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Supporting Information for

Identifying Abnormal Tank Emissions Using Ethane to Methane Signatures of Oil and Natural Gas Production in the Permian Basin

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Introduction

The supplemental information contains the following:

S1. Detailed explanation of the CH_4 and C_2H_6 parsing method

S2. More details of Sites S02/S03 on 22 January 2020

S1. Multiple EMR Signatures Parsing Method

This section describes the derivation of equations used to parse the total CH_4 emission to contributing sources from sites with two EMRs. In order to separate the EMR signals, principal component analysis (PCA) was performed. PCA was used to identify distinct groups which were subsequently analyzed separately. The results from an example of such an analysis are shown in Figure S1. Analysis of the wind direction data was used to identify the probable sources based on site notes and photographs when possible. Figure S1 shows an example of a site with distinct wind directions associated with each signal.

The following sections describes the system of equations used to solve for the individual fluxes. All fluxes are in units of mol/s and EMRs are in fractional form. Eqs. 1.1-1.4 represent the initial system of equations (4 equations, 4 unknowns). In Eq. 1.1 $F_{CH_4,T}$ is the total CH_4 flux at a given site, $F_{CH_4,A}$ is the CH_4 flux corresponding to signal A and $F_{CH_4,B}$ is the CH_4 flux corresponding to signal B. The analogous components of the total C_2H_6 flux ($F_{C_2H_6,T}$) are represented using A and B subscripts in Eq. 1.2. The ratio between the signal A and B C_2H_6 and CH_4 fluxes are constrained by the observed EMRs for signal A and B in Eqs. 1.3 and 1.4. Rearranging Eqs. 1.3 and 1.4 and substituting into 1.2 yields Eq. 2.1. Rearranging Eq. 2.1 to solve for $F_{CH_4,B}$ gives Eq. 2.2. Substituting Eq. 2.2 into Eq. 1.1 gives Eq. 3.1, which contains only one unknown, $F_{CH_4,A}$. Eqs. 3.2-3.4 show the process of solving for $F_{CH_4,A}$ and the final equation for $F_{CH_4,A}$ is given in Eq. 4. From this step, Eqs 1.1, 1.3 and 1.4 can be solved to produce all four unknowns.

$$F_{CH_4,A} + F_{CH_4,B} = F_{CH_4,T} \qquad \text{Eq. 1.1}$$

$$F_{C_2H_6,A} + F_{C_2H_6,B} = F_{C_2H_6,T} \qquad \text{Eq. 1.2}$$

$$\frac{F_{C_2H_6,A}}{F_{CH_4,A}} = EM_A \qquad \text{Eq. 1.3}$$

$$\frac{F_{C_2H_6,B}}{F_{CH_4,B}} = EM_B \qquad \text{Eq. 1.4}$$

$$F_{CH_4,A} \times EM_A + F_{CH_4,B} \times EM_B = F_{C_2H_6,T} \qquad \text{Eq. 2.1}$$

$$F_{CH_4,B} = \frac{F_{C_2H_6,T} - F_{CH_4,A} \times EM_A}{EM_B} \qquad \text{Eq. 2.2}$$

$$F_{CH_4,A} + \frac{F_{C_2H_6,T} - F_{CH_4,A} \times EM_A}{EM_B} = F_{CH_4,T} \qquad \text{Eq. 3.1}$$

$$F_{CH_4,A} + \frac{F_{C_2H_6,T}}{EM_B} - \frac{F_{CH_4,A} \times EM_A}{EM_B} = F_{CH_4,T} \qquad \text{Eq. 3.2}$$

$$F_{CH_4,A} - \frac{F_{CH_4,A} \times EM_A}{EM_B} = F_{CH_4,T} - \frac{F_{C_2H_6,T}}{EM_B} \qquad \text{Eq. 3.3}$$

$$F_{CH_4,A}\left(1 - \frac{EM_A}{EM_B}\right) = F_{CH_4,T} - \frac{F_{C_2H_6,T}}{EM_B} \qquad \text{Eq. 3.4}$$

$$F_{CH_4,A} = \frac{F_{CH_4,T} - \frac{F_{C_2H_6,T}}{EM_B}}{\left(1 - \frac{EM_A}{EM_B}\right)} \qquad \text{Eq. 4}$$

Due to the assumptions that go into emission calculations combined with reliance on additional meteorological data, the error associated with emission calculation is much higher than the error associated with EMRs. This can result in situations where the site combined EMR as determined from the ratio of the molar C_2H_6 and CH_4 fluxes is higher or lower than should be possible. For example, Site 1030 S03 (see Table S1) has a flux EMR of 13.2% while the contributing signals from the regression analysis are 47% and 15.1%. The combined site EMR should be within these two limits. However, the error on the flux EMR is also large. By adding the expected OTM 33A error estimates calculated by Edie et al., (2020) in quadrature the resulting error on the flux EMR is +76%/-37%.

Error on the calculated CH_4 and C_2H_6 fluxes for signals A and B arises primarily from the error on the total flux calculations and the addition/subtraction terms. Errors from addition/subtraction are propagated by added the absolute error in quadrature, and thus will differ based on the magnitude of each site. As an example, the 95% CI on the CH_4 and C_2H_6 fluxes for 0122 S03 is ±177% for Signal A and ±52% for Signal B. In this case, the contribution of Signal A is not statistically significant. For 1030 S02 the 95% CI on the CH_4 and C_2H_6 fluxes is ±190% for Signal A and ±68% for Signal B. Again, Signal A is not statistically significant.

S2. Sites S02/S03 on 22 January 2020

This section presents further discussion of the case study on 22 January 2020 (Section 3.1 in the main text) where a site was measured twice, and the second measurement produced results with two EMR signals. The CH_4 emissions calculated by OTM 33A actually decreased from S02 to S03 by 16%. These emission rates are not ideal for comparison because Gaussian theory predicts that the signals for both sources should be partially mixed along the road. Because the tank signal is not observable in the S02 data, this emission rate may be attributable to the separator, however, it is also possible that the tank signal was diluted and impossible to distinguish from the dominant separator signal. S03 shows clear signal mixing so it does not solely represent the emission from the tank. Using the parsing method, the contribution of the total CH_4 emission from the tank to the S03 emission is small (7% of the total emissions). This suggests the repositioning to catch the tank signal excluded some of the overall CH_4 emission, which appeared to primarily be coming from a separator.

In order to investigate this attribution further, we analyzed the pre-measurements transects. Because the transects represent individual realizations of the plume, the observed plumes are narrower than the Gaussian model predicts. The Gaussian plume model is meant to predict an average plume profile over ~20 minutes (Fritz et al., 2005). For the narrow transect plumes, the individual plumes can be isolated and quantified. We had only two transects to analyze and there is significant uncertainty of emissions from this approach with few transects (Caulton et al., 2018). Regressing the transect data shows that the plumes have distinct EMRs, with the tank producing a clear ratio ~21% (Figure S2). The separator signal is more variable, but is clearly the source of the ~3% signal (Figure S2). Based on the transect source specific emission estimates, the tank contributed 13% of the total site emissions, in line with the estimate from the parsing method.

References

Caulton, D. R., Li, Q., Bou-Zeid, E., Lu, J., Lane, H. M., Fitts, J. P., et al. (2018). Quantifying uncertainties from mobile-laboratory-derived emissions of well pads using inverse Gaussian methods. *Atmospheric Chemistry and Physics*, *18*(20), 15145–15168. https://doi.org/10.5194/acp-18-15145-2018

Edie, R., Robertson, A. M., Field, R. A., Soltis, J., Snare, D. A., Zimmerle, D., et al. (2020). Constraining the accuracy of flux estimates using OTM 33A. *Atmospheric Measurement Techniques*, *13*(1), 341–353. https://doi.org/10.5194/amt-13-341-2020

Fritz, B. K., Shaw, B. W., & Parnell, C. B. (2005). INFLUENCEOF METEOROLOGICAL TIME FRAMEANDVARIATIONON HORIZONTAL DISPERSION COEFFICIENTSIN GAUSSIAN DISPERSION MODELING. *Transactions of the American Society of Agricultural Engineers*, *48*(3), 1185–1196. https://doi.org//10.13031/2013.18501

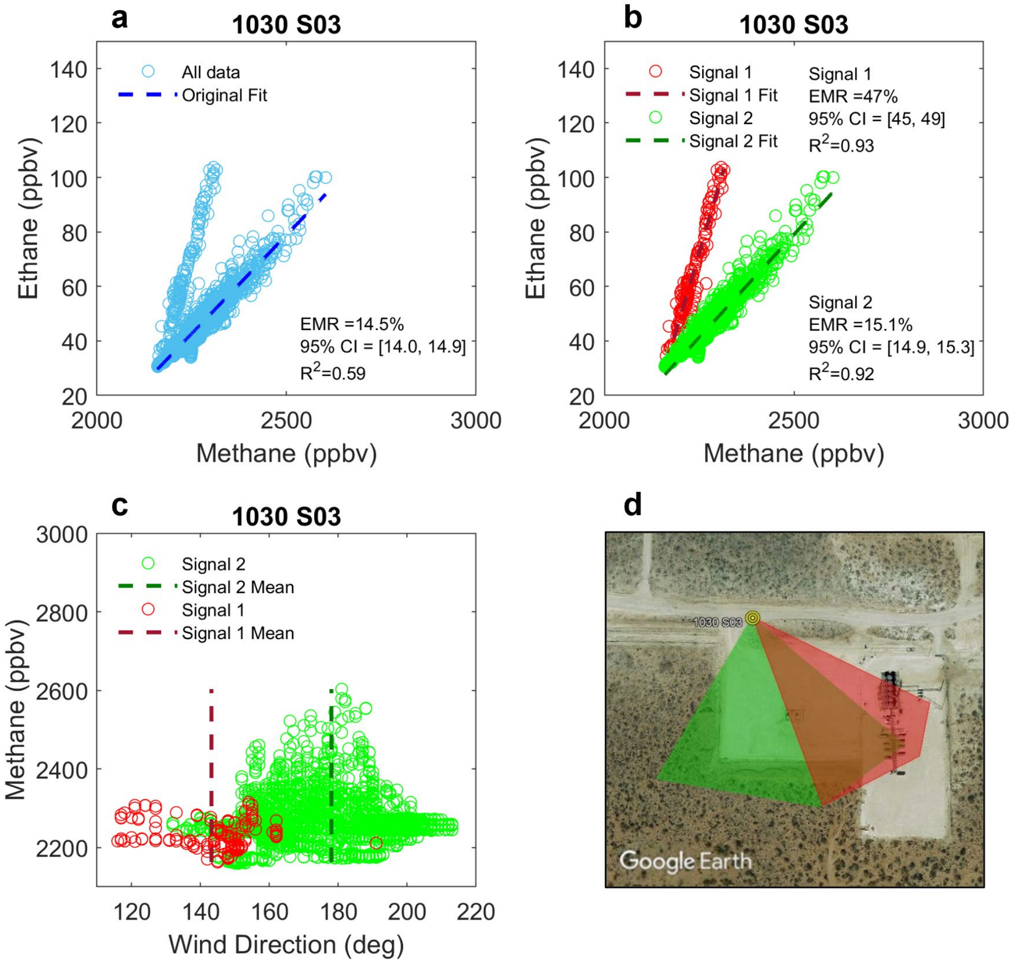

Figure S1. Scatter plot of data for site S03 sampled on 30 Oct. 2020 showing (a) two distinct signals that are not captured by single regression, (b) the signal parsed using PCA, (c) the wind direction data associated with each signal, and (d) the wind direction projected onto site imagery from Google Earth (© Google).

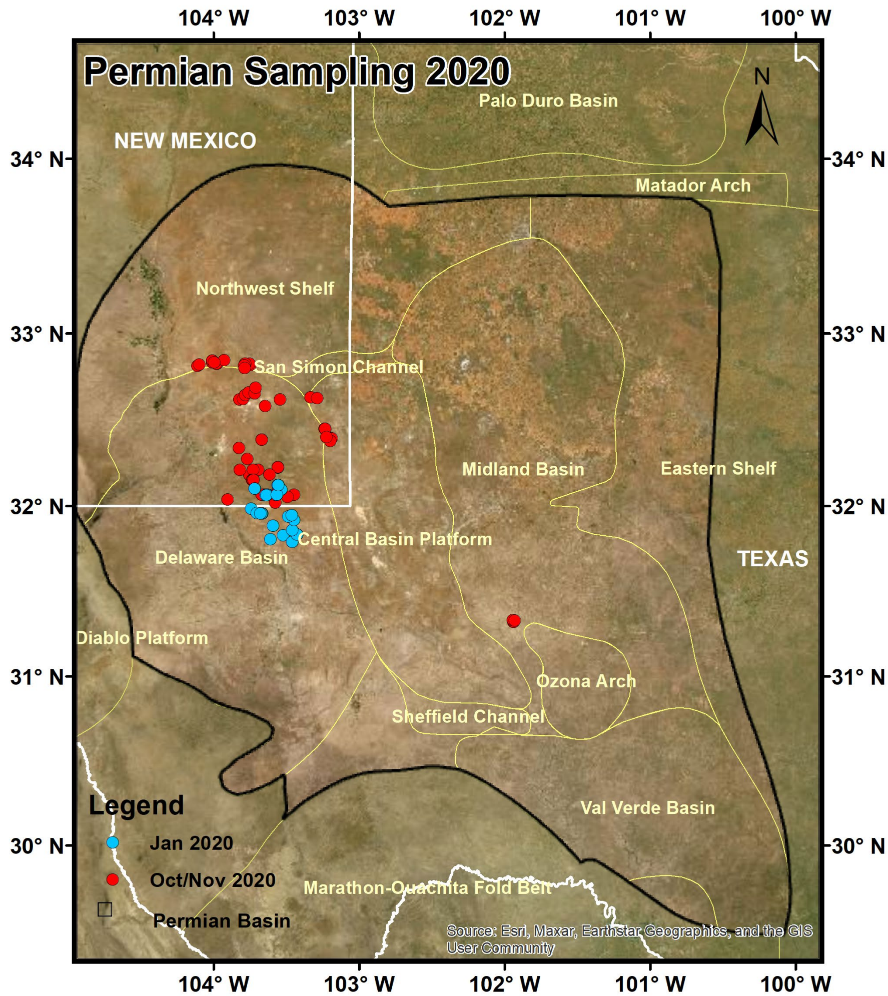

Figure S2. Sampling locations in the Permian Basin in 2020 relative to the entire region. The Permian basin extent is denoted by the thick black line, while individual formations are outlined in yellow. State and international boundary lines are shown in white. The red and blue markers represent the sites sampled. This map was created using ESRI ArcMap 10.8.1 and follows their attribution requirements and terms of use for academic publications, which are available here: https://doc.arcgis.com/en/arcgis-online/reference/static-maps.htm#ESRI_SECTION1_21347CA4FAB14A7E95CE6B738DCA2843

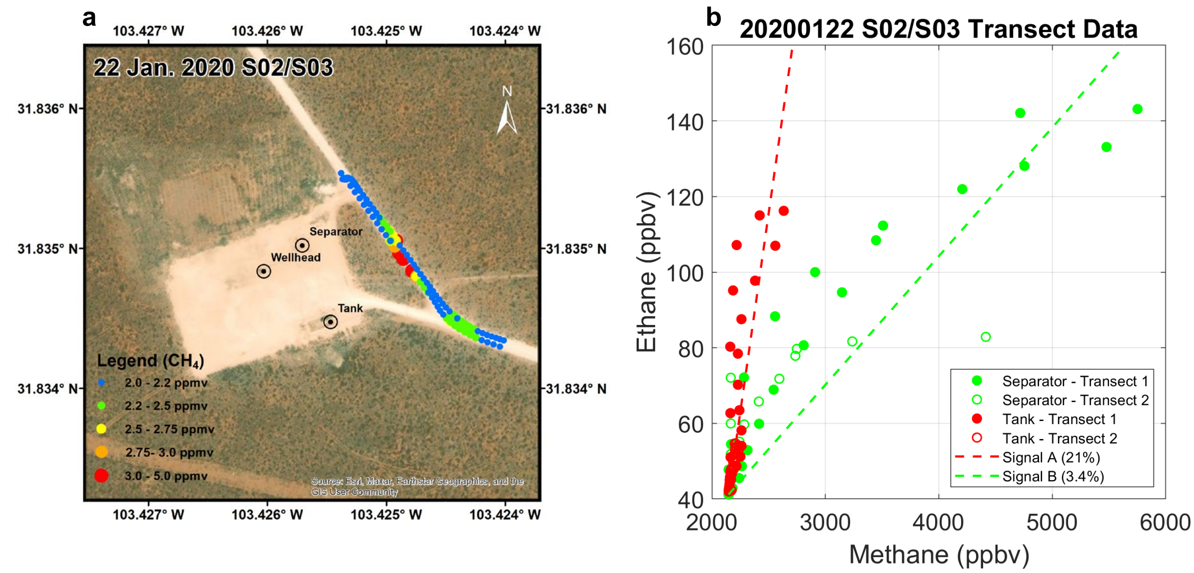

Figure S3. Panel (a) shows an image of sites S02/S03 on 22 Jan. 2020 with the sources on site indicated and the downwind transect colored by CH_4 enhancements. The nominal wind direction was ~245º (SW). This map was created using ESRI ArcMap 10.8.1 and follows their attribution requirements and terms of use for academic publications. Panel (b) shows the regression of the transect data. Plumes have been attributed to the separator and tanks and the ratios from the regression analysis of the OTM have been plotted.

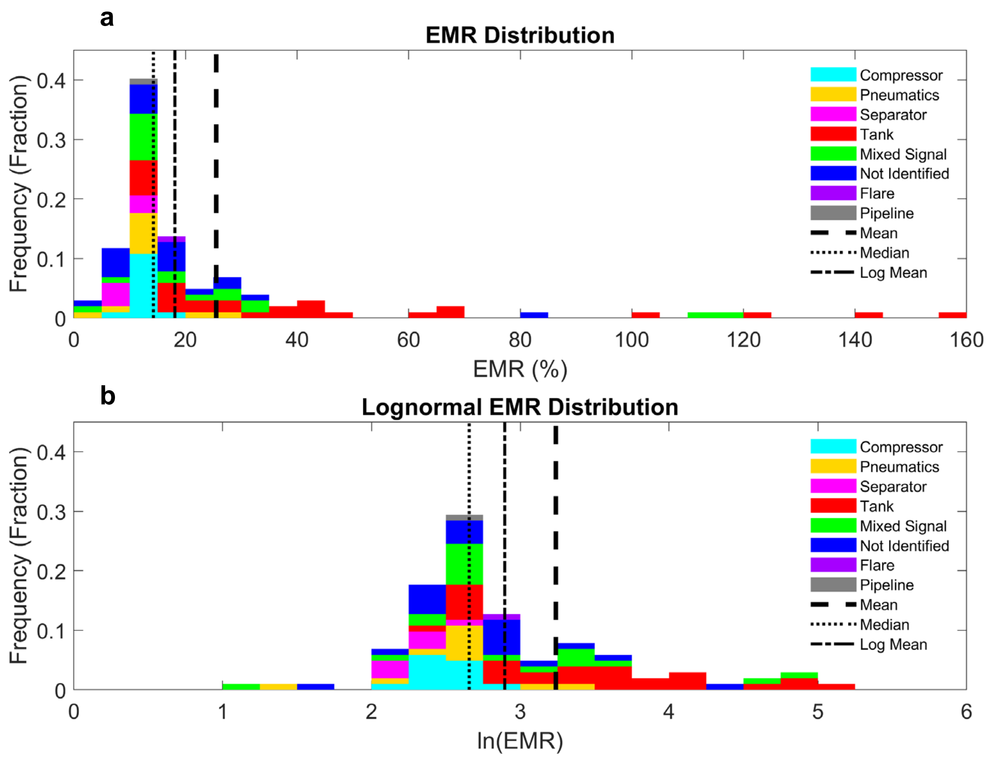

Figure S4. Distribution of EMRs on (a) normal and (b) lognormal axes. Colors represent the contribution to each bin from the specific source type. Also shown are the mean (black dash), median (black dot) and logarithmic mean (black dot/dash) lines.

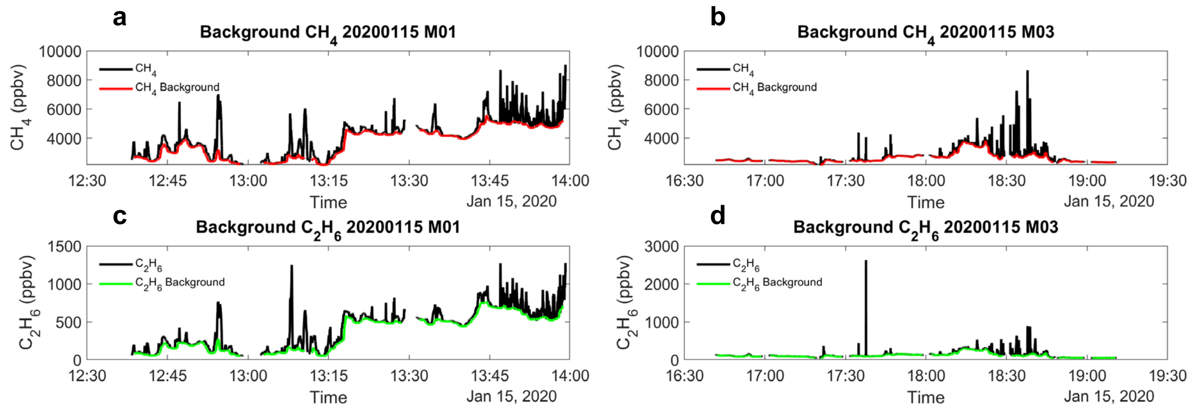

Figure S5. Plots showing the calculated background values for CH_4 (a/b) and C_2H_6 (c/d).

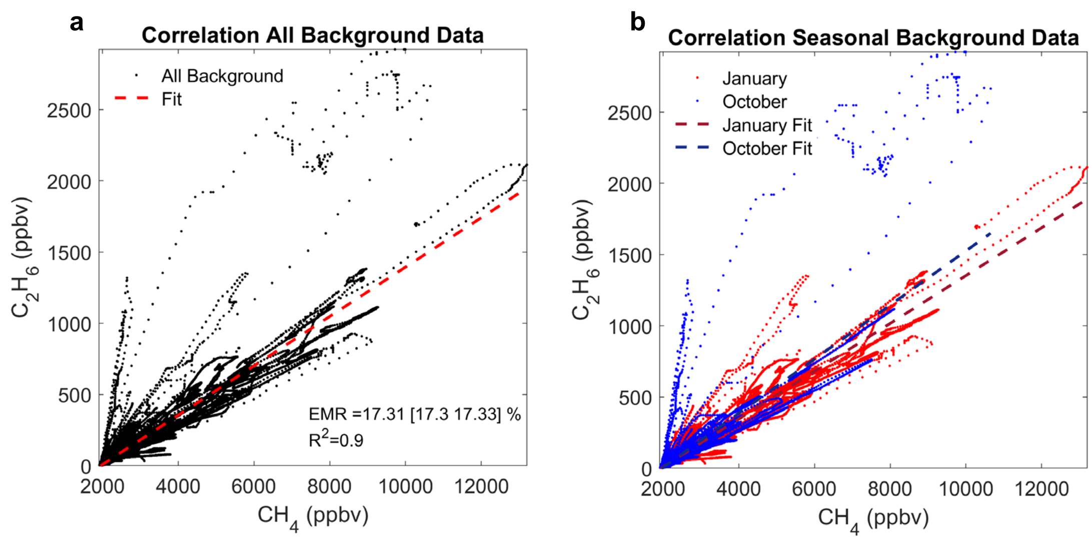

Figure S6. Correlation plots for (a) all background data and (b) background data colored by season collected.

Table S1. Sites with two EMRs and the associated CH_4 and C_2H_6 fluxes for sites where both signals were significant (R^2>0.65).

Site	Signal	EMR (± 95% CI)	R^2	CH_4 Flux (kg hr^{-1})*	C_2H_6 Flux (kg hr^{-1})*	Flux EMR (%)†	Probable Source‡
0115 S01	**Total**	**14.6 (0.3)**	**0.82**	**N/A**	**N/A**	**--**	**Unknown (Tanks, Separator & Compressor present)**
	A	*29.1 (0.8)*	*0.92*	--	--		*CND*
	B	*14.7 (0.1)*	*0.96*	--	--		*CND*
0122 S03	**Total**	**3.32 (0.07)**	**0.82**	**2.02**	**0.18**	**4.7**	**Tank & Pneumatic**
	A	*21 (1)*	*0.9*	*0.14*	*0.06*		*Tank*
	B	*3.48 (0.06)*	*0.9*	*1.88*	*0.12*		*Pneumatic*
1030 S02	**Total**	**11.0 (0.4)**	**0.60**	**1.97**	**0.54**	**14.7**	**Tank & Compressor**
	A	*43 (6)*	*0.71*	*0.25*	*0.20*		*Tank*
	B	*10.6 (0.1)*	*0.94*	*01.72*	*0.34*		*Compressor*
1030 S03	**Total**	**14.5 (0.5)**	**0.59**	**0.58**	**0.15**	**13.2**	**No obvious source (Tanks, Wellhead & Compressor present)**
	A	*47 (2)*	*0.93*	*0*	*0*		*Tanks*
	B	*15.1 (0.2)*	*0.92*	*0.58*	*0.15*		*Compressor/ Wellhead*
1101 S01	**Total**	**10.1 (0.3)**	**0.64**	**N/A**	**N/A**	**--**	**Tank & Separator**
	A	*33 (1)*	*0.86*	--	--		*Tank*
	B	*8.6 (0.1)*	*0.96*	--	--		*Separator*
1103 S04	**Total**	**10.1 (0.2)**	**0.85**	**1.90**	**0.36**	**10.0**	**Tank & Compressor**
	A	*157 (6)*	*0.73*	*0*	*0*		*Tank*
	B	*10.6 (0.1)*	*0.95*	*1.90*	*0.36*		*Compressor*
1105 S06	**Total**	**59 (3)**	**0.43**	**N/A**	**N/A**	**--**	**Tank, Separator, & Intermittent Flare**
	A	*116 (6)*	*0.81*	--	--		*CND*
	B	*15.8 (0.4)*	*0.77*	--	--		*CND*

* Error estimates for OTM 33A derived fluxes are reported to be +54%/-26% (Edie et al., 2020).
† Error estimates for the OTM 33A derived EMRs are calculated to be +76%/-37%.
‡ CND = Could not distinguish. This means that the wind direction did not show sufficient separation and/or sources on site were too close to reasonably distinguish by wind direction analysis.

Table S2. Sites with two EMRs and the associated CH_4 and C_2H_6 Fluxes for sites where only one signal was significant (R^2>0.65).

Site	Signal	EMR (%) (± 95% CI)	R^2	CH_4 Flux (kg hr^{-1})*	C_2H_6 Flux (kg hr^{-1})*	Flux EMR (%)†	Probable Source‡
0116 T02	**Total**	**31.4 (0.8)**	**0.68**	**19.1**	**10.8**	**30.2**	**Unknown**
	A	*33 (4)*	*0.50*	--	--		
	B	*14.3 (0.2)*	*0.90*	--	--		
0117 S01	**Total**	**12.9 (0.3)**	**0.74**	**2.43**	**0.83**	**18.2**	**Compressor (also Separator and Wellhead on site)**
	A	*14.0 (0.2)*	*0.93*	--	--		*CND*
	B	*2.3 (0.3)*	*0.57*	--	--		*CND*
0118 S01	**Total**	**2.2 (0.1)**	**0.35**	**0.28**	**0.03**	**5.5**	**Unknown (Tanks, Combustor and Wellhead on site)**
	A	*25.0 (0.8)*	*0.69*	--	--		*Combustor/ Tanks*
	B	*1.6 (0.3)*	*0.27*	--	--		*Wellhead*
0120 S07	**Total**	**5.9 (0.2)**	**0.64**	**0.39**	**0.07**	**9.6**	**Unknown (Tanks, Compressor, and Wellhead on site)**
	A	*9.7 (0.1)*	*0.91*	--	--		*CND*
	B	*0.8 (0.5)*	*0.41*	--	--		*CND*
1105 S01	**Total**	**3.9 (0.2)**	**0.58**	**0.47**	**0.06**	**6.9**	**Tank (Oil derrick on site)**
	A	*8.7 (0.2)*	*0.87*	--	--		*CND*
	B	*3.6 (0.3)*	*0.60*	--	--		*CND*

*Error estimates for OTM 33A derived fluxes are reported to be +54%/-26% (Edie et al., 2020) and +170%/-50% for transect derived fluxes (Caulton et al., 2018).

† Error estimates for the OTM 33A derived EMRs are calculated to be +76%/-37%.

‡ CND = Could not distinguish. This means that the wind direction did not show sufficient separation and/or sources on site were too close to reasonably distinguish by wind direction analysis.

Table S3. Source categories and the full observations recorded for each site

Source Category	Serial Date	Site	Full Observations
Compressors	20201029	S01	Compressor
	20201030	S03	Compressor
	20201030	S04	Compressor
	20201030	S05	Compressor
	20201030	S06	Compressor
	20201103	S01	Compressor
	20201103	S02	Compressor
	20201103	S03	Compressor
	20201115	S01	Compressor
	20200117	S01	Emissions from compressor stack
	20200120	S01	Emissions from compressor stack
	20200117	T01	Emissions from compressor stack
	20200120	T01	Emissions from compressor stack
Pneumatics	20201031	S02	Emissions from pump wellhead
	20201031	S06	Emissions from pneumatic near pump wellhead
	20200123	S02	Emissions from pneumatic valves on several separators
	20200123	S03	Emissions from pneumatics on separator
	20200123	S04	Emissions from pneumatics on separator
	20200123	S05	Emissions from pneumatics on separators
	20201115	S02	Kimray pneumatic in front of wellhead
	20201115	S05	Pneumatic on separator
	20201108	S02	Pneumatic valve
	20201106	S03	Pneumatic valves near separators
Separators	20201031	S01	Emissions from separator - separator was rusty and had a large nest built on it
	20201105	S03	Separator
	20201105	S04	Separator
	20201105	S05	Separator
	20201110	S02	Separator
	20201110	S06	Separator
Tanks	20200120	S03	Combustor stack on processing tank
	20200118	S02	One of tanks, base of burner
	20201102	S04	Back of tanks - stopped emitting before we could find with FLIR
	20200122	S04	stack on tanks
	20200122	S05	Emissions from stack on tank battery
	20201102	S02	2 tank vent pipes
	20201031	S03	Emissions from tank vent
	20201105	S01	Lower vent hatch on tank
	20201030	S07	Large continuous emissions from tank vent
	20201102	S01	Tank vent
	20201106	S02	Tank vent pipe
	20201107	S05	Tank vent pipe
	20201107	S06	Tank vent pipe
	20201101	S02	Tank vent pipe
	20201025	S01	Vent pipe on tank
	20201106	S01	Tank vent pipes
	20201112	S03	3 tank thief hatches
	20201112	S04	3 tank thief hatches
	20201115	S03	Tank thief hatch
	20201115	S04	Tank thief hatch
	20201105	S02	Tank thief hatch

	20201107	S02	Tank thief hatch
	20201104	S01	Thief hatches on tanks
	20201104	S02	Thief hatches on tanks
	20201107	S01	Thief hatches on tanks
Mixed Signal	20201102	S03	Tank vent pipe and separator
	20201110	S03	Tank thief hatch and pipe going into produced saltwater tan
	20201107	S07	Tank thief hatch and pneumatics near separators
	20201110	S04	Tank thief hatch, pneumatic on separator, and torn pipe going into separator
	20201110	S05	Tank thief hatch, pneumatic on separator, and torn pipe going into separator
	20200120	T03	Leaking from flare, pneumatic valve on separator, and tank vent
	20201105	S06	2 of the separators, vent pipes on 2 of the tanks
	20200109	S01	Leaking everywhere (seps, flare, tanks)
	20200120	S04	Leaking from flare, pneumatic valve on separator, and tank vent
	20200122	S06	Intermittent emissions from flare, emissions from stacks on tanks
	20201112	S02	Flare, thief hatch, tanks
	20200122	S02	Emissions from pneumatic valve on separator and from thief hatch on tanks
	20200122	S03	Emissions from pneumatic valve on separator and from thief hatch on tanks
	20201030	S02	Compressor and tank vent
	20201101	S01	Continuous emissions from tank vent pipe, intermittent emissions from separator
	20201112	S01	3 front tanks, tall back tank, and compressor
	20201103	S04	Compressor and produced saltwater tank
	20201107	S03	Combustor and tank vent pipe
	20201107	S04	Combustor and tank vent pipe
	20201108	S01	Emissions from compressor box near tanks, but flare emitting a lot more
Not Identified	20200123	S01	No obvious source
	20200115	S01	No obvious source
	20200115	S02	No obvious source
	20200120	S02	No obvious source
	20200120	S05	No obvious source
	20200120	S06	No obvious source
	20200120	S07	No obvious source
	20200122	S07	No obvious source
	20201030	S01	No obvious source
	20201031	S05	No obvious source
	20201107	S08	No obvious source
	20201108	S03	No obvious source
	20200120	T04	No obvious source
	20201110	S01	No obvious source
	20201106	S04	No obvious source
	20200118	S01	No obvious source
	20200109	S02	Blank (Aborted)
	20200116	T01	Blank (Transect)
	20200116	T02	Blank (Transect)
	20200116	T03	Blank (Transect)
	20200120	T02	Blank (Transect)

Table S4. EMR and CH_4 Statistics by Source Category

Source	EMR (%)				CH_4 Emission (kg hr^{-1})			n (CH_4)*
	Mean	Weighted Mean	Median	Std. error	Mean	Median	Std. error	
Compressor	12.3	12.4	11.6	0.6	4	2	1	13 (12)
Pneumatics	14	11	13	2	0.7	0.5	0.3	11 (6)
Separator	9.8	9.1	9.5	0.5	0.8	0.5	0.4	7 (5)
Tanks	44	17	27	7	12	1	5	29 (18)
Mixed Signal	27	14	14	7	21	3	17	19 (9)
None	19	16	15	3	2.1	1.8	0.6	21 (11)
Flare	16.3	--	--	--	1.1	--	--	1 (1)
Pipeline Leak	13.7	--	--	--	28	--	--	1 (1)

* n = the number of EMR observations. The number in parentheses is the number of CH_4 emission rate observations.

Table S5. EMR and CH_4 Statistics for Tanks

Tanks	EMR (%)		CH_4 Emission (kg hr^{-1})		Gas Production (Mfc $month^{-1}$)		n (CH_4)*
	Mean	Std. error	Mean	Std. error	Mean	Std. error	
Low EMR	16	1	25	10	4,138	2,016	12 (8)
High EMR	63	10	0.7	0.2	9,040	3,634	17 (12)

* n = the number of EMR observations. The number in parentheses is the number of CH_4 emission rate observations.