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Variability observed over time in methane emissions from abandoned oil and gas wells

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ABSTRACT

Recent studies have reported methane (CH_4) emissions from abandoned oil and gas wells across the United States and the United Kingdom. These emissions can reach hundreds of kg CH_4 per year per well and are important to include in greenhouse gas emission inventories and mitigation strategies. Emission estimates are generally based on single, short-term measurements that assume constant emission rates over both short (hours) and longer (months/years) time periods. To investigate this assumption, we measure CH_4 emissions from 18 abandoned oil and gas wells in the USA and the UK continuously over 24 h and then make repeat 24 -h measurements at a single site over 12 months. While the lack of historical records for these wells makes it impossible to determine the underlying leakage-pathways, we observed that CH_4 emissions at all wells varied over 24 h (range 0.2-81,000 mg CH_4 hr^{-1}) with average emissions varying by a factor of 18 and ranging from factors of 1.1–142. We did not find a statistically significant relationship between the magnitude of emissions and variability or that variability is correlated with temperature, relative humidity or atmospheric pressure. The results presented here suggest high CH_4 emission events tend to be short-lived, so short-term (< 1 h) sampling is likely to miss them. Our findings present the dynamic nature of CH_4 emissions from abandoned oil and gas wells which should be considered when planning measurement methodologies and developing greenhouse gas inventories/mitigation strategies. Incorporation of these temporal dynamics could improve national greenhouse gas emissions inventories.

1. Introduction

The US Environmental Protection Agency (US EPA) estimates that over 6 Tg of methane (CH_4) gas leaks from natural gas systems to the atmosphere each year. This includes emissions from field production, processing, transmission/storage, and distribution (US EPA, 2018). However, discrepancies between top-down and bottom-up CH_4 emission estimates suggest this inventory is underestimating sources (Cerri et al., 2017; Miller et al., 2013; Schwietzke et al., 2014; Yang et al., 2017; Zavala-Araiza et al., 2015). Recent measurements identified abandoned oil and gas wells as a source of CH_4 emissions (Kang et al., 2016, 2014; Townsend-Small et al., 2016) which led them to be added to the US EPA greenhouse gas emissions inventory (US EPA, 2018). However, the uncertainty associated with methane emissions from abandoned wells is large due to the lack of measurements and challenges associated with measuring a representative sample. To reduce these uncertainties, it is important to understand variability in emission rates.

Recent studies estimating CH_4 emissions from abandoned oil and gas wells implicitly assume that emissions are constant over time, and often base annual emissions estimates from each well on short (~ 20 min), one-time measurements (Boothroyd et al., 2016; Kang et al., 2016; Riddick et al., 2019; Townsend-Small et al., 2016). These "instantaneous" emission estimates are then used to calculate emission factors applied to many other wells to produce a national annual emission estimate based on the number of abandoned wells. Although repeat multi-year measurements at high-emitting abandoned wells in Pennsylvania were found to be of the same order of magnitude (Kang et al., 2016), the role of emissions variability at the minute and hourly time scales on estimated state-wide or nation-wide emissions is unknown.

In systems emitting biogenic methane, trace gas emissions to the

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atmosphere are rarely constant and can be affected by environmental conditions. Methane emissions from landfills are highly affected by both temperature and atmospheric pressure, where colder temperatures decrease methanotrophic bacteria activity (Riddick et al., 2017), higher temperature increase methanogenic activity (Avery et al., 2003; Mønster et al., 2015) and negative changes in pressure result in CH_4 being hydraulically pulled from the landfill (Riddick et al., 2018; Xu et al., 2014). In permafrost, short-term variability in CH_4 fluxes are controlled by temperature and height of the water table (Tagesson et al., 2013; Turetsky et al., 2014), while long-term patterns depend on the rate of decomposition of various types of organic matter (Whalen, 2005). The effects of changes in air pressure were also observed in a recent study that aimed to simulate wellbore leakage by injecting gas into the shallow subsurface (Forde et al., 2019), where methane emissions were higher away from the injection site during periods of low pressure. These studies typically involve three-dimensional transport of methane, sometimes including multi-phase flow through complex geological systems. Such leakage systems involve spatially distributed methane fluxes along the land surface.

In contrast, the oil and gas wells measured in this work exhibit leakage only at, or in the immediate vicinity of (a few centimetres away), the wellbore. Measurements have consistently shown thermogenic methane to be emitted from the wellbore, with measurements away from the wellbore consistently showing only background-level biogenic soil emissions (see, for example, Kang et al., 2014). This means the leakage is essentially one-dimensional, along the wellbore. With regards to leakage along these oil and gas wells, thermogenic methane originating from much deeper in the earth could rise through zones of oil or water within the borehole in complex ways, thereby giving intermittent emissions (Davies and Taylor, 1950; Dusseault and Jackson, 2014). Day-to-day variability in CH_4 emissions from *active* wells has been observed (Lavoie et al., 2017). However, to our knowledge, no study to date has measured how CH_4 emissions from abandoned oil and gas wells change over time, specifically over a timeframe of hours.

Herein we report measurements of CH_4 emissions from abandoned conventional gas and oil wells to determine if temporal variability exists and, if so, whether it is significant. Our objectives are to: 1. Report CH_4 emissions from abandoned wells as a function of time over a 24 -h time period; 2. Investigate whether measurements made over a period of less than an hour, henceforth termed instantaneous, can be used to effectively quantify emissions from abandoned wells; 3. Determine whether CH_4 emissions from high-emitting wells vary less than those from low-emitting wells; and 4. Investigate if there are any environmental factors that can explain observed variability in methane emissions. To our knowledge this is the first time that variability of fugitive CH_4 emissions from individual abandoned conventional gas and oil wells has been measured over a 24 -h period of time. Understanding the variability of methane emissions is essential to accurately estimate emissions and design effective mitigation strategies.

2. Methods

2.1. Measuring 24 -h methane emissions from abandoned oil and gas wells

Continuous measurements of CH_4 emissions from abandoned oil and gas wells over a 24 -h period had significant logistical challenges: 1. Remoteness of the wells meant that grid power could not be used; 2. The setup was left unattended overnight in public areas; 3. The distance from roads to the wells was in some cases significant (> 2 miles) with a limitation on what could be carried over rough ground and; 4. Weather could be inclement and could change markedly in 24 h. Given these considerations, a dynamic flux chamber method was employed as it is relatively easy to carry, inexpensive, requires little power to measure continuously and has all the electronics contained within the waterproof chamber (Fig. 1). This dynamic flux chamber has been deployed previously in similar measurements of CH_4 emissions from abandoned oil and gas wells in West Virginia (Riddick et al., 2019).

The chamber is comprised of a rigid polyethylene plastic cylinder closed at one end with a diameter of 50 cm and a height dependent on the dimensions of the abandoned well. The base of the flux chamber was inserted into the soil and a seal was made with the ground by pressing the chamber 5 cm into the ground. A motor and propeller, set at 60 rpm, were used to continuously circulate the air inside the chamber and an air pump was used to draw air through the chamber. The size of the pump depended on the expected concentration of CH_4 in the chamber: for high concentrations (> 40,000 ppm) an air flow of 60 L min^{-1} was used and for lower concentrations (< 40,000 ppm) an air flow of 5 L min^{-1} was used. Flow rates were measured using a Cole Palmer mechanical flow meter (www.colepalmer.com). Power was supplied to the fan and pump by a 100 Ah lead acid 12 V battery and the chamber was left *in-situ* at each abandoned well for 24 h. These experiments were designed to measure all direct emissions from the well bore, and included emissions from any soil outside the well casing that was also inside the 0.2 m^2 area of the chamber base. The size of the chamber footprint was selected to be slightly larger than the typical abandoned wellhead girth to minimize the amount of soil measured.

An MQ4 semiconductor gas sensor (Hanwei Electronics, Zhengzhou, China) was used to continuously measure the CH_4 concentration inside the chamber. The MQ4 was used because it is a low-power, low-cost device that showed stability when measuring CH_4 concentration over 24 -hs inside the chamber. This solid-state sensor uses tin dioxide (SnO_2) as the sensing material which has a fixed resistance in clean air (R_0, Ω). The resistance of SnO_2 decreases in the presence of CH_4 (R_s, Ω) and the ratio of these resistances (R_s/R_0) gives a measure of the CH_4 mixing ratio in air. Data on CH_4 concentration, air temperature, relative humidity, soil moisture and air pressure were sampled at 1/second frequency using DHT22, FC-28 and BMP-180 sensors, respectively, and the one-minute averages were logged. The CH_4 concentration and meteorological data were then retrieved and analysed using the software package R (R Project, 2018). Using the manufacturer's empirically derived equation (Eq. 1), the raw CH_4 count values (C_m) can be calculated from the sensor resistance (R_s), the resistance in clean air (R_0), temperature (T, ºC) and relative humidity (RH, %), with an uncertainty of ± 12 % (Hanwei, 2018; Honeycutt et al., 2019).

$$C_m = 13743 - 12754\frac{R_s}{R_0}(1.267 - (0.003159\,RH) - (0.00698\,T)) \quad (1)$$

These raw CH_4 count data were then calibrated against a handheld HXG-2D (Sensit Technologies, USA) CH_4 sensor (range 10 ppm to 40,000 ppm), which had been calibrated against gas standards of 2 ppm, 5000 ppm and 1% CH_4 before and after deployment, October 2016 and October 2017, respectively. We saw that the MQ4 CH_4 count, C_m as calculated in Eq. 1., is non-linear with increasing CH_4 concentration (Supplementary Material Section 1 Figure SM1.1) between 10 ppm and 3 % CH_4. Following this analysis, we generated calibrated concentrations ($[CH_4]_c$, ppm) using the algorithm in Eq. 2. Repeat calibrations in October 2016 and October 2017 show no significant drift on the sensor.

$$[CH_4]_c = 5x\,10^{-9}.(C_m)^{0.445} \quad (2)$$

In addition to measuring the CH_4 concentrations with the MQ4 sensor, intermittent gas samples were also taken from the chamber and analysed using a Shimadzu GC-2014 gas chromatograph (GC). The GC, as used here, has a detection limit of 1.5 ppb methane and an uncertainty of ± 0.8 %, based on triplicate analysis of 5000 ppm methane, ethane, propane, and n-butane standards. To identify the source of the emission as biogenic or thermogenic, the concentrations of C_2 to C_4 hydrocarbons were also measured by the GC, where for biogenic sources (C_2 - C_4)/C_1 < 0.01 and for thermogenic sources (C_2 - C_4)/C_1 > 0.01 (Molofsky et al., 2013; Taylor et al., 2000). Gas standards used in the GC analysis were 100 %, 1%, 5000 ppm and 200 ppm for C_1 to C_4.

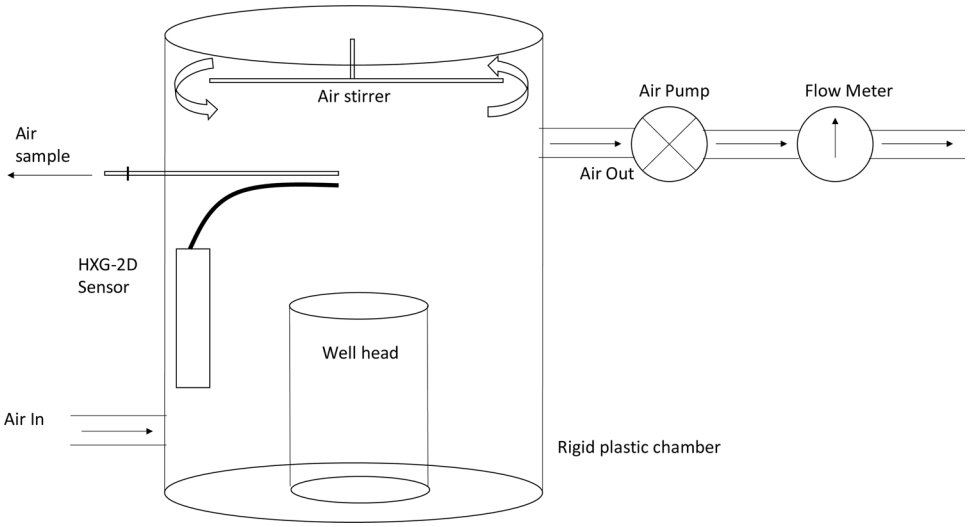

Fig. 1. Schematic of the dynamic flux chamber used to measure emissions from the well head. The dynamic flux chamber is made from a rigid plastic cylinder closed at one end with a diameter of 0.5 m, height of 1.5 m and volume of 0.3 m^3. A propeller was used to circulate the air and a pump drew air through the chamber with flowrate measured throughout using a Cole-Palmer flowmeter.

Methane emissions (Q, g s^{-1}) were calculated using the algorithm presented in Eq. 3 and following the methods in Aneja et al. (2006) and Riddick et al. (2019). Emissions are derived from the CH_4 concentration in the chamber ($[CH_4]_c$), the background CH_4 concentration ($[CH_4]_b$), the height of chamber (h), the flow of air through the chamber (q), and the volume of the chamber (V). During each measurement the height, volume and flow were kept constant and changes in CH_4 concentration inside the chamber were a function of changes in emissions. The flow rate of air through the chamber was measured using a Cole-Palmer volumetric flowmeter (Fig. 1) at the beginning, after the first hour and at the end of the experiment. The relevant equation for the methane flux is

$$Q = \frac{([CH_4]_c - [CH_4]_b)hq}{V} \quad (3)$$

2.2. Field measurements

Field measurements of CH_4 emissions from abandoned oil and gas wells were conducted between November 2016 and September 2017 in Volcano, Wood Co., West Virginia (WV), USA, as published in Riddick et al. (2019), at wells in Pennsylvania (PA), USA, identified in Kang et al. (2016) and at Tibshelf, Derbyshire, UK (Fig. 2). WV and PA measurements were used to examine similarities and differences between basins in the same geographic region, while the measurements in the UK were used to study similarities between CH_4 emissions in geographically disparate oil-producing regions.

2.2.1. Hardstoft 1 oil Well, Tibshelf, Derbyshire, UK

The Hardstoft 1 oil well in Tibshelf is the oldest oil well on the UK mainland. First drilled in 1918, the vertical well in carboniferous limestone reached a depth of 997 m (Craig et al., 2015). Oil production decreased afterwards and the well was finally closed and capped in the late 1940s. The well was rediscovered during landscaping works in the 1990s and was found to be leaking oil. This site was chosen because of its historical significance and because it is on fenced private land with gates that were locked at night. The time-variable measurements over a 24 -h period were repeated monthly between February and September 2017, thereby providing a second time scale (monthly) to analyse temporal variability. In each monthly measurement, the chamber was secured to the ground and left in place for 24 h.

2.2.2. Volcano, Wood County, West Virginia, USA

Oil was first discovered in Volcano, Wood County in 1865 100 feet below the surface and erupted from the surface “like a volcano”. Between 1865 and 1879 an unknown number of oil wells were drilled. On August 4th 1879, a fire burned down the entire town, after which the majority of residents left Volcano for other oil fields and few new wells were drilled. Volcano was chosen for our study site because the site has many abandoned wells close together to measure. None of these wells are documented in the WV Department of Environmental Protection well database (TAGIS, 2017) and no data describing well attributes are available.

The 24 -h methane emissions measurements were taken at the leaking abandoned oil wells in Volcano, Wood Co., WV, which are described in Riddick et al. (2019). The Riddick et al. (2019) measurements were made in November 2016 and comprised 12 abandoned WV wells with instantaneous CH_4 emissions ranging from 0.2 to 6,919 mg CH_4 hr^{-1}. The measurements in the current study were made between between the 20th and 30th May 2017 in Mountwood Park, Wood County, WV (the site of Volcano).

2.2.3. Pennsylvania

To investigate the behaviour of higher emitting ($> 10^4$ mg CH_4 hr^{-1}) abandoned wells, five sites in Pennsylvania were chosen with wells emitting between 31,000 and 81,000 mg CH_4 hr^{-1}, as described in Kang et al. (2016). Measurements for the current study were made in September 2017. The sites were all on state land: Well P1 in Allegheny National Forest near Bradford, PA; Wells P2, P4 and P5 in Parker Dam State Park near Penfield, PA; and Well P3 in Hammersley Wild Area near Coudersport, PA (Fig. 2). Some well attributes were estimated by Kang et al. (2016), as shown in Table SM3.1 (in Supplementary Material Section 3). Plugging status was determined from surface inspection of wells, while the type and depth of well were assigned based on the formation(s) beneath the surface location of the well (see Kang et al. (2016) for details).

2.3. Environmental variability in CH_4 emissions using meteorological data

In addition to presenting emissions from abandoned wells over 24 h, we also investigate how meteorological conditions and corresponding subsurface changes affect emission rates. For the Hardstoft 1 data, we compare CH_4 emission to the average temperature, average relative humidity, average air pressure during the 24 h over which the measurements took place and the cumulative precipitation in the days preceding measurement. In this study we present cumulative rainfall from 1 to 21 days before measurement. To identify variable(s) that have the largest effect on emission rates we report the R^2, gradient and p-value of the regression.

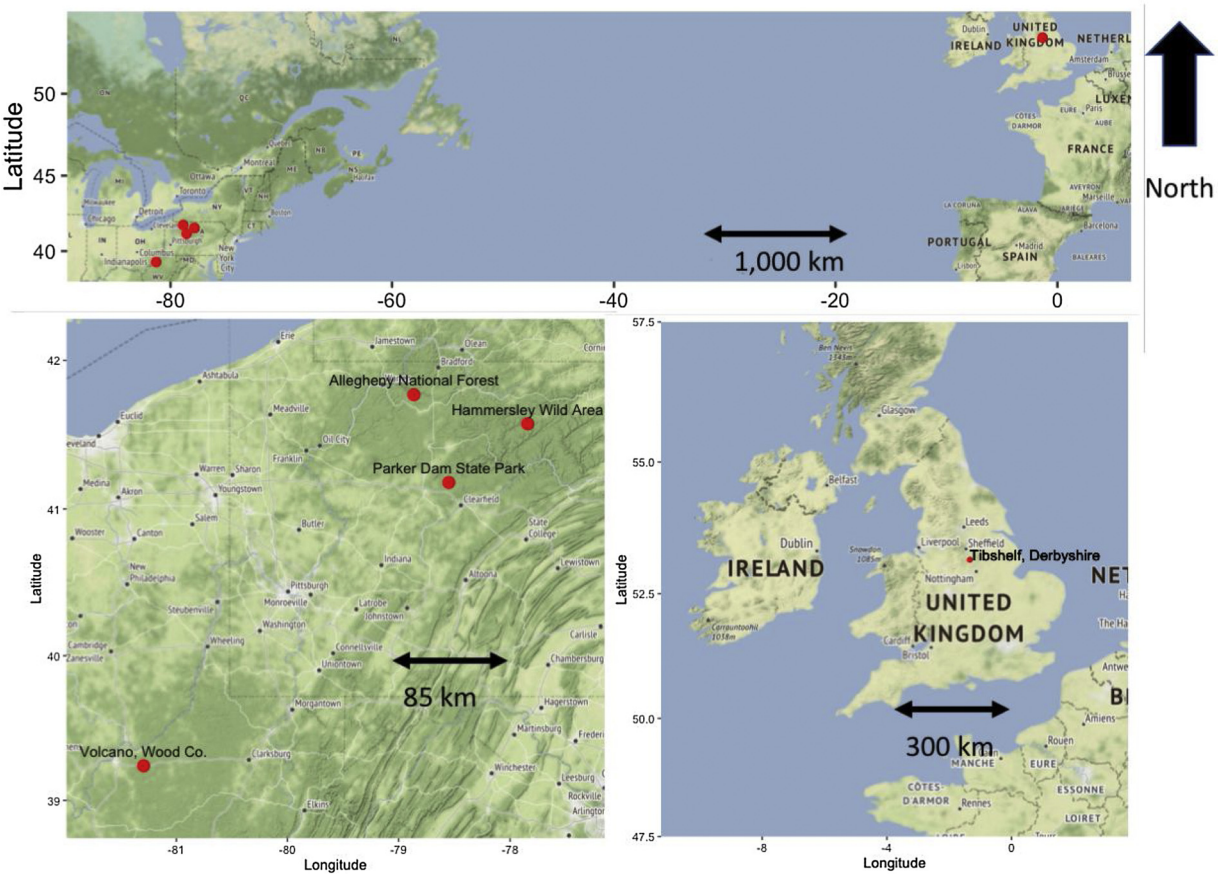

Fig. 2. Map of wells measured in Pennsylvania (two wells in Parker Dam State Park, two wells in Allegheny National Forest and one in Hammersley Wild area), West Virginia (12 wells in Volcano, Wood Co.), both USA and one well in Tibshelf, Derbyshire, UK. Image courtesy of Google maps (www.google.com/maps).

3. Results

3.1. MQ4 methane sensor

The MQ4 methane sensor is an inexpensive (< $10) instrument, not designed for precision CH_4 measurement and, in this application, was calibrated against a low-precision handheld methane sensor. Our goal was not to use the MQ4 sensor to accurately determine CH_4 concentrations, but rather to monitor relative changes in methane concentration. However, we compared the calculated $[CH_4]_c$ values in the chamber with the air samples collected from the chamber and analysed on the GC to determine how representative the calculated CH_4 concentrations were. We found that $[CH_4]_c$ were in good agreement with time-matched GC measurements (Supplementary Material Section 1 Figure SM1.2; m = 1.05, R^2 = 0.99, p-value = 0.001) between 100 ppm and 9% CH_4. This gave us confidence that the MQ4 sensor could feasibly be used to differentiate between high and low concentrations of CH_4.

3.2. Characterisation of methane emission sources

For the wells measured here, the hydrocarbon (C_2 - C_4)/C_1 ratios range from 1.73 (well W6) to 0.006 (well W12) and suggest that all CH_4 emitted from the wells originated from thermogenic sources, as (C_2 - C_4)/C_1 > 0.01, except for W12 which appears to be from a biogenic source (Supplementary Material Section 5).

3.3. Using instantaneous emission measurements to estimate emissions

When instantaneous CH_4 emission estimates, (i.e. averages of multiple instantaneous emission measurements as reported in Kang et al. (2016) for PA and Riddick et al. (2019) for WV), are compared to average CH_4 emissions over 24-hs, only four CH_4 emissions estimates based on instantaneous measurements fall within the range of measurements observed over 24-hs (minimum and maximum CH_4 emissions represented as error bars in Fig. 3). Four of the seventeen show the average of the 24-h CH_4 emission measurements to be more than two orders of magnitude lower than the instantaneous measurements. Nine out of the 17 have 24-h averages as much as four orders of

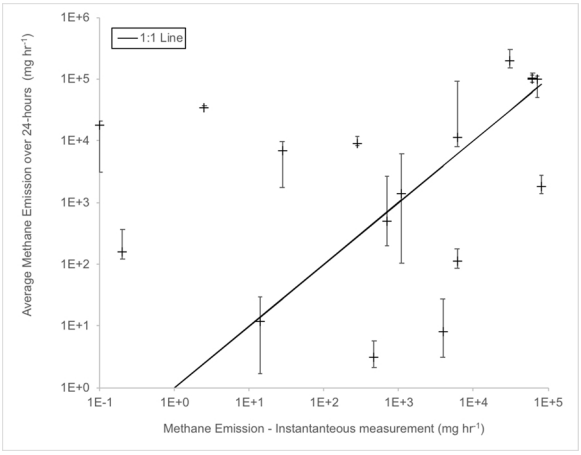

Fig. 3. Methane emissions estimated using instantaneous measurements (data taken from Riddick et al. (2019) and Kang et al. (2016)) compared to average emissions measured over 24 h (as measured in this paper with minimum and maximum emissions during 24-h measurement presented as error bars).

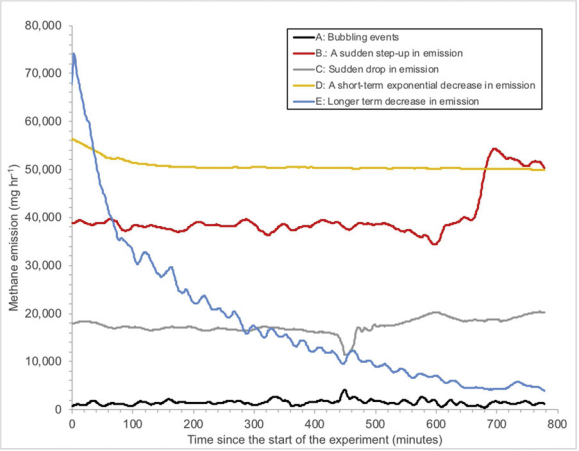

Fig. 4. Five common emission features that were identified in the 24 -h emission profiles of wells measured in West Virginia, Pennsylvania and the UK. The common features were: A. Sporadic emission events e.g. abandoned well W3 in West Virginia, B. Sudden step-up in emissions e.g. abandoned well P4 in Pennsylvania, C. Sudden short-term drop in emissions followed by a recovery and increase in emissions e.g. abandoned well W7 in West Virginia, D. Short-term exponential decrease in emissions e.g. abandoned well P2 in Pennsylvania, E. Slow large longer term decrease in emissions e.g. abandoned well W8 in West Virginia.

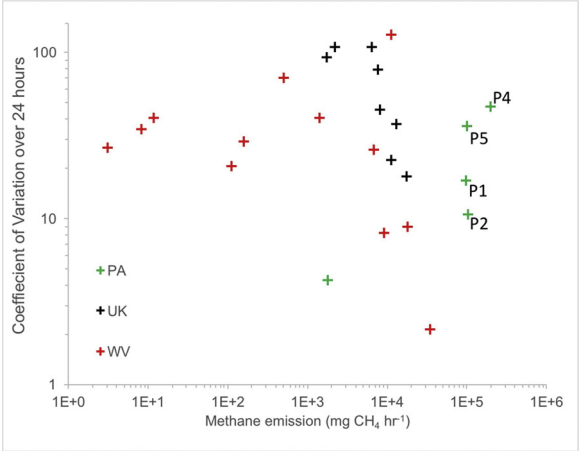

Fig. 5. The average CH_4 emission over 24 -hs is plotted against the coefficient of variance (CV) within the 24 -hs of measurement at each site in Pennsylvania (PA), West Virginia (WV) and the UK (UK).

magnitude higher than the instantaneous measurements.

3.4. CH_4 emissions per well over 24 -hs

The plots from all abandoned wells showed varying CH_4 emission over 24 -hs are shown in Supplementary Material Sections 2; 3; 4. From the collection of transient measurements, five common features are identified and are shown in Fig. 4 using five different plot lines of emissions versus time. From these plots, the five common features are identified as: 1. Sporadic emissions e.g. abandoned well W3 (e.g. Fig. 4A) (a short-term spike in emissions, usually involving an increase on the order of 1000 mg hr^{-1}, over a time interval of several minutes); 2. A sudden large step-up in emission e.g. abandoned well P4 (e.g. Fig. 4B) (an increase of 20,000–30,000 mg hr^{-1} in 10 to a few tens of minutes); 3. A sudden drop in emission followed by a recovery and increase in emissions e.g. abandoned well W7 (e.g. Fig. 4C) (17,000–4,000 mg hr^{-1} in 10 min); 4. A short-term exponential decrease in emissions e.g. abandoned well P2 (e.g. Fig. 4D) (decrease from 120,000–100,000 mg hr^{-1} in 2 h); and 5. Longer term decreases in emissions e.g. abandoned well W42 (e.g. Fig. 4E) (decrease from 10,000–3,000 mg hr^{-1} in 20 h). The 24 -h emission plots for all wells measured in WV, PA and Hardstoft 1 are shown in the Supplementary Material Sections 2,3 and 4, respectively. Of the 17 wells measured in WV and PA seven showed evidence of sporadic emissions, eight showed a sudden step-up, two showed a sudden drop, six showed an exponential decrease, and four showed a slow decrease over an extended period of time. Collectively, this shows that wells were not limited to a single behaviour and displayed a wide range of behaviours over 24 h.

3.5. Variability of emissions and methane emission rates

To investigate the variability of CH_4 emissions from both high emitters ($> 1 \times 10^5$ mg CH_4 hr^{-1}) and lower-emitting wells ($< 1 \times 10^5$ mg CH_4 hr^{-1}), the average CH_4 emission over 24 h is plotted against the coefficient of variance (CV), within the 24 -h time frame (Fig. 5). Here, the CV is the standard deviation of each minute-averaged emission over 24 -hs divided by the mean emission in 24 -hs multiplied by 100. A linear regression between all average CH_4 emissions over 24 h and the corresponding coefficients of variance indicates that there is no statistical significance between the rate of emissions and variability in emissions within a 24 -h time period ($R^2 = 0.09$, m = -0.000, p-value = 0.14). In addition, the plots of the highest emitters, P4 and P5, show substantial CV of 30–50 % change in emission (Supplementary Material Section 3). The average percentage change of lower-emitting wells ($< 1 \times 10^5$ mg CH_4 hr^{-1}) is 26 %, which indicates that the overall magnitude of variability is similar at all emission rates when measured using the coefficient of variance.

3.6. Meteorological drivers of CH_4 emissions

Previous studies have suggested that the CH_4 emissions from high-emitting abandoned wells have little seasonal variability (Kang et al., 2016), however the variability in CH_4 emissions between the instantaneous and 24 -h average measurements was not investigated. To investigate this, we compare a 24 -h emission measurement taken each month at the Hardstoft 1 well to 24 -h average air temperature, relative humidity, air pressure and cumulative precipitation.

The variability in the average 24 -h CH_4 emission for each month at Hardstoft 1 appears to show seasonal effects (Fig. 6). The highest emissions rate of 17,386 mg CH_4 hr^{-1} was observed in August and the lowest of 1726 mg CH_4 hr^{-1} in April. The relationship between the coefficient of variance over 24 -hs and the average 24 -h CH_4 emission is statistically significant ($R^2 = 0.76$, m = -0.0061, p-value = 0.005), indicating a decrease in variability as the average emission increases.

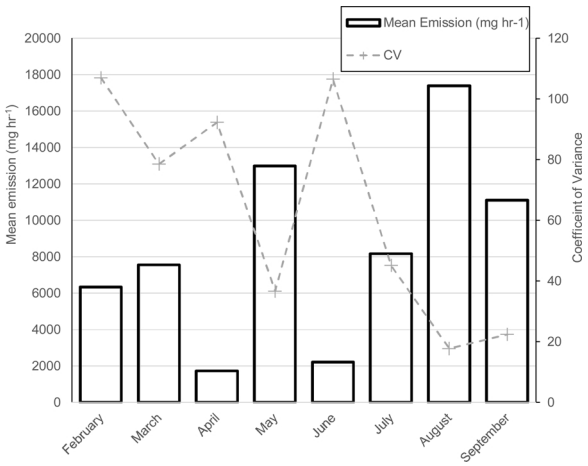

Fig. 6. Variability in the average of the 24 -h methane emissions from the Hardstoft 1 oil well in Tibshelf, UK, in 2017.

Changes in the average 24 -h CH_4 emissions from the Hardstoft 1 well are not statistically significantly related to average air temperature (p-value = 0.91), average relative humidity (p-value = 0.81) or average atmospheric pressure (p-value = 0.22). However, methane emission rates are statistically significantly related to the cumulative precipitation in the days preceding the measurement, where the highest R^2 and lowest p-value was found for the cumulative rainfall in the 7 days before the measurement (R^2 = 0.79, m = 1053, p-value 0.001; Supplementary Material Section 6 Figure SM 6.1). While a detailed mechanistic investigation is beyond the scope of the current work, we note that mixed lateral and vertical gas migration in shallow unsaturated soils (see, for example, Forde et al., 2018) is significantly influenced by meteorology. The effect of meteorology may be influenced by the underlying mechanisms that influence flux from our wells because the well settings and flow pathways may differ notably between wells.

4. Discussion

4.1. Methane emissions from abandoned wells over 24 -h periods

We present the first data showing essentially continuous measurements of emissions over 24 -h time periods from abandoned oil and gas wells at sites in the UK and the USA. This study used a low-cost sensor inside a dynamic chamber to continuously monitor changing CH_4 concentrations. Comparisons of the concentration derived from the sensor output to concentrations measured using a GC show that calibrated low cost sensors can feasibly be used to facilitate widespread monitoring of abandoned oil and gas wells. For these wells, the alkane ratios show that the methane emitted is from a thermogenic source at all but one well out of the 18 wells measured. The measurements indicate that CH_4 emissions vary by between 1.1–142 times, with an average of a factor of 18, over the 24 -h measurement period (Supplementary Material Section 5). Data presented here strongly suggest the amount of precipitation falling the week before measurements are made may affect variability in emissions (Supplementary Material Section 6 Figure SM 6.1). This is contrary to the findings of Forde et al. (2019), who looked at horizontally extensive gas transport associated with gas injected into the shallow subsurface; in our case, we have essentially vertical transport of gas along the wellbore that is open at the land surface.

Given that the majority of the methane appears to be migrating through an open wellbore filled with another fluid (most likely water, possibly some oil) or through a conductive zone just outside the well casing, we hypothesize that flow variability may be associated with buoyancy combined with threshold blockage and release. These kinds of flows can lead to a uniform bubbly flow (simple buoyancy) or a periodic slug-type flow. The periodic nature of gas slugs (or Taylor bubbles) and associated emissions is likely to be driven by how gas enters/leaves the wellbore and migrates upwards (Dusseault and Jackson, 2014). Therefore, the variability likely reflects the complex leakage flow paths within a wellbore (Davies et al., 2014; Gasda et al., 2004). We note the important studies of Forde et al. (2019).

Database analysis studies on wellbore leakage have identified a wide range of factors including drilling and completion methods, geographic location, geology, and surface casing depth (Bachu, 2017; Cahill et al., 2019; Lackey et al., 2017; Montague et al., 2018; Watson and Bachu, 2009). However, it is impossible to apply these approaches to the current wells because of a lack of historical information for the wells. Many of the measured wells date from the 19th century and are completely undocumented without the details of date of drilling, how much oil was produced or the height of the water table. While some attributes can be inferred from historical studies (for example, Kang et al., 2016), a systematic study like those referenced is not possible. Given the age of the wells and the lack of regulatory statutes at the time of their abandonment, it could be that these very old wells were never sealed after use. In those cases, when oil production became unprofitable, the operator simply moved to the next well. This practice was common before modern plugging regulations were put in place. Well drilling practices and technology have evolved over time from cable tool drilling with no cement isolation in the 19th century to rotary drilling in the 1930s to modern drilling and completion techniques (King and Valencia, 2014). Even though we offer some possible explanations above, the main finding of this study is that methane does not leak from abandoned wells at a constant rate and that the variability can be significant within a 24 -h period.

4.2. Instantaneous CH_4 emission measurements from abandoned wells

Even though many studies have used instantaneous (< 1 h) CH_4 measurements to make emission estimates from abandoned oil and gas wells (Boothroyd et al., 2016; Kang et al., 2016, 2014; Townsend-Small et al., 2016), observations made in this study indicate that CH_4 emissions calculated from short term CH_4 concentration measurements (~ 1 h) can be substantially different from the daily average CH_4 emissions because large changes in emissions can occur over minutes to hours (e.g. short-term, < 5 min, sporadic emission events can clearly be seen during 70 % of our measurements; Supplementary Material Section 2). These variations over the 24 -h time period should be considered when assigning emission factors.

Longer term methane measurements (with each measurement representing a daily average) can provide a more representative annual average emission. For example, the difference in average CH_4 emissions at the same site can vary by a factor of 6 between consecutive months (May to June; Fig. 6). This suggests that instead of a single average one-hour emission for each well, as has been used previously to calculate fugitive emissions from abandoned oil and gas wells (Riddick et al., 2019), a more dynamic approach may need to be employed to estimate changing emissions throughout the day and throughout the year.

We suggest that emission estimates should be based on longer-term measurements. Ideally, continuous measurements for at least 24 h repeated in various seasons would provide a more accurate representation of well leakage. However, we acknowledge that 24 -h measurements at every site would be prohibitively expensive. Instead, we suggest that, for most of the wells measured in this study, measurements lasting three-hours could make emission estimates representative of the mean 24 -h emission by averaging out emission behaviours A to D, as identified in Section 3.4. The results presented here suggest high emission events tend to be short-lived (less than one hour), so random sampling is likely to miss them. Single measurements in time therefore likely underestimate actual cumulative emissions, thus potentially leading to underestimates of emissions from abandoned oil and gas wells in GHG emission inventories.

From a policy viewpoint, this study highlights the shortcomings in our understanding of what drives emissions from abandoned oil and gas wells. Our results show that wells emitting almost no CH_4 can be revisited and emissions 10,000 times higher can be observed, i.e. WV5 (Supplementary Material Section 5). Conversely, higher emitting wells can be 500 times less emissive when re-measured (WV1). This uncertainty must be resolved through further measurements of a successful plugging program targeting constantly high emitting wells if a plugging strategy is to be implemented that reduces overall GHG emissions to the atmosphere.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Stuart N. Riddick: Conceptualization, Data curation, Formal analysis, Writing - original draft, Writing - review & editing. **Denise L. Mauzerall:** Conceptualization, Supervision, Writing - original draft, Funding acquisition, Writing - review & editing. **Michael A. Celia:** Supervision, Funding acquisition, Writing - review & editing. **Mary Kang:** Funding acquisition, Writing - review & editing. **Karl Bandilla:** Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ijggc.2020.103116.

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