
BASELINE AIR QUALITY ASSESSMENT

Deep River Basin, Lee County North Carolina

JULY 12, 2018

NORTH CAROLINA DEPARTMENT OF ENVIRONMENTAL QUALITY

DIVISION OF AIR QUALITY

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1.0 EXECUTIVE SUMMARY

The North Carolina Division of Air Quality, or DAQ, has completed the hydraulic fracturing baseline air quality monitoring project at the Blackstone site in the Deep River geological basin located south-southwest of the city of Sanford in Lee County, North Carolina. This study focused on collecting several air quality measurements, namely ozone, particulate matter, or PM, oxides of nitrogen, or NO_x, sulfur dioxide, or SO₂, aldehydes, speciated volatile organic compounds, or VOC, and meteorological data. DAQ currently operates long-term air monitoring sites that are upwind and downwind from the Blackstone site. The DAQ measured all pollutants included in this study at both the Blackstone site and the Millbrook downwind site located in Raleigh, North Carolina. The DAQ measured the same pollutants, except for NO_x and SO₂, at the upwind Candor site in Montgomery County, North Carolina. To provide a general comparison of the air shed in Lee County with these two other air sheds in North Carolina, an assessment was made between the air quality measurements obtained at the Blackstone site to air quality measurements collected at the rural upwind site in Candor and the urban downwind Millbrook site.

Prevailing winds out of the southwest and west-southwest direction characterize the Lee County air shed. The ozone data exhibited very similar maximum daily 8-hour averages for both Candor and Blackstone, with the downwind urban site being slightly higher as expected. The PM data showed a slow rise in levels of PM as one traveled from the southern tip of the basin towards the downwind site. Nitrogen dioxide levels in Lee County were lower than those measured at the downwind urban site in Raleigh, as expected. The SO₂ values at the urban downwind site in Raleigh showed the highest concentrations of the two sites, yet both sites appeared to exhibit a downward trend over time. Based on collected VOC data and statistical analysis during the study period, the air sheds at Blackstone and Candor measured the same types of VOC at similar concentration levels.

This report further discusses the findings of this baseline study.

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2.0 INTRODUCTION

North Carolina General Assembly Session Law 2011-276 directed the Department of Environment and Natural Resources, currently, the Department of Environmental Quality, in conjunction with other agencies, “to study the issues of oil and gas exploration in the state and the use of horizontal drilling and hydraulic fracturing.”¹ Session Law 2012-143, Section 2(c), requires rules related to collection of baseline data in areas where oil and gas exploration and development activities are proposed.² The study recommended, among other things, the collection of baseline air quality information. Thus, the DAQ planned and initiated a baseline ambient air monitoring program. The Project Plan for Baseline Ambient Air Monitoring near Potential Shale Gas Development Zones in Lee County, North Carolina, provides additional information about this baseline ambient air monitoring program.³ This document contains the results of the baseline assessment where, in 2012, there was thought to be a high potential for shale gas exploration and extraction in the future.

Implicit in “baseline monitoring” is that monitoring occurs before well development, production and gas treatment. This data can be used when making a “before-during-after” comparison to characterize possible air quality impacts due to hydraulic fracturing. Because hydraulic fracturing has not occurred in North Carolina, this report contains a summary of the air quality in Lee County prior to hydraulic fracturing.

Objectives of the baseline study were to:

1. Measure target pollutant concentrations over a minimum one-year period to characterize baseline ambient conditions. (The actual study period lasted over four years. This report contains a summary of the first three years of monitoring).
2. Collect enough data to estimate annual average concentrations.
3. Implement monitoring consistent with existing state monitoring for ease of data comparability.
4. Use standard monitoring protocols to ensure consistent data of high quality.
5. Use conventional data reduction, data summary and analysis techniques to characterize the data.

This project plan recommended establishing a Lee County air monitoring site that would employ monitoring methods and equipment as used at other monitoring sites. Therefore, data collected would be directly comparable between the Lee County air monitoring site, named Blackstone, and DAQ’s existing air monitoring sites. The DAQ selected the Blackstone site, along with the two existing sites in Candor and Raleigh, referred to as Candor and Millbrook, to characterize air quality within, upwind and downwind of the Sanford sub-basin. Figure 1 displays the orientation of

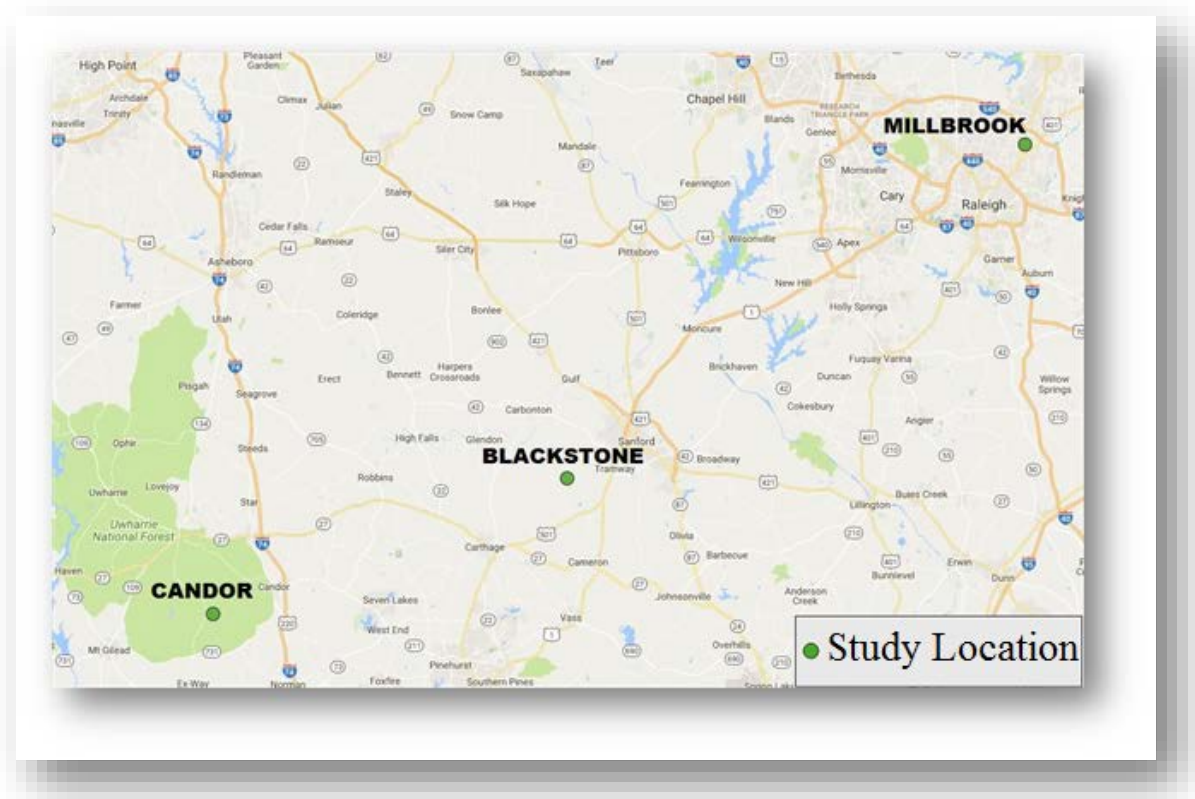
¹ General Assembly of North Carolina, Session 2011, Session Law 2011-276, House Bill 242, available on the worldwide web at <https://www.ncleg.net/Sessions/2011/Bills/House/PDF/H242v7.pdf>, accessed May 26, 2018.

² General Assembly of North Carolina, Session 2011, Session Law 2012-143, Senate Bill 820, available on the worldwide web at <https://www.ncleg.net/Sessions/2011/Bills/Senate/PDF/S820v6.pdf>, accessed May 26, 2018.

³ North Carolina Department of the Environment and Natural Resources, Project Plan for Baseline Ambient Air Monitoring near Potential Shale Gas Development Zones in Lee County, NC, updated Nov. 8, 2013, available on the worldwide web at https://files.nc.gov/ncdeq/Air%20Quality/monitor/specialstudies/DAQ_Project_Plan.pdf, accessed May 26, 2018.

these three monitoring stations, which are aligned with the axis of the Triassic Basin,⁴ southwest to northeast and with climatological wind directions in central North Carolina.⁵

Figure 1. Map of Monitoring Locations at Blackstone, Candor and Millbrook.



DAQ considers the Candor site as the “upwind” site. The study needed an “upwind” site to serve as a reference location to characterize ambient air typical to North Carolina. DAQ considers the Millbrook site as the “downwind” site. DAQ uses the “downwind” site to characterize the possible influence of emission sources located downwind from the reference site. The study site at Blackstone is located between the upwind site at Candor and the downwind site at Millbrook.

The United States Environmental Protection Agency, or EPA, uses core-based statistical areas, or CBSAs, as designated by the Office of Management and Budget, or OMB, to determine whether an area is urban or rural by EPA’s definition.⁶ The OMB designates CBSAs as metropolitan statistical areas, or MSAs, if they have at least one

⁴ U.S. Geological Survey, Assessment of Undiscovered Oil and Gas Resources of the East Coast Mesozoic Basins of the Piedmont, Blue Ridge Thrust Belt, Atlantic Coastal Plain and New England Provinces, 2011, available on the worldwide web at <https://pubs.usgs.gov/fs/2012/3075/fs2012-3075.pdf>, accessed on May 26, 2018.

⁵ North Carolina Climate Office, General Synopsis, available on the worldwide web at <http://www.nc-climate.ncsu.edu/climate/synopsis>, accessed May 25, 2018.

⁶ Office of Management and Budget, OMB Bulletin NO. 18-03, Revised Delineations of Metropolitan Statistical Areas, Micropolitan Statistical Areas and Combined Statistical Areas and Guidance on uses of the Delineations of These Areas, April 10, 2018, available on the worldwide web at <https://www.whitehouse.gov/wp-content/uploads/2018/04/OMB-BULLETIN-NO.-18-03-Final.pdf>, accessed May 25, 2018.

urban area of 50,000 or more population, plus adjacent territory that has a high degree of social and economic integration with the core as measured by the number of people from the adjacent territory who commute to the urban core for work. Micropolitan statistical areas have at least one urban cluster of at least 10,000 but less than 50,000 population plus adjacent territory that has a high degree of social and economic integration with the core as measured by the number of people from the adjacent territory who commute to the urban cluster for work. Based on population statistics, Candor is not in an MSA or a micropolitan statistical area so EPA considers it a rural site. Millbrook and Blackstone are in CBSAs so the EPA considers them urban sites. However, Blackstone is in the micropolitan statistical area of Sanford, which has significantly less population and less urban area than the Raleigh MSA where Millbrook is located. The urbanization trends based on overall population statistics often follow the concentration trends when comparing pollutant concentrations at each site.

For the criteria pollutants, ozone, PM, NO₂ and SO₂, the EPA determines ambient air quality status by measuring pollutant concentrations in outdoor air and comparing the measured concentrations to corresponding standards. The EPA defines the ambient air as “that portion of the atmosphere, external to buildings, to which the public has access.” The EPA classifies ambient air quality standards as primary and secondary. Primary standards are those established to protect public health. Secondary standards are those established to protect the public welfare from adverse pollution effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility, climate, property, transportation, economy and personal comfort and well-being. The EPA periodically reviews the scientific criteria used to establish the standards. Depending on its findings, the EPA may reestablish or change the standards. The EPA defines a pollutant measurement that is greater than the ambient air quality standard for a specific averaging time as an exceedance.

3.0 METEOROLOGICAL DATA

3.1 INTRODUCTION

The Blackstone site, as well as the upwind site at Candor, is equipped with meteorological sensors that record data at 1 and 5-minute intervals at a height of 2 meters and 10 meters. The downwind site at Millbrook is also equipped with meteorological sensors that record data at a height of 2 meters and 10 meters. The DAQ collected data for wind speed, wind direction, variability in wind direction, temperature and relative humidity. The DAQ used the wind speed and wind direction data to construct wind roses, showing the frequency of winds blowing from specific directions over a specified period, which may help identify contributing sources in the event of high pollutant readings during the study period.

3.2 MONITORING METHODOLOGY

The meteorological sampling and analysis methods used followed reference documents published by the EPA. The DAQ followed equipment manufacturer's operating manuals, agency standard operating procedures and preventative maintenance procedures. The DAQ measured temperature and relative humidity data using a Rotronics HC2 sensor located in a solar radiation shield at 2 meters above ground level. Wind data was continuously measured by a cross arm with an attached Met One 010C wind speed sensor and a Met One 020 wind direction sensor. The DAQ placed these two sensors on a tower at 10 meters above ground level.

The wind roses show the direction from which the wind was blowing and present the wind speeds from those directions as rays of varying lengths and colors. The length of each "spoke" around the circle equates to the frequency the wind blows from a specific direction per unit time and color coded to the range of speeds observed. Each wind rose consists of wind data for the entire 3-year study period. The wind rose does not give information about wind direction variations and only indicates the relative amount of time during the sampling period that the winds originated from a specific direction. While the wind direction provides a generalized directional location of a potential impact source, the wind speed can provide a generalized distance from the air monitoring site to a potential impact source.

3.3 WIND ROSE DATA

Figure 2 through Figure 4 on the following pages contain examples of wind roses generated by wind speed and wind direction sensors at the Blackstone, Candor and Millbrook monitoring sites during the study period.

Figure 2. Blackstone Wind Rose (2014-2016).

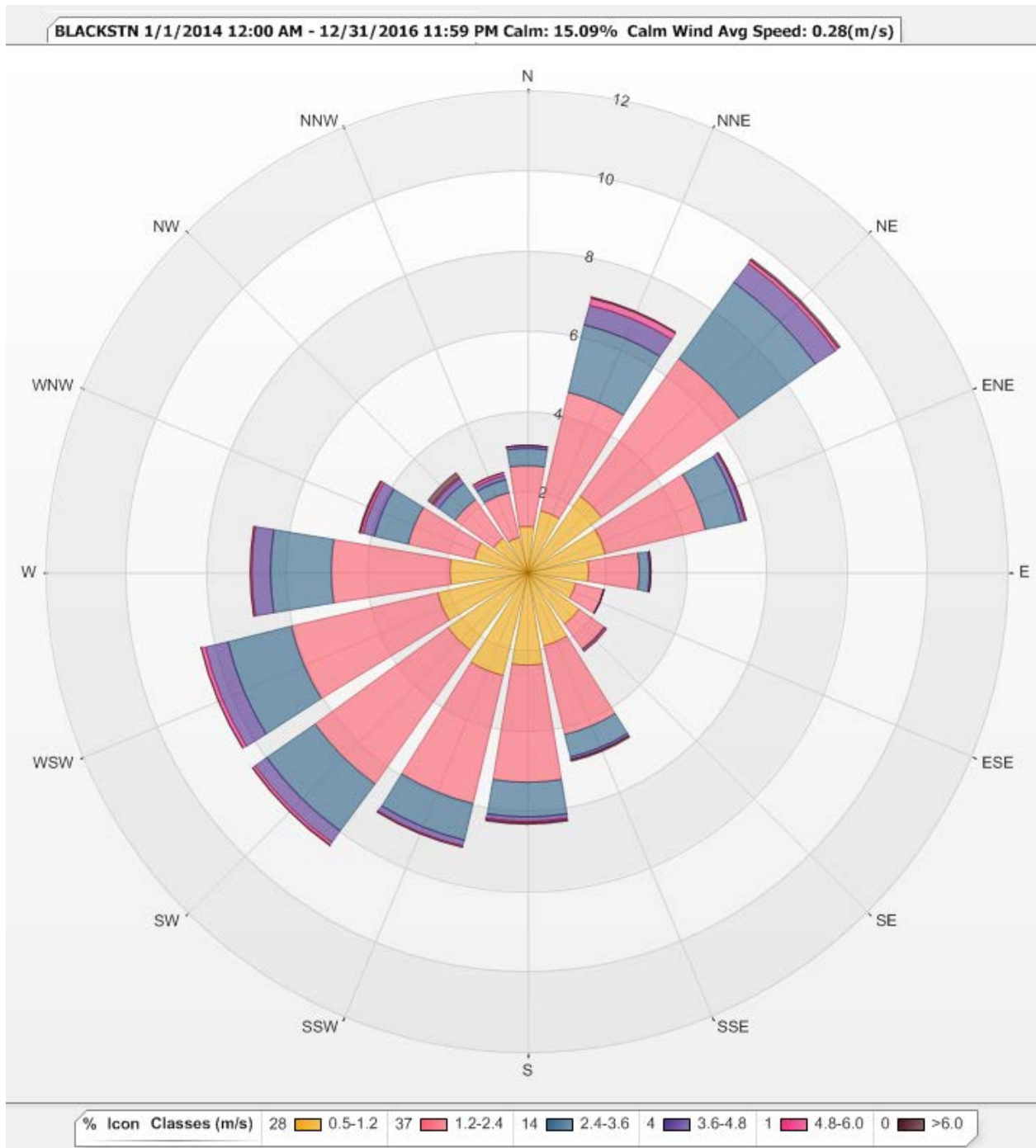


Figure 3. Candor Wind Rose (2014-2016).

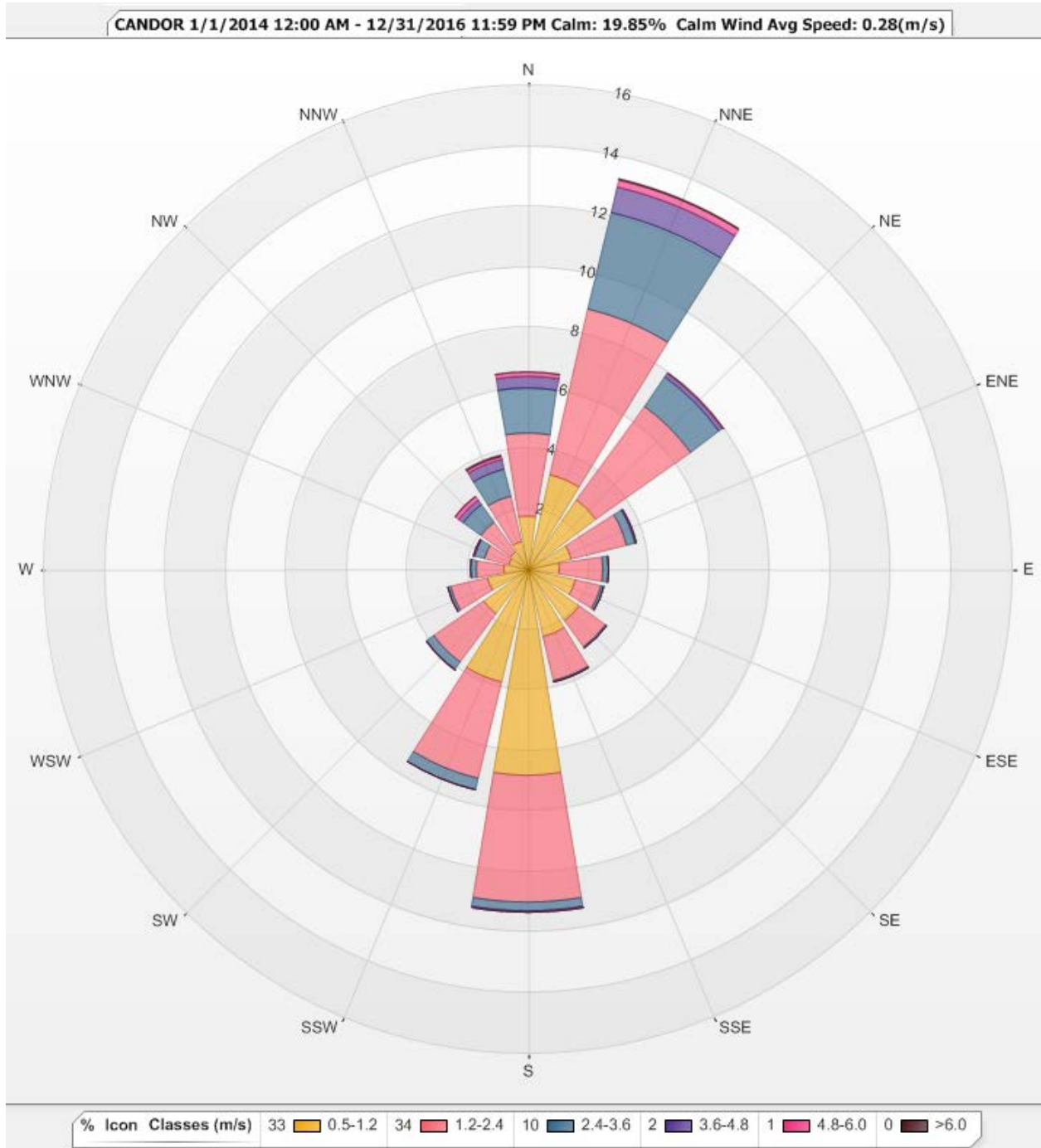
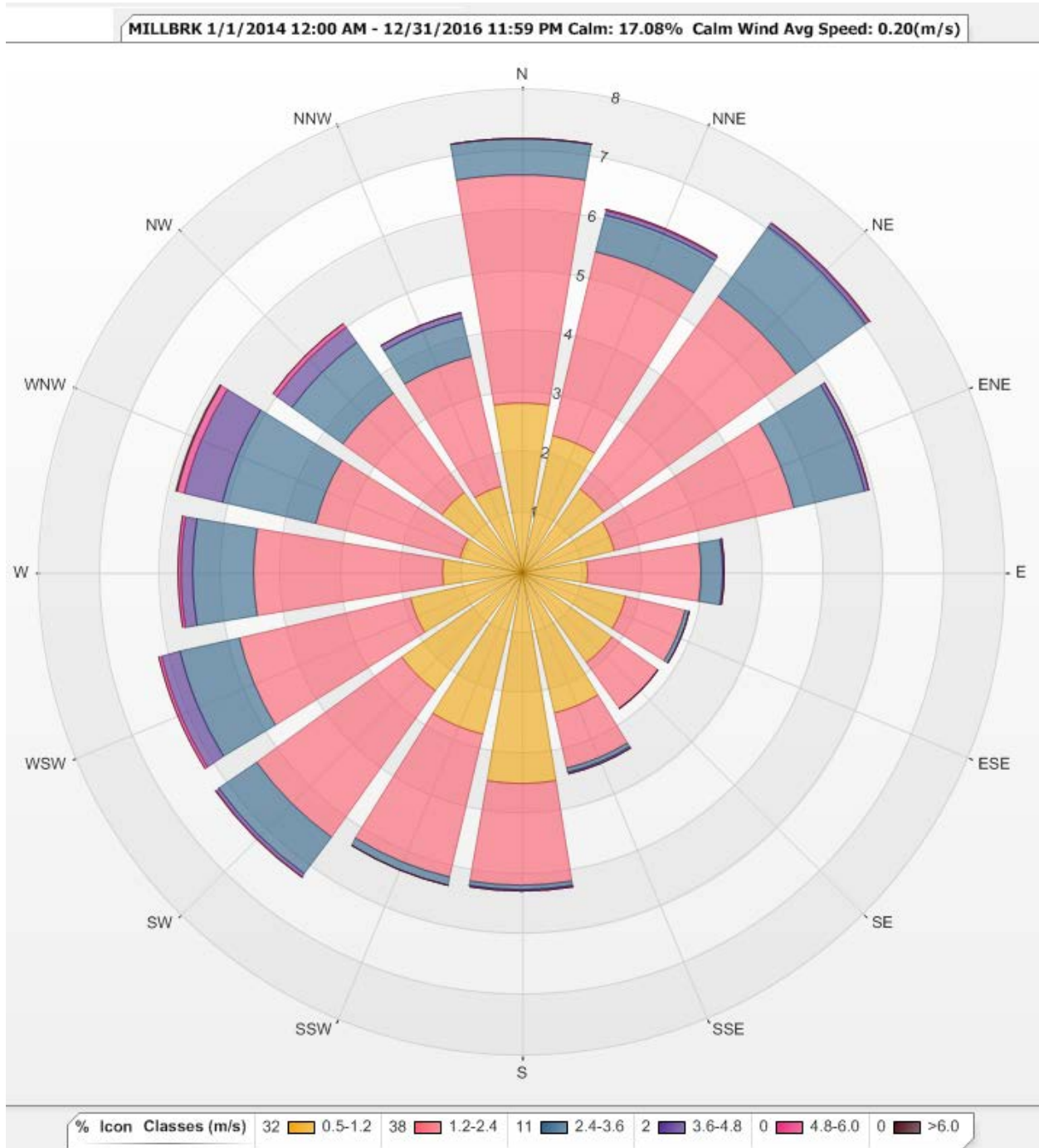


Figure 4. Millbrook Wind Rose (2014-2016).



3.4 SUMMARY OF MONITORING DATA

The Blackstone wind rose indicates the wind generally blows either from the southwest, west southwest and west or from the northeast with a predominant wind speed range of 1.2-2.4 meters per second, or m/s. Candor's wind rose indicates the wind generally blows from the south, north northeast and northeast with a predominant wind speed range of 1.2-2.4 m/s. Millbrook's wind rose indicates the wind generally blows from all directions with a predominant wind speed range of 1.2-2.4 m/s.

3.5 CONCLUSION

Wind roses can provide stake holders the ability to locate potential impact sources relative to the air monitoring site location. The Blackstone, Candor and Millbrook wind roses indicate similar wind speed ranges at all three sites during the study period. The wind direction data tend to vary from site to site, but overall the wind generally blows from the south, southwest direction at all sites. According to the North Carolina Climate Office, the winds in North Carolina come predominately from a westerly direction due to North Carolina's geographical location.⁷ The prevailing winds come from the southwest 10 months of the year and from the northeast in September and October.⁸

Wind roses can also be a useful tool in confirming the validity of a site location for air monitoring. The Blackstone site is located northeast of potential shale gas well sites in the deep river basin. Thus, DAQ positioned the site in a location that would measure the potential air emissions from the deep river basin on days when the wind was blowing from the southwest, west and south.

⁷ North Carolina Climate Office, General Synopsis, available on the worldwide web at <http://www.nc-climate.ncsu.edu/climate/synopsis>, accessed May 25, 2018.

⁸ *Ibid.*

4.0 OZONE

4.1 INTRODUCTION

Natural gas development and production emit criteria pollutants as defined by the Clean Air Act (EPA, 2012). The main pollutants produced in shale gas extraction are NO_x and VOCs. In the presence of sunlight, these react to form ozone and contribute to regional air problems. Ozone is the most widespread and serious criteria air pollutant in North Carolina and even moderate concentrations can be harmful to people, animals, vegetation and materials.

Ozone is a pulmonary irritant, affecting the respiratory mucous membranes, as well as other lung tissues and respiratory functions. Studies show ozone impairs normal function of the lung causing shallow, rapid breathing and a decrease in pulmonary function. Other symptoms of exposure include chest tightness, coughing and wheezing. People with asthma, bronchitis or emphysema will develop breathing difficulty when exposed to high, short-term concentrations. Continued or repeated long-term exposure may result in permanent lung damage.

Ozone damages vegetation by injuring leaves. It enters the plant's leaves through its gas exchange pores, or stomata, just as other atmospheric gases do in normal gas exchange. Ozone dissolves in the water within the plant and reacts with other chemicals, causing a variety of problems such as slowed photosynthesis, lower yields and greater susceptibility to pests.

Ozone also accelerates material aging by cracking rubber and fading dyes and paint. Ozone in the air will attack the double bonds in rubber chains, with natural rubber and nitrile rubber being the most sensitive to degradation. Ozone increases the oxidation rate of paints and dyes; primarily fading many of the natural dyes and dye-based pigments used by artists.

Table 1 summarizes the national primary, secondary and North Carolina ambient air quality standards in effect during the study. At the beginning of the study, the primary and secondary standards were set at 0.075 parts per million, or ppm, up to and including 2014 and 2015. In October 2015, the EPA revised the standard, starting in 2016, to 0.070 ppm. In 2015, EPA directives and Code of Federal Regulations, or CFR, guidance also changed the hours of day used to calculate the maximum 8-hour average for the day. The DAQ revised and back calculated design values, or DVs, with the 'new' standard, i.e. 0.070 ppm, back to 2014 and forward through 2016 data.

Table 1. National and North Carolina Ambient Air Quality Ozone Standards as of 2016.

Pollutant/ Ambient Measurement/ (Reference)	Averaging Period	Type of Summary	Primary National (Health Related) Standard	Secondary National (Welfare Related) Standard	North Carolina Standard
Ozone (40CFR50, App. I)	8 hours	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years	0.070 ppm	0.070 ppm	0.070 ppm

4.2 MONITORING METHODOLOGY

All air monitoring sampling and analysis methods followed reference methodologies published by the EPA.⁹ For the two DAQ-operated monitors at Blackstone and Millbrook, the DAQ followed equipment manufacturer's operating manuals, agency standard operating procedures and preventative maintenance procedures. Ozone data were continuously measured by Thermo Environmental Instruments Model 49i ozone analyzers with Thermo Environmental Instruments Model 49CPS or 49i Calibrators and ESC 8832 Data loggers. The DAQ used a Teledyne API Model 701 Zero Air Generator for zero-point generation and to provide zero air for the ozonated precision and span points via the calibrator. This instrumentation is consistent with monitoring equipment and methods used at all DAQ ozone monitoring sites. The ozone monitor at Candor is part of the Clean Air Status and Trends Network and EPA's contractor operates it according to the protocols of that program, which includes year-round operation.¹⁰ The DAQ periodically conducts a performance evaluation on the Candor ozone monitor by testing the monitor with three to four concentrations of ozone. The results of these evaluations indicate the monitor meets DAQ's performance criteria.

The DAQ also operated its two ozone monitors year-round to obtain a larger database of baseline data at all three sites. The normal ozone season established by EPA ran from April through October, up to and including year 2016. In October 2015 when the EPA revised the ozone standard, they also revised the ozone season.

⁹ U.S. EPA, List of Designated and Equivalent Methods, available on the worldwide web at https://www.epa.gov/sites/production/files/2018-01/documents/amtic_list_dec_2017_update_1-20-2018_0.pdf, accessed May 25, 2018.

¹⁰ U.S. EPA, CASTNET ozone monitoring, available on the worldwide web at <https://www.epa.gov/castnet/castnet-ozone-monitoring>.

4.3 SUMMARY OF MONITORING DATA

The EPA revised and updated the primary and secondary national ambient air quality standards, or NAAQS, for ozone during 2016 to 0.070 ppm or 70 parts per billion, or ppb. Due to the new standard, an escalation of exceedance events across the state occurred. During 2016, a total of 39 exceedance events occurred across the state with the new standard in place. Even with the 39 exceedances observed in 2016, North Carolina achieved attainment status in all counties across the state. It is significant that of the three sites presented in this report, only the Millbrook urban downwind site exhibited two ozone exceedance values. As shown in Table 2 one exceedance occurred during 2015 and the other during 2016.

Table 2. First through Fourth Daily 8-Hour Average Maximum Ozone Values in Parts per Billion for 2014 through 2016.

	First Maximum Daily 8-Hour Average	Second Maximum Daily 8-Hour Average	Third Maximum Daily 8-Hour Average	Fourth Maximum Daily 8-Hour Average
2014				
Blackstone	69	66	64	62
Candor	65	64	62	62
Millbrook	70	64	64	63
2015				
Blackstone	65	60	60	60
Candor	64	63	61	59
Millbrook	71	68	65	65
2016				
Blackstone	69	66	65	64
Candor	66	66	63	62
Millbrook	74	70	69	69

Per 40 CFR Part 50, the EPA uses design values, or DVs, to classify areas consistent with the NAAQS. For ozone, the EPA based the DV on the 4th highest daily maximum 8-hour average value for a site, averaged over a three-year period. The DAQ used the 70-ppb standard for the 2014 thru 2016 DV calculations. The data completeness requirement is no less than 75 percent per year and a 3-year average of 90 percent completeness. If the DV exceeds the 70-ppb standard, then EPA classifies the area as “non-attainment” and the area violates the standard. Figure 5 displays the DVs throughout the state for 2014 through 2016. All monitors throughout the state attained the standard. The DVs increase going from the rural Candor site to the urban Millbrook site.

Figure 5. Ozone Design Values for 2014 Through 2016 at Blackstone, Millbrook and Candor Sites.

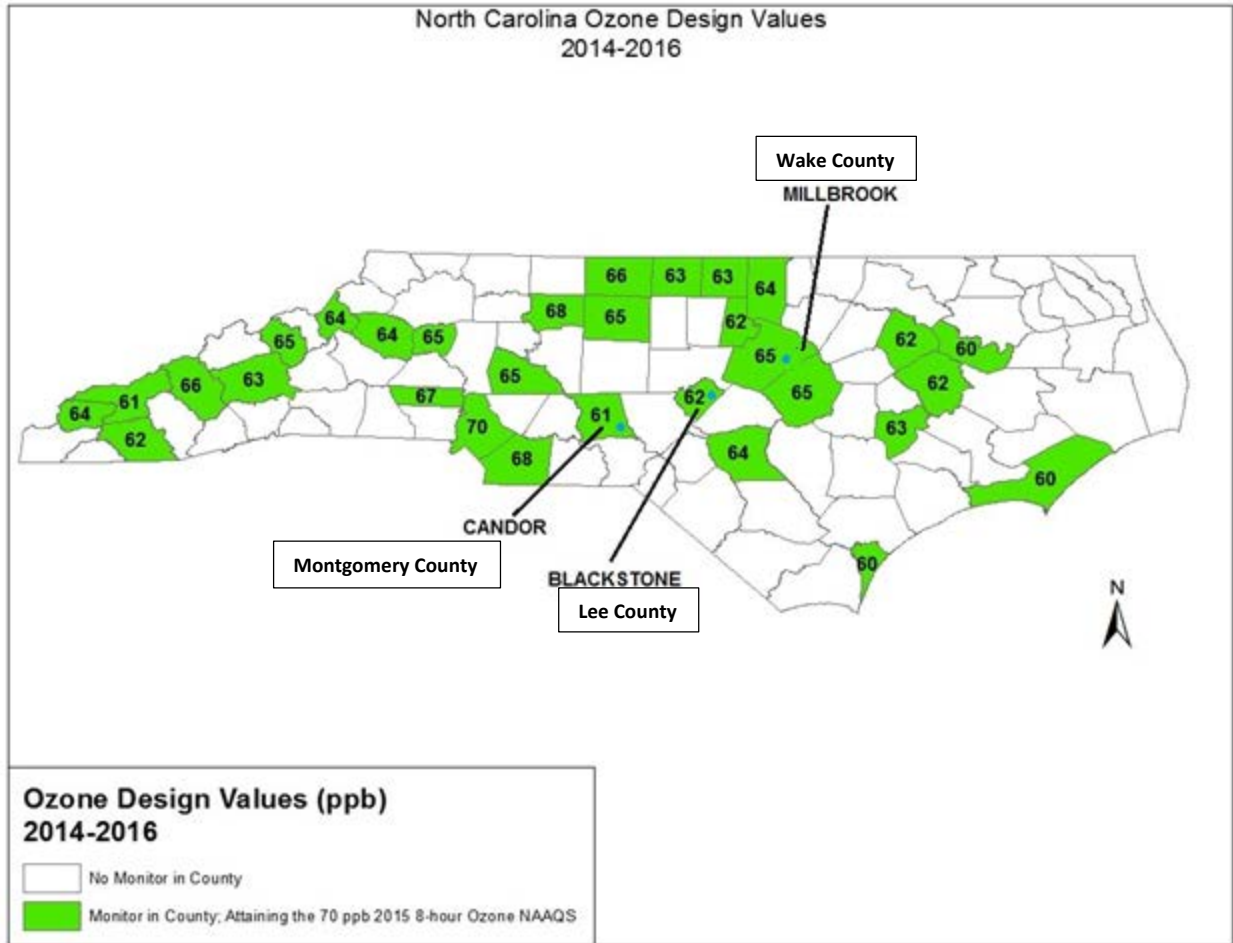


Figure 6 displays the ranked maximum daily 8-hour ozone concentrations at Millbrook for 2014, 2015 and 2016. All three years show a similar pattern with most concentrations being less than 60 ppb. Table 3 summarizes the average of the maximum daily 8-hour average; the 98th percentile of the maximum daily 8-hour average and the 4th maximum daily 8-hour average ozone concentrations at Millbrook for the three years. These statistics remained the same in 2014 and 2015.

Figure 6. Ranked Millbrook Maximum Daily 8-Hour Ozone Concentrations.

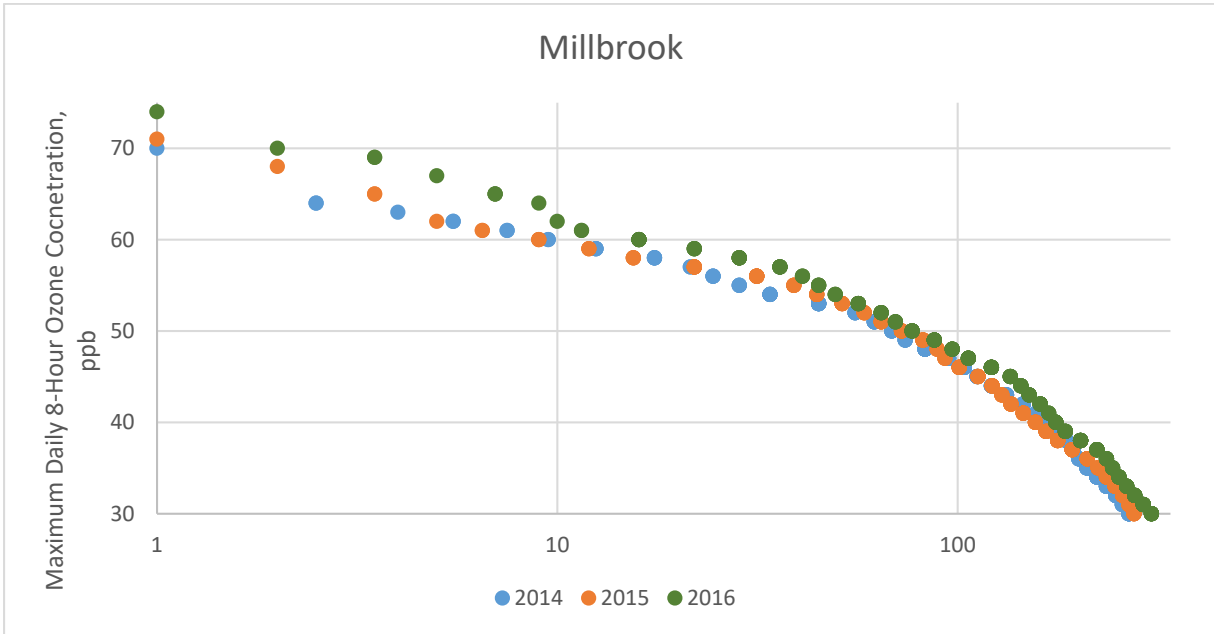


Table 3. Millbrook 4th Maximum, 98th Percentile and Average Maximum Daily 8-Hour Average Ozone Concentrations.

Millbrook	2014	2015	2016
<i>Average of the maximum daily 8-hour average, ppb</i>	39	39	41
<i>98th percentile of the maximum daily 8-hour average, ppb</i>	61	61	65
<i>4th maximum daily 8-hour average, ppb</i>	63	65	69

Figure 7 displays the ranked maximum daily 8-hour ozone concentrations at Blackstone for 2014, 2015 and 2016. All three years show a similar pattern with most concentrations being less than 60 ppb. Table 4 summarizes the average of the maximum daily 8-hour average; the 98th percentile of the maximum daily 8-hour average and the 4th maximum daily 8-hour average ozone concentrations at Blackstone for the three years. These statistics were very close to one another in 2014 and 2016 and appeared to go down in 2015.

Figure 7. Ranked Blackstone Maximum Daily 8-Hour Ozone Concentrations.

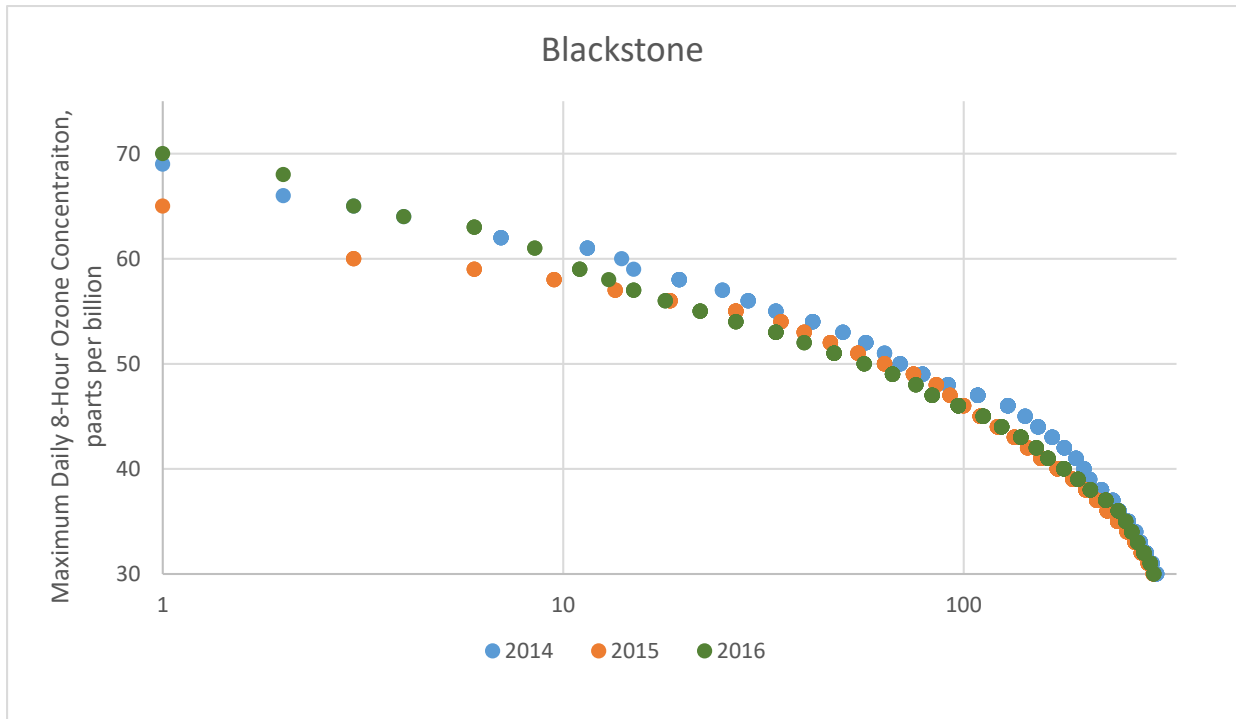


Table 4. Blackstone 4th Maximum, 98th Percentile and Average Maximum Daily 8-Hour Average Ozone Concentrations.

Blackstone	2014	2015	2016
<i>Average of the maximum daily 8-hour average, ppb</i>	41	39	41
<i>98th percentile of the maximum daily 8-hour average, ppb</i>	62	59	64
<i>4th maximum daily 8-hour average, ppb</i>	64	60	64

Figure 8 displays the ranked maximum daily 8-hour ozone concentrations at Candor for 2014, 2015 and 2016. All three years show a similar pattern with most concentrations being less than 60 ppb. Table 5 summarizes the average of the maximum daily 8-hour average; the 98th percentile of the maximum daily 8-hour average and the 4th maximum daily 8-hour average ozone concentrations at Candor for the three years. These statistics may indicate a slight downward trend between 2014 and 2016.

Figure 8. Ranked Candor Maximum Daily 8-Hour Average Ozone Concentrations.

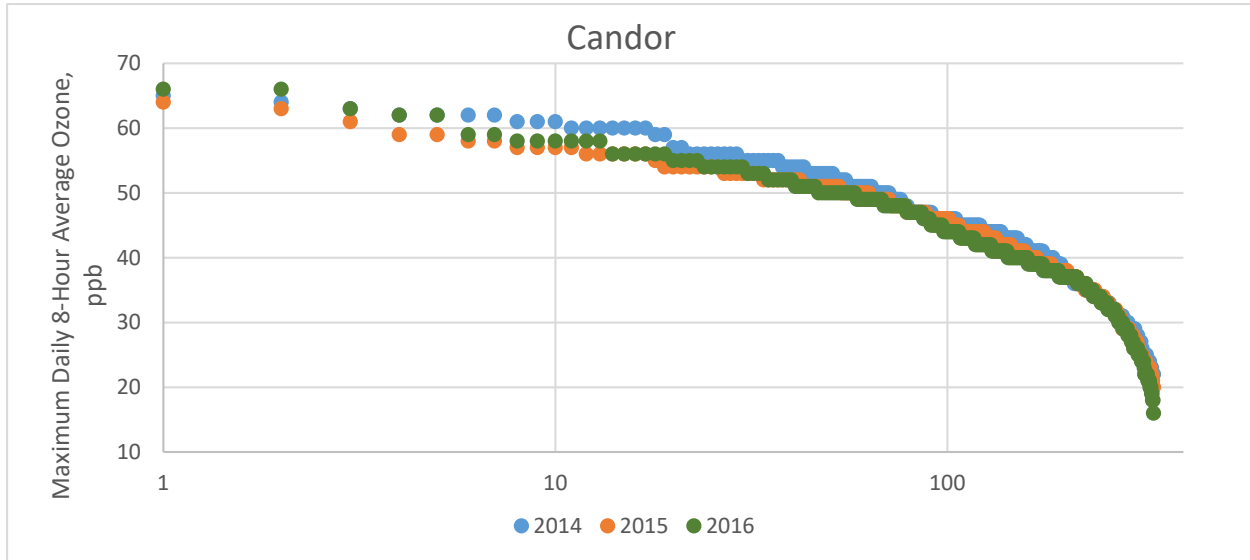
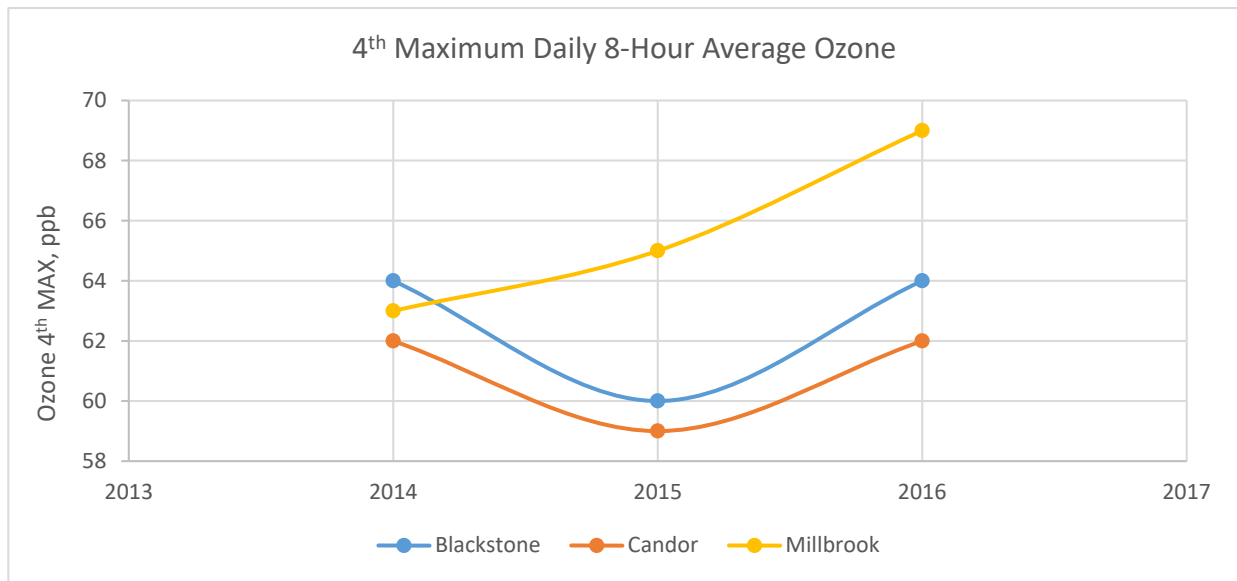


Table 5. . Candor 4th Maximum, 98th Percentile and Average Maximum Daily 8-Hour Average Ozone Concentrations.

Candor	2014	2015	2016
<i>Average of the maximum daily 8-hour average, ppb</i>	40	39	39
<i>98th percentile of the maximum daily 8-hour average, ppb</i>	62	58	59
<i>4th maximum daily 8-hour average, ppb</i>	62	59	62

Figure 9 displays the trends in the fourth maximum daily 8-hour ozone concentrations at Candor, Blackstone and Millbrook for 2014, 2015 and 2016. The fourth maximum daily 8-hour ozone concentrations at Candor and Blackstone display a similar trend for this three-year period. At the Millbrook site, the fourth maximum daily 8-hour average ozone concentrations displayed an upward trend from 2014 to 2016.

Figure 9. Fourth Maximum Daily 8-Hour Average Ozone Concentrations.



4.4 STATISTICAL ANALYSIS

The DAQ performed a Wilcoxon nonparametric test that compares two paired groups on the three datasets. The DAQ used the test to determine whether a statistically significant difference exists between two populations that have the same continuous distribution. The DAQ used the test to calculate the difference between each set of pairs and analyze these differences. Table 6 and Table 7 present the results of these tests. Based on the Wilcoxon Statistical Test, the DAQ does not have sufficient evidence to conclude the ozone dataset at Blackstone differs from the Candor ozone dataset in 2014, 2015 and 2016. Based on the Wilcoxon Statistical Test, the DAQ does not have sufficient evidence to conclude the ozone dataset at Blackstone differs from the Millbrook ozone dataset in 2014. However, the DAQ does have statistically significant evidence at $\alpha = 0.05$ to show that the ozone dataset at Blackstone is not equal to the ozone dataset at Millbrook in 2015 and 2016.

Table 6. Wilcoxon Statistical Test for Maximum Daily 8-Hour Average Ozone at Candor and Blackstone.

	2014	2015	2016
α	0.05	0.05	0.05
Tails	2	2	2
W(Candor)	45	49	45
W(Blckstr)	60	56	60
W_crit	36	36	36
	(45>36)	(49>36)	(45>36)

Table 7. Wilcoxon Statistical Test for Maximum Daily 8-Hour Average Ozone at Millbrook and Blackstone.

	2014	2015	2016
α	0.05	0.05	0.05
Tails	2	2	2
W(Millbro)	48	73	70
W(Blckstr)	57	32	35
W_crit	36	36	36
	(48>36)	(32<36)	(35<36)

4.5 CONCLUSION

The comparisons of more than three years of daily maximum 8-hour average ozone data for all three sites indicated consistency in data for each site from year to year. Millbrook exhibited slightly higher daily 8-hour average values, as expected, in general, from an urban site with a much denser population and greater potential for source emissions. Candor and Blackstone exhibited very similar maximum daily 8-hour averages throughout the study. Only the Millbrook site exhibited exceedances of the NAAQS during 2015 and 2016. The DVs were slightly higher for Millbrook. The DVs for Blackstone and Candor were very similar in value. The fourth highest daily maximum 8-hour average used to calculate the DVs was positive and linear for Millbrook and increasing for all three years of the study. Both Candor and Blackstone exhibited a negative slope during year 2015 and then a return to values like 2014 for 2016. It is uncertain what caused this dip. The dip could possibly be attributable to meteorological events or other influences beyond the scope of this report.

The DAQ performed Wilcoxon statistical analysis on the data collected at the Blackstone site and compared it with data collected at both the upwind Candor site and the downwind Millbrook site. There was no statistical significance between the Blackstone and Candor sites ozone data for the duration of the study. However, at $\alpha = 0.05$ we have statistically significant evidence to show that the Millbrook ozone data are not equal to the Blackstone ozone during years 2015 and 2016.

In conclusion, this study collected over three years of continuous ozone data that DAQ can use with a high degree of confidence for baseline reference data if needed at a future date. The ozone data is of interest since it can be

impacted from many of the byproducts of shale gas extraction processing depending on activity levels. Scientists have known and established many of these byproducts as precursors of ozone formation. Thus, the DAQ believes the data collected from the Blackstone site and the data generated from the downwind Millbrook site provide excellent datasets to compare against should the energy industry implement a shale gas extraction operation in the foreseeable future.

5.0 PARTICULATE MATTER

5.1 INTRODUCTION

Atmospheric PM is defined as any airborne material, except uncombined water (liquid, mist, steam, etc.), that exists in a finely divided form as a liquid or solid at standard temperature (25° C) and pressure (760 mm mercury) and has an aerodynamic diameter of less than 100 micrometers, or μm . Two of the most common monitored sizes of PM are PM with an aerodynamic diameter less than or equal to 10 μm , or PM_{10} , and PM with aerodynamic diameter less than or equal to 2.5 μm , or $\text{PM}_{2.5}$. The DAQ has performed PM_{10} sampling in North Carolina since 1985. Monitoring $\text{PM}_{2.5}$ became a separate requirement in 1999 and the DAQ has performed sampling in North Carolina since that year.

Many human activities, such as fuel combustion, motor vehicle operation, industrial processes, grass mowing, agricultural tilling and open burning, emit PM. Natural sources include windblown dust, forest fires, volcanic eruptions and plant pollen.

$\text{PM}_{2.5}$ can cause health problems affecting the respiratory system, including aggravation of existing lung and heart disease, limitation of lung clearance, changes in form and structure of organs and the development of cancer. Individuals most sensitive to the effects of PM include those with chronic obstructive lung or heart disease, those suffering from the flu, asthmatics, the elderly and children.

Table 8 summarizes the national primary, secondary and North Carolina ambient air quality standards in effect during the study.

Table 8. National and North Carolina Ambient Air Quality $\text{PM}_{2.5}$ Standards.

Pollutant/ Ambient Measurement/ (Reference)	Averaging Period	Type of Summary	Primary National (Health Related) Standard	Secondary National (Welfare Related) Standard	North Carolina Standard
Particle Pollution ($\text{PM}_{2.5}$) (40CFR50, App. N)	1 year	Annual mean, averaged over 3 years	12 $\mu\text{g}/\text{m}^3$	15 $\mu\text{g}/\text{m}^3$	12 $\mu\text{g}/\text{m}^3$
	24 hours	98 th percentile, averaged over 3 years	35 $\mu\text{g}/\text{m}^3$	35 $\mu\text{g}/\text{m}^3$	35 $\mu\text{g}/\text{m}^3$

5.2 MONITORING METHODOLOGY

The DAQ conducted ambient monitoring for calendar years 2014 through 2016. The DAQ continuously measured $\text{PM}_{2.5}$ data using Met One Instruments, Inc. BAM-1020 $\text{PM}_{2.5}$ samplers at all three sites. All air monitoring sampling and analysis methods followed reference methodologies published by the EPA.¹¹ The DAQ followed manufacturer's operating manuals, agency standard operating procedures and preventative maintenance procedures.

¹¹ U.S. EPA, List of Designated and Equivalent Methods, available on the worldwide web at https://www.epa.gov/sites/production/files/2018-01/documents/amtic_list_dec_2017_update_1-20-2018_0.pdf, accessed May 25, 2018.

5.3 SUMMARY OF MONITORING DATA

Figure 10 displays the ranked 24-hour average PM_{2.5} concentrations at Candor for 2014, 2015 and 2016. All three years show a similar pattern with most concentrations falling within the range of 5 to 15 micrograms per cubic meter or µg/m³. Table 9 summarizes the 98th percentile and average 24-hour average PM_{2.5} concentrations at Candor for the three years. These statistics show a downward trend from 2014 to 2016. Please note that the annual averages used in this report are not the same as the weighted annual averages used to calculate design values, although the annual average and weighted annual average will be very close to one another.

Figure 10. Ranked 24-Hour Average PM_{2.5} Concentrations at Candor.

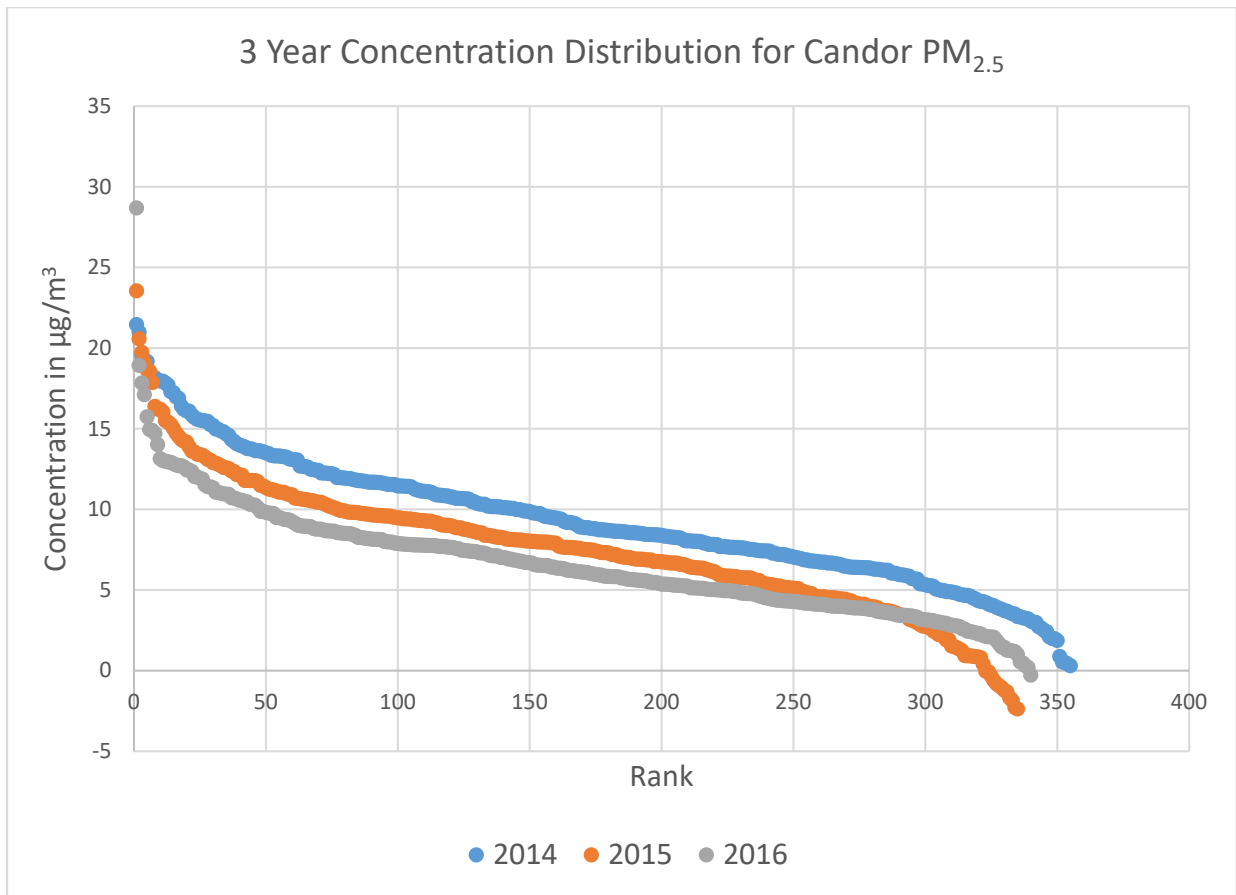


Table 9. Candor 98th Percentile and Annual Average of 24-Hour Average PM_{2.5} Concentrations.

Candor	2014	2015	2016	Three-Year Average Value for 2014-2016
Annual Average, µg/m ³	9.3	7.6	6.6	7.8
98 th Percentile, µg/m ³	18.2	18.0	14.9	17

Figure 11 displays the ranked 24-hour average PM_{2.5} concentrations at Blackstone for 2014, 2015 and 2016. All three years show a similar pattern with most concentrations falling within the range of 5 to 15 µg/m³. Table 10 summarizes the 98th percentile and average 24-hour average PM_{2.5} concentrations at Blackstone for the three years. These statistics show an increase in PM_{2.5} in 2015. This increase in 2015 is most likely due to the loss of three months of data from Feb. 23 to March 16, April 9 to May 8 and June 30 to July 23. Almost all data lost were due to problems with tape breaks caused by high humidity and improper orientation of the downtube, which caused punctures in the tape.

Figure 11. Ranked 24-Hour Average PM_{2.5} Concentrations at Blackstone.

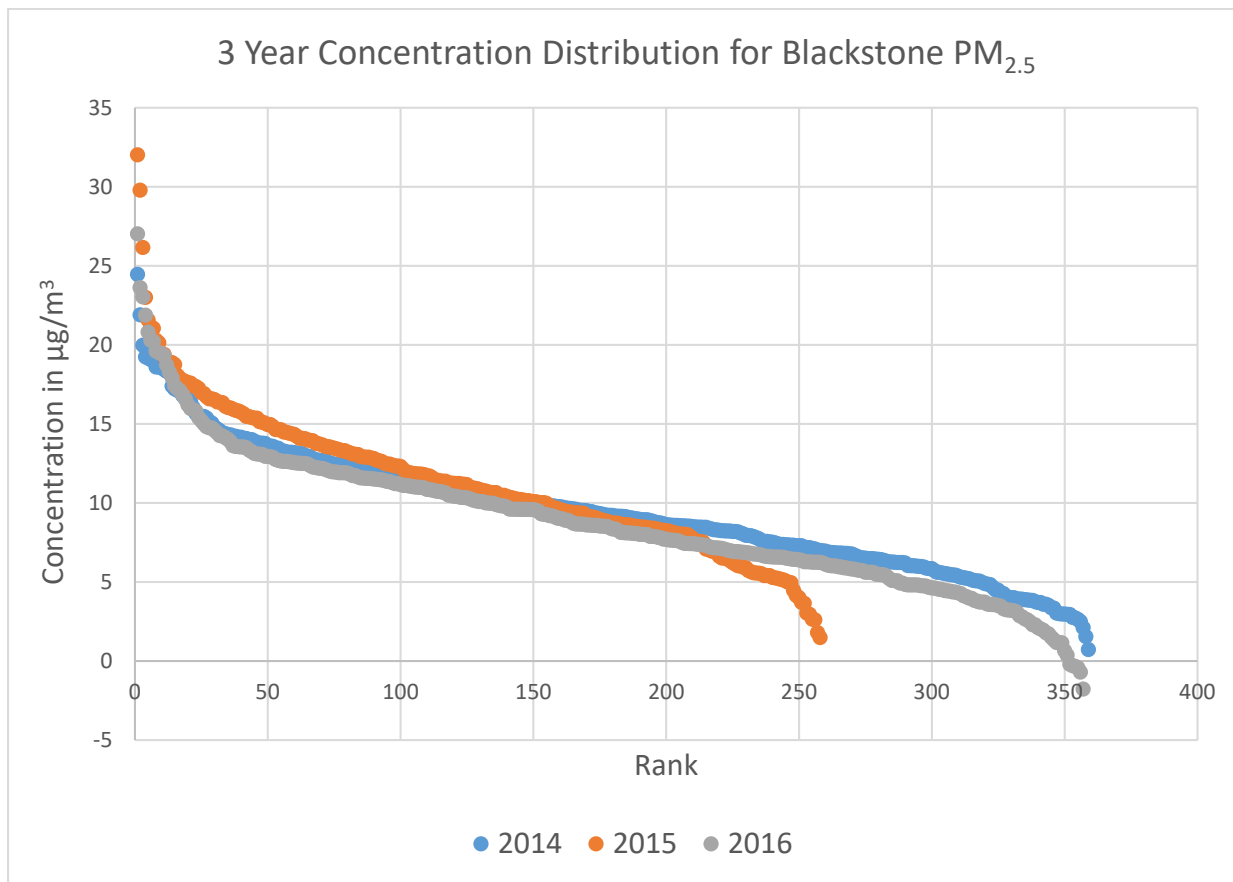


Table 10. Blackstone 98th Percentile and Annual Average of 24-Hour Average PM_{2.5} Concentrations.

Blackstone	2014	2015	2016	Three-Year Average Value for 2014-2016
Annual Average, µg/m ³	9.5	11.3	8.8	9.9
98 th Percentile, µg/m ³	18.9	21.5	20.1	20

Figure 12 displays the ranked 24-hour average PM_{2.5} concentrations at Millbrook for 2014, 2015 and 2016. All three years show a similar pattern with most concentrations falling within the range of 10 to 20 µg/m³. Table 11 summarizes the 98th percentile and average 24-hour average PM_{2.5} concentrations at Millbrook for the three years. These statistics show a downward trend for the annual average for the three-year period but an increase in the 98th percentile concentration in 2015.

Figure 12. Ranked 24-Hour Average PM_{2.5} Concentrations at Millbrook.

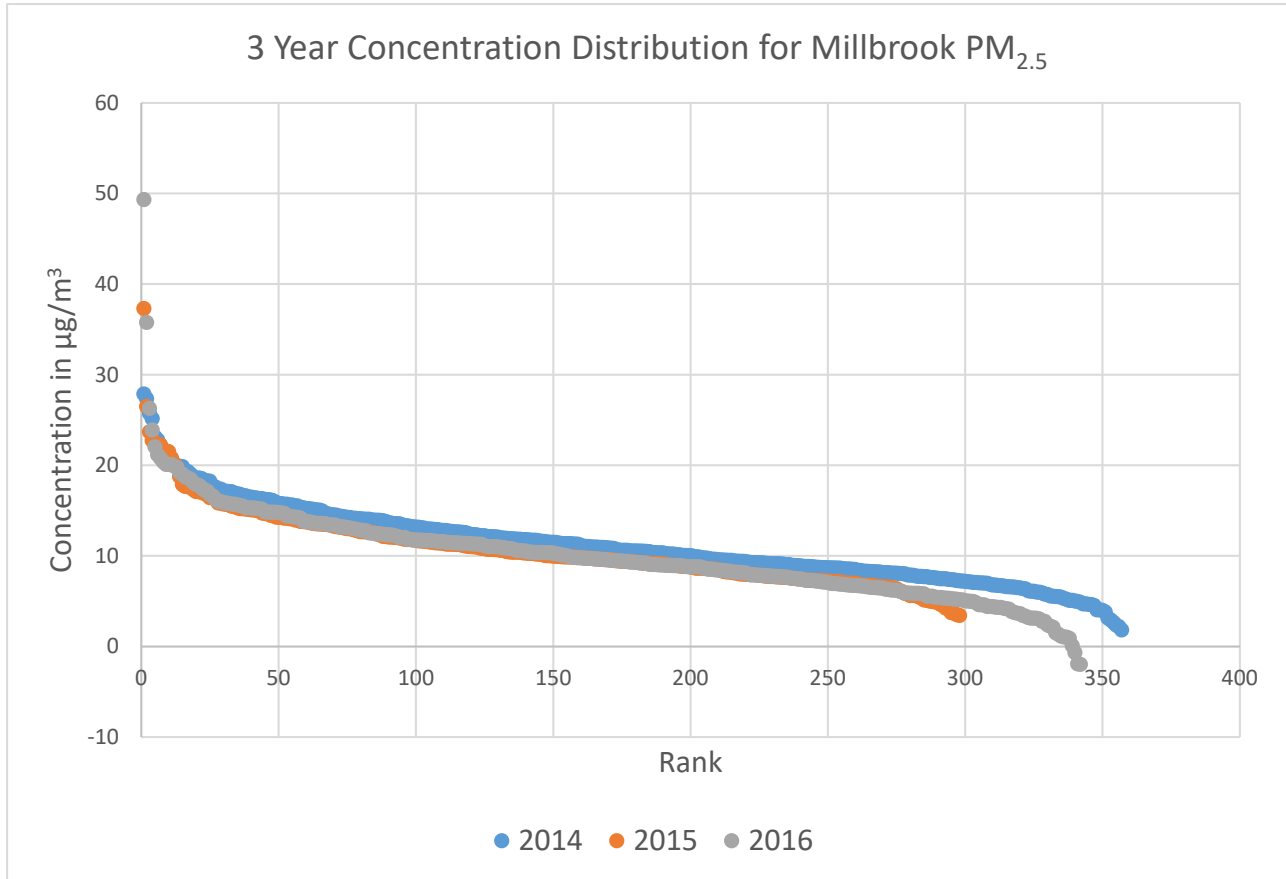


Table 11. Millbrook 98th Percentile and Annual Average of 24-Hour Average PM_{2.5} Concentrations.

Millbrook	2014	2015	2016	Three-Year Average Value for 2014-2016
Annual Average, µg/m ³	11.2	10.8	10.0	10.7
98 th Percentile, µg/m ³	22.1	22.2	20.8	22

Figure 13 and Figure 14 display the trends in the annual means and the 98th percentile of the 24-hour PM concentrations at Candor, Blackstone and Millbrook for 2014, 2015 and 2016. Candor and Millbrook show similar trends. The PM concentrations at Blackstone increased during 2015.

Figure 13. Annual Average PM_{2.5} Concentration at Candor, Blackstone and Millbrook.

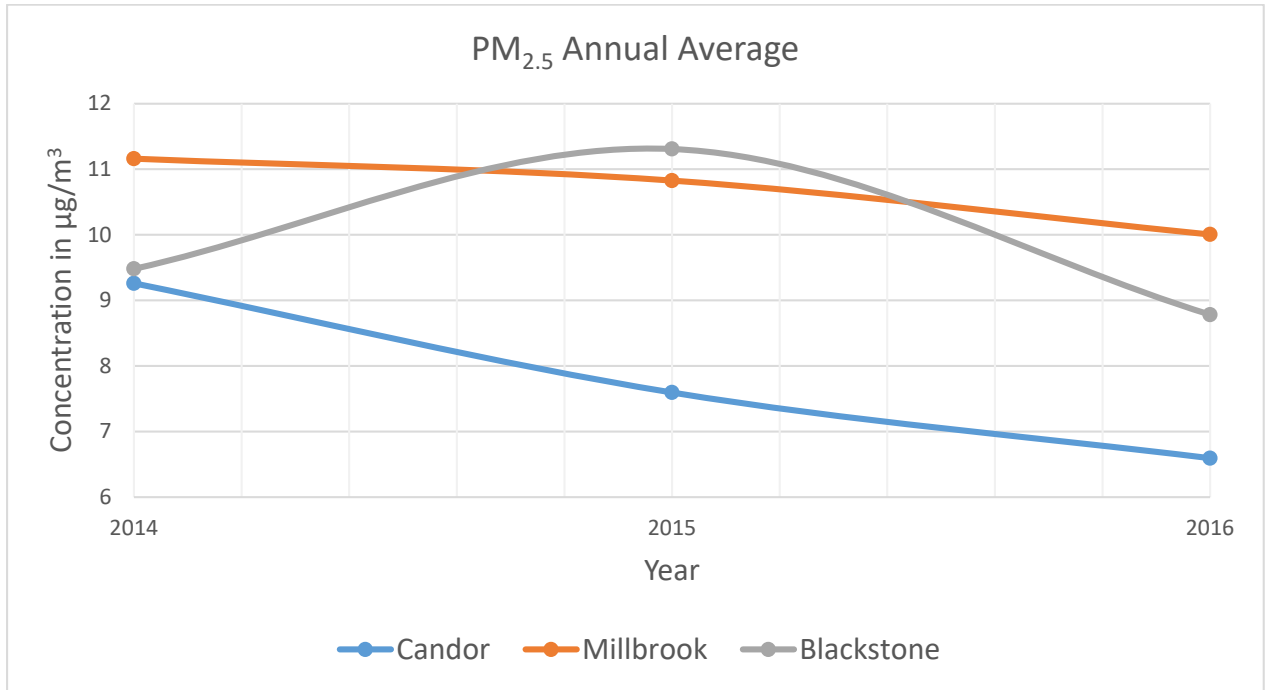
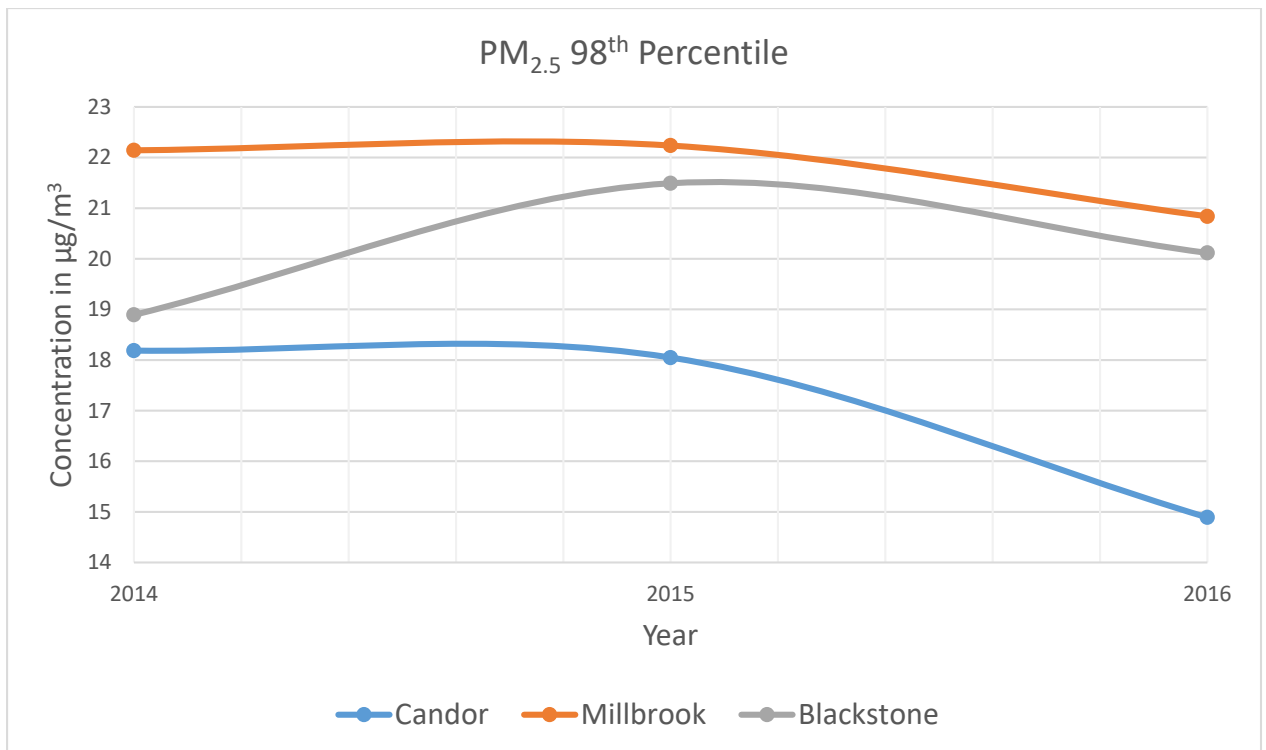


Figure 14. 98th Percentile PM_{2.5} Concentrations at Candor, Blackstone and Millbrook.



5.4 STATISTICAL ANALYSIS

The Wilcoxon test is a nonparametric test that compares two paired groups. The DAQ used it to test whether a statistically significant difference exists between two populations that have the same continuous distribution. The test essentially calculates the difference between each set of pairs and analyzes these differences. Table 12 and Table 13 provide the results of the Wilcoxon Statistical Tests.

Table 12. Wilcoxon Statistical Test for PM_{2.5} between Candor and Blackstone.

	2014	2015	2016
α	0.05	0.05	0.05
Tails	2	2	2
W (Candor)	200	150	140
W (Blckstn)	265	315	325
W_crit	184	184	184
	(200>184)	(150<184)	(140<184)

Based on the results of the Wilcoxon Statistical Test, the DAQ lacks sufficient evidence to conclude the 98th percentile PM_{2.5} data at Blackstone differ from the 98th percentile PM_{2.5} data at Candor in 2014. The DAQ has statistically significant evidence at $\alpha = 0.05$ to show that the 98th percentile PM_{2.5} data at Blackstone differ from the 98th percentile PM_{2.5} data at Candor in 2015 and 2016.

Table 13. Wilcoxon Statistical Test for PM_{2.5} between Millbrook and Blackstone.

	2014	2015	2016
α	0.05	0.05	0.05
Tails	2	2	2
W(Millbrook)	324	258	269
W(Blckstn)	141	207	196
W_crit	184	184	184
	(141<184)	(207>184)	(196>184)

We do not have sufficient evidence to conclude that the 98th percentile PM_{2.5} data at Blackstone differ from 98th percentile PM_{2.5} data at Millbrook in 2015 and 2016. We have statistically significant evidence at $\alpha = 0.05$ to show that the 98th percentile PM_{2.5} data at Blackstone differ from 98th percentile PM_{2.5} data at Millbrook in 2014.

5.5 CONCLUSION

This portion of the study was conducted to determine baseline PM levels in Lee County prior to shale gas well development and extraction. Because the DAQ used the same monitoring equipment at all three sites and operated them following the same procedures, the DAQ can directly compare the datasets collected at the Lee County air monitoring site and the two existing sites in Candor and Raleigh. This ability to compare the data helped characterize air quality upwind and downwind of the Sanford sub-basin.

Table 14 presents the three-year average for 2014 to 2016 for the annual averages and 98th percentiles of the 24-hour averages. On average, the Candor upwind monitoring site showed the lowest PM values, the Millbrook downwind monitoring site showed the highest PM values and the Blackstone site showed PM values between the other two sites. Further statistical analysis indicates there is evidence that these differences in PM levels are not due to random chance but rather to the specific surroundings near each monitoring site, with the more populated areas having higher PM values.

Table 14. Three Year Average and 98th Percentile PM_{2.5} Concentrations in $\mu\text{g}/\text{m}^3$ at All Sites.

	Three Year Average	Three Year Average 98th
Candor	7.8	17.0
Blackstone	9.9	20.0
Millbrook	10.7	22.0

6.0 OXIDES OF NITROGEN

6.1 INTRODUCTION

Several gaseous forms of NO_x are normally found in the atmosphere, including nitrous oxide or N₂O, nitric oxide or NO and nitrogen dioxide, or NO₂. Nitrous oxide is a stable gas with anesthetic characteristics. Ambient concentrations are typically well below the threshold concentration for a biological effect. Nitric oxide is a colorless gas with ambient concentrations generally low enough to have no significant biological effect. Nitrogen dioxide is reddish-brown, but is not usually visible at normal ambient concentrations.

The most significant NO_x emissions result from the burning of fossil fuels such as coal, oil and gasoline, due to the oxidation of atmospheric nitrogen and nitrogen compounds in the fuel. The primary combustion product is NO, which reacts to form NO₂.

At high concentrations, nitrogen dioxide has significant health effects as a pulmonary irritant, especially upon asthmatics and children. In North Carolina, a much greater health concern is the formation of ozone, because the presence of NO₂ and other NO_x promote its formation.

Some types of vegetation are very sensitive to NO₂, including oats, alfalfa, tobacco, peas and carrots. Chronic exposure causes chlorosis (yellowing) and acute exposure usually causes irregularly shaped lesions on the leaves.

Nitric oxide and NO₂ do not directly damage materials. However, NO₂ can react with moisture in the air to produce nitric acid, which corrodes metal surfaces and contributes to acid rain. High concentrations of NO₂ may reduce visibility. Much of the brownish coloration sometimes observed in polluted air in winter months may be due to NO₂.

Table 15 summarizes the national primary, secondary and North Carolina ambient air quality standards that were in effect during the study.

Table 15. National and North Carolina Ambient Air Quality Nitrogen Dioxide Standards.

Pollutant/ Ambient Measurement/ (Reference)	Averaging Period	Type of Summary	Primary National (Health Related) Standard	Secondary National (Welfare Related) Standard	North Carolina Standard
Nitrogen Dioxide (NO ₂)	1 hour	98 th percentile of 1 hour daily maximum concentrations, averaged over 3 years	100 ppb		100 ppb
	1 year	Annual mean	53 ppb	53 ppb	53 ppb

6.2 MONITORING METHODOLOGY

The DAQ conducted ambient monitoring for calendar years 2014 through 2016 at the Millbrook site and from December 2014 through 2016 for the Blackstone site. The DAQ continuously measured NO, NO₂ and NO_x using a

Teledyne Model T200UP NO-NO₂-NO_x Analyzer which uses a photolytic convertor to convert NO₂ to NO. All air monitoring sampling and analysis methods followed reference methodologies published by the EPA.¹² The DAQ followed equipment manufacturer’s operating manuals, agency standard operating procedures and preventative maintenance procedures.

6.3 SUMMARY OF MONITORING DATA

This report compares and discusses NO₂ data for two sites, Blackstone and Millbrook, during calendar years 2014, 2015 and 2016. Data analysis for calculating the 98th percentile values was performed by taking the highest hourly measurement for each day reporting 18 or more hours of data. From these numbers the 98th percentile was selected for each calendar period. The annual average was calculated by taking all of the hourly values for the calendar year and averaging them.

The Blackstone monitor reported the highest one-hour NO₂ measurement for each of the 695 days sampled from December 2014 through the end of 2016. Table 16 gives the 98th percentile concentrations and the annual arithmetic means of the NO₂ data. The arithmetic means are about 2 percent of the annual standard and the 98th percentile values are about 8 percent of the hourly standard.

Table 16. Blackstone Annual Average and 98th Percentile of 1-Hour Average NO₂ Concentrations.

Blackstone	2014	2015	2016	Two Year Average Value
Annual Average, ppb	*	1.39	1.17	1.28
98 th Percentile, ppb	*	9	7	8
*Sample size too small to meet statistical standards for reliability				

The Millbrook monitor reported the highest one-hour NO₂ measurement for each of the 1,060 days sampled over the three-year period. Table 17 gives the 98th percentile concentrations and the annual arithmetic means of the NO₂ data. The arithmetic means are about 11 percent of the annual standard and the 98th percentile values are about 37 percent of the hourly standard.

¹² U.S. EPA, List of Designated and Equivalent Methods, available on the worldwide web at https://www.epa.gov/sites/production/files/2018-01/documents/amtic_list_dec_2017_update_1-20-2018_0.pdf, accessed May 25, 2018.

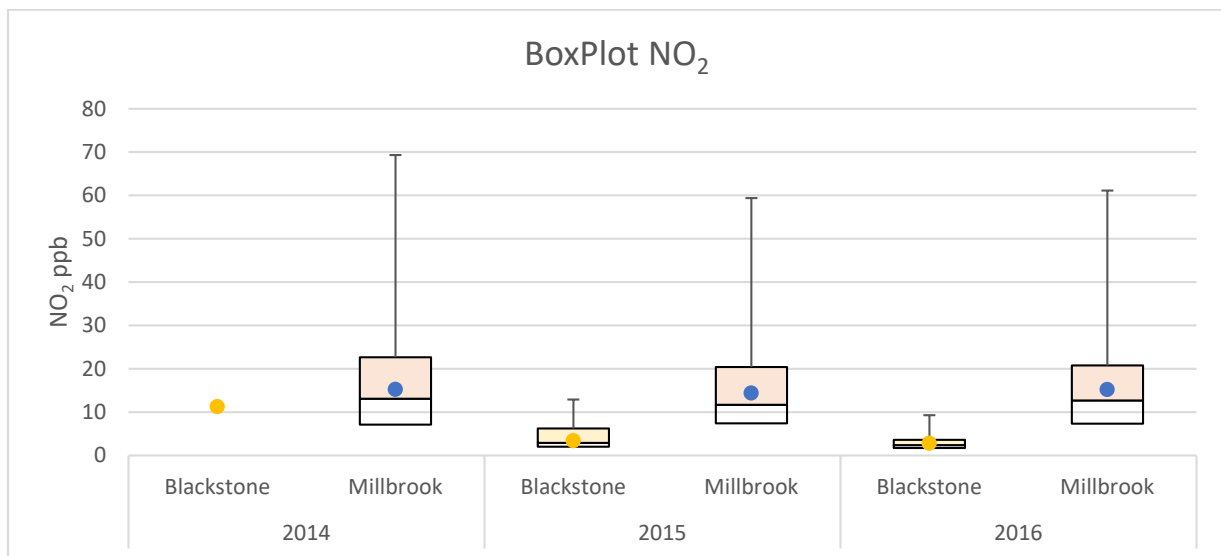
Table 17. Millbrook Annual Average and 98th Percentile of 1-Hour Average NO₂ Concentrations.

Millbrook	2014	2015	2016	Three Year Average Value
Annual Average, ppb	6.01	5.64	5.64	5.76
98 th Percentile, ppb	39	32	39	37.7

6.4 STATISTICAL ANALYSIS

The DAQ generated box plots to compare nitrogen dioxide concentration statistics at both sites. Figure 15 displays the box plots. The box plot presents the following information. The upper whisker represents the maximum, excluding outliers. The top of the box represents the first quartile. Twenty-five percent of the measured values are greater than this value. The dot in the box represents the mean. The line inside the box represents the median. Fifty percent of the measured values are greater than this value and 50 percent are lower. The bottom of the box represents the third quartile. Twenty-five percent of the measured values are less than this value. As expected the box plots show that the NO₂ concentrations at Millbrook tend to be higher than those measured at Blackstone.

Figure 15. Box Plots of Daily Maximum 1-Hour Average Nitrogen Dioxide Concentrations at Blackstone and Millbrook.



*2014 sample size at Blackstone is too small to meet statistical standards for reliability

Figure 16 displays the trends in the annual average of 1-hour NO₂ concentrations and Figure 17 displays the trends in the 98th percentile of the maximum daily 1-hour concentrations at Blackstone and Millbrook for 2014, 2015 and 2016. The annual average 1-hour NO₂ concentrations show a similar trend with time while the 98th percentile of the maximum daily 1-hour concentrations at Millbrook and Blackstone display a different trend going from 2015 to 2016.

Figure 16. Nitrogen Dioxide Annual Average Concentrations at Blackstone and Millbrook.

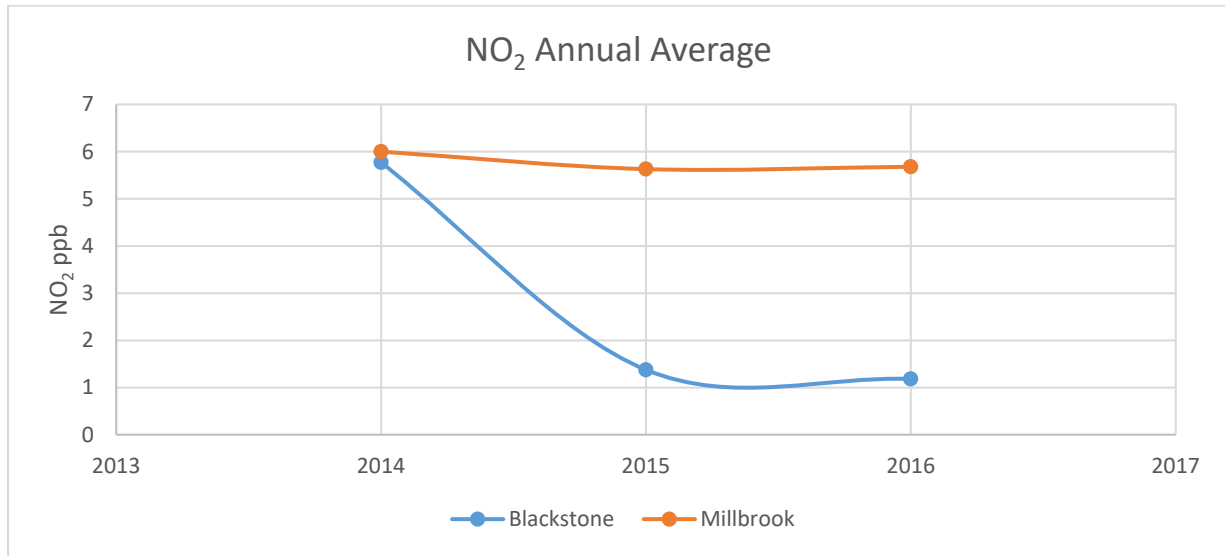


Figure 17. Nitrogen Dioxide 98th Percentile Concentrations at Blackstone and Millbrook.

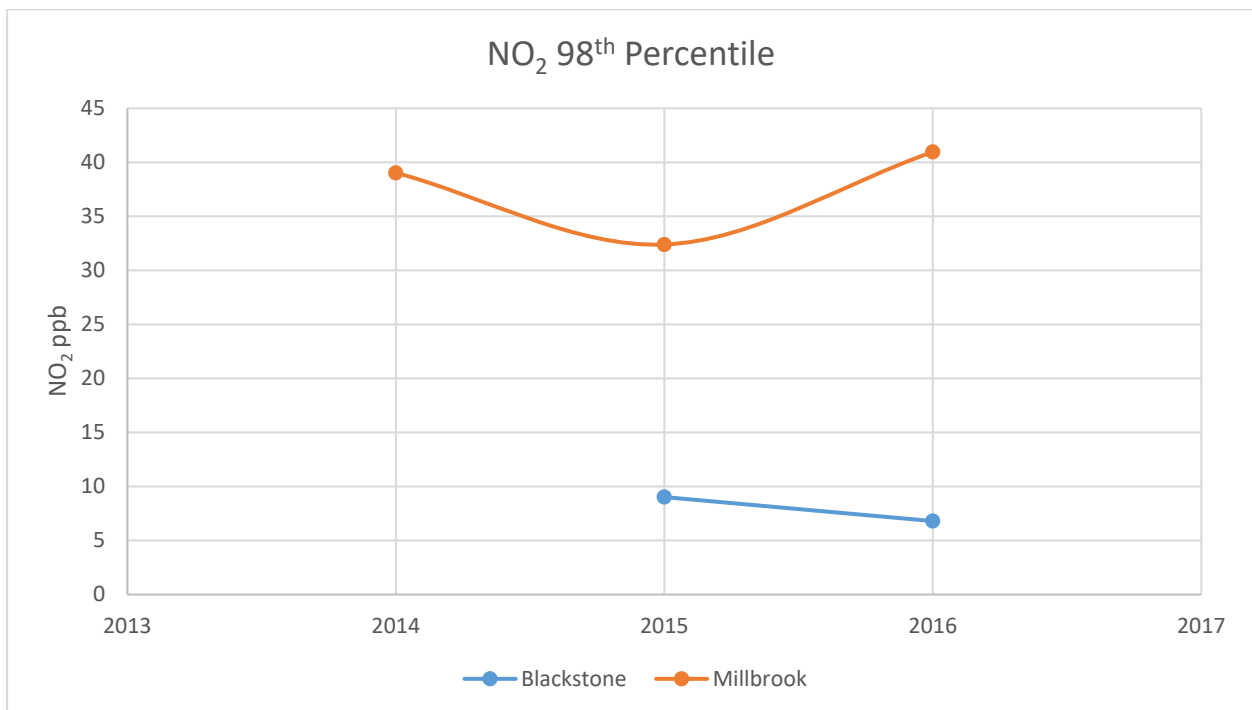


Figure 18 and Figure 19 displays the ranked maximum daily 1-hour NO₂ concentrations at Blackstone and Millbrook for 2014, 2015 and 2016, respectively. Note that the Blackstone plot uses a logarithmic scale for concentration and both plots use a logarithmic scale for the rank. At Blackstone, most of the daily maximum 1-hour average NO₂ concentrations are less than 10 parts per billion. At Millbrook about half the daily maximum 1-hour average NO₂ concentrations are between 10 and 40 parts per billion.

Figure 18. Ranked Nitrogen Dioxide Daily Maximum 1-Hour Average Concentrations at Blackstone.

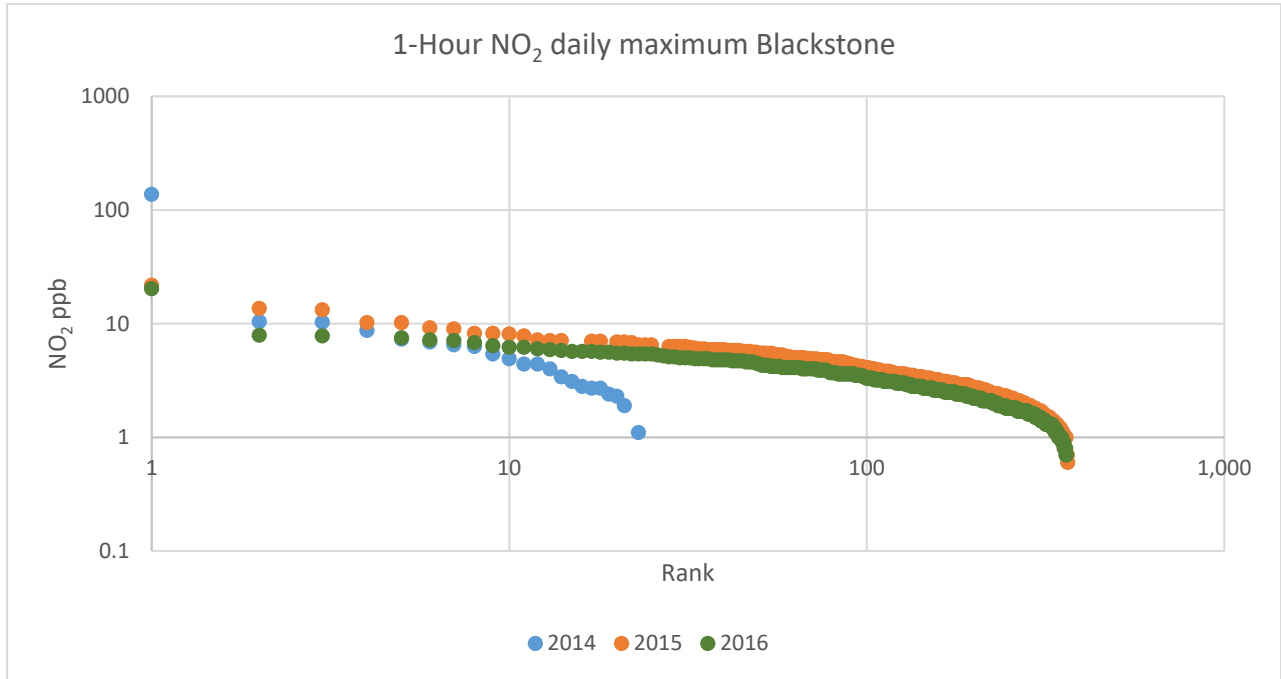
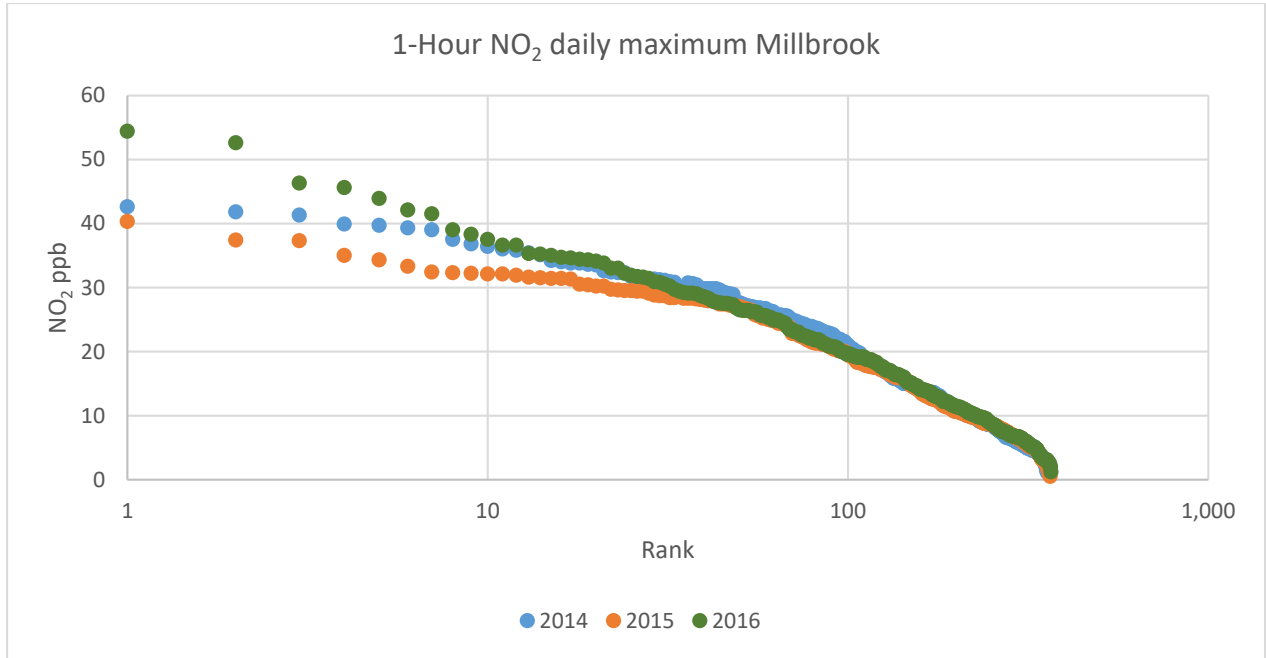


Figure 19. Ranked Nitrogen Dioxide Daily Maximum 1-Hour Average Concentrations at Millbrook.



6.5 CONCLUSION

The DAQ conducted this portion of the study to determine baseline NO₂ levels in Lee County before well development, production and gas treatment. Because the DAQ used the same monitoring equipment and procedures at both locations, the DAQ can directly compare the datasets collected at the Lee County air monitoring site and Raleigh Millbrook monitoring site. In general, as shown in Table 18, the NO₂ values at the Raleigh downwind site showed the higher NO₂ values.

Table 18. Three Year Average and 98th Percentile NO₂ Concentrations.

Site	Three Year Average of Annual Average of 1-Hour Averages, ppb	Three Year Average of 98 th Percentile of 1-Hour Averages, ppb
Blackstone	1.28*	8*
Millbrook	5.763	37.7

*Two-year average only

7.0 SULFUR DIOXIDE

7.1 INTRODUCTION

The EPA listed sulfur oxides, or SO_x as one of the criteria air pollutants for which they have established a NAAQS. These standards use SO₂ as the indicator pollutant. Sulfur dioxide is a colorless, corrosive, toxic gas and is the most prevalent compound of SO_x found in our lower atmosphere. It has a pungent odor and is detectable by taste and smell at levels between 1 and 3 ppm. Sulfate aerosols are other sulfur oxides of concern; they occur at levels considerably lower than SO₂ and contribute to PM air pollution.

The combustion of fossil fuels, such as coal, distillate fuel oil and gasoline produce SO₂. There are other minor sources such as ore smelting and other industrial processes that contribute as well. These sources emit SO_x into the atmosphere. When they emit SO_x at higher levels, they can have a direct impact on human health and the environment.

Human exposure to SO₂ has been associated with reducing pulmonary function and is a respiratory irritant. Especially susceptible groups are asthmatics, the elderly and children.

Sulfur dioxide can adversely affect forests, agricultural crops and other vegetation. High ambient concentrations in the air can act as a defoliant and lead to soil acidification. The formation of sulfurous and sulfuric acids when combined with moisture can increase the pH of ground and surface waters.

Higher levels of SO₂ in the ambient air can react with moisture in the atmosphere to produce acidic precipitation, which corrodes both ferrous and non-ferrous metals, limestone, marble and sandstone. Sulfate in the presence of moisture will rapidly form sulfuric acid which is a strong acid and can further lead to the chemical erosion of buildings and monuments.

Table 19 summarizes the national primary, secondary and North Carolina ambient air quality standards that were in effect during the study.

Table 19. National and North Carolina Ambient Air Quality Sulfur Dioxide Standards.

Pollutant/ Ambient Measurement/ (Reference)	Averaging Period	Type of Summary	Primary National (Health Related) Standard	Secondary National (Welfare Related) Standard	North Carolina Standard
Sulfur Dioxide	1 hour	99 th percentile of 1-hour daily maximum concentrations, averaged over 3 years	75 ppb		75 ppb
	3 hours	Not to be exceeded more than once per year		0.5 ppm	0.5 ppm

7.2 MONITORING METHODOLOGY

The DAQ conducted ambient monitoring for calendar years 2015 through 2016 for both the Blackstone study site and the Millbrook downwind site. The DAQ continuously measured SO₂ at the Millbrook site using a Thermo 43C-TLE Enhanced Trace Level SO₂ Analyzer until being replaced later with a newer 43i-TLE model. At the Blackstone site, the DAQ used a Thermo 43C SO₂ Analyzer, which DAQ later replaced with a newer 43i model. These instruments employ pulsed fluorescence technology and optical detection to precisely measure down to parts per trillion levels and conform to EPA approved monitoring methods.¹³

7.3 SUMMARY OF MONITORING DATA

The DAQ collected SO₂ data for calendar years 2014 through 2016 for the Millbrook site and 2015 and 2016 for the Blackstone site. DAQ achieved a high degree of data capture as illustrated in Table 20.

Table 20. Number of Valid SO₂ Sampling Days at Blackstone and Millbrook.

Year	2014	2015	2016
Blackstone		360	356
Millbrook	360	347	355

When comparing the two sites, DAQ considered the 99th percentile of daily maximum 1-hour values or the values below which nominally 99 percent of all daily maximum 1-hour concentration values fall. Table 21 provides the 99th percentile of the daily maximum 1-hour averages at both sites.

Table 21. Annual 99th Percentile of Daily Maximum 1-Hour Averages.

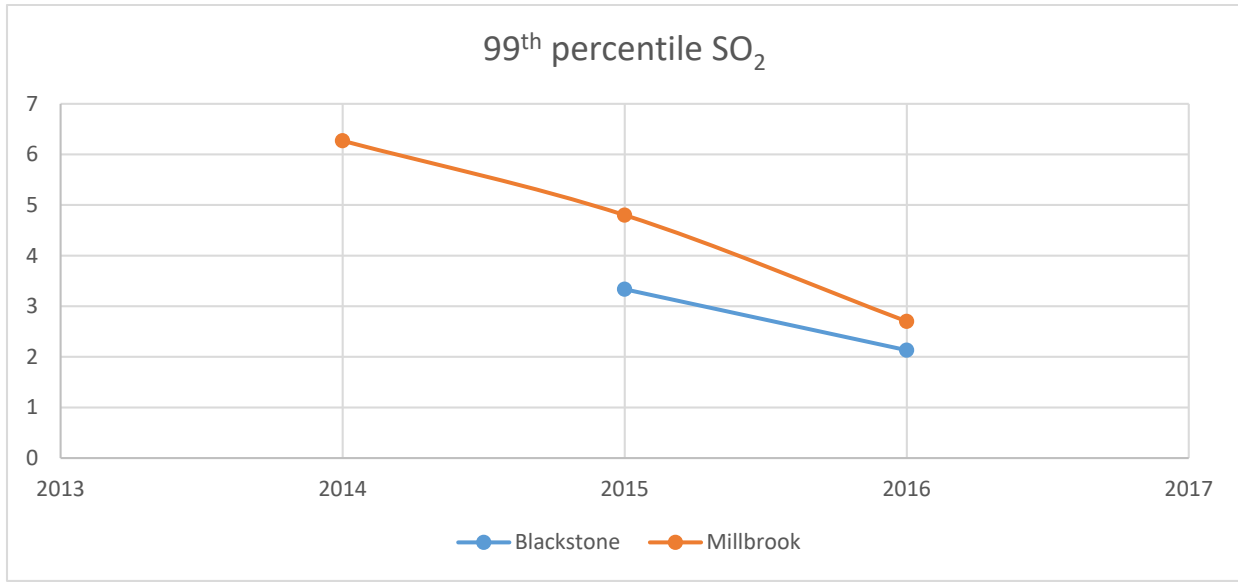
Year	2014	2015	2016
Blackstone, ppb		3	2
Millbrook, ppb	6	5	3

¹³ U.S. EPA, List of Designated and Equivalent Methods, available on the worldwide web at https://www.epa.gov/sites/production/files/2018-01/documents/amtic_list_dec_2017_update_1-20-2018_0.pdf, accessed May 25, 2018.

7.4 STATISTICAL ANALYSIS

Figure 20 displays the trend in the 99th percentile of the daily maximum 1-hour SO₂ concentrations measured at the two sites. The 99th percentile at both sites declined over the study period. As expected, the DAQ measured lower SO₂ concentrations at the Blackstone site.

Figure 20. 99th Percentile Daily Maximum 1-Hour SO₂ Concentrations (PPB).



7.5 CONCLUSION

The DAQ conducted this portion of the study to determine baseline SO₂ levels in Lee County before any well development, production and gas treatment. The DAQ collected the data using methods and procedures that allows direct comparability of the collected data at the Lee County and the downwind site at Millbrook. The SO₂ values at Millbrook showed the highest concentrations. Both sites appeared to exhibit a downward trend with overall lower concentrations in the ambient air in 2016.

8.0 ALDEHYDES

8.1 INTRODUCTION

Atmospheric aldehydes contribute to ozone formation through complex chemical reactions in the atmosphere. Potential sources of atmospheric aldehydes include mobile sources, industrial emissions, non-mobile sources, farming and agriculture. Additional aldehyde emission sources include oil and gas extraction and combustion of various fossil fuels.

8.2 MONITORING METHODOLOGY

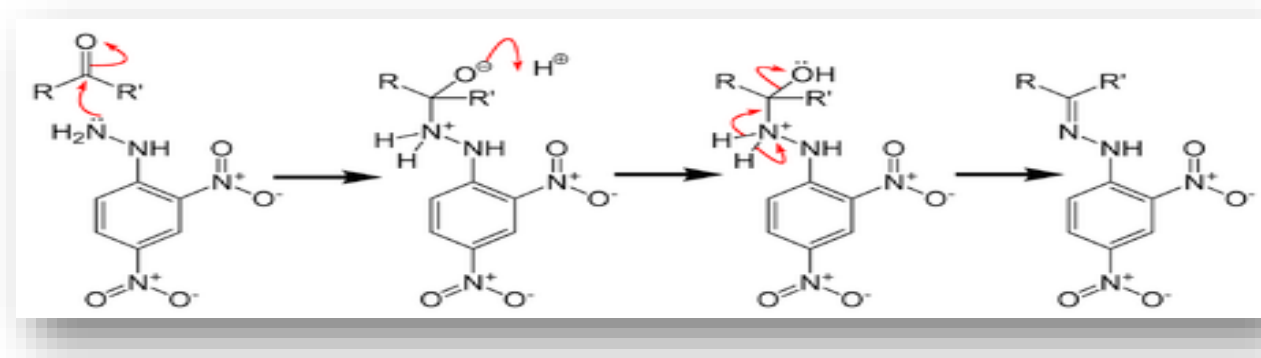
The DAQ collected atmospheric aldehydes using established EPA methods and procedures¹⁴ using ATEC 2200 air samplers that pull a known volume of ambient air through a sampling cartridge. The supplier packs the sampling cartridge, shown in Figure 21, with a bed of silica beads coated with dinitrophenylhydrazone, or DNPH. The DNPH reacts with the aldehyde as shown in Figure 22 to form a DNPH-aldehyde derivative that DAQ quantified using chromatographic techniques.

Figure 21. DNPH Sampling Cartridge.



¹⁴ U.S. EPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-11A, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High-Performance Liquid Chromatography (HPLC), January 1999, available on the worldwide web at <https://www3.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>, accessed May 25, 2018.

Figure 22. The DNPH Reaction Mechanism with Atmospheric Aldehydes and Ketones.



The field operator retrieves the sampled cartridges within 24-hours of collection and sends them to the North Carolina DAQ Laboratory Analysis Branch, or LAB, for extraction and analysis. At the LAB, the analyst removes the collected DNPH-aldehydes from the sampling cartridge via liquid extraction using a known volume of acetonitrile. The analyst separates and quantifies the DNPH-aldehyde extracts using an HPLC system fitted with a reversed phase separation column and multi-wavelength detector. To identify and quantify the ambient air sample extracts, the analyst compares the DNPH-aldehyde derivatives to known National Institute of Standards and Technology, or NIST, traceable DNPH-aldehyde derivative standards.

Aldehyde samples are collected on a six-day frequency, following the national sampling schedule,¹⁵ and are collected over a 24-hour period from midnight to midnight local standard time, that is Eastern Standard Time. Sample volume is determined using calibrated mass flow controllers at standard atmospheric conditions.

8.3 SUMMARY OF MONITORING DATA

This report discusses aldehyde data for all three sites during calendar years 2014, 2015 and 2016. This report focuses on comparing two main aldehyde compounds - formaldehyde and acetaldehyde - because they are the most predominant aldehydes found in the atmosphere. During this timeframe, the DAQ collected on DNPH cartridges a total of 756 aldehyde samples from all three sites. The total number of valid samples from all three sites was 738 DNPH cartridges. The sample completeness during this three-year period was 96 percent. The DAQ attributed the 18 missed or invalid DNPH cartridges to sample collection errors, power failures and laboratory errors.

8.4 STATISTICAL ANALYSIS

The DAQ compared the annual average concentration of formaldehyde and acetaldehyde at Candor, Blackstone and Millbrook. Figure 23 and Figure 24 present the trends in the annual average concentrations. Secondly, the DAQ generated box plots to compare formaldehyde and acetaldehyde concentration statistics at all three sites. Figure 25 and Figure 26 display the box plots.

¹⁵ U.S. EPA, Sampling Schedule Calendar, available on the worldwide web at <https://www3.epa.gov/ttn/amtic/calendar.html>, accessed May 24, 2018.

Figure 23. Annual Average Formaldehyde Concentrations.

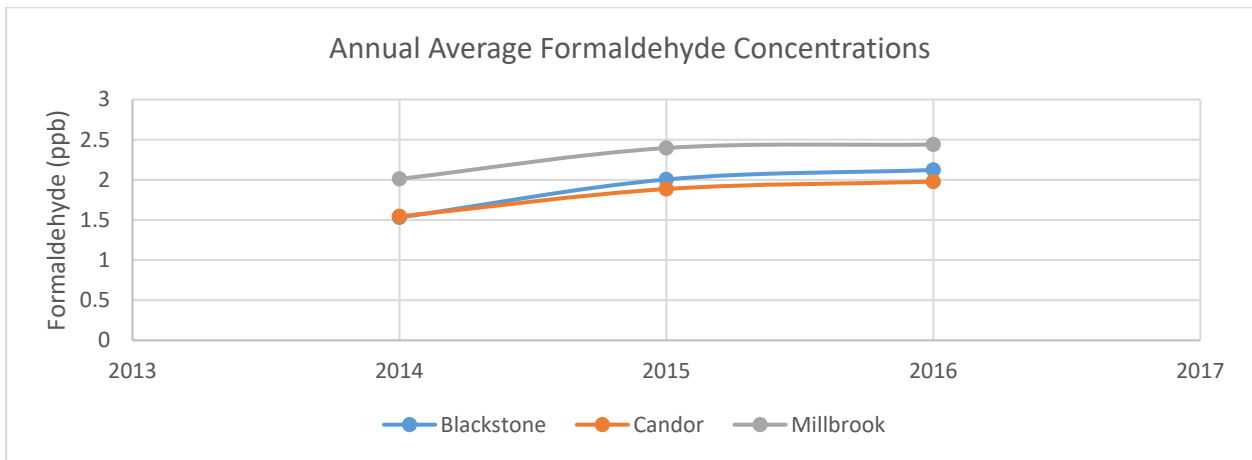


Figure 24. Annual Average Acetaldehyde Concentrations.

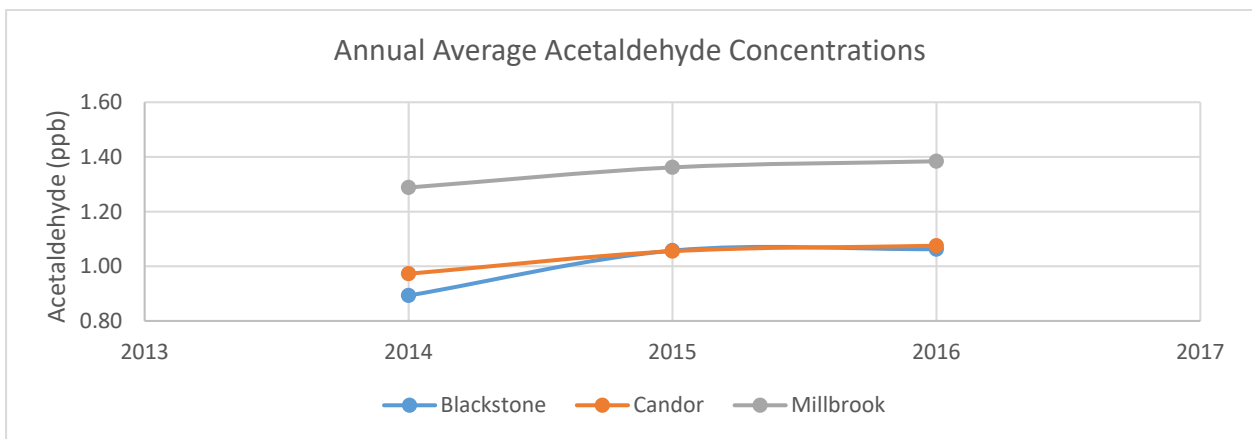


Figure 25. Box Plots of Formaldehyde Concentrations (PPB).

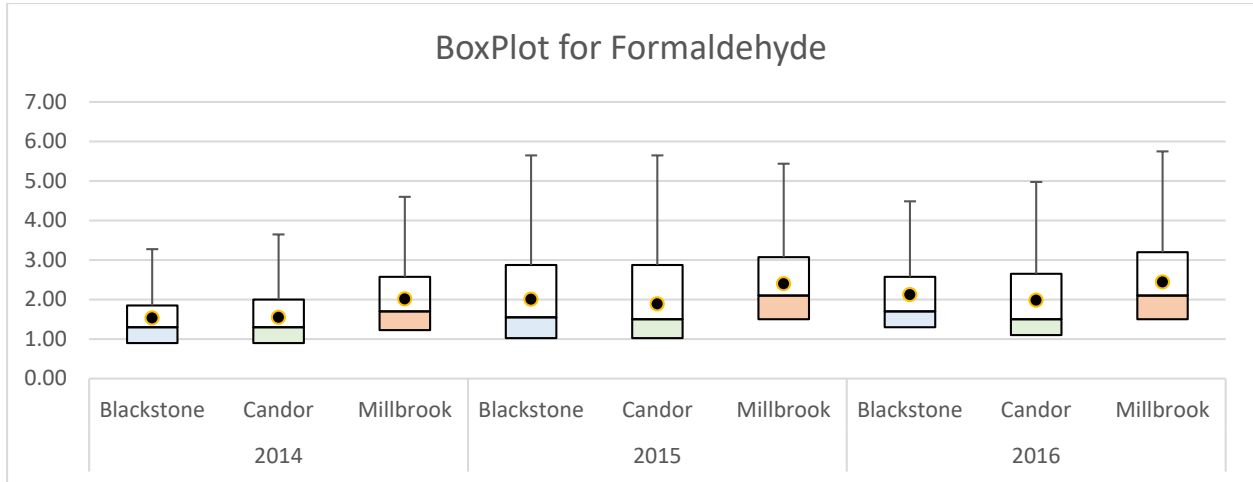
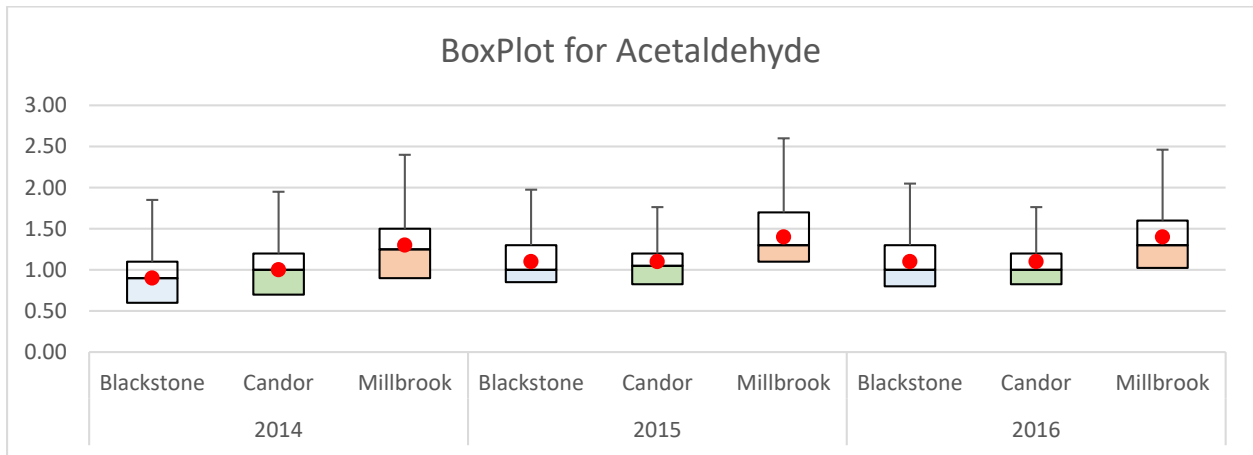


Figure 26. Box Plots of Acetaldehyde Concentrations (PPB).



8.5 CONCLUSION

The annual average formaldehyde and acetaldehyde concentration charts shows similar concentrations at Blackstone and Candor. One can use annual average aldehyde concentrations to deduce the urbanization of each site. One would expect formaldehyde and acetaldehyde concentrations at Candor to be the lowest values because Candor is a rural site. Based on the data collected during the study the following trend holds true, Millbrook detected the highest values of formaldehyde and acetaldehyde meaning it was the most urban site. Blackstone detected concentrations values somewhere between Candor and Millbrook. Specifically, formaldehyde values at Blackstone were much closer to Candor with a measured annual average difference between the two sites of approximately 0.15 ppb in 2016. Alternatively, the difference between measured annual average formaldehyde values at Blackstone and Millbrook was approximately 0.43 ppb in 2016.

The DAQ expected to see this larger difference between the measured values at Millbrook and Blackstone because the Millbrook site is in a larger urban area than Blackstone. The box plots of formaldehyde and acetaldehyde at all

three sites show a similar trend with Blackstone and Candor concentration statistics being more alike than the concentration statistics between Blackstone and Millbrook.

9.0 VOLATILE ORGANIC COMPOUNDS (VOC)

9.1 INTRODUCTION

Volatile organic compounds contribute to ozone formation through complex chemical reactions in the atmosphere. Potential sources of VOCs include mobile sources, industrial emissions, non-mobile sources, farming and agriculture. Additional VOC emission sources include oil and gas extraction and combustion of various fossil fuels. The VOC compounds of interest include benzene, toluene, ethylbenzene, xylenes, hexanes, 2,2,4 trimethylpentane and styrene.

9.2 MONITORING METHODOLOGY

DAQ collected and analyzed the VOCs following established EPA methods and procedures.¹⁶ The DAQ used a Xontech 911 air sampler to force ambient air into 6-liter Summa canisters to a predetermined final canister pressure. The DAQ cleaned and certified the canisters at the LAB using established procedures before sending them to the field. The field operators shipped the sampled canisters to the LAB where the analyst checks the canister for leaks and analyzes the samples by gas chromatography mass spectrometry. The DAQ analyst compared the sampled canister analysis results to known NIST-traceable VOC standards. The vendor provides approximately 75 VOCs in the NIST-traceable standard.

The DAQ collected VOC samples on a six-day frequency following the EPA national sampling calendar.¹⁷ The DAQ collected VOC samples over a 24-hour period from midnight to midnight local standard time, or Eastern Standard Time in North Carolina. The DAQ determined the sample volume collected using certified pressure gauges calibrated at standard atmospheric conditions, or 25 degrees Celsius and 760 millimeters mercury.

9.3 SUMMARY OF MONITORING DATA

This report discusses VOC data for all three sites during calendar years 2014, 2015 and 2016.

Based on available study data and the DAQ's Blackstone site project plan, VOCs associated with oil and gas extraction emissions include benzene, toluene, ethylbenzene, xylenes, hexanes, 2,2,4-trimethylpentane and styrene. The 2,2,4-trimethylpentane and styrene concentrations detected during the study period were too low to create meaningful annual average concentration charts or box plots. This report will not further discuss these compounds due to their concentration values being at or below reportable limits throughout the study period.

The total number of VOC canister samples collected from all three sites during this timeframe was 789 canisters. The total number of valid samples from all three sites was 755 canisters. The sample completeness during this

¹⁶ U.S. EPA, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS), January 1999, available on the worldwide web at <https://www3.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf>, accessed May 25, 2018.

¹⁷ U.S. EPA, Sampling Schedule Calendar, available on the worldwide web at <https://www3.epa.gov/ttn/amtic/calendar.html>, accessed May 24, 2018.

three-year period is 96 percent. The DAQ attributed the 34 missed or invalid canisters to sample collection errors, power failures and laboratory errors.

9.4 STATISTICAL ANALYSIS

Figure 27 through Figure 32 compare the annual average concentration of benzene, toluene, ethylbenzene, xylenes, hexanes, 2,2,4-trimethylpentane and styrene at Candor, Blackstone and Millbrook. Lastly, the DAQ used box plots as a tool to compare the benzene and toluene concentration statistics between all three sites. Figure 33 through Figure 38 provide the box plots for all VOCs of interest.

Figure 27. Annual Average Benzene Concentrations at All Sites.

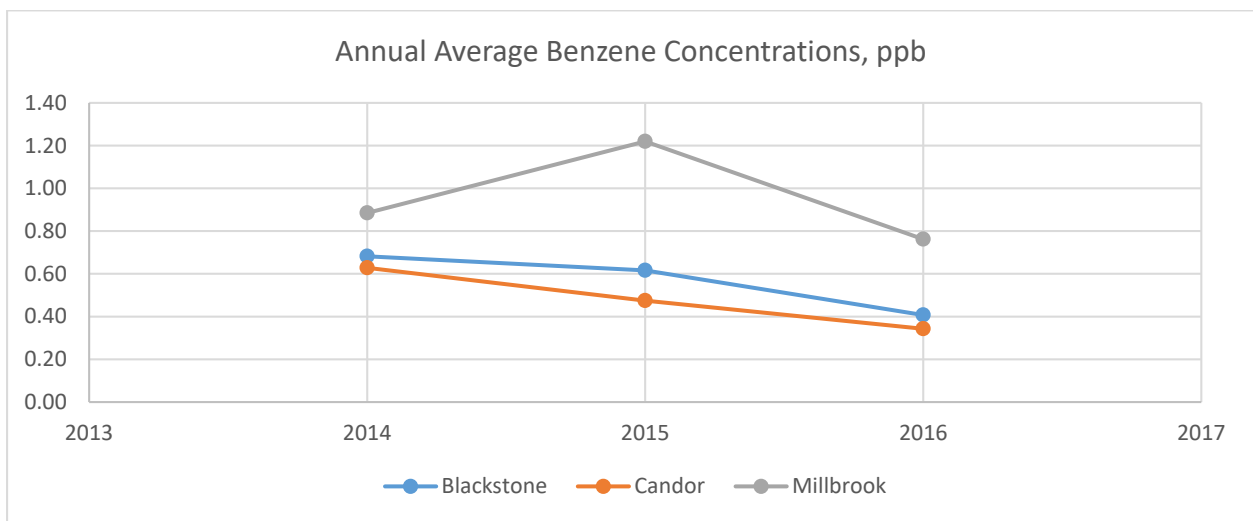


Figure 28. Annual Average Toluene Concentrations at All Sites.

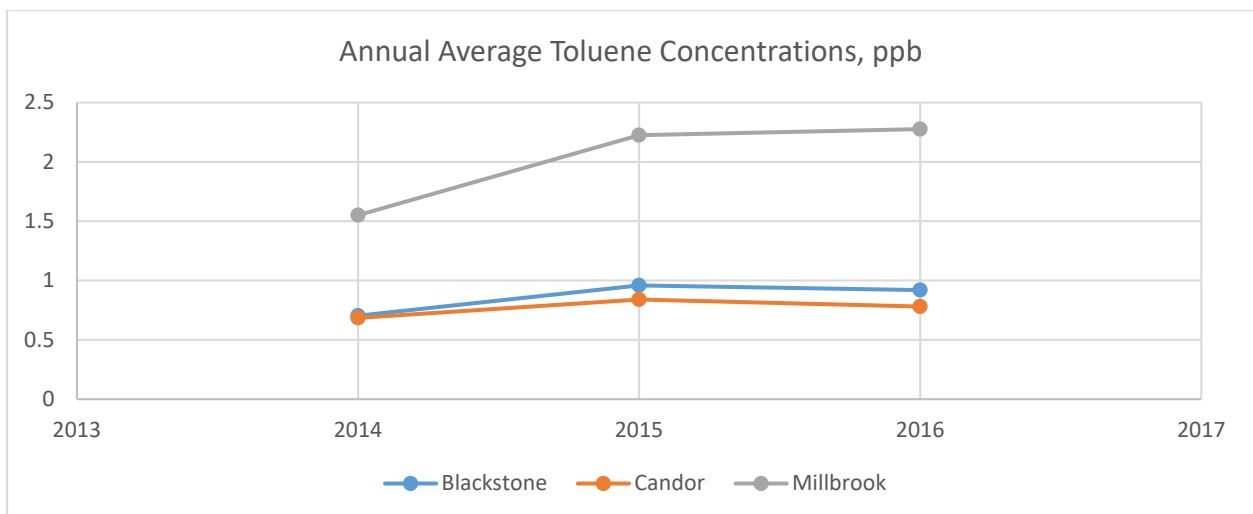


Figure 29. Annual Average Ethylbenzene Concentrations at All Sites.

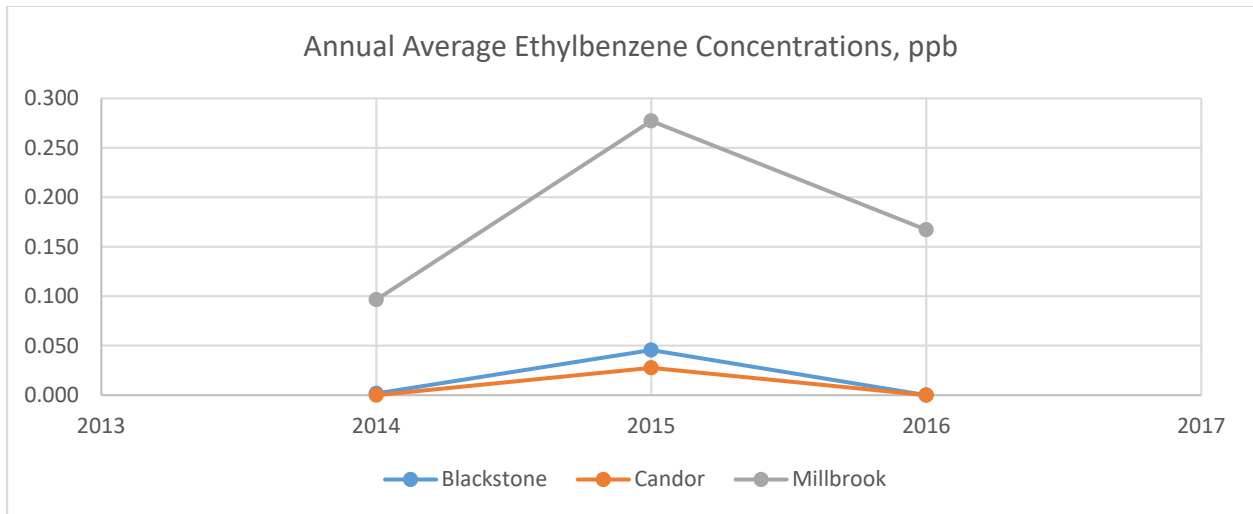


Figure 30. Annual Average m/p-Xylene Concentrations at All Sites.

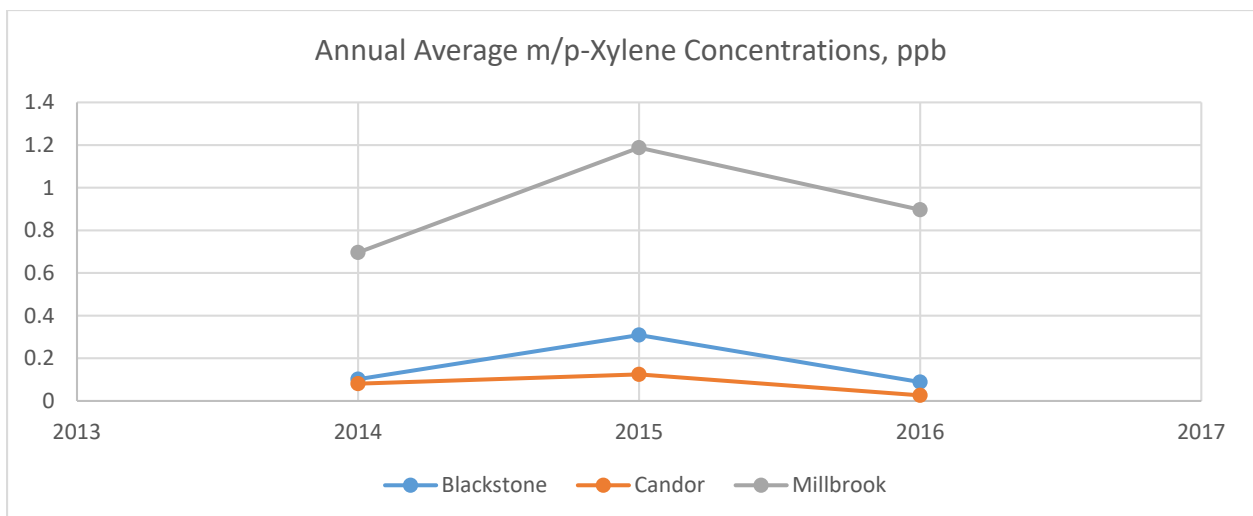


Figure 31. Annual Average o-Xylene Concentrations at All Sites.

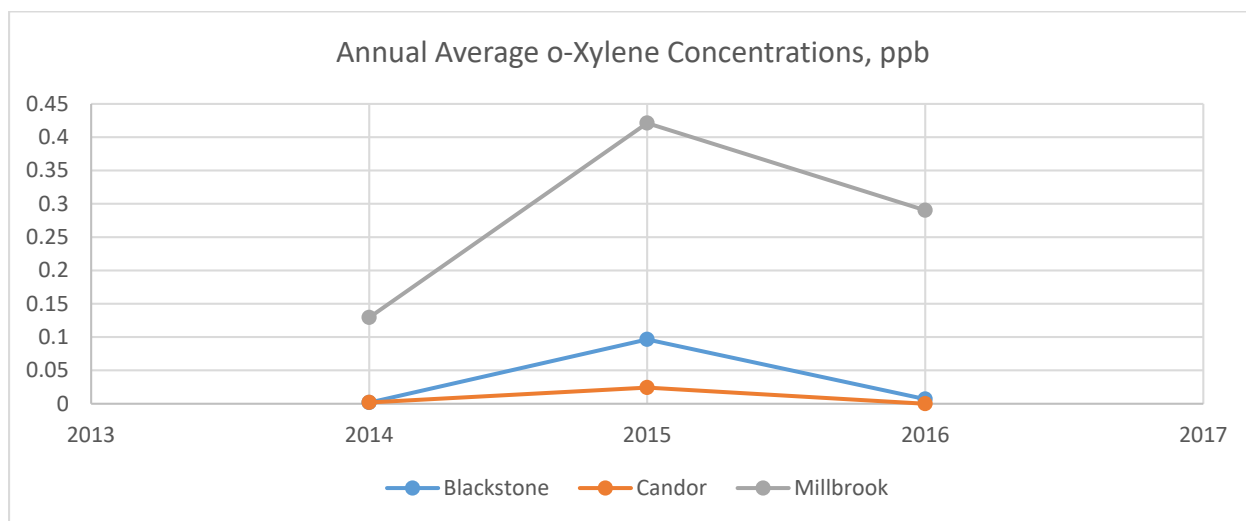


Figure 32. Annual Average n-Hexane Concentrations at All Sites.

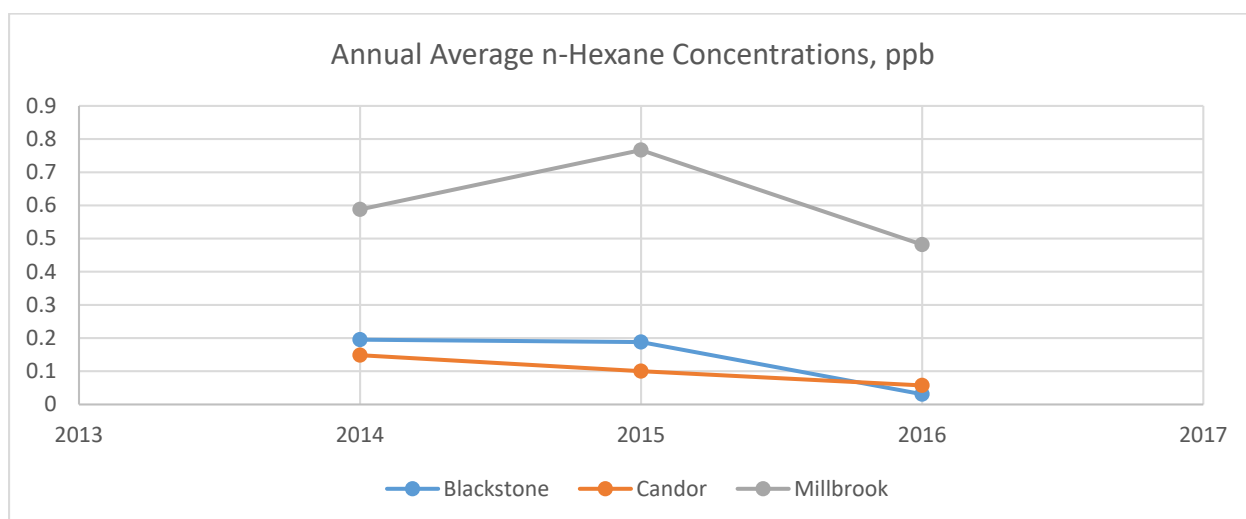


Figure 33. Box Plot of Benzene Concentrations at All Sites.

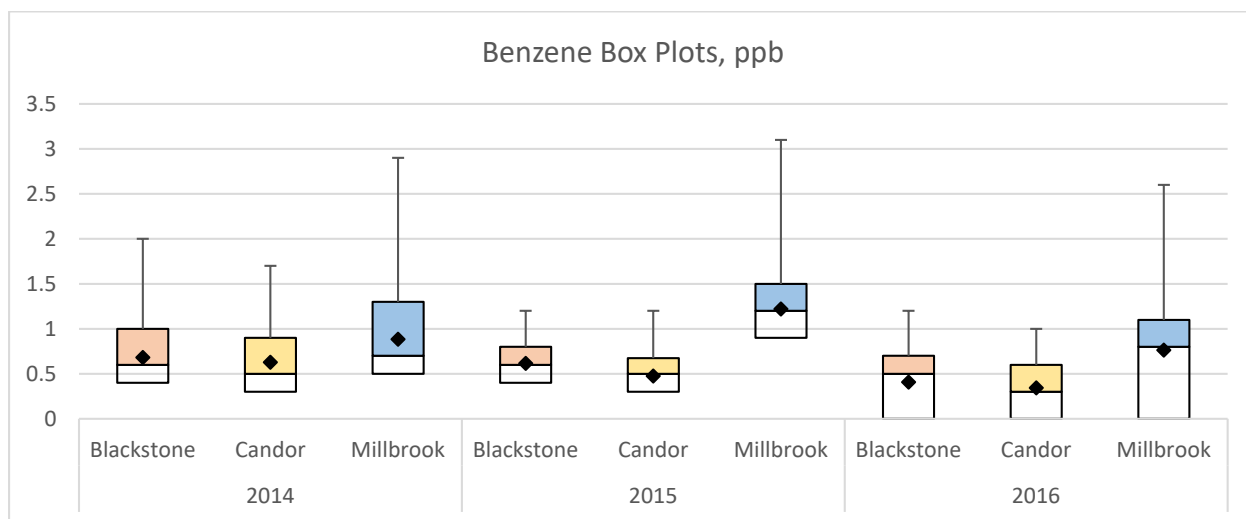


Figure 34. Box Plot of Toluene Concentrations at All Sites.

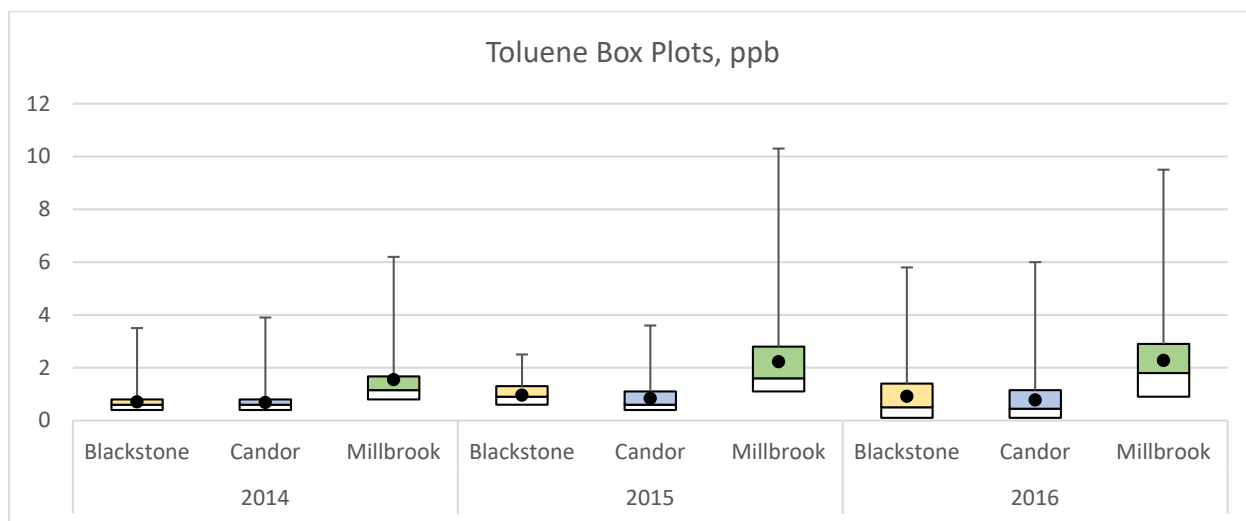


Figure 35. Box Plot of Ethylbenzene Concentrations at All Sites.

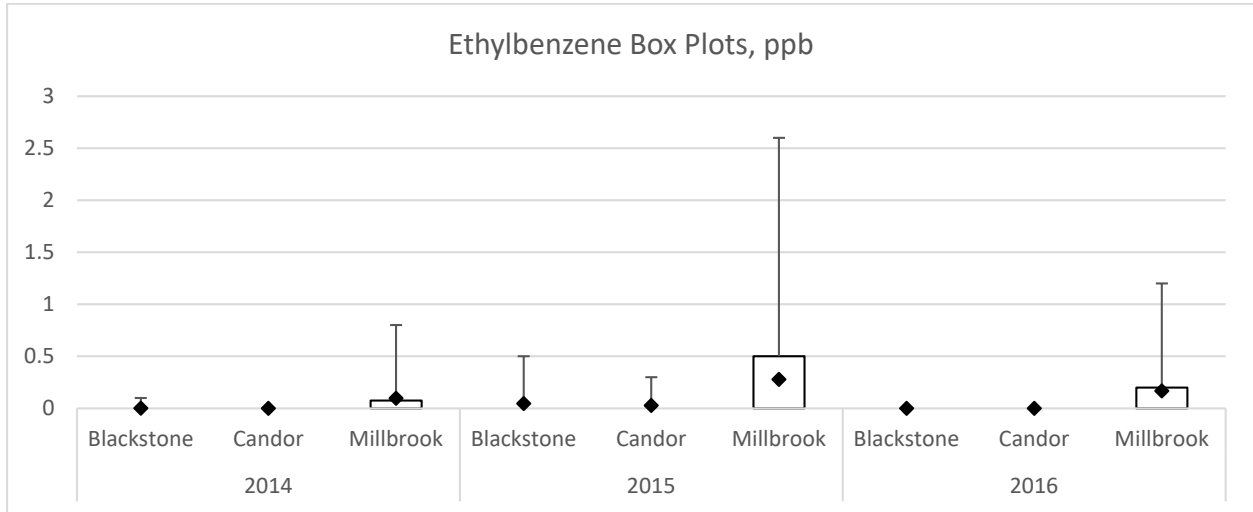


Figure 36. Box Plot of m/p-Xylene Concentrations at All Sites.

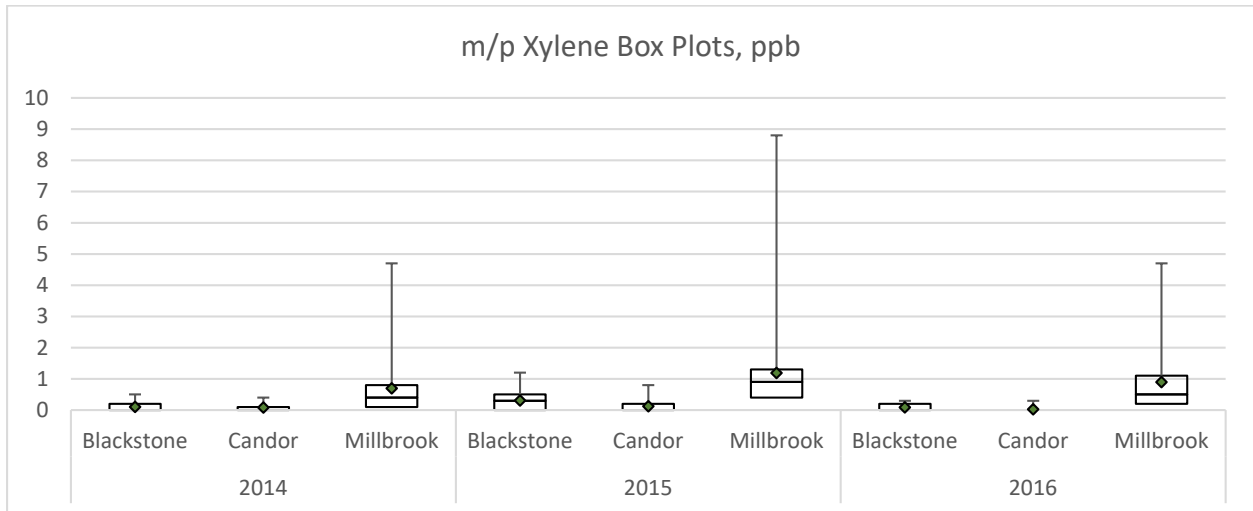


Figure 37. Box Plot of o-Xylene Concentrations at All Sites.

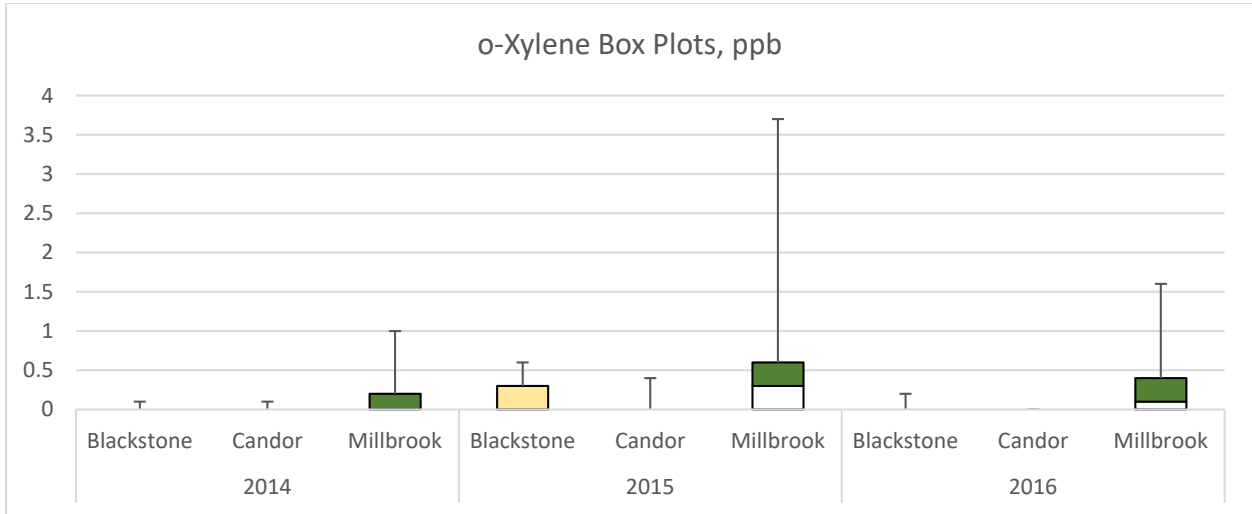
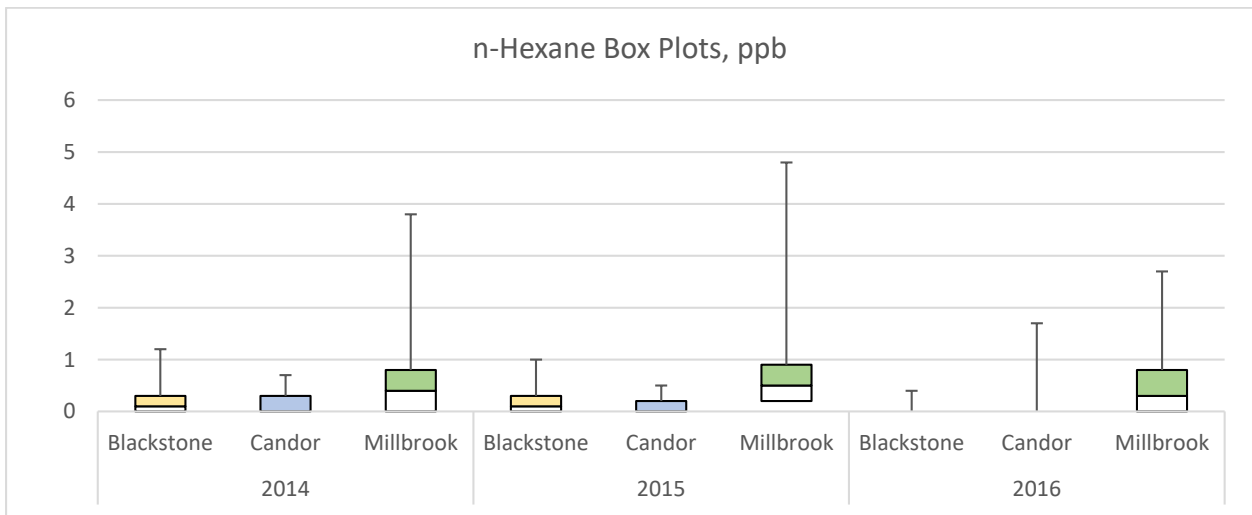


Figure 38. Box Plot of n-Hexane Concentrations at All Sites.



9.5 CONCLUSION

Based on collected VOC data and statistical analysis during the study period, one can infer that air sheds at Blackstone and Candor are similar. Focusing on annual average benzene and toluene concentrations during the study period one can conclude that Blackstone and Candor air sheds are similar. The annual average benzene concentration difference between Blackstone and Candor was approximately 0.07 ppb in 2016. Conversely, in 2016 the annual average benzene concentration difference between Blackstone and Millbrook was approximately 0.35 ppb or 5 times higher. The DAQ expected these results because concentrations of VOCs are heavily dependent on the size of the urban area near the site. Millbrook is in the largest urban area, Blackstone is in a much smaller urban area and Candor is a rural site. The VOC trends between annual average concentrations and concentration statistics show a similar trend with the aldehyde annual average concentrations and concentrations statistics during the study period.

10.0 CONCLUSIONS

The DAQ has completed the hydraulic fracturing baseline air quality monitoring project at the Blackstone site in the Deep River geological basin located south-southwest of the city of Sanford, North Carolina. This study focused on collecting several air quality measurements, namely ozone, PM, NO_x, SO₂, aldehydes, speciated VOCs, and meteorological data. DAQ currently operates long-term air monitoring sites that are upwind and downwind from the Blackstone site. To provide a general comparison of the air shed in Lee County, an assessment was made between the air quality measurements obtained at the Blackstone site to air quality measurements collected at a rural upwind site in Candor, North Carolina, and an urban downwind site in Raleigh, North Carolina.

Prevailing winds out of the southwest and west-southwest direction characterize the Lee County air shed. The ozone data exhibited very similar maximum daily 8-hour averages for both Candor and Blackstone, with the downwind urban site being slightly higher as expected. The PM data showed a slow rise in levels of PM as one traveled from the southern tip of the basin towards the downwind site. Nitrogen dioxide levels in Lee County were lower than those measured at the downwind urban site in Raleigh, as expected. The SO₂ values at the urban downwind site in Raleigh showed the highest concentrations of the two sites, yet both sites appeared to exhibit a downward trend over time. Based on collected VOC data and statistical analysis during the study period (2014 through 2016), the air sheds at Blackstone and Candor measured the same types of VOC at similar concentration levels. Ambient monitoring data was also collected during the 2017 calendar year at each of the three sites; however, this data was not quality assured and certified early enough to be evaluated in this report. However, preliminary analysis of the 2017 data does not reveal any unexpected or anomalous results.

11.0 LIST OF ACRONYMS

CBSA – Core-based statistical area

CFR – Code of Federal Regulations

DAQ – North Carolina Division of Air Quality

DNPH – Dinitrophenylhydrazone

DV – design values

EPA – United States Environmental Protection Agency

LAB – North Carolina DAQ Laboratory Analysis Branch

m – meta

$\mu\text{g}/\text{m}^3$ – micrograms per cubic meter

μm – micrometer

m/s – meters per second

MSA – Metropolitan statistical areas

n – normal or straight-chained

NAAQS – National ambient air quality standards

NIST – National Institute of Standards and Technology

NO_x – Oxides of nitrogen

o – ortho or adjacent

OMB – Office of Management and Budget

p – para or opposite

PM – Particulate matter

PM_{10} – PM with an aerodynamic diameter less than or equal to 10 μm

$\text{PM}_{2.5}$ – PM with aerodynamic diameter less than or equal to 2.5 μm

ppb – parts per billion

ppm – parts per million

SO_2 – Sulfur dioxide

SO_x – Sulfur oxides

VOC – Volatile organic compounds