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RESEARCH ARTICLE

Analysis of local-scale background concentrations of methane and other gas-phase species in the Marcellus Shale

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The Marcellus Shale is a rapidly developing unconventional natural gas resource found in part of the Appalachian region. Air quality and climate concerns have been raised regarding development of unconventional natural gas resources. Two ground-based mobile measurement campaigns were conducted to assess the impact of Marcellus Shale natural gas development on local scale atmospheric background concentrations of air pollution and climate relevant pollutants in Pennsylvania. The first campaign took place in Northeastern and Southwestern PA in the summer of 2012. Compounds monitored included methane (CH_4), ethane, carbon monoxide (CO), nitrogen dioxide, and Proton Transfer Reaction Mass Spectrometer (PTR-MS) measured volatile organic compounds (VOC) including oxygenated and aromatic VOC. The second campaign took place in Northeastern PA in the summer of 2015. The mobile monitoring data were analyzed using interval percentile smoothing to remove bias from local unmixed emissions to isolate local-scale background concentrations. Comparisons were made to other ambient monitoring in the Marcellus region including a NOAA SENEX flight in 2013. Local background CH_4 mole fractions were 140 ppbv greater in Southwestern PA compared to Northeastern PA in 2012 and background CH_4 increased 100 ppbv from 2012 to 2015. CH_4 local background mole fractions were not found to have a detectable relationship between well density or production rates in either region. In Northeastern PA, CO was observed to decrease 75 ppbv over the three year period. Toluene to benzene ratios in both study regions were found to be most similar to aged rural air masses indicating that the emission of aromatic VOC from Marcellus Shale activity may not be significantly impacting local background concentrations. In addition to understanding local background concentrations the ground-based mobile measurements were useful for investigating the composition of natural gas emissions in the region.

Keywords: methane; climate change; hydraulic fracturing

1. Introduction

The Marcellus Shale is a large-scale unconventional natural gas resource that underlies part of the Appalachian region. As of January 2015, the natural gas (NG) production rate in the Marcellus region was about 16 billion cubic feet per day, or 2 times the production rate of any other unconventional NG resource in the United States and 8 times its 2010 rate (EIA, 2016). The Energy Information Administration (2015) estimated that shale gas production in the US is projected to increase to about 150% of 2010 values by 2040. As Marcellus Shale development increases it is estimated to contribute 30–40% production share of the total US natural gas consumption east of the Mississippi River (EIA, 2014), establishing its potential role in the US energy market.

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Although the Marcellus Shale and similar NG resources are important to the future energy portfolio of the United States (EIA, 2016), there has been growing concern about the emissions of greenhouse gases (largely methane), criteria pollutants, and air toxics from all stages of shale gas development (Field et al., 2014; Moore et al., 2014). Novel extraction technologies like directional drilling and hydraulic fracturing, as well as other practices used to prepare an unconventional well for gas extraction, are known to emit pollutants associated with diesel combustion including carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur dioxide (SO_2), particulate matter (PM), and volatile organic compounds (VOC) (Goetz et al., 2015; Roy et al., 2013). In addition to combustion products, several well development practices including directional drilling and well completion have been observed to emit methane (CH_4), the primary component of NG (Caulton et al., 2014; Goetz et al., 2015).

The local atmospheric impacts of the above emission sources per well are short-lived because each process typically has a maximum lifetime of several weeks. Furthermore, the role of emissions from well development practices in the region are likely declining with the observed drop in drilling activity throughout the region since 2012 (EIA, 2016). Persistent sources of emissions involved in shale gas manufacturing include active well pads, compressor stations, processing facilities, liquid unloading, and pipelines, or sources associated with routine production and distribution (Allen et al., 2013; Goetz et al., 2015; Litovitz et al., 2013; Roy et al., 2013). Natural gas leaks are prevalent throughout the production and distribution stream (Allen et al., 2013; Burnham et al., 2011; EPA, 2015b). Emissions of VOC, CO, NO_x, and ultrafine PM have been reported from several stages of the shale gas production sector (i.e. active well pads, compressor stations, and processing facilities) (Goetz et al., 2015; Pekney et al., 2014; Rich et al., 2014; Warneke et al., 2014).

Despite the known increase of unconventional natural gas extraction and corresponding increase in atmospheric emissions there have been limited measurements of ambient air quality in regions that could be impacted. In the Marcellus region, Carlton et al. (2014) suggest that there is an air monitoring data gap and that increased monitoring is needed to assess the air quality impact of shale gas activity. The importance of improved monitoring is further demonstrated by Ogneva-Himmelberger and Huang (2015) who determined that clusters of populations vulnerable to poor air quality (e.g. young, elderly, low-income residents) are found in some areas of the Marcellus basin with high densities of shale gas activity. On a regional scale, Vinciguerra et al. (2015) observed increased ethane (C_2H_6), an alkane that is the second largest component of NG, downwind of the Marcellus basin corresponding to increased Marcellus Shale production rates. Another ambient air study in the Marcellus basin observed elevated methane and light alkanes near clusters of shale gas wells, but determined that the wells were only a minor source of alkenes and hazardous air pollutants (HAPs) (Swarthout et al., 2015). Similar results were observed by Goetz et al. (2015), where aromatic VOC and other HAPs were not detected at elevated levels in NG emissions from Marcellus Shale infrastructure.

Although non-alkane VOC may not be readily emitted from Marcellus shale development, the impact of other primary pollutants (e.g. CO, NO_x, PM) and secondary pollutants (e.g. O_3) on regional air quality remains uncertain. Studies focusing on other unconventional NG regions have attributed high summertime (Kemball-Cook et al., 2010) and wintertime (Ahmadov et al., 2015; Schnell et al., 2009) ozone events to VOC emitted from NG development. In northeastern Colorado, Gilman et al. (2013) found that alkanes from oil and natural gas activity contributed 60% of the total hydroxyl radical (OH) reactivity, an important metric that indicates a compound's potential to contribute to photochemical O_3 production. Given the known increase of alkanes in the Marcellus region it is possible that NG emissions from Marcellus shale activity play an increasing role in O_3 production in the region and especially in areas with high NO_x concentrations. However, other work has shown that in the summer of 2012 biogenic VOC dominated OH reactivity in part of the Marcellus Shale region in Southwestern Pennsylvania (Swarthout et al., 2015).

As Marcellus Shale development expands, its impact on local and regional air quality from direct emissions of criteria pollutants or ozone production may intensify, though the roles of decreasing well development practices and the projected increase in production are unknown. Additionally, because NG production from the Marcellus Shale is projected to increase, the emission of climate forcing compounds like methane may also increase in the region. Therefore, ambient air quality measurements are necessary to monitor the evolution of potential impacts from changes in Marcellus Shale development. The objective of this study is to utilize ground-based mobile measurements to determine concentrations of air quality and climate relevant pollutants in the Marcellus region during the early development stages of the NG play. Because future atmospheric measurements in the Marcellus region could be on other platform types (e.g. stationary monitoring, aircraft, etc.) methods have been developed in this study to identify "local background" concentrations in an attempt to create a cross platform metric that can be used by other researchers to investigate trends in the region. The local background in this work is defined as the observed concentration of a compound in a location due to the atmospheric mixing of local, regional, and global contributions. The contributions to the mixed air mass could be due to any type of anthropogenic or biogenic source. In addition to characterizing local background concentrations, this study will interpret the local background in the context of spatial distribution and composition of natural gas emissions in two areas of the Marcellus basin with high densities of production activity.

2. Methodology

This work combines results from two ground-based mobile measurement campaigns. The first campaign was conducted in the summer of 2012 using the Aerodyne Research Inc. Mobile Laboratory (AML) (Herndon et al., 2005). The second campaign took place in the summer of

2015 with the Drexel University Mobile Laboratory (DML). Details on instrumentation and where measurements took place can be found in the following sections.

2.1 2012 Measurements overview

The two major goals of the 2012 campaign were to characterize ambient concentrations of measured atmospheric species in areas of the Marcellus basin with high densities of shale gas activity and to characterize emission rates of climate-relevant compounds and air pollutants from Marcellus Shale infrastructure. The emission characterization aspect of the study was completed using tracer release ratio methods and the results were published in Goetz et al. (2015). The ambient measurement portion of the campaign, and the focus of this work, was located in sections of Southwestern and Northeastern Pennsylvania (SW PA and NE PA). Measurements were made while driving on-road and also while the AML was parked at night. Sampling locations are shown in **Figure 1**. In NE PA, ambient sampling was conducted in Sullivan and Bradford counties and the AML sampled overnight while parked in Laporte, PA. Sampling in the region began on August 22nd and ended on August 27th 2012. In SW PA, measurements were made in Fayette, Green, Somerset, Washington, and Westmoreland counties between the 23rd and 29th of September 2012. Stationary overnight sampling took place in Hidden Valley, PA (**Figure 1**). It should be noted that when parked overnight, the AML was powered using the residential power grid to prevent contamination from vehicle and generator exhaust. In addition to being located in areas with concentrated shale gas extraction activity, the study locations were also chosen because of differences in natural gas composition. Marcellus Shale in SW PA is known to contain areas of wet-gas (methane and other light alkanes), while the remainder of the shale layer in PA is known to contain dry-gas (mostly methane) (PADEP, 2010, 2011a, 2011b).

2.2 AML instrumentation

The AML was equipped with both commercial and research grade instruments that utilize real-time rapid response measurements, with most instruments sampling at ~1 Hz. An overview of the AML setup including layout, power setup, and inlet systems can be found in Kolb et al. (2004). A detailed list of particle and gas phase instrumentation installed on the AML for this campaign can be found in Goetz et al. (2015) and its supporting information.

This work will focus on ambient measurements of methane, ethane, CO, NO_2, and select volatile organic compounds. Methane, CO, and ethane were measured using Aerodyne Research, Inc. quantum cascade laser (QCL) trace gas monitors. Mobile detection limits for the species measured by the QCL trace gas monitors were <1 ppbv. Ethane monitoring took place only in the SW PA study area because the development of a QCL monitor for ethane detection occurred after measurements were made in Northeast PA. An Aerodyne Inc. cavity attenuated phase shift monitor (CAPS) was used to measure NO_2. Because

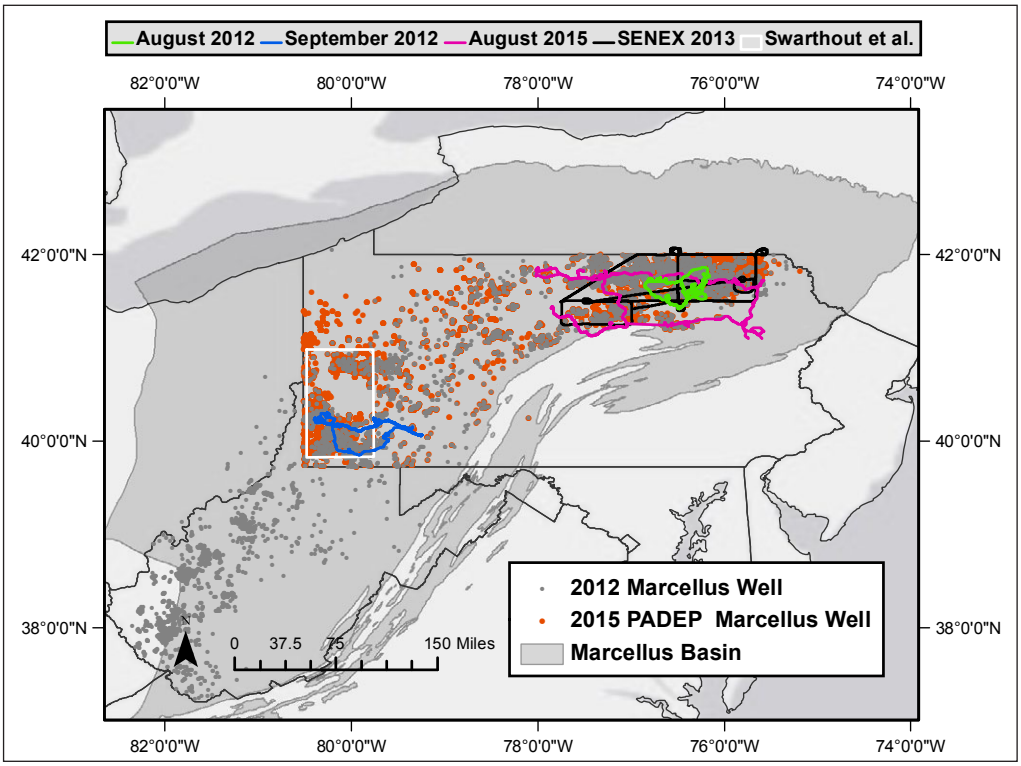


Figure 1: Map of study region. Mobile sampling tracks in Northeastern PA (green and pink) and Southwestern PA (blue) and NOAA SENEX flight (black). The sampling area of Swarthout et al. (2015) is shown in white. The extent of the Marcellus Basin in displayed in grey and overlaid by well sites in 2012 (red marker) and 2015 (orange marker). DOI: https://doi.org/10.1525/elementa.182.f1

of a technical issue CAPS-NO_2 measurements were only available in SW PA. The CAPS-NO_2 mobile detection limit was estimated to be ~0.25 ppbv. Various volatile organic compounds including aromatics and oxygenated hydrocarbons were measured using a proton-transfer reaction mass spectrometer (PTR-MS). A full list of compounds monitored by the PTR-MS and their associated detection limits can be found in Goetz et al. (2015). Additionally, all calibration procedures can be found in the supplemental material of Goetz et al. (2015). All measurements were adjusted based on derived calibration factors. Data processing and analysis was performed in Igor Pro 6.37 (Wavemetrics, Lake Oswego, OR).

2.3 2015 Measurements overview

Ground-based mobile measurements using the DML were conducted in NE PA between August 3rd and the 7th of 2015. Unlike the 2012 campaign, measurements were only active during the day while driving and were not active while parked at night. The DML made ambient measurements while driving in Bradford, Clinton, Columbia, Luzerne, Lycoming, Potter, Susquehanna, and Tioga counties (**Figure 1**). All of the counties investigated are known to contain Marcellus shale NG wells and supporting infrastructure. Some measurements were in similar locations as the 2012 campaign, but generally the 2015 measurements investigated areas outside the 2012 domain. Similar to the 2012 campaign, another objective of the 2015 campaign was to estimate emission rates from Marcellus shale infrastructure. The results from the emissions portion of the 2015 campaign are not included in this work and will be available elsewhere.

2.4 DML instrumentation

The DML is a late 1990s Ford cargo van that is equipped for gas-phase and particle-phase ambient mobile monitoring. The platform is modular in design and allows for the installation of any combination of instrumentation using a shock-mounted military grade 19-inch rack. Instrumentation is powered through the vehicle's alternator and a 2000-watt DC to AC power inverter. The inlet system is adaptable to the instrumentation and for this study PTFE tubing was used. The inlet was attached to a PTFE gooseneck positioned in front of the vehicle and at a height of ~2 meters. The sampling point of the inlet was positioned to be in free flow and not impacted by vehicle emissions in the boundary layer of the vehicle. The gas-phase inlet was equipped with inline Teflon disc filters to remove particulate contamination. The inlet flow rate is adjustable based on excess flow and for this study was set to a fixed flow rate that provided an inlet residence time of ~1 second. The DML was equipped with a ~1 Hz GPS to provide geopositioning.

This work will focus on methane and CO measurements made using a Picarro Inc. Cavity Ring Down Spectrometer (CRDS), Picarro G2401. The CRDS has a sampling rate of ~1 Hz and the mobile detection limits for all compounds analyzed were estimated to be <1 ppbv. The CRDS was factory calibrated prior to the measurement campaign and dilution calibrations were performed at the end of the campaign. The multi-point dilution calibrations were completed by using zero air and a custom calibration standard of methane, CO, and CO_2 balanced with N_2 produced by Airgas Inc. (Radnor, PA). The calibrations for both methane and CO determined that the CRDS measured ~6.5% low for the campaign compared to the calibration standard for a span up to 2 ppmv for CO and 5 ppmv for methane. All campaign measurements were adjusted to reflect the calibration results.

2.5 Percentile interval smoothing

Ambient concentrations from ground-based mobile monitoring provide insight into local-scale air quality of the area monitored, but they are not useful for direct comparison to other monitoring studies because unprocessed ground-based mobile measurements are biased by a number of factors that do not impact other measurement platforms. For example, changes in topography coupled with spatial changes in local scale meteorology are factors that affect ground-based mobile monitoring, but do not have the same significance for stationary monitoring. Disregarding the effects of extremes in topography (e.g. mountains), aircraft and satellite monitoring are largely independent of topography, and are typically impacted by larger scale (rather than local) meteorology. One of the largest differences between ground-based mobile ambient monitoring and other types of measurement platforms is the degree of mixing of emissions at the local scale. Depending on proximity to emission sources, a stationary ambient monitoring site can be influenced by local unmixed emissions, but the extent of that influence is typically based on wind direction and regularity of emissions. Consequently, when the sampling location is fixed, and distances to emission sources are known, background concentrations can often be isolated from unmixed emission signals and conclusions can be made about the magnitude of emissions. Aircraft measurements are mobile, however, depending on altitude often sample air masses assumed to be well mixed vertically in the boundary layer (Peischl et al., 2015). Alternatively, the degree of emission mixing observed by ambient ground-based mobile monitoring is constantly changing with its location, and the magnitude of an emission source is difficult to estimate because the scale is dependent on the rate of emission, local scale meteorology and distance. Therefore, local scale unmixed emissions need to be removed from mobile datasets to make them comparable to other types of atmospheric monitoring.

In order to generate a cross platform dataset, the data in this study were transformed using percentile smoothing over a defined "averaging" time. The developed processing technique generates a dataset at a user-selected percentile that best represents the background concentrations over a time interval with sufficient resolution to remove rapid changes in the time series due to emission source plumes and acute changes due to topographically dependent meteorology. The percentile smoothed dataset was calculated by using a custom script written in Igor Pro 6.37. The method was developed to be functionally similar to median smoothing, but with the option of smoothing at other percentile values. The following methods establish

how the percentile and the time interval were chosen to best represent the local-scale background concentrations in the Marcellus basin from our combined datasets.

The percentile smoothing analysis was conducted at a range of time intervals and at percentiles ranging from 5 to 60 to determine which percentile best represents the local background for all of the atmospheric species monitored. Time intervals at multiples of 10 minutes ranging from 10 to 60 minutes were investigated. It was qualitatively determined that the 20 minute interval provided the best balance of spatial and temporal resolution for our mobile dataset to represent the local background concentration for all species given our mean sampling speed of 32 km per hour. This value may be different for other mobile platforms and is based on both platform velocity (e.g. car vs plane) and sampling rate of the measurement. The percentile that best represents the local background was determined through comparison with lognormal fits of the measurement data histograms over the same 20-minute section of data for the entire dataset. Histograms were calculated for each interval because it was assumed that the most frequent concentrations represent the local-scale background for that sampling interval. Example histograms of 20-minute sections of ethane measurements that display three common sampling scenarios encountered in the dataset are shown **Figure 2c**. The figure demonstrates how the mode of the lognormal fit of each histogram approximates the most frequent value for each sampling interval. The mode of a lognormal fit of a histogram is assumed to reasonably characterize the local-scale background as seen in the time series from one sampling day shown in **Figure 2**. However, the log normal fit analysis is less robust compared to percentile smoothing and can create unpredictable results when the fitted histogram is not log normally distributed. Therefore, the mode of lognormal fit methodology was used only as a standard to determine which 20-minute percentile best represents the most frequent concentrations for each species. **Figure 3** provides an example of the mode of the log normal fit for each 20-minute interval of the ethane dataset plotted against the concentration percentiles for the same intervals. Results from the bulk comparisons determined that percentiles between 30 and 40 were the most closely related (i.e. slope = 1) to the lognormal fits for all of the species analyzed. A qualitative assessment of the percentile smoothed dataset for ethane compared to the lognormal fit time series and the 1-Hz time series can be seen in **Figure 2b**. Based on the three sampling scenarios presented in **Figure 2**, it is clear that the 35th percentile is the percentile that is most closely related to the lognormal fit

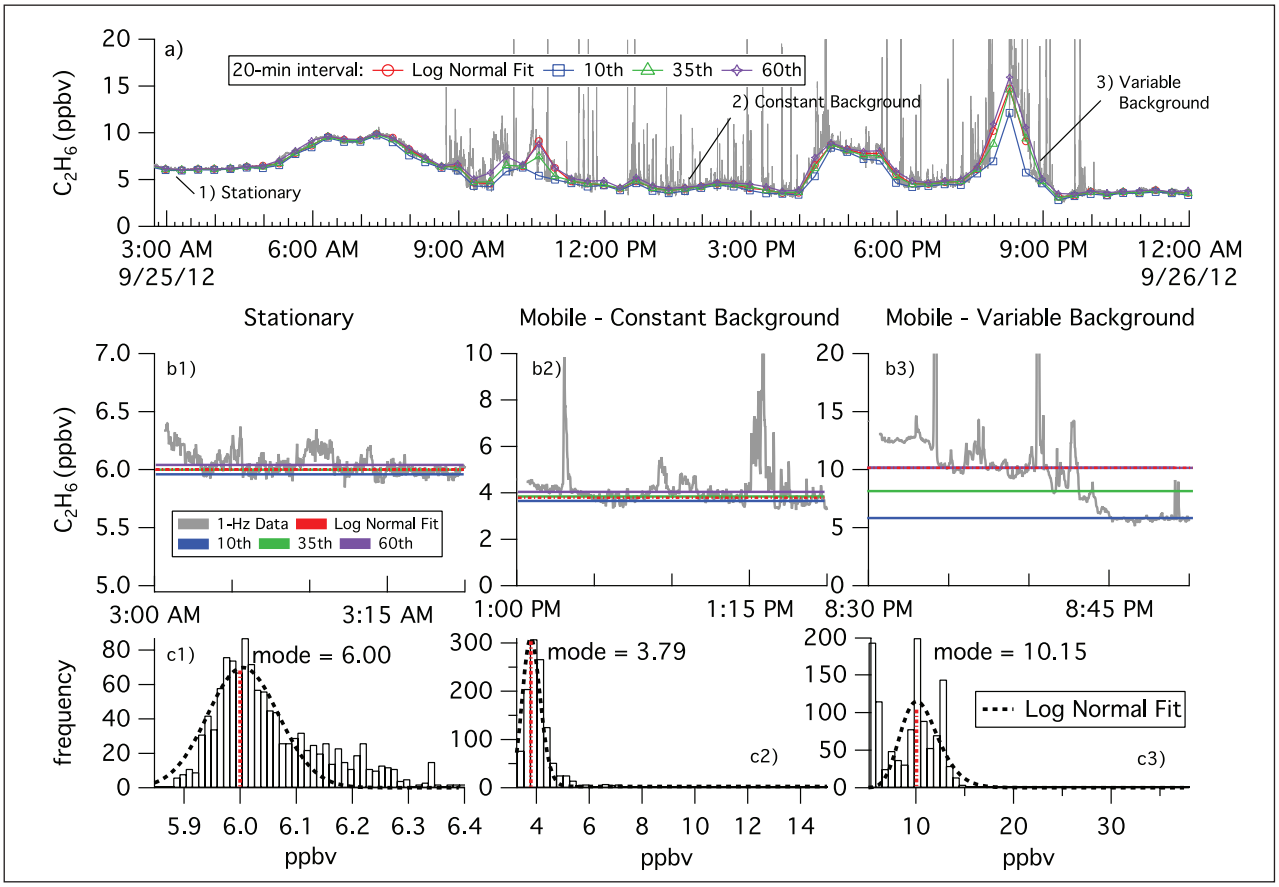
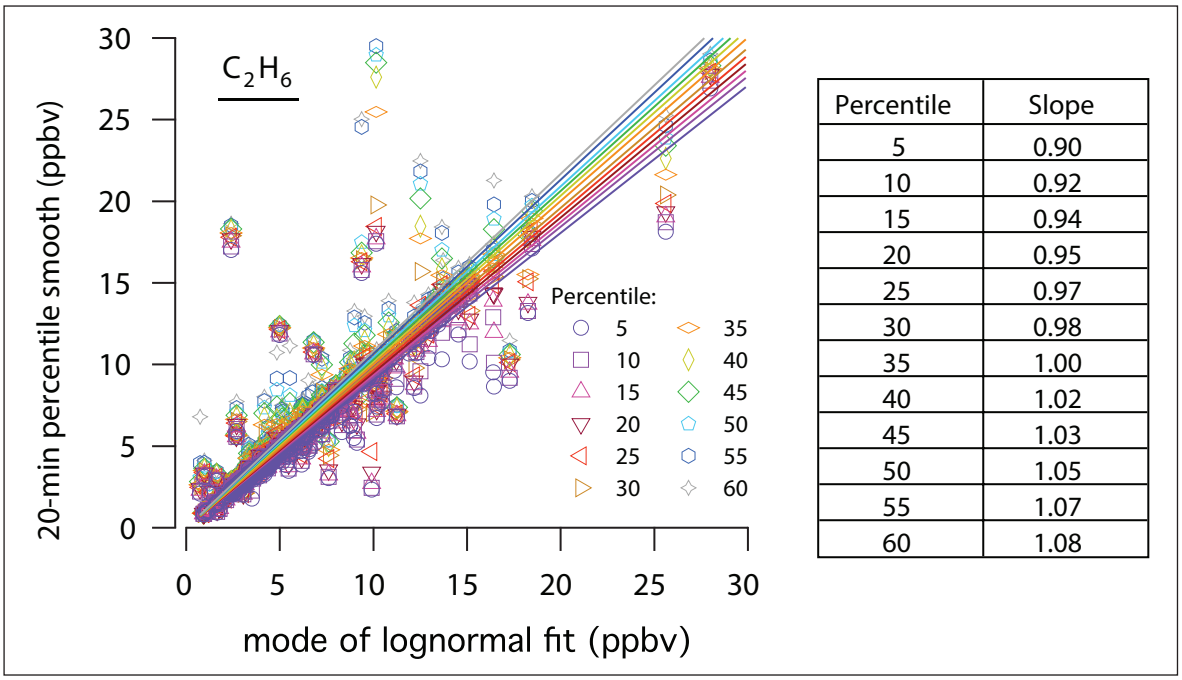


Figure 2: Examples of local background estimates. Time series (panel b) and histograms (panel c) of ethane with examples of stationary data (1), mobile data with a constant background (2), and mobile data with a variable background (3). Lognormal fits of each histogram (black dotted line) and the mode of the log normal fit (red dotted line) are displayed. Panel a contains a 1-Hz time series for ethane from one example sampling day. The log normal mode fits, 10th, 35th, and 60th percentiles are overlaid on the 1-Hz time series for comparison. DOI: https://doi.org/10.1525/elementa.182.f2



Percentile	Slope
5	0.90
10	0.92
15	0.94
20	0.95
25	0.97
30	0.98
35	1.00
40	1.02
45	1.03
50	1.05
55	1.07
60	1.08

Figure 3: Correlation of percentile smoothed data to lognormal fits of the data. Scatter plot of 20-minute percentile smoothed ethane data at percentiles ranging from 5 to 60 versus the mode of the log normal fit for the same 20-minute intervals. Linear fits of the data with results slopes are shown. DOI: https://doi.org/10.1525/elementa.182.f3

dataset during stationary sampling and while mobile sampling is conducted in a location with a stable background. More significant differences between the 35th percentile and lognormal fits were observed when in variable backgrounds (**Figure 2b**). Large variable backgrounds were not commonly observed in during mobile sampling and it was determined that 85% of the ethane, methane, and CO 35th percentile datasets were within 10% of the lognormal mode dataset for each species (Figure S2). The low frequency of differences greater than 10% between the 35th percentile and lognormal mode datasets suggests that variable backgrounds had little effect on the role of the 35th percentile as a proxy for the local-scale background. Based on these analysis results, 20-minute 35th percentile smoothing is used to represent the local-scale background concentrations for the remainder of this work.

2.6 Other sources of data

Aside from the ground-based mobile measurements conducted on the AML and DML, other data from other ambient air quality studies in the Marcellus region were retrieved and used for comparison. Results from flask samples detailed in the supporting information of Swarthout et al. (2015) were used for comparisons of methane, ethane, acetone, methanol, acetonitrile, acetaldehyde, benzene, and toluene mole fractions in SW PA. Major comparisons were made between the mobile results and results from PTR-MS and Picarro CRDS measurements taken during the National Oceanic and Atmospheric Administration's (NOAA) 2013 Southeast Nexus (SENEX) field study (Warneke et al., 2016). The SENEX campaign performed multiple flights using the NOAA WP-3D aircraft in Southeast U.S. and also directed several flights that focused on areas with unconventional natural gas activity including the Haynesville, the Fayetteville, and the Marcellus Shale regions (Peischl et al., 2015; Yuan et al., 2015). Summary statistics are derived from data collected on the July 6th 2013 flight when in the Marcellus region (>41.0°N latitude) and below an altitude of 2000 meters above sea level (ASL). Measurements below 2000 meters ASL were assumed to be at or near the planetary boundary layer height and therefore to have similar characteristics to ground-based measurements (Peischl et al., 2015). The majority of the SENEX measurements were made at 500 meters above ground level and an effort was made to position the aircraft within the planetary boundary layer. It should be noted that because the other sources of data did not occur simultaneously with the ground-based mobile measurements conducted in this work, the other sources of data could not be used to assess the performance of the percentile smoothing data for characterizing the local-scale background.

3. Results and discussion

Summary statistics of the ambient mole fractions of atmospheric species monitored by both mobile labs can be found in the supporting information (SI) Figure S1. The following sections provide results of local-scale background mole fractions derived from percentile interval smoothing. Discussion points are based on the analysis of the local-scale background mole fractions and not from the summary statistics of the ambient mole fractions contained in the SI.

Box and whisker plots are presented in **Figure 4** to show local-scale background mole fractions of methane, ethane, CO, NO_2, methanol, and acetone estimated from interval percentile smoothing for SW PA and NE PA from

both measurement campaigns. Results from other studies and other data sources are also provided for comparison to concentrations observed elsewhere in the Marcellus region, concentrations observed in other unconventional natural gas plays, and also to make comparisons to urban measurements and larger regions. Most notably, comparisons were made to mole fractions observed by the above mentioned SENEX campaign and Swarthout et al. (2015).

3.1. Methane

As seen in **Figure 4**, the median local-scale background mole fraction of methane was estimated to be 2100 ppbv in SW PA and 1960 ppbv in NE PA during the 2012 field study. The results indicate that the local background methane mole fractions were significantly elevated in the Southwest compared to the Northeast study area, and that similar local background mole fractions were never observed between the two areas in the summer of 2012. For example, there was approximately a 50 ppbv difference between the 10th percentile value in SW PA and the 90th percentile value in the NE PA in 2012. An analysis of boundary layer heights, taken from the North American Region Reanalysis (NARR) model (NCEP, 2015) during the two study periods, can be found in the SI (Figure S3). This analysis found that the boundary layer height was typically greater during the SW PA study period compared to

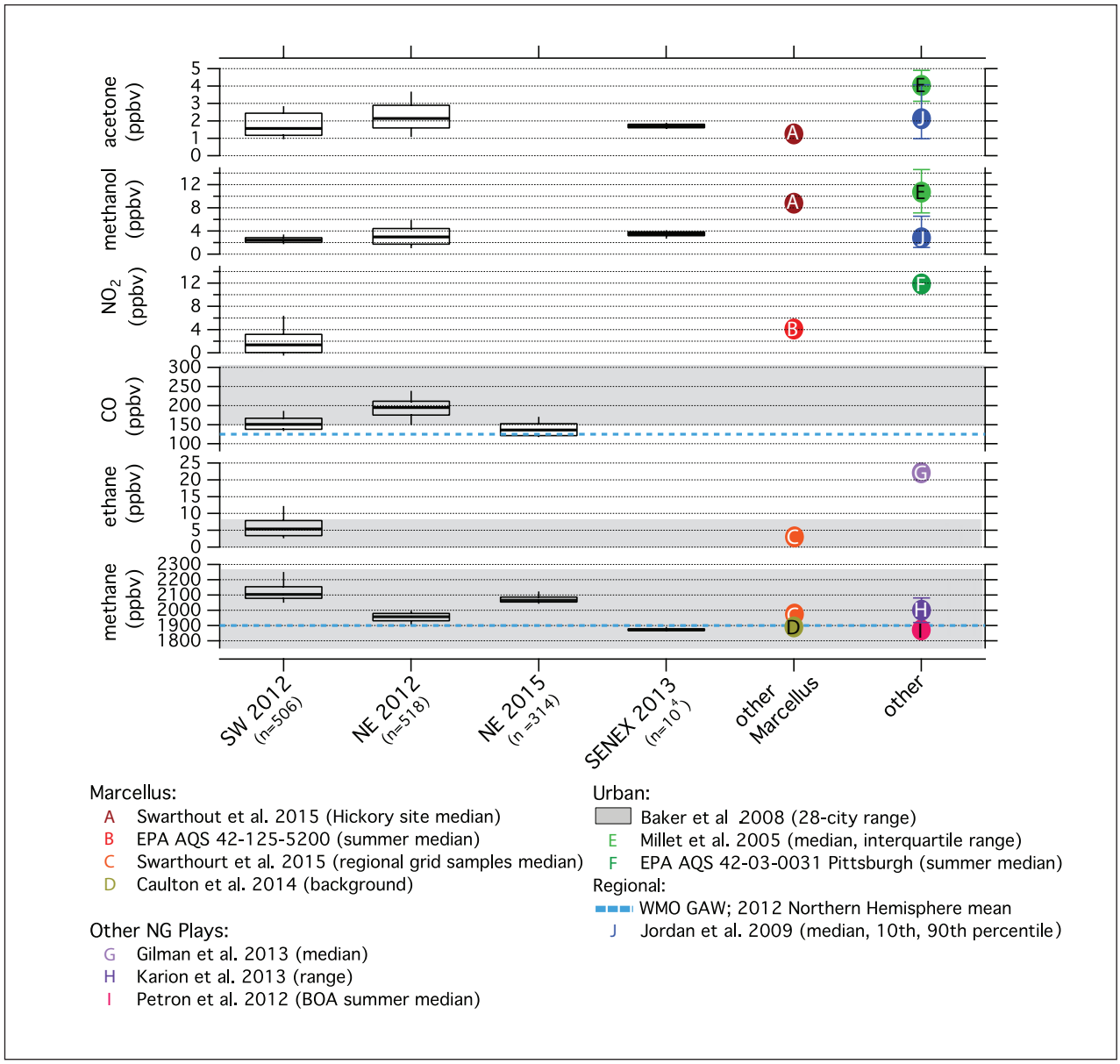


Figure 4: Summary of local-scale background estimates. Box and whisker plots (10th, 25th, 50th, 75th, and 90th percentiles) of local-scale background estimates from Southwestern PA and Northeastern PA in 2012 for methane, ethane, CO, NO_2, methanol and acetone. Also included are estimates of methane and CO from the 2015 Northeastern PA field study. Box and whisker plots for methane, acetone, and methanol from the SENEX 2013 field study are displayed. The Baker et al. (2008) 28-city range is for select species is shown in grey. WMO mean is displayed as the blue dashed line. Important values from relevant studies and other data sources displayed as lettered markers (circles). DOI: https://doi.org/10.1525/elementa.182.f4

the NE PA study period in 2012. Furthermore, an analysis of wind speed observed by the AML, located in the supporting information, determined that the median wind speed during the NE PA study period was approximately 50% of the median of the SW PA study period (Figure S6), which would lead to less atmospheric dilution compared to SW PA. Back trajectories for each study day were produced using NOAA's HYSPLIT (Rolph, 2016; Stein et al., 2015) to look at the air mass source regions as a potential explanation of mole fraction differences between locations and years. The back trajectories indicate that the majority of the 48 hour air masses originated in rural areas to the west of the Marcellus Shale basin during the SW PA study period in 2012 (Figure S5). Additionally, there are no indications that the SW PA air masses originated in other natural gas regions. The 48-hour back trajectories from the NE PA 2012 study period show that the majority of the air masses originated within the Marcellus Shale basin and two trajectories originated from the urbanized Atlantic Coast (Figure S5). The period originating from the Atlantic coast was found to have an average methane local background mole fraction of ~70 ppbv less than when the air masses originated from within the Marcellus Basin.

Results from the 2015 campaign indicate that the median local-scale background of methane was enhanced by 100 ppbv compared to the 2012 Northeast study area. In addition to enhancements of the median local-scale background there were enhancements in all percentiles when comparing 2012 to 2015 datasets with no overlap in local background values. Since mobile routes differed between 2012 and 2015 measurements, we can compare measurements made in the same area to remove this potential source of error. When comparing sampling locations within 10 km proximity, the median local methane background was found to be 125 ppbv greater in 2015 compared to 2012. The World Meteorological Organization (WMO) Global Atmospheric Watch estimated global methane mole fractions increased by an average of 6 ppb per year over that same time period (WMO, 2016). An analysis of boundary layer heights and wind speed during the two study periods shows that the atmosphere was likely more dilute in 2015 compared to 2012 in NE PA with boundary layer heights equal to or greater than 2012 (Figure S4) and with greater wind speeds (Figure S6). Consequently, the elevated background levels observed in NE PA in 2015 were not due to boundary layer height and wind speed differences. The 48-hour HYSPLIT back trajectories indicate that the air masses observed in 2015 primarily originated in areas west of the Marcellus Basin (Figure S5). Although the trajectories show some differences in source regions between to two study periods, the lack of overlapping local backgrounds suggests that regional enhancements in methane were likely occurring in the region.

Additional comparisons can be made between local-scale methane backgrounds in the two study areas and measurements from other studies in the Marcellus region. In NE PA, the SENEX flight provided a median methane mole fraction of 1880 ppbv in July 2013, which is lower than any local-scale background estimate made in this study. From two flights in SW PA in June 2012, Caulton et al. (2014) estimated the methane background to be 1890 ppbv. Another study that took place in June 2012 in SW PA used a regional grid of ground-based flasks and found methane to have a median value of 1970 ppbv from 144 samples (Swarthout et al., 2015). It is noteworthy that both aircraft studies observed lower methane concentrations than those observed by ground-based measurements in this work and by Swarthout et al. (2015), all of which took place in the summertime and within a 13 month span. Additionally, median daytime local background CH_4 estimates between 11am and 5pm, when vertical mixing within the boundary layer is assumed to be greatest, were approximately 4% to 12% greater than the SENEX median. The difference between the ground-based and aircraft platforms suggests that there may be some inherent systematic difference between the two measurement approaches, and assumptions of equivalently mixed boundary layers may not be appropriate. The aircraft measurements were within 20 ppbv of the WMO's 2012 estimated mean for methane of 1900 ppbv for the Northern Hemisphere between 30°N and 60°N latitude (WMO, 2016), which could indicate that the methane background in the Marcellus region at that time was not elevated compared to the mid-latitude average. Alternatively, if there is a systematic difference between the two measurement approaches, and ground-based measurements, which often have longer sampling durations, are considered to be more representative of a regional air mass, then the ground-based results from this study and in Swarthout et al. (2015) demonstrate that methane in the Marcellus region is elevated compared to the Northern Hemisphere mid-latitude (30–60°N) mean.

Methane mole fractions from other unconventional natural gas regions (Karion et al., 2013; Pétron et al., 2012) and from a 28-city air study (Baker et al., 2008) can be found in **Figure 4**. All local-scale methane backgrounds estimated in this study were within the 28-city urban range, suggesting that methane concentrations in the Marcellus are more similar to urban air masses than rural, despite being a mostly rural region. It is important to note however that the 28-city study values may no longer be representative of urban methane because the study was conducted over ten years ago and therefore does not represent the increasing global background on top of which urban emissions accumulate and changes in urban methane emissions over that time period. For example, between 2007 and 2012 the global mean mole fraction increased by 29 ppbv (WMO, 2016). Comparisons to Pétron et al. (2012), demonstrate that background methane mole fractions were greater in the Marcellus region than the summertime median at Boulder Atmospheric Observatory (BAO) located in the Denver-Julesburg basin in Colorado. In the Uintah Basin in Utah, Karion et al. (2013) found that downwind methane ranged from 1920 to 2080 from one flight in February 2012. The results from the Uintah basin flight reveal that the local-scale methane backgrounds estimated in this study are within the mole fraction range observed in another large unconventional natural gas basin.

3.2 Carbon monoxide

The median local-scale background for CO was estimated to be 150 ppbv in SW PA (**Figure 4**). Northeastern PA in 2012 was estimated to have a local-scale background mole fraction nearly 50 ppbv larger than SW PA. The larger CO median in NE PA is unexpected because NE PA is considered the more rural of the two study areas and the counties contained in the study area have a lower population density compared to the counties in SW PA, though all counties had a population density of less than 20% of the urbanized local Allegheny County (Bureau, 2012). While both study areas were in rural areas, the median background CO was within the 28-city range of Baker et al. (2008) and above the WMO mid-latitude average of 125 ppbv (WMO, 2016). Additionally, because there is evidence that urban mole fractions in the US have decreased in the last decade (Warneke et al., 2012) it is possible that the CO backgrounds observed in this study are greater than some urban air masses. The comparison to the 28-city study indicates that although the areas are rural there is a source of CO emissions that is amplifying CO to urban levels. However, the larger CO local-scale background in NE PA in 2012 could partially be explained by lower boundary layer heights (Figure S3) and windspeed (Figure S6) over the study period compared to SW PA. Additionally, the differing source regions identified from the HYSPLIT trajectories (Figure S5) and previously discussed with methane could explain the differences in CO local background, though more monitoring is needed to assess the role of emissions from eastern urbanized areas on CO levels in the region.

In 2015 CO was estimated to have a median local-scale background mole fraction of 136 ppbv. The estimated background was lower than what was observed in either study area in 2012, and when investigating measurements within the same 10 km vicinity the 2015 median was ~75 ppbv lower than the 2012 median. The 2015 median was also lower than the 28-city range and the 25th percentile was within the 30–60°N mean (**Figure 4**). The comparisons suggest that NE PA in 2015 had CO backgrounds more similar to rural areas despite the observation of larger CO emission signals in the ambient dataset as seen in the SI (Figure S1). The significant drop in median local-scale background provides some evidence that CO emission may have decreased from 2012 to 2015 in the NE PA, though the lower median background in 2015 can also be explained by the increased boundary layer height (Figure S4), increased wind speed (Figure S6), and differences in air mass source regions (Figure S5) estimated for that study period.

3.3 Carbon monoxide and methane ratios

Although the absolute local background mole fractions provide insight to the range of methane and CO concentrations observed in the Marcellus shale region in 2012 and 2015, it is difficult to ascertain inter-annual and regional trends because of inconsistency due to meteorology. Here we evaluate the local background ratios of CO and methane to better understand trends between the mobile datasets. This type of analysis has been found to provide internal consistency for comparisons of datasets containing observations of long-lived atmospheric species because concentration ratios are conserved regardless of meteorology (Parrish et al., 1998). **Figure 5** provides box and whisker results of collocated concentration ratios of local background CO to local background methane as well as the WMO mid-latitude value.

Southwestern PA in 2012 the median local background CO to methane ratio was observed to be 0.071 (ppbv/ppbv). Northeastern PA in 2012 was observed to have a median local background ratio of 0.099. The median CO to methane ratios in each region in 2012 were above the WMO mid-latitude ratio of 0.066, though in SW PA observations in the 25th percentile and lower were at or below the mid-latitude range ratio (**Figure 5**). Because the observed background CO to methane ratios were generally above the mid-latitude ratio it is likely that background CO was universally enhanced in the region compared to the mid latitude background. The lower ratios in SW PA compared to NE PA in 2012 are thought to be due to enhanced CO mole fractions observed in NE PA and enhanced methane in SW PA. The large differences in background mole fractions were possibly due to differences in the quantity of emissions and emission types between the two study areas in 2012. Natural gas activity, for example, is thought to be a major source of methane emissions, but differences in the extent of emissions between the two study areas are unknown. Additionally, there are a number of other natural and anthropogenic emission sources of methane that could contribute to enhanced backgrounds in SW PA (IPCC, 2013). Although natural gas development is likely a major emission source in the region, the role of other emissions sources (e.g. landfills, biomass burning, biogenic, NG distribution leaks, coal mines etc.), which may be significant in some areas, is outside the scope of this work.

Northeastern PA in 2015 was determined to have a local background CO to methane median of 0.066 with a 25th percentile of 0.059 and a 75th percentile of 0.073 (**Figure 5**). The CO to methane ratios in 2015 were found to be significantly lower than observations in the same area in 2012 and similar to WMO mid-latitude mean. Because the local background CO mole fractions were often near or below the mid-latitude average any background CO to methane value lower than the mid latitude average is thought to be due to enhanced methane in the study area. Additionally, based on the local background observations, the decreased CO to methane ratios observed in 2012 compared to 2015 are likely due to a decrease in background CO and an increase in methane. The enhancement of methane from 2012 to 2015 suggests that emissions of methane have increased in NE PA. Since the scale of agricultural activity has likely not changed to the same extent as Marcellus Shale development in the region, it is possible that the major contributor to the elevated local backgrounds in 2015 is increased Marcellus Shale NG production. The supposed trend in CO emissions corresponds with a decrease in Marcellus Shale spuds, or the point at which a new NG well is drilled, in Pennsylvania over the same time period. New unconventional NG wells have decreased at a rate of ~170 wells per year in Pennsylvania, though 2011 and 2014 were outside

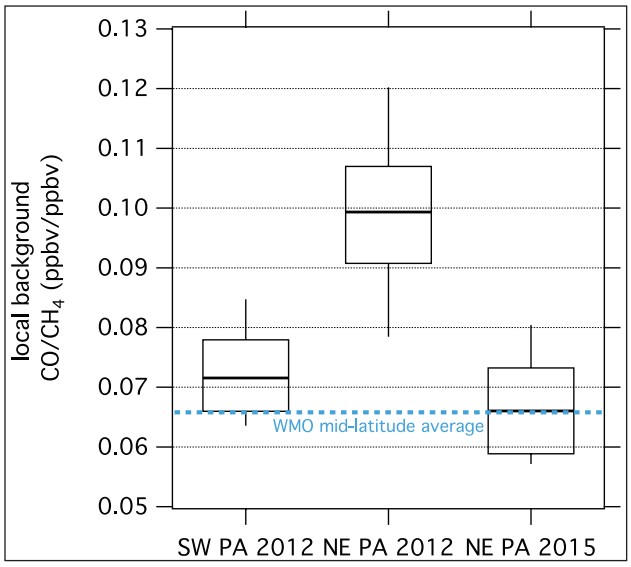


Figure 5: Carbon monoxide to methane local background ratios. Box and whisker plots (10th, 25th, 50th, 75th, and 90th percentiles) of local-scale background CO to local background methane from Southwestern PA and Northeastern PA in 2012. WMO mid-latitude mean CO to mean methane ratio is displayed as the blue dashed line. DOI: https://doi.org/10.1525/elementa.182.f5

that trend, and the total spuds in 2015 were only 58% of the total for 2012 (PADEP, 2016). A decrease in new NG well development would induce a decrease in the use of heavy duty diesel trucks, directional drilling, hydraulic fracturing, flow-back flaring, and well pad construction all of which are sources of CO emissions and is one possible explanation for the decreased CO levels. However, while spuds have decreased in PA, the total production in the Marcellus Basin has more than doubled (110% increase from 2012 to 2015), which provides further explanation for the observed methane enhancements in the region (EIA, 2016). The increase in production with the coupled decrease in spuds suggests that distribution infrastructure (i.e. compressor stations, pipelines, processing facilities) is starting to become accessible to many of the started and capped wells in the region. Increased methane and CO monitoring combined with emission inventories are needed to understand the evolving role of emissions from well pad development and distribution infrastructure on air quality in the Marcellus region and its climate impact.

3.4 Ethane

Ethane was observed to have a local-scale background median of 5.4 ppbv and interquartile values of 2.7 ppbv and 7.9 ppbv in SW PA (**Figure 4**). Unfortunately, because ethane monitoring was limited to SW PA comparisons cannot be made between study areas or between years to determine emission trends. Most of the local-scale ethane background estimates were within the Baker et al. 28-city range (0.5–8.74 ppbv), but the 90th percentile was outside the range with a mole fraction of 12.2 ppbv. Due to hydroxyl radical (OH) chemistry in the summertime, ethane has been observed to have strong seasonal variability at an amplitude of ~0.8 ppbv in the high Northern Hemisphere (Simpson et al., 2012). Consequently, it is difficult to estimate a global or hemispheric average. From WMO (2016) and Simpson et al. (2012), it can be estimated that the summertime mole fraction of ethane in 2009 was ~1 ppbv in the Northern Hemisphere between 30°N and 60°N latitude. Given the approximated mid-latitude average it is likely that ethane in SW PA is enhanced compared to other rural mid-latitude locations. Further evidence that ethane is enhanced in SW PA can be found in Swarthout et al. (2015), who observed a summertime median of 2.86 ppbv. While ethane appears to be enhanced in SW PA, it is not as enhanced as in the Denver-Julesburg Basin (median of 22 ppbv) based on measurements made at the BAO in 2011 (Gilman et al., 2013). The large differences between the two NG regions could be due to the quantity of emissions in the region, differences in NG composition, and seasonal effects. Further monitoring of ethane in the Marcellus region is needed to understand seasonal trends and how increased NG activity influences ozone production in the region.

3.5 Nitrogen dioxide

Nitrogen dioxide, a criteria pollutant under the National Ambient Air Quality Standards (NAAQS), was estimated to have a median local-scale background of 1.4 ppbv in SW PA in 2012. The median was lower than the 2012 summertime NO_2 median of 4.0 ppbv at an US Environmental Protection Agency (USEPA) monitoring station (AQS 42–125–5200), which is located in rural Washington County in an area with a high density of Marcellus Shale well pads (EPA, 2016a). Additionally, the SW PA median was ~10 ppbv lower than the 2012 summertime median at a USEPA monitoring station located in Pittsburgh, PA (AQS 42–03–0031) (EPA, 2016a). Although comparisons to other studies are difficult because of the short lifetime of NO_2 in daytime hours, the values shown in **Figure 4** provide a baseline that represents mole fractions observed in the early development of the Marcellus Shale.

3.6 Acetone

Acetone is known to be prevalent in the troposphere and is emitted by solvents, vehicles, biogenic sources, oceans, biomass burning, and secondary production from propane oxidation (Jordan et al., 2009). Past measurements in the troposphere have observed ambient mole fractions ranging from 0.2–3 ppbv (Jacob et al., 2002). Globally, the largest sources of acetone are terrestrial vegetation (35%) exchange with oceans (28%), and oxidation of propane (22%) (Jacob et al., 2002). In the Marcellus region the major sources are expected to be vegetation and the oxidation of propane from NG leaks.

In SW PA acetone was estimated to have a median local-scale background of 1.6 ppbv (**Figure 4**). Based on measurements in NE PA in 2012 acetone was estimated to have a median local scale background of 2.1 ppbv. Similar results have been observed by the SENEX 2013 field study in Northeastern PA (median of 1.7 ppbv) and by Swarthout et al. (2015) in SW PA at their Hickory monitoring station (median of 1.3 ppbv) located within an area of with a high density of NG activity. The analogous results from the

listed field studies indicate that the acetone mole fractions were consistent throughout the Marcellus region in the summertime of 2012 and 2013 and acetone was likely emitted from a constant source or was transported from other regions. The local background estimates were also similar to findings from Jordan et al. (2009), who observed a summertime median mole fraction of 2.1 ppbv at a rural monitoring site in New Hampshire. Further evidence that the local-scale background estimates are most similar to rural concentrations can be found in Millet et al. (2005), who observed large acetone mole fractions in the summertime in Pittsburgh. Given that propane has an atmospheric lifetime of 10 days due to OH oxidation (Atkinson, 2000), which allows for significant transport outside the region, and that acetone measurements are not enhanced compared to literature values it is likely natural gas development is not significantly adding to acetone concentrations in the Marcellus region. Future acetone measurements collocated with propane measurements would be valuable in constraining the role of propane oxidation in acetone production in the Marcellus region and how it compares to biogenic production.

3.7 Methanol

Methanol is ubiquitous in the atmosphere and emissions have been attributed to terrestrial vegetation, plant decay, biomass burning, oxidation of methane, and direct anthropogenic sources (Holzinger et al., 2005; Singh et al., 2000; Wells et al., 2012). Methanol has also been observed from unconventional NG wells in the Uintah Basin in Utah and from a compressor station in the Marcellus Basin because of its use as a pipeline antifreeze (Goetz et al., 2015; Warneke et al., 2014). Methanol was estimated to have a local-scale background median of 2.5 ppbv in SW PA and 3.0 ppbv in NE PA in 2012. In 2013, methanol observed by the SENEX field study was slightly larger with a median mole fraction of 3.5 ppbv, but generally methanol followed the same trend in the three field studies compared to acetone. Methanol observations by Swarthout et al. (2015) produced a median mole fraction of 8.96 ppbv in SW PA at their Hickory monitoring site. The observations by Swarthout et al. (2015) were more similar to the urban summertime median of 10.72 ppbv observed by Millet et al. (2005) than the rural summertime median of 2.69 observed by Jordan et al. (2009). The observations of urban scale methanol at the Hickory monitoring site and consistent rural scale concentrations observed by this study and SENEX suggest that the Hickory site likely detected methanol emissions from natural gas infrastructure that was not detected at the same extent by the other studies. The observation of methanol emissions at the Hickory site is possibly due to the intensity of NG activity in the area, but could also be due to other factors like operator practices in the study area.

3.8 Hazardous air pollutants

Hazardous air pollutants are atmospheric pollutants, mostly VOCs, that are known to cause cancer or serious health impacts. Consequently, emissions of the compounds are regulated by the US EPA (EPA, 2015a). The PTR-MS aboard the AML monitored several signals that are attributable to volatile organic compounds classes that have been listed as hazardous air pollutants and the complete list of monitored masses can be found in Goetz et al. (2015). The HAPs monitored in this study include oxygenated VOC such as methanol, acetonitrile, acetaldehyde, and aromatic compounds including benzene, toluene, and C_8-aromatics (107 amu). C_8-aromatics species measured at 107 amu include ethyl benzene, (m+p)-xylene and o-xylene (de Gouw and Warneke, 2007). The same HAPs were monitored by a PTR-MS on the July 6 2013 SENEX flight. Local-scale background estimates for the monitored HAPs and observations of the same compounds during the SENEX flight can be found in **Figure 6**, excluding methanol for which results were discussed previously.

Median local-scale background mole fractions of the monitored HAPs were generally larger in NE PA in 2012 compared to SW PA and the SENEX flight, with the exception of C_8-aromatics, which were found to have the largest mole fractions in SW PA. Acetonitrile is known to be emitted from the combustion of biomass and is often used as a biomass burning tracer (de Gouw, 2003). The

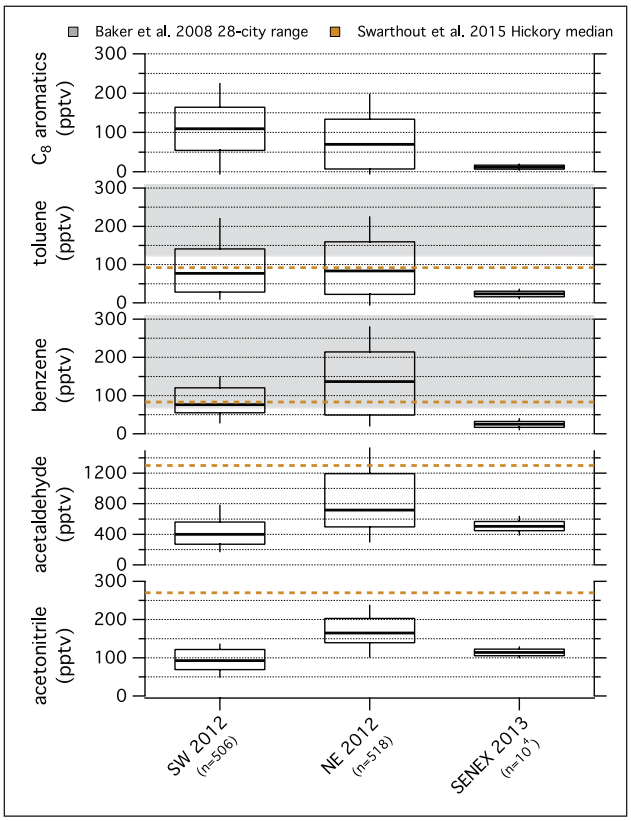


Figure 6: Summary of local-scale background estimates for HAPs. Box and whisker plots (10th, 25th, 50th, 75th, and 90th percentiles) of local-scale background estimates from Southwestern PA and Northeastern PA in 2012 for acetonitrile, acetaldehyde, benzene, toluene, C_8-aromatics. Box and whisker plots of mole fractions of the same compounds monitored during the July 6 2013 SENEX flight are also included. DOI: https://doi.org/10.1525/elementa.182.f6

presence of enhanced acetonitrile in NE PA by this study and SENEX compared to SW PA suggests that biomass burning was likely prevalent in NE PA or from regions upwind (**Figure 6**). Median mole fractions of the HAPs found in **Figure 6** were generally lower than observations at the Hickory site by Swarthout et al. (2015), with the exception of benzene in NE PA which was ~50 pptv greater.

Benzene in both SW PA and NE PA had median mole fractions within the Baker et al. 28-city range, but toluene was found to have medians below the urban range (Baker et al., 2008). Because aromatic compounds are often emitted from similar sources (e.g. fuel combustion, biomass burning, oil, and natural gas) and have different atmospheric lifetimes, molar ratios of the compounds can be used to understand the photochemical age of the compounds if the molar ratio at the point of emission is known (Monod et al., 2001; Rogers et al., 2006). The atmospheric lifetimes of benzene, toluene, and C8-aromatic compounds due to reaction with the OH radical are estimated to be 9.4, 1.9, and <1.6 days respectively based on standard atmospheric conditions (Atkinson, 2000; Monod et al., 2001). While the dominant source or sources of aromatics in the Marcellus basin are not known, the emission ratios of common sources provided in the literature can be used to make inferences about potential sources and the age of aromatic compounds in the region. As seen in **Table 1**, the emission of toluene is greater than benzene from common emissions sources like vehicle emissions, oil wells, and NG wells, but has been found to be lower from biomass burning and from diesel combustion (Heeb et al., 1999; Jobson et al., 2005; Monod et al., 2001; Warneke et al., 2014). Molar ratios of toluene to benzene were determined to be 1.45 in SW PA and 0.77 in NE PA based on linear fits of the local-scale backgrounds (**Table 1**), though correlation was shown to be poor in SW PA with an r^2 of 0.24. Based on a linear fit of 1-minute averaged data the SENEX flight observed a toluene to benzene molar ratio of 0.93 ($r^2 = 0.22$). Comparisons with toluene to benzene ratios reported in different types of ambient air masses shown in **Table 1** demonstrate that the molar ratios observed in the Marcellus region were less than what has been observed in urban and suburban air masses (Heeb et al., 2000; Monod et al., 2001; Parrish et al., 1998; Rogers et al., 2006). The toluene to benzene molar ratio in SW PA was also slightly less than the daytime summer rural ratio observed by Jordan et al. (2009), but was also within 2% of the benzene to toluene ratio observed in oil well emissions in the Uintah Basin, another unconventional fossil fuel resource located in Utah (Warneke et al., 2014). Although there are NG liquid producing wells in the Marcellus region, which could potentially contribute to enhanced toluene and benzene, evidence from another study shows that unconventional natural gas wells only contribute ~10% of the ambient benzene and toluene in SW PA (Swarthout et al., 2015). Additionally, the molar ratio of C8-aromatics to benzene in SW PA was estimated to be 1.6 ($r^2 = 0.37$), which is more similar to the ratio of gasoline automobile emissions than oil and NG emissions that have been observed at molar ratios <1 (**Table 1**) (Heeb et al., 1999; Warneke et al., 2014). The evidence indicates that aged emissions similar to what has been found in other rural locations, likely from vehicular emissions, may be the dominant source of aromatics in SW PA, though the contribution from other sources is unknown.

Table 1: Molar ratios of local-scale background mole fractions in SW PA and NE PA, 1-minute average data from the July 6 2013 SENEX flight, and literature values of aromatic compounds. DOI: https://doi.org/10.1525/elementa.182.t1

Location or source		toluene/benzene ratio (r^2)	c^8-aromatics/benzene ratio (r^2)
This study	SW PA	1.45 (0.24)	1.6 (0.37)
	NE PA	0.77 (0.68)	0.64 (0.66)
	SENEX (1-min mean)	0.93 (0.22)	0.45 (0.14)
Emissions	natural gas wells[a]	1.22	0.5
	oil wells[a]	1.42	0.78
	biomass burning[b]	0.45 (0.95)	–
	automobile emissions[c]	1.89	2.04
	diesel emissions[d]	0.50[i]	0.64[i]
Ambient	rural[e] (daytime summer)	1.49	–
	suburban[f] (1998)	1.72	–
	urban[b]	1.93 (0.66)	–
	urban[g] (U.S. average)	2.27	–
	Mexico City[h]	4.35	–
Uintah Basin	downwind of NG field[a]	0.60	0.92

[a]Warneke et al., 2014; [b]Monod et al., 2001; [c]Heeb et al., 1999; [d]Jobson et al., 2005; [e]Jordan et al., 2009; [f]Heeb et al., 2000; [g]Parrish et al.,1998; [h]Rogers et al., 2006; [i]means from idle and 20%, 40%, and 80% loading of generators.

The molar ratios of toluene and C8-aromatics to benzene in NE PA were significantly lower than what was observed in SW PA, as seen in **Table 1**. The toluene to benzene molar ratio of 0.77 was also >35% less than any emission source listed in **Table 1** except for biomass burning and diesel emissions. The low ratio in NE PA suggests that either the sampled air masses were well aged, that emission sources like biomass burning or diesel combustion were large contributors to background concentrations in the area, or the combination of both scenarios were true especially since the ratio is significantly lower than what has been observed in other rural areas. As previously discussed, the presence of elevated acetonitrile in NE PA suggests that biomass burning was prevalent in the region. Although biomass burning is likely a contributor to the aromatics in NE PA it does not preclude the contribution of aged NG or diesel emissions from Marcellus Shale development in the region. For example, the C8-aromatics to benzene molar ratio in NE PA was 0.64, which is similar to the ratio observed from oil and NG by Warneke et al. (2014). Warneke et al. (2014) found that the toluene to benzene ratio at the edge of the NG field in the Uintah Basin was approximately half the ratio measured directly from NG wells in the basin, demonstrating that significant mixing and ageing can occur within a NG basin. It is possible that the same type of ageing occurred during the NE PA study period which took place in the summertime when photochemical activity is expected to be high and the majority of the 48-hour back trajectories (Figure S5) show that the air masses originated from within the Marcellus Shale basin. The C8-aromatics to benzene ratio observed in NE PA was closest to the ratio produced by diesel exhaust (Jobson et al., 2005) demonstrating that on and off road diesel engines used in well pad development and transport may have an impact on air quality in the region.

Further monitoring of HAPs is needed to understand their air quality impacts in the Marcellus Basin and how concentrations evolve over time. Yet the estimated local-scale background mole fractions of benzene and toluene in the Marcellus Basin in the summer of 2012 were below or within the lower range of urban levels. Furthermore, molar ratios of light aromatics to benzene have shown that the monitored areas do not have urban characteristics and that aromatic emissions from NG production are not obvious. These results coincide with results by Goetz et al. (2015), where HAPs were not detected above detection limits from Marcellus Shale production and infrastructure.

3.9 Well area density and production

In addition to being useful for comparisons to other studies, local-scale background estimates from ground-based mobile monitoring are suitable for discerning relationships between spatial parameters and ambient concentrations. One spatial parameter that is thought to be a useful proxy for the intensity of NG extraction activity is the density of permitted NG wells in an area. Permits for unconventional NG wells in the Marcellus region in 2012 were retrieved from the HDPI database (HPDI, 2012), an independent clearinghouse for oil and natural gas data. Marcellus Shale well permit information for Pennsylvania in 2015 was retrieved from the Pennsylvania Department of Environmental Protection (PADEP) (PADEP, 2016).

Well locations retrieved from permit information were used to determine the density of unconventional NG wells within 2.5 km of the sampling track for all of the sampling locations in NE PA and SW PA. **Figure 7** shows the cumulative frequency of the unconventional well density when the sampling location was at least within 2.5 km of 1 well for SW PA and NE PA in 2012 and 2015. Based on **Figure 7**, it is apparent that measurements in SW PA (2012) and NE PA in 2015 were taken in locations with more even distributions of well density compared to NE PA in 2012. While areas with the largest densities of unconventional wells (>4.0 km^{-2}) were sampled in NE PA in 2012, the density range was not well distributed and nearly 75% of the sampling locations were within 2.5 km of ~20 (1 km^{-2}) unconventional wells.

The disparity in distributions of unconventional well density observed between the 2012 and 2015 sampling tracks may be responsible for the lower methane local-background concentrations estimated in NE PA in 2012 compared to the other sampling campaigns. However, when the methane local-scale background for each study area is plotted against unconventional well density there does not appear to be any relationship between well density and increasing mole fractions (**Figure 8**). Notably, local-scale background methane does not increase when comparing low well density areas (≤ 0.5 km^{-2}) to high well density areas (≥ 2.5 km^{-2}) in any study region from our

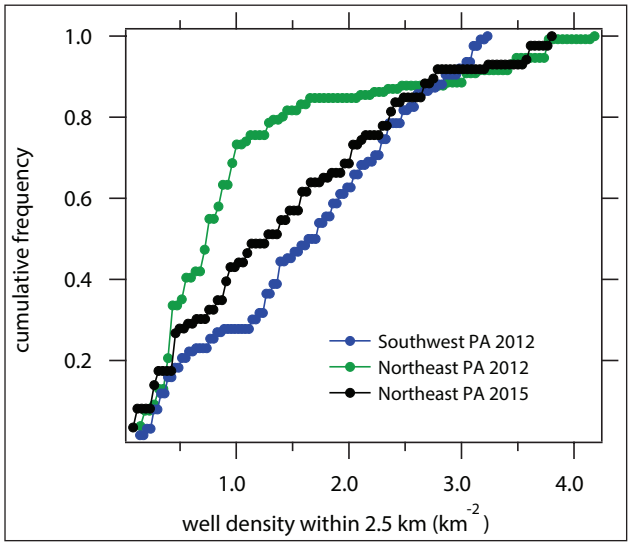


Figure 7: Cumulative frequency of unconventional well density. Cumulative frequency of unconventional well density (km^{-2}) within 2.5 km of the sampling locations with more than 1 well within 2.5 km in Southwestern PA (blue), Northeastern PA in 2012, (green), and Northeastern PA in 2015 (black). DOI: https://doi.org/10.1525/elementa.182.f7

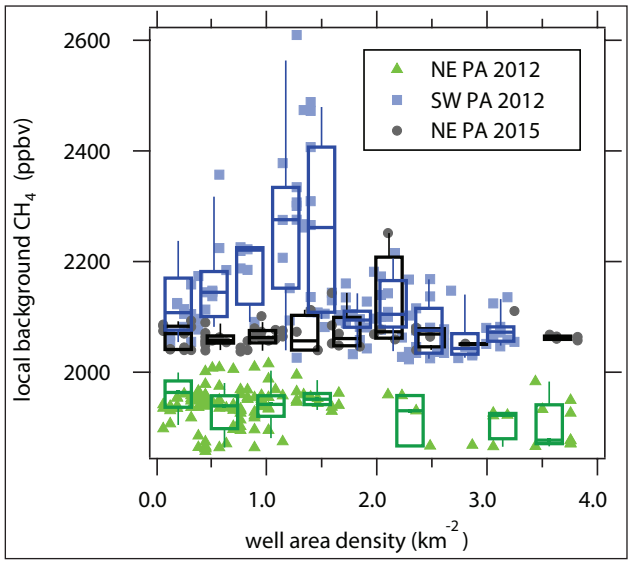


Figure 8: Correlation of the methane local-scale background to well area density. Scatter plot of methane local-scale background estimates for NE PA and SW PA versus the unconventional well area density within 2.5 km of each sampling location. Box and whisker plots (10th, 25th, 50th, 75th, 90th percentiles) are used to approximate trends within 10 well density bins. Any bin containing less than 3 data points is not included as a box and whisker. DOI: https://doi.org/10.1525/elementa.182.f8

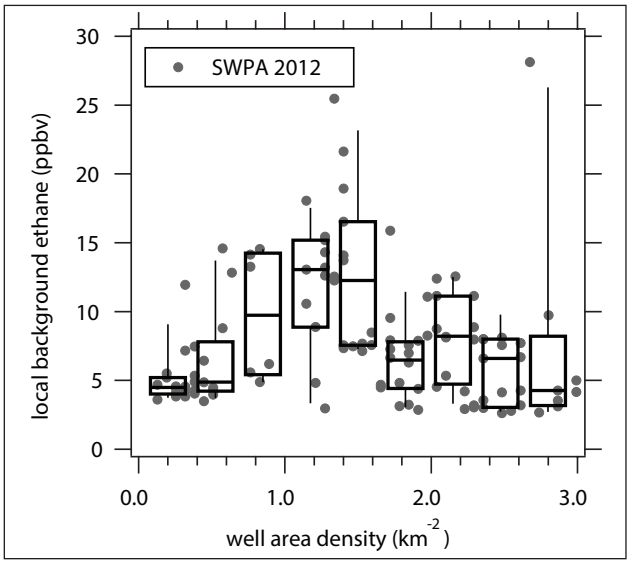


Figure 9: Correlation of the ethane local-scale background to well area density. Scatter plot of local-scale background mole fractions ethane in SW versus the unconventional well area density within 2.5 km of each sampling location. Box and whisker plots (10th, 25th, 50th, 75th, 90th percentiles) are used to approximate trends within 10 well density bins. Any bin containing less than 3 data points is not included as a box and whisker. DOI: https://doi.org/10.1525/elementa.182.f9

sampling data. The results are contradictory to findings by Swarthout et al. (2015) who observed increased methane mole fractions in areas with more unconventional wells. The data does however illustrate increased methane mole fractions in areas with unconventional well densities ranging from 0.5 to 1.5 km^{-2} in SW PA. The increased methane mole fractions in mid-range density areas in SW PA suggest that factors other than well area density likely affected local-background concentrations in the Marcellus regions.

Similar results were observed when comparing the local-scale background estimates for ethane to unconventional well density in SW PA (**Figure 9**). The primary source of ethane in the atmosphere is emissions from fossil fuel activities (e.g. natural gas leaks from production, transmission and processing) (Simpson et al., 2012). Because natural gas production is a major source of ethane, the elevated methane in mid-range well density areas in SW PA was most likely due to NG sources and not other sources of methane emission (e.g. biological and combustion). Since we do not observe a relationship between the background mole fractions of methane and ethane and well area density, the elevated mole fractions observed throughout the study may be due to emissions from other natural gas infrastructure (e.g. compressor stations, processing plants, pipelines) or due to atypically large emissions rates of NG from a few wells commonly called "super-emitters".

In addition to investigating well area density, natural gas production was investigated as a factor that controls local background mole fractions of methane in the Marcellus Shale region. Natural gas production rates of actively producing unconventional wells from June through December of 2012 were obtained from the PADEP (PADEP, 2012). Production rates from active wells within 2.5 km of the local background sampling locations were averaged and compared to the methane local background (**Figure 10**). Based on **Figure 10** it is clear that background methane did not have a clear relationship with the mean NG production rates of actively producing wells in SW PA in 2012. If the leak rates of NG corresponded to production at a site there would likely be an observable relationship between production and local-scale background concentrations of methane in an area. Additionally, some of the largest methane background estimates were in locations with low NG production rates and low well density.

The above results suggest that other factors outside of mean production rates of unconventional wells and well area density likely control local background concentrations in the region. Recent attention has been given to the prevalence of super-emitters, or a small amount NG production sites that account for the majority of emissions in an area (Yacovitch et al., 2015; Zavala-Araiza et al., 2015). Furthermore, methane emissions have been reported from other types of infrastructure associated with unconventional natural gas development (Allen et al., 2013; Goetz et al., 2015). While the above results provide inferences regarding major NG emission sources in the Marcellus region, further ambient observations combined with emission rate measurements are needed to evaluate

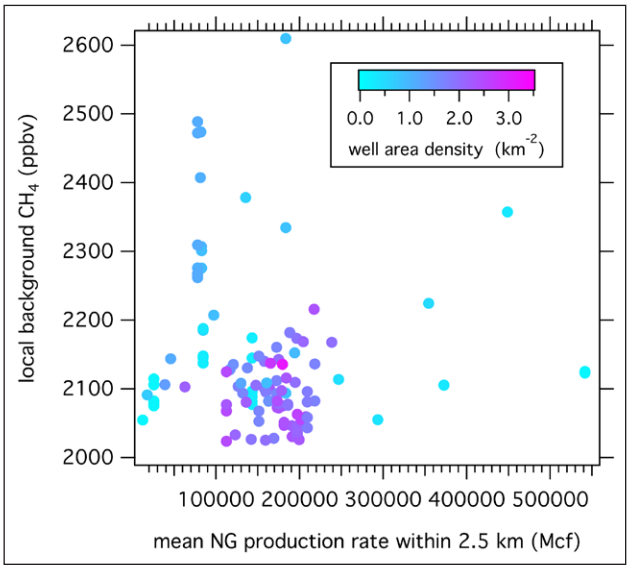


Figure 10: Correlation of the methane local-scale background to mean natural gas production rate. Scatter plot of local-scale background mole fractions of methane in SW PA versus the mean production rate of NG (Mcf) from July to December of 2012 of wells within 2.5 km of the sampling locations. The markers are colored by the well area density within the same sampling locations. DOI: https://doi.org/10.1525/elementa.182.f10

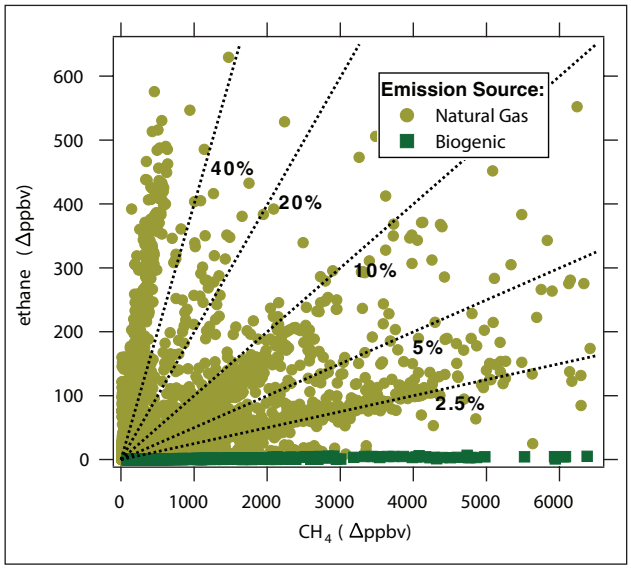


Figure 11: Correlation of excess ethane to excess methane in SW PA. Scatter plot of 1-Hz molar enhancements (Δppb) of ethane and methane attributed to biogenic (green) and natural gas sources (gold). Enhancement ratios are displayed as dotted lines. DOI: https://doi.org/10.1525/elementa.182.f11

the role of super-emitters and sources of methane outside of active well pads, and their impact on emission inventories in the region.

3.10 Characteristics of natural gas emissions

Molar enhancement ratios of ethane to methane have been used in the past for methane source identification and to characterize NG composition (Goetz et al., 2015; Yacovitch, 2014, 2015). Yacovitch et al. (2014) found that methane emissions attributed to biogenic sources (e.g. landfills, wastewater treatment, ruminants) are only associated with very low levels of ethane (<0.2%) and that sources from NG production and distribution had emission ratios ranging from 1% to >30% depending on the source of the NG emissions. Using this reference, methane enhancements observed in this study are investigated to determine sources and spatial characteristics of NG emissions in parts of the Marcellus Shale region.

The ethane to methane enhancement ratio (Δppbv/Δppbv) of plumes encountered throughout SW PA was determined by subtracting the continuous local-background estimates from the enhancements encountered throughout SW PA within the same time interval. The 1-Hz measurements of the encountered emissions are plotted in **Figure 11**. Emissions from biogenic sources were assumed to have molar ratios <0.01 and NG emissions were attributed to any emissions with ethane to methane enhancement ratios greater than 0.01. Any enhancement of methane due to a combustion source was removed by using CO emissions as a combustion tracer. Based on **Figure 11**, it is clear that methane attributed to NG was observed with a large distribution of ethane enhancements and that molar emission ratios ranged from ~0.01 to >0.40. The wide distribution of emission ratios suggests that a variety of NG emissions sources were sampled while surveying in SW PA, that there is spatial variability in NG composition, or the combination of the two possibilities. Although a wide distribution of enhancement ratios were observed only 28% of the observations were found to have ratios greater than 0.055, indicating that raw dry-gas or pipeline grade NG emissions were prevalent in SW PA (Yacovitch et al., 2014). In other work, large ethane to methane enhancement ratios have been observed from wet-gas (>0.06) NG wells, NG processing plants (>0.30), and chemical feedstock facilities (Yacovitch et al., 2014). Additionally, Goetz et al. (2015) observed molar ratio enhancements >0.85 from suspected condensate tank flashing emissions at one investigated well pad. The enhancement ratios above 0.06 demonstrate that emissions from wet-gas or NG processing were observed by the AML.

The spatial distribution of the methane enhancements attributed to NG was investigated by dividing the SW PA study area into three subregions (**Figure 12a**). The subregions were chosen because extended sampling took place in the areas and because the areas contained high densities of Marcellus Shale wells. **Figure 12b** shows a scatter plot of 1-Hz ethane and methane enhancements for each sub-region. We find that the majority of large enhancements from NG encountered in SW PA with ethane to methane molar ratios above 0.05 were located in subregion 1, located in Washington County, PA (**Figure 12b**). Additionally, ~65% of the enhancements due to NG emissions in subregion 1 had ethane to methane ratios above 0.06. In subregions 2 and 3 it was determined that <10% of the enhancements encountered were found to have molar emission ratios greater than 0.06. Subregion 2 was observed to have larger enhancements of both ethane and

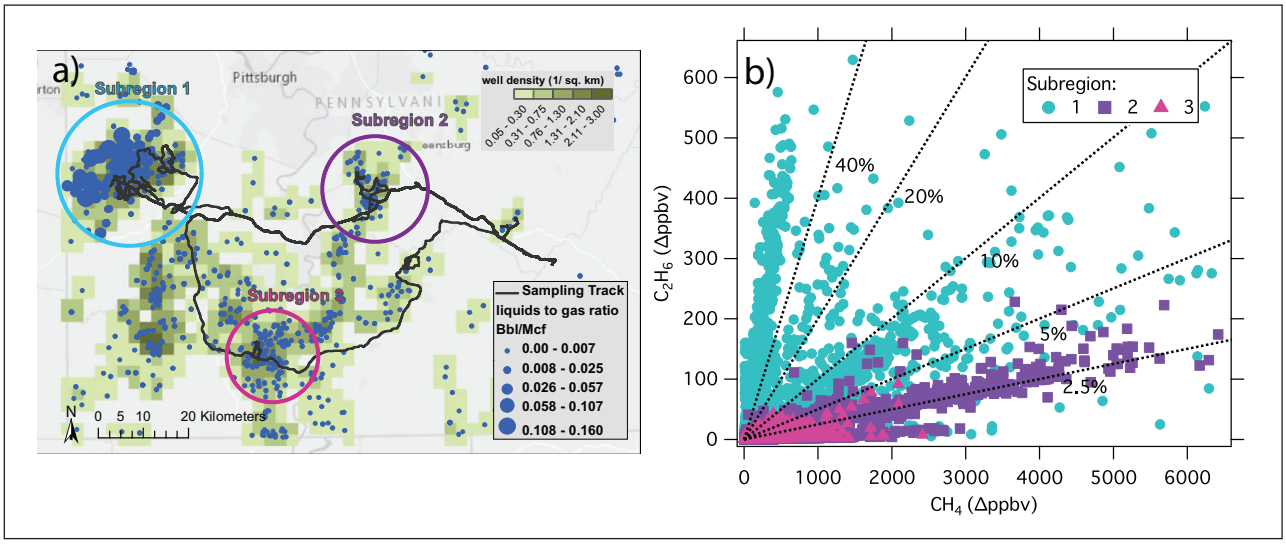


Figure 12: Correlation of excess ethane and excess methane by subregion. a) Map of Southwestern PA study are with the sample track (black trace) and Marcellus Shale well locations (blue markers) displayed. The well locations are sized by the condensate liquids production (barrel) to the natural gas production (million cubic feet) ratio (Bbl/Mcf). Well area density is displayed in green. **b)** Scatter plot of 1-Hz molar enhancements (Δppb) of ethane and methane attributed divided into three major spatial sub-regions. Enhancement ratios are displayed as dotted lines. DOI: https://doi.org/10.1525/elementa.182.f12

methane than subregion 3 and the large enhancements were found to have ratios of ~0.025 (**Figure 12b**). The low frequency of molar enhancements above 0.06 in subregions 2 and 3 indicate that the areas predominately emit dry-gas or pipeline quality NG. However, the major source of the low ethane NG is unknown.

The contrast in ethane to methane enhancement ratios between subregion 1 (high ethane to methane ratios) and the other subregions indicates that the sources of NG emissions or the composition of produced NG are not homogenous throughout SW PA. Further evidence of this is illustrated with well production data from the same time period that highlights that the high condensate (natural gas liquids) producing wells are located in subregion 1, whereas subregions 2 and 3 produced little or no NG liquids (**Figure 12a**) (PADEP, 2012). Therefore, the high ethane to methane enhancement ratios observed in SW PA by the AML were due to emissions in a wet-gas producing sub-section of the region. Because ethane and other light alkanes contained in the wet-gas are known to contribute more strongly to photochemical ozone production, areas in the Marcellus Shale basin known to contain wet-gas, like subregion 1 in Washington County PA, should be considered to be more at risk for ozone events than other parts of the basin. Additionally, the counties in SW PA monitored in this study have been in non-attainment with the NAAQS for 8-hour ozone since 2012 (EPA, 2016b), indicating that there is an acute risk of ozone events in wet-gas areas from NG emissions. The above results demonstrate that ground-based mobile sampling is an effective tool for characterizing the spatial distribution of natural gas emissions. Further air quality monitoring and modeling inside and outside of wet-gas producing areas of the Marcellus basin is needed to assess the influence of wet-gas and NG liquids production on ozone production in the region.

4. Conclusion

Ground-based mobile monitoring has been used to understand the concentrations and sources of climate relevant pollutants, combustion products, and compounds that have previously been associated with natural gas production and distribution in the Marcellus Shale basin. The mobile datasets from 2012 and 2015 were transformed to remove biases from topography and local unmixed emission sources to generate a dataset that represents local-scale background concentrations. Data from the NOAA SENEX flight over the Marcellus Shale region and literature values were used to make comparisons to other observations and to characterize concentrations observed in this study.

Methane was observed to be at higher concentrations in SW PA than NE PA in 2012, demonstrating that there is spatial variability in methane concentrations across the region. In 2015 methane mole fractions were observed to be ~125 ppbv greater than what was observed in 2012, indicating the background concentrations have likely increased possibly due to increased emissions in the region. However, methane levels were not influenced by well area density or by average production rates at the mobile sampling locations. Methane, ethane, and CO mole fractions were all within urban levels and above estimated mid-latitude Northern Hemispheric backgrounds, although CO mole fractions were decreased by ~60 ppbv in 2015 compared to 2012 in NE PA. The Marcellus Shale region is primarily rural with few conventional urban emission sources, and therefore the presence of urban concentrations suggest that emissions from Marcellus Shale development may be responsible for the enhanced concentrations in the region. While ethane was found to be elevated in the region, other VOC monitored (i.e. oxygenated VOC and aromatics) did not appear to follow the same

trend. Two exceptions being benzene and acetonitrile in NE PA, which are thought to be due to biomass burning emissions. Methanol and acetone concentrations in 2012 were observed to be at rural levels and the primary source of the compounds was thought to be biogenic emissions and not primary emissions from NG infrastructure or the oxidation of NG. Additionally, the observed toluene to benzene molar ratios in SW PA and NE PA were less than what has been observed in urban air masses and were inferred to be most similar to aged rural air masses, though low toluene to benzene ratios have also been observed in the Uintah Basin.

In addition to being used to understand background concentrations the mobile local-background estimates were used as a baseline to characterize ethane and methane enhancements observed in SW PA. It was determined that methane enhancements due to NG in SW PA were found with a large distribution of ethane enhancements indicating that differing emission sources or NG composition exists in the region. However, the majority of the NG emissions (72%) were found to have ethane to methane molar enhancement ratios similar to dry-gas. An analysis of three subregions in SW PA determined that wet-gas like emissions were almost exclusively found in an area of Washington County, PA.

Overall ground-based mobile monitoring and the percentile smoothing method were found to be useful tools for understanding ambient concentrations and emissions of relevant atmospheric pollutants during the early phases of NG development in the Marcellus Shale region. This work has expanded the body of literature on the potential atmospheric impacts of Marcellus Shale development and provided an early development baseline to help understand how the impacts change with the evolution of shale gas development. Future ambient monitoring is needed to understand how ambient concentrations change as the shale play increases in NG production and the construction of new wells declines. Additional monitoring is also needed to understand the potential impact of aging NG production and distribution infrastructure as Marcellus Shale production matures.

Data accessibility statement

The local background results are archived and available at the Dryad data repository. High time resolution and processed data for this manuscript can be obtained free of charge at: DOI: https://doi.org/10.5061/dryad.g8h54

Supplemental material

The supporting information contains information about ambient concentrations observed from the three ground-based mobile monitoring campaigns and gives a comparison of the percentile smoothing and lognormal mode methodologies for estimating the local-scale background. The document also contains information about regional meteorology and HYSPLIT modeling results that were used for the interpretation of the local background results. The material is available free of charge.

Supplemental Files

Supplemental file S1: Figures and Tables. https://doi.org/10.1525/elementa.182.s1

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Competing Interests

The authors have no competing interests to declare.

Contributions

- Concept and design: JG, PD
- Acquisition of data: JG, AA, BW, CF, EF, JW, PM, WK, SH, JP, TR, CW, JdG, PD
- Analysis and interpretation of data: JG, PD
- Drafting of the article or revising it for important intellectual content: JG, AA, JW, PM, WK, JP, CW, JdG, SS, PD
- Final approval of the version to be published: JG, AA, BW, CF, EF, JW, PM, SH, CK, WK, JP, TR, CW, JdG, SS, PD

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