

Direct measurements of methane emissions from abandoned oil and gas wells in Pennsylvania

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Edited* by Stephen W. Pacala, Princeton University, Princeton, NJ, and approved November 10, 2014 (received for review May 6, 2014)

Abandoned oil and gas wells provide a potential pathway for subsurface migration and emissions of methane and other fluids to the atmosphere. Little is known about methane fluxes from the millions of abandoned wells that exist in the United States. Here, we report direct measurements of methane fluxes from abandoned oil and gas wells in Pennsylvania, using static flux chambers. A total of 42 and 52 direct measurements were made at wells and at locations near the wells (“controls”) in forested, wetland, grassland, and river areas in July, August, October 2013 and January 2014, respectively. The mean methane flow rates at these well locations were 0.27 kg/d/well, and the mean methane flow rate at the control locations was 4.5×10^{-6} kg/d/location. Three out of the 19 measured wells were high emitters that had methane flow rates that were three orders of magnitude larger than the median flow rate of 1.3×10^{-3} kg/d/well. Assuming the mean flow rate found here is representative of all abandoned wells in Pennsylvania, we scaled the methane emissions to be 4–7% of estimated total anthropogenic methane emissions in Pennsylvania. The presence of ethane, propane, and n-butane, along with the methane isotopic composition, indicate that the emitted methane is predominantly of thermogenic origin. These measurements show that methane emissions from abandoned oil and gas wells can be significant. The research required to quantify these emissions nationally should be undertaken so they can be accurately described and included in greenhouse gas emissions inventories.

methane emissions | oil and gas | abandoned wells | hydrocarbons | isotopes

Abandoned oil and gas wells provide a potential pathway for subsurface migration and emissions to the atmosphere of methane and other fluids (1). According to one recent study, there are an estimated 3 million abandoned oil and gas wells throughout the United States (2). Methane emissions from these wells are assumed to be the second largest potential contribution to total US methane emissions above US Environmental Protection Agency estimates and are not included in any emissions inventory (2). There is a lack of empirical studies that can be used to estimate the methane emission potential of these wells (2).

Methane is a greenhouse gas (GHG) and its oxidation produces ozone (O_3) that degrades air quality and adversely impacts human health, agricultural yields, and ecosystem productivity (3). Therefore, it is important to understand methane emission sources so that appropriate mitigation strategies can be developed and implemented.

Efforts to improve estimates of methane emissions to the atmosphere from oil and gas production in the United States are being driven, in part, by growth in unconventional production. Estimates of methane emissions from activities on producing oil and gas sites, including well completion, routine maintenance, and equipment leaks, are used to develop bottom–up estimates (4, 5). Overall, a comparison of bottom–up and top–down estimates indicate that there may be missing sources in bottom–up estimates (2, 6–8, 9). Here, we focus on one missing source: abandoned oil and gas wells.

There is no regulatory requirement to monitor or account for methane emissions from abandoned wells in the United States. Methane leakage through abandoned wells linked to recent growth in unconventional oil and gas production is being studied as a groundwater contamination issue (10–14), but no direct evidence for leakage through abandoned wells to groundwater aquifers currently exists. Abandoned wells have been connected to subsurface methane accumulations that have caused explosions, which are major concerns in urban areas with oil and gas development or natural gas storage reservoirs, as well as in coal mines (15, 16). Therefore, existing monitoring is focused on detecting large concentrations. The result is a lack of information to quantify methane emissions from abandoned oil and gas wells.

To characterize abandoned oil and gas wells’ potential as a significant methane source, we made first-of-a-kind direct measurements of methane flow rates from 19 wells in various locations across McKean and Potter counties in Pennsylvania (PA) (Fig. 1). The measured wells were selected mainly based on logistical and legal access (*Supporting Information*). As of January 17, 2014, only 1 of the 19 wells was on the PA Department of Environmental Protection’s (DEP’s) list of abandoned and orphaned wells. (Orphaned wells can be defined as abandoned wells with no

Significance

Recent studies indicate that greenhouse gas emission inventories are likely missing methane emission sources. We conducted the first methane emission measurements from abandoned oil and gas wells and found substantial emissions, particularly from high-emitting abandoned wells. These emissions are not currently considered in any emissions inventory. We scaled methane emissions from our direct measurements of abandoned wells in Pennsylvania and calculate that they represent 4–7% of current total anthropogenic methane emissions in Pennsylvania. Millions of abandoned wells exist across the country and some are likely to be high emitters. Additional measurements of methane emissions from abandoned wells and their inclusion in greenhouse gas inventories will aid in developing and implementing appropriate greenhouse gas emission reduction strategies.

Author contributions: M.K., C.M.K., M.C.R., X.Z., and Y.C. designed research; M.K., C.M.K., M.C.R., X.Z., D.L.M., M.A.C., Y.C., and T.C.O. performed research; M.K. analyzed data; and M.K., D.L.M., and M.A.C. wrote the paper.

The authors declare no conflict of interest.

*This Direct Submission article had a prearranged editor.

Freely available online through the PNAS open access option.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1408315111/-DCSupplemental.

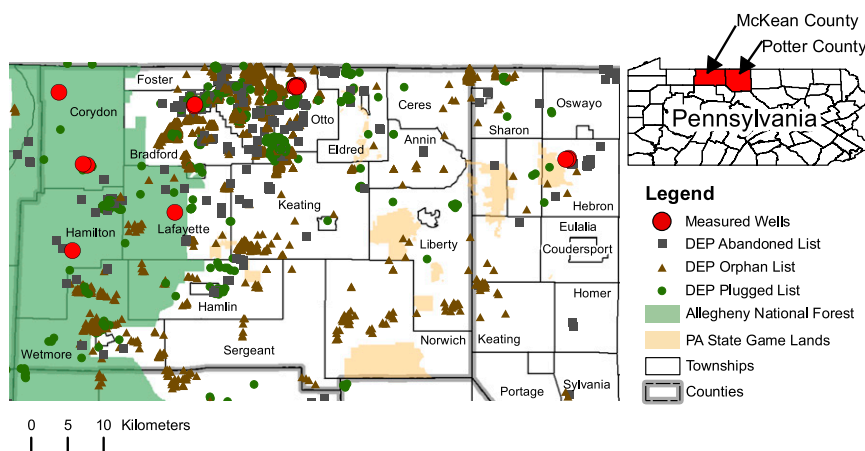


Fig. 1. The 19 measured wells are located in McKean County and Potter County in Pennsylvania. There are 12,127 abandoned, orphaned, and plugged wells on the Pennsylvania DEP's website (as of January 17, 2014), with 4,273 in McKean County and 188 in Potter County. The map shows the DEP wells that are in the region of our field study. Note that only the western portion of Potter County is shown in the detailed map.

responsible party available, other than the state.) The DEP database provides information on the well status (abandoned, plugged, or orphan) and well type (gas, oil, combined oil and gas, or undetermined) but does not provide other information such as well age and depth. No additional information on the measured wells is available. This is indicative of the general scarcity of available information on this class of old wells in PA. Given the lack of records on the wells we measured, no distinction was made between oil and gas wells; the wells were simply categorized as plugged or unplugged, based on surface evidence of cementing and/or presence of a marker. With this criterion, 5 of the 19 measured wells (26%) were classified as plugged.

In addition to methane, we also analyzed the collected samples for ethane, propane, n-butane, and carbon isotopes of methane, to provide insight on the potential sources of the emitted methane. This work provides previously unavailable data on methane leakage rates and other emissions from abandoned oil and gas wells.

Results

Methane Flow Rates. Mass flow rates, in units of mass per time per well, were measured using a static chamber methodology (17, 18) (*Materials and Methods* and *Supporting Information*). Methane flow rates from wells and controls were measured at various sites over five sampling campaigns that took place in July, August, and October 2013, and January 2014. At each well site, measurements of one to six controls located 0.1–62 m from the measured well were taken. (Flow rates at each control were scaled to reflect the same areal footprint as that of the nearest well to ensure that measurements for wells and controls were consistent.)

Methane flow rates from abandoned wells were found to be significantly higher than methane flow rates observed at controls (Fig. 2). The mean flow rate at well locations was 11,000 mg/h/well (0.27 kg/d/well), and the mean flow rate at control locations was 0.19 mg/h/location (4.5×10^{-6} kg/d/location). The median flow rate at well locations was 56 mg/h/well (1.3×10^{-3} kg/d/well), which is still higher than both the mean and median flow rate at control locations. The median flow rate at controls was 0 mg/h/location (or 0 kg/d/location) considering all values, and 6.7×10^{-3} mg/h/location (1.6×10^{-7} kg/d/location) considering nonzero values. Positive methane flow rates were observed at all 19 wells with values, averaged over multiple sampling events, ranging from 6.3×10^{-1} to 8.6×10^4 mg/h/well. Average methane flow rates over multiple sampling events at control locations ranged from -1.2×10^{-1} to 4.2 mg/h/location.

Methane flow rates at wells were based on good linear fits with 88% of the flow rates having R^2 values greater than 0.8 (*Supporting Information*). Sources of uncertainty included flux chamber design, deployment, sampling, laboratory analysis of samples, and data selection for regression analysis (*Supporting Information*). We estimate that the combined effect of the various sources of uncertainties in flow rate estimates will lead to errors within a factor of 2 of our estimate. This error is small relative to the seven orders of magnitude variation in measured flow rates. Furthermore, most of the sources of measurement uncertainty would bias the measured flow rates to be lower than their actual value.

Methane flow rates at well locations appeared to be unaffected by land cover, which included forest, grassland, river, and wetland. In contrast, we found that methane fluxes at control locations were dependent on land cover. A large proportion of flow rates from controls in forests and grasslands were negative (i.e., methane sinks) and ranged from -1.2×10^{-1} to 1.8 mg/h/location, and the flow rates from controls in wetlands were consistently positive and relatively high, ranging from 1.6×10^{-2} to 4.2×10^1 mg/h/location. We found seasonal effects were present in controls, with lower methane fluxes observed in the January 2014 sampling round. Although there is no evidence of significant seasonal effects in the methane flow rates from wells, additional measurements are needed to reach a firm conclusion.

According to regulations on well abandonment, wells are plugged to limit vertical migration from subsurface source

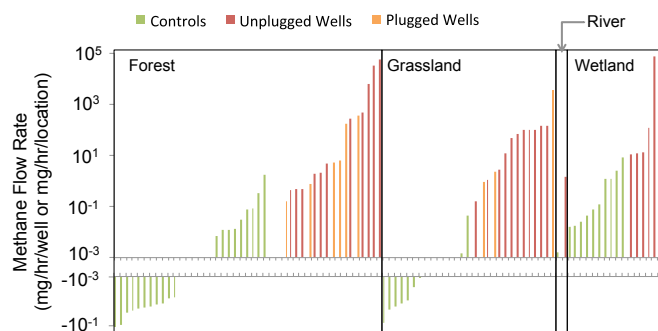


Fig. 2. A total of 42 and 52 measurements were made at wells and at locations near the wells (controls), respectively, in forested, wetland, grassland, and river areas in July, August, October 2013 and January 2014.

formations (oil and gas reservoirs and coal beds), which includes minimizing impacts on groundwater. We found that methane flow rates from plugged wells were not necessarily lower than methane flow rates at unplugged wells. For example, in the grassland area, both the largest and the second lowest methane fluxes originated from plugged wells. Evaluation of plugging status and wellbore integrity was difficult using only visual inspection at the surface and lack of additional information.

Presence of Ethane, Propane, and n-Butane. The presence and concentration of ethane, propane, and n-butane are useful for identifying the methane source as thermogenic or microbial. Because ethane is not coproduced during microbial methanogenesis, the presence of ethane-to-methane ratios greater than 0.01 indicates gas of largely thermogenic origin (14, 19). A similar threshold is not readily available in literature for propane-to-methane and n-butane-to-methane ratios, but we expect this threshold value to be less than 0.01. Ratios of ethane, propane, and n-butane relative to methane were more frequently greater than 0.01, and at higher values, for wells than for controls (Fig. 3). Nonetheless, the presence of these nonmethane hydrocarbons in controls indicates that there may be subsurface horizontal gas flow away from the well and subsequent emissions to the atmosphere. We also did not find a consistent ratio for wells or controls and obtained alkane ratios ranging from 1×10^{-5} to 0.8. The high variability in alkane ratios may be a result of mixing between various microbial and thermogenic (deeper) sources.

Carbon Isotopes of Methane. Carbon isotope information provides additional evidence suggesting that the source of methane from the wells is likely to represent a mixture of microbial and thermogenic sources. In general, methane originating from thermogenic sources is more enriched in ^{13}C ; whereas, methane originating from microbial sources is relatively depleted in ^{13}C . We found that the samples collected at wells were likely to be more enriched in ^{13}C than those collected at controls (Fig. 4). A comparison of the methane $\delta^{13}\text{C}$ values to that of known thermogenic and microbial sources (20) indicates that most of the methane flow rates from wells are thermogenic or a mixture of microbial and thermogenic sources. Only 3 of the 26 measurements at wells had methane $\delta^{13}\text{C}$ values in the microbial range. The methane $\delta^{13}\text{C}$ values of the measured wells ranged from -71‰ to -21‰ . This range is broader than published methane $\delta^{13}\text{C}$ values of thermogenic methane in natural gas in the northern Appalachian basin, which range from -47.9‰ to -30.7‰ (21). The methane $\delta^{13}\text{C}$ values at controls ranged from -85‰ to 75‰ , indicating control sources were more likely to be of primarily microbial origin.

Fig. 4 also shows that locations with larger methane flow rates emitted methane that was more enriched in ^{13}C . Wells with methane flow rates that were greater than 10^3 mg/h/well were likely to be emitting methane of thermogenic origin; and wells

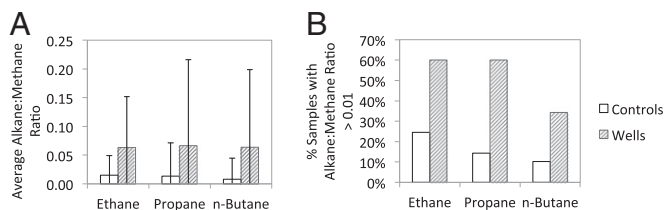


Fig. 3. Average alkane ratios ($[\text{C}_2\text{H}_6]/[\text{CH}_4]$, $[\text{C}_3\text{H}_8]/[\text{CH}_4]$, and $[\text{n-C}_4\text{H}_{10}]/[\text{CH}_4]$) (A) and proportions of samples with alkane ratios greater than 0.01 (B) at control and well location with detectable ethane, propane, and n-butane concentrations are calculated for samples collected in July, August, and October 2013 and January 2014. The error bars in A represent the SDs of the dataset.

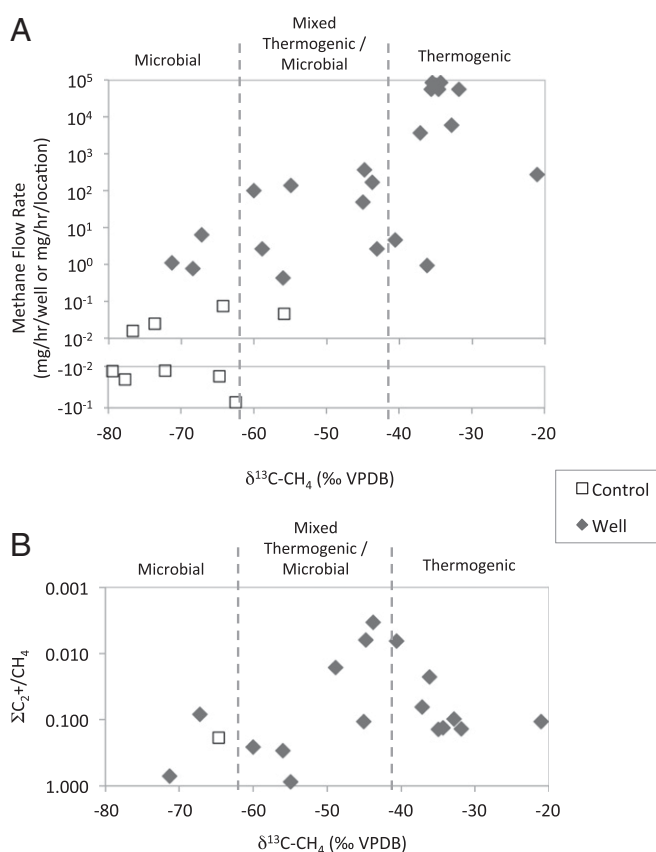


Fig. 4. Composition of carbon isotopes of methane for select samples collected at well and control locations in July, August, and October 2013 and January 2014 are compared with the methane flow rate (A) and the sum of ethane, propane, and n-butane concentrations divided by methane concentrations (B).

with flow rates in the order of 10^0 to 10^1 mg/h/well emitted methane of microbial, thermogenic, or mixed thermogenic/microbial origin. Methane emitted from most control locations is in the microbial range; however, one measurement reveals that methane emitted from control sources can contain thermogenic sources of methane as well. If we consider the integrated fluxes from all these wells, the methane emitted is primarily of thermogenic origin because the high-emitting wells would represent a large fraction of the total methane emitted from abandoned wells.

We expected the ratio of the sum of ethane, propane, and n-butane concentrations divided by methane concentrations ($\Sigma \text{C}_2+/\text{CH}_4$) to be higher for samples more enriched in methane $\delta^{13}\text{C}$ (19). Instead, we observed the opposite with quite a few of the samples depleted in methane $\delta^{13}\text{C}$ with large values of $\Sigma \text{C}_2+/\text{CH}_4$ (Fig. 4). This trend may indicate that there may be complex microbial cycling occurring in and around the wells.

Methane Emissions from Abandoned Wells in PA

Total methane emissions from all abandoned oil and gas wells in PA can be estimated from the number of wells and the emissions per well. If we assume the 19 measured wells are representative of wells across the state, we can use the mean of measured methane flow rates from the wells (0.27 kg/d/well) as a gross estimate of the statewide emission rate per well. As shown in Fig. 5, the mean is ~ 3 orders of magnitude larger than the median, indicating that the mean value is controlled by a few high emitters. We note that site selection was not based on knowledge about a well's emission potential (*Supporting Information*). It is difficult to quantitatively assess the ability of our measurements

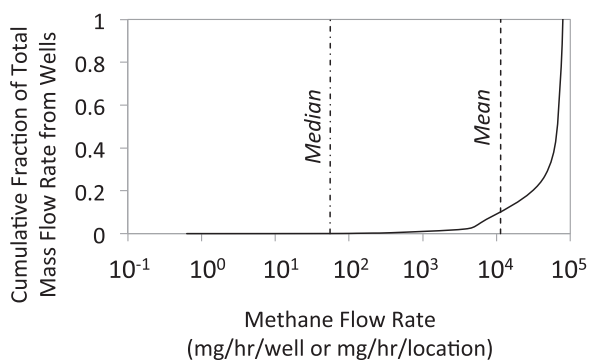


Fig. 5. Cumulative fraction of total measured methane mass flow rate from wells with respect to mass flow rate order of magnitude.

to capture the distribution from all abandoned wells in PA and the representativeness of the mean flow rate for all wells in PA remains uncertain.

The number of abandoned oil and gas wells in the United States and abroad is also highly uncertain. The numbers are complicated by the fact that many of the abandoned wells are “lost” with no evidence of their existence at the surface and/or via public records. Based on the history of oil and gas production in PA, 300,000–500,000 abandoned and orphaned wells have been estimated to exist in PA (*Supporting Information*).

Using these numbers, we estimate methane emissions from abandoned oil and gas wells in PA to be 0.03–0.05 Mt CH₄ per year, which corresponds to 4–7% of estimated total anthropogenic methane emissions in PA for 2010 (22) (*Supporting Information*). We also calculate methane emissions from abandoned wells to be ~0.3–0.5% in 2010 and 0.1–0.2% in 2011 of gross gas withdrawal in PA. These percentages are relatively close to methane leakage from US natural gas production estimated at 0.53–0.59% of gross US gas production in 2011 (5). We provide the scaled estimates to give some context for the relative significance of methane emissions from abandoned wells. We acknowledge that the sample may not be representative of all wells in PA and the denominator used to determine the percentage in terms of total anthropogenic methane emissions is uncertain (*Supporting Information*). (Also, recall that the measurement error in flow rates is estimated to be up to a factor of 2.) We also note that the millions of abandoned oil and gas wells across the country will increase the current contribution to methane emissions from natural gas and petroleum systems, which are 23% and 5% of total methane emissions, respectively, for 2010 (23).

Conclusions

Methane emissions from abandoned oil and gas wells appear to be a significant source of methane emissions to the atmosphere. An improved understanding of abandoned oil and gas wells as a methane emission source may help bridge the current gap in local, regional, and global methane budgets. Additional measurements are required to characterize and determine the distribution of methane flow rates from these wells. Also, lost wells

must be identified, located, and recorded to improve estimates of the number of abandoned oil and gas wells.

The measured wells presented in this paper are likely to be half a century old or older, and the positive flow rates measured at these wells indicate that the methane emissions from these wells may have been occurring for many decades and possibly more than a century. Therefore, the cumulative emissions from abandoned wells may be significantly larger than the cumulative leakage associated with oil and gas production, which has a shorter lifetime of operation.

As oil and gas development continues to grow in the United States and abroad, the number of abandoned oil and gas wells will continue to grow. Inclusion of abandoned wells in methane emissions accounting (e.g., GHG emissions inventories) will facilitate an improved understanding of their impact on the environment and the development and implementation of effective mitigation strategies and policies. In addition, the measurements provided here may be useful for characterizing groundwater contamination sources and estimating subsurface accumulations of methane and other fluids.

Materials and Methods

We selected the abandoned wells to be measured based on location information, access (legal and logistical), wellhead configuration/geometry above ground, land cover, and plugging status (*Supporting Information*). A static chamber methodology was adapted from techniques to measure trace gas fluxes from soil–plant systems (17, 18). The chambers were designed to enclose the wellhead and measure the methane and other trace gas fluxes from the well and surrounding areas. This is discussed further in the *Supporting Information*. Air samples were analyzed for CH₄, C₂H₆, C₃H₈, and n-C₄H₁₀ using flame ionization gas chromatography on a Shimadzu GC-2014 instrument (*Supporting Information*). To measure the C isotopic composition of CH₄, a near-IR continuous wave-cavity ring-down spectrometer (CW-CRDS) was used (24) (*Supporting Information*).

Mass flow rates, in units of mass per time per well, beginning from the moment of chamber deployment, were calculated using linear regression in MATLAB on the concentration data, c [mass/volume], over time.

$$F = \frac{dc}{dt} \cdot V_e, \quad [1]$$

where dc/dt is the slope of the fitted line for $c(t)$ and V_e is the effective chamber volume. For control locations, F is scaled based on the land area covered by the chamber for the control and the nearest well location.

ACKNOWLEDGMENTS. We thank Princeton Environmental Institute for the Science, Technology, and Environmental Policy Fellowship and the National Sciences and Engineering Research Council of Canada for the Postgraduate Scholarship-Doctoral Program (to M.K.). We thank Princeton University for awards (to M.A.C. and D.L.M.) and Yale Center for Environmental Law and Policy award (to X.Z.) for providing funding for equipment and travel. This work was supported in part by National Oceanic and Atmospheric Administration Grant NA140AR4310131, “Constraining methane leakage from abandoned oil and gas wells.” We also thank Joseph/Cheryl Thomas, Joann Parrick, and Save Our Streams PA for aiding in site identification and access; Joseph Vocaturo for assisting with chamber construction; Tsering W. Shawa for helping with map creation and geospatial analysis; Professor Anthony Ingrassia for providing contacts in Pennsylvania; Ryan Edwards, Evan Leister, Levi Golston, and David Pal for assisting in the field and with chamber construction; Peter Jaffe for allowing the use of laboratory equipment/facilities; and David Pal for assisting with laboratory equipment setup and usage.

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