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Hydrocarbon and Carbon Dioxide Fluxes from Natural Gas Well Pad Soils and Surrounding Soils in Eastern Utah

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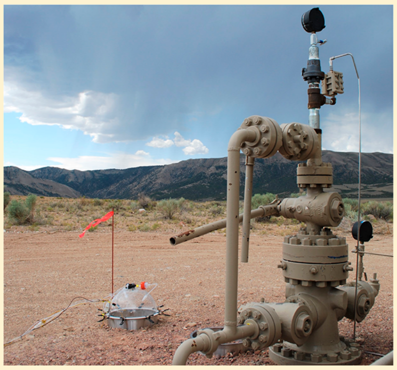
Supporting Information

ABSTRACT: We measured fluxes of methane, nonmethane hydrocarbons, and carbon dioxide from natural gas well pad soils and from nearby undisturbed soils in eastern Utah. Methane fluxes varied from less than zero to more than 38 g m^{-2} h^{-1}. Fluxes from well pad soils were almost always greater than from undisturbed soils. Fluxes were greater from locations with higher concentrations of total combustible gas in soil and were inversely correlated with distance from well heads. Several lines of evidence show that the majority of emission fluxes (about 70%) were primarily due to subsurface sources of raw gas that migrated to the atmosphere, with the remainder likely caused primarily by re-emission of spilled liquid hydrocarbons. Total hydrocarbon fluxes during summer were only 39 (16, 97)% as high as during winter, likely because soil bacteria consumed the majority of hydrocarbons during summer months. We estimate that natural gas well pad soils account for 4.6×10^{-4} (1.6×10^{-4}, 1.6×10^{-3})% of total emissions of hydrocarbons from the oil and gas industry in Utah's Uinta Basin. Our undisturbed soil flux measurements were not adequate to quantify rates of natural hydrocarbon seepage in the Uinta Basin.



INTRODUCTION

Oil and natural gas operations are significant sources of emissions of greenhouse gases[1−4] and pollutants that impair air quality,[5−7] including the air quality of eastern Utah.[8−10] Characterization of oil and gas industry emission sources is needed to better understand their potential impact on climate change and air quality,[11,12] and to provide operators with information that allows them to increase efficiency and reduce emissions.

While emissions from many potential oil and gas-related sources have been studied extensively, emissions from oil and gas well pad soils have been measured only infrequently,[13] and most work to date has focused on plugged and abandoned wells.[14−17] In October 2015, a subsurface casing failure at Southern California Gas Company's well SS-25 in the Aliso Canyon Storage Field near Los Angeles, California resulted in extremely high soil emissions of natural gas. 97,100 tonnes of natural gas were emitted before the leak was contained,[18] highlighting the potential importance of well pad soil emissions and the necessity of quantifying this emission source. Emissions from well pad soils (in excess of what is natural) could originate from failure of subsurface infrastructure, as was the case in Aliso Canyon,[18] or from re-emission of liquid hydrocarbons spilled on the soil.[19] Ingraffea et al.[20] and Jackson[21] indicate that possible sources of subsurface infrastructure failure include (1) failure of cement due to inappropriate cement density, inadequately cleaned boreholes, premature gelation, cement fluid loss, high permeability, shrinkage, radial cracking because of pressure changes, poor bonding with rock or casing, or age-related deterioration and (2) casing failure due to leaking joints, casing collapse, or corrosion.

In addition to studies of the Aliso Canyon leak, several other studies have quantified emissions of natural gas from well pad soils. Day et al.[13] used a flux chamber to measure methane flux from well pad soils on active oil and gas wells in Australia, but they did not detect any emissions. Kang et al.[15] used a flux chamber to measure methane flux from abandoned oil and gas wells in Pennsylvania. They observed significant emissions and found that abandoned wells could constitute 4−7% of total anthropogenic methane emissions in the state. Their chamber enclosed not just soil, but also above-ground well heads, so emissions from soil alone cannot be determined from this study. Boothroyd et al.[16] measured surface soil gas concentrations of methane at plugged and abandoned wells in the U.K., and estimated fluxes based on Fick's law. They estimated

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emissions of 15 ± 28 kg methane well^{-1} year^{-1}. Townsend-Small et al.[17] measured emissions from abandoned wells in Ohio, Wyoming, Colorado, and eastern Utah. They found that only 6.5% of plugged wells emitted methane, but their prescreening method may have resulted in omission of wells with low emissions. They estimated that emissions from abandoned wells account for 0.01–0.03% of total methane emissions in Utah's Uinta Basin. While the results of these studies vary, they indicate that soil emissions can be significant in some cases, at least for abandoned wells. Soil emissions from abandoned wells tend to have a non-normal, heavy-tailed distribution,[17] as do many oil and gas-related emissions data sets.[22−24]

In this Research Article, we discuss measurements of soil emissions from active and shut-in natural gas wells in eastern Utah. We used a dynamic flux chamber to measure methane, nonmethane hydrocarbon (NMHC), and carbon dioxide fluxes at 31 natural gas wells. We visited some of these wells several times from 2013 to 2016. For comparison, we also measured fluxes from undisturbed soils within active oil and gas fields and from several hydrocarbon-bearing outcrops. We discuss these results below, including analyses of the spatial and temporal variability in fluxes, influence from soil bacteria on the composition of emitted gases, probable subsurface sources of observed fluxes, and the importance of well pad soil emissions relative to the remainder of the oil and gas industry.

■ METHODS

Study Locations. We measured soil fluxes at wells in the Uinta Basin (n = 17), Paradox Basin (n = 5), and Clay Basin (n = 9) of eastern Utah during 2013–2016. Prior to our visits, scientists at the United States Geological Survey's (USGS) Utah Water Science Center measured concentrations of total combustible gas in soil at a larger subset of wells in these basins (n = 220 wells), as they have done elsewhere.[25] Selection of wells sampled by USGS was random in that they had no prior knowledge about which wells or fields might have higher or lower soil gas concentrations. We visited a subset of wells sampled by USGS. We did not select wells to visit randomly. Instead, we purposely chose wells with a range of measured total combustible soil gas concentrations and several operational states. We measured fluxes from the well pads of producing, shut-in, and storage wells. Producing wells were listed by the Utah Division of Oil, Gas, and Mining as actively producing natural gas during the month of our visit. Shut-in wells were listed as shut-in during the month of our visit, meaning that the well was not actively producing, but still had all production equipment in place. The producing and shut-in wells we visited all produced "wet" gas, meaning that the gas contained significant concentrations of nonmethane hydrocarbons. The gas storage wells we visited were used to store natural gas in a subsurface gas reservoir. Many of the wells alternated between producing and shut-in during the study period. Additional information about selection of measurement locations, frequency of visits, etc. is available in the Supporting Information.

Dynamic Flux Chamber. We used a polycarbonate dynamic flux chamber attached to a stainless steel ring that pressed into the soil to measure fluxes, following the method of and using the same dimensions as Eklund.[26] Our chamber departed from the method of Eklund in that (1) it had a fan at the top with a polyethylene blade that rotated at about 100 rotations min^{-1} and (2) rather than utilizing a sweep gas, it had a 1.2 cm hole in one side to allow ambient air to enter the chamber, and we sampled air inside and outside the chamber using two PFA tubes with PTFE filters. All chamber measurements were collected over at least 30 min, and averages over the sampling period are presented. We calculated flux as

$$F = (\Delta C \times Q)/S$$

where F is the soil–air flux in mg m^{-2} h^{-1}, ΔC is the difference in concentrations of the compound of interest inside versus outside the chamber in mg m^{-3}, Q is the flow rate in m^3 h^{-1}, and S is the surface area covered by the chamber in m^2.[27]

Field and Laboratory Analysis of Gas Samples From Flux Chamber. The flow rate through the chamber was 10 sL min^{-1} (standard conditions of 25 °C and 1 atm). We measured methane and carbon dioxide from the inside and outside lines with a Los Gatos Research (LGR) Ultra-Portable Greenhouse Gas Analyzer. The LGR analyzer sampled sequentially from the two lines at 120 s intervals. Detection limits (calculated as 3 times the standard deviation of blanks) were 0.06 and 18.9 mg m^{-2} h^{-1} for methane and carbon dioxide. We checked the LGR analyzer against NIST-traceable compressed gas calibration standards daily. Calibration standard recovery was 99 (99, 100)% for methane and 100 (99, 101)% for carbon dioxide (95% confidence).

For 34% of flux chamber measurements, we collected silonite-coated 6 L stainless steel canister samples from the inside and outside air streams and analyzed them for a suite of 54 nonmethane hydrocarbons (NMHC) using a derivation of the U.S. Environmental Protection Agency Photochemical Assessment Monitoring Stations (PAMS) method.[28] We used stainless steel Alicat mass flow controllers to regulate flow into the canisters. Canisters filled over the entire flux measurement period (at least 30 min). After collection, we used an Entech 7200 preconcentrator and a 7016D autosampler to concentrate samples and introduce them to a gas chromatograph (GC) system for analysis. The 7200 preconcentrator used cold trap dehydration to concentrate the gases of interest and reduce water vapor.[29]

The GC system consisted of two Shimadzu GC-2010 GCs, one with a flame ionization detector (FID) and one with a Shimadzu QP2010 Mass Spectrometer (MS). Sample introduced to the GC system first passed through a Restek rtx1 ms column (60 m, 0.32 mm ID), and then entered a heated VICI four-port valve with a Valcon T rotor. For the first few minutes after injection, the sample then passed into a Restek Alumina BOND/Na_2SO4 column (50 m, 0.32 mm ID) and into the FID. After the first few minutes, the valve position changed and the sample was directed into another Restek rtx1 ms column (30 m, 0.25 mm ID), and then into the MS. Light hydrocarbons (ethane, ethylene, acetylene, propane, and propylene) were quantified by FID, whereas all other compounds were quantified by MS. Each analysis included two calibration checks and duplicate analysis of an ambient air sample. Calibration checks had an average recovery of 104 (103, 104)% (95% confidence). Duplicate samples were −2 (−3, 0)% different. Detection limits for individual NMHC were 0.05 (0.04, 0.06) mg m^{-2} h^{-1}.

We measured fluxes periodically from a clean, 3 mm thick PTFE sheet (n = 8). Methane, carbon dioxide, individual NMHC, and total NMHC fluxes from this surface were 0.02 (−0.01, 0.04), 16 (−31, 109), 0.01 (0.00, 0.02), and 0.24 (−0.14, 0.72) mg m^{-2} h^{-1}, respectively (95% confidence).

Measured fluxes within these confidence limits cannot be statistically distinguished from zero.

We also injected undiluted gas from the same compressed gas standards used for calibration into the center of the chamber via a PFA tube that extended 1 cm above the measurement surface. We injected methane, carbon dioxide, and NMHC calibration gases at 200 mL min^{-1} at concentrations of 1620, 152 000, and 1 ppm, respectively (balance nitrogen). Recovery was 101 (99, 104)% for methane ($n = 5$), 103% for carbon dioxide ($n = 2$), 104 (101, 107)% for all hydrocarbons, and 114 (111, 117)% for aromatics ($n = 5$ for hydrocarbons; 95% confidence). The reason for high recovery of aromatics is unclear. It was not likely to have been the result of system contamination, since flux measurements on the PTFE sheet showed very low aromatic fluxes (see above). An intercomparison of hydrocarbon measurement laboratories showed that analysis of the majority of compounds agreed within ±20%.[30]

Analysis of Soil Gas and Other Soil Properties. USGS installed soil probes at various distances and directions from the wellhead (4−12 per well) at most of the wells visited for this study. We measured total combustible soil gas concentrations with a Bascom Turner Gas Rover at all the probes we encountered, and we measured soil flux within about 0.3 m of each probe. We sometimes collected additional flux measurements that were not near a soil probe, and we measured fluxes at some wells that did not have soil probes. We calibrated the Gas Rover daily using clean ambient air and 100 ppm and 100% methane certified calibration gas standards. Calibration checks had an average recovery of 98 (95, 101)% (95% confidence).

The soil gas probes consisted of PFA tubing with a PVC sheath. The tubing was placed into the ground at a depth of 0.6 m, whereas the PVC sheath extended less than 0.2 m. Sand was placed between the tubing and the PVC sheath. The lowest 15 cm of the PFA tubing was perforated, and it was closed off at the bottom. We connected to the top of the PFA tubing with the Gas-Rover to measure combustible soil gas concentrations. We recorded and used the soil gas reading collected at 30 s of sampling (flow rate of ~0.6 L min^{-1}).

We collected soil samples from each measurement location visited in 2015. We used a shovel to excavate to a depth of 15 cm and transferred the soil to a plastic bag. We analyzed these soils in the laboratory for texture, pH, and conductivity (a proxy for the salt content of the soil). Methods used to measure these soil properties are given in the Supporting Information.

Meteorological Measurements. We measured temperature and relative humidity (Campbell CS215 or New Mountain NM150WX), wind speed and direction (Gill WindSonic or New Mountain NM150WX), barometric pressure (Campbell CS100 or New Mountain NM150WX), and total incoming solar radiation (Campbell CS300) at 6 m above ground. We measured soil moisture with a Campbell CS655 soil water content reflectometer.

Raw Gas Analyses and Additional Well Property Data. We obtained raw gas analyses (which provide the composition of raw natural gas at each well) and information about casing and tubing pressures from operators of most of the wells we visited. These data were specific to the time periods of our sampling events. We obtained data about well status, age, and other properties from the Utah Division of Oil, Gas and Mining.[31]

Statistical Analyses and Units of Measurement. r^2 values shown are for Pearson correlations. We used student's t tests to compare data sets. Because of the high variability in measured fluxes, we determined statistical significance at $\alpha = 0.10$. We determined statistical significance at $\alpha = 0.10$. We calculated bootstrapped 90% confidence limits (except when noted otherwise) using the BCa method.[32] We present results as bootstrapped means with lower and upper confidence limits in parentheses.

We calculated an average per-well emission rate by averaging the emissions at different distances from the well head and multiplying these averages by the areas of concentric rings around the well head. Because our flux measurement locations were not randomly chosen, we weighted our results using USGS soil gas data. Additional details are available in the Supporting Information.

In most cases, we report flux measurements in units of mg $\text{m}^{-2}\ \text{h}^{-1}$. We use the flux of the carbon mass of each compound or compound group in analyses that compare hydrocarbon and carbon dioxide fluxes. Since the raw gas analyses we obtained give gas composition in mole percent, we compare flux speciation with raw gas composition using units of mol $\text{m}^{-2}\ \text{h}^{-1}$.

An anonymized version of our measurement data set is available.[33]

RESULTS AND DISCUSSION

Non-Well Soil Fluxes. Methane fluxes from undisturbed soils in oil and gas fields were consistently low (−0.06 (−0.09, −0.02) mg $\text{m}^{-2}\ \text{h}^{-1}$). 86% of methane fluxes from nonwell soils were negative, but none of the carbon dioxide fluxes were (carbon dioxide fluxes were 176 (147, 210) mg $\text{m}^{-2}\ \text{h}^{-1}$). Methane and carbon dioxide fluxes from nonwell soils were significantly different from fluxes measured from a PTFE sheet.

Negative methane fluxes have been measured in desert soils by others,[34] and are likely caused by methanotrophic oxidation of methane to carbon dioxide. Methane fluxes were less negative during winter (0.00 (−0.10, 0.16) mg $\text{m}^{-2}\ \text{h}^{-1}$) than summer (−0.04 (−0.7, −0.1) mg $\text{m}^{-2}\ \text{h}^{-1}$) for a subset of 6 nonwell locations that were measured during August 2015 and then again during January 2016. This difference was not significant, however, and was driven by measurements in the Natural Buttes Field in the Uinta Basin, where methane was negative during summer (−0.06 mg $\text{m}^{-2}\ \text{h}^{-1}$) and positive during winter (0.26 mg $\text{m}^{-2}\ \text{h}^{-1}$). Average methane fluxes measured by Klusman and Jakel from soils in the Denver-Julesburg Basin in Colorado were slightly positive (0.02 (0.00, 0.04) mg $\text{m}^{-2}\ \text{h}^{-1}$), but subsequent measurements by Klusman et al. in other oil and gas-producing basins were usually negative.

Methane generated in subsurface oil and gas reservoirs may migrate to the surface and emit to the atmosphere via so-called natural seepage,[35−37] but small seeps could still result in negative methane fluxes at the surface, since methanotrophic bacteria could consume as much or more methane than migrates to the surface. Thus, our measurements were inadequate to determine the influence of natural seepage at our study locations.

Fluxes of total NMHC were usually positive from nonwell soils (0.50 (−0.05, 1.05) mg $\text{m}^{-2}\ \text{h}^{-1}$) but were not significantly different from fluxes from the PTFE sheet ($p = 0.46$).

Fluxes of methane from oil shale, coal, and gilsonite outcrops were very close to zero (−0.02 (−0.04, 0.00) mg $\text{m}^{-2}\ \text{h}^{-1}$), but were significantly different from the PTFE sheet, and fluxes of NMHC from these surfaces were low and not different from fluxes from the PTFE sheet (−0.30 (−0.77, −0.04) mg m^{-2} h^{-1}, $p = 0.12$).

Methane fluxes from nonwell soils were not significantly correlated with any of the meteorological variables or soil properties measured. Carbon dioxide fluxes were significantly positively correlated with temperature ($r^2 = 0.20$), and total NMHC fluxes were significantly negatively correlated with temperature ($r^2 = 0.41$). This could be because warmer temperatures promote bacterial consumption of NMHC, resulting in lower NMHC fluxes and higher carbon dioxide fluxes.

Well Pad Soil Fluxes. Methane fluxes from well pad soils were extremely variable, but 79% were higher than the average flux from nonwell soils. Total hydrocarbon (methane + total NMHC) fluxes correlated poorly with total combustible soil gas concentrations ($r^2 = 0.01$), but the log of fluxes and soil gas concentrations correlated better ($r^2 = 0.31$; see Supporting Information for a more detailed analysis of this relationship). Figure 1 shows that soils with more total combustible soil gas tended to have higher fluxes of all the compounds measured. Total combustible soil gas concentrations exhibited a heavy-tailed distribution (see Figure S2). Our measurement locations were not randomly selected, but were instead chosen based on soil gas measurements. Thus, we cannot use our data set to independently determine the distribution of well pad soil fluxes, but we assume it is heavy tailed.

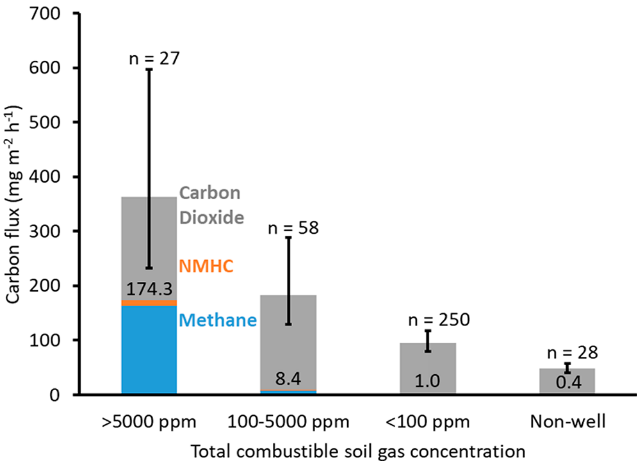

Figure 1. Average flux of the carbon content of carbon dioxide, total NMHC, and methane from well pad soils, binned by the total combustible soil gas concentration. Nonwell fluxes are also shown. The number above the NMHC bar is the average carbon flux of total hydrocarbons. Whiskers represent 90% confidence limits.

Observed hydrocarbon fluxes were extremely spatially variable. Figure 2 shows that fluxes could vary dramatically across the same well pad, even over distances of less than 1 m. In most cases, we measured fluxes at far fewer locations than the example shown in Figure 2, and it is possible that we failed to locate the point of highest emissions at many of these wells.

Methane fluxes were not significantly correlated with distance from wellheads ($r^2 = 0.02$), but when we averaged all flux measurements over intervals of 0.3 m from wellheads, the correlation improved ($r^2 = 0.44$ and 0.52 for methane and total NMHC) and assumed a logarithmic distribution (Figure 3; $r^2 = 0.88$ and 0.56 for log of methane and total NMHC fluxes).

Hydrocarbons were thus more likely to be emitted near the wellhead, which could have been due to (1) raw gas lost from wellbores or other subsurface infrastructure or (2) liquid hydrocarbons that had been spilled on the soil near well heads (see discussion below). The weakness of the relationship prior to data binning reflects that (1) some well pads exhibited high fluxes at relatively large distances from the wellhead (e.g., Figure 2), and (2) some well pads had small or no subsurface emission sources (even close to the well head), while others had very large subsurface sources, leading to a high degree of variability in flux data.

Methane fluxes binned by distance from the wellhead (0−2.5 m) were not significantly different from each other, but methane fluxes greater than 2.5 m from the wellhead were significantly lower than those 0−2.5 m from the wellhead. Because our measurements at some wells included locations greater than 2.5 m from the wellhead, while others did not, we excluded measurements greater than 2.5 m from the wellhead from subsequent analyses to avoid creating a low bias for wells with measurements distant from the wellhead. We did not use distance from the well head to correct flux measurements in these analyses because the relationship between distance and flux was variable, and some wells did not exhibit a meaningful distance-flux relationship.

Fluxes measured within 2.5 m of the wellhead were lower for producing wells than for shut-in wells (Figure 4). The reason for this difference is unclear. Producing wells tended to be older than shut-in wells (33 (29, 38) versus 27 (23, 30) years old), so well age cannot be assumed to be the reason for this difference. Producing and shut-in wells had similar casing pressure at the time of our measurements (365 (296, 430) versus 340 (328, 348) psi), so casing pressure that may have built up after the well was shut in cannot explain the difference (casing pressure was not significantly correlated with hydrocarbon flux or total combustible soil gas concentration). We also were unable to find any relationship of fluxes with monthly gas production, well depth, the number or depth of perforations in the well bore, the amount of cement used to seal the casing, or the amount or depth of surface cement used.

We also measured fluxes at three natural gas storage wells. Total hydrocarbon flux measured within 2.5 m of the wellhead at storage wells was 248.9 (103.9, 613.6) mg m^{-2} h^{-1}, lower than shut-in wells, but higher than producing wells. We regard these data as preliminary because of the low number of storage wells sampled.

Completion dates for the wells we sampled ranged from 1935 to 2013. The date of well completion was not correlated with methane fluxes measured within 2.5 m of the wellhead, regardless of whether we used all individual data points, or whether we averaged flux data by decade of well completion. Ingraffea et al.[20] found that newer wells in Pennsylvania were as likely as older wells to have integrity problems.

We visited 11 wells three or more times. Figure 5 shows a time series of the average of all methane flux measurements within 2.5 m of the wellhead for those 11 wells. Methane flux at many of those wells varied dramatically over time for reasons, in most cases, that we do not understand. Shut-in wells did not consistently increase in methane flux over time, as might be expected if the natural gas pressure built up in these wells over years of disuse. Some wells alternated between shut-in and producing over our visits, but we did not observe a consistent pattern of higher fluxes for shut-in periods and lower fluxes for producing periods at those wells. Except for winter/summer

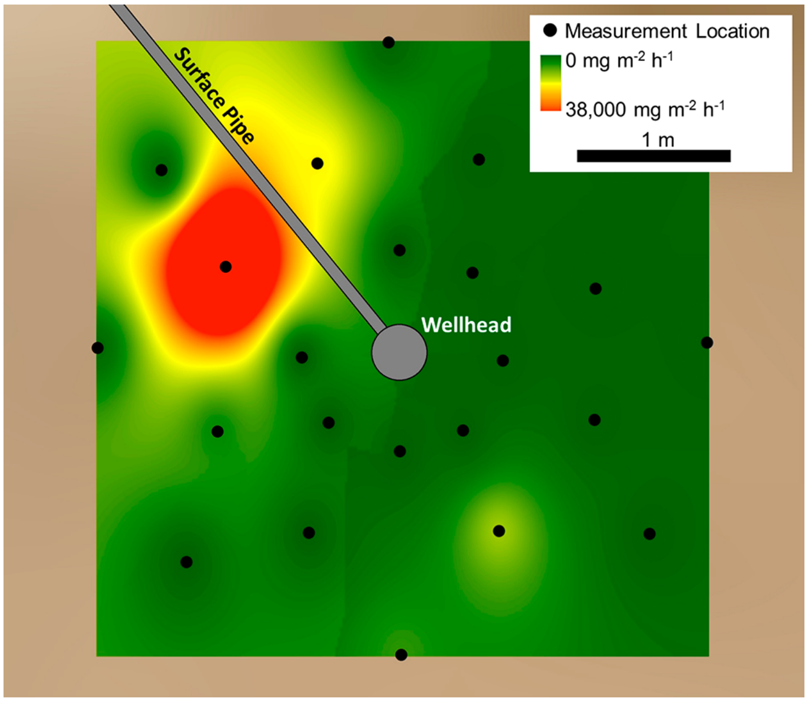

Figure 2. Interpolation of methane flux measured at 24 locations around a gas well in April 2016. Coloring indicates flux magnitude.

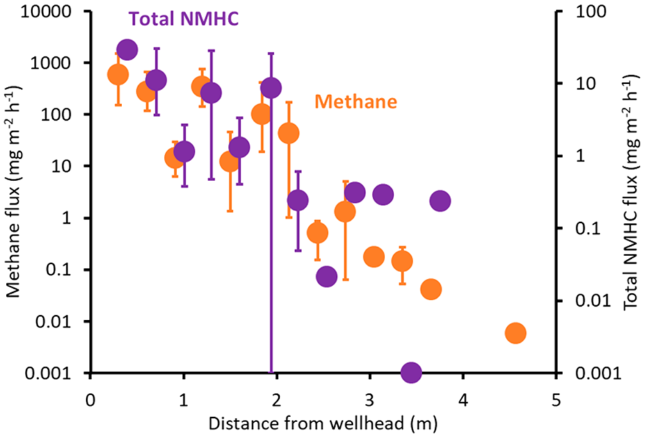

Figure 3. Average methane and total NMHC flux versus distance from the wellhead. Whiskers represent 90% confidence limits. *Y* axes are in log scale.

differences (discussed below), we did not observe any meaningful relationships of fluxes, or flux/soil gas ratios, with temperature, atmospheric pressure, soil moisture, or any of the other meteorological or soil properties we investigated.

At one well ("A" in Figure 5), the well owner installed a bradenhead vent, which can be used to relieve pressure on the well's casing, between our 2014 and 2015 visits, and the average soil flux at that well decreased from 2014 to 2015 (The casing pressure recorded by the operator at this well decreased from 360 psi in 2014 to 317 psi in 2015). Soil flux at this well was already declining from 2013 to 2014, however, so we cannot be sure whether the new vent led to the observed decrease in soil flux.

At another well (not shown in Figure 5 because it was only visited twice), total combustible soil gas concentrations were 256 007 (142 000, 372 000) ppm on 22 July 2014 but were only 1451 (600, 2750) ppm at the same sampling locations on

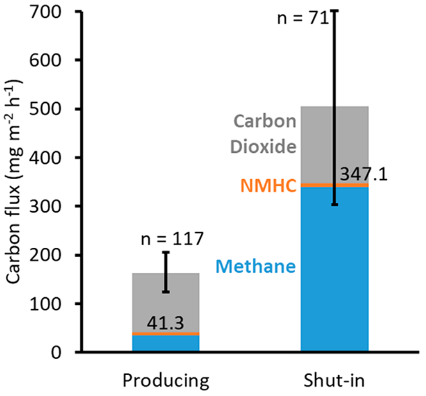

Figure 4. Average flux of the carbon content of carbon dioxide, total NMHC and methane measured within 2.5 m of the wellhead from producing and shut-in wells. The number above the NMHC bar is the average carbon flux of total hydrocarbons. Whiskers represent 90% confidence limits. *n* = the total number of measurements. Results from 18 producing wells and 10 shut-in wells are shown.

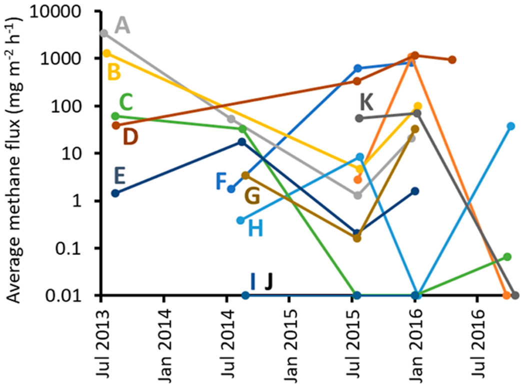

Figure 5. Time series of average methane fluxes at 11 wells we visited three or more times. Each well is shown as a different color.

16 September 2014 (soil flux was not measured in July and was near zero in September). Evidence at the well pad and logs submitted to the Utah Division of Oil, Gas, and Mining[31] indicate that this well was hydraulically fractured to stimulate production between the first and second sampling events. It is possible that, in addition to hydraulic fracturing, the work at this well included new components or repairs that reduced hydrocarbon gas migration into the soil. A subsequent visit in 2015 showed that soil gas concentrations and soil fluxes were in the same range as we observed during September 2014.

The high temporal variability in fluxes observed at these natural gas wells is in contrast to relatively stable fluxes observed by Kang et al.[14] for abandoned wells in Pennsylvania. This could be because the wells in this study were actively utilized, maintained, changed, and repaired, and changes in operations at the wells resulted in changes in fluxes. For the abandoned wells in the Kang et al. study, no changes would be likely, so constant fluxes over time can be expected.

We measured soil flux at 15 wells during July and August 2015 and again during January 2016. Soil fluxes of methane and NMHC tended to be higher during winter than during other months, while carbon dioxide flux tended to be lower (Figure 6). In a comparison of average fluxes within 2.5 m of each wellhead, 60% of wells exhibited higher methane flux during winter than during other seasons. When we excluded wells with methane flux less than 10 mg m^{-2} h^{-1}, 86% had higher methane flux during winter. This difference was not due to a greater proportion of wells being shut-in during winter (three of the 15 wells were shut in during summer, while only one was shut in during winter). Because of high variability in the sample data, the difference in total hydrocarbon flux between winter and summer was not significant ($p = 0.14$). The seasonal difference in carbon dioxide flux was statistically significant, however ($p = 0.02$).

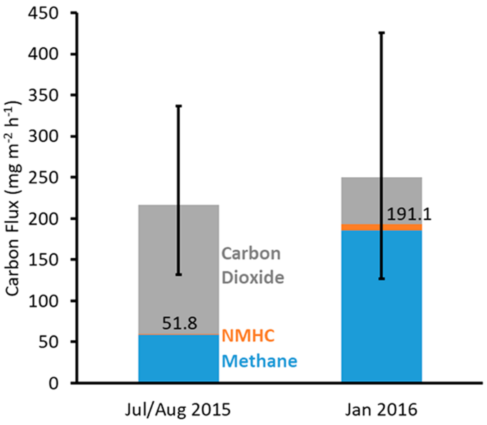

Figure 6. Average flux of the carbon content of carbon dioxide, total NMHC and methane measured within 2.5 m of the wellhead from 15 wells that were sampled in July and August 2015, and then again in January 2016. The number above the NMHC bar is the average carbon flux of total hydrocarbons. Whiskers represent 90% confidence limits.

Methane and carbon dioxide fluxes were significantly, but weakly correlated ($r^2 = 0.16$). When only summer data were used, the correlation improved ($r^2 = 0.51$; see Figure S3). Thus, to some extent at least, methane and carbon dioxide emitted from well pad soils likely originated from a common source. At the wells for which raw gas analyses were available, carbon dioxide was 81 (74, 87)% of the total flux (units of mol m^{-2} h^{-1}) but only 0.6 (0.6, 0.7)% (mole percent) of raw natural gas, so raw gas was clearly not the direct source of observed carbon dioxide fluxes. Instead, we postulate that a large percentage of hydrocarbon gas within the soil were consumed by soil bacteria,[38,39] resulting in a reduction in hydrocarbon fluxes and an increase in carbon dioxide fluxes. Wintertime decreases in carbon dioxide fluxes, and (while they are not statistically significant) increases in hydrocarbon fluxes, were likely caused by a reduction in soil bacterial activity during winter[40−44] (air temperature during summer 2015 measurements was 25.5 (24.3, 26.8)°C, while temperature during winter 2016 measurements was −4.4 (−5.3, −3.5)°C). This means that soil bacteria at these wells lessen the atmospheric impact of hydrocarbons leaked into the soil by converting hydrocarbons to carbon dioxide (at least during warmer months).

Methane comprised only 78 (68, 85)% of total hydrocarbon flux in the subset of measurements for which raw gas analyses were available, but it comprised 89 (88, 89)% of raw natural gas. For 72% of flux measurements, the ratio of the percent of total hydrocarbon flux that was due to methane to the percent methane in raw gas was greater than 0.9. We subsequently refer to this ratio as percent methane in flux/percent methane in raw gas or the PMF/PMG ratio.

For measurements with a PMF/PMG ratio greater than 0.9, methane comprised 96 (95, 98)% of hydrocarbon flux, but methane comprised only 30 (20, 42)% for the remainder of our samples. Ririe and Sweeney[19] compared gas samples from soils with natural gas seeps against samples from soils contaminated by liquid hydrocarbons. They showed that gas samples from soils contaminated with liquid hydrocarbons were depleted in methane and ethane relative to gas samples from natural gas seeps, in which methane and ethane were the dominant hydrocarbons in emitted gas. Figure 7 shows that for our measurements, flux samples with a PMF/PMG ratio greater than 0.9 have a nonmethane hydrocarbon flux speciation that is similar to the speciation of raw natural gas, while those with a ratio below 0.9 have a flux speciation that is depleted in light hydrocarbons relative to raw gas. We hypothesize that soils with

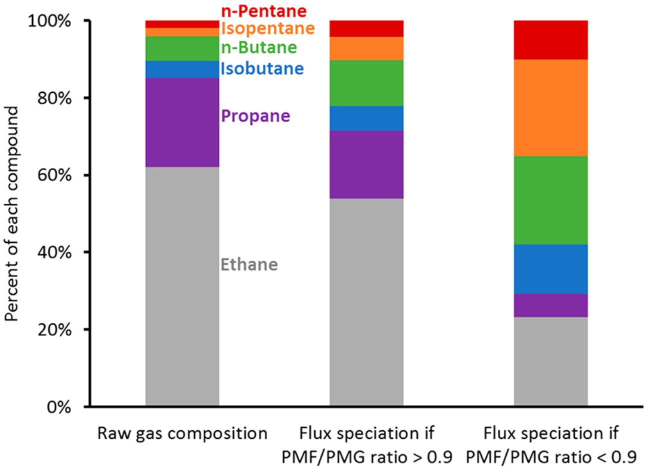

Figure 7. Average raw natural gas composition of the compounds indicated (mole percent) at a subset of wells sampled, flux speciation of the same compounds if the PMF/PMG ratio was greater than 0.9, and flux speciation if the ratio was less than 0.9. The compounds shown were chosen because they were consistently explicitly measured in available raw gas analyses.

a lower PMF/PMG ratio were influenced by contamination from liquid hydrocarbon spills, leading to low methane and ethane fluxes, while those with a high PMF/PMG ratio were influenced primarily by subsurface sources of raw natural gas. Liquid storage tanks (a possible source of spills) at wells with a PMF/PMG ratio less than 0.9 were not closer to well heads than at wells with a ratio greater than 0.9 (37 (32, 40) m for ratios less than 0.9, 30 (28, 33) m for ratios greater than 0.9).

For flux measurements with a PMF/PMG ratio greater than 0.9, methane fluxes were correlated with light hydrocarbon fluxes, as would be expected if the source of fluxes was raw natural gas. Methane was significantly correlated with total alkanes ($r^2 = 0.49$), ethane ($r^2 = 0.54$), propane ($r^2 = 0.27$), isobutane ($r^2 = 0.50$), *n*-butane ($r^2 = 0.40$), and isopentane ($r^2 = 0.55$), among other compounds. For measurements with a PMF/PMG ratio less than 0.9, methane fluxes were not significantly correlated with any of the nonmethane hydrocarbons measured.

Flux measurements with a PMF/PMG ratio less than 0.9 had much lower total hydrocarbon flux (18.8 (4.1, 62.2) mg m^{-2} h^{-1}) than measurements with a ratio greater than 0.9 (328.2 (76.0, 1123.9) mg m^{-2} h^{-1}). This may indicate that subsurface raw gas is a more significant source of hydrocarbons to the atmosphere than re-emissions from spilled liquid hydrocarbons. The vast majority of emissions from hydrocarbon spills occur very soon after the spill occurs, however, so this conclusion is far from certain and more work is needed to characterize emissions from liquid hydrocarbon spills.

Significance of Well Pad Soil Emissions Relative to Other Oil and Gas-Related Sources. We estimate that 1.2 (0.4, 4.2) and 0.1 (0.0, 0.2) g day^{-1} of methane and total NMHC are emitted from well pad soils per natural gas well in Utah (note that 90% confidence limits show variability in flux measurement results, not uncertainty in our measurement method). Soil emissions of methane from the highest-emitting well we sampled were 0.26 kg day^{-1}. For comparison, Robertson et al.[45] measured average whole-well emissions (which would include soil emissions and emissions from above-ground infrastructure) from Uinta Basin gas wells of 88.8 (28.8, 218.4) kg day^{-1}. The Uinta Basin contained 6,492 producing and shut-in gas wells in July 2016 (out of 11,726 total oil and gas wells), which would lead to 2.9 (1.0, 10.0) and 0.2 (0.0, 0.5) metric tons yr^{-1} of methane and total NMHC. Ahmadov et al.[46] used aircraft-based measurements of total fossil methane emissions from the Uinta Basin[4] and surface measurements of nonmethane organics to estimate that Uinta Basin methane and nonmethane organic compound emissions are 482 130 and 184 511 t $year^{-1}$, respectively. Using these numbers, well pad soils emit 6.0×10^{-4} (2.1×10^{-4}, 2.1×10^{-3})% and 1.1×10^{-4} (1.9×10^{-5}, 2.9×10^{-4})% of total methane and NMHC emissions from all oil and gas-related sources in the Uinta Basin.

Averages of data sets with heavy-tailed distributions, especially ones that sample only a small part of the entire population, are likely to underestimate the true mean because they are likely to miss the small subset of the population that has the highest values. In other words, emissions from a single, extremely high-emitting well pad could make the difference between soil emissions being a significant or insignificant hydrocarbon source. The Aliso Canyon leak provides a poignant reminder that this could be true for soil emissions from well pads.[18] The small sample size of our study (<1% of all natural gas wells in eastern Utah) and high variability in measured fluxes add to the uncertainty of our emissions estimate. Our estimated well pad soil emission total for the Uinta Basin is extremely low, however, and even if it is biased low by several orders of magnitude, emissions of hydrocarbons from well pad soils in Utah would still be a small emission source compared to emissions from the oil and gas industry overall.

Regardless of their significance relative to the oil and gas industry overall, emissions of hydrocarbons from well pad soils are indicative of spilled hydrocarbon liquids or malfunctioning subsurface infrastructure, and flux or soil gas concentration measurements are useful in that they can alert operators that repairs or changes to operating practices are needed. Additional research is needed to determine whether soil emissions are associated with or caused by certain well construction practices and materials or well maintenance and operation techniques.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b03408.

> Additional information about our methods, including measurements of the pressure differential inside vs outside the chamber, the impact of above-ground natural gas leaks on measurement precision, study location selection and sampling frequency, soil analysis methods, how we scaled up fluxes to the whole Uinta Basin, additional discussion of our results, and additional figures (PDF)

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Notes

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Supporting Information for:

Hydrocarbon and Carbon Dioxide Fluxes from Natural Gas Well Pad Soils and Surrounding Soils in Eastern Utah

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This document contains additional information about our methods, some additional discussion, and additional figures.

1. DATA AVAILABILITY

An anonymized version of our measurement data are publicly available at http://digitalcommons.usu.edu/all_datasets/25/.[1]

2. PRESSURE DIFFERENTIAL INSIDE VERSUS OUTSIDE THE FLUX CHAMBER

We used a Dwyer 616KD differential pressure transducer to measure the difference between pressure inside and outside the chamber. We used a Campbell Scientific CR1000 data logger to measure and record the transducer's voltage output (0-5 V, or 0.05 Pa per mV). The transducer's accuracy (stated by the manufacturer) was ±2.5 Pa. The sensitivity of the transducer (observed) was 0.05-0.1 Pa. We observed no significant change in the differential pressure when the flow rate through the chamber was 10 L min^{-1} (0.00 (-0.01, 0.01) Pa) versus 0 L min^{-1} (0.00 (-0.01, 0.01) Pa).

3. IMPACT OF ABOVE-GROUND NATURAL GAS LEAKS ON MEASUREMENT PRECISION

Our dynamic flux chamber pulled ambient outside air into the chamber. Most of our measurements were collected near above-ground well heads, and well heads or other above-ground well pad equipment can leak natural gas, leading to fluctuating concentrations of methane and non-methane hydrocarbons in ambient air. This had the effect of lowering our measurement precision in some cases, since short-term spikes in concentrations could lead to artificially high or low fluxes. When these impacts were obvious, we removed the offending measurements or the entire 30-min averaged sample. These impacts were not obvious in some cases but could have still influenced our measurement results.

Figure S1 shows 72 h of continuous flux measurements collected 1 m from a well head with an obvious natural gas leak, and the impact of the leak was obvious in our measurement data. The maximum methane concentration in air outside the chamber during the sampling period was 29.9 ppb, which was as high as we measured at any of the wells we visited. The rolling 30-min average methane flux shown in Figure S1 varied from -10 to 15 mg m^{-2} h^{-1}. The average flux over the 72-h period, which can be assumed to approximate the actual soil flux at the location, was 0.12 mg m^{-2} h^{-1}. We did not collect NMHC data during the 72-h period shown in Figure S1, but if we assume an NMHC/Methane flux ratio of 4% (the average for all of our flux measurements), this could lead to bias in NMHC fluxes of between -0.4 and 0.6 mg m^{-2} h^{-1}. For comparison, methane and NMHC fluxes from our entire study were 141.6 (89.1, 235.7) and 5.2 (2.5, 10.1) mg m^{-2} h^{-1}, respectively. Figure S1 represents a worst-case scenario; we normally would have discarded these data because of the obvious influence of a nearby leak.

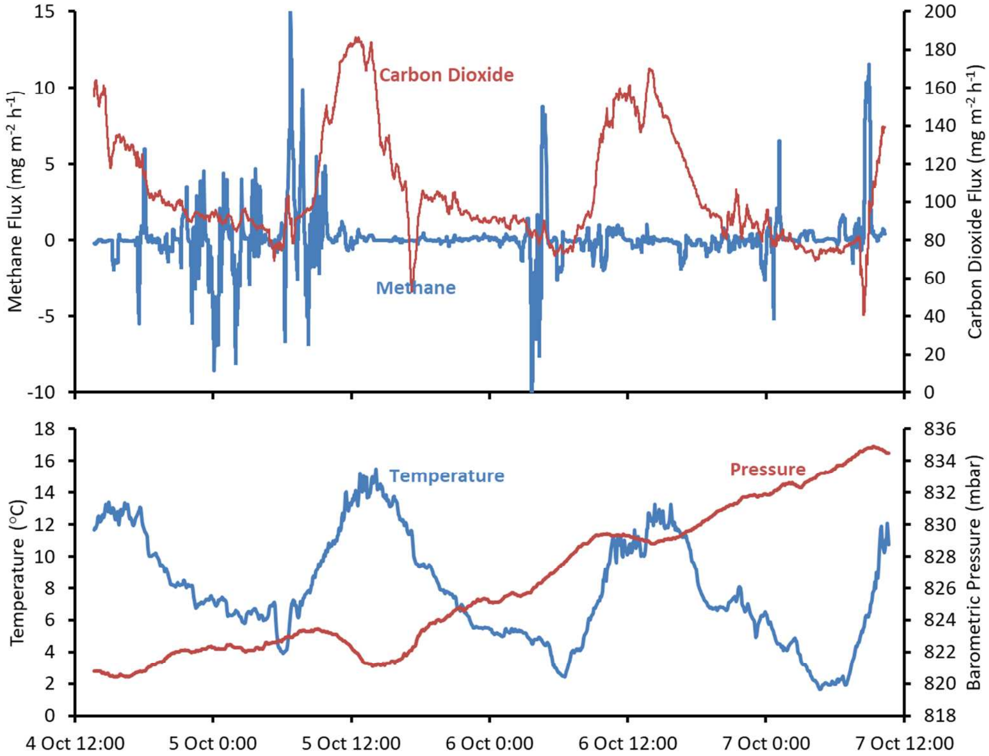

Figure S1. 30-min rolling average flux chamber measurements of methane and carbon dioxide over a 72-h period. Temperature and pressure are also shown. These measurements were collected 1 m from a well head with an obvious leak.

4. ADDITIONAL INFORMATION ABOUT STUDY LOCATIONS AND SAMPLING FREQUENCY

All wells we visited had a well head, at least one above-ground liquid storage tank, and a heater/separator unit. Some wells had additional equipment, and the configuration and type of equipment at each well was unique. Since we only measured soil fluxes within a few m of well heads, and since our measurements were always at least 5 m from other well-site equipment, we did not make a detailed attempt to catalog above-ground equipment at the wells we visited.

We visited most of the wells at least twice, and sometimes as many as five times. Most of the wells were visited annually between July and October. We visited a subset of 15 wells in July 2015 and again in January 2016. We also visited one well in April 2016 to measure flux at high spatial density.

We measured fluxes from at least two undisturbed non-well locations within each of the three basins during each measurement campaign. Also, during summer 2015 we collected flux measurements from an undisturbed oil shale outcrop, an undisturbed gilsonite outcrop, and an undisturbed coal outcrop (n = 4 measurements for each).

We typically collected between two and eight measurements from each well pad or other measurement site during each site visit. We collected 23 flux chamber measurements from a single well pad in April 2016 to better understand the spatial distribution of fluxes. For well pad measurements, locations varied between 0.3 and 5.2 m from the well head and were collected in all directions from the well head. The majority (93%) of the measurements were within 3.1 meters of the wellhead.

5. METHODS FOR ANALYSIS OF SOIL SAMPLES

Soil Texture

Soil samples were sieved to <2 mm grain size for soil texture characterization. 40-50 g of each sample were then weighed and mixed with 100 mL of sodium hexametaphosphate (solid) and 200 mL of distilled deionized water. The suspension was poured into a 1000 mL hydrometer sedimentation cylinder. The remaining 1000mL in the cylinder was filled with distilled deionized water. After the solution was mixed and sediment began to settle, temperature and hydrometer measurements were collected after 60 seconds and again after 7 hours. The mass of the soil, temperature, and hydrometer measurements were used to calculate the percent sand, silt, and clay.[2] Computed soil texture of the percent sand, silt, and clay were entered into the United States Department of Agriculture (USDA) Natural Resource Conservation Service (NCRS) Soil Texture Calculator.[2]

Soil pH and Conductivity

Soil pH and conductivity were measured using water extraction. 100 mg of each soil sample was sieved to a 2 mm grain size and then ground to <1 mm grain sizes. Distilled deionized water was added to the soil to create a slurry. A Mavco Extractor was used to extract liquid from the mixture, and a Vernier pH/conductivity meter measured the pH and conductivity of the extracted liquid. The pH/conductivity meter was calibrated using pH levels of 4, 7, and 10 and conductivity levels of 84, 1280, 80,000, and 111,800 millisiemens cm^{-1}.

6. CALCULATING PER-WELL EMISSION RATES FROM FLUX MEASUREMENTS

Since soil flux was inversely correlated with distance from wellheads, we determined per-well emission rates (E) in g day^{-1} as:

$$E = e_{<1} + e_{1\text{-}2} + e_{2\text{-}3}$$

Where $e_{<1}$, $e_{1\text{-}2}$, and $e_{2\text{-}3}$ are the total emissions at distances of less than 1 m, 1-2 m, and 2-3 m from the wellhead. $e_{<1}$, $e_{1\text{-}2}$, and $e_{2\text{-}3}$ were determined by multiplying the average flux within the three distance bins ($f_{<1}$, $f_{1\text{-}2}$, and $f_{2\text{-}3}$; units of g m^{-2} day^{-1}) by the area of concentric rings around the wellhead with inner and outer diameters of 0 and 1 m, 1 and 2 m, and 2 and 3 m. We collected some flux measurements more than 3 m from wellheads, but fluxes were uniformly very low, and sample sizes were small, so we only used data collected less than 3 m from wellheads to calculate per-well emission rates.

Since the wells sampled by USGS were randomly chosen, while the wells we sampled were not, we used USGS total combustible soil gas measurements to weight the average flux within each distance bin. Fluxes and total combustible soil gas concentrations were positively related, and Figure 1 shows average fluxes for each of three total combustible soil gas bins (>5000 ppm, 100-5000 ppm, and <100 ppm). We averaged all flux data for each combination of the three distance bins and three soil gas bins, and we determined the final flux for each distance bin as:

$f_d = f_1 \times freq_1 + f_2 \times freq_2 + f_3 \times freq_3$

Where f_x is the average flux associated with each soil gas bin x (bins are shown in Figure 1) for each distance bin d (i.e., distances of less than 1 m, 1-2 m, and 2-3 m from the wellhead), and $freq_x$ is the frequency of occurrence (as a fraction) of each combination of soil gas bins and distance bins, obtained from the USGS combustible soil gas dataset.

We calculated $e_{<1}$, $e_{1\text{-}2}$, $e_{2\text{-}3}$ as:

$e_d = f_d \times a$

Were a is the area of each concentric ring.

7. DISCUSSION ABOUT THE WEAK RELATIONSHIP BETWEEN COMBUSTIBLE SOIL GAS CONCENTRATIONS AND SOIL FLUXES

The relatively weak relationship between combustible soil gas and hydrocarbon fluxes could have been caused by (1) enhanced methanotrophy near the surface relative to the depth of soil gas measurements, (2) poor soil porosity, which would tend to trap gases beneath the surface, and/or (3) a high degree of spatial heterogeneity in fluxes and/or soil gas concentrations, in which case the 0.3 m distance between the two measurements could be enough to lead to large discrepancies.

We did not measure combustible soil gas concentrations at multiple depths, so we cannot be sure about the relationship between hydrocarbons at the depth of soil sampling versus the surface. Kightley et al.[3] showed that methane oxidation rates are highest at soil depths were the concentrations of methane and oxygen are both maximized, and we thus expect the zone of maximum methanotrophy to occur near the surface in well pad soils we sampled. If this were the cause of the disconnect between soil gas concentrations and soil flux, we would expect the total carbon flux to correlate better with soil gas than the hydrocarbon flux alone (since methane lost to methanotrophy would become carbon dioxide), but the total carbon flux was poorly correlated with total combustible soil gas ($r^2 < 0.01$; $r^2 = 0.01$ for the correlation between the log of the two variables).

Well pads consist of level, packed soils, usually mixed with gravel. Because of compaction[4] and/or high clay content,[5-6] surface well pad soils could have low porosity, preventing migration of hydrocarbons to the atmosphere. We did not measure soil compaction, but soils we collected were sandy, with medium-low clay content (59 ± 2% sand, 17 ± 1% silt, 23 ± 1% clay, n=34). Soil moisture, which could swell clays and further limit porosity, was not correlated with hydrocarbon fluxes or hydrocarbon fluxes normalized for soil gas concentration. True and normalized hydrocarbon fluxes were also not significantly correlated with any of the measured meteorological parameters.

Spatial variability may have been a cause of the relatively weak correlation between hydrocarbon fluxes and total combustible soil gas concentrations. Figure 2 shows that well pad soil fluxes exhibited a high degree of spatial variability. For a subset of well pad soils sampled in fall 2016, total combustible soil gas measured via a probe pounded at the center of flux chamber measurement locations correlated better with methane flux ($r^2 = 0.35$; n = 9) than soil gas measured from USGS-installed probes that were 0.2-0.4 m away from flux chamber measurement locations ($r^2 = 0.11$; n = 9).

8. HISTOGRAM OF TOTAL COMBUSTIBLE SOIL GAS MEASUREMENTS

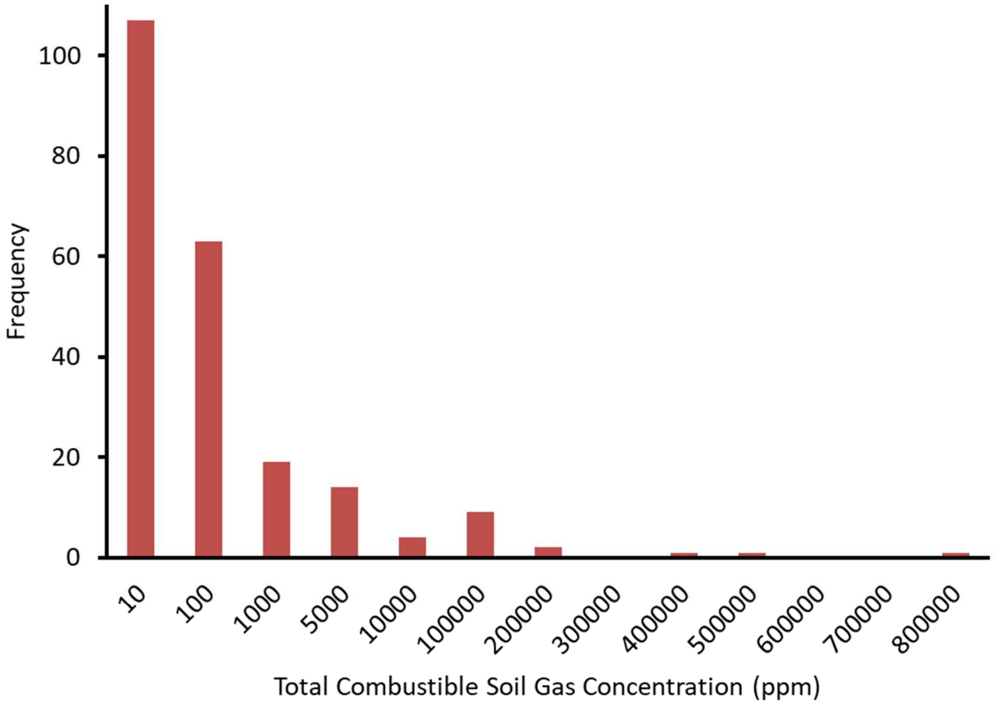

Figure S2. Histogram of total combustible soil gas measurements collected by USGS. Values represent the average soil gas concentration from all measurements collected less than 2 m from the well head at each well (n = 220 wells visited). Values on the x-axis indicate the upper bound of each concentration bin. These data were provided by USGS with the understanding that they are preliminary and subject to revision.

9. METHANE VERSUS CARBON DIOXIDE FLUXES

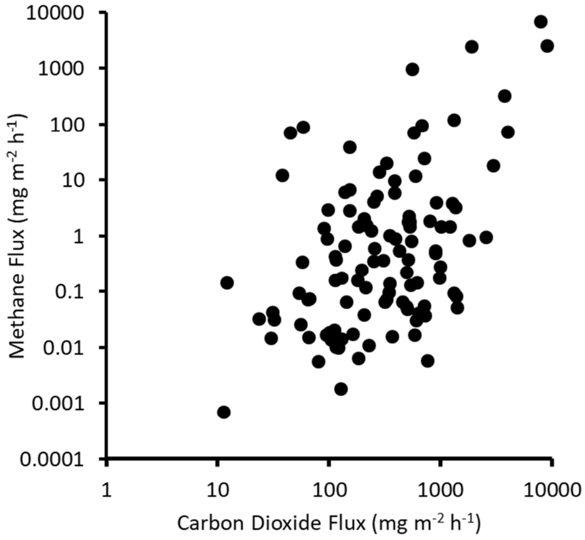

Figure S2. Scatterplot showing the relationship between methane and carbon dioxide fluxes (summer data only).

10. REFERENCES

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