

# Atmospheric Emission Characterization of Marcellus Shale Natural Gas Development Sites

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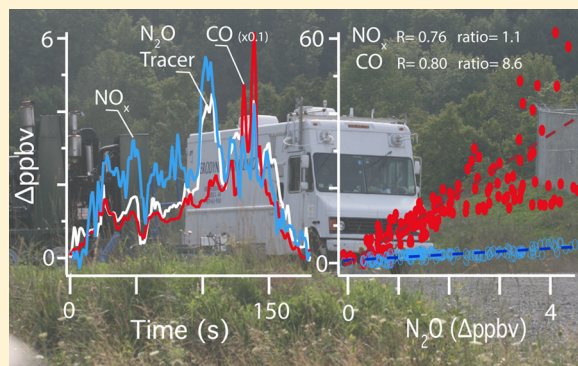
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## Supporting Information

**ABSTRACT:** Limited direct measurements of criteria pollutants emissions and precursors, as well as natural gas constituents, from Marcellus shale gas development activities contribute to uncertainty about their atmospheric impact. Real-time measurements were made with the Aerodyne Research Inc. Mobile Laboratory to characterize emission rates of atmospheric pollutants. Sites investigated include production well pads, a well pad with a drill rig, a well completion, and compressor stations. Tracer release ratio methods were used to estimate emission rates. A first-order correction factor was developed to account for errors introduced by fenceline tracer release. In contrast to observations from other shale plays, elevated volatile organic compounds, other than CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, were generally not observed at the investigated sites. Elevated submicrometer particle mass concentrations were also generally not observed. Emission rates from compressor stations ranged from 0.006 to 0.162 tons per day (tpd) for NO<sub>x</sub>, 0.029 to 0.426 tpd for CO, and 67.9 to 371 tpd for CO<sub>2</sub>. CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> emission rates from compressor stations ranged from 0.411 to 4.936 tpd and 0.023 to 0.062 tpd, respectively. Although limited in sample size, this study provides emission rate estimates for some processes in a newly developed natural gas resource and contributes valuable comparisons to other shale gas studies.



## INTRODUCTION

The Marcellus shale is the largest shale gas resource in the contiguous United States.<sup>1</sup> Found in the Appalachian region, the Marcellus basin has an area of 240 000 km<sup>2</sup> underlying parts of Maryland, New York, Ohio, Pennsylvania, and West Virginia<sup>1,2</sup> and it is estimated to contain 84 billion cubic feet of technically recoverable natural gas.<sup>3</sup> The U.S. Energy Information Agency estimated that the Marcellus shale gas resource could support up to 90 000 individual wells;<sup>4</sup> four times more than any other shale gas resource in the United States, and approximately 8 times the number of Marcellus wells as of 2012.<sup>4,5</sup>

As the development and production of unconventional natural gas resources continues, there has been growing concern about its impact on the environment and human health due to the potential degradation of local and regional air quality (AQ).<sup>6</sup> Likewise, there has been significant debate regarding the extent of greenhouse gas emissions from the entire lifecycle of shale gas compared to other fossil fuels like

coal.<sup>7–12</sup> Natural gas (NG) is known to produce less carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), black carbon (BC), and other pollutants than oil or coal combustion per unit of energy.<sup>13</sup> A study by de Gouw et al.<sup>14</sup> found that since 1997, emissions from fossil fuel power plants in the United States have decreased their CO<sub>2</sub> emissions by 23% and NO<sub>x</sub> emissions by 40% due in part to the replacement of coal by NG systems. However, the extent of AQ relevant emissions from upstream shale gas activities like extraction, processing, and transmission is poorly known.

The shale gas extraction process includes minor, but widely distributed, transitory emission sources including well pad construction, horizontal well drilling, hydraulic fracturing, and well completion.<sup>6</sup> Off-road diesel (e.g., generators, pumps, and

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**Table 1. Tracer Release Site List with the Study Area, Relative Size, Number of Tracer Release Experiments Performed at the Site, The Sampling Duration in Hours, The Average Downwind Distance of Sampling from the Site in Meters, and Estimated Average Correction Factor Applied to the Emission Rate Estimates**

source type	site name <sup>a</sup>	region	capacity (bhp) <sup>c</sup>	experiments	sample duration (h)	sample downwind distance (m)	corr. factor
compressor station	C-A	SW	5285	1	2.5	1100	1.27
	C-B	NE	5360	1	1.1	480	0.67
	C-C	SW	8165	1	1.8	980	0.58
	C-D	NE	9000	1	1.7	1020	1.54
	C-E	SW	14000	1	2.0	660	0.88
	C-F	NE	14200	2	1.2, 2.3	730, 710	2.68, 1.89
	C-G	NE	15300 <sup>b</sup>	1	1.5	900	2.98
	C-H	NE	16560	2	1.0	500	1.30
wells in production	W-A	SW	7 wells	1	2.5	750	1.48
	W-B	SW	9 wells	1	2.2	700	1.06
	W-C	SW	9 wells	1	2.0	560	0.61
gas processing	P-A	SW	N/A	1	2.0	N/A	N/A
well drilling	T-A	NE	N/A	1	1.0	890	1.28
completion	T-B	NE	N/A	2	3.3	650	1.66

<sup>a</sup>See the Supporting Information, Section 1 for more information about tested facilities. <sup>b</sup>Electric powered compressor station. <sup>c</sup>1 bhp is equivalent to 746 watts (W).

drill rigs) and on-road diesel (e.g., trucking and transport) engines are used throughout the extraction process. Heavy-duty diesel engines are known to emit a variety of pollutants including carbon monoxide (CO), CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, organic and inorganic particulate matter (PM), BC, heavy metals, and volatile organic compounds (VOC).<sup>15–18</sup> Well completion, one of the final steps before production, involves the recovery of residual liquids and sand, or flowback, from the hydraulic fracturing process. The flowback can contain dissolved gases such as methane (CH<sub>4</sub>) and other components of NG. Once the flowback is recovered, the gases contained in the flowback are either directly emitted to the atmosphere, flared, or the NG is reclaimed and emissions are reduced by a “green completion” process. An environmental impact statement indicates that flowback gas flaring can emit criteria pollutants, VOC, and hazardous air pollutants (HAPS), with the quantity of SO<sub>2</sub> and HAPS increasing with heavier hydrocarbon content (e.g., wet gas).<sup>19</sup> A recent study that investigated CH<sub>4</sub> emissions from shale gas operations throughout the United States found that emissions from well completions had a wide range of values (from 0.01 to 17 Mg), suggesting that the quantity emitted is likely controlled by variable factors such as completion procedures.<sup>2</sup>

The routine production and distribution aspect of Marcellus shale development involves small but persistent sources of both combustion and NG related emissions including production well pads, pipelines, compressor stations, and gas processing facilities. On an annual per well basis, it is estimated that production sites in the Marcellus Basin emit between 46 and 1200 kg VOC, 520–660 kg NO<sub>x</sub>, 9.9–50 kg PM<sub>2.5</sub>, and 3.1–4.0 kg SO<sub>x</sub>.<sup>20</sup> Allen et al.<sup>2</sup> estimated that equipment leaks from the natural gas production sector are responsible for an average of 291 Gg of CH<sub>4</sub> per year nationally. Because few measurements of AQ relevant pollutants have been made in the Marcellus Shale region, these estimates are typically based on emissions from other plays. Compressor stations generally utilize NG fired compressor engines that run continuously to transport gas from local well sites to larger pipelines. A review of air quality permits for compressor stations in Pennsylvania shows that a single facility can have an average of 4 compressor engines (with a range of 1 to 12), each with a power capacity ranging

from 800 to 3500 bhp.<sup>21</sup> Compressor stations also typically have other sources of emission including process equipment such as glycol dehydrators and in-line heaters. In a similar review of Pennsylvania air quality permits, Litovitz et al.<sup>20</sup> found that if operating at full capacity a compressor station in Pennsylvania has the potential to emit 11–45 Mg of VOC and 46–90 Mg of NO<sub>x</sub> per year.

As much of the Marcellus shale production is recent, there has been scant research into the characteristics and potential impacts of emission sources on AQ. Additionally, there is very limited ambient AQ monitoring coverage in the Marcellus region, particularly in rural areas with high densities of NG development activity.<sup>22</sup> Carlton et al.<sup>22</sup> suggest that the data gap in air quality monitoring in the Marcellus Shale basin could be limiting air quality management for the region. The objective of this study is to improve the current understanding of potential regional air quality impacts through the characterization of the emissions of criteria air pollutants, hazardous air pollutants, and greenhouse gases from emission sources associated with Marcellus shale development by the use of real-time mobile measurements. This study investigates both transient and persistent sources of emission, with the goal of characterizing emissions from several sites that are part of the shale gas extraction and distribution process.

## ■ MATERIALS AND METHODS

The Aerodyne Research Inc. Mobile Laboratory (AML)<sup>23</sup> was used during the summer of 2012 to collect ambient air data in two regions of Pennsylvania within the Marcellus Shale Basin with NG development activity. The first campaign took place in Northeast Pennsylvania (NE) centering on Sullivan and Bradford counties in August of 2012. The second took place in September 2012 in several counties of Southwestern Pennsylvania (SW). The sampling locations were chosen because these areas are known to have a high-density NG activity (See Figure SI-1 of the Supporting Information). Furthermore, the two areas are known to have compositional differences in NG, with dry gas (mostly CH<sub>4</sub>) in the NE and both wet gas (CH<sub>4</sub> with other light hydrocarbons) and dry gas in the SW.<sup>24</sup>

Mobile measurements were made at specifically targeted sites of interest and while driving in areas of high development and production activity. A master list of potential sites of interest was created to identify facilities representing all major steps of shale gas extraction, production, and distribution. The master site list was developed from publicly available Pennsylvania databases and contained 54 compressor stations of various sizes, 460 wells where drilling had recently commenced (SPUD), approximately 3800 wells that were known to be in production, and other site types all within the study area.<sup>21,25,26</sup> A refined list was developed after premeasurement surveys that verified site activity, and adequate road conditions and topography. Subsequently, final site selection was made on each measurement day, and decisions were based primarily on local meteorology and drive time. Site selection was not based on the observation of emission downwind of the site. Tracer release ratio methods based on work by Lamb et al.<sup>27</sup> were utilized to estimate the emission rate of measured pollution species at each targeted site similar to other recent studies,<sup>2</sup> although without site access. Tracer release ratio experiments were conducted 17 times at 13 separate sites over the course of both measurement campaigns. Table 1 indicates the assigned name of the site, site type, the relative size, and the number of tracer release experiments performed at each site. The table also shows the sampling duration of each site, the average downwind distance of the measurements from the site, and the average correction factor applied to the emission estimates, which will be discussed later in this work.

**Instrumentation.** For this study, the AML was deployed to measure most regulated pollutants, including criteria pollutants and HAPs, and major constituents of NG. All of the instruments equipped on the AML utilized real-time rapid response measurements, typically with sampling rates of  $\sim 1$  Hz. A list of calibration procedures for the instrumentation equipped on the AML can also be found in the Supporting Information, Section 3.

**Quantum Cascade Laser (QCL) Trace Gas Monitors.** Select gas phase species including methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), acetylene ( $\text{C}_2\text{H}_2$ ), carbon monoxide, and nitrous oxide ( $\text{N}_2\text{O}$ ) were measured using three Aerodyne Research Inc. QCL trace gas monitors. The QCL monitors use tunable infrared laser direct absorption spectroscopy (QCL-TILDAS) and have measurement sensitivity ranging from 0.3 to 1 ppbv.<sup>23</sup> It is important to note that  $\text{C}_2\text{H}_6$  was only measured in the SW because the development of the QCL-TILDAS for the measurement of  $\text{C}_2\text{H}_6$  occurred after measurements in the NE.

**Thermo Scientific 42i NO/NO<sub>2</sub> Monitor.** The nitrogen oxide species, NO and NO<sub>y</sub>, were measured using commercial chemiluminescence analyzers. For this study, NO<sub>y</sub> (total reactive nitrogen) was assumed to be NO<sub>x</sub> (NO+NO<sub>2</sub>) because we directly measured primary emissions plumes, which contain negligible secondary reactive nitrogen species.<sup>28</sup>

**Cavity Attenuated Phase Shift NO<sub>2</sub> Monitor.** Nitrogen dioxide (NO<sub>2</sub>) was directly measured using an Aerodyne Research, Inc. cavity attenuated phase shift NO<sub>2</sub> monitor (CAPS-NO<sub>2</sub>).<sup>29</sup> Because of technical issues, CAPS-NO<sub>2</sub> measurements were only available for the campaign in the SW.

**Licor 6262 CO<sub>2</sub> monitor.** Carbon dioxide (CO<sub>2</sub>) was measured using a nondispersive infrared unit.

**TSI Condensation Particle Counter 3022.** Particulate number concentration was measured using a condensation particle counter.

**Aerodyne Research Inc. Soot-Particle Aerosol Mass Spectrometer (SP-AMS).** Submicrometer particulate matter mass (PM<sub>1</sub>) and composition, including nonrefractory aerosols and black carbon, were measured using an SP-AMS.<sup>30</sup> This data was gathered on a 1 s time scale.

**Proton-Transfer Reaction Mass Spectrometer (PTR-MS).** A PTR-MS measured oxygenated and unsaturated volatile organic compounds including NG constituents, HAPs, and biogenic species.<sup>31</sup> A full list of masses monitored by the PTR-MS and their corresponding detection limits can be found in Table 2. For this study, the PTR-MS had a sampling period of  $\sim 3$  s.

**Table 2. Ion Mass and Limit of Detection (LOD) of Compounds Monitored by the PTR-MS**

mass (amu)	major chemical species monitored	LOD (ppbv)
21	O-18 isotope $\text{H}_3\text{O}^+$ reagent ion	
34	$\text{O}_2^+$ O-18 isotope	
33	methanol	3.8
39	O-18 isotope $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ reagent ion	
42	acetonitrile	0.4
43	propene, fragment ion of acetic acid and larger alkenes	1.5
45	acetaldehyde	1.9
49	methyl mercaptan	0.2
57	butenes, fragment ion of butanol and larger alkenes	1.7
59	acetone	1.4
61	acetic acid	1.2
69	isoprene	0.7
71	methacrolein + methyl vinyl ketone, fragment ion of larger alkenes	0.6
79	benzene	0.7
93	toluene	0.3
107	C2-benzenes	0.5
121	C3-benzenes	0.5
137	monoterpenes	0.2

**Additional Measurements on the AML.** In addition to ambient air monitoring instrumentation, the AML was also equipped with high precision GPS and meteorological instruments to establish position, bearing, driving speed, wind direction, wind speed, temperature, pressure, and other parameters necessary for data analysis. All instrument data was processed and analyzed using Igor Pro 6.34, (Wavemetrics, Lake Oswego, OR).

**Tracer Release Ratio Measurements.** Dual tracers were implemented at targeted sites to estimate whole site emissions. For each tracer ratio experiment,  $\text{N}_2\text{O}$  and  $\text{C}_2\text{H}_2$  were used as tracer gases and were released at a fixed rate from tanks attached to the bed of a stationary pick-up truck at a height of 3 m. They were chosen because they are routinely available in industrial grade, cost-effective, and inert on the time scale of these experiments. The relative detection sensitivity of the QCL monitors to  $\text{C}_2\text{H}_2$  and  $\text{N}_2\text{O}$  are adequate and exceptional, respectively. Typically,  $\text{N}_2\text{O}$  was released at a rate of 24 standard liters per minute (SLPM) and  $\text{C}_2\text{H}_2$  was released at 5 SLPM. However, at some sites the tracer gases were released at different fixed rates because of site conditions. The flow rate from each tank was controlled by Alicat MC-series mass flow controllers. A high-precision GPS was used to determine the location of each tracer release. 1 Hz measurements of wind speed and wind direction were recorded at a height of 3 m at the tracer release point.



At each site, the location of tracer release was chosen in order to be as close as feasible to the presumed emission release point. For this study, we did not have access to the tested facilities and therefore were unable to release tracer gases on-site, and colocated with emission sources. Consequently, we released tracers at the fenceline and attempted to position the tracers so the direction of their plume was in line with the expected site emission plume based on prevailing wind conditions. Once the tracer was positioned and activated at a site, the AML would make ambient measurements while driving on the downwind roads in the vicinity of the site. Out-of-plume measurements were used to characterize the nonplume “background” concentrations of the measured species and to distinguish other emission sources in the area. Downwind of the site and tracer release location, the AML transected the tracer-containing emission plumes. Five or more transects through emission plumes were made, which typically took  $\sim 2$  h (Table 1). The resulting downwind source and dual tracer plume measurements above the background were used to estimate the emission rate of pollution species at each site.<sup>2,27</sup> The background concentration for each plume transect was determined by the average of ten measurements before the plume intercept and ten measurements after the plume. This background value was then subtracted from plume transect measurements to determine a  $\Delta$ ppbv value (see Figure SI-2 of the Supporting Information). A first-order correction factor was determined for each plume transect to correct for the fact that tracers were not colocated with sources as described below. This method allows for the identification of point source emissions, but is not ideal for identifying large area sources that would appear as an elevated background value rather than a distinct plume.

**Site Emission Rate Calculation.** Two techniques were used to estimate site emission rates of the measured pollution species. The first technique utilizes an orthogonal distance linear regression analysis of the downwind plume  $\Delta$ ppbv values of the source emission versus the downwind plume  $\Delta$ ppbv values of the dual tracer to determine the emission ratio of emitted pollutant species to tracer for each plume intercept (Figure 1c). The second technique utilizes the downwind plume-integrated mixing ratios ( $\Delta$ ppbv-s) of the source emission and the tracer to determine an emission ratio for

each plume intercept at each site (Figure 1b). Average emission ratios for each measured species for each site were calculated as follows. Based on a preliminary survey of regression method (RM) results, only plume transects where the regression analysis of the species of interest versus the  $N_2O$  tracer resulted in a correlation coefficient (Pearson's  $R$ ) greater than 0.60 were included in the average emission ratio calculation. Using the integration method (IM), only plume transects with an average  $\Delta$ ppbv value greater than 3 times the instrument noise were accepted. The resulting emission ratios for each plume transect of each chemical species observed at concentrations above background for plume intercepts at each site can be found in the Supporting Information, Section 8. Site emission rates were then calculated by multiplying the known tracer release rate by the average emission ratio for the site. It should be noted that  $N_2O$  was used as the primary tracer species for analysis because of it had lower noise and background variability compared to  $C_2H_2$ .

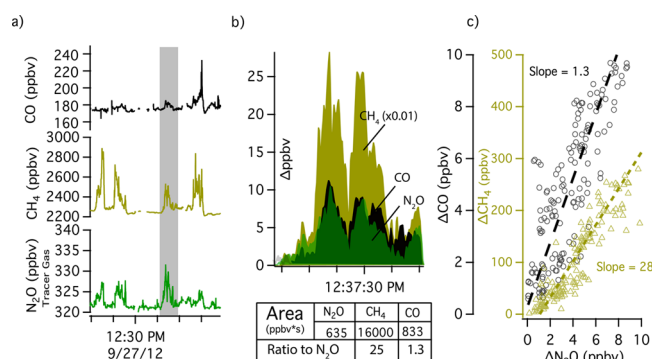
**First-Order Correction Factor.** Because the tracer release was never exactly colocated with each targeted site, the release locations were always spatially offset from the site emission source. The tracer offset distance was different for each site with an average of  $\sim 200$  m, and ranged from 40 to 750 m. Due to the tracer offset, errors in our emission rate estimates depend on the distance between the tracer release and source, the distance downwind where the tracer and emission plume is encountered and the direction of the offset with respect to the wind (see Figure SI-3 of the Supporting Information). These factors lead to differences in dispersion characteristics of the two plumes at the AML intercept location due to differing dilution of the plume during transport. To correct for this dilution effect, a correction factor for emission rates was developed utilizing Gaussian dispersion theory. An explanation and derivation of the correction factor can be found in the Supporting Information, Section 5. The correction factor was applied to the site emission estimates for each species. This correction factor was calculated for each plume transect based on meteorological parameters at the time of sampling, and ranged from 0.52 to 3.2, with 94% of correction factors within a factor of 2. Emission rates for each plume utilize the correction factor as follows

$$TR \times M \times CF = ER \quad (1)$$

where TR is the tracer emission rate, M is the species emission ratio determined by the integration or regression method (IM or RM), and CF is the correction factor for each plume transect. Table 1 presents the average correction factor estimated for each tracer release experiment.

## RESULTS

The emission rate results for  $CH_4$ ,  $C_2H_6$ , CO,  $CO_2$ ,  $NO_x$ , VOC, and  $PM_{10}$  with correction factors applied are presented in the following sections. All emission rate values are shown in metric tons per day (tpd). The results indicate that the RM was often not applicable for some pollution species at some sites because none of the plume transects met the criteria ( $R > 0.6$ ) to be included in the average emission rate results. An error assessment of the different emission ratio techniques using the known release ratios of the dual tracers can be found in the Supporting Information, Section 6. Although the error assessment indicates that the RM has a smaller error distribution than the IM, comparisons to literature and other



**Figure 1.** (a) Time series of CO, CH<sub>4</sub>, and N<sub>2</sub>O (tracer gas) during tracer release at a Marcellus Shale site with one plume intercept highlighted in gray. (b) Time series of select plume intercept with crosswind integrated concentration denoted and emission ratios. (c) Regression analysis of plume intercept with resulting emission ratios denoted. The Pearson's  $R$  value for the  $\Delta$ CO regression is 0.86 and the  $\Delta$ CH<sub>4</sub> regression is 0.92.

discussion points are made with IM results because it contains the larger dataset.

The ambient VOC concentrations for many of the compounds monitored by the PTR-MS were at or near the mobile mode detection limit for the instrument. Most notably, we did not observe elevated levels of any of the light aromatic compounds (benzene, toluene etc.) that have been previously observed in oil and NG emissions.<sup>32–34</sup> With the exception of CH<sub>3</sub>OH, which was observed at one compressor station and has been observed at NG well pads,<sup>34</sup> all of the other VOCs detected have been attributed to on-road engine exhaust.<sup>35</sup> The absence of light aromatics in NG emissions observed the Marcellus basin is not surprising because the play does not have associated oil deposits, and consequently nonalkane VOCs are not expected to be widely present.<sup>19</sup> It should be noted that CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were the only short-chain alkanes measured in this study, therefore we cannot comment on emissions of other alkanes that have previously been observed in other NG plays.<sup>32,33</sup> Enhancements in particle number concentration with sizes >7 nm were observed downwind of most compressor and transient activity well sites. Conversely, enhancements in the submicron mass concentration of organic, nitrate, sulfate, ammonium, and chloride aerosols were not observed at any site, with the exception of a single plume intercept at one compressor station in which elevated organic aerosol concentrations were observed. The absence of significant enhancement of PM<sub>1</sub> mass with enhancements in number concentration suggests that particulate emissions from these sites were mostly ultrafine particles which do not contribute significant mass, and are likely from NG combustion.<sup>36</sup> In situ mobile measurement of C<sub>2</sub>H<sub>6</sub> in conjunction with CH<sub>4</sub> was found to be useful tool for the location and characterization of NG related emissions, as discussed in Yacovitch et al.<sup>37</sup>

Compressor stations and transient sites (e.g., drill site and completion) were observed to be the largest emitters of most of the measured species (i.e., CH<sub>4</sub>, CO, NO<sub>x</sub>, CO<sub>2</sub>), followed by producing well sites. Production well pads were expected to have the lowest emissions because they have fewer potential emissions sources (e.g., combustion sources) compared to other site types, and handle lower volumes of NG compared to compressor stations.<sup>19</sup> The following results provide a source type analysis and insight into their role on local air quality. Results from the single gas processing facility tested are not included due to an unsuccessful tracer release experiment associated with site size and topography. The IM results for emission factors will be presented first with values derived from the RM following in parentheses if available.

**Well Sites.** Three well sites located in the SW in Washington County were sampled using the tracer release method. The sites are within 2 miles of each other, they are of similar in size, and coincidentally operated by the same company. More information on these sites can be found in the Supporting Information. The variability between these sites is informative, but it is important to note that it might not be representative of the variability of all sites of this type in the Marcellus Basin. Emission rate results are reported in Table 3.

The W-A well pad was the smallest of the well sites investigated with tracer release. The pad had 7 individual wells and ancillary site equipment. The W-A well pad was observed to have the second largest CH<sub>4</sub> emissions of the well sites with a value of 0.204 (0.219) tpd for the IM and (RM) analyses, respectively (Table 3). Ethane had an estimated emission rate of 0.120 (0.082) tpd. This well site appears to produce

**Table 3. Emission Rate Estimates of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO, CO<sub>2</sub>, NO<sub>x</sub>, PM<sub>1</sub>, and VOC for Production Well Pad, Well Drilling, and Well Completion Tracer Release Sites Represented in Metric Tons Per Day**

site name	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO	CO <sub>2</sub>	NO <sub>x</sub>	PM <sub>1</sub>	VOC
well site							
W-A	0.204(0.219) ± 0.28(0.13)	0.120(0.082) ± 0.19(0.05)					
W-B	0.081(0.084) ± 0.08(0.05)	0.025(0.025) ± 0.01(0.01)					
W-C	0.340 (0.036) ± 0.49(0.01)	0.416(0.043) ± 0.81(0.03)	0.034(0.043) ± 0.03(0.05)	83.6 ± 105	0.021 ± 0.01		
well drilling							
T-A	0.923 ± 0.66	§	0.200(0.156) ± 0.20(0.13)	152 ± 125	0.047(0.042) ± 0.02(0.03)	*	
completion							
T-B	7.72(10.1) ± 8.54(10.0)	§	0.386(0.102) ± 0.81(0.09)	250(669) ± 250(490)	0.072(0.044) ± 0.13(0.04)	*	

The values were estimated using the integration and (regression) methods reported in tons per day (tpd). Bold print represent the mean emission rate estimated at the site, and the standard deviation is represented by the nonbold values. A dashed line (–) represents undetected species and the symbol (§) represents unmeasured species. The symbol (\*) indicates that in-plume elevated particle number concentrations were observed.

relatively wet gas as indicated by the high content of  $C_2H_6$  at roughly 35% of  $CH_4$  emissions. Combustion emissions (e.g., CO,  $CO_2$ ,  $NO_x$ ),  $PM_{10}$ , and VOC were not observed at the site.

The W-B well pad had 9 individual wells and ancillary site equipment. The site had the smallest correction factor with a value of  $1.06 \pm 0.02$  and had the lowest  $CH_4$  emission of any site at 0.081 (0.084) tpd. Ethane emissions were found to be 0.025 tpd by both emission ratio estimation methods. Ethane to  $CH_4$  molar emission ratios found here were  $\sim 30\%$ . Like the previous well site, combustion products and VOC other than  $CH_4$  or  $C_2H_6$  were not observed.

The W-C well pad also had 9 individual wells and site equipment. This well pad is notable because of its large  $C_2H_6$  emissions. Using the IM,  $C_2H_6$  emissions were estimated to be 0.416 tpd, which was significantly larger than either of the nearby well sites. The  $CH_4$  emission rate at the site, using the IM, was estimated to be 0.340 tpd. Based on the IM emission rate results W-C had a large  $C_2H_6$  to  $CH_4$  emission ratio with a value of  $\sim 120\%$ . The RM yielded markedly lower emission values of 0.043 and 0.036 tpd for  $C_2H_6$  and  $CH_4$ , respectively. The considerable differences between the two methods are a result of the exclusion of several plume transects with large emissions ratios from the final site averaging using the RM. The excluded plume transects did not meet the averaging criteria for the RM ( $>0.6 R$  value), but did meet the averaging criteria for the IM ( $>3\times$  instrument noise). The low correlation between the dual tracer plume and the site emission plume is likely due to site specific characteristics as described in the dual tracer error assessment. Therefore, for this site the IM values should be considered the more complete emission estimate.

The molar ratio of  $\Delta C_2H_6$  and  $\Delta CH_4$  for the transects at the W-C site yielded different values for the same site, with some transects resulting in ratios  $<0.2$  and others resulting in ratios  $>0.85$  (see Figure SI-5 of the Supporting Information). The differences in  $\Delta C_2H_6$  to  $\Delta CH_4$  ratios indicate that there may have been transient emissions (e.g., flash emissions, possibly from a condensate tank) that were not emitting during the full tracer release experiment, which took  $\sim 2$  h. Variability in emission characteristics was seen throughout the study for many of the investigated sites (see Figure SI-7 of the Supporting Information).

Unlike the other well sites, CO,  $CO_2$ , and  $NO_x$  were observed at the W-C site with emission rates of 0.034 (0.043), 83.60, and 0.021 tpd, respectively. To the best of our knowledge, this study is the first to quantify the emissions of criteria pollutants from Marcellus shale gas well pads. However, estimates based on other data have been reported.<sup>20</sup> Although there are differences in VOC and PM emission estimates by this study and Litovitz et al.,<sup>20</sup> the  $NO_x$  emission rate from W-C is within a factor of 2 of 0.0128–0.0162 tpd for a 9 well site estimated by Litovitz et al.

In comparison to another study that investigated well pad emissions, our results indicate that the average  $CH_4$  emissions at the tested well pads were about 16, 4, and 23 times greater than the upper range ( $\mu + 1\sigma$ ) of well pad equipment leak estimates in Allen et al.<sup>2</sup> This large disparity between the two studies suggests that there are other factors such as operating practices, production volume decline, location of leaks, scheduled versus unscheduled monitoring, as well as the number and representativeness of sites sampled that may be important considerations when compiling a bottom-up inventory.

**Transient Sites.** The T-A well pad in Bradford County was being developed at the time of our sampling and was in the drilling stage, although the state of the drill rig (e.g., drilling, stopped, etc.) was unknown. The drill site emissions were 0.200 (0.156) tpd of CO, 152.8 tpd of  $CO_2$ , and 0.047 (0.042) tpd of  $NO_x$  (Table 3). Compared to engineering emission factors for a drill rig in Roy et al.,<sup>38</sup> and assuming the drill rig had the average power rating of 4000 bhp, our calculated  $NO_x$  emission rate is about 10 times less than the engineering estimate.<sup>38</sup> Similarly, there are emission factors for PM and VOC from drill rigs, but we did not observe elevated concentration of either pollutant type downwind of the drill rig. The lower emissions from the drill site we sampled compared to engineering emission factors could indicate that the drill rig was not operating at full capacity, that there was pollution control on the site, or that the values in Roy et al.<sup>38</sup> are overestimated.

Unexpectedly,  $CH_4$  emissions were observed at the drill site with an estimated emission rate of 0.923 tpd (Table 3). The  $CH_4$  emissions were likely associated with a gas “kick”, or when a gaseous zone is encountered during drilling and the NG is directed to a mud-gas separator then vented away from the drill rig.<sup>19</sup> Similar results were observed in the Marcellus Shale play by Caulton et al.<sup>39</sup> via aircraft measurements. That study concluded that wells in the drilling phase in a portion of Southwestern Pennsylvania had a  $CH_4$  flux of  $2.94 \pm 0.95$  tpd.<sup>39</sup>

A flow-back flaring event, denoted in this work as T-B, was observed at a well pad in Sullivan County. Two tracer release experiments were performed at this site; however, the results from one experiment are not shown because it was unsuccessful due to unfavorable and variable wind conditions. Because of the large buoyancy of the hot flare, two distinct emission plumes were observed during the successful tracer release experiment. Plume-1, thought to be direct emissions from the temporary flare, was located  $\sim 1500$  m downwind. Plume-2, thought to be from ground-based fugitive losses, NG leakage not combusted by the flare, and emissions from site process equipment, was located with the dual tracer plume  $<500$  m downwind of the site.

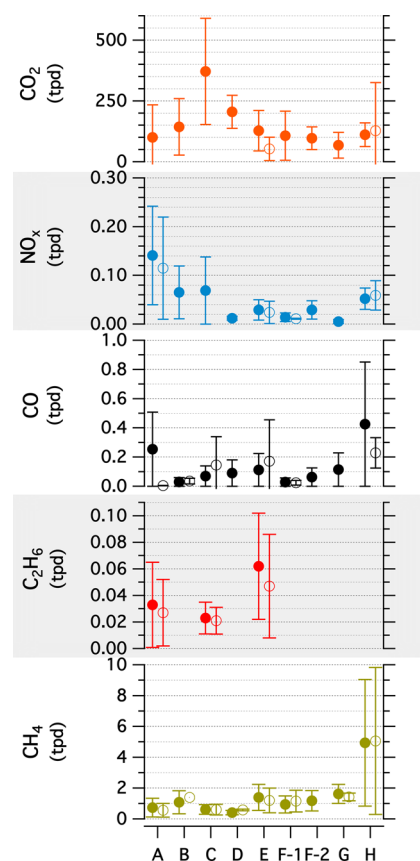
Plume-1 was observed to have elevated mixing ratios of CO and  $CO_2$ , with no enhancements in  $NO_x$ , and decreased concentrations of  $CH_4$ ,  $CH_3OH$ , and acetone relative to the background. The modified combustion efficiency, or  $\Delta[CO_2]/(\Delta[CO_2] + \Delta[CO])$ , for the flare plume was determined to be greater than 0.99, indicating that the flare efficiently combusted flowback gases.<sup>40</sup> Alternatively, the ground-based  $NO_x$  emissions in Plume-2 were observed to have average center plume mixing ratio of 19 ppbv and a maximum 1 Hz value of 140 ppbv over a 3 h sampling period. The emission factors obtained from the dual tracers and Plume-2 indicated large emission rates of combustion species, with CO emissions at 0.386 (0.102) tpd,  $CO_2$  at 251 (669) tpd, and  $NO_x$  at 0.072 (0.044) tpd (Table 3). There was large variability in transect emission ratios for each species, which indicates that the site emissions were not constant throughout the sampling period. Although the emission rate of the temporary flare is unknown, the large emission rates of incomplete combustion species from the ground-based operations compared to the relatively efficient flaring of flowback gases suggests that the ground-based emission sources could have a larger impact on local air quality compared to the temporary flaring during completion events.



The largest  $\text{CH}_4$  emissions measured in the study were observed at this site in Plume-2 with a value of 7.7 (10.1) tpd with a median center-plume  $\Delta\text{CH}_4$  mixing ratio of 1.3 ppmv and a maximum of 38 ppmv. The daily  $\text{CH}_4$  emission rate observed at this completion event, if constant over the entire event, was significantly in excess of any completion event observed by Allen et al.<sup>2</sup> ( $\mu = 1.7 \text{ Mg}$ ; 95% CI = 0.67–3.3 Mg), because well completion events can often last several weeks.<sup>2,41</sup>

**Compressor Stations.** Site size information for all of the compressor stations investigated in the study was found in PA DEP air quality permits. Permits from the closest available date before our measurements were used to gather site information. Sites are permitted to operate based on the full capacity of the site equipment. It is not known whether any of the compressor stations investigated were operating at full capacity during our sampling period. Additional site information can be found in the Supporting Information, Section 1. Eight compressor stations of various sizes were investigated in this study. Compressor stations C-B, C-D, C-F, C-G, and C-H were located in Bradford County in NE Pennsylvania. Two tracer release experiments were conducted at the C-F compressor station. Compressor stations C-A, C-C, and C-E were located in the SW study area, located in Greene, Fayette, and Westmoreland counties, respectively. All compressor stations investigated utilize NG fired compressor engines with total power capacities ranging from 5285–16 560 bhp, with the exception of C-G, which is equipped with an electric powered 15 300 bhp centrifugal turbine. All of the sites had various amounts of process equipment (e.g., glycol dehydrators, separators, in-line heaters, liquids tanks), and air quality controls, which was verified by PA DEP air quality permits and by visual inspection.

Emission rates of measured combustion related species from the tested compressor stations are shown in Figure 2. Carbon monoxide emission rates ranged from 0.029 (0.005) to 0.426 (0.229) tpd with a median emission rate of 0.09 (0.145) tpd. The largest CO emission rate was observed at the largest compressor station (C-H). The tested compressor stations had a minimum  $\text{NO}_x$  emission rate of 0.005 (0.011) tpd, a median of 0.029 (0.042) tpd, and a maximum of 0.141 (0.115) tpd. Unlike CO, the largest emitter of  $\text{NO}_x$  was C-A, which was the smallest compressor station, suggesting that site processes other than compressor engines and differences in pollution control may play a large part in the magnitude of site emissions. The electric powered compressor station (C-G) had the lowest  $\text{NO}_x$  emissions, as expected. However, the observation of combustion emissions at site C-G indicates that site process equipment plays a role in the total emissions from compressor stations. Carbon dioxide emission rates ranged from 68.0 (52.7) to 371 (128) tpd, with a median emission rate of 111 (90.2) tpd. Elevated particle number concentrations were observed at 6 of the compressor stations where particle number was measured, and undetected at the C-G compressor station. Center-plume number concentrations above the background ( $\Delta\text{conc.}$ ) ranged from 75 to 9600  $\#/\text{cm}^3$  with a median of 1400  $\#/\text{cm}^3$ . Elevated  $\text{PM}_{10}$ , however, was only observed in the emission plume of the C-A compressor station. The emission plume contained only organic aerosol and had an emission rate of 0.419 (0.548) tpd. As previously mentioned, no VOC enhancements, other than  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , were observed downwind of any compressor station, with the exception of  $\text{CH}_3\text{OH}$  at the C-F compressor station. Methanol was observed in the site plume during both tracer release experiments at the site. The emission rate of



**Figure 2.** Emission rate estimates for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , CO,  $\text{NO}_x$ , and  $\text{CO}_2$  from the compressor stations in metric tons per day. The average integration method results are represented by a solid circle. The average regression method results are represented with open circles when applicable. The standard deviations for both methods are represented with caps and whiskers.

$\text{CH}_3\text{OH}$  at the first tracer release experiment at the site had an estimated value of 0.384 (0.432) tpd and the second had a value of 0.300 tpd. The relatively similar emission values for  $\text{CH}_3\text{OH}$  for tracer release experiments that occurred several days apart suggest that the emission source was likely not from a transitory site process and instead was from a constant process (e.g., antifreeze). Additionally, similar emission rates from a constant source like pipeline antifreeze provides evidence for the success of our tracer ratio methods.

Methane emission rates ranged from 0.411 (0.565) to 4.94 (5.06) tpd with a median emission rate of 1.09 (1.18) tpd. The largest emission rates and the largest variability between plume transects was observed at the C-H compressor station, which has the largest compression power of the tested facilities. The observed  $\text{C}_2\text{H}_6$  emission rates at the tested facilities ranged from 0.023 (0.021) to 0.062 (0.047) tpd with a median emission rate of 0.033 (0.027) tpd. The emission ratio of  $\text{C}_2\text{H}_6$  to  $\text{CH}_4$  at the three compressor stations where  $\text{C}_2\text{H}_6$  was measured had an average of  $\sim 0.04$ .

There was no significant relationship between emission rates of the measured chemical species and the compression power at the site. Although a positive trend was observed between total permitted compressor power and  $\text{CH}_4$  emissions, indicating that there may be a relationship between the volume of NG a facility handles and fugitive losses. However, the role of compressor power in site emissions is unclear because of the small sample size of this study and also because information

about the operating state of compressor stations studied was not available to us. There are likely many other factors besides compression power that lead to differences in emission rates. Future sampling at these sites and others throughout the region is key to understanding how factors like size, operation state, NG processing, pollution control, and age affect the emission rates of pollutants from compressor stations in the Marcellus Shale region.

Although this study adds critically needed measurements to the existing literature, the extent to which the results can be generalized to the Marcellus basin as a whole remains uncertain. Although the sample size of this study is too small to make statistical conclusions about different emission source types, it provides crucial comparisons to recent literature about emissions from NG well pads, pads with active drilling, and completions. Additionally, we have shown that in contrast to other unconventional NG gas resources there are few emissions of nonalkane VOCs (as measured by PTR-MS) from Marcellus shale development. The low emission of nonalkane VOC in the Marcellus play indicates that emission estimates should not be generalized across shale plays in regional models or in emission inventories. The study has also provided useful methodology for quantifying emissions from NG development without the advantage of site access. Based on the results from this study we recommend that future studies increase the monitoring time at each site in order to better characterize daily variability in emission composition and quantity.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Detailed site information, a map of the study region, and calibration procedures for the chemical species reported in this study. Detailed discussions about the background subtraction technique, the first-order correction factor, and site emissions variability. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00452.

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All authors have given approval for the final version of the paper.

### Notes

The authors declare no competing financial interest.

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