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Comment on "Hydrocarbon emissions characterization in the Colorado Front Range — A Pilot Study"

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Abstract. *Petron et al.* [2012] have recently observed and analyzed alkane concentrations in air in Colorado's Weld County and used them to estimate the volume of methane vented from oil and gas operations in the Denver-Julesburg Basin. They conclude that "the emissions of the species we measured are most likely underestimated in current inventories", often by large factors. However, their estimates of methane venting, and hence of other alkane emissions, rely on unfounded assumptions about the composition of vented natural gas. We show that relaxing those assumptions results in much greater uncertainty. We then exploit previously unused observations reported in *Petron et al.* [2012] to constrain methane emissions without making assumptions about the composition of vented gas. This results in a new set of estimates that are consistent with current inventories but inconsistent with the estimates in *Petron et al.* [2012]. The analysis also demonstrates the value of the mobile air sampling method employed in *Petron et al.* [2012].

1. Introduction

Several studies reporting unexpectedly high methane leakage from natural gas operations have recently attracted attention and sparked debate [*Howarth et al.*, 2011; *Jiang et al.*, 2011; *Cathles et al.*, 2011]. *Petron et al.* [2012] (henceforth P12) have now attempted to infer rates of methane emissions from oil and gas operations in the Denver-Julesburg Basin directly from novel measurements of alkane (notably methane and propane) concentrations in air near those operations. They report much higher rates of methane emissions than have been previously estimated through bottom up methods based on industry inventories. Here, we show that their results rely on unsupported assumptions about the molecular composition of vented natural gas. We then use additional observations reported (but not exploited) in P12 to estimate the rate of methane leakage without resort to assumptions about the composition of vented methane gas. Our conclusions are consistent with the more modest emissions rates indicated by bottom-up inventories but not with the top-down estimates presented in P12. In addition, our emissions estimates could, in principle, be further constrained by additional observations.

2. Method of P12

P12 analyze alkane concentrations in air samples collected both by the National Oceanographic and Atmospheric Administration (NOAA) Boulder Atmospheric Observatory (BAO) and by mobile air surveys in the Denver-Julesburg Basin area. The former finds a C_3H_8-to-CH_4 (C_3/C_1) molar ratio of 0.104 ± 0.005 for summertime samples (0.105 ± 0.004 for wintertime) originating near oil and gas producing areas, while the latter finds a C_3/C_1

molar ratio of 0.095 ± 0.007. The authors use a C_3/C_1 ratio of 0.1 in their subsequent analyses.

To estimate methane leakage based on their air observations, the authors begin by noting that most observed alkane emissions come from either raw gas venting or condensate tank flashing. They then create two equations. The first describes the vented gas:

$$v_{m/p} = \frac{M_p}{M_m}\frac{x_m}{x_p} \tag{1}$$

where $v_{m/p}$ is the basin-average C_1/C_3 molar ratio of vented raw gas, $M_p = 44g/mol$ and $M_m = 16g/mol$ are the molar masses of C_3H_8 and CH_4 respectively, x_m is the mass of methane vented, and x_p is the mass of propane vented.

The second relates emissions to observed concentrations of CH_4 and C_3H_8:

$$\frac{M_p(x_m + y_m)}{M_m(x_p + y_p)} = a_{m/p} \tag{2}$$

where y_m is the mass of methane released by flashing, y_p is the mass of propane released by flashing, and $a_{m/p} = 10$ is the observed ratio of CH_4 to C_3H_8 in air.

These are solved thusly:

$$x_p = \frac{a_{m/p}y_p - y_m M_p/M_m}{v_{m/p} - a_{m/p}} \tag{3}$$

$$x_m = v_{m/p}\frac{x_p M_m}{M_p} \tag{4}$$

The authors use three different values for $v_{m/p}$ to evaluate equations 3 and 4: (1) 18.75, which is the mean value of $v_{m/p}$ used in the Western Regional Air Partnership (WRAP) Phase III inventory of oil and gas emissions in the Denver-Julesburg Basin; (2) 15.43, which is the median of the molar ratios of methane to propane in seventy seven wells studied by the Colorado Oil and Gas Conservation Commission (COGCC) Greater Wattenberg Area Baseline Study (henceforth referred to as the GWA survey); and (3)

24.83, which is the mean of the molar ratios for the same seventy seven wells. For each of these, P12 evaluate x_p and x_m for each of 16 pairs of Y_m and Y_p, each of which is based on an observed profile of flashed gas for a single condensate tank. (This data is provided to them by the Colorado Department of Public Health and the Environment (CDPHE); it has been provided to the present author by the Western Energy Alliance, personal communication.) This gives them minimum, maximum, and average (across all 16 flashing profiles) levels of methane venting for each of the three values for $v_{m/p}$. The authors also create bottom-up estimates of methane venting based on figures from the WRAP Phase III study.

Table 1 reproduces relevant results from Table 4 of P12. Columns 2 and 3 in Table 4 have been reversed in the original paper, which is corrected here. As emphasized in P12, estimates for methane venting done through the top-down method are much higher than the bottom-up ones.

3. Methodological Limitations

There is, however, no reason given for believing that the three values of $v_{m/p}$ used in P12 actually bracket the possible range of C_1/C_3 ratios that might characterize vented gas. Indeed the results in P12 suggest that the choice of potential values for $v_{m/p}$ may be incorrect.

There is no overlap between the ranges of possible methane emissions estimated from the bottom up and the top down solely using WRAP III figures. This can only be true if either the choice of $v_{m/p}$ is wrong or if some of the underlying WRAP III figures themselves are incorrect; neither allows one to give credence to this particular top-down estimate.

That said, the top-down estimates based on the GWA survey do not rely on the WRAP III-based assumption about the value of $v_{m/p}$. They thus have the potential to provide independent insight into methane venting. However, P12 rely on an assumption that the molar ratio of CH_4 to C_3H_8 in vented gas is equal to either the median of that ratio in the 77 wells in the GWA survey (Case 2 above, $v_{m/p} = 15.43$) or the average of those wells (Case 3, $v_{m/p} = 24.83$). But the authors make no contention that the 77 wells sampled in the GWA survey are representative of producing wells in Weld Country. Moreover, and most importantly, there is no reason to assume that the typical venting-prone well has $v_{m/p}$ bounded by the median and mean for all 77 wells.

Indeed the full range of wells sampled show $v_{m/p}$ ranging from 4.11 to 260.2; ninety percent of the wells have $v_{m/p}$ between 8.79 and 61.7. Applying formulas 3-4 above together with lower bound for flashing emissions (reported in P12) yields a lower bound on methane venting emissions of 48 Gg/yr, well below any of the uncertainty ranges reported for the top-down estimates in P12. Moreover, even if one uses the average over the full ensemble of condensate tank flashing profiles reported, instead of the minimum, the estimated lower bound on methane venting emissions is 66 Gg/yr, still outside any of the uncertainty ranges reported for the top-down estimates in P12. Meanwhile, combining the observations of $a_{m/p}$ used in P12 with the full range of $v_{m/p}$ that characterizes potential venting-prone wells, yield no upper bound on methane venting emissions. Indeed it is entirely plausible that venting is biased toward wells with either high or low $v_{m/p}$, since those tend to characterize different types of production wells (gas and oil wells, respectively). The upshot is that, absent difficult to support assumptions about the composition of vented natural gas, the top-down methods used in P12 give no new constraints on methane emissions.

4. Constraining Methane Emissions

While P12 use only the observed C_1/C_3 ratio to constrain methane emissions, they note that the observed C_1/nC_4 (methane-to-butane) ratio can be used to do the same thing. In this section, we combine the observed C_1/C_3 and C_1/nC_4 ratios to remove the need to make assumptions about $v_{m/p}$, and hence better constrain estimates of methane emissions.

As in P12, we have

$$X_m/X_p = v_{m/p} \tag{5}$$

$$\frac{X_m + Y_m}{X_p + Y_p} = a_{m/p} \tag{6}$$

where we have defined $X_i = x_i/M_i$ for all species i in order to simplify our equations.

In addition, we have two similar constraints related to observed butane levels:

$$X_m/X_b = v_{m/b} \tag{7}$$

$$\frac{X_m + Y_m}{X_b + Y_b} = a_{m/b} \tag{8}$$

where $v_{m/b}$ is the ratio of methane to butane in vented gas, X_b is the number of moles of butane vented, Y_b is the number of moles released through condensate tank flashing, and $a_{m/b}$ is the observed ratio of methane to butane in air. We also define $a_{b/p} = a_{m/p}/a_{m/b}$.

To avoid the assumptions made in P12 about the composition of vented gas, we let

$$v_{m/p} = \sum_N Q_N v^N_{m/p} \tag{9}$$

$$v_{m/b} = \sum_N Q_N v^N_{m/b} \tag{10}$$

where N is an index that ranges over all wells, Q_N is the fraction of total venting due to well N, $v^N_{m/p}$ is the ratio of methane to propane in well N, and $v^N_{m/b}$ is the ratio of methane to butane in well N.

C_1/C_3 and C_1/nC_4 are consistently correlated in the 77 wells sampled in the GWA assessment [COGCC, 2007]. Specifically, if

$$v^N_{m/b} = b v^N_{m/p}, \tag{11}$$

we can estimate $b = 4.15\pm^{2.43}_{1.65}$ (95 percent confidence interval). In obtaining these values, we discard one outlying well for which C_1/C_3 (260) and C_1/nC_4 (2277) are much greater than for all other wells. (This observation indicates unusually dry gas for the area under investigation.) One can obtain a slightly better fit, and hence sharper constraints on X_i, by introducing a constant term in equation (11). Doing so, however, makes the analysis below considerably more complex and opaque while producing similar results.

Equation 11 can be substituted in equation 10, which can then be combined with equation 9 to yield

$$v_{m/b} = b v_{m/p} \tag{12}$$

Equations 5-8 and 12 can now be combined to yield

$$X_p = \frac{Y_b - Y_p a_{b/p}}{a_{b/p} - 1/b} \tag{13}$$

$$b X_b = X_p \tag{14}$$

$$X_m = a_{m/p} \frac{b Y_b - Y_p}{b a_{b/p} - 1} - Y_m \tag{15}$$

At a similar point in the P12 analysis, the authors continue by evaluating X_m for the maximum, minimum, and average values of Y_p and Y_m over their ensemble of 16 condensate tank flashing profiles, thus obtaining a range of estimates for X_m. In the present case, though, one finds that for all but one set of flashing profiles, the implied X_p (based on equation 13) is negative. Thus, in order to understand the full range of possible venting rates, we first need to determine the space of Y_m, Y_p, and Y_b for which X_m, X_p, and X_b are all non-negative. (We always assume, as in P12, that Y_m, Y_p, and Y_b are obtained by some linear combination of the 16 flashing profiles used in P12.) Specifically, we need to determine the sets of Y_m, Y_p, and Y_b that maximize and minimize implied X_m.

We find that X_m is maximized for $Y_m = 0.51$, $Y_p = 0.32$, and $Y_b = 0.17$. The similar values that minimize X_m depend on $a_{b/p}$. We find that for observations using the mobile lab ($a_{b/p} = 0.490$), X_m is minimized for $Y_m = 0.56$, $Y_p = 0.33$, and $Y_b = 0.16$, while for observations using the BAO ($a_{b/p} = 0.447$), X_m is minimized for $Y_m = 0.58$, $Y_p = 0.33$, and $Y_b = 0.16$ (detailed justifications for these figures are in the online supplementary materials).

Equation 15 now allows us to calculate the range of most likely values for X_m, and hence x_m. (We present no expected value within this range because we have no way of determining which values of Y_i are most likely.) We also estimate uncertainties (95 percent confidence intervals) in the maximum and minimum values for these ranges by propagating known uncertainties in b, $a_{m/p}$, and $a_{b/p}$. Uncertainties in $a_{m/p}$ are given in Table 3 of P12. Table 3 of P12 also reports uncertainties for $a_{b/p}$, but these exclude systematic uncertainty of as much as 20 percent (total) due to provisional calibration of the equipment used to measure n-butane concentrations (Gabrielle Petron, personal communication); we combine both sources of uncertainty in our estimates. The uncertainty for b reported above ($b = 4.15\pm^{2.43}_{1.65}$) is for a single well; the uncertainty for a sample with a large number of wells will be lower unless we assume that all wells are of the same profile. We estimate uncertainties both in the conservative case where all venting emissions come from wells with one consistent profile, and for the more realistic (but still arguably somewhat conservative) case where 100 different profiles are represented among wells that vent significantly. This is still somewhat conservative but it more likely to be more realistic, and reduces uncertainty in b by a factor of 10. Since b is only weakly correlated with $a_{m/p}$ — their correlation coefficient is 0.24, or 0.19 if we exclude wells drilled in the Sussex zone, which are rare — this is still much weaker than the implicit assumption made in P12 that wells that vent significantly have random $a_{m/p}$. The results are summarized in Table 2 and Figure 1.

With the exception of the combination of BAO observations and highly conservative uncertainty estimates, all of the inferred methane emissions rates are consistent with those derived from accepted bottom-up inventories, but inconsistent with the top-down estimates reported in P12. Indeed the method used here places considerably tighter constraints on methane emissions than previous ones have. The one exception is in the case of observations at the BAO using highly conservative uncertainty estimates: there, there remains a very small chance that annual methane venting emissions are greater than 118 Gg/yr. It is most likely, though, that this simply indicates that observations at a single point (the BAO) are insufficient to tightly constrain possible methane emissions across the entire Denver-Julesburg basin.

5. Conclusion

P12 infer from air measurements of methane-to-propane ratios that methane leakage from oil and gas operations in Weld County, Colorado, is considerably higher than previously believed. However, this inference is based on assumptions about the molecular profile of vented natural gas that lack support. Using observed methane-to-propane and butane-to-propane ratios, both of which are reported in P12, we have made independent estimates of methane emissions that do not rely on assumptions about the composition of vented gas. These estimates are largely consistent with previous bottom-up predictions of methane emissions from oil and gas operations. The coincidence of bottom-up and new top-down estimates reported here for estimates using the mobile lab, as well as the modest uncertainties in methane leakage inferred from those observations, also indicates the potential value of carefully monitoring alkane concentrations in air near oil and gas operations, particularly through sampling across entire areas of operations. Additional observations, including statistically meaningful samples of flashing emission profiles from condensate tanks, could be used to further constrain estimates of methane emissions. Moreover, the prominent role of uncertainty in $a_{b/p}$ in the analysis suggests that repeating the observations reported in P12 but with more careful calibration of n-butane measurements could further constrain estimates of alkane venting from oil and gas operations.

Appendix A: Online supplementary material to Comment on Hydrocarbon emissions characterization in the Colorado Front Range — A Pilot Study

Estimating methane emissions requires that we determine the sets of Y_m, Y_p, and Y_b that maximize and minimize implied X_m.

Denote the constituent emissions for the sixteen flashing profiles used in P12 as Y_m^L, Y_p^L, and Y_b^L, where L is an index that ranges from 1 to 16, and Y_i^L is rate of emissions of species i due to flashing that one would observe if all flashing emissions came from condensate tanks with the profile of tank L. The values for Y_i^L are given in Table 3. We have

$$Y_i = \sum_L P_L Y_i^L \tag{A1}$$

where P_L is the fraction of condensate tanks that generate flashing emissions with the same profile as that of tank L in the reference ensemble. To determine the set of P_L that maximizes implied X_m, note from equation 15 that X_m is linear in Y_m, Y_p, and Y_b. We thus have

$$X_m = \sum_L P_L X_m^L \tag{A2}$$

where X_m^L is X_m evaluated for $Y_i = Y_i^L$. Substituting the values of Y_i^L into A1 reveals that $X_m^{14} > X_m^L$ for all $L \neq 14$, which implies that X_m is maximized for $P_{14} = 1$ and $P_L = 0$ for $L \neq 14$. This corresponds to $Y_m = 0.51$, $Y_p = 0.32$, and $Y_b = 0.17$, all in Gmol/yr.

To determine the set of P_L that minimizes implied X_m, note from equation 13 that X_p is linear in Y_b and Y_p. We thus have

$$X_p = \sum_L P_L X_p^L \tag{A3}$$

where X_p^L is X_p evaluated for $Y_i = Y_i^L$. Substituting the values of Y_i^L into A3 reveals that $X_p^{14} > 0$ and $X_p^L < 0$ for all $L \neq 14$. In order to have $X_p > 0$, then, we must have $P_{14} > 0$. In addition, for any choice of Y_b and Y_p such that implied $X_p > 0$, we can lower the implied X_p and X_m by lowering P_{14} and increasing any of those P_L for which $X_m^L < 0$. This implies that X_m will be minimized for a set of P_L such that $X_p = 0$, or $Y_b = Y_p - a_{b/p}$.

We can rewrite equations A2 and A3 to get

$$X_m = \sum_{L \neq 14} P_L (X_m^L - X_m^{14}) + X_m^{14} \tag{A4}$$

$$X_p = \sum_{L \neq 14} P_L (X_p^L - X_p^{14}) + X_p^{14} \tag{A5}$$

Define $R_L = (X_m^L - X_m^{14})/(X_p^L - X_p^{14})$ for all $L \neq 14$. Note that R_L is maximized for $L = 8$. We now show that X_m is minimized only if $P_L = 0$ for all $L \notin \{8, 14\}$. To do that, assume that we have some set of P_L than minimizes X_m. For any $K \notin \{8, 14\}$, decreasing P_K by Δ while increasing P_8 by $\Delta(X_p^K - X_p^{14})/(X_p^8 - X_p^{14})$ and P_{14} by $\Delta(X_p^8 - X_p^K)/(X_p^8 - X_p^{14})$, where Δ is an arbitrarily small positive number, leaves $X_p > 0$. It does, however, decrease X_m by $(X_p^{14} - X_p^K)/(R_8 - R_K)$. This implies that X_m could only have been a minimum if P_L was zero for all $L \notin \{8, 14\}$ in the first place.

We thus know that X_m is minimized for some P_L such that P_8 and P_{14} are nonzero and $P_L = 0$ for all other L. As noted above, this minimum will occur as X_p approaches zero. We can thus calculate P_8 and P_{14} that minimize X_m for each possible value of $a_{b/p}$. For observations made using the mobile lab ($a_{b/p} = 0.490$), this is obtained for $P_8 = 0.10, P_{14} = 0.90$ ($Y_m = 0.56$, $Y_p = 0.33$, $Y_b = 0.16$). For observations using the BAO ($a_{b/p} = 0.447$), this is obtained for $P_8 = 0.14$ and $P_{14} = 0.86$ ($Y_m = 0.58$, $Y_p = 0.43$, $Y_b = 0.16$).

References

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Figure 1. Estimated methane emissions from venting in Gg/yr. Top plot shows top-down estimates based on mobile lab observations; middle plot shows top-down estimates based on BAO observations; lower plot shows bottom-up estimates from P12. Shaded boxes show range of expected values (due to irreducible uncertainty in flashing emissions). Solid lines show 95 percent confidence intervals for expected values with realistic assumptions about variation of $\nu_{b/p}$ among venting-prone wells as described in the text; dashed lines show 95 percent confidence intervals under the more conservative assumption that all wells that vent have the same $\nu_{b/p}$.

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Table 1. Estimates of Methane Emissions From P12 in Gg/yr

	Bottom Up Emissions			Top Down Venting Emissions		
	Flashing	Venting	Flashing + Venting	$v_{m/p}$=18.75	$v_{m/p} = 15.43$	$v_{m/p} = 24.83$
Average	11.2	53.1	64.3	118.4	157	92.5
Minimum	4	42	46	86.5	114.7	67.6
Maximum	23	63	86	172.6	228.9	134.9

Table 2. Revised Estimates of Methane Emissions in Gg/yr

	Mobile Lab			BAO		
	Expected	Realistic Errors	Conservative Errors	Expected	Realistic Errors	Conservative Errors
Maximum	52.5	+15.9/-10.9	+19.5/-11.0	58.8	+20.1/-12.8	+62.2/-13.8
Minimum	46.4	+4.4/-3.9	+4.5/-3.9	49.4	+2.9/-9.6	+28.5/-9.9

Table 3. Flashing Profiles For Reference Tank Ensemble

Tank #	Y_m	Y_p	Y_b
1	1.537	0.424	0.107
2	0.369	0.498	0.173
3	0.551	0.476	0.168
4	0.787	0.383	0.135
5	0.235	0.446	0.145
6	0.611	0.411	0.079
7	0.501	0.398	0.147
8	1.034	0.355	0.095
9	1.357	0.393	0.120
10	0.810	0.378	0.109
11	0.271	0.396	0.146
12	0.749	0.38	0.125
13	1.122	0.396	0.125
14	0.507	0.322	0.167
15	0.352	0.463	0.171
16	0.427	0.544	0.168