Supporting Information

Temporal Variations in Methane Emissions from an Unconventional Well Site

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Introduction

Additional supporting information is provided within the following Text, Figures, and Tables. Data are included to support the analysis provided in the main article.

S1 Site Details.

The unconventional well site under consideration included four unconventional wells targeting the Marcellus shale formation. Two of the wells have been in production since late 2011 while two newer wells started production in late 2015. The site produces a dry gas and Table S1 presents a summary of the gas composition for two different samples and the average composition. Additional details on this site, including its natural gas and water production can be found at the following website – mseel.org.

|                | Units | Sample 1 | Sample 2 | Average  |
|----------------|-------|----------|----------|----------|
| Methane        | %     | 97.3064  | 97.2962  | 97.3013  |
| Ethane         | %     | 2.0614   | 2.0703   | 2.06585  |
| Propane        | %     | 0.071    | 0.0709   | 0.07095  |
| i-Butane       | %     | 0.001    | 0.009    | 0.005    |
| n-Butane       | %     | 0.0031   | 0.0029   | 0.003    |
| i-Pentane      | %     | <MDL     | <MDL     | <MDL     |
| n-Pentane      | %     | <MDL     | <MDL     | <MDL     |
| Nitrogen       | %     | 0.2494   | 0.2527   | 0.25105  |
| Oxygen         | %     | <MDL     | <MDL     | <MDL     |
| Carbon Dioxide | %     | 0.3077   | 0.3061   | 0.3069   |
| Hexanes        | %     | <MDL     | <MDL     | <MDL     |
| LHV            | BTU/ft3 | 1008.4  | 1008.4   | 1008.4   |
Table S1. Dry-gas composition. Note: <MDL was below the measurement detection limit of the equipment used by the third party that provided gas analysis.

An overview of the site is shown in Figure S1. For spatial reference, the black line is 125 meters in length. The site contains four unconventional wellheads; Figure S2 includes a diagram of the wellheads used at this site along with a picture of an actual wellhead. As discussed below, tenting was used to quantify all wellhead losses – including those that are below the deck grade and within the cellar.

Figure S1. Satellite image of the audited well site.
In addition to the wellheads, there was also a produced water tank onsite. The API 12F tank had a nominal capacity of 210 barrels and was 19 feet in diameter and 15 feet high - see Figure S3. The site also included two six feet vertical sand separators of which one is shown in Figure S4. The site contained two production units shown in Figure S5 and a PIG launcher station shown in Figure S6. Site electrical power was provided by a combination of solar and a thermoelectric generator from Global Thermoelectric, see Figure S7.
Figure S3. Produced water storage tank and impoundment. Photograph courtesy of Derek Johnson.

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Figure S4. Vertical sand separator. Photograph courtesy of Derek Johnson. Copyright 2016.
Figure S5. Production units. Photograph courtesy of Derek Johnson. Copyright 2016.

Figure S6. PIG launcher station. Photograph courtesy of Derek Johnson. Copyright 2016.
In addition to the equipment above, the site included two enclosed gas-processing units (EGPUs) and during one audit a methanol injection system. Details were collected from one of the EGPUs for which exhaust gas samples were collected. Figure S8 shows an example of an EGPU. As noted below, instead of quantifying each source within the unit, the units were sampled as a whole. The sampling hose was placed within the unit near the top of all plumbing equipment. The doors were closed and plastic taped over the doors since they remained ajar to allow for the sampling hose installation. Sampling occurred for varied durations until a steady state reading was achieved or until multiple cyclic events were recorded. The units were not sealed at the bottom of the skid, which allowed fresh dilution air to enter.
at the bottom, mix with any sources, and to be sampled near the top. This particular EGPU was a modified 750M BTU/hr unit which included horizontal three phase separators.

Figure S8. Onsite enclosed gas-processing unit. Photograph courtesy of Derek Johnson. Copyright 2016.

S2 Methods.

The full flow sampling systems (FFS) operates on a principle similar to automotive emissions sampling systems whereby the emissions stream is captured and mixed with dilution air, the total combined flowrate is measured, and an emissions analyzer draws a constant volume sample from the mixed stream to determine species concentrations. The FFS system uses an explosion proof blower, grounded wire wound sampling hose, a calibrated mass airflow sensor (MAF), and an Ultraportable Greenhouse Gas Analyzers (UGGA). For increased accuracy, the system can use a low or high range
analyzer for variable methane concentrations. The MAF is calibrated on a flow bench using a laminar flow element and calibrated pressure transducers and thermocouples. The methane analyzer was calibrated with bottled certification gases (≤±2%). It was previously reported that the system was capable of uncertainties of ≤4.4% based on propagation of error, which was verified with controlled methane releases that showed an accuracy of ±2%. For simplicity in this research a single analyzer was used which increased measurement uncertainty to about ±10%. All FFS data were collected at a rate of one Hz. Literature includes additional details on the design and use of the FFS system.

An example of a 12-point calibration of the MAF against a NIST traceable laminar flow element is shown in Figure S9. The calibration was completed across the entire possible flow range but it should be noted that the targeted total flow rate during audits was between 100 and 200 CFM. For the entire calibration range, the MAF error ranged from -3.5 to +2.2%. Over the targeted range the error ranged from -0.4 to +2.2%. Note that standard reference conditions were 70°F and 14.697 PSIA.

Prior to leak or loss measurements, components were examined using a handheld methane detector capable of measuring up to 50,000 parts per million (ppm) of methane. The units used in
audits were Eagle II methane detectors from RKI Instruments. These units were zeroed on ambient air and had a sensitivity of 5 ppm above background. Handheld units were calibrated prior to use with a flooded probe and bottled methane with a concentration of 19,500 ppm (±2%). Researchers followed recommendations set forth in EPA Method 21 for assessing possible leak sources and we quantified all sources that were identified with concentrations of around 500 ppm and above. Once sources were detected with the handheld units, they were photographed and marked for subsequent quantification with the FFS.

The wellheads, which include all above grade tree components, also included below grade components and the well casing. These below grade components were inaccessible (housed within the well cellar). Therefore, methane emissions from a wellhead were quantified as single value using the FFS and a tented enclosure. Figure S10 illustrates a tented wellhead and its connection to the FFS through a length of the grounded wire wound hose. Prior to measurement of the wellhead flux, the tent and FFS were set up onsite overtop bare ground. A background flux measurement was used to background correct wellhead flux values. Each well was tented separately and measurements ranged from 20-30 minutes depending on leak and operation conditions. A separate ambient background measurement was obtained and used to background correct emissions from other sources. Note that during the third audit a background flux was not collected and the wells were corrected with the average site background. Table S2 includes information on weather conditions and background emissions during each audit.
Figure S10. Tented well (left) and FFS system on rear of research vehicle (right). Photograph courtesy of Derek Johnson. Copyright 2016.

|                      | Audit 1       | Audit 2       | Audit 3       | Audit 4       | Audit 5       | Audit 6       |
|----------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Date                 | 11/22/2016    | 4/10/2017     | 7/19/2017     | 11/20/2017    | 5/23/2018     | 8/7/2014      |
| Daily High Temperature (°F) | 44           | 80           | 90           | 44           | 70           | 84           |
| Daily Average Temperature (°F) | 34           | 70           | 79           | 36           | 64           | 77           |
| Daily Low Temperature (°F) | 23           | 60           | 67           | 28           | 57           | 70           |
| Average Wind Speed (mph) | 8            | 7            | 2            | 8            | 7            | 6            |
| Average Background Concentration of Methane (ppm) | 2.45         | 2.04         | 2.47         | 2.79         | 2.45         | 2.35         |
| Average Tent Background (g/hr) | 0.55         | 0.69         | N/A          | 0.15         | 0.16         | 0.18         |
| Number of Active Wells | 4            | 4            | 1            | 2            | 3            | 4            |
| Number of Active EGPUs | 2            | 1 - Intermittent | 1          | 2            | 0            | 0            |

Table S2. Audit information.

During Audit 2 a pneumatic valve operated intermittently on a wellhead and caused significant variability in wellhead emissions. Figure S11 shows the raw, uncorrected methane concentration from the same well from Audit 1 (steady and low) and from Audit 2 (intermittent and high). During this same audit, the tank emissions were also higher and variable in nature due to the intermittent operation and
dumping of the separator unit. Figure S12 shows the variability in raw, uncorrected methane emissions from the opened tank thief hatch.

**Figure S11.** Extended wellhead flux data collection (~30 minutes). Comparison of steady wellhead flux compared with the variable emissions due to intermittent operation of pneumatic valve.
Figure S12. Example of variations in methane concentration during tank measurements. Variations due to intermittent operation of the EPGU and dumps to the tank.
S3 Stack Emissions.

Stack emissions data were collected during the first four audits, however after the first two audits it was determined that the sampling pump had a tear in its gasket allowing for dilution of the sample and those data are not reported here. Table S3 presents the data from EGPU 1, which included a sampling port. Methane emissions from the single EGPU ranged from 5.7 to 7.7 g/hr, which are on the order of total leak rates (defined as other) during both audits. Neither of the burners were active on either EGPUs during Audits 5 and 6.

| Stack Emission Component | Audit 3 | Audit 4 |
|--------------------------|---------|---------|
| Carbon Dioxide           | 9126 g/hr | 12,354 g/hr |
| Carbon Monoxide          | 5.70 g/hr | 7.71 g/hr |
| Oxides of Nitrogen       | 0.22 g/hr | 0.30 g/hr |
| Methane                  | 3.90 g/hr | 5.30 g/hr |

Table S3. EGPU stack emissions for Audits 3 and 4.
| Wellhead | Audit 1 | Audit 2 | Audit 3 | Audit 4 | Audit 5 | Audit 6 |
|----------|---------|---------|---------|---------|---------|---------|
|          | CH₄ g/hr | NG g/hr | Water Bbl/day | CH₄ g/hr | NG g/hr | Water Bbl/day | CH₄ g/hr | NG g/hr | Water Bbl/day | CH₄ g/hr | NG g/hr | Water Bbl/day | CH₄ g/hr | NG g/hr | Water Bbl/day |
| 1        | 0.17    | 1823    | 0.59    | 0.00    | 3136    | 8.75    | 0.96    | 4397    | 7.26    | 0.41    | 1433    | 0.99    | 0.00    | 1720    | 0.37    |
| 2        | 0.16    | 2778    | 0.90    | 0.00    | 2027    | 3.82    | 0.30    | 0.00    | 0.00    | 0.24    | 5393    | 6.75    | 4.65    | 0.52    | 2521    | 3.23    |
| 3        | 0.14    | 1576    | 0.51    | 4.29    | 801     | 1.51    | 0.00    | 0.00    | 0.24    | 0.00    | 0.44    | 712     | 0.00    | 0.16    | 902     | 0.20    |
| 4        | 0.39    | 1040    | 0.34    | 0.00    | 312     | 0.59    | 1.33    | 0.00    | 0.00    | 0.24    | 0.00    | 0.32    | 833     | 0.57    | 0.00    | 517     | 0.11    |
| Total    | 0.85    | 7217    | 2.34    | 1.64    | 3136    | 11.0    | 1.68    | 9791    | 14.0    | 5.82    | 2978    | 2.05    | 0.68    | 5660    | 3.91    |

**Table S4.** Specific wellhead emissions along with natural gas and water production – by well and totals.
**S4 Comparison with other Site-wide Studies.**

We compared our direct quantification data for site-wide emissions with those reported in literature which included multiple direct and indirect measurement campaigns. Table S5 presents a summary of these data.
| Region       |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|              | Our Data        | Allen et al.    | Allen et al.    | Rella et al.    | Yacovitch et al.| +               | Robertson et al.| w/ unloading    | Robertson et al.| w/ unloading    | Robertson et al.| w/ unloading    | Robertson et al.| w/out unloading | Omara et al.    | Unconventional  |
|              | Marcellus       | Rocky Mountain  | Appalachian     | Barnett         | Barnett         | Uintah          | Denver-Julesburg| Upper Green      | River            | Fayetteville     | Marcellus        | Marcellus        | Marcellus        | Fayetteville     | Denver-Julesburg |
| Method       | Direct          | Hi-Flow         | Hi-Flow         | Downwind Flux   | Downwind Flux   | Downwind Flux   | Downwind Flux   | Downwind Flux   | Downwind Flux   | Downwind Flux   | Downwind Flux   | Downwind Flux   | Downwind Tracer  | Downwind Tracer  | Downwind Tracer  | Downwind Tracer  |
|              |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |                 |
| n            | 6               | 10              | 5               | 115             | 7               | --              | --              | --              | --              | 17              | 18              | 3               | 17              | 5               |                 |
| Min          | 86              | 109             | 473             | 27              | 6000            | 1200            | 880             | 1700            | 380             | 12,000          | 590             | 3500            | 0               | 2000            |                 |
| Max          | 4102            | 5373            | 5761            | 47,600          | 287,000         | 9100            | 3500            | 3100            | 1100            | 26,800          | 1100            | 14,170          | 802,000         | 74,000          |                 |
| Mean         | 1371            | 1180            | 1992            | 1720            | 137,000         | 3700            | 1400            | 2300            | 680             | 18,800          | 820             | 8932            | 48,391          | 33,000          |                 |

**Table S5.** Comparison of our direct temporal measurements with indirect geospatial measurements from literature. Note our data were from direct measurements while the other studies all used indirect quantification methods. (n = sample size, min, max, mean are in g/hr) * Minimum and maximum are presented as the 95% CI of the average. + Indicates studies that were excluded from Figure 2 based on a modified z-score analysis.
**S4 Trends Analysis.**

We examined both wellhead emissions and site wide emissions with gas and water production data. A regression analysis showed no significant correlations between individual wellhead emissions with water or gas production. No correlations were found from a cumulative wellhead emissions rate and production data. We then examined total site emissions as compared with total natural gas production and water production as shown in Figure S13 and S14. No strong trends were indicated. We noted that the main source of variability and in many cases the main source of emissions was the water tank which should have some correlation with the amount of water produced based on dump activity from the separators. We therefore removed tank emissions and compared non-tank methane emissions with natural gas production and found a weak positive correlation of increasing methane emissions from increased natural gas production, see Figure S15. However, when we compared the tank emissions with daily water production no improvement in correlation was found as was the case with non-tank emissions, see Figure S16. But since uncontrolled tank emissions are a function of the desorption of methane from liquids, the active dumps, and the displacement of gases by liquid volume we realized that the tank methane emissions could be influenced by previous activity. We specifically focused on Audit 2 which had the highest tank emissions. We saw that water production rates from two days prior were significantly higher. Therefore, we examined the tank methane emissions with the total water production from the audit day and two prior days. This in fact showed the strongest correlation between any methane emissions category and site activity, see Figure S17.
Figure S13. Total site emissions as a function of daily NG production.
Figure S14. Total site emissions as a function of daily water production.
**Figure S15.** Non-tank methane emissions as a function of daily NG production showing a weak positive correlation with increased natural gas production.
Figure S16. Results of plotting tank methane emissions against daily water production. Note a weaker correlation than was shown for total site emissions and water production.
Figure S17. Results of plotting tank methane emissions against three-day water production. This produced the highest $R^2$ of any regression analyses between two variables.