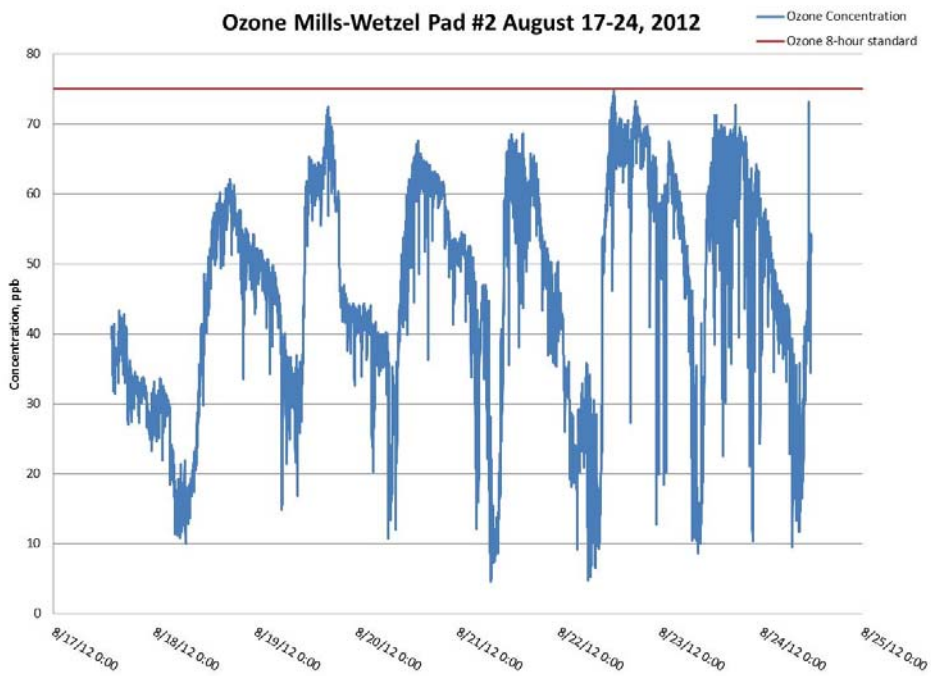

Figure 19: 1-minute average ozone concentrations at the Mills-Wetzel pad #2.

***NO_x*.** Data for NO_x are available for the entire monitoring period at the Mills-Wetzel pad site, August 17–24 (Figure 20). The average of the 1-minute NO_x concentration measurements was 7 ppb with an hourly average maximum of 38 ppb. The 1-hour average for NO_2 ranged from 0.77–24.2 ppb.

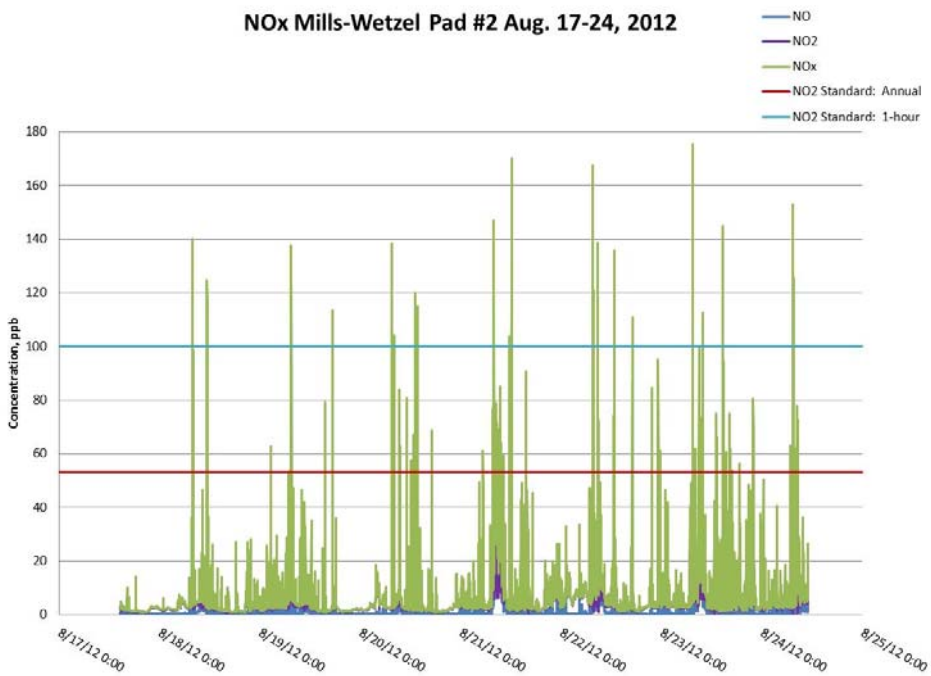

Figure 20: 1-minute average NO_x concentrations at the Mills-Wetzel pad #2.

CH_4 and CO_2. The ambient CH_4 concentration at the Mills-Wetzel pad #2 site averaged 2.0 ppm (±0.1) with an average isotopic composition of -46.8‰ (±1.2‰), which are typical background atmospheric values (Figures 21–22). For the duration of the 1-week monitoring period at this site, the CH_4 concentration was near ambient levels, exceeding 4 ppm on only two occasions. The maximum observed CH_4 concentration was 4.6 ppm with a $\delta^{13}C$ value of -46.0‰, indicating a very minor contribution from a thermogenic source.

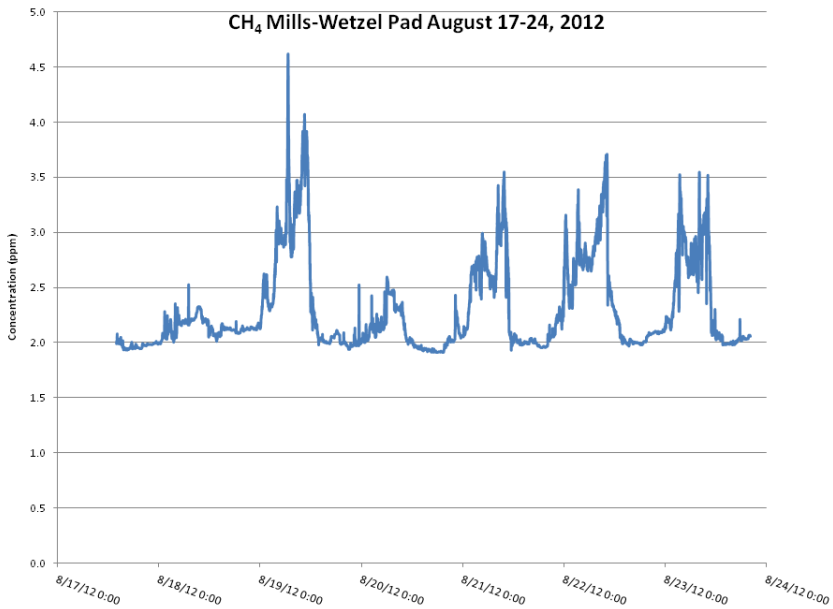

Figure 21: 1-minute average CH_4 concentrations at the Mills-Wetzel pad.

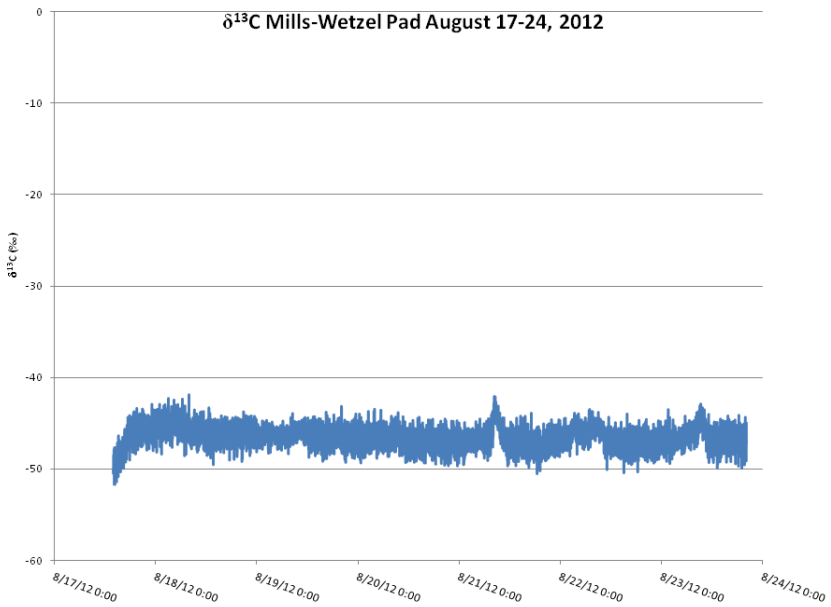

Figure 22: 1-minute average $\delta^{13}C$ of CH_4 at the Mills-Wetzel pad.

Over the 1 week of monitoring at the Mills Wetzel pad #2 site, the CO_2 concentration averaged 384 ppm (±13 ppm) with $\delta^{13}C$ averaging -10.8‰ (±1.0‰) (Figure 23). The maximum CO_2 concentration at the site was 509 ppm with a corresponding $\delta^{13}C$ value of -14.8‰. The CO_2 concentrations and $\delta^{13}C$ values at the site cycled daily. Starting at approximately 8 p.m., the CO_2 concentration increased gradually to values occasionally greater than 410 ppm before dropping back to near ambient levels by 7 a.m. During these times, the corresponding $\delta^{13}C$ values become more depleted, approaching -12‰.

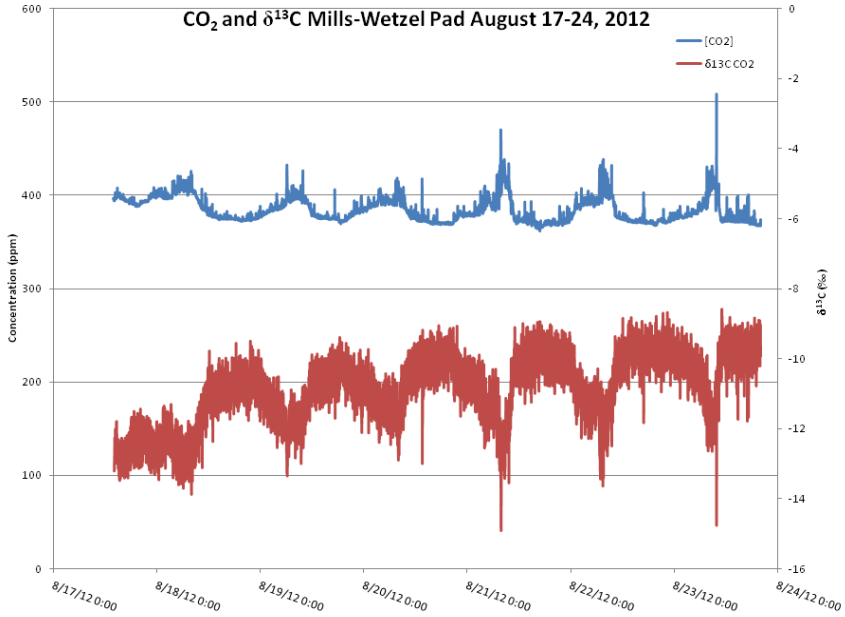

Figure 23: 1-minute average CO_2 concentrations and $\delta_{13}C$ of CO_2 at the Mills-Wetzel pad.

PM_{10} and $PM_{2.5}$. Data are available for August 17–24 (Figure 24). At the Mills-Wetzel pad, average PM_{10} concentration was 30 μg/m^3 and average $PM_{2.5}$ concentration was 12 μg/m^3. Maximum 1-hour average concentrations of PM_{10} and $PM_{2.5}$ were 546 μg/m^3 and 36 μg/m^3, respectively. The substantial peaks in PM_{10} concentration at this site were likely due to the mobile air monitoring laboratory's position on the side of a gravel well pad access road as well as the nearby earth-moving activity for pipeline construction.

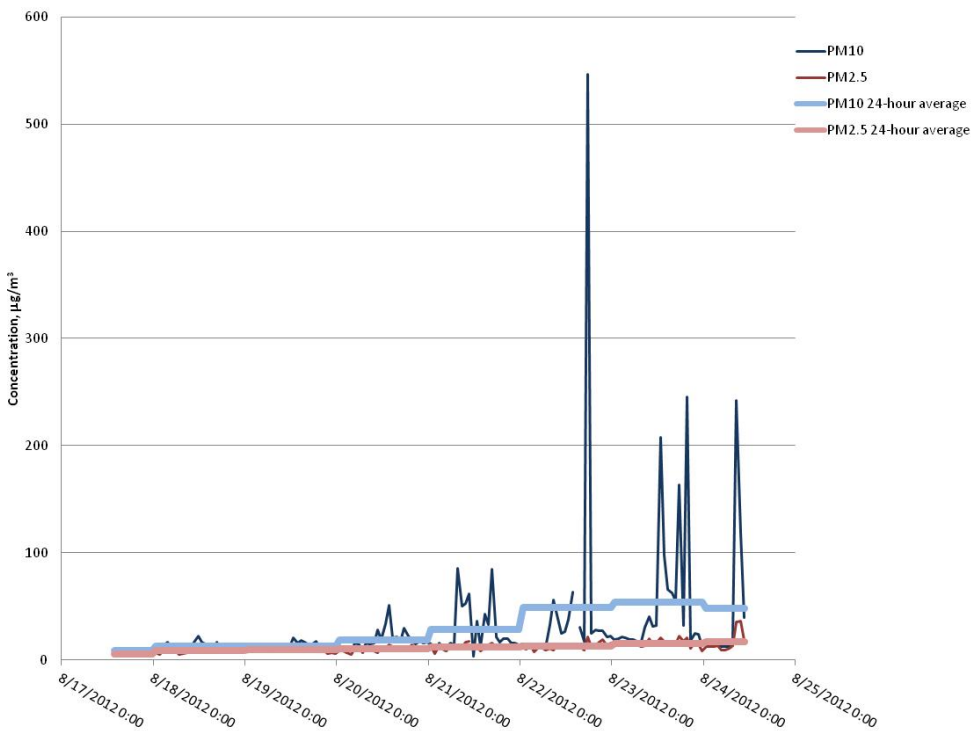

Figure 24: 1-hour average PM_{10} and $PM_{2.5}$ concentrations at the Mills-Wetzel pad #2.

SO_2. Data for SO_2 are available for the entire monitoring period, August 17–24 (Figure 25). The average concentration of SO_2 at the Weekley pad was 3.0 ppb, with peaks not exceeding 17 ppb. One-hour averages ranged from 1.4–9.5 ppb. Similarly, calculating 3-hour averages from the 1-minute data results in a range of 1.6–8.4 ppb.

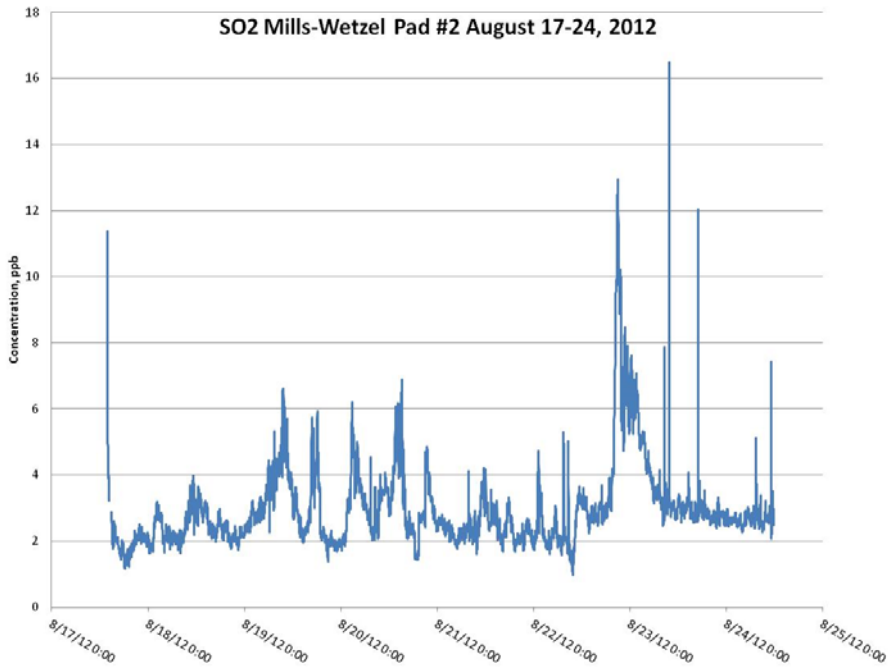

Figure 25: 1-minute average SO_2 concentrations for the Mills-Wetzel pad #2.

Site Summary. At this site, there was no evidence of thermogenic CH_4 and concentrations were always less than 5 ppb. Concentrations for criteria pollutants measured were below NAAQS. There were many incidences of short-lived peaks in NO_x concentrations but due to the proximity of both the diesel generator used to power the laboratory and the equipment used for pipeline construction nearby, distinction between these emissions and the activity on the well pad is not easily possible. Average VOCs concentrations were reflective of background air quality and were below PELs for the entire duration of monitoring at this site. Due to the unfavorable wind speed and direction for the 1 week of monitoring at this site as well as the potential for picking up emissions from the diesel generator and pipeline construction equipment, it was not feasible to adequately evaluate the impact of the well stimulation activities that occurred.

3.4 MAURY PAD

The laboratory was deployed to the Maury pad site near New Martinsville, WV in western Wetzel County on August 24, 2012. The laboratory was located approximately 190 m northeast of the well pad on the side of a gravel well pad access road with coordinates of 39°37'5.48"N, 80°46'57.45"W. As there was no available electric service at this site, the laboratory was operated using a diesel fuel-powered generator provided by Stone Energy. The generator was approximately 5 m from the laboratory in the opposite direction of the well pad. After unpacking, installing, and calibrating, some instruments were fully operational and collecting data on August 24. The remaining instruments were calibrated and began collecting data on August 29. Hydraulic fracturing operations began on August 30 and ended on September 14, with a break in operations September 1–3 for the Labor Day holiday. From September 15–18, frac equipment was moved out and a service rig and snubbing unit were moved in and rigged up for plug drillouts. From September 15–25, the operator was conducting drillout operations and running of production tubing. For a 30-hour period September 25–26, one well was opened to flowback (flared). Monitoring at this site ended on September 26, 2012. Figure 26 shows a wind rose and histogram for the wind direction and speed during monitoring at the Maury pad location. Wind speed was typically very low, with calm conditions 82% of the time. When there was wind, it was most frequently blowing from the south. At almost all times the laboratory was either monitoring during stagnant conditions or was almost directly downwind of the well pad. Figures for other measured meteorological parameters (temperature, relative humidity, rainfall, and solar intensity) are included in Appendix B.

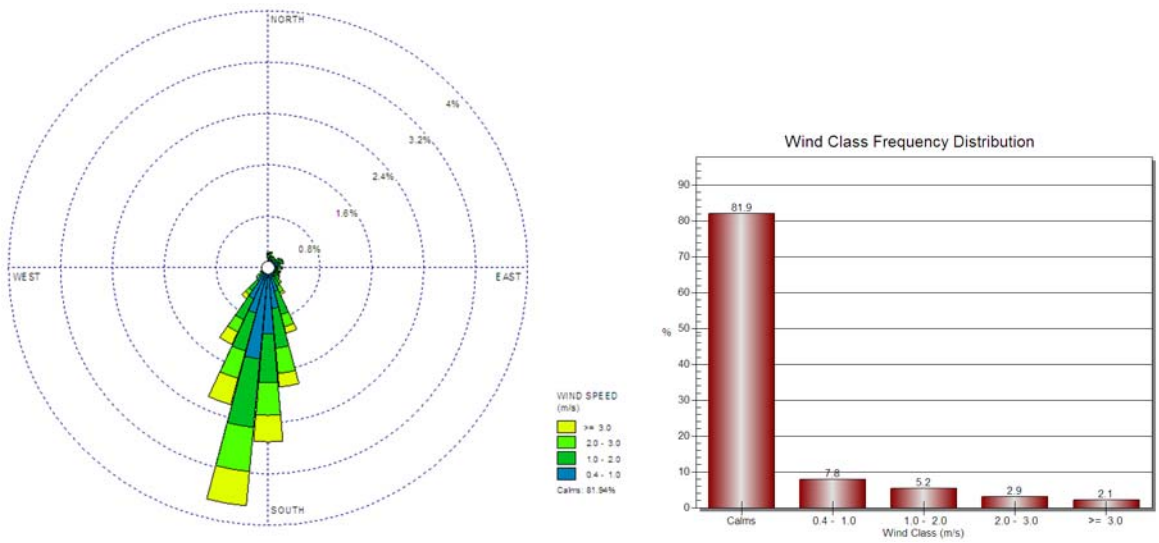

Figure 26: Wind rose and histogram for wind direction and speed during monitoring at the Maury pad location. For the wind rose, radial axis is percent of the time that the wind was coming from a particular direction.

VOCs. At this site the analyzer ran continuously from August 29–September 29. However, there were a large number of samples that had to be discarded due to moisture entering the gas chromatograph columns that caused an unstable baseline in the chromatograms, including all of the samples collected after the morning of September 23. Table 5 lists the average concentration, standard deviation, minimum and maximum concentrations, and frequency of detection for compounds that were detected in at least 10% of the samples. The VOCs analyzer has two columns; one is for the lighter hydrocarbons and one is for the heavier hydrocarbons. In Table 4, for the lighter hydrocarbons ethane-isporene, there were a total of 535 samples with data for August 29–September 23. For the heavier compounds hexane-undecane, there were 353 samples, with intermittent periods of invalid data.

Table 5: VOCs concentrations for the Maury pad

Compound	Average (ppb)	Standard Deviation (ppb)	Minimum (ppb)	Maximum (ppb)	Frequency of Detection (%)
Hexane	1.2	2.9	0.0	28.2	37
n-heptane	0.3	1.2	0.0	14.2	11
Methylcyclohexane	0.2	0.8	0.0	7.0	10
Toluene	0.3	0.7	0.0	4.3	17
Nonane	0.2	0.7	0.0	3.8	12
Decane	0.4	1.0	0.0	6.9	16
Undecane	0.3	0.8	0.0	5.2	15
Ethane	40.2	62.1	3.3	840.5	100
Ethylene	1.7	1.4	0.0	8.7	74
Propane	24.1	31.3	0.0	453.3	100
Isobutane	6.4	6.5	0.0	72.0	96
n-butane	11.3	13.9	0.0	184.0	99
Isopentane	5.9	6.2	0.0	64.3	96
n-pentane	5.1	5.7	0.0	59.2	95
2-methylpentane	1.0	1.7	0.0	14.8	42
3-methylpentane	0.5	1.2	0.0	11.2	28
Isoprene	4.0	3.6	0.0	17.7	76

Ozone. Ozone data are available for most of the monitoring duration at this site, August 24–September 26, with a gap in the data from September 15–18 due to a power outage (Figures 27–31). The average ozone concentration using 1-minute data at the Maury pad was 21 ppb, and the maximum hourly average concentration was 76 ppb. Day-to-night variations ranged from 30–70 ppb. The 8-hour average ranged from 2–69 ppb.

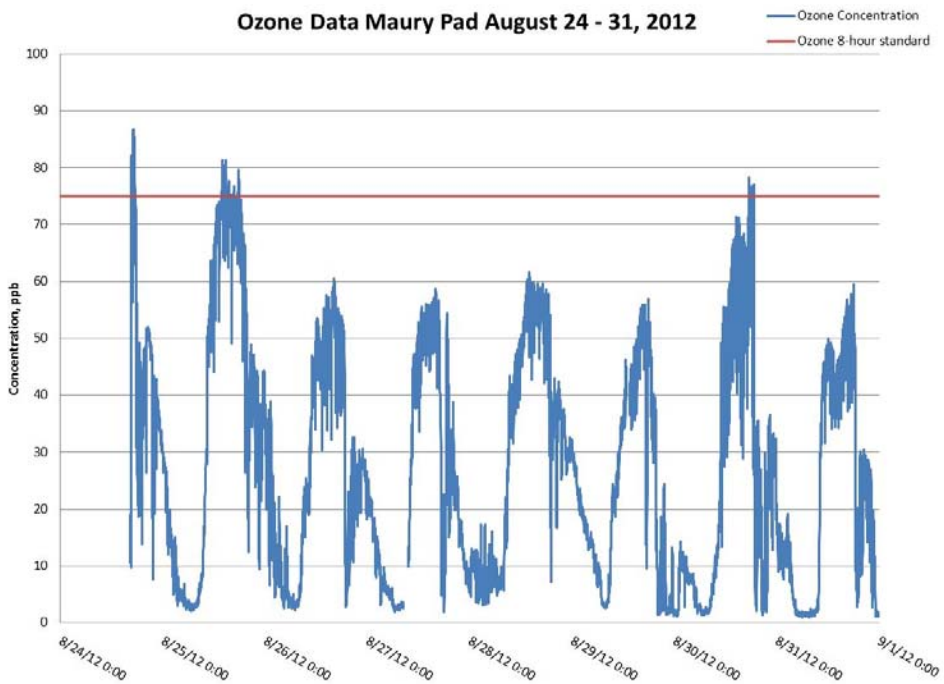

Figure 27: 1-minute average ozone concentrations for the first week at the Maury pad.

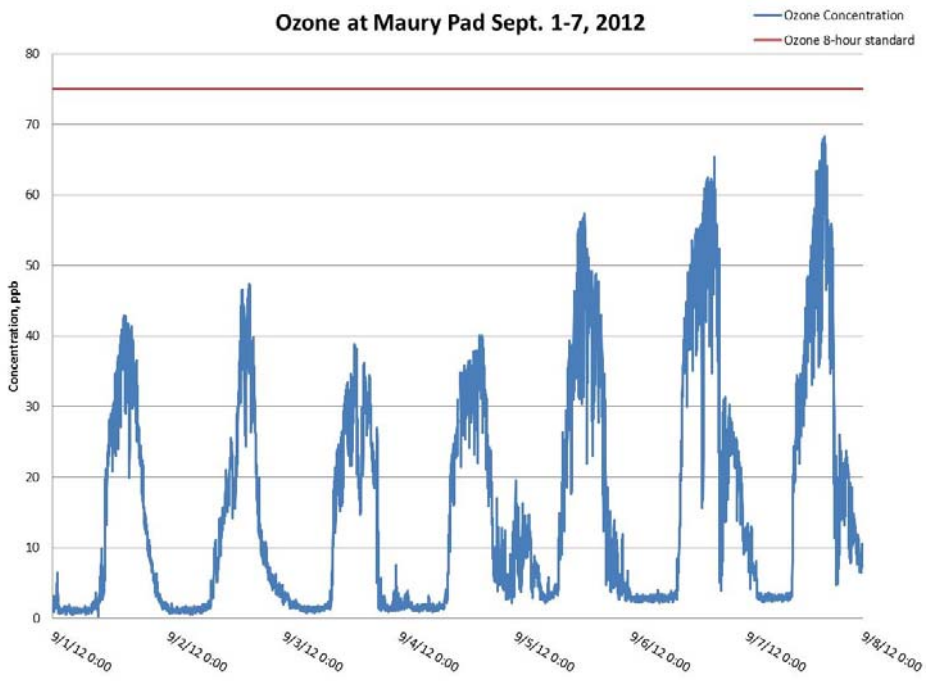

Figure 28: 1-minute average ozone concentrations for the second week at the Maury pad.

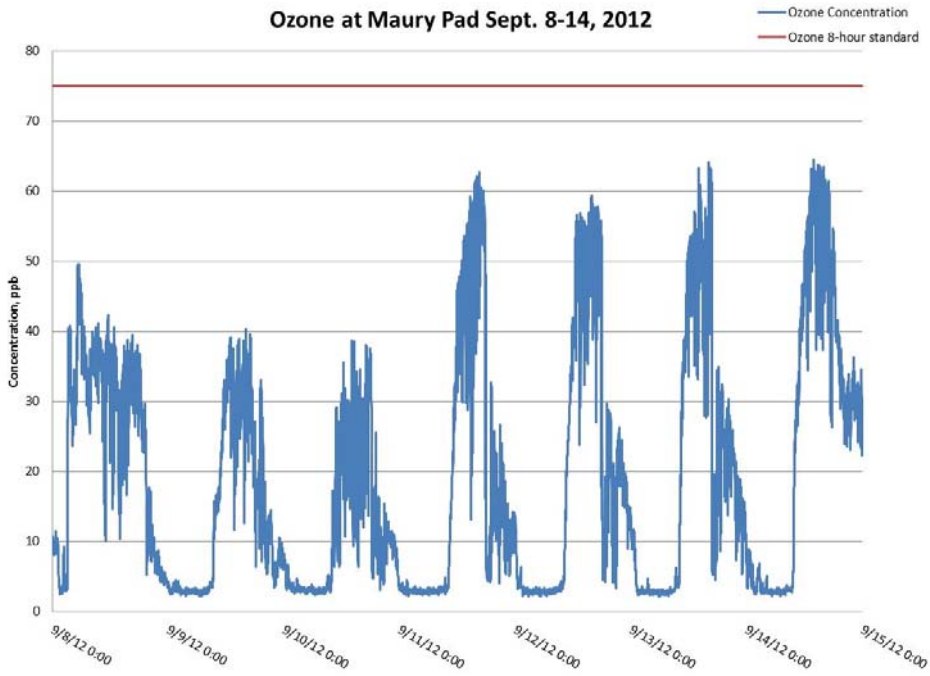

Figure 29: 1-minute average ozone concentrations for the third week at the Maury pad.

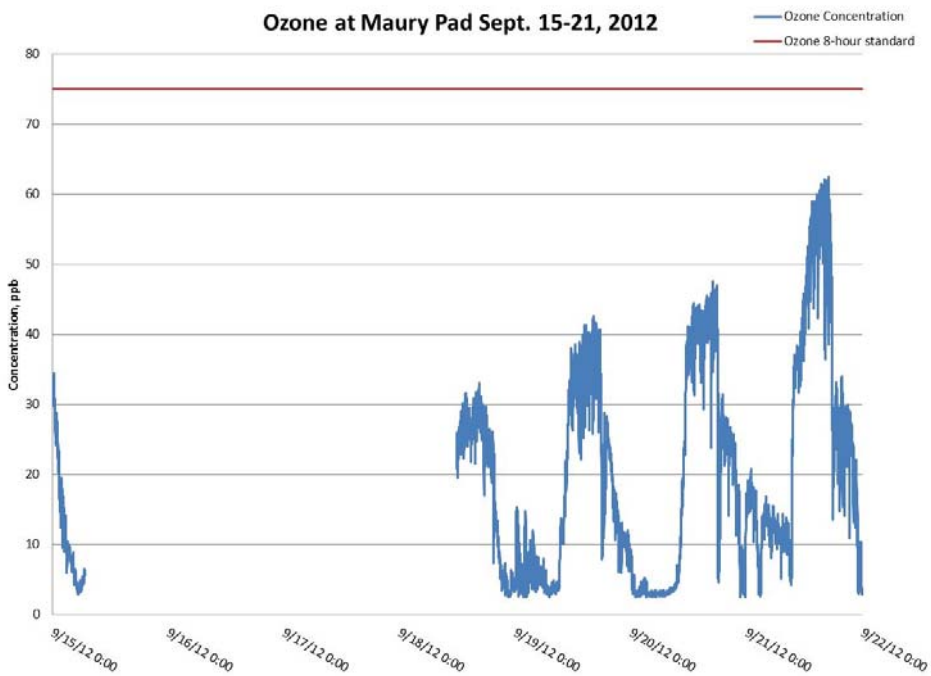

Figure 30: 1-minute average ozone concentrations for the fourth week at the Maury pad.

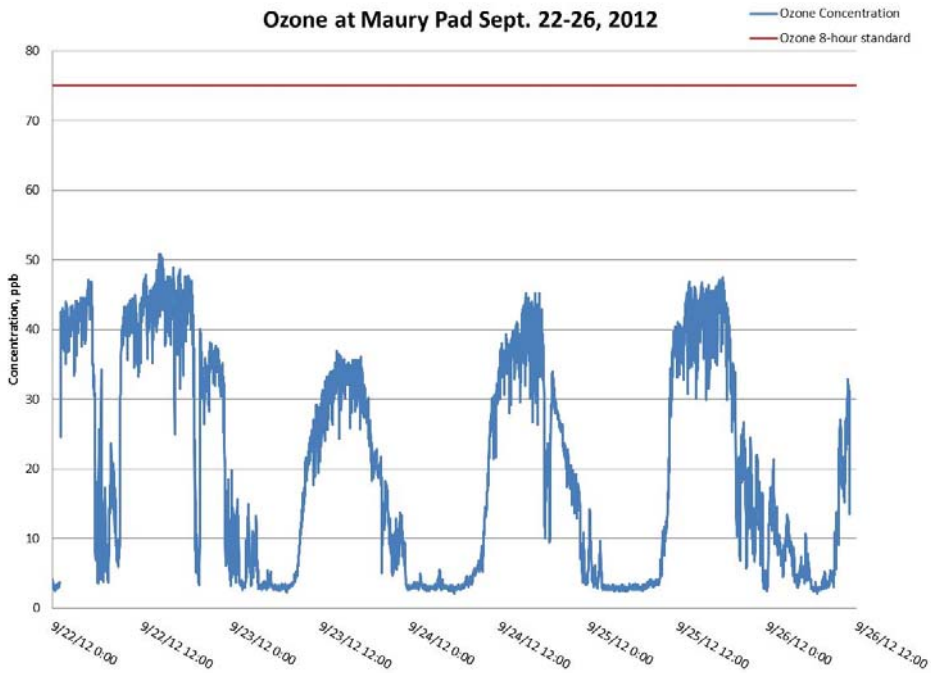

Figure 31: 1-minute average ozone concentrations for the fifth week at the Maury pad.

Maury Pad. NO_x data for the Maury pad site are available for the entire monitoring duration, August 24–September 26, with the exception of a period from September 15–18 (Figures 32–36). During this time a software glitch froze up the computer and prevented data from being recorded. The average of the 1-minute measurements at the Maury pad site was 23 ppb with an hourly average maximum of 138 ppb. The 1-hour average for NO_2 ranged from 0.66–52.7 ppb.

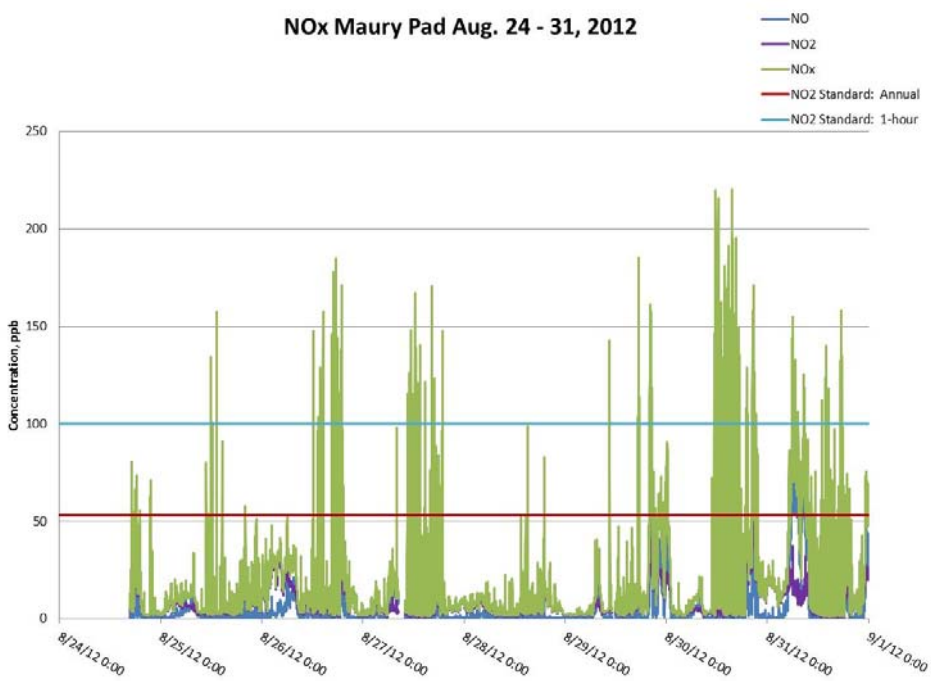

Figure 32: 1-minute average NO_x concentrations for the first week at the Maury pad.

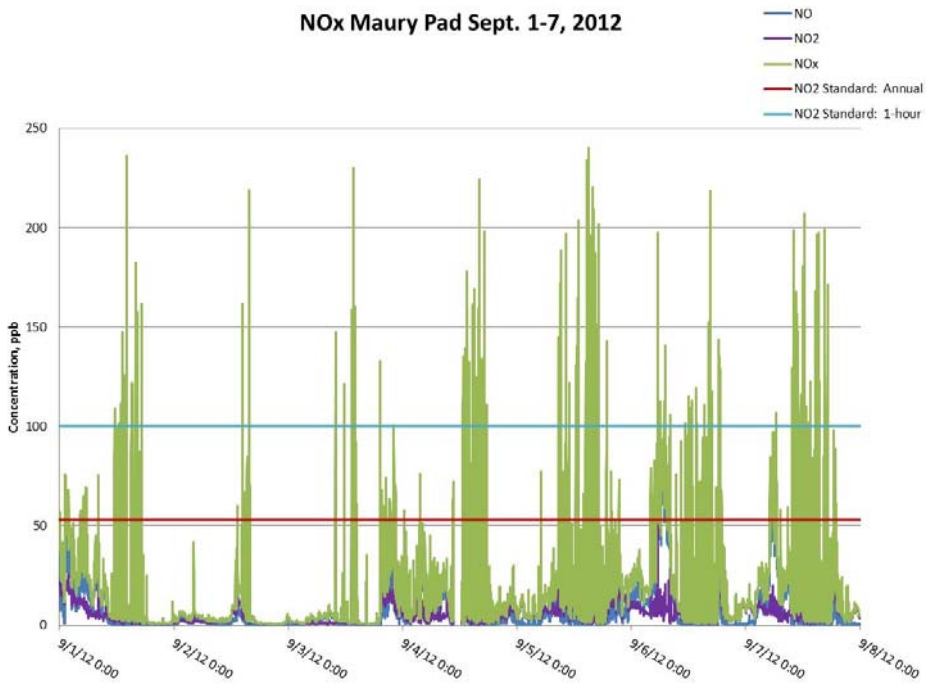

Figure 33: 1-minute average NO_x concentrations for the second week at the Maury pad.

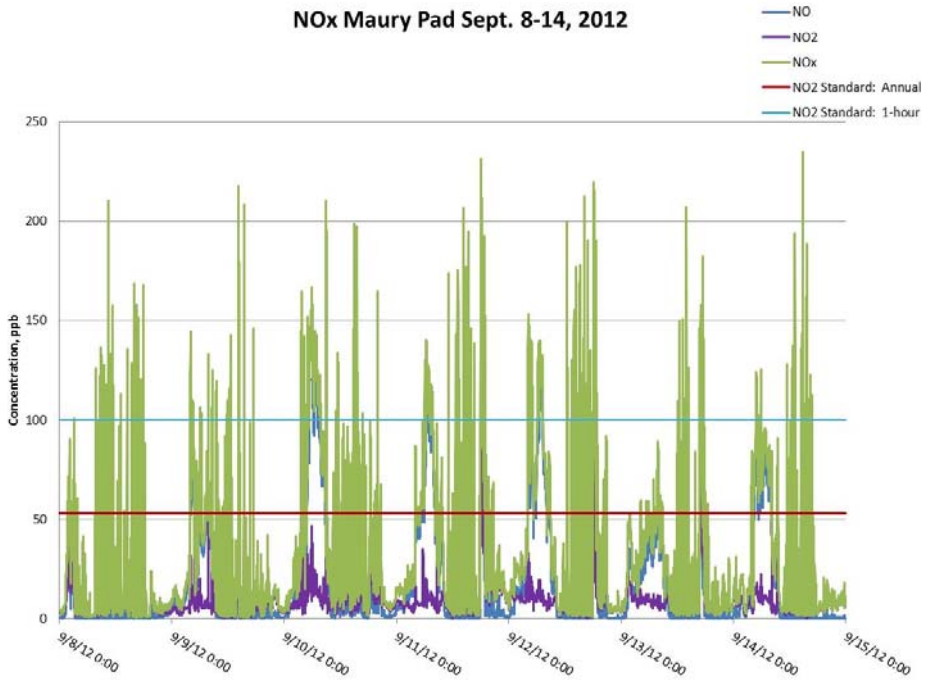

Figure 34: 1-minute average NO_x concentrations for the third week at the Maury pad.

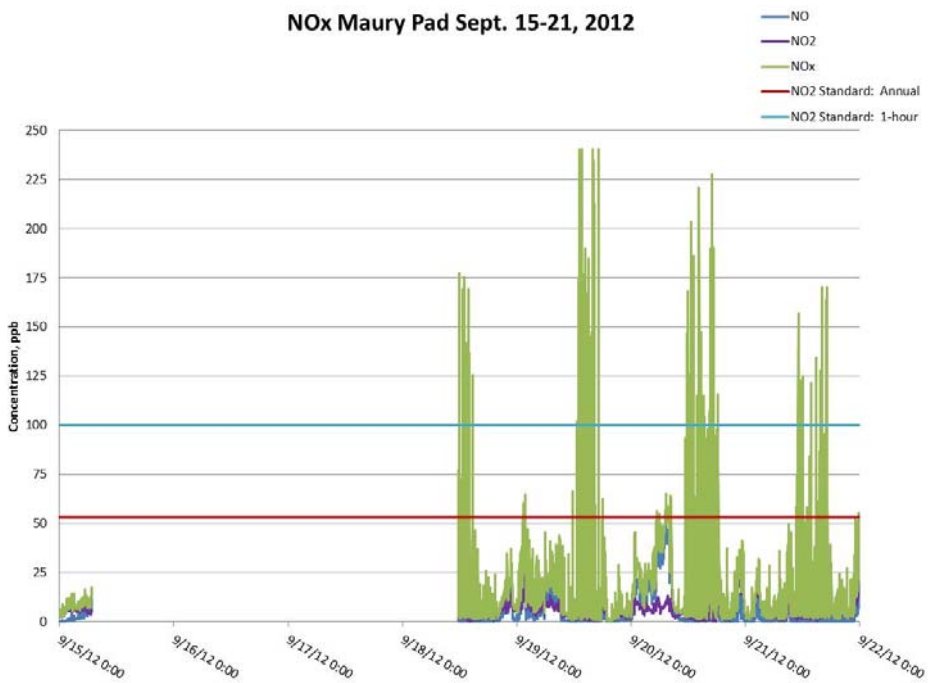

Figure 35: 1-minute average NO_x concentrations for the fourth week at the Maury pad.

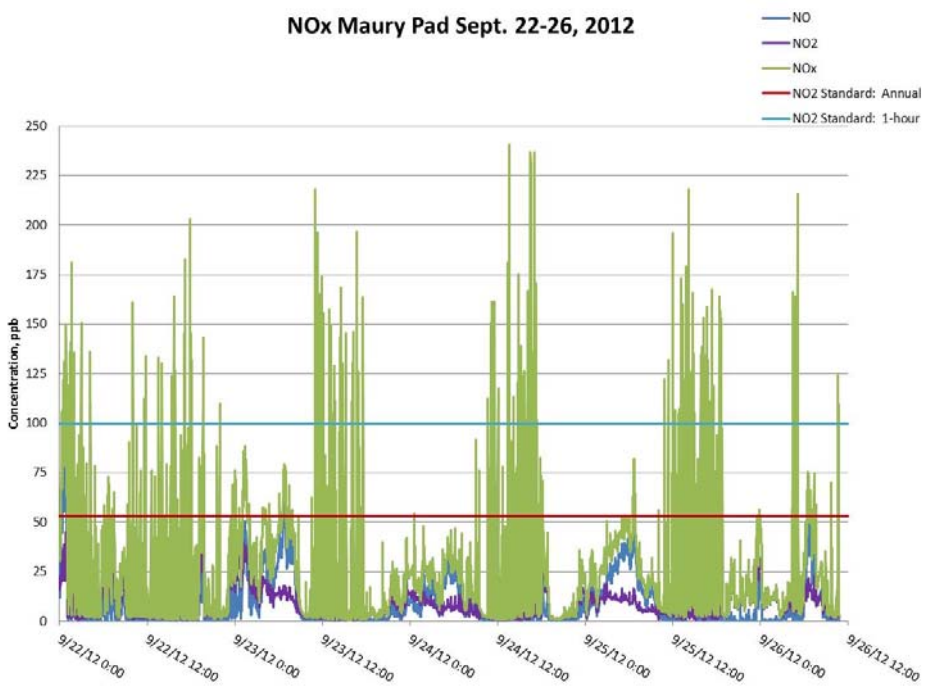

Figure 36: 1-minute average NO_x concentrations for the fifth week at the Maury pad.

CH_4 and CO_2. The ambient CH_4 concentration at the Maury pad averaged 2.0 ppm (±0.1 ppm) with an average isotopic composition of -49.4‰ (±1.7‰), which are typical background atmospheric values (Figures 37–40). For the majority of the 4-week monitoring period at this site, the CH_4 concentration was near ambient levels, exceeding 5 ppm on only four occasions. The maximum observed CH_4 concentration was 40.8 ppm on August 30. Unfortunately, the corresponding $\delta^{13}C$ value is not available due to an instrument error. For concentrations greater than 5 ppm (n=50), however, the $\delta^{13}C$ averaged -41.5‰ (±1.5‰) reflecting a significant contribution from a thermogenic source. The CH_4 peak on September 7 occurred during hydraulic fracturing operations, which ran from August 30–September 14. The CH_4 peak on September 23 occurred while the operator was running production tubing. The elevated CH_4 concentration on September 26 corresponds to the 30-hour time period that one of the wells was opened to flowback (flared).

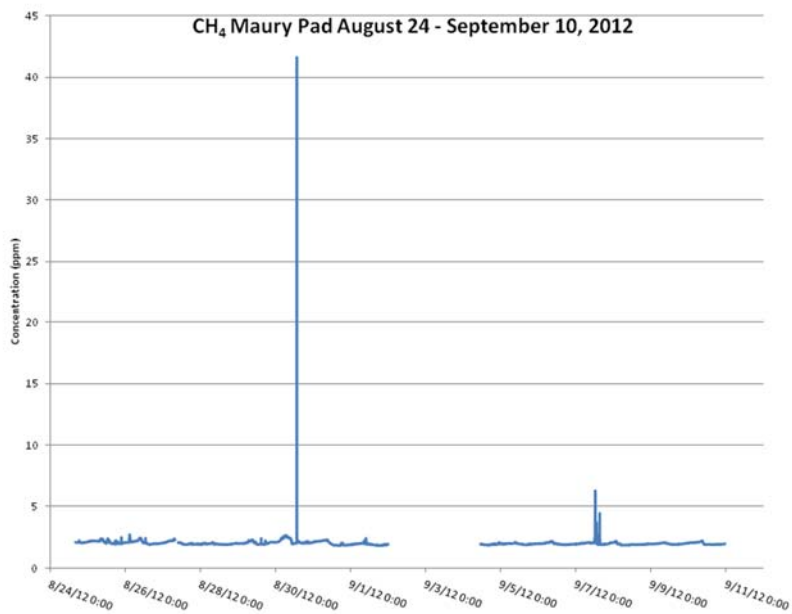

Figure 37: 1-minute average CH_4 concentrations at the Maury pad, August 24–September 10.

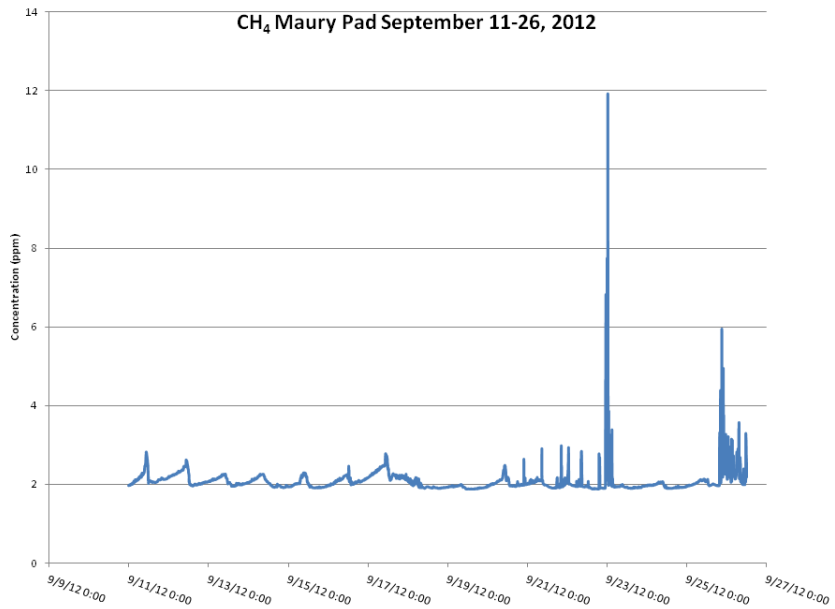

Figure 38: 1-minute average CH_4 concentrations at the Maury pad, September 11–26.

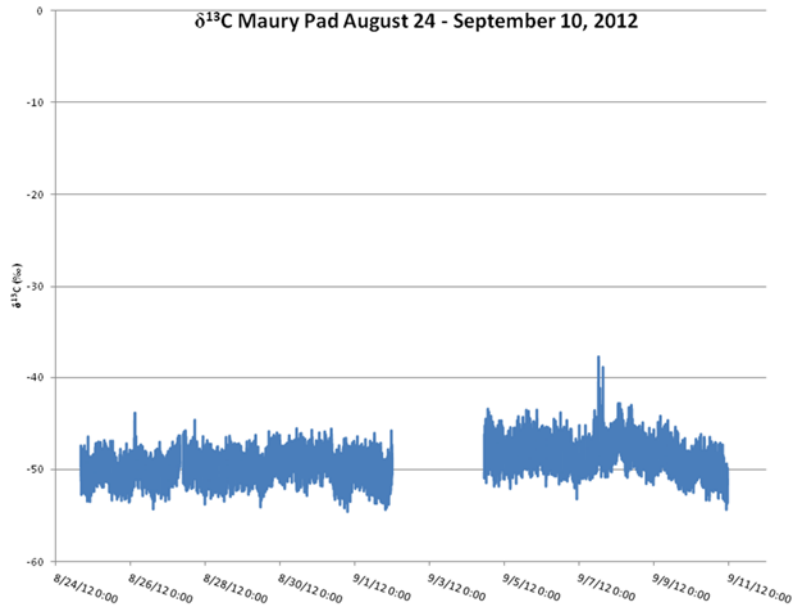

Figure 39: 1-minute average $\delta^{13}C$ of CH_4 at the Maury pad, August 24–September 10.

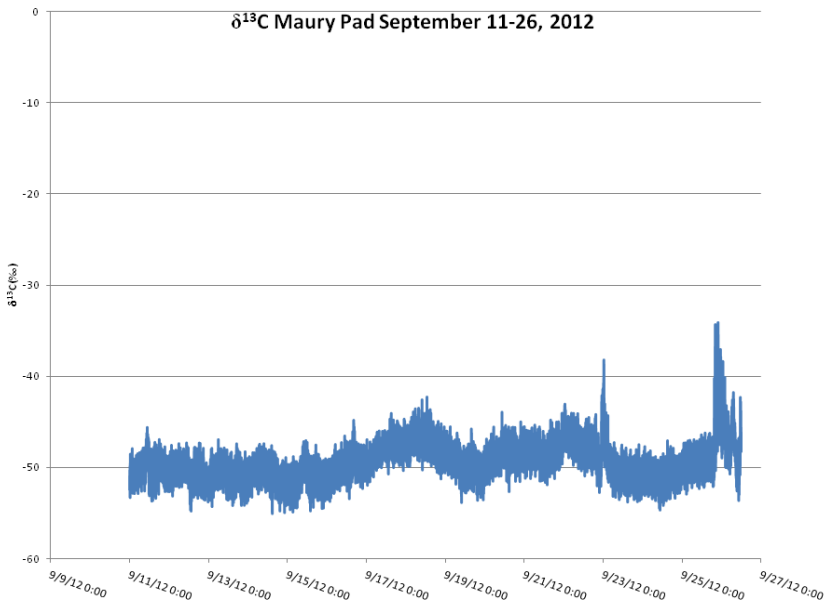

Figure 40: 1-minute average $\delta^{13}C$ of CH_4 at the Maury pad, September 11–26.

Over the 4 weeks of monitoring at the Maury pad site, the CO_2 concentration averaged 414 ppm (±30 ppm) with $\delta^{13}C$ averaging -12.6‰ (±1.5‰) (Figures 41–42). The maximum CO_2 concentration at the site was 551 ppm with a corresponding $\delta^{13}C$ value of -16.7‰. The CO_2 concentrations and $\delta^{13}C$ values at the site cycled daily. Starting at approximately 8 p.m., the CO_2 concentration increased gradually to values typically greater than 450 ppm, and occasionally greater than 500 ppm, before dropping back to near ambient levels by 7 a.m. During these times, the corresponding $\delta^{13}C$ values become more depleted, approaching -14‰ and as occasionally as low as -16‰.

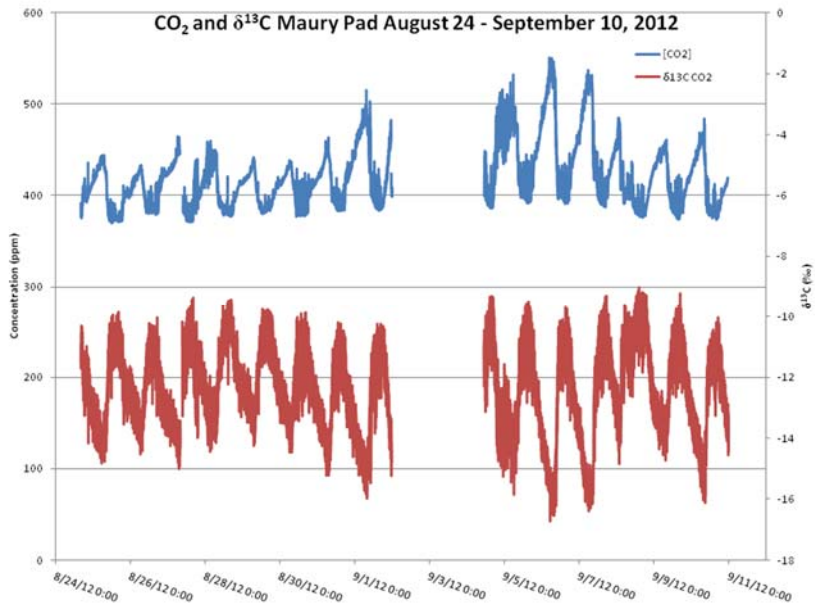

Figure 41: 1-minute average CO_2 concentrations and $\delta^{13}C$ of CO_2 at the Maury pad, August 24–September10.

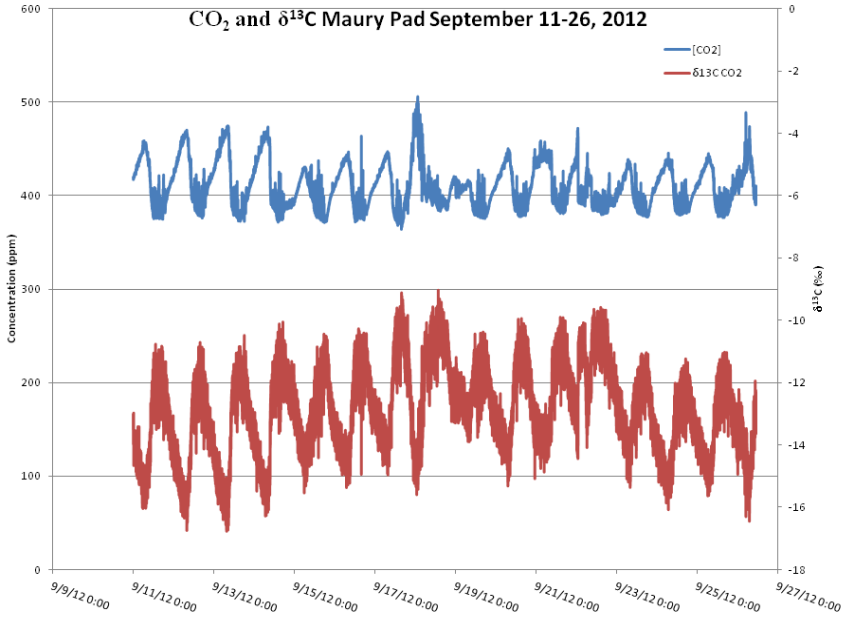

Figure 42: 1-minute average CO_2 concentrations and $\delta^{13}C$ of CO_2 at the Maury pad, September 11–26.

PM_{10} and $PM_{2.5}$. Data are available for August 24–September 26 (Figure 43). At the Maury pad, average PM_{10} concentration was 30 μg/m^3 and average $PM_{2.5}$ concentration was 12 μg/m^3. Maximum 1-hour average concentrations of PM_{10} and $PM_{2.5}$ were 768 μg/m^3 and 129 μg/m^3, respectively. The substantial peaks in PM_{10} concentration at this site were likely due to the mobile air monitoring laboratory's position on the side of a frequently traveled gravel well pad access road.

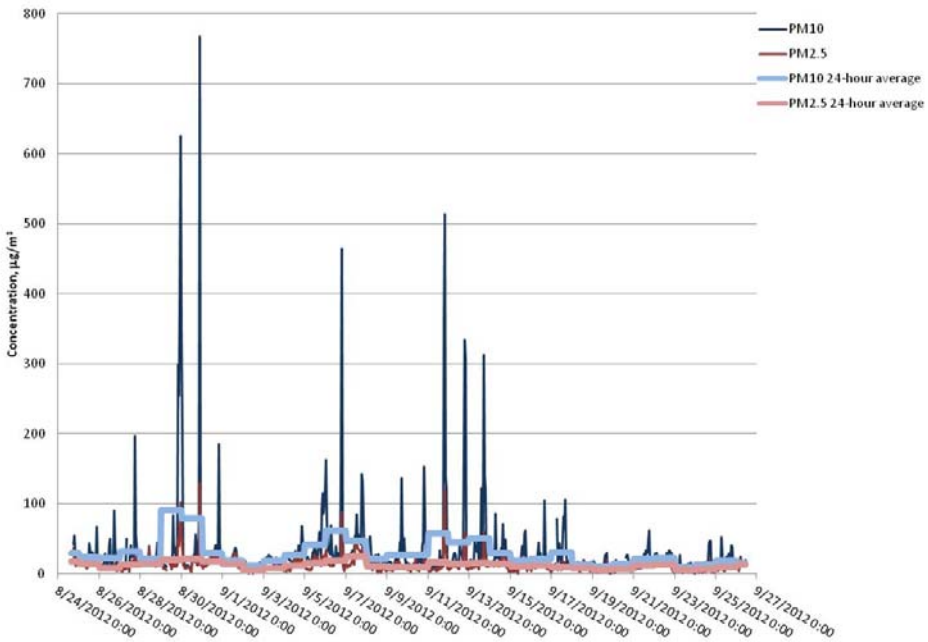

Figure 43: 1-hour average PM_{10} and $PM_{2.5}$ concentrations at the Maury pad.

SO_2. Data for SO_2 are available for the entire monitoring period, August 24–September 26 with the exception of a period from September 15–18 due to a computer software problem (Figures 44–48). The average concentration of SO_2 at the Maury pad was 2.3 ppb, with peaks not exceeding 13 ppb. One-hour averages ranged from 0.9–12.2 ppb. Similarly, calculating 3-hour averages from the 1-minute data results in a range of 1.1–9.6 ppb.

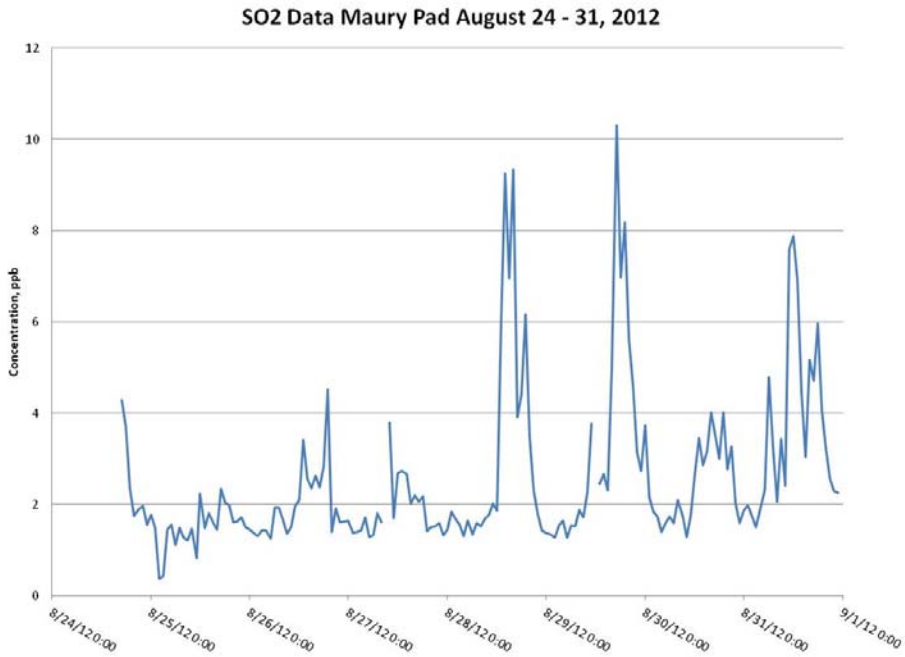

Figure 44: 1-minute average SO_2 concentrations for the Maury pad, August 24–31.

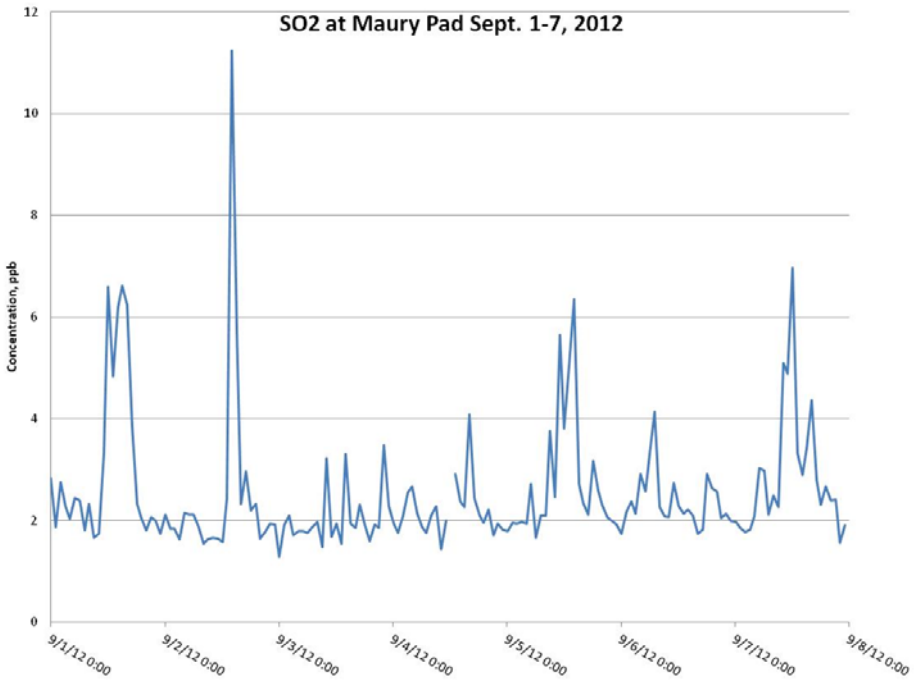

Figure 45: 1-minute average SO_2 concentrations for the Maury pad, September 1–7.

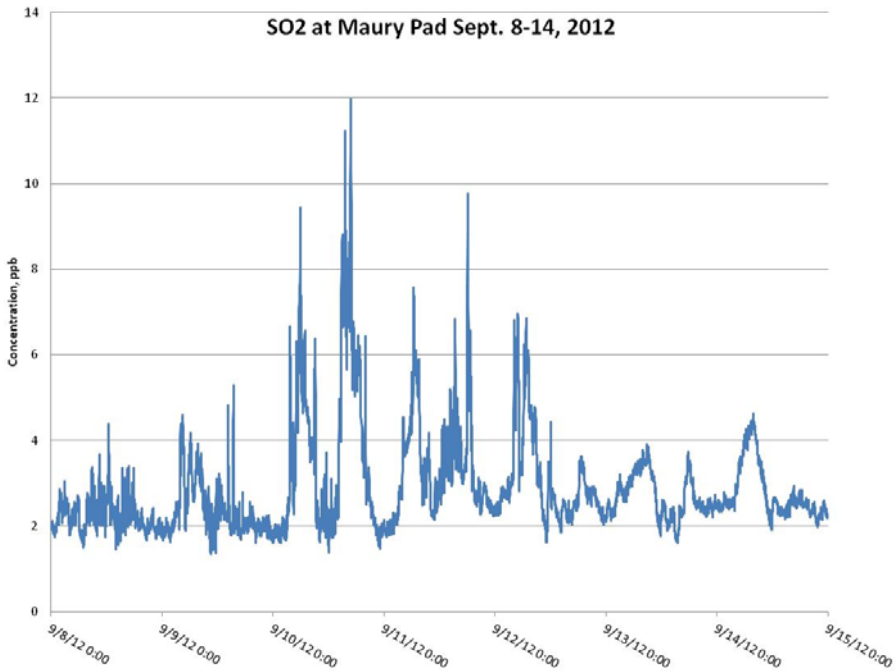

Figure 46: 1-minute average SO_2 concentrations for the Maury pad, September 8–14.

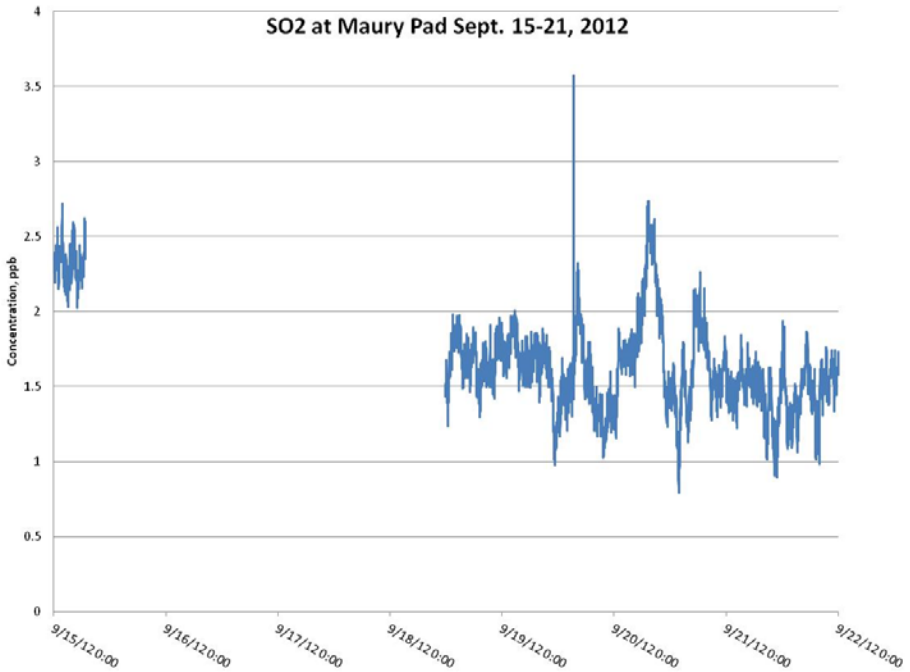

Figure 47: 1-minute average SO_2 concentrations for the Maury pad, September 15–21.

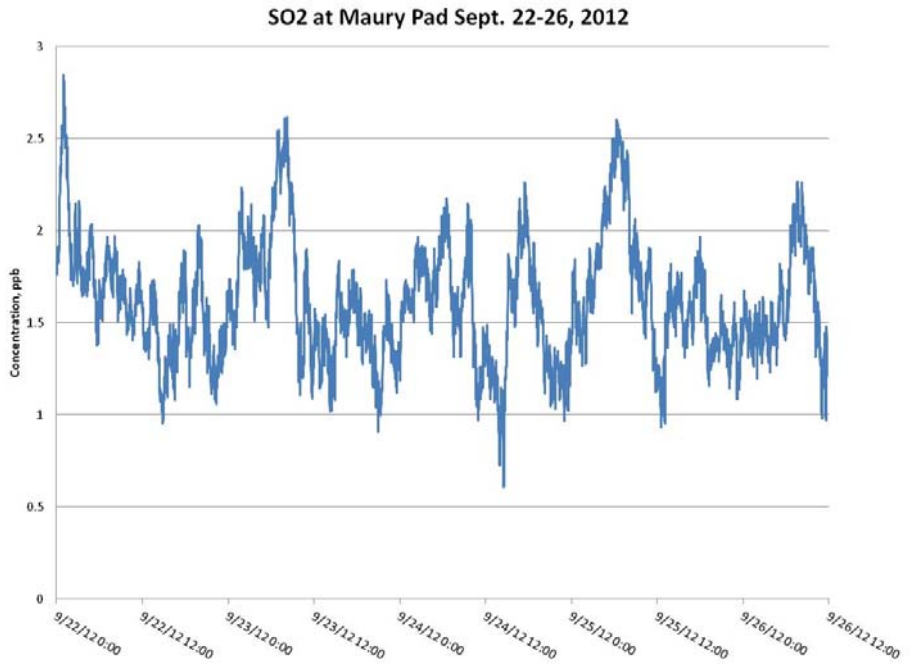

Figure 48: 1-minute average SO_2 concentrations for the Maury pad, September 22–26.

OC and EC. At the Maury pad, data are available for the entire monitoring period with the exception of September 15–18, when a software problem froze the computer and stopped the analysis (Figure 49). The data show high variability, with an average OC concentration of 2.7 μgC/m^3, ranging from 1.3–6.7 μgC/m^3, and an average EC concentration of 1.4 μgC/m^3, ranging from >0.1–6.2 μg/m^3.

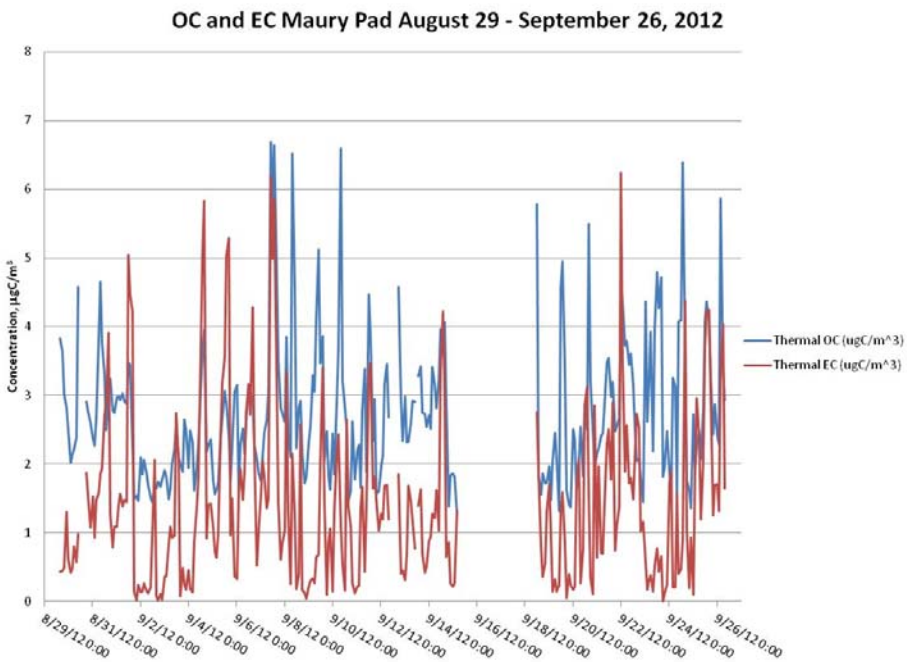

Figure 49: 2-hour average OC and EC concentrations for the Maury pad.

Site Summary. This site had a very distinct wind pattern that affected the measurements. Due to a channeling effect, wind direction was always from the south in the direction of the well pad. Wind speeds were very low at night and higher in the afternoon. Concentrations of NO_x and EC were effected, showing this same diurnal pattern. CH_4 concentrations also showed a clear diurnal pattern, although the peak time was several hours earlier than the wind speed peak time. Concentrations peaked at mid-morning, sharply dropped to ambient background levels (approximately 2 ppm) around noon, then slowly increased to the mid-morning peak on the following day. Peaks in concentration were typically modest (approximately 4 ppm). Isotopic signature of the CH_4 indicated typical ambient background, and not thermogenic CH_4. For the period of time for which VOCs data are available, August 29 through September 24, concentrations of alkanes were highly correlated with CH_4, also showing the distinct diurnal pattern. There were a few instances of elevated CH_4 concentration that were due to emissions of thermogenic CH_4. The CH_4 peak on September 7 occurred during hydraulic fracturing operations, which ran from August 30–September 14. The CH_4 peak on September 23 occurred while the operator was running production tubing. The elevated CH_4 concentration on September 26 corresponds to the 30-hour time period that one of the wells was opened to flowback (flared). Concentrations for criteria pollutants measured were below NAAQS and VOCs were below PELs for the entire duration of monitoring at this site.

3.5 LEMONS PAD

The laboratory was moved to the Lemons pad site near New Martinsville, WV in western Wetzel County on September 27, 2012. The laboratory was located approximately 200 m northwest of the well pad on a grassy knoll off the side of the main well pad access road with coordinates of 39°39'8.73"N, 80°47'44.69"W. As there was no available electric service at this site, the laboratory was operated using a diesel fuel-powered generator provided by Stone Energy. The generator was approximately 20 m northeast from the laboratory. After unpacking, installing, and calibrating, instruments were fully operational and collecting data on September 27. Monitoring at this site ended on October 15, 2012 due to power interruption. The laboratory was moved from the site on October 17, 2012. The operator was drilling (vertical) during the time that the air monitoring laboratory was collecting data. Wind most frequently came from the southwest; winds from the southeast would have been optimal for carrying any plumes from the well pad toward the monitoring laboratory, but the frequency of winds from the southeast was very low (less than 5%). Figure 50 shows a wind rose and histogram for the wind direction and speed during monitoring at the Lemons pad location. Figures for other measured meteorological parameters (temperature, relative humidity, rainfall, and solar intensity) are included in Appendix B.

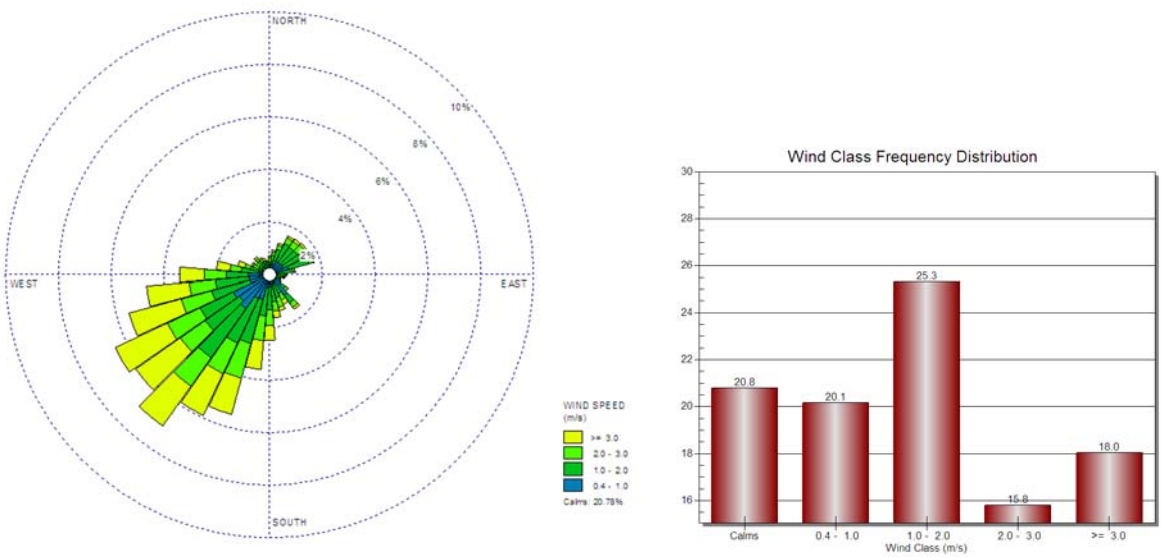

Figure 50: Wind rose and histogram for wind direction and speed during monitoring at the Lemons pad location. For the wind rose, radial axis is percent of the time that the wind was coming from a particular direction.

VOCs. VOCs data are available from October 2–15 at this site for a total of 278 samples. The samples collected from September 27–October 2 had to be discarded due to excess moisture in the gas chromatograph columns that caused an unstable baseline in the chromatograms. Table 6 lists the average concentration, standard deviation, minimum and maximum concentrations, and frequency of detection for compounds that were detected in at least 10% of the samples. Ethylene was the only non-alkane compound detected.

Table 6: VOCs concentrations for the Lemons pad

Compound	Average (ppb)	Standard Deviation (ppb)	Minimum (ppb)	Maximum (ppb)	Frequency of Detection (%)
Ethane	30.4	49.9	4.7	638.6	100
Ethylene	0.8	1.2	0.0	6.8	43
Propane	25.1	65.8	0.6	860.0	100
Isobutane	5.7	10.0	0.0	122.7	95
n-butane	9.6	21.3	1.2	273.8	100
Isopentane	4.5	5.0	0.0	53	98
n-pentane	4.0	5.0	0.0	57.7	96
2-methylpentane	0.7	1.2	0.0	10.1	37
3-methylpentane	0.3	1.0	0.0	9.4	18

Ozone. Ozone data are available for most of the monitoring duration at this site, September 26–October 15, with a gap in the data from September 28–October 2 due to a power outage (Figures 51–53). The average ozone concentration using 1-minute data at the Lemons pad was 33 ppb, and the maximum hourly average concentration was 65 ppb. Day-to-night variations were 20–40 ppb. The 8-hour average ranged from 11–61 ppb.

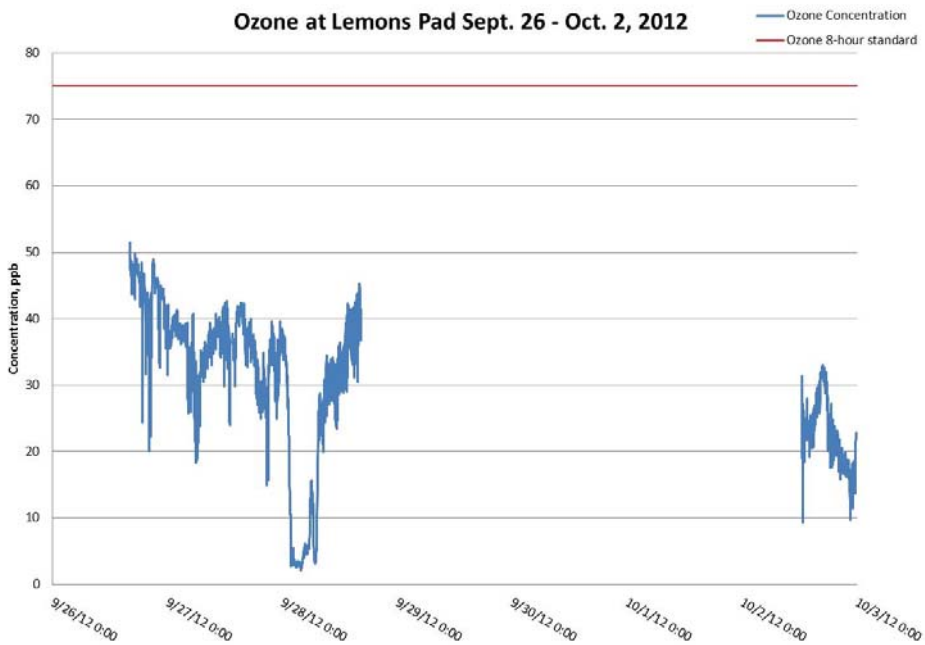

Figure 51: 1-minute average ozone concentrations for the first week at the Lemons pad.

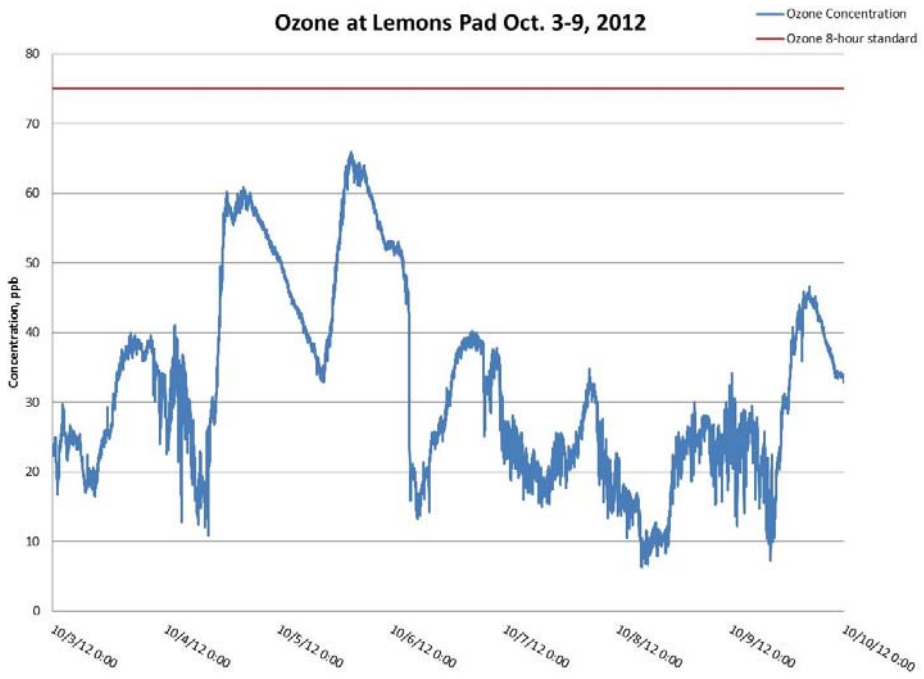

Figure 52: 1-minute average ozone concentrations for the second week at the Lemons pad.

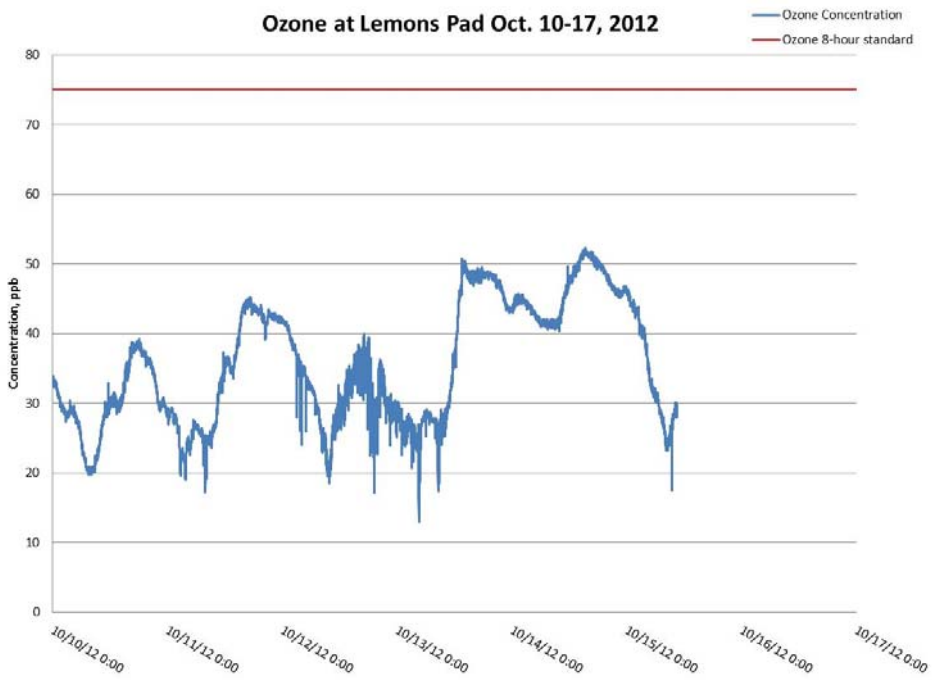

Figure 53: 1-minute average ozone concentrations for the third week at the Lemons pad.

***NO_x*.** NO_x data for the Lemons pad site are available for the entire monitoring duration, September 26–October 15, with a gap in the data from September 28–October 2 due to a power interruption caused by the diesel generator running out of fuel (Figures 54–56). The average of the 1-minute measurements at the Lemons pad site was 9 ppb with an hourly average maximum of 151 ppb. The 1-hour average for NO_2 ranged from 0.24–63.1ppb.

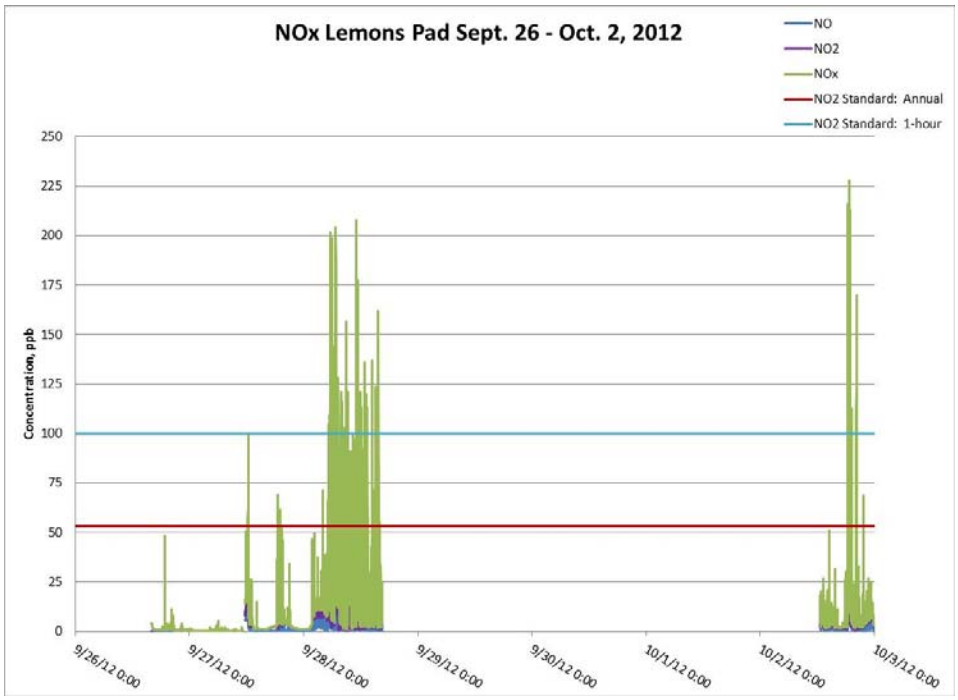

Figure 54: 1-minute average NO_x concentrations for the first week at the Lemons pad.

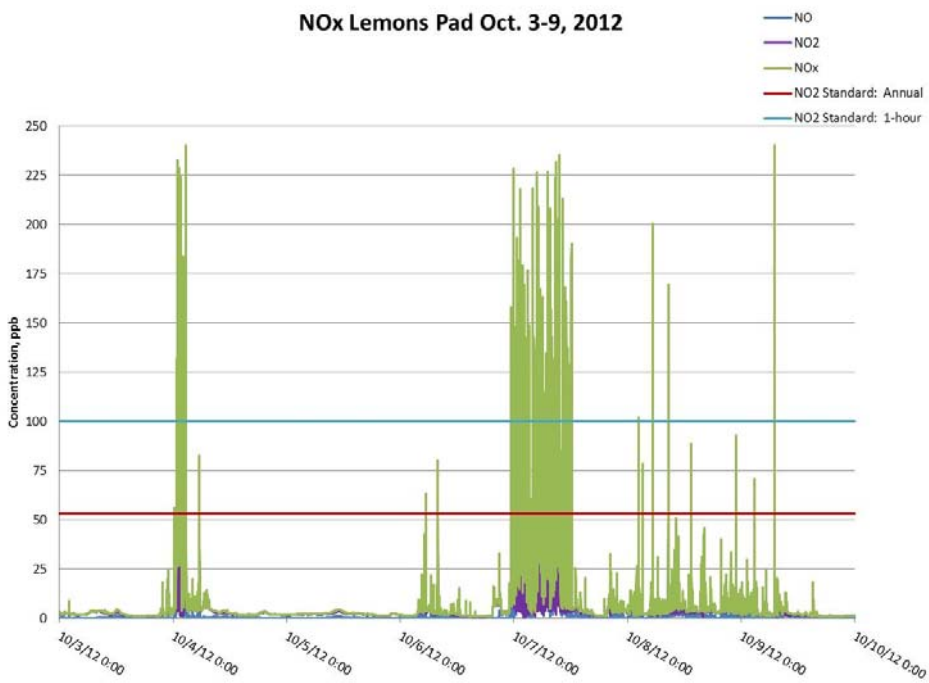

Figure 55: 1-minute average NO_x concentrations for the second week at the Lemons pad.

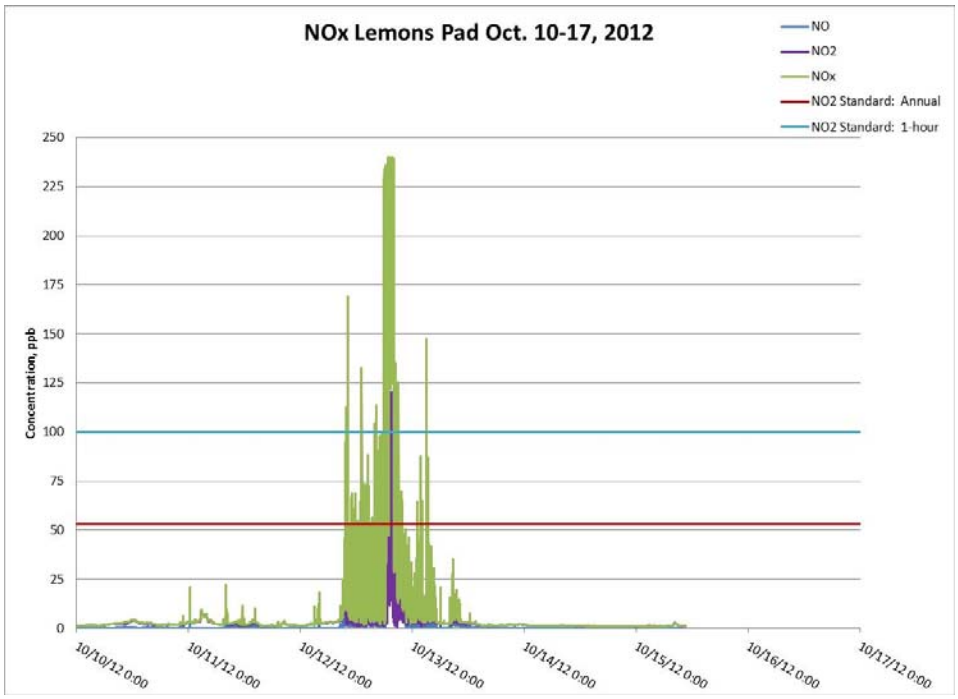

Figure 56: 1-minute average NO_x concentrations for the third week at the Lemons pad.

CH_4 and CO_2. At this site there was a gap in the data due to a power interruption that started on September 28 and ended on October 2. The ambient CH_4 concentration at the Lemons pad averaged 2.1 ppm (±0.1) with an average isotopic composition of -46.7‰ (±1.8‰) which are typical background atmospheric values (Figures 57–58). For the duration of the 3-week monitoring period at this site, the CH_4 concentration was near ambient levels. A maximum concentration of 2.9 ppm was recorded a total of 41 times with an average $\delta^{13}C$ value of -45.7‰ (±0.7‰), indicating a very minor contribution from a thermogenic source.

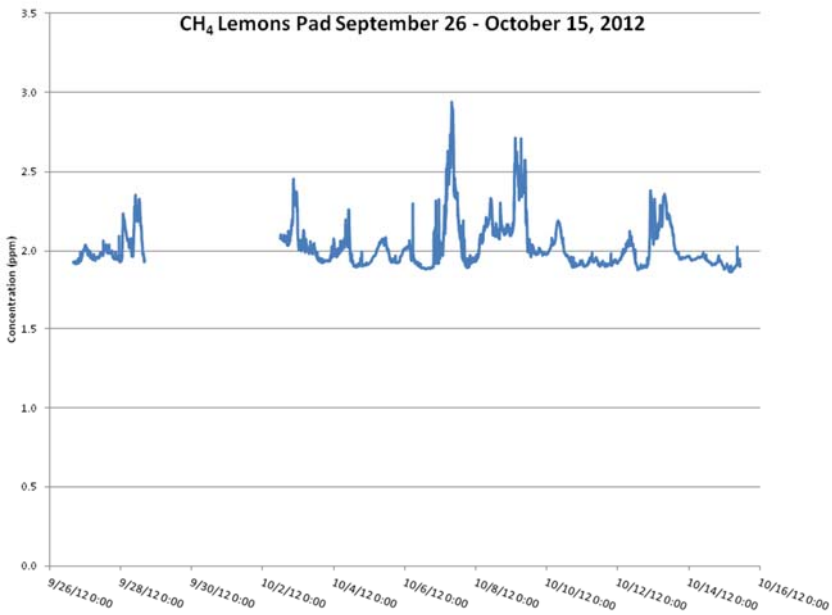

Figure 57: 1-minute average CH_4 concentrations at the Lemons pad.

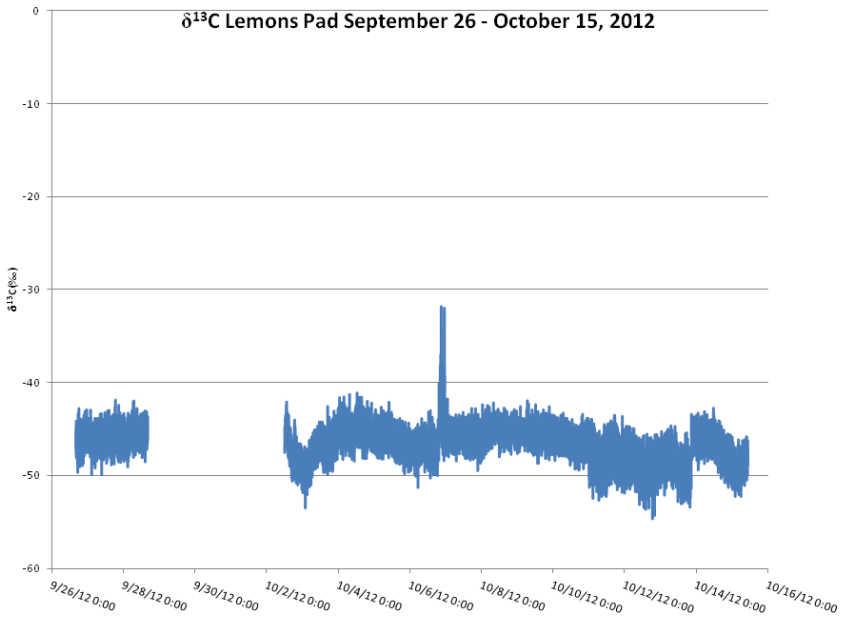

Figure 58: 1-minute average $\delta^{13}C$ of CH_4 at the Lemons pad.

Over the 3 weeks of monitoring at the Lemons pad site, the CO_2 concentration averaged 395 ppm (±9) with $\delta^{13}C$ averaging -11.7‰ (±0.8‰) (Figure 59). The CO_2 concentrations and $\delta^{13}C$ values at the site cycled daily. Starting at approximately 8 p.m., the CO_2 concentration increased gradually to values typically greater than 415 ppm and occasionally greater than 440 ppm before dropping back to near ambient levels by 7 a.m. During these times, the corresponding $\delta^{13}C$ values become more depleted, dropping to less than -13‰ and occasionally approaching -14‰. The maximum CO_2 concentration at the site was 446 ppm with a corresponding $\delta^{13}C$ value of -13.6‰.

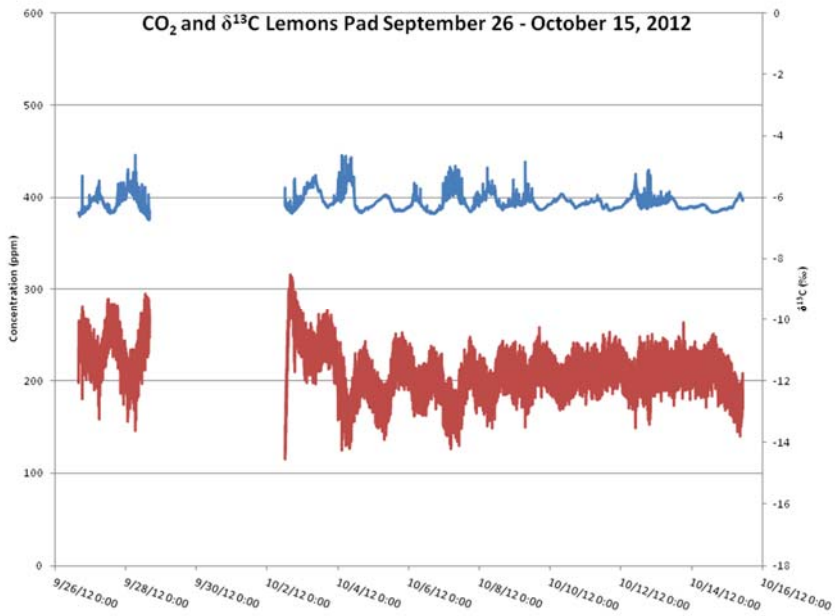

Figure 59: 1-minute average CO_2 concentrations and $\delta^{13}C$ of CO_2 at the Lemons pad.

PM_{10} and $PM_{2.5}$. Data are available for September 26–October 17 with gaps in the data from September 28–October 2 and October 15–16 due to power interruption (Figure 60). At the Lemons pad, average PM_{10} concentration was 12 μg/m^3 and average $PM_{2.5}$ concentration was 7 μg/m^3. Maximum 1-hour average concentrations of PM_{10} and $PM_{2.5}$ were 188 μg/m^3 and 25 μg/m^3, respectively.

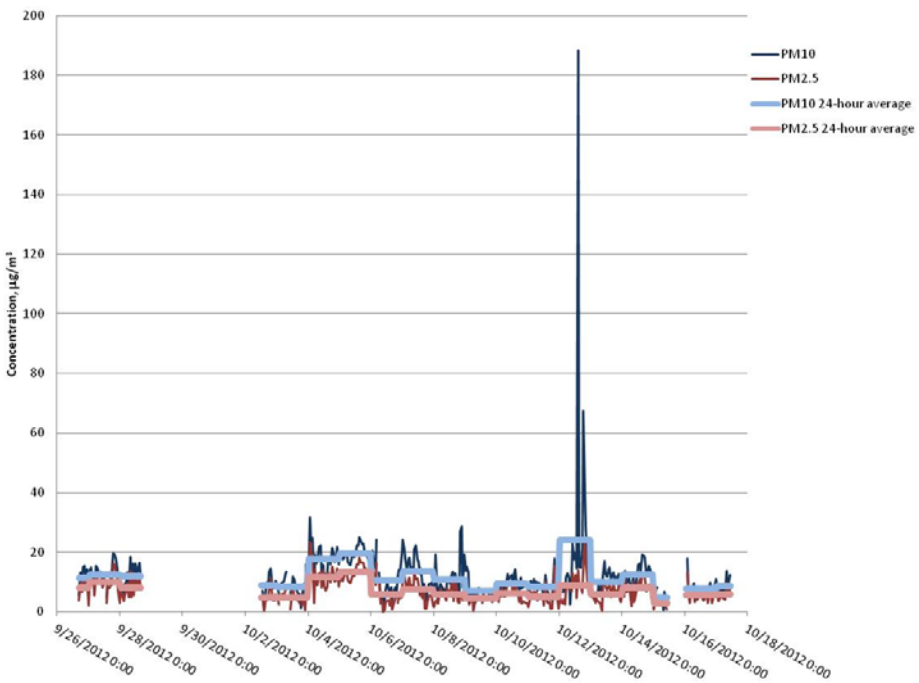

Figure 60: 1-hour average PM_{10} and $PM_{2.5}$ concentrations at the Lemons pad.

SO_2. Data for SO_2 are available for September 27–October 15 with sections of data missing due to power interruptions (Figures 61–63). The average concentration of SO_2 at the Lemons pad was 2.6 ppb, with peaks not exceeding 4.5 ppb. One-hour averages ranged from 1.6–3.8 ppb. Similarly, calculating 3-hour averages from the 1-minute data results in a range of 1.7–3.7 ppb.

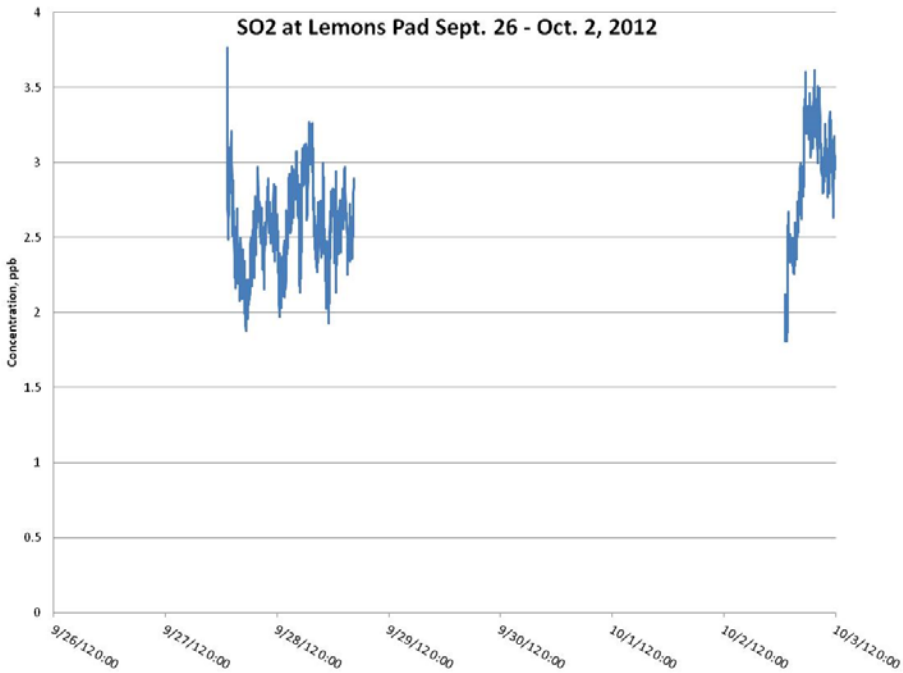

Figure 61: 1-minute average SO_2 concentrations for the Lemons pad, September 26–October 2.

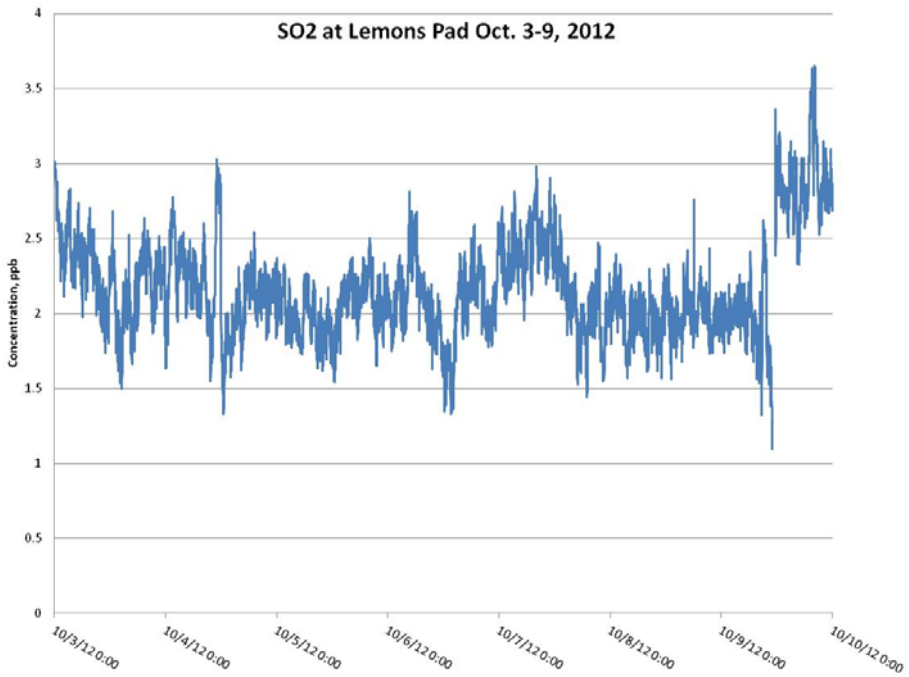

Figure 62: 1-minute average SO_2 concentrations for the Lemons pad, October 3–9.

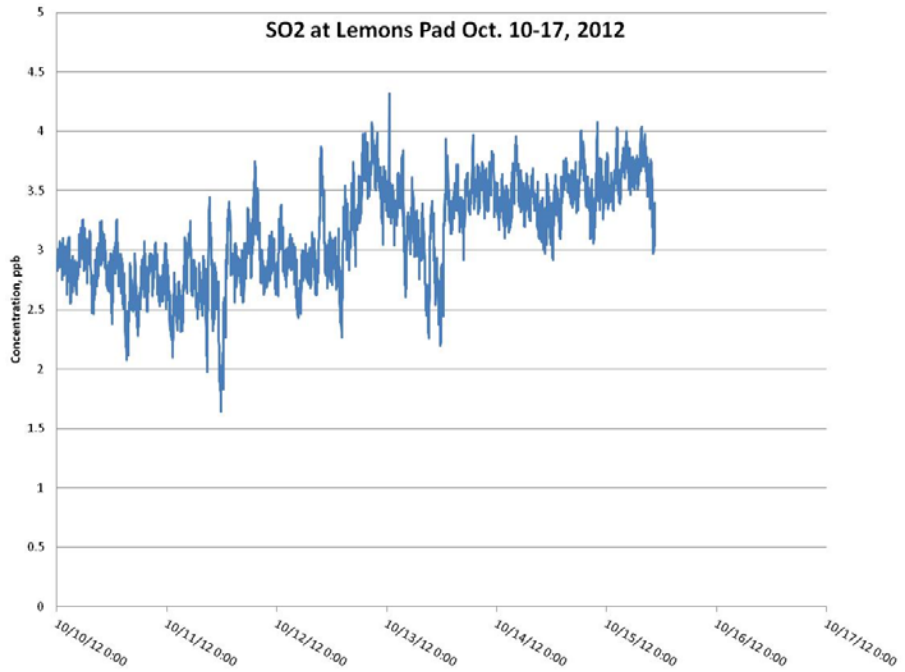

Figure 63: 1-minute average SO_2 concentrations for the Lemons pad, October 10–17.

OC and EC. At the Lemons pad, data are available for the entire monitoring period with the exception of September 28–October 2 due to a loss of electric power (Figure 64). The data are less noisy than what was recorded at the Maury pad, and have more distinct peaks in concentration, with an average OC concentration of 2.4 μgC/m^3, ranging from 1.2–17.7 μgC/m^3, and an average EC concentration of 0.8 μgC/m^3, ranging from >0.1–6.6 μg/m^3.

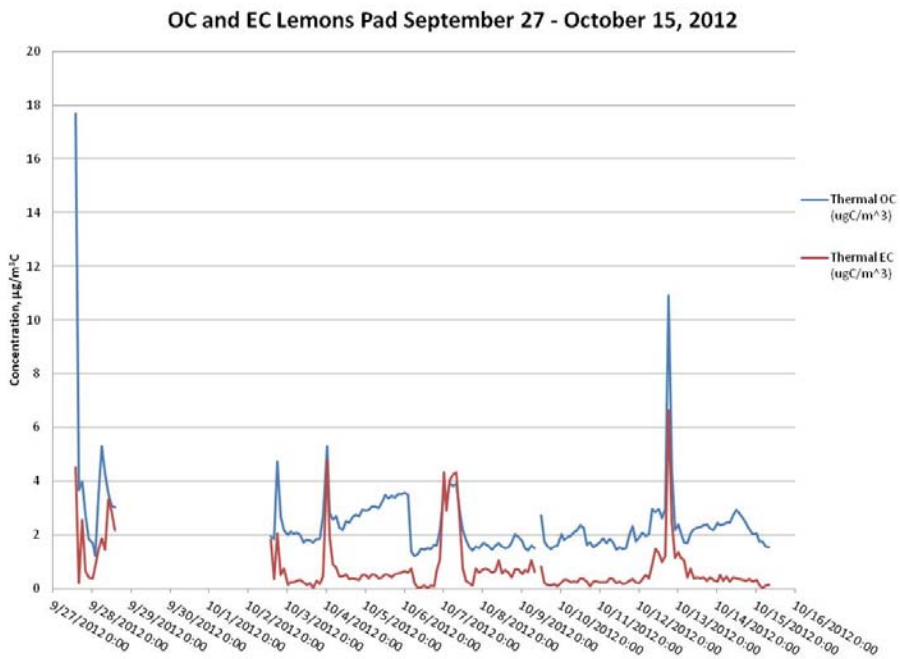

Figure 64: 2-hour average OC and EC concentrations for the Lemons pad.

Site Summary. On the evening of October 12 into the morning of October 13, there were sustained high concentrations of NO_x, PM, OC, and EC. Events similar but less in magnitude were observed on October 4 and 7. CO_2 concentrations may also have been slightly elevated during these events but concentrations are difficult to distinguish from background. As the concentration of CH_4 was at background levels during these times, these events are likely associated with combustion engine emissions. Winds were coming from the northeast during the events, which is not in the direction of the well pad but the diesel-powered generator used to power the laboratory. Therefore the elevated concentrations of NO_x, PM, OC and EC that were observed when the wind was from the northeast are assumed to be due to the generator emissions. The only instance of detection of thermogenic CH_4 was on the evening of October 6. Concentrations of VOCs were usually at typical background levels, but the one instance of a peak in concentration of the alkanes occurred at the same time that the thermogenic CH_4 was detected. During this time the wind was coming from the northwest, which is not in the direction of the well pad and therefore the source is unknown. Concentrations for criteria pollutants measured were below NAAQS and VOCs were below PELs for the entire duration of monitoring at this site. Unfortunately due to unfavorable wind direction for most of the study period and influence from the laboratory generator's emissions, the data are not adequate for evaluating the impact of the drilling activity happening on the well pad.

3.6 WVDNR A PAD

The laboratory was moved to the West Virginia Division of Natural Resources (WVDNR) A pad site in Brooke County off of Putney Ridge Road on October 17, 2012. The laboratory was located approximately 200 m southwest of the well pad off the side of the main well pad access road with coordinates of 40°19'15.5"N, 80°32'12.2"W. As there was no available electric service at this site, the laboratory was operated using a diesel fuel-powered generator provided by Chesapeake Energy. The generator was approximately 10 m from the laboratory in the opposite direction of the well pad. After unpacking, installing, and calibrating, instruments were fully operational and collecting data on October 19. Monitoring at this site ended on November 2, 2012 due to Chesapeake Energy shutting down the generator. The operator was drilling (vertical and horizontal) during the time that the air monitoring laboratory was collecting data. The laboratory was moved from the site on November 6, 2012. During this period, wind most frequently came from the southwest; winds from the northeast would have been optimal for carrying any plumes from the well pad toward the monitoring laboratory but there were no instances of winds from the northeast. Figure 65 shows a wind rose and histogram for the wind direction and speed during monitoring at the WVDNR A pad location. Figures for other measured meteorological parameters (temperature, relative humidity, rainfall, and solar intensity) are included in Appendix B.

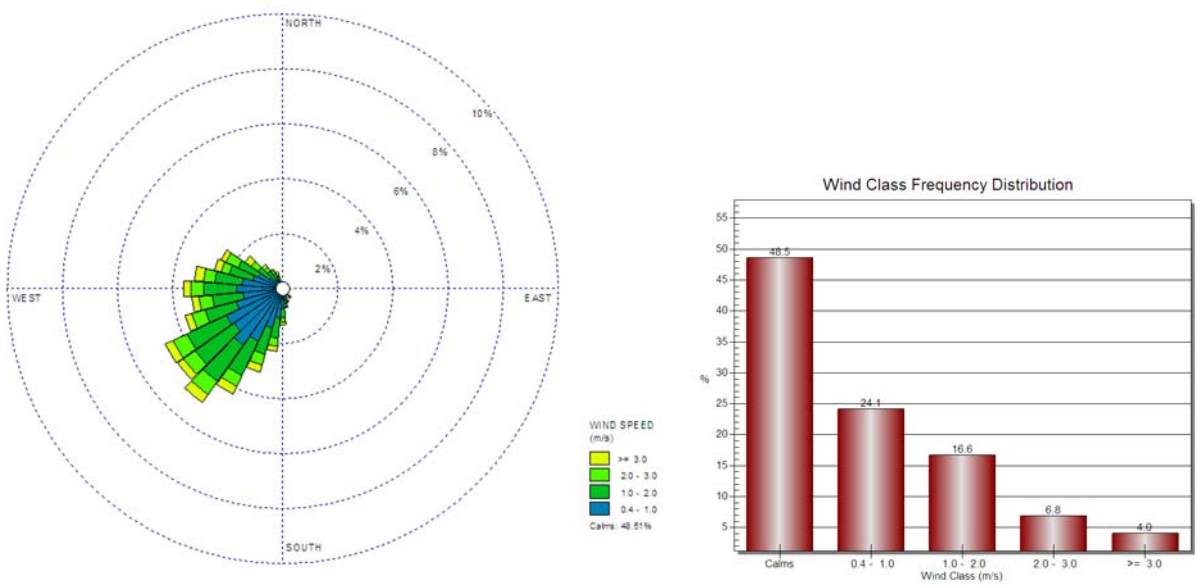

Figure 65: Wind rose and histogram for wind direction and speed during monitoring at the WVDNR A pad location. For the wind rose, radial axis is percent of the time that the wind was coming from a particular direction.

VOCs. The VOCs analyzer was running continuously at this site from October19–November 2 with a gap in the data from October 25–31 due to a power interruption. There were a total of 162 samples. Table 7 lists the average concentration, standard deviation, minimum and maximum concentrations, and frequency of detection for compounds that were detected in at least 10% of the samples. Measured concentrations at this site were comparatively low, with all averages less than 20 ppb and all maximums less than 140 ppb.

Table 7: VOCs concentrations for the WVDNR A pad

Compound	Average (ppb)	Standard Deviation (ppb)	Minimum (ppb)	Maximum (ppb)	Frequency of Detection (%)
Hexane	0.4	1.3	0.0	8.7	13
Toluene	1.0	1.0	0.0	8.8	82
m-diethylbenzene	0.5	1.8	0.0	12.5	14
n-undecane	3.4	14.3	0.0	122.3	40
n-dodecane	3.6	12.7	0.0	95.8	43
Ethane	17.8	20.6	4.9	139.3	100
Ethylene	1.6	0.9	0.0	5.3	92
Propane	11.6	13.5	0.6	99.3	100
Propylene	0.2	0.5	0.0	3.7	20
Isobutane	2.5	3.1	0.0	22.2	86
n-butane	6.2	8.4	0.0	58.6	99
Acetylene	0.3	0.6	0.0	3.2	25
Isopentane	2.3	2.5	0.0	15.8	83
n-pentane	2.2	3.1	0.0	22.7	77
2-methylpentane	0.2	0.7	0.0	4.6	10

Ozone. Ozone data are available from October 19–November 2 (Figure 66). The gap in the data from October 25–31 is due to a generator switch that interrupted the power. The average ozone concentration using 1-minute data at the WVDNR A Pad was 31 ppb, and the maximum hourly average concentration was 60 ppb. Day-to-night variations were typically around 20 ppb. The 8-hour average ranged from 14–56 ppb.

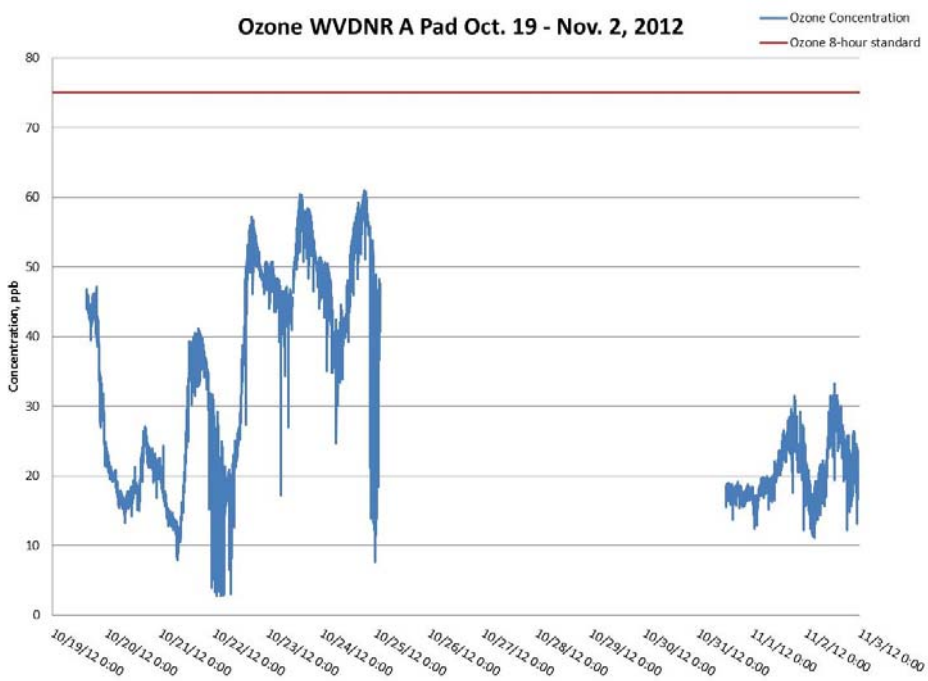

Figure 66: 1-minute average ozone concentrations at the WVDNR A pad.

NO_x. At the WVDNR A pad site, there was a gap in the NO_x data from October 25–31 due to a power interruption (Figure 67). The average of the 1-minute measurements was 9 ppb with an hourly average maximum of 49 ppb. The 1-hour average for NO_2 ranged from 1.4–25.0 ppb.

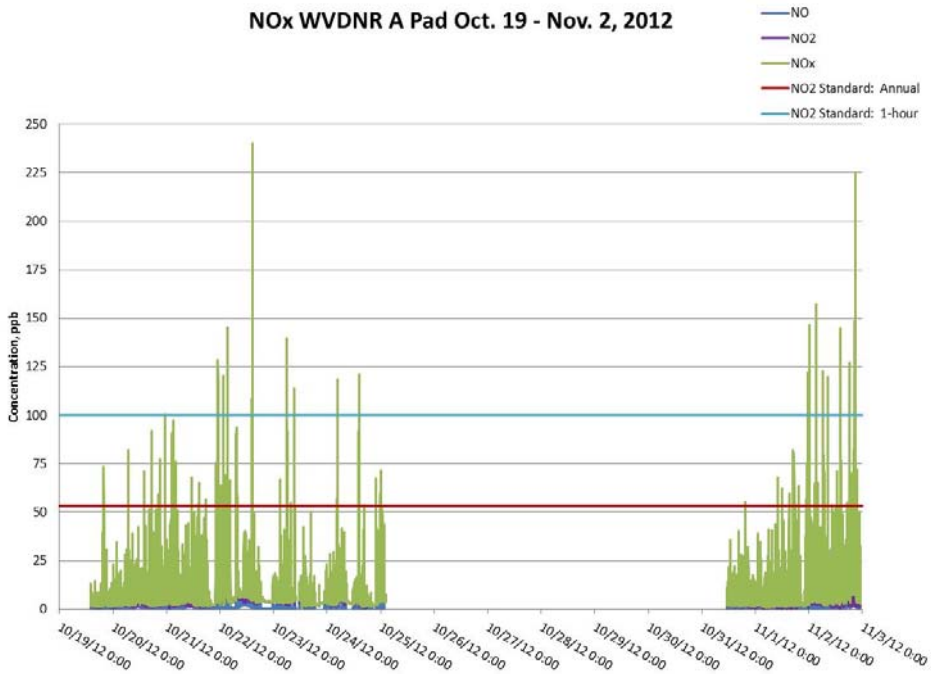

Figure 67: 1-minute average NO_x concentrations for the WVDNR A pad.

CH_4 and CO_2. There are limited data available for this site to due to multiple power interruptions. The concentration of CH_4 at the WVDNR A pad averaged 1.9 ppm (±0.1 ppm) with an average isotopic composition of -50.1‰ (±1.5‰) over the course of the 2-week monitoring period (Figure 68). A maximum concentration of 2.8 ppm was recorded ($\delta^{13}C$ = -47.2‰) before an unexpected power failure.

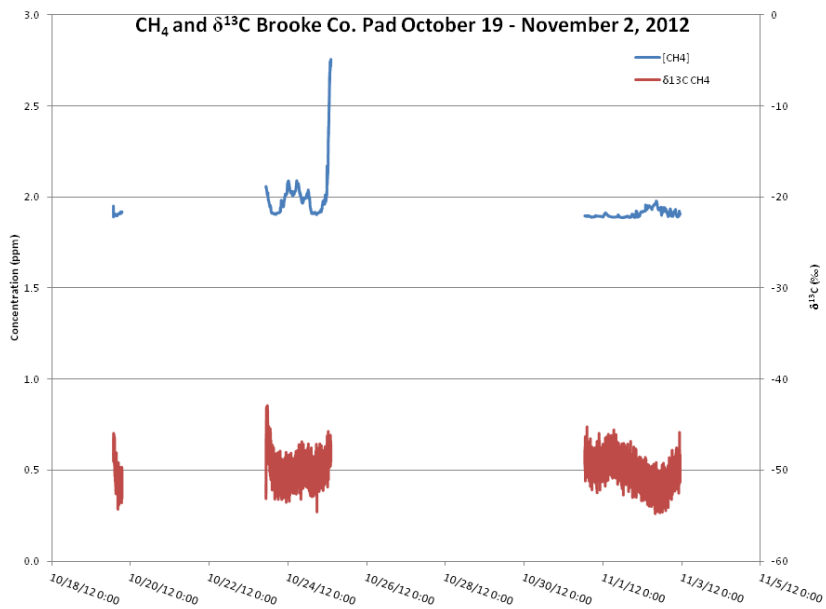

Figure 68: 1-minute average CH_4 concentrations and $\delta^{13}C$ of CH_4 at the WVDNR A pad.

The concentration of CO_2 at the WVDNR A pad site averaged 405 ppm (±7 ppm) with an average isotopic composition of -12.5‰ (±0.9‰) over the course of the 2-week monitoring period (Figure 69). The maximum CO_2 concentration at the site was 449 ppm with a corresponding $\delta^{13}C$ value of -13.4‰.

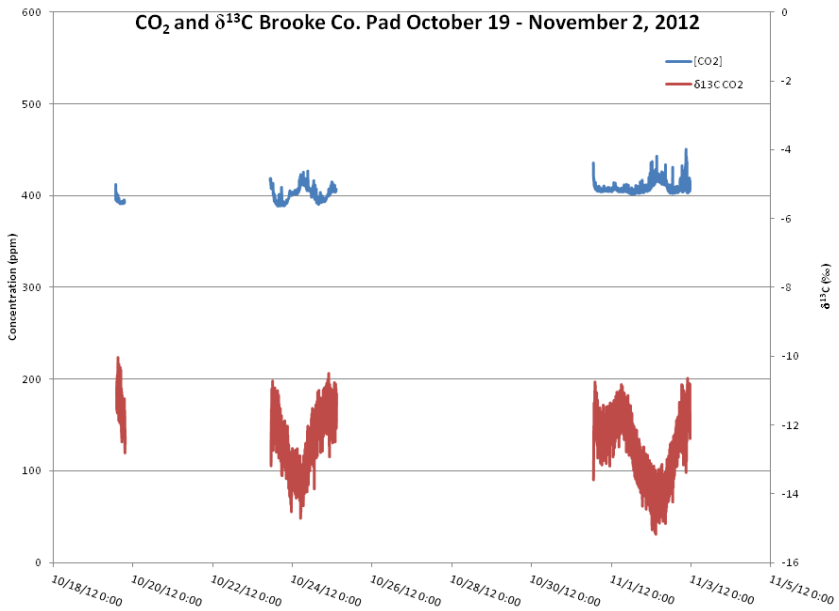

Figure 69: 1-minute average CO_2 concentrations and $\delta^{13}C$ of CO_2 at the WVDNR A pad.

PM_{10} and $PM_{2.5}$. Data are available for October 19–November 2 with a 32-hour gap in the data starting on October 25 due to a power interruption (Figure 70). Beginning on October 28, there were many samples that were discarded because they did not meet a data quality control objective; in all reported data, PM_{10} concentrations must be greater than $PM_{2.5}$ concentrations. Frequently the concentrations were near equal, with the slightly higher $PM_{2.5}$ concentrations attributed to instrument signal variability. At the WVDNR A pad, average PM_{10} concentration was 15 μg/m^3 and average $PM_{2.5}$ concentration was 8 μg/m^3. Maximum 1-hour average concentrations of PM_{10} and $PM_{2.5}$ were 129 μg/m^3 and 24 μg/m^3, respectively.

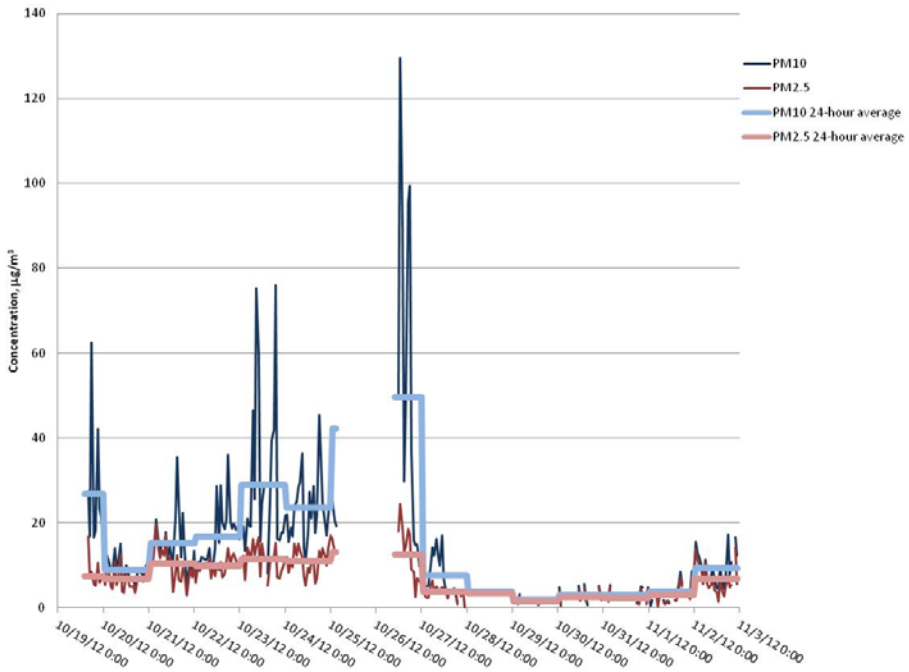

Figure 70: 1-hour average PM_{10} and $PM_{2.5}$ concentrations at the WVDNR A pad.

SO_2. Data for SO_2 are available for October 19–November 2 with a section of data from October 25–31 missing due to a power interruption (Figure 71). The average concentration of SO_2 at the WVDNR A pad was 2.5 ppb, with peaks not exceeding 9 ppb. One-hour averages ranged from 1.9–7.0 ppb. Similarly, calculating 3-hour averages from the 1-minute data results in a range of 2.1–5.3 ppb.

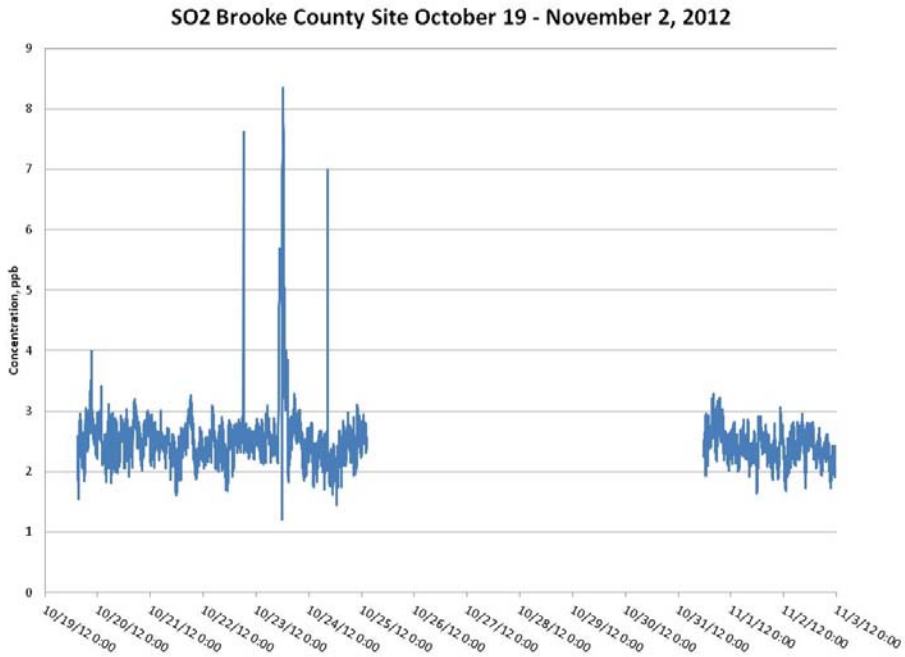

Figure 71: 1-minute average SO_2 concentrations for the WVDNR A pad.

Site Summary. Data collection at this site was limited due to power outages. The small amount of CH_4 and CO_2 data collected are of little use. Because there were no instances of winds from the northeast, an evaluation of the impact of the activity on the well pad cannot made. There was one instance of a modest peak in concentrations of alkanes in the early morning hours of October 22 during which time conditions were stagnant. Concentrations for criteria pollutants measured were below NAAQS and VOCs were below PELs for the entire duration of monitoring at this site.

4. REFERENCE

AIRNow. www.airnow.gov (accessed Jan 2014).

EPA. U.S. Environmental Protection Agency (EPA), National Ambient Air Quality Standards. https://www.epa.gov/criteria-air-pollutants/naaqs-table (accessed Sept 2012).

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APPENDIX A: LIST OF MEASURED VOCS

Where applicable, OSHA 8-hour time-weighted average permissible exposure limits (PELs) are given in parts per million. From: OSHA Standard 1910.1000 Table Z-1.

Compound	PEL	Compound	PEL	Compound	PEL
Acetylene		Trans-2-pentene		Methylcyclohexane	500
n-Butane		Propane	1,000	Methylcyclopentane	
1-Butene		Propylene		2-Methylheptane	
Cis-2-butene		Benzene	1	3-Methylheptane	
Trans-2-butene		Cyclohexane	300	2-Methylhexane	
Cyclopentane		n-Decane		3-Methylhexane	
2,2-Dimethylbutane		m-Diethylbenzene		n-Nonane	
2,3-Dimethylbutane		p-Diethylbenzene		n-Propylbenzene	
Ethane		2,3-Dimethylpentane		Styrene	100
Ethylene		2,4-Dimethylpentane		Toluene	200
1-Hexene		n-Dodecane		1,2,3-Trimethylbenzene	
Isobutane		Ethyl Benzene	100	1,2,4-Trimethylbenzene	
Isopentane		o-Ethyltoluene		1,3,5-Trimethylbenzene	
Isoprene		m-Ethyltoluene		2,2,4-Trimethylpentane	
n-Pentane	1,000	p-Ethyltoluene		2,3,4-Trimethylpentane	
1-Pentene		n-Heptane	500	n-Undecane	
2-Methylpentane		n-Hexane	500	o-Xylene	100
3-Methylpentane		Isopropylbenzene		m-Xylene	100
Cis-2-pentene		n-Octane	500	p-Xylene	100

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APPENDIX B: METEOROLOGICAL DATA

Meteorological data (temperature, relative humidity, barometric pressure, wind speed and direction, rainfall, and solar intensity) were collected using a Davis Instruments Vantage Pro2 Plus meteorological station. One-minute averaged values were obtained. Results for temperature, relative humidity, rainfall, and solar intensity for each of the six monitoring locations are shown in Figures B1–B28.

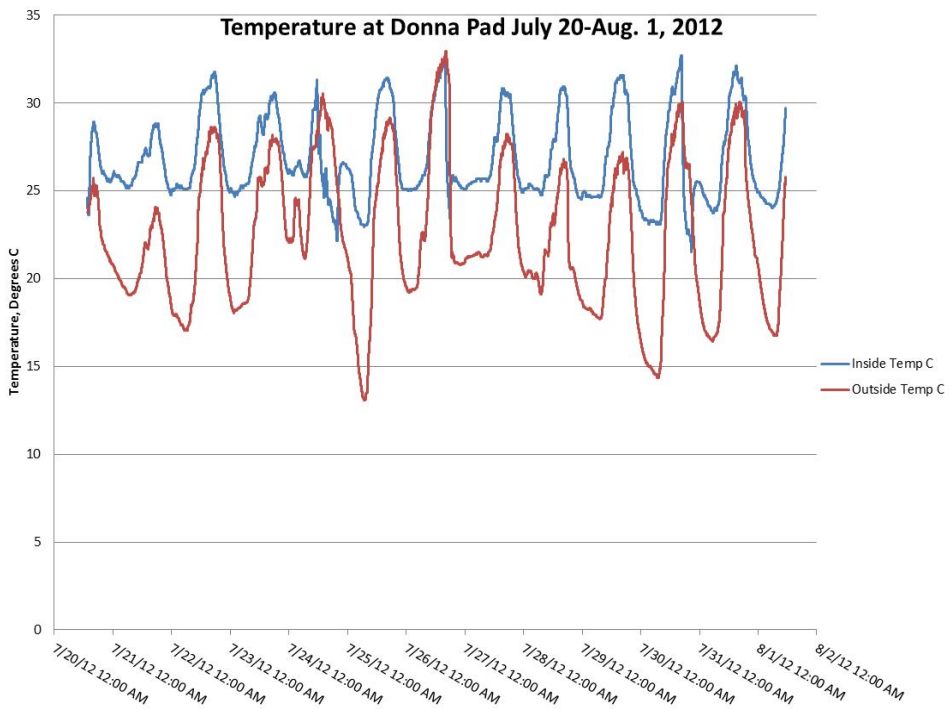

Figure B1: Air temperature inside and outside of the air monitoring laboratory at the Donna pad.

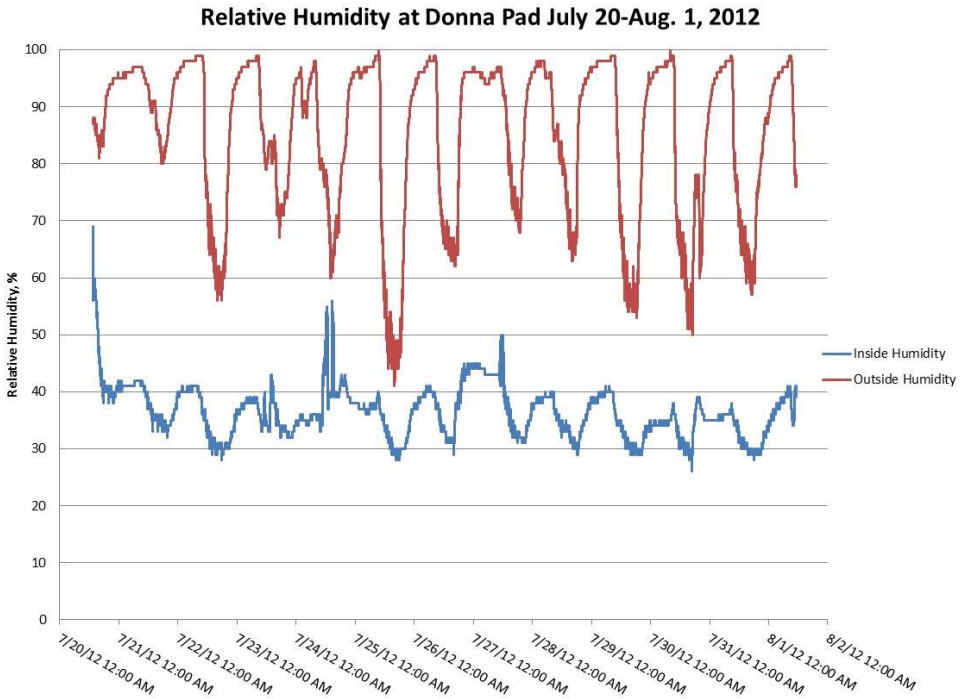

Figure B2: Relative humidity inside and outside of the air monitoring laboratory at the Donna pad.

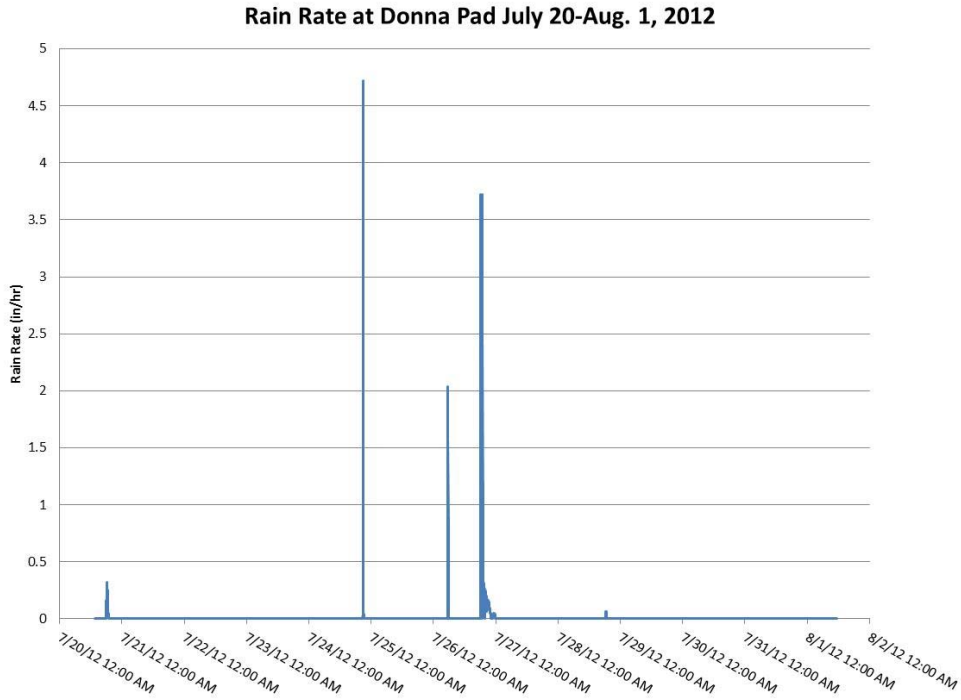

Figure B3: Rainfall events at the Donna pad.

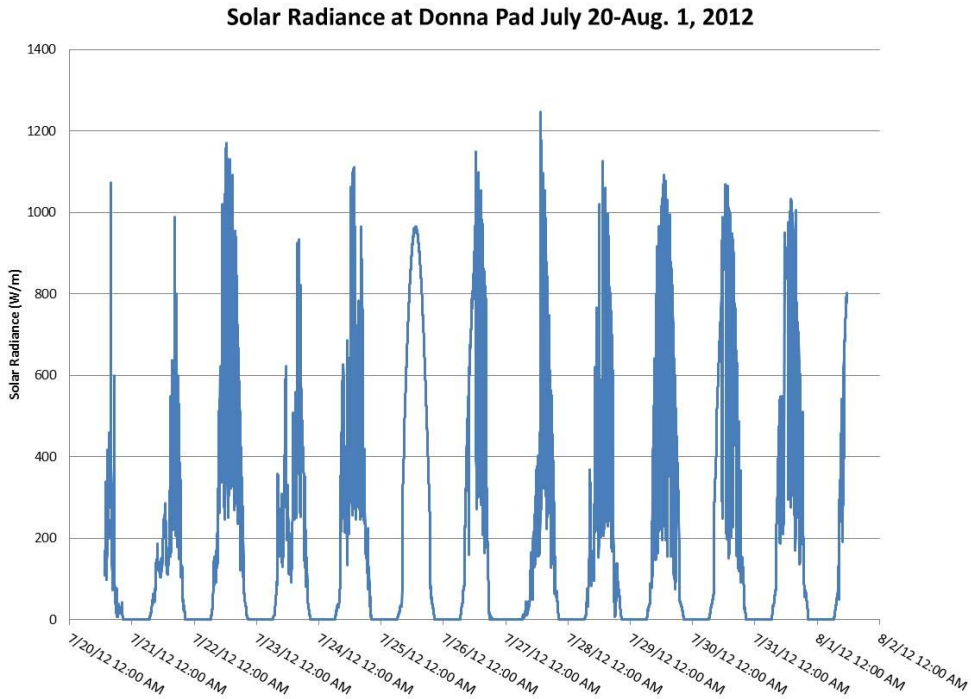

Figure B4: Solar intensity at the Donna pad.

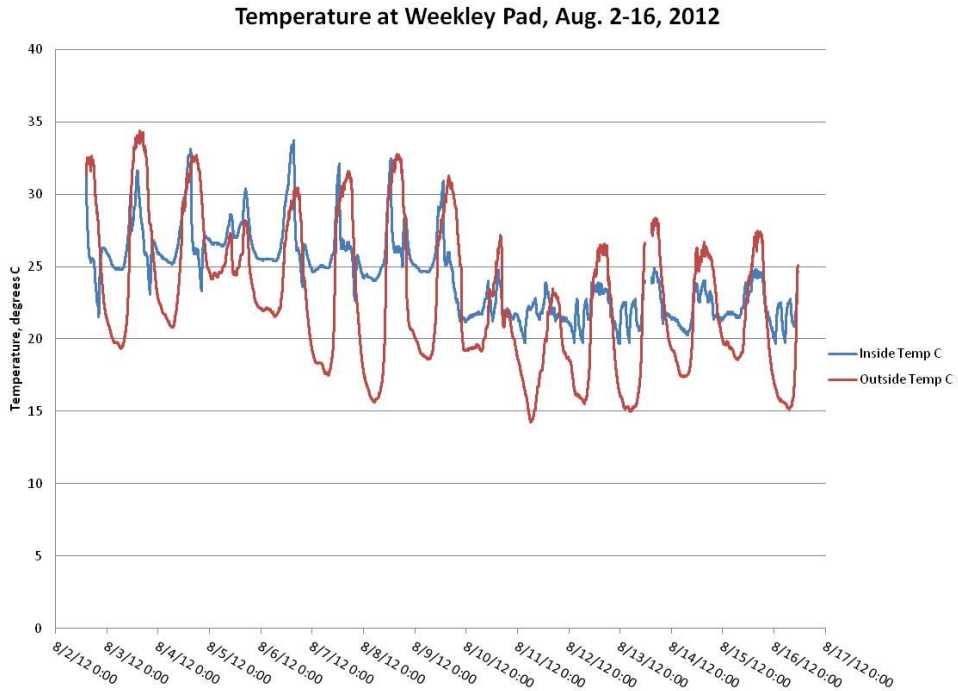

Figure B5: Air temperature inside and outside of the air monitoring laboratory at the Weekley pad.

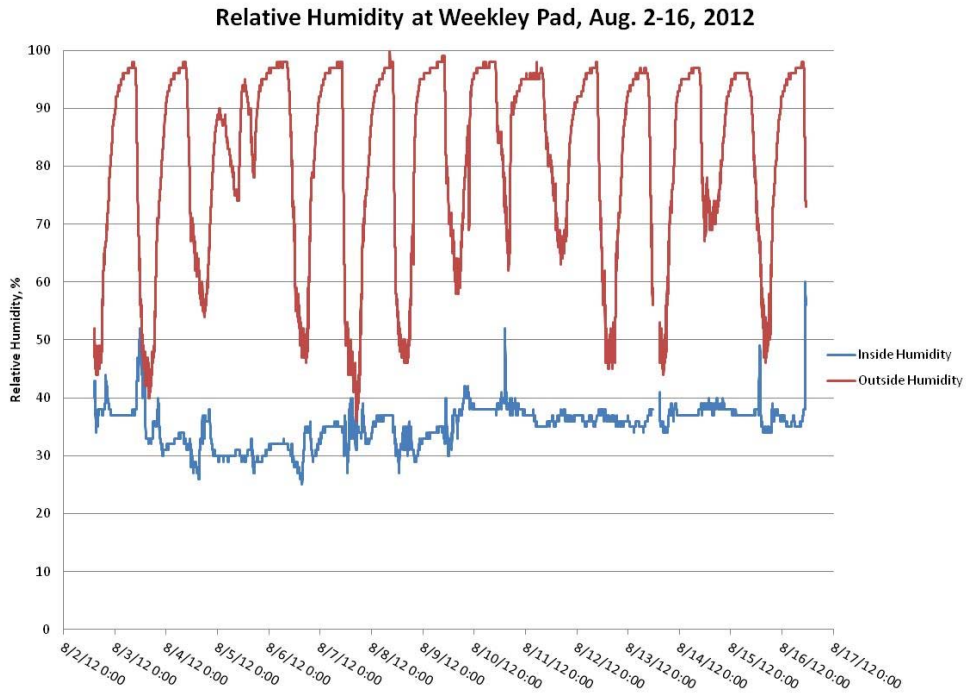

Figure B6: Relative humidity inside and outside of the air monitoring laboratory at the Weekley pad.

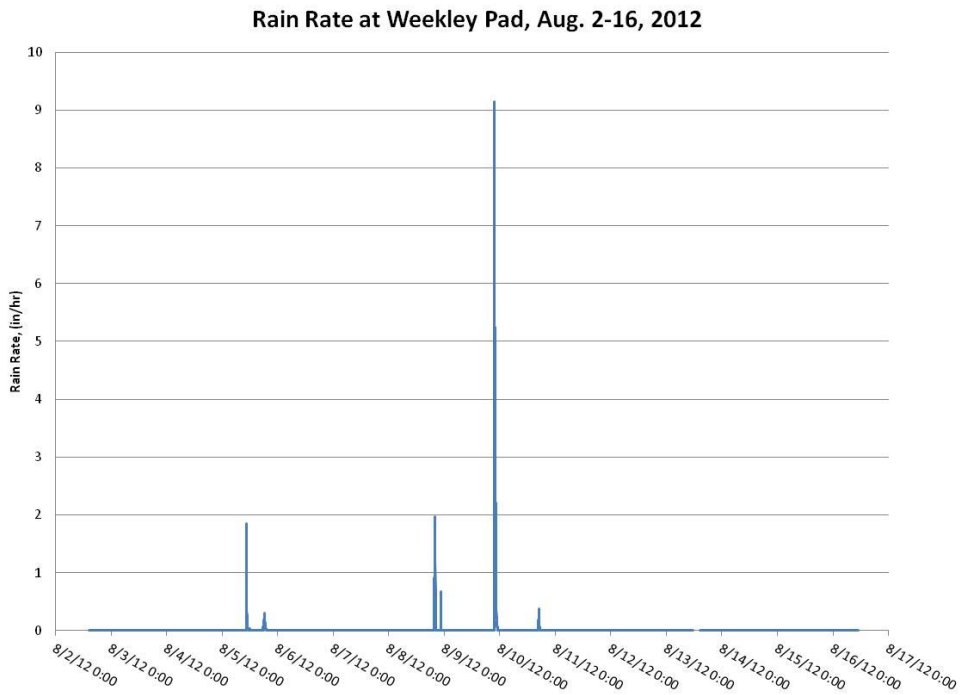

Figure B7: Rainfall events at the Weekley pad.

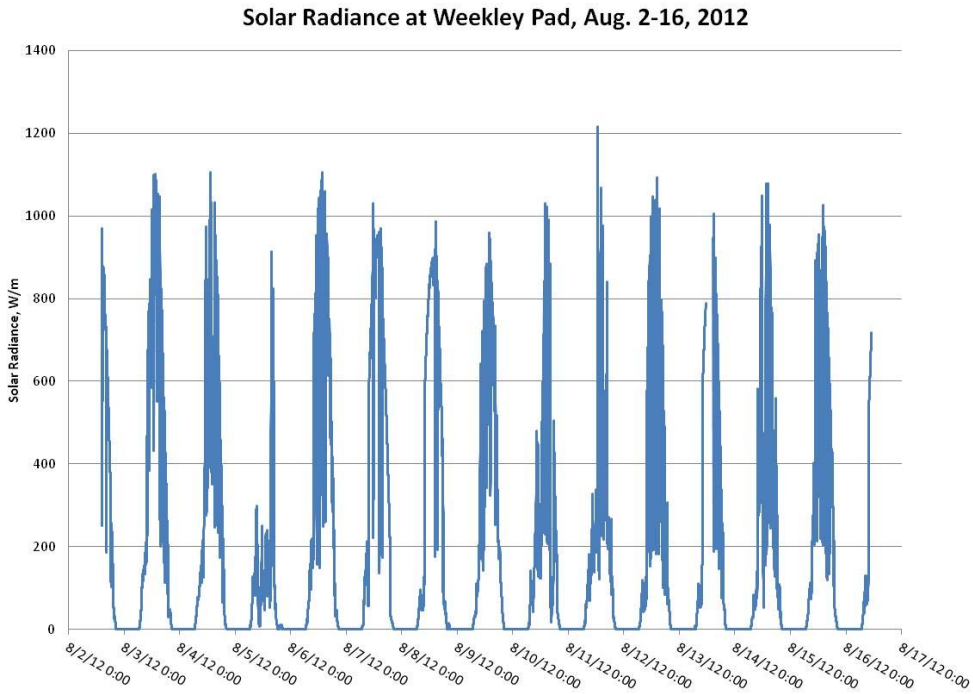

Figure B8: Solar radiance at the Weekley pad.

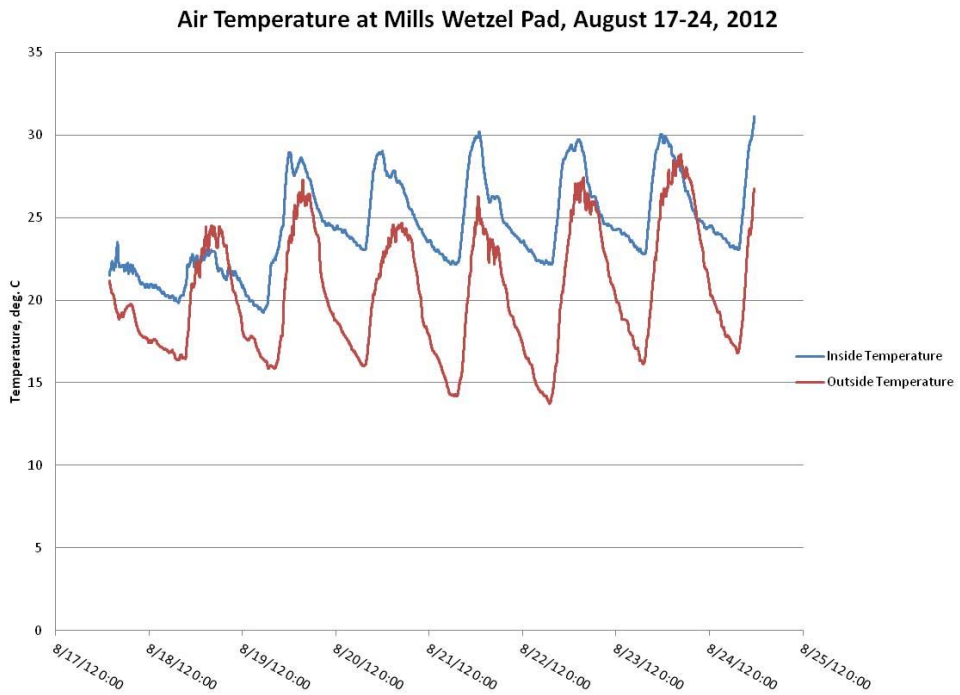

Figure B9: Air temperature inside and outside of the air monitoring laboratory at the Mills-Wetzel pad.

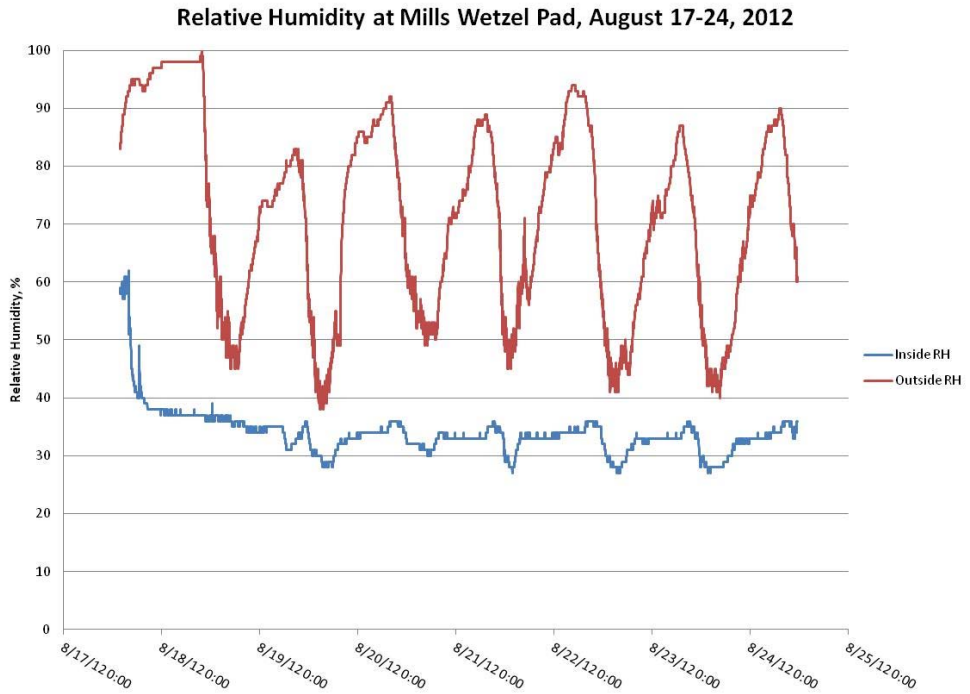

Figure B10: Relative humidity inside and outside of the air monitoring laboratory at the Mills-Wetzel pad.

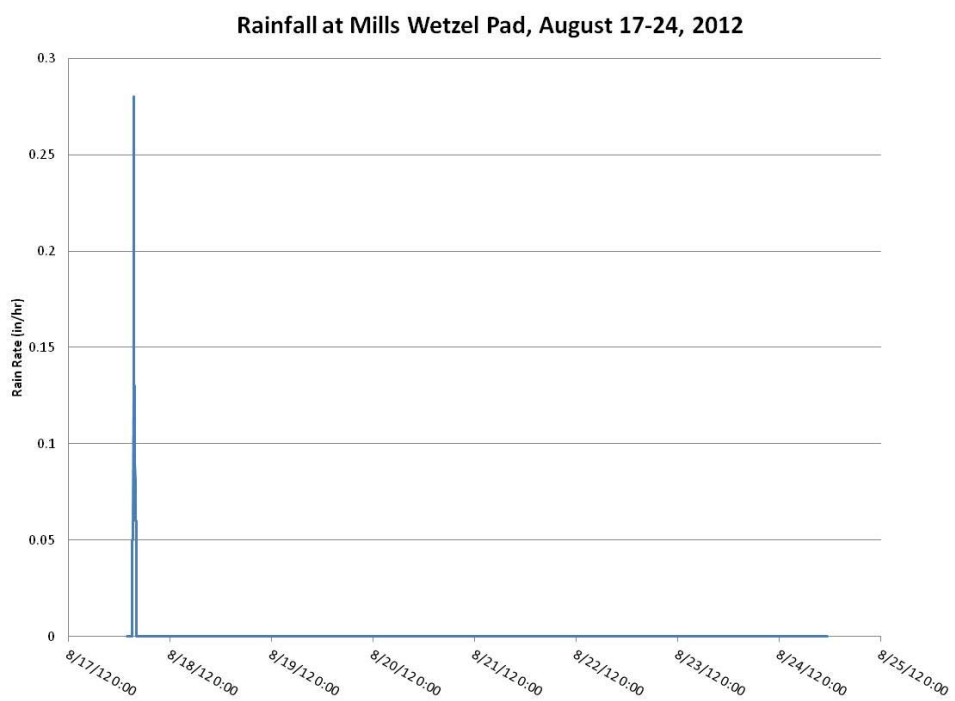

Figure B11: Rainfall events at the Mills-Wetzel pad.

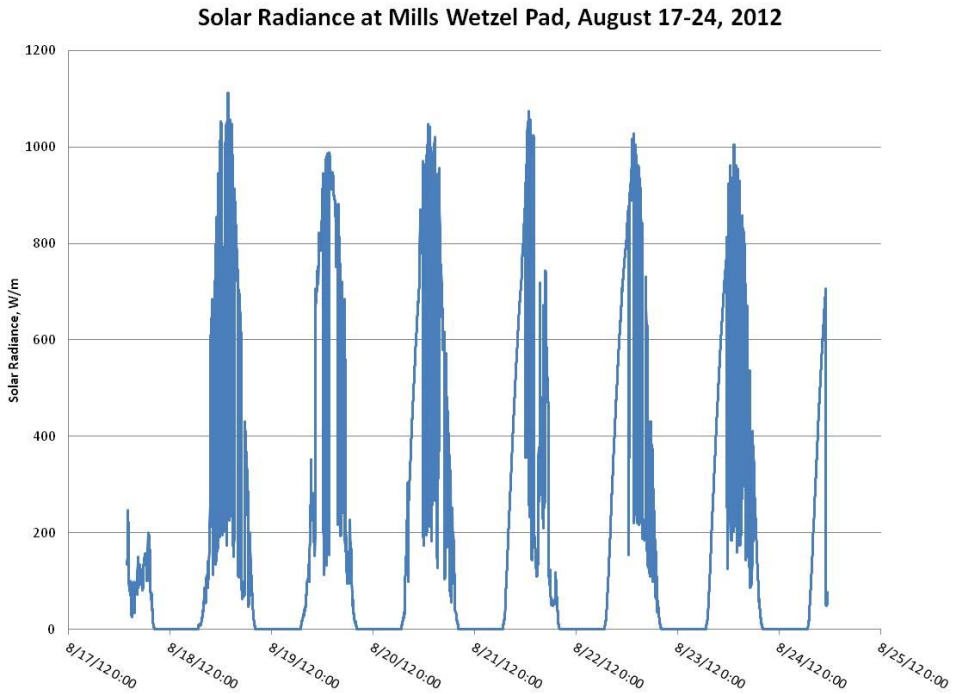

Figure B12: Solar radiance at the Mills-Wetzel pad.

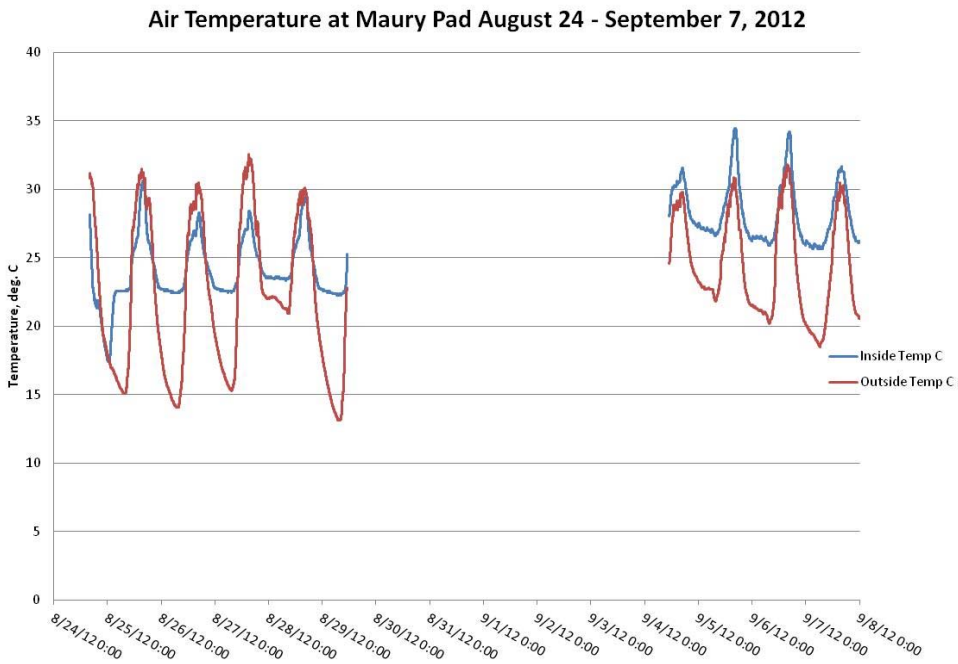

Figure B13: Air temperature inside and outside of the air monitoring laboratory for the first 2 weeks of monitoring at the Maury pad. The gap in the data was due to a software error.

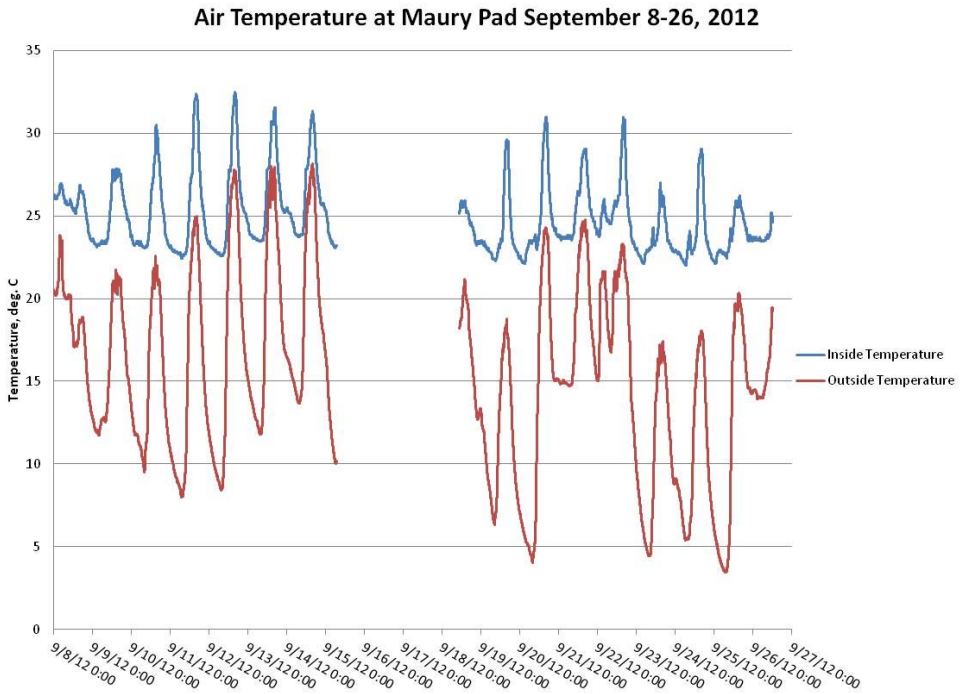

Figure B14: Air temperature inside and outside of the air monitoring laboratory for the second 2 weeks of monitoring at the Maury pad. The gap in the data was due to a software error.

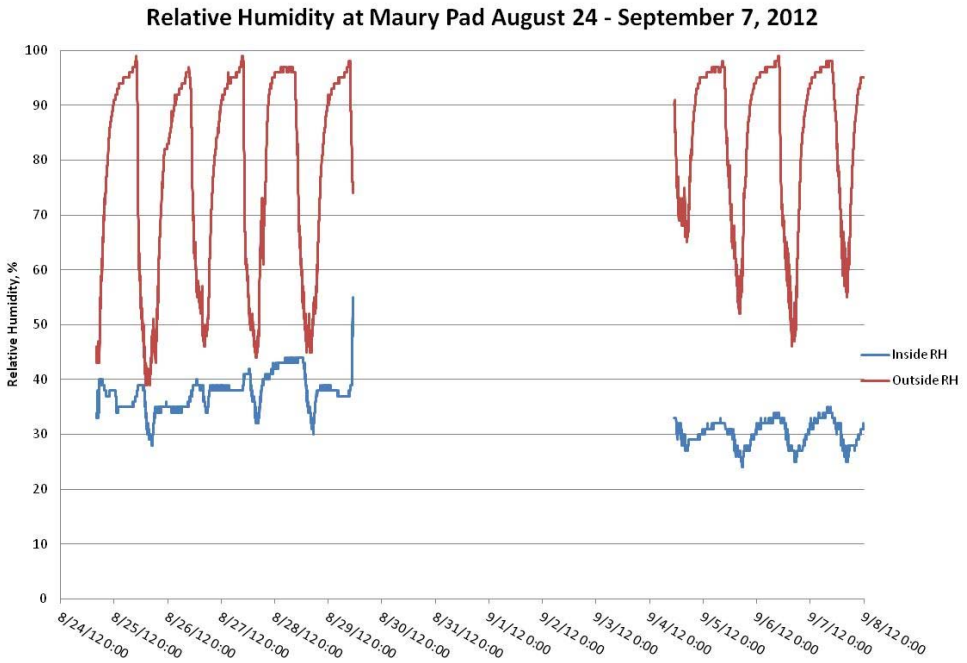

Figure B15: Relative humidity inside and outside of the air monitoring laboratory for the first 2 weeks of monitoring at the Maury pad. The gap in the data was due to a software error.

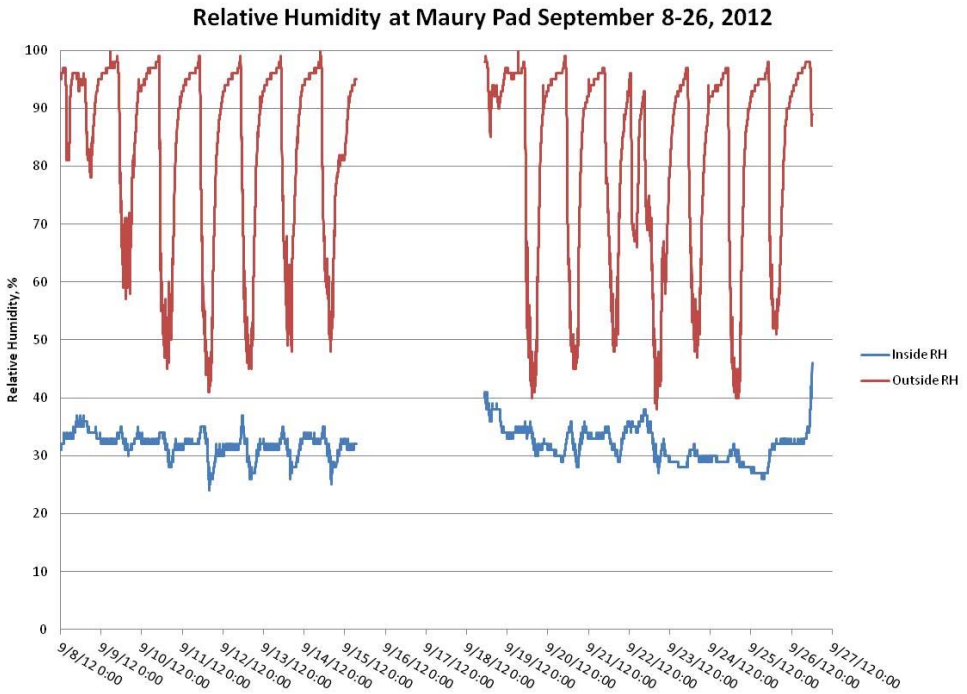

Figure B16: Relative humidity inside and outside of the air monitoring laboratory for the second 2 weeks of monitoring at the Maury pad. The gap in the data was due to a software error.

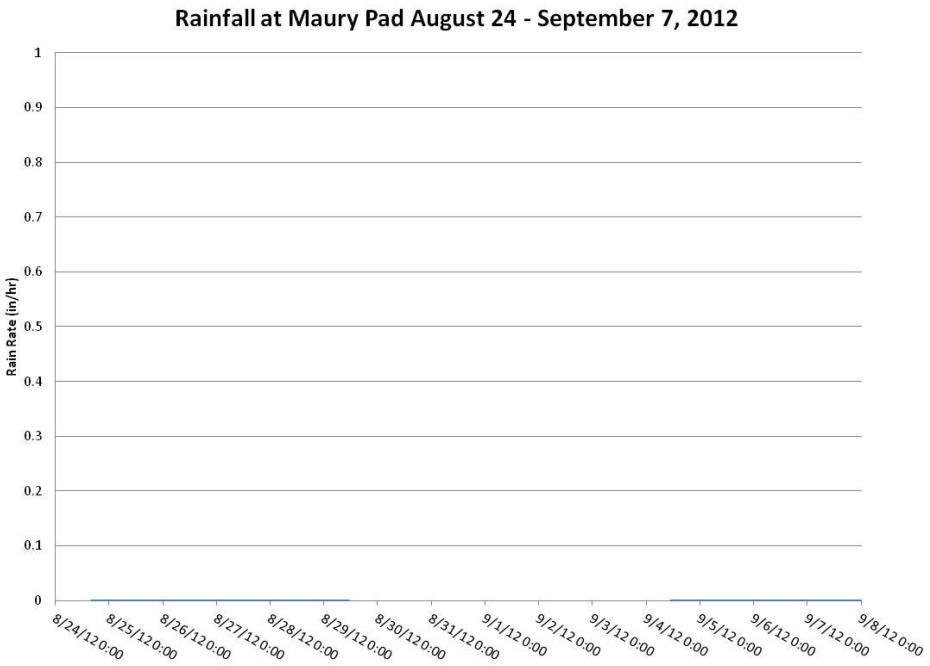

Figure B17: Rainfall events for the first 2 weeks of monitoring at the Maury pad. The gap in the data was due to a software error.

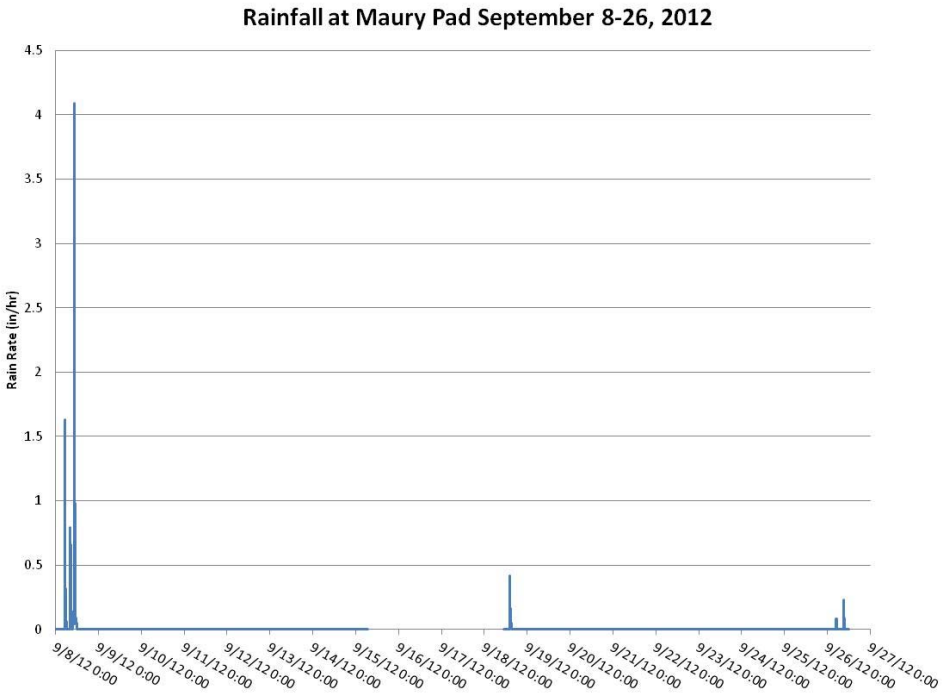

Figure B18: Rainfall events for the second 2 weeks of monitoring at the Maury pad. The gap in the data was due to a software error.

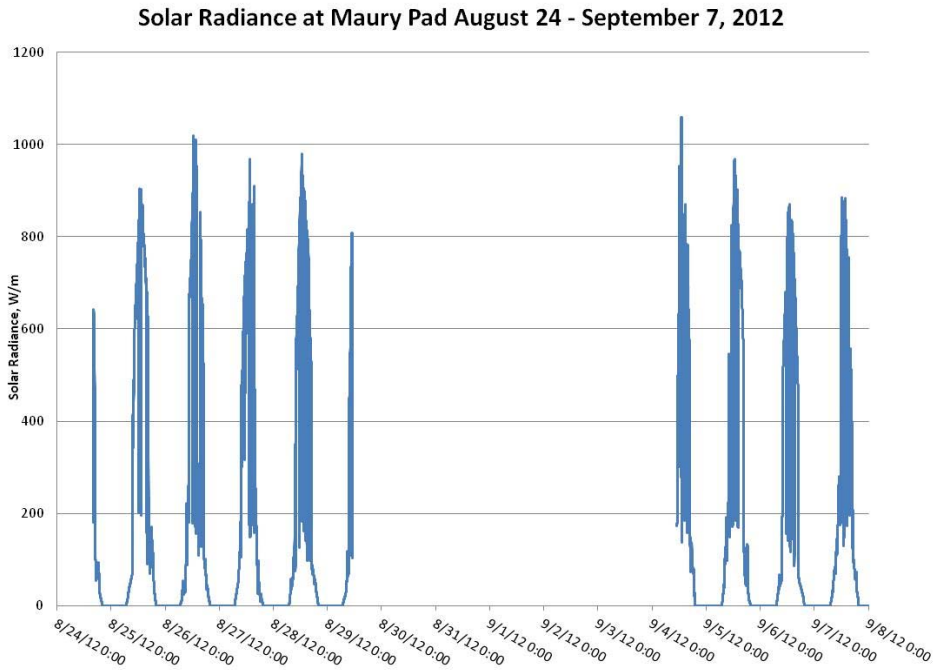

Figure B19: Solar radiance for the first 2 weeks of monitoring at the Maury pad. The gap in the data was due to a software error.

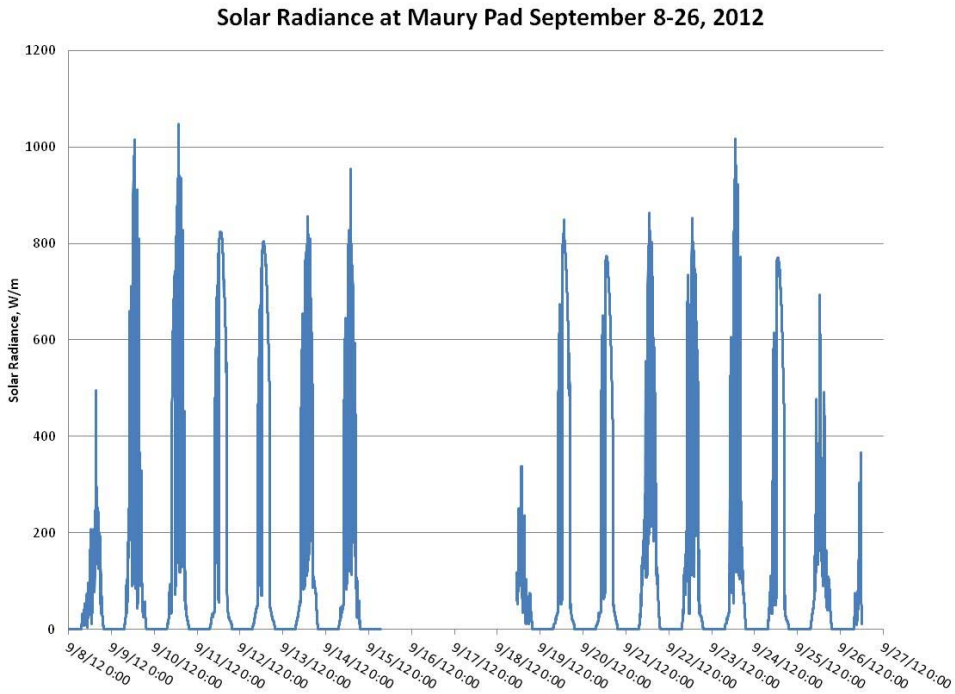

Figure B20: Solar radiance for the second 2 weeks of monitoring at the Maury pad. The gap in the data was due to a software error.

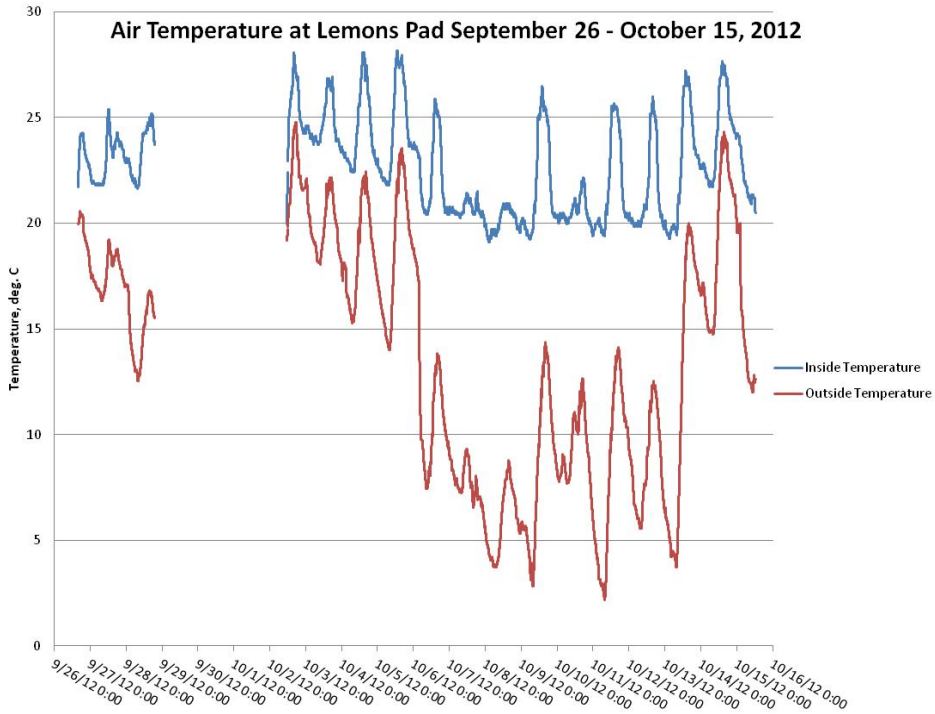

Figure B21: Air temperature inside and outside of the air monitoring laboratory at the Lemons pad. The gap in the data was due to a power interruption.

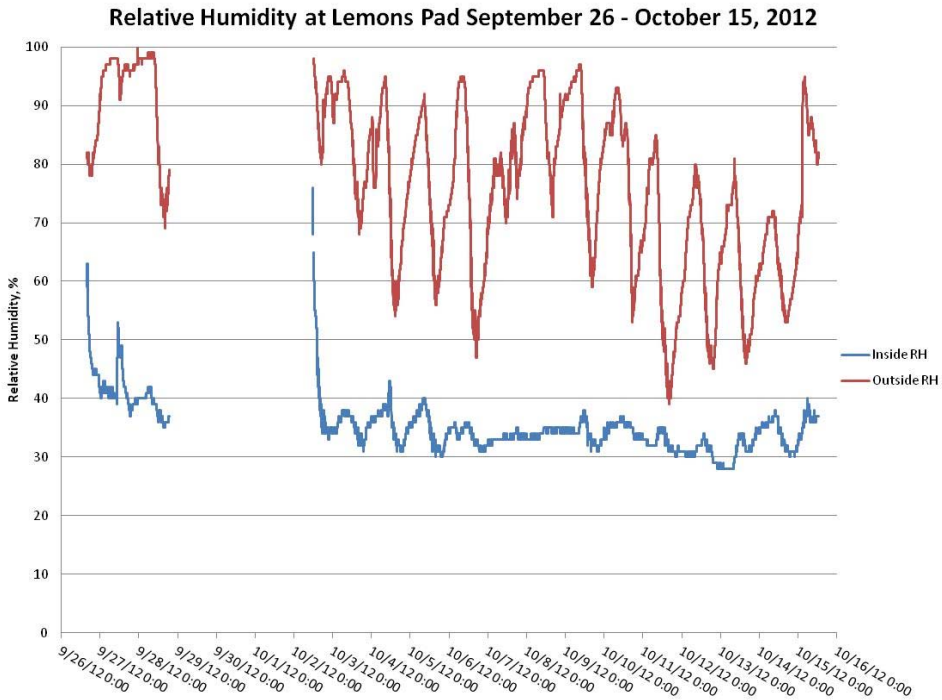

Figure B22: Relative humidity inside and outside of the air monitoring laboratory at the Lemons pad. The gap in the data was due to a power interruption.

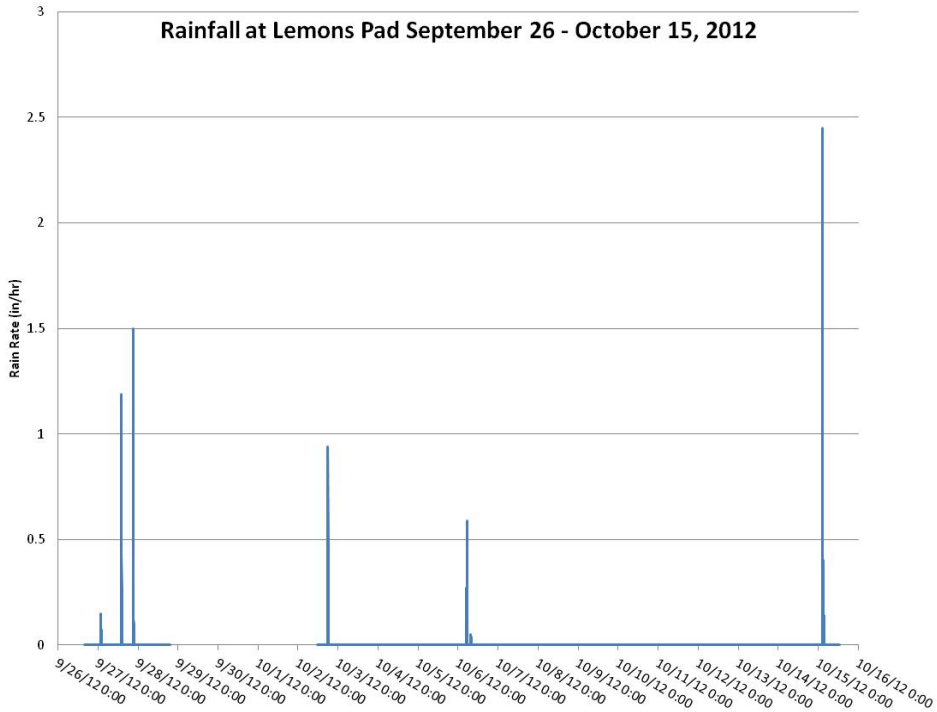

Figure B23: Rainfall events at the Lemons pad. The gap in the data was due to a power interruption.

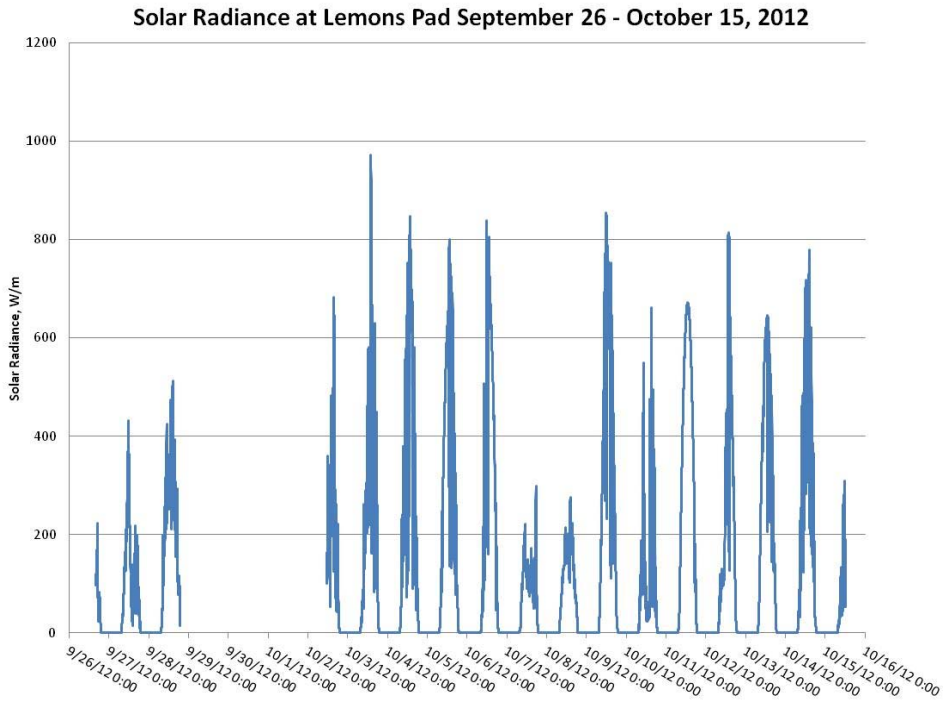

Figure B24: Solar radiance at the Lemons pad. The gap in the data was due to a power interruption.

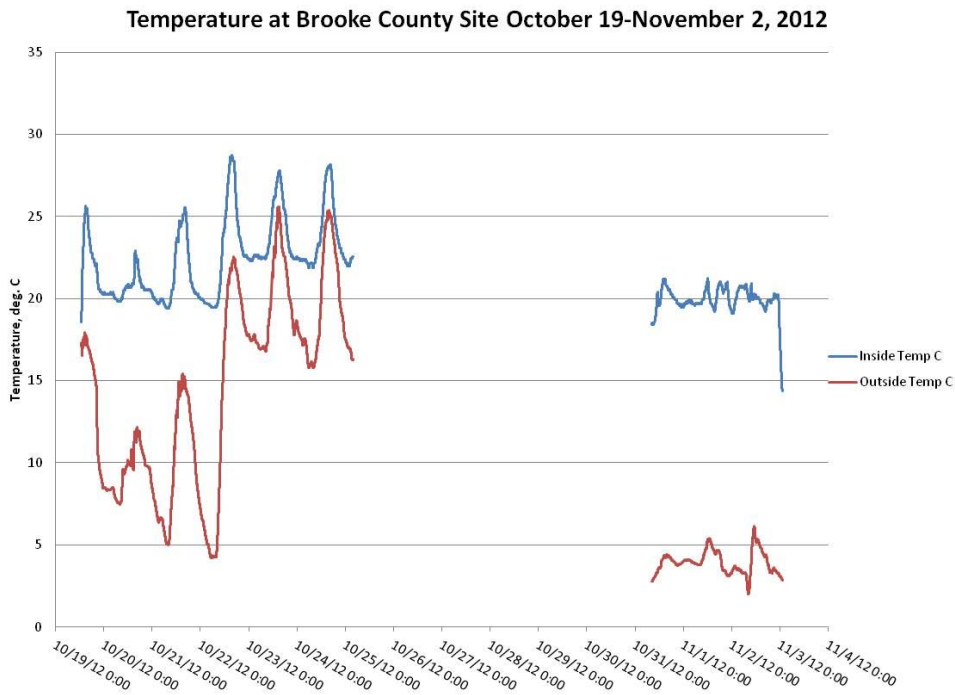

Figure B25: Air temperature inside and outside of the air monitoring laboratory at the WVDNR A pad. The gap in the data was due to a power interruption.

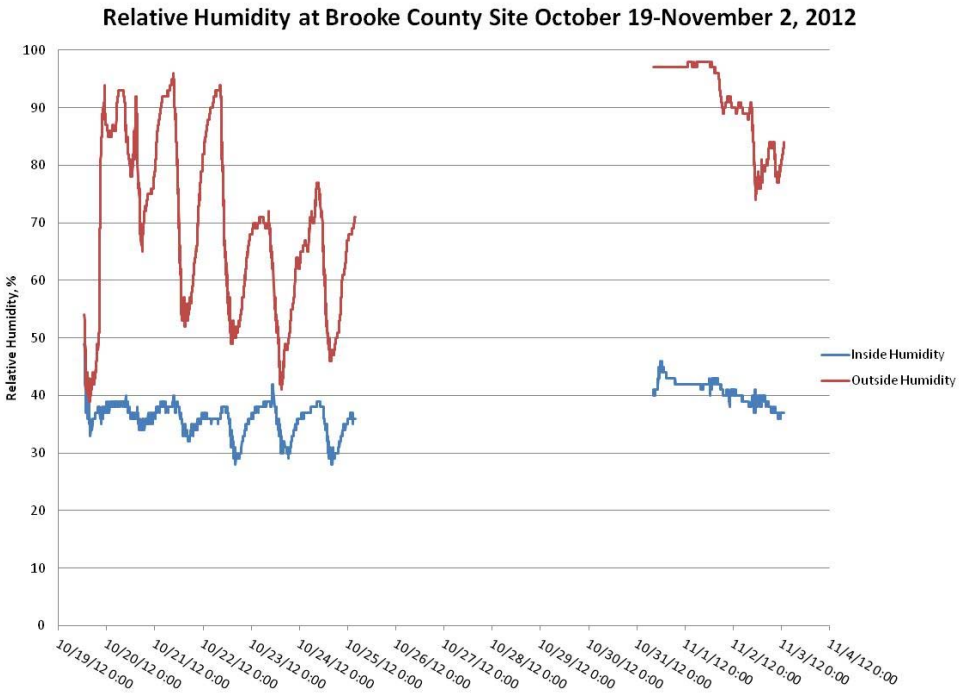

Figure B26: Relative humidity inside and outside of the air monitoring laboratory at the WVDNR A pad. The gap in the data was due to a power interruption.

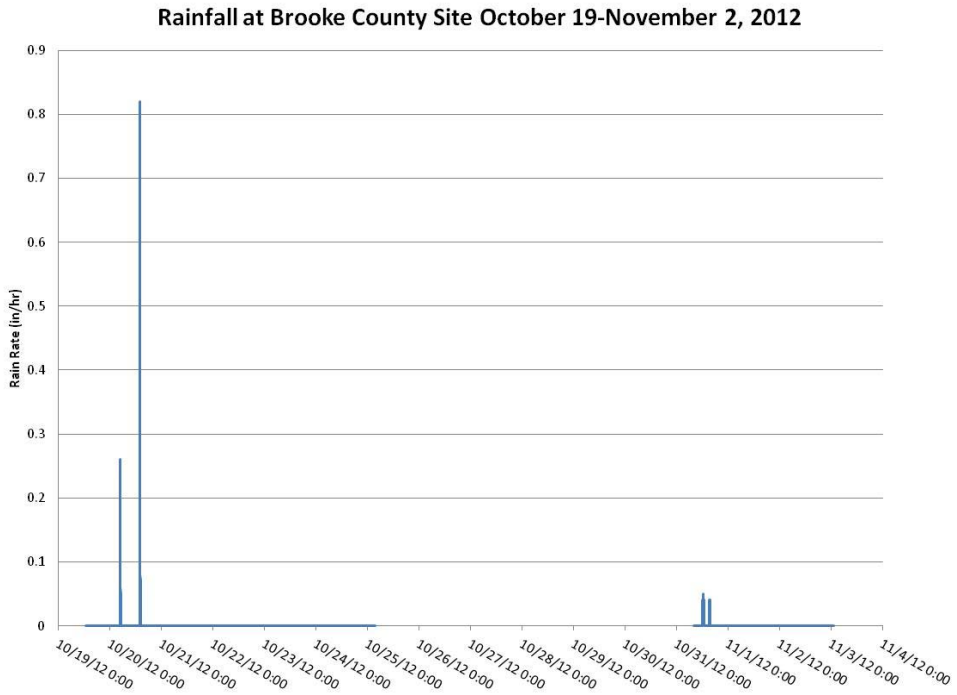

Figure B27: Rainfall events at the WVDNR A pad. The gap in the data was due to a power interruption.

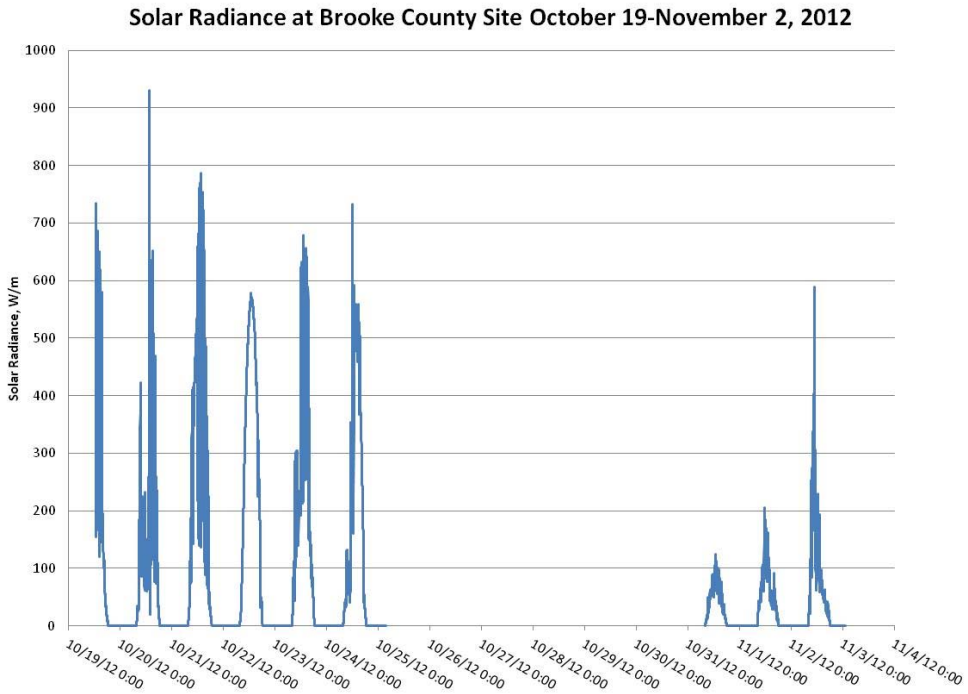

Figure B28: Solar radiance at the WVDNR A pad. The gap in the data was due to a power interruption.

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