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Tower-based Measurements of CH_4 Dry Mole Fraction and $\delta^{13}CH_4$ in the Northeastern Pennsylvania Marcellus Shale Gas Region

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Introduction

Fugitive emissions of atmospheric methane (CH_4) from natural gas drilling, production, processing, and distribution activities in the Marcellus Shale geologic formation have the potential to impact the current state of the climate. Thus, it is useful to quantify these emissions from natural gas activities, as well as other sources, both biogenic and anthropogenic (e.g., wetlands, cattle, landfills). Sources can be distinguished via the isotopic signature: heavy isotope ratios (e.g., -23.9‰) are characteristic of thermogenic CH_4 sources and light isotope ratios (e.g., -66.5‰) are characteristic of biogenic sources. Regional emissions can be quantified using an atmospheric transport model with a Bayesian inversion to minimize differences between simulated and observed atmospheric CH_4 concentrations. Towards that end, high-accuracy atmospheric observations of CH_4 dry mole fractions and its stable isotope ($^{13}CH_4$) are made on four communications towers. We present results from one year of measurements, focusing on characterizing the enhancements of CH_4 and the calibration technique for the isotopic ratio ($\delta^{13}CH_4$).

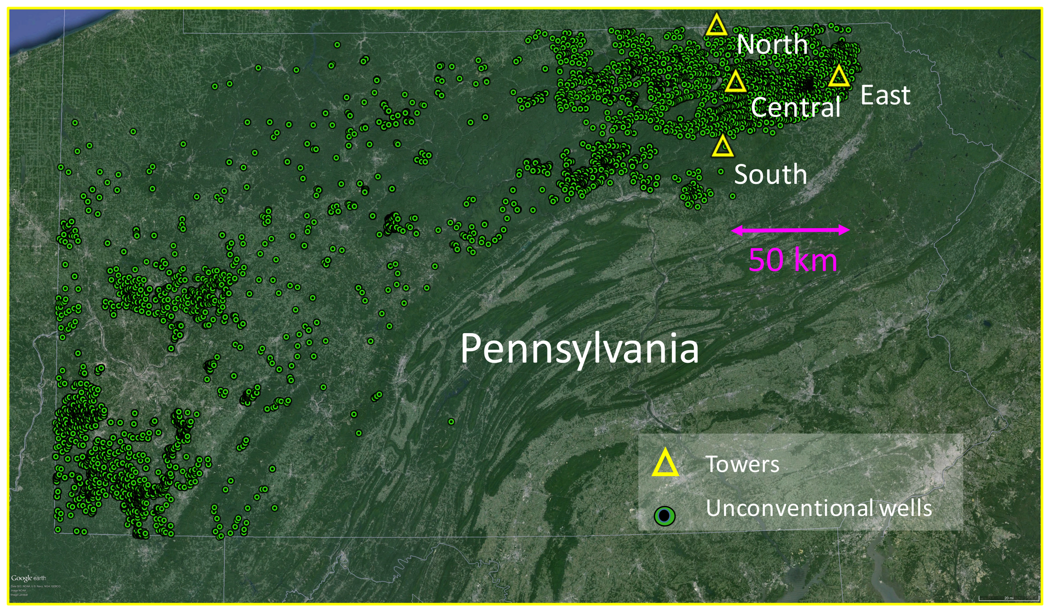


Figure 1. Map of Pennsylvania with permitted unconventional natural gas wells (green circles) and network of towers with methane and stable isotope insturments (Picarro G2132-i). The measurement heights are between 46 and 61 m AGL; the instruments were deployed in May 2015. Towers East and South are also equipped with NOAA flask samples, measuring a suite of > 55 gases (including greenhouse gases, hydrocarbons, and halocarbons) and $\delta^{13}CH_4$.

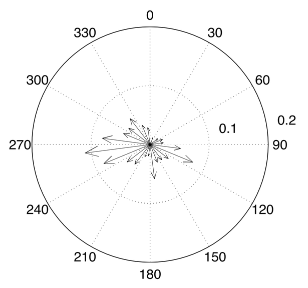


Figure 2. Angular probability distribution function of wind direction, as measured at the Binghamton, NY airport for the period Apr 2015 - Apr 2016. Arrows point to the direction of origin and the magnitude indicates the relative frequency. Winds in the study area are most often from the west-south-west.

Objective

Establish a netowrk of precise and accurate measurements of methane and its stable isotope to estimate and attribute regional emissions from anthropogenic and biogenic sources using an atmospheric inversion technique.

Methods: in-situ measurements

- Prior to deployment, the instruments were calibrated for CH_4 and CO_2 mole fraction using four NOAA-calibrated tanks.
- Field calibration: Target tank calibrated by NOAA/INSTAAR (1868 ppb, -47.2‰); sampled every ~21 hours; offset applied.
- In-situ dry mole fraction data (CH_4 and CO_2) has been corrected for water vapor effects and averaged to 10-min segments.

- Prior to deployment, the instruments were calibrated for $\delta^{13}CH_4$ using 4 Isometric Instruments standards (-23.9/-38.3/-54.5,/66.5‰) diluted to varying degrees with zero air to obtain mixing ratios 1.8 - 10 ppm.
- Field calibration: Tanks filled by Scott-Marrin using Isometric Instruments standard to spike and calibrated at PSU
  - High tank: ~10 ppm, -38.9‰; sampled every 90 min; peak-to-peak noise within the calibration cycles is < 10 ppb CH_4 and < 4‰
  - Low tank: ~2 ppm, -23.6‰; sampled every 90 min; peak-to-peak noise within the calibration cycles is < 2 ppb CH_4 and < 20‰

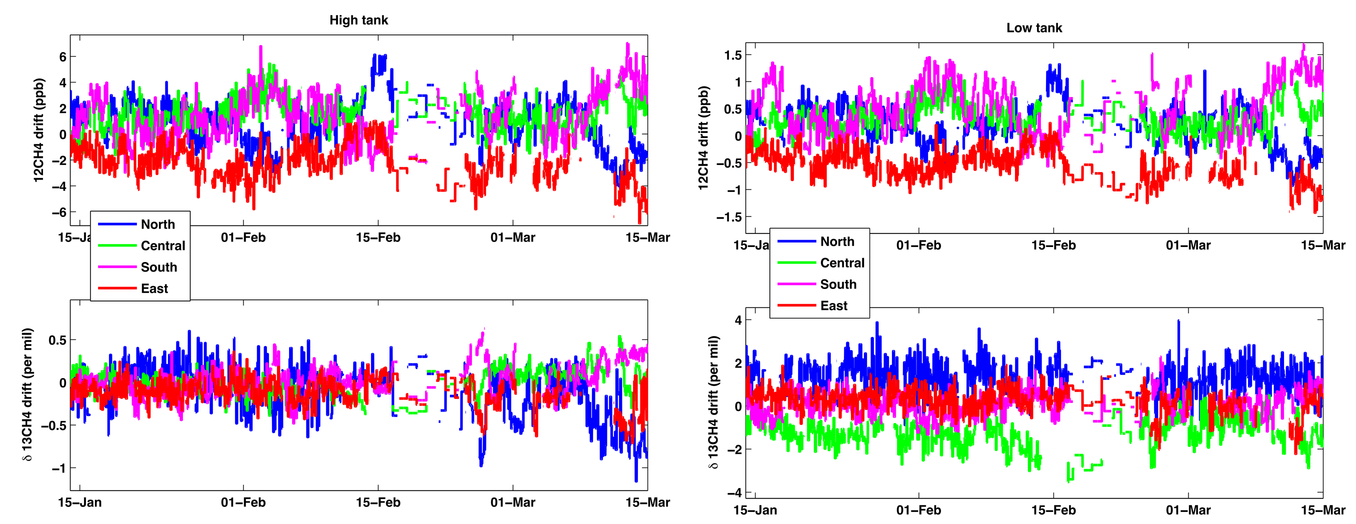


Figure 3. Tank drift of $^{12}CH_4$ (top panels) and isotopic ratio (bottom panels), for the "High" tank (left panels) and the "Low" tank (right panels). The drift of the "High" tank is within 9 ppb/‰ Comparitively, the drift of the "Low" tank is within 2 ppb for $^{12}CH_4$ and the isotopic ratio signal is noisier: within a 3‰ range.

Methods: Flask measurements

- Flasks are filled over a 1-hour time period in the late afternoon (14-15 LST), thereby yielding a more representative measurement, compared to most flask sampling systems, which collect nearly instantaneous samples (e.g. ~10 sec). The integrative sampling approach is particularly useful for flask samples taken nearby areas with large or variable surface flux processes (compared to those taken in remote regions).
- Samples are measured only when winds were blowing steadily out of the west or north, to ensure that the samples were sensitive to and representative of the broader Marcellus shale gas production region that is the focus of this study.
- Back-trajectories from the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) atmospheric transport and dispersion model are analyzed for each flask sample.
- The flask measurements are essential for independent validation and error-estimation of the continuous in-situ CO_2, CH_4, and $\delta^{13}CH_4$ measurements.

In-situ/NOAA Flask Comparisons

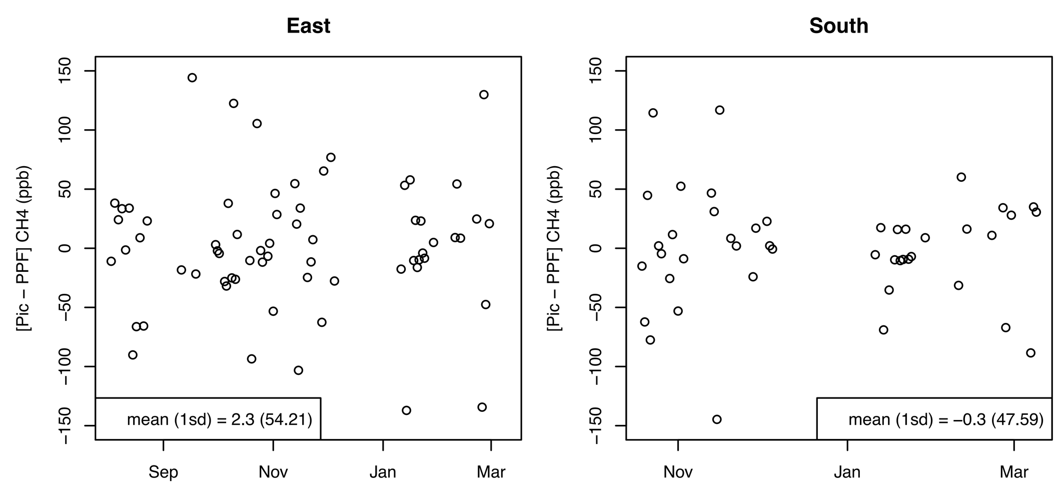


Figure 4. Difference between in-situ and flask CH_4 dry mole fraction at the South tower (left) and the East tower (right).

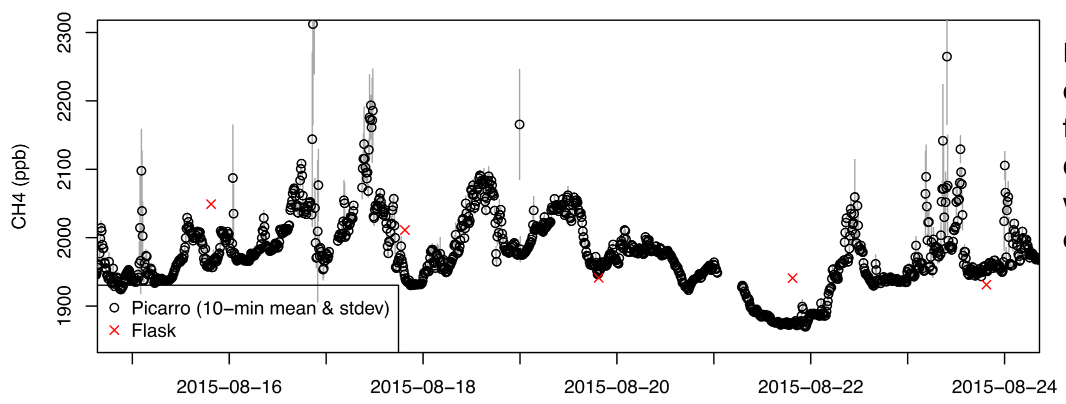


Figure 5. Time series of in-situ CH_4 dry mole fraction for several days at the East tower, with flask values overlaid.

The in-situ/flask comparison of the CH_4 dry mole fraction indicates the mean difference to be 2.3 ppb at the East site and -0.3 ppb at the South site. The standard deviation, however, is large: 54 ppb and 48 ppb, respectively (Figures 4 and 5). For comparison, in INFLUX with G2301 instruments, we see 0.62+-4.6 ppb in-situ to flask to Picarro differences. The Picarro datasheet for the G2301 indicates precision (1-σ) of <0.5 ppb for 5 sec and < 0.22 ppb for 5 min and for the G2132-i (isotope instrument) precision (1-σ) of <5 ppb +-0.05% of reading -> 6 ppb (at 2000 ppb reading) for high precision mode. The cause for the large variability is under further investigation.

Results: Flasks

The many trace gases measured in the flasks provide information about the upwind source types. In the example below (Figure 6), the highly correlated relationships between ethane and methane, and propane and methane, are consistent with the hypothesis of a common CH_4 source from natural gas upwind to the towers.

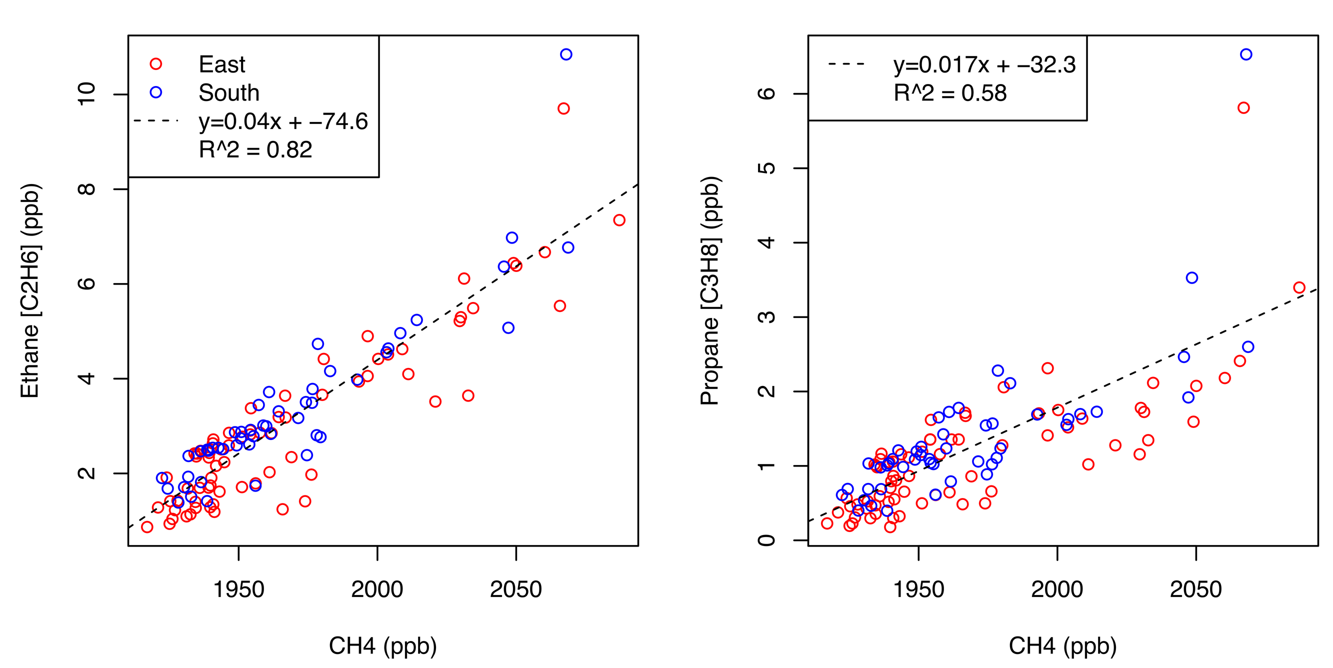


Figure 6. Flask measurements of ethane (C_2H_6) and propane (C_3H_8) as a function of CH_4.as measured by flasks at the East and South towers.

Results: In-situ measurements

Daily afternoon-averaged CH_4 dry mole fraction is shown in Figure 7 (top left panel) for each of the tower in-situ sites. There is significant overlap between the sites on this scale. 67% (1-σ) of the daily afternoon-averaged CH_4 dry mole fractions measured during the period May 2015 – Apr 2016 are within 34 ppb at the South site. For comparison, the variability at the Central tower is somwhwat larger: 53 ppb.

After smoothing with a 15-day running mean filter (Figure 7, middle left panel), we can see the effects of synoptic-scale (~3 day cycles) weather systems on the measurements. A large excursion is noted at all four sites for the period 6-13 December 2015 (DOY 340-347). This may be representative of a larger-scale event occurring outside of the study region. A smaller excursion occurred 28 August - 4 September 2015 (DOY 240-247). Wind directions, as measured at the Binghampton, NY airport, are variable during these periods. On 26-27 January 2015, the North tower measured elevated CH_4 compared to the other sites for 2 days. On the second day, the North tower measured 300 ppb higher than the other towers. Unfortunately wind data is not available from the airport that day, but this event was likely local.

A longer (61-day) running mean filter (Figure 7, bottom left panel) yields the regional overall signal. The South tower measures the lowest overall methane. The East tower is within 5-8 ppb of the South tower for much of the measurement period in terms of the smoothed value, except during the December event when it was 40 ppb larger than the South tower. (Figure 7, bottom right panel). The Central tower measures the highest CH_4 overall, with the enhancement above the South tower being 50 ppb during the December event, and 15 ppb during October 2015 (presumably capturing the "normal" regional enhancement). The signal from the North tower is in between these extremes.

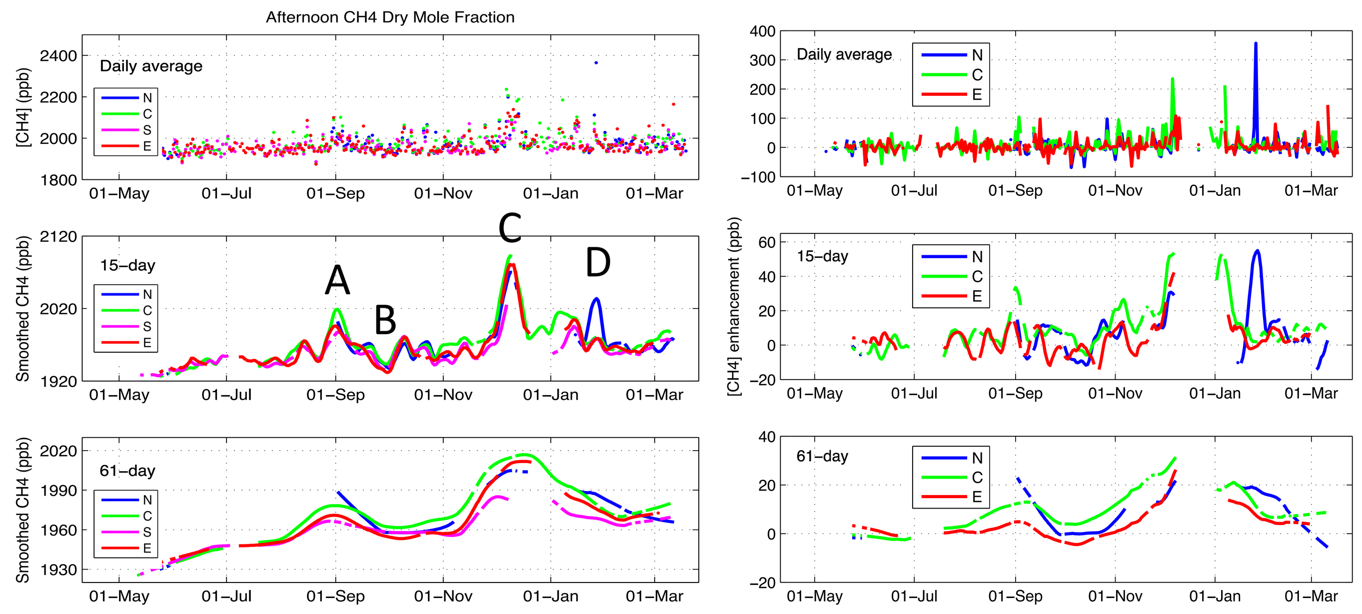
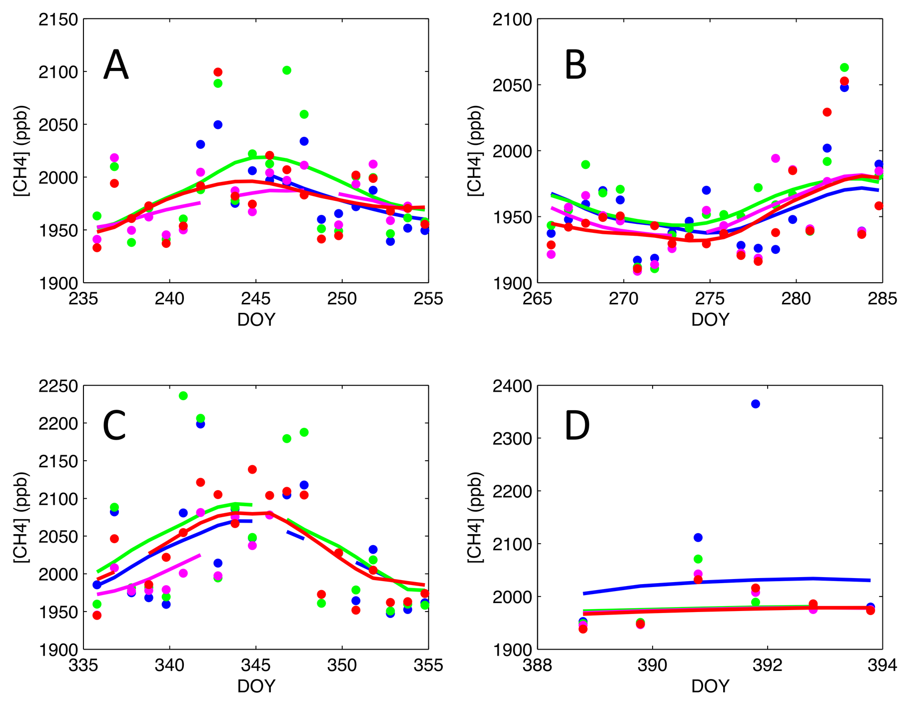


Figure 7. Top left panel: Daily afternoon-averaged CH_4 dry mole fraction as a function of time for each of the four tower locations. Middle left panel: Same data as the top panel, but smoothed with a 15-day running mean filter. Bottom left panel: Same data as the top panel, but smoothed with a 61-day running mean filter. The panels on the right are equivalent to those on the left, but are enhancements above the South site.

Figure 8. Daily afternoon-averaged CH_4 (dots) with 15-day smoothed curves shown as well for four events during the measurement period. The events are labeled A, B, C, D in the 15-day smoothed plot (Figure 7, middle left panel).



Conclusions

The long-term (~months) regional enhancement is about 15 ppb, with the South tower measuring the lowest overall CH_4 dry mole fraction and the Central tower the largest. The enhancement at the East tower is much smaller, although that site was expected to be a "downwind" site. The North tower was chosen as an alternative background site and is in New York State, where horizontal fracking is not allowed. However, it appears to capture the regional signal much of the time. Therefore, careful calibration comparison to NOAA flasks, and round robin testing with NOAA tanks will be especially important. Although the overall signal is small, the signal is, of course, variable, and larger deviations do occur.

Contact: Natasha Miles (nmiles@psu.edu) http://sites.psu.edu/marcellus Funding This work was funded by the Department of Energy National Energy Technology Laboratory (DE-FOA-0000894).