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Chemical Characterization of Natural Gas Leaking from Abandoned Oil and Gas Wells in Western Pennsylvania

Dominic C. DiGiulio,* Robert J. Rossi, Eric D. Lebel, Kelsey R. Bilsback, Drew R. Michanowicz, and Seth B.C. Shonkoff

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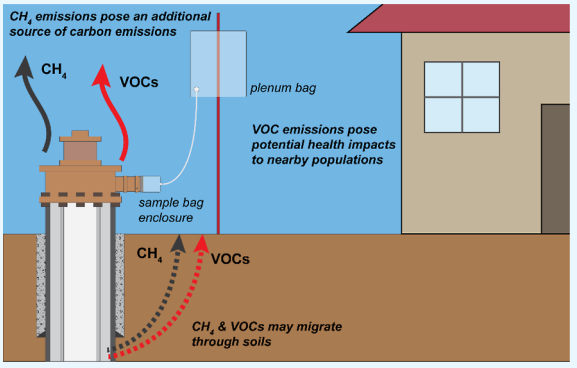
ABSTRACT: The U.S. Environmental Protection Agency estimates that there are over 3.2 million abandoned wells in the United States. Studies conducted on gas emissions from abandoned wells have been limited to methane, a powerful greenhouse gas, due to concerns regarding climate change. However, volatile organic compounds (VOCs), including benzene, a known human carcinogen, are known to be associated with upstream oil and gas development and hence could also be released when methane is emitted to the atmosphere. In this investigation, we analyze gas from 48 abandoned wells in western Pennsylvania for fixed gases, light hydrocarbons, and VOCs and estimate associated emission rates. We demonstrate that (1) gas from abandoned wells contains VOCs, including benzene; (2) VOCs are emitted from abandoned wells, the magnitude of which depends on the flow rate and concentration of VOCs in the gas stream; and (3) nearly one-quarter of abandoned wells are located within 100 m of buildings, including residences, in Pennsylvania. Together, these observations indicate that further investigation is necessary to determine whether emissions from abandoned wells pose an inhalation risk to people living, working, or congregating near abandoned wells.



1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) estimates that there are over 3.2 million abandoned wells in the United States.[1] This number includes oil and gas wells with no recent production (plugged, inactive, temporarily abandoned, shut-in, and idle), with or without a responsible owner (orphaned). An on-line review of records from the Pennsylvania Department of Environmental Protection (PADEP)[2] indicates that there are 24,619 documented abandoned wells in Pennsylvania, of which 18,608 have associated geographical coordinates (Figure 1). However, the PADEP estimates that there are approximately 200,000 abandoned oil and gas wells that remain unaccounted for in state records.[3,4]

Leakage of natural gas to the atmosphere at the wellhead at active and abandoned wells can occur through poorly sealed joints, flanges, and valves. Leakage can also occur through a casing vent engineered to allow gas flow between the annular spaces of the surface, intermediate, and production casing, collectively commonly referred to as surface casing vent flow (SCVF).[7] Venting effectively eliminates pressure buildup in an annular space, which can cause the entry of gas into groundwater.[8] Casing vents are commonly used in Canada, especially Alberta,[9] British Columbia,[10] and Quebec.[11] However, the use of casing vents in the United States appears limited to Pennsylvania.[7] In Pennsylvania, plugged oil and gas wells penetrating "marketable" coal must be equipped with a 5 cm (2 in.) vent pipe 9.1 m (30 ft) below the coal bed.[12]

When subsurface gas leakage occurs along or away from the borehole, it is often referred to as gas migration.[13] Gas migration can result in the efflux of gas through soil to the surface near oil and gas wells or transport to water wells[14] or surface water[15,16] through deeper and more extensive lateral migration in groundwater. Between 1987 and 2013, there were 133 confirmed cases of gas migration to water wells in Pennsylvania attributed to abandoned wells.[3] Gas migration from abandoned wells into buildings and residences has resulted in emergency plugging actions[17,18] and contributed to explosions in Pennsylvania[19] and elsewhere.[20] Gas migration and SCVF are believed to be due to a lack of cement in non-producing but gas-containing strata overlying reservoirs, defects in cement during setting, poor bonding between cement and casing or cement and boreholes, drilling induced fractures outside boreholes,[21,22] and corrosion of casing,

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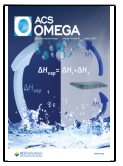

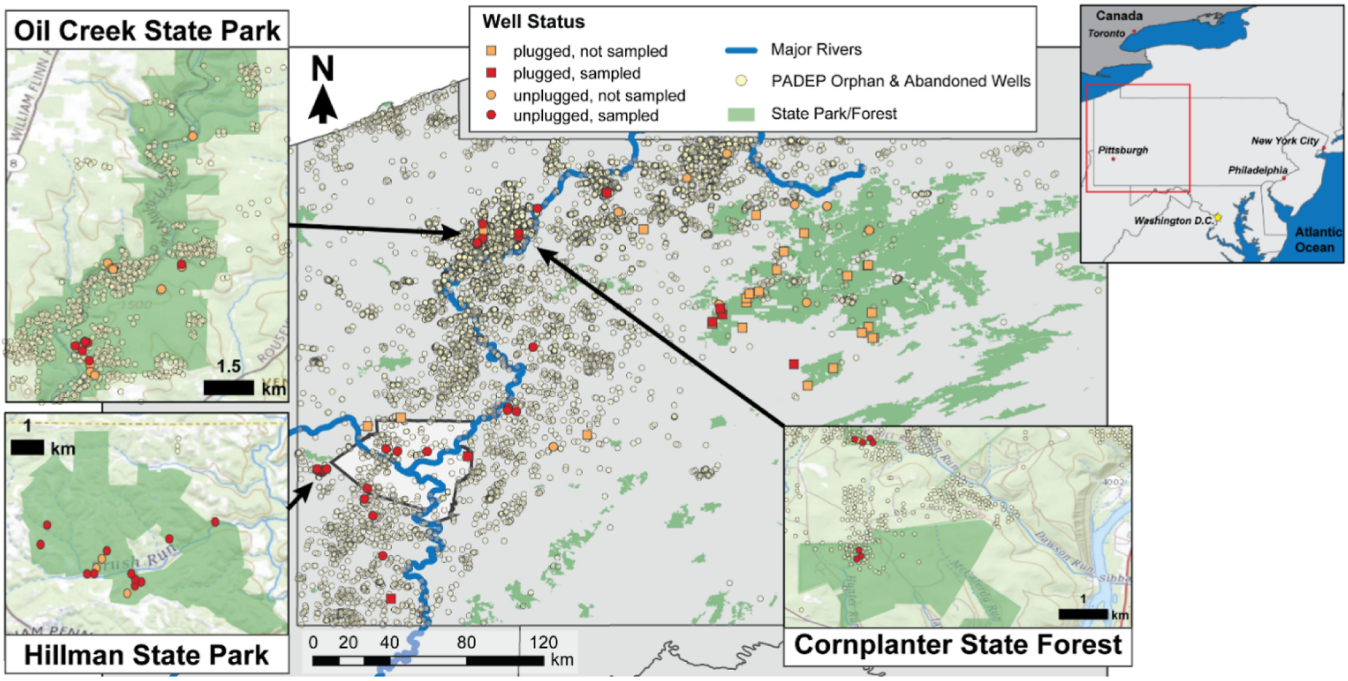

Figure 1. Locations of documented abandoned wells in western Pennsylvania having coordinates,[2] plugged and unplugged abandoned wells screened but not sampled in this investigation, and plugged and unplugged abandoned wells both screened and sampled in this investigation. State park[5] and state forest[6] boundaries are included where screening and sampling occurred. The polygon in southwestern Pennsylvania represents the outline of Allegheny County.

especially in the presence of gas containing hydrogen sulfide (H_2S).[20]

Concern regarding climate change has led to considerable interest in quantifying emissions rates (mass per unit time) of methane, a powerful greenhouse gas, from active[23,24] and abandoned oil and gas wells.[25−36] To date, there is only one published study where the measurement of volatile organic compounds (VOCs) in gas from an abandoned well was attempted.[29] However, after dilution of gas from the well with air inside an enclosure covering the well, benzene was not detected at the reporting limit of 4.2 parts per billion volume (ppbv).

In addition to fixed gases, which include oxygen (O_2), argon (Ar), nitrogen (N_2), carbon dioxide (CO_2), and hydrogen (H_2), and light hydrocarbons, which include methane, ethane, propane, isobutane, *n*-butane, isopentane, and *n*-pentane, natural gas is known to contain H_2S[25] and VOCs such as benzene, toluene, ethylbenzene, and xylene (BTEX components).[37−40] Benzene, a known human carcinogen,[41] is of particular concern when abandoned wells are in close proximity to buildings, including residences. The EPA estimates that continuously breathing air containing 1.3−4.5 $\mu g\ m^{-3}$ (equivalent to 0.40−1.4 ppbv at 293 K and 1 atm) would result in not greater than a one-in-a hundred thousand increased chance of developing cancer.[41] The California chronic reference exposure level (REL) for benzene is 3 $\mu g\ m^{-3}$ (~0.94 ppbv at 293 K and 1 atm).[42]

The objectives of this investigation are to determine the (1) composition (fixed gases, light hydrocarbons, VOCs, and H_2S) of gas emitted from wellheads or open casings of abandoned wells; (2) emission rates of light hydrocarbons and VOCs from these wells; and (3) proximity of abandoned wells to buildings, including residences, in western Pennsylvania. Taken together, the presence of these conditions would indicate the need for further investigation to determine whether emissions from abandoned wells pose an inhalation risk to people living, working, or congregating near abandoned wells.

2. MATERIALS AND METHODS

2.1. Abandoned Well Screening. Between May and August 2021, the PADEP screened 90 abandoned wells (29 plugged, 61 unplugged) for natural gas leakage in western Pennsylvania (Figure 1). Abandoned wells were screened by placing the probe extension of a Bascom-Turner Explorer EGA 612 portable gas analyzer directly over the open casing, joints, fittings, and valves of unplugged wells and the riser vent pipe of plugged wells (Figure S1). The instrument is equipped with a dual catalytic combustion and thermal conductivity detector for measurement response readings between 20 parts per million volume (ppmv) and 100% gas.[43] The EGA 612 was calibrated daily to 1.0% methane. The instrument is also equipped with electrochemical cells for the detection of H_2S and carbon monoxide (CO) at a lower limit of detection of 1 ppmv.[43] Additional information on the EGA 612 is provided in Section S1.

To measure gas flow from abandoned wells and instrument response in the absence of interference from ambient air, following initial screening at abandoned wells exhibiting leakage, the PADEP enclosed primary points of leakage and repeated measurements with the EGA 612. Depending on the configuration of leakage, enclosure materials included 3.8−363 L (1−96 gallon) polyethylene bags, ziploc sandwich bags, flexible couplings and adapters, poly(vinyl chloride) reducer fittings, and 0.95 cm (3/8″) brass fittings. A stainless-steel Marlin spike was used to create a hole in polyethylene and ziploc bags for the insertion of 0.95 cm internal diameter polyethylene tubing (Figure S2). With the exception of a plugged well (059-01162), where an orifice meter was used

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because of high flow (146 m^3 d^{-1}), polyethylene tubing was connected to a low-flow Alicat Whisper flowmeter (details on operating principles provided in Section S2) for flow measurement. Since readings often fluctuated during measurement, a maximum value was recorded after relative stabilization (minimum oscillation). Fluctuation during flow measurement resulted in an unknown level of error. The flowmeter was factory calibrated with methane prior to field use, with minimum and maximum flow detections of 20 mL min^{-1} and 9.4 L min^{-1}, respectively.

A polycarbonate cone (to minimize the effect of wind) attached at the end of the EGA 612 sample hose was then used to screen gas concentration directly above soil (Figure S3) within 1 m of abandoned wells in at least three locations around each well. The cone was held in place for at least 3 s prior to advancement. At some locations, the presence of standing water prevented soil screening. The results of all screening activities between May and August 2021 to support this investigation were provided by the PADEP.

2.2. Abandoned Well Sampling and Analysis. Between September and November 2021, with assistance from the PADEP, we screened (using the same procedures previously described) and sampled gas from 8 plugged abandoned wells and 40 unplugged abandoned wells for fixed gases, light hydrocarbons, and VOCs. At one well (053-25266), we collected two samples because of the detection of leakage from two open pipes—one from the production casing (053-25266p) and one from the annular space outside production casing (053-25266a). Seven active wells were sampled but not screened for leakage of gas (as per the access agreement). Flow measurements using the Alicat Whisper flowmeter were corrected based on the viscosities and molecular weights of fixed gases and light hydrocarbons detected in gas mixtures (Section S2). After flow correction, the lower range of detectable flow varied from 12 to 17 mL min^{-1}.

Well names, API numbers, geographic coordinates, and information on completion dates, target depths, and formations (where known) of sampled abandoned wells are provided in Table S1. Sampled abandoned unplugged well locations included 7 wells in Oil Creek State Park (OCSP), 11 wells in Hillman State Park (HSP), and 7 wells in Cornplanter State Park (CPSP) (Figure 1). Sample locations were selected based on public accessibility and locations where the PADEP could obtain private access to abandoned wells. A brief background on oil and gas development at OCSP, HSP, and CPSP is provided in Supporting Information (Section S3).

After field screening and flow measurement, we used scissors to cut the base of 18 × 18 cm (7″ × 7″), 30 × 30 cm (12″ × 12″), or 47 × 47 cm (18.5″ × 18.5″) 5.0 mil perfluoroalkoxy (PFA) or 2.5 mil fluorinated ethylene propylene (FEP) gas sampling bags equipped with an open Kynar valve to secure an area of leakage using rigid plastic zip ties. We utilized the smallest PFA or FEP bag size as practical to enclose leakage locations to minimize the surface area for sealing, heat transfer (condensation) during enclosure, and time to reach equilibrium, as recommended in the EPA's Protocol for Equipment Leak Estimates.[44] Condensation on the inside of sampling bags was absent during sampling.

We then connected a short section (30−60 cm) of 0.48 × 0.64 cm (3/16″ × 1/4″) polytetrafluoroethylene (PTFE) tubing to the Kynar valve and connected the tubing to another 30 × 30 cm PFA or FEP sample bag acting as a plenum (Figure S4). This sampling procedure was pursued to enable passive sample collection (no active gas extraction from the enclosure) to avoid, to the extent possible, the intrusion of atmospheric air into the plenum. We used PFA and FEP sample bags and PTFE tubing to minimize off-gassing or adsorption of VOCs commonly associated with Tedlar bags and polyethylene tubing.[45,46] When necessary, we used electrical tape completely on the outside of sample bags to assist in securing sampling bags.

Depending on conditions at abandoned wells, we allowed plenum bags to inflate between 0.5 and 42 h (Table S2) prior to extraction of gas from the plenum bags into one-liter evacuated summa canisters using 67, 200, and 1000 mL min^{-1} single-use stainless-steel flow regulators. Summa canisters and regulators were provided by Eurofins Air Toxics Laboratory, Folsom, California. We collected duplicate samples at one plugged abandoned well and at two active wells using single-use 0.64 cm outside diameter stainless-steel tees. We also collected one replicate sample at an abandoned unplugged well by sampling the well twice within a ten-minute period. Variation in concentration was calculated as the relative percent difference (RPD), defined as 2*100|R1-R2|/(R1+R2), where R1 = sample 1 and R2 = sample 2. RPDs of fixed gases and light hydrocarbons were below 10%. The RPDs for VOCs were below 20%.

We collected equipment blanks in three 30 × 30 cm FEP bags, two 30 × 30 cm PFA bags, and one 47 × 47 cm PFA bag by inflating sample bags with ultra-pure N_2 gas. We sealed the sample bags using PTFE tubing and 1000 mL min^{-1} dedicated flow controllers and allowed the sample bags to equilibrate for a 24 h period. Samples were subsequently extracted into one-liter evacuated summa canisters. At one abandoned well (125-21260), sample collection necessitated the use of duct and electrical tape overlapping cut sample bags and metal from the well, thereby providing a potential pathway for sampled air to contact adhesive. To evaluate the potential effect of off-gassing from electrical or duct tape at this well, we cut two 18 × 18 cm FEP bags at the base and sealed one using electrical tape and the other using duct tape. We handled these equipment blanks in the same manner as other equipment blanks. We also collected two samples of atmospheric air distant (e.g., >1 km) from abandoned wells (one at OCSP and one at HSP) in six-liter evacuated summa canisters to evaluate the presence of VOCs in the background atmospheric air.

We shipped summa canisters to the Eurofins Air Toxics Laboratory for analysis of fixed gases and light hydrocarbons using Modified ASTM D-1945 (gas chromatography/flame ionization detector or thermal conductivity detector) and for analysis of VOCs plus naphthalene using the EPA Method TO-15 (gas chromatography/mass spectrometry) in the full scan mode using the same canister. Analysis of fixed gases included N_2, O_2 + Ar, (on the analytical column used for analysis, O_2 coeluted with Ar), CO_2, and H_2. Analysis of light hydrocarbons included methane, ethane, propane, isobutane, *n*-butane, neopentane, isopentane, *n*-pentane, and hexane-plus. VOCs (as defined in EPA Method TO-15) analyzed are summarized in Table S3. Compound reporting limits were determined by the gas dilution necessary to quantitate compounds detected at high concentrations. Eurofins is accredited by the National Environmental Laboratory Accreditation Program. Eurofins provided full documentation on quality assurance procedures and results associated with analysis.

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To determine the stable isotope ratio of carbon in methane (δ13C−CH_4) relative to the Vienna Peedee belemnite standard, we extracted 200−400 mL of gas from a plenum or secured sample bag using a bulb syringe into a 1 L 5 mil (0.14 mm) thick multi-layer foil Cali-5 Bond bag for transportation and storage.

We analyzed samples using a Picarro Cavity Ring Down Spectrometer (model G2210-i) within 2−5 weeks of sample collection with an accuracy of ±0.5‰. We periodically checked the analyzer with isotopic standards to ensure that the results were within 10% of the certified values. Additional information on stable carbon isotope analysis is provided in Section S4.

2.3. Estimation of Intrusion of Air into Sample Bags. During initial sampling efforts, it became apparent that 5.0 mil PFA sample bags were too thick and pressure at leakage locations on abandoned wells was too low to allow inflation of most plenum bags. In some instances, this necessitated sample collection directly from secured PFA bags. In addition, the rigidity of PFA bags made it difficult to obtain a good seal around a point of leakage. While we achieved greater success transitioning to 2.5 mil FEP sample bags, in some cases, flow from abandoned wells was still too low to allow inflation of FEP plenum bags even at inflation times exceeding 40 h. This necessitated sample collection directly from secured FEP sample bags. Information on flow rates during sampling, enclosure times, and flow rates of controllers during sampling is summarized in Table S2.

Intrusion of atmospheric air into a sampling vessel will result in elevated O_2 and N_2 concentrations and, without adjustment, will result in biased low estimates of light hydrocarbons and VOCs. To estimate concentrations of fixed gases, light hydrocarbons, and VOCs in samples, we used ratios of N_2, O_2 + Ar, and CO_2 in atmospheric air to adjust sample results when air intrusion was plausible (N_2 levels above detection). We calculated upper and lower bounds of fixed gas, light hydrocarbon, and VOC concentrations by assuming concentrations of O_2 + Ar in samples at 0.0 and 3.0%, respectively, based on available information from oil and gas wells in Devonian-age reservoirs in Pennsylvania[37,47−49] (Figure S5) and three abandoned wells at HSP having non-detectable levels of N_2 (<0.19%) and levels of O_2 + Ar between 2.4 and 2.9% (indicating that O_2 + Ar levels in samples this high were not due to air intrusion). When N_2 levels were above detection limits, we used the midpoint of the upper and lower bounds to report concentrations. A detailed discussion of concentration adjustment and equation development is provided in Section S5.

2.4. Statistical Analysis. Environmental datasets containing sample results are often left-censored (sample results below reporting limits). Substitution methods such as assigning values of zero, one-half of a reporting limit, or a reporting limit itself to sample results below a reporting limit are commonly used to calculate the mean and standard deviation of left-censored data.[50] However, substitution methods have no statistical basis,[51] perform poorly in datasets with multiple reporting limits,[51] and commonly result in overestimation or underestimation of a mean and standard deviation.[52] The EPA now discourages the use of substitution methods in calculating the mean, standard deviation, and other statistical parameters (e.g., 95% upper confidence limit) of left-censored data.[53] Several methods have been used for calculating statistical parameters of left-censored data, including maximum likelihood estimation, regression on order statistics,[51] and the non-parametric Kaplan−Meier (KM) method.[54] The KM method used here appears to provide the most accurate estimate of statistical parameters containing up to 70% left-censored data.[55] Hypothesis testing was conducted using the non-parametric Tarone−Ware test,[56] which also accounts for left-censored data. The EPA's ProUCL (version 5.2) software package[53] was used to calculate the KM mean, KM standard deviations, and conduct hypothesis testing. The calculation of median levels was handled by ranking reporting limits. When more than one-half of a dataset contained left-censored data, a median was reported as less than the reporting limit.

2.5. Proximity Analysis. During our sampling campaign, we observed several abandoned wells located within 100 m of residential buildings. To better understand how commonly this occurs, we determined the distance from the nearest building to the location of abandoned wells. The locations of abandoned wells were taken from the PADEP orphaned and abandoned wells report.[2] Building locations were taken from building footprint polygons generated by Microsoft using deep learning algorithms.[57] The distance of each well from any building was determined using the sf package in R.[58] We limited a proximity analysis of residential buildings to one county (Allegheny County) because of the ease of accessibility of parcel tax assessment data.[59] Parcels having residents were identified by first excluding any assessment with descriptor codes of "utilities" or "industrial" in R.[60] We then selected every assessment with a descriptor code of "residential" and appended these with use codes containing keywords, such as "single family" or "condominium". After identifying the parcels containing residents, buildings contained within these parcels[61] were identified via spatial joining in the sf package in R.[58] To account for edge effects, a 2.5 km buffer was extended from the edge of Allegheny County, and the proximity of wells contained within this buffer to Allegheny County residential buildings was calculated.

To assess the accuracy of the proximity analysis, we randomly selected 5% (n = 213) of abandoned wells that were found to be within 100 m of a building and cross-referenced them with the building footprint dataset with either 0.6 m (Surdex Corporation)[62] or 15.4 cm (Quantum Spatial, Inc.)[63] resolution aerial imagery captured in 2019 and 2018, respectively. In some cases, we also used historic imagery in Google Earth Pro[64] for cross-referencing. For each well, we classified the observation as a "true positive" (i.e., a structure in which people would reasonably be inside of), a "false positive" (e.g., ruins of a former building, oil and gas development infrastructure), and in one case "demolished". Additional detail is provided in Section S6.

2.6. Comparison with Published Sources of VOCs from Active Oil and Gas Wells. Finally, we conducted a database search to compare the sample results of VOCs from gas collected from active and abandoned wells in this investigation with those from active wells at other locations. The Colorado Oil and Gas Conservation Commission maintains an extensive electronic database[38] of bradenhead (annular space between surface and production casing) (n = 115) and production gas (PG) samples (n = 251) which contain data on VOCs including benzene. Search terms for PG included production, production casing, production string, oil/gas wellhead, intermediate casing, separator, gas stream, and gas sales point. We also extracted data from a database[37] maintained by the United States Geological Survey with PG

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Table 1. Summary Statistics for the Levels of Fixed Gases, Light Hydrocarbons, and VOCs in Gas Samples from Active and Abandoned Wells in Western Pennsylvania[a]

	active wells						abandoned wells					
compound	frequency of left-censored data	minimum	maximum	KM mean	KM standard deviation	median	frequency of left-censored data	minimum	maximum	KM mean	KM standard deviation	median
Fixed Gases as Measured using ASTM-D-1945 (%)												
oxygen + argon	4/7	<0.17	1.8	0.45	0.56	<0.18	5/49	<0.19	2.9	1.4[b]	0.60[b]	1.5[b]
nitrogen	6/7	<0.17	4.3			<0.19	16/49	<0.18	20	7.9	6.9	8.9
carbon dioxide	0/7	0.024	0.084	0.044	0.020	0.040	4/49	<0.18	26	2.9	5.5	0.43
hydrogen	0/7	0.023	0.27	0.13	0.086	0.15	37/49	<0.018	7.2	0.26	1.1	<0.056
Natural Gas constituents as Measured using ASTM-D-1945 (%)												
methane	0/7	28	97	83	83	91	0/49	17	98	78	78	83
ethane	0/7	2.7	29	8.2	9.3	5.5	2/49	<0.039	20	3.8	4.7	2.2
propane	0/7	0.18	26	4.8	9.4	1.5	4/49	<0.0019	25	2.5	4.6	0.42
isobutane	0/7	0.017	3.7	0.73	1.3	0.22	4/49	<0.0019	4.6	0.61	1.1	0.10
butane	0/7	0.025	8.5	1.5	3.1	0.33	5/49	<0.0019	10	1.2	2.2	0.13
neopentane	0/7	0.0045	0.011	0.012	0.012	0.0087	31/49	<0.0018	0.10	0.0092	0.017	<0.0064
isopentane	0/7	0.0087	1.9	0.37	0.68	0.15	7/49	<0.0019	5.5	0.54	1.0	0.058
pentane	0/7	0.002	1.5	0.29	0.54	0.12	13/49	<0.0018	4.7	0.43	0.83	0.042
hexane+	1/7	<0.018	1.5	0.34	0.48	0.15	18/49	<0.018	6.2	0.67	1.2	0.13
VOCs as Measured using the EPA Method TO-15 (ppmv)												
hexane	0/7	1.8	3900	790	1400	310	2/49	<0.00094	14000	1400	2400	160
cyclohexane	0/7	0.38	780	180	270	79	2/49	<0.00094	2700	340	533	56
heptane	0/7	0.32	1000	232	350	94	6/49	<0.00094	2400	400	570	79
benzene	1/7	<0.22	170	33	56	12	14/49	<0.00094	250	36	65	2.8
toluene	1/7	<0.22	180	36	59	16	29/49	<0.00094	250	21	50	<2.1
ethylbenzene	7/7	<0.22	<22			<2.0	41/49	<0.00094	40	2.7	7.7	<1.3
m,p-Xylene	2/7	<0.22	58	12	19	5.3	28/49	<0.00094	340	22	57	<2.1
o-Xylene	5/7	<0.22	3.2			<3.2	37/49	<0.00094	55	4.2	10	<1.7
1,3,5-trimethylbenzene	7/7	<0.22	<22			<2.0	39/49	<0.00094	30	1.8	4.9	<1.7
1,2,4-trimethylbenzene	7/7	<0.22	<22			<2.0	40/49	<0.00094	40	1.6	6.2	<1.4
4-ethyltoluene	7/7	<0.22	<22			<2.0	40/49	<0.00094	30	1.6	4.8	<1.4
propylbenzene	7/7	<0.22	<22			<2.0	46/49	<0.00094	5.7	0.26	0.99	<1.3
cumene	7/7	<0.22	<22			<2.0	45/49	<0.00094	5.5	0.25	0.93	<1.1

[a]Midpoints of adjusted fixed gas, light hydrocarbon, and VOC concentration data were used for all calculations. KM mean and standard deviations were not calculated for data sets having less than 3 detected values. All data reported two significant figures. [b]Mean and median values of 1.5% for O_2 + Ar in abandoned wells are an artifact of using 0.0 and 3.0% O_2 + Ar to estimate the upper and lower bounds of air intrusion.

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samples (n = 23) containing data on benzene concentration. Published sources of information on VOCs in natural gas include production and bradenhead (n = 25 each) samples from the Pavillion, WY Field,[39] and a report[40] to the Texas Commission on Environmental Quality summarizing results of gas samples (n = 117) in the Anadarko, Ben Arch-Fort Worth, East Texas, Permian, and Western Gulf Basins prior to glycol dehydration.

3. RESULTS AND DISCUSSION

3.1. Field Screening. During open screening, the frequency of EGA 612 instrument response above detection (20 ppmv) at plugged wells (9/27 ~ 33%) was less than that of unplugged wells (53/60 ~ 88%) (p < 0.001) (only enclosed screening was conducted at 3 abandoned wells). This observation is consistent with the findings of others[10,27,34] that plugging decreases the incidence of leak detection at the wellhead of abandoned wells. Gas leakage at unplugged wells was due to the presence of ground-level open casing when wellheads were absent or open pipe attached to wellheads or corroded casing when wellheads were present. When detected, the mean concentrations of gas during open screening were 26 and 14% at plugged and unplugged wells, respectively, while the mean concentrations of gas screened with enclosure were 38 and 37% at plugged and unplugged wells, respectively. Hence, detected gas concentrations from leakage locations at abandoned wells were generally high (often above the lower explosive limit of methane of 5%) and increased, as expected, with enclosure using sample bags (Figure S6) due to a lack of dilution from atmospheric air.

During field screening, H_2S was detected at 3 of 90 (~3.3%) abandoned wells. H_2S concentrations were 1.5 and 5.0 ppmv at leakage locations of two unplugged wells and 11.2 ppmv from the vent of plugged well (059-01162), which, because of a high flow rate, had an H_2S emission rate of 2.3 g d^{-1}. The gas from this well consisted of 92% methane and 6.6% N_2 with no detection of VOCs. El Hachem and Kang[25] detected H_2S emissions at 3 of 20 (~15%) abandoned wells in Ontario, Canada, with a maximum emission rate of 144 g d^{-1}. Given the toxicity of H_2S (California acute and chronic inhalation REL at 42 and 10 μg m^{-3}, respectively, or 29 and 7 ppbv, respectively, at 293 K and 1 atm),[42] H_2S should be routinely screened at abandoned wells, especially in areas where gas from oil and gas wells are known to have high levels of H_2S. We also detected CO at 17 of 90 (~19%) abandoned wells at a maximum concentration of 290 ppmv and a maximum emission rate of 5.7 g d^{-1}. The California acute REL for CO is 20 ppmv.[42] This finding indicates that CO should also be routinely screened at abandoned wells.

Gas was detected at the ground surface at 7 of 61 (~11%) unplugged wells and 3 of 29 (~10%) plugged wells within a 1 m radius of the wells. At one plugged well, ground-level gas was measured at a concentration of 6% with no detection at the vent pipe of the well. At another plugged well, ground-level gas was measured at a concentration of 0.05%. There was no vegetation within 2 m of this well, suggesting high root zone gas concentrations, potentially from displacement of oxygen. These observations highlight the need to evaluate gas flux at the surface before and after plugging.

Soil screening, as performed here, has been utilized by others[65] to detect natural gas migration to the surface. However, soil screening is generally recognized as having insufficient sensitivity to effectively detect gas efflux from soil to the atmosphere.[66] Soil-gas sampling and flux chambers are more sensitive methods of detection and measurement of gas migration in soil near and distant from abandoned oil and gas wells[67−71] especially when methane-oxidizing microorganisms reduce methane efflux,[72−74] and efflux is affected by variation in barometric pressure.[68] Hence, the frequency of detection of gas emissions at the soil surface (~10%) from abandoned wells observed in this investigation could be an underestimate to some unknown degree.

3.2. Composition of Gas from Active and Abandoned Wells. Gas from active and abandoned wells sampled in this investigation was from Devonian-age reservoirs (Table S1), as is the case for conventional oil and gas production throughout the Appalachian Basin.[75] At the abandoned well where two samples were collected, the gas sample from the annular space (053-25266a) indicated a greater proportion of microbial to thermogenic gas ($\delta^{13}C-CH_4$ = −60.3‰) compared to the gas sample from production (053-25266p) ($\delta^{13}C-CH_4$ = −54.3‰) (Figure S7). With the exception of gas sample 053-25266a, δ13C−CH_4 values and ratios of methane to ethane and propane were within the range of expected values for thermogenic gas originating from Devonian-age reservoirs.[47−49] These observations suggest that gas from abandoned wells originated from Devonian-age reservoirs or that gas in overlying strata potentially in contact with corroded or compromised casing had stable isotopic values for methane similar to those of Devonian-age reservoirs.

Analyses of gas samples from equipment blanks indicated no impact on sample results (Section S7 and Figure S8). Despite observations of atmospheric intrusion into enclosures during sampling at some locations (Figure S9), the estimation technique utilized here effectively constrained lower and upper estimates of fixed gas, light hydrocarbon, and VOC concentrations (Tables S4 and S5, lower and upper estimates of benzene illustrated in Figure S10). For instance, the maximum difference in the lower and upper bound estimates for benzene was only 32 ppmv (lower and upper bound estimates of 196 and 228 ppmv, respectively, at well 125-21260).

Summary statistics for fixed gases, light hydrocarbons, and VOCs in gas samples from active and abandoned wells in western Pennsylvania are provided in Table 1. Differences in concentrations of fixed gases, light hydrocarbons, and VOCs in active and abandoned wells (Figure S11) were not statistically significant (p > 0.05). Hexane, cyclohexane, and heptane were frequently detected (4.1−8.1% left-censored data sets) in gas samples from abandoned wells (Table 1) and dominated VOC analysis (Figures S12 and S13). The maximum concentration of hexane (14,000 ppmv) was greater than the California chronic REL[42] (7000 μg m^{-3} or 1.99 ppmv at 293 K and 1 atm) by a factor of 7000.

Benzene was also frequently detected in gas from abandoned wells (28.6% left-censored data set), with less detection frequency of toluene (59.2% left-censored data set) and m,p-xylene (57.1% left-censored data set) (Table 1). The maximum concentrations of benzene (250 ppmv), toluene (250 ppmv), and m,p-xylene (340 ppmv) were greater than the California chronic RELs[42] by factors of 250,000, 2000, and 2000, respectively (REL for toluene = 420 μg m^{-3} or 0.111 ppmv and REL for xylenes = 700 μg m^{-3} or 0.161 ppmv at 298 K and 1 atm). Hence, while VOCs other than benzene were detected in gas from abandoned wells, observed benzene concentrations largely the dominated potential risk of exposure. The mean

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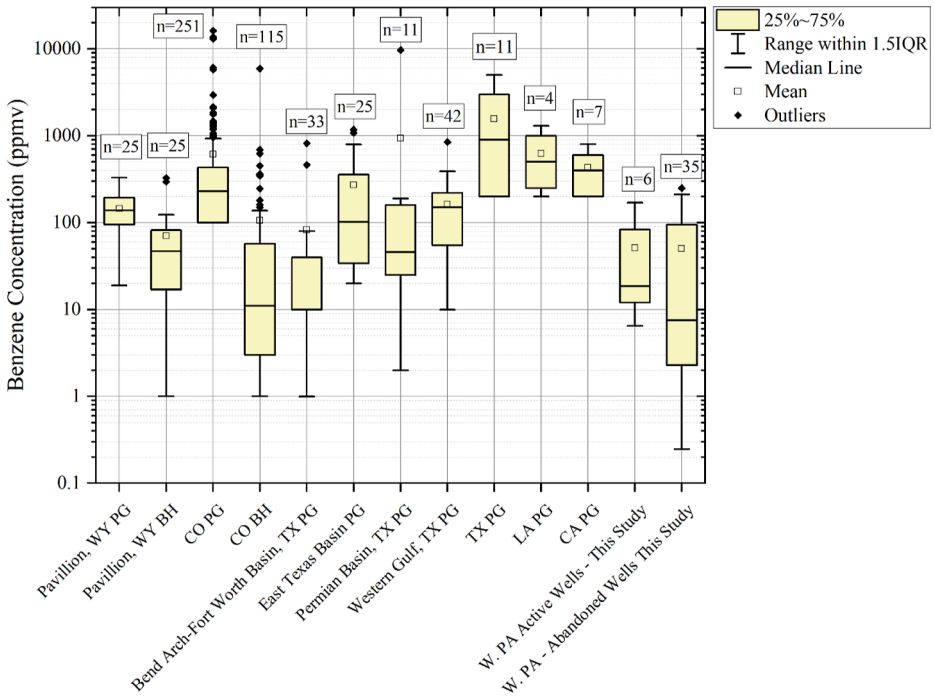

Figure 2. Detected benzene concentrations reported in PG and bradenhead gas (annular space between production or intermediate casing and surface casing) at the Pavillion Field, WY;[39] in Colorado (CO);[38] in Bend Arch-Fort Worth, East Texas, Permian, and Western Gulf Basins[40] in Texas (TX); additional locations in Texas, Louisiana (LA), and California (CA);[37] and midpoints of lower and upper bounds of detected (above reporting limits) concentrations in this study. The mean and median of detected concentrations of benzene in abandoned wells in this study were 53 and 2.8 ppmv, respectively.

Table 2. Summary Statistics of Emission Rates (g D^{-1}) of Light Hydrocarbons and VOCs from Abandoned Wells in Western Pennsylvania[a]

compound	frequency of left-censored data	minimum	maximum	KM mean	KM standard deviation	median
Natural Gas Constituents as Measured using ASTM-D-1945 (g d^{-1})						
methane	15/48	$<1.8 \times 10^{+0}$	$8.3 \times 10^{+4}$	$2.2 \times 10^{+3}$	$1.2 \times 10^{+4}$	$6.9 \times 10^{+1}$
ethane	15/48	$<4.2 \times 10^{-3}$	$3.8 \times 10^{+2}$	$1.8 \times 10^{+1}$	$5.7 \times 10^{+1}$	$1.5 \times 10^{+0}$
propane	18/48	$<5.3 \times 10^{-3}$	$6.8 \times 10^{+1}$	$3.9 \times 10^{+0}$	$1.3 \times 10^{+1}$	4.2×10^{-1}
isobutane	18/48	$<1.8 \times 10^{-3}$	$1.3 \times 10^{+1}$	7.5×10^{-1}	$2.4 \times 10^{+1}$	1.1×10^{-1}
butane	18/48	$<8.5 \times 10^{-4}$	$2.3 \times 10^{+1}$	$1.2 \times 10^{+0}$	$3.9 \times 10^{+1}$	1.5×10^{-1}
neopentane	24/38	$<3.5 \times 10^{-4}$	7.3×10^{-1}	3.0×10^{-2}	1.1×10^{-1}	$<5.4 \times 10^{-3}$
isopentane	18/48	$<8.5 \times 10^{-4}$	$8.8 \times 10^{+0}$	5.0×10^{-1}	$1.5 \times 10^{+1}$	7.2×10^{-2}
pentane	26/48	$<7.3 \times 10^{-4}$	$7.1 \times 10^{+0}$	3.5×10^{-1}	$1.2 \times 10^{+1}$	5.7×10^{-2}
VOCs as Measured using EPA Method TO-15 (g d^{-1})						
hexane	17/48	$<5.7 \times 10^{-6}$	$1.4 \times 10^{+1}$	7.2×10^{-1}	$2.3 \times 10^{+1}$	1.1×10^{-1}
cyclohexane	17/48	$<1.2 \times 10^{-5}$	$3.0 \times 10^{+0}$	1.6×10^{-1}	4.9×10^{-1}	2.7×10^{-2}
heptane	21/48	$<5.9 \times 10^{-6}$	$5.7 \times 10^{+0}$	3.8×10^{-1}	$1.1 \times 10^{+1}$	5.2×10^{-2}
benzene	24/48	$<3.0 \times 10^{-6}$	7.4×10^{-1}	2.2×10^{-2}	1.1×10^{-1}	2.2×10^{-3}
toluene	35/48	$<3.5 \times 10^{-6}$	8.7×10^{-1}	2.7×10^{-2}	1.3×10^{-1}	$<1.0 \times 10^{-3}$
ethylbenzene	43/48	$<4.0 \times 10^{-6}$	4.4×10^{-2}	1.8×10^{-3}	8.1×10^{-3}	$<7.2 \times 10^{-4}$
m,p-xylene	31/48	$<4.0 \times 10^{-6}$	4.3×10^{-1}	2.1×10^{-2}	8.3×10^{-2}	$<1.9 \times 10^{-3}$
o-xylene	40/48	$<4.0 \times 10^{-6}$	8.4×10^{-2}	3.9×10^{-3}	1.6×10^{-2}	$<9.9 \times 10^{-4}$
1,3,5-trimethylbenzene	40/48	$<4.6 \times 10^{-6}$	4.4×10^{-2}	1.6×10^{-3}	6.5×10^{-3}	$<1.1 \times 10^{-3}$
1,2,4-trimethylbenzene	41/48	$<4.6 \times 10^{-6}$	5.8×10^{-2}	1.7×10^{-3}	8.4×10^{-3}	$<1.0 \times 10^{-3}$
4-ethyltoluene	41/48	$<4.6 \times 10^{-6}$	4.2×10^{-2}	1.4×10^{-3}	6.3×10^{-3}	$<1.0 \times 10^{-3}$
propylbenzene	46/48	$<4.6 \times 10^{-6}$	8.1×10^{-3}			$<7.7 \times 10^{-4}$
cumene	45/48	$<4.6 \times 10^{-6}$	6.2×10^{-3}	1.7×10^{-4}	9.4×10^{-4}	$<7.7 \times 10^{-4}$

[a]The product of the lower limits of flow detection and reporting limits was used for the calculation of minimum emission rates. Midpoints of adjusted light hydrocarbon and VOC concentration data were used for all calculations. KM mean and standard deviations were not calculated for data sets having less than three reportable values. All data and calculations are reported in two significant figures.

values of these compounds were substantially greater than the median values, indicating a highly skewed distribution of data with high concentrations controlling the calculation of the mean.

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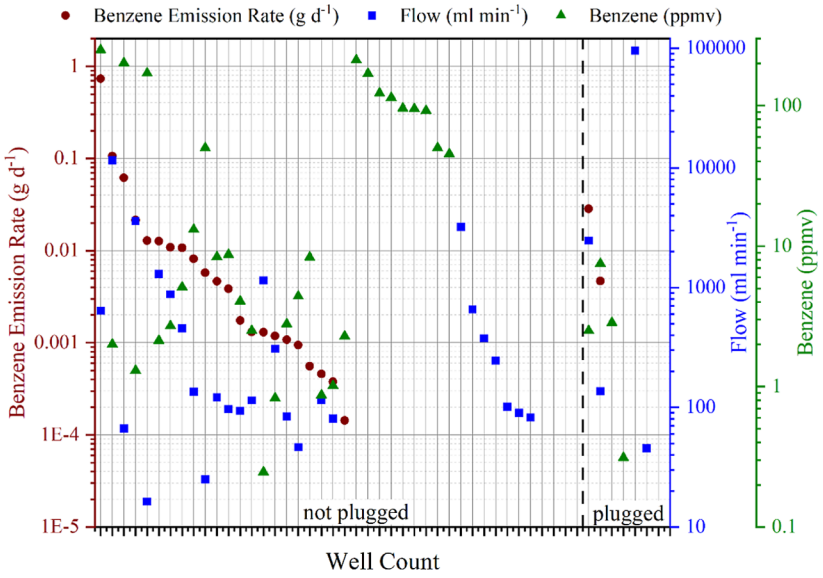

Figure 3. Emission rates for benzene when detectable flow and benzene concentrations are present, detectable concentrations of benzene, and detectable flow rates (plotted in this order) for unplugged and plugged abandoned wells in western Pennsylvania. Wells with both non-detectable flow and benzene concentrations are left blank.

Ethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 4-ethyltoluene, propylbenzene, and cumene (isopropylbenzene) were detected infrequently (75.5−93.9% left-censored data sets) in abandoned wells at maximum concentrations of 40, 30, 40, 30, 5.7, and 5.5 ppmv, respectively (Table 1). Summary statistics with left-censored data sets in excess of 70% are considered to be unreliable.[53] Halogenated compounds, ketones (acetone, 2-butanone, 2-hexanone, 4-methyl-2-pentanone), alcohols (ethanol, propanol), styrene, naphthalene, and 1,3-butadiene were not detected in any samples. Other compounds (e.g., methyl cyclohexane and mixed isomers of butane and pentane) that have been detected in gas samples collected directly from oil and gas wells elsewhere[38] were not included in the EPA Method TO-15 utilized for this investigation. With the exception of the detection of acetone and 2-propanol at maximum levels of 7.2 and 2.7 ppbv, respectively, VOCs were not detected in atmospheric air samples distant from abandoned wells. Hence, background air quality had no impact on the sample results.

The mean and median concentrations of benzene detected in gas from active and abandoned wells in this investigation were generally less than those observed in active wells elsewhere in the United States (Figure 2). This finding suggests that VOC concentrations in gas from abandoned wells in other areas of the United States could be higher than those measured in this investigation, necessitating further investigation elsewhere.

3.3. Emission Rates of Light Hydrocarbons and VOCs from Abandoned Wells. Summary statistics for emission rates of light hydrocarbons and VOCs from abandoned wells in western Pennsylvania are provided in Table 2. Methane dominated emissions of light hydrocarbons at mean values of 2.2 kg d^{-1}—more than two orders of magnitude greater than the mean values of the next highest emitting light hydrocarbon, ethane, at 18 g d^{-1}. The mean and median emission rates of light hydrocarbons generally decreased with increased carbon numbers (methane > ethane > propane > butane ≈ isobutane > isopentane ≈ pentane > neopentane).

We observed mean values of methane emission rates for plugged and unplugged abandoned wells in western Pennsylvania of 12 kg d^{-1} (n = 7) and 550 g d^{-1} (n = 42), respectively, compared to 360 g d^{-1} (n = 35) and 530 g d^{-1} (n = 53), respectively, measured by Kang et al.[27,28] (Table S6). The mean value for plugged wells in this investigation was dominated by one well (059-01162) having a methane emission rate of 83 kg d^{-1} (Figure S14). In the absence of this well, the mean emission rate for plugged wells would be 390 g d^{-1} similar to that measured by Kang et al.[27,28] At OCSP and HSP, we observed mean emission rates for unplugged wells at 54 g d^{-1} (n = 7) and 285 g d^{-1} (n = 11) compared to 27 g d^{-1} and (n = 129) and 700 g d^{-1} (n = 22) observed by Saint-Vincent et al.[33] and Pekney et al.,[30] respectively. Hence, our methane emission rate measurements are in general agreement with others conducting similar measurements in western Pennsylvania. We observed median methane emission rates for plugged and unplugged abandoned wells of 36 and 74 g d^{-1}, respectively. As observed by others,[29,32,34−36] methane emissions from both plugged and unplugged wells follow a "long tail distribution" where measurements from a few wells dominate total emissions as reflected in mean values being much higher than median values.

Mean methane emission rates from abandoned wells in Pennsylvania appear to be lower than those measured through SCVF for active wells. Ingraffea et al.[7] estimated a daily flow of 110,400 m^3 d^{-1} of methane to the atmosphere from SCVF at 62,483 conventional, unconventional, and coal-bed active wells, equivalent to 1.16 kg d^{-1} per well at 298 K and 1 atmosphere. This is greater than a factor of two for mean methane emissions at unplugged abandoned wells measured in this investigation and by Kang et al.[27,28]

Emission rates of VOCs from abandoned wells in this investigation were dominated by hexane, heptane, and cyclohexane, followed by BTEX compounds (Table 2 and Figure S15). We observed KM mean emission rates of hexane, heptane, cyclohexane, and benzene at 0.72, 0.38, 0.16, and 0.022 g d^{-1}, respectively. For active marginal or stripper wells (less than 1 barrel oil equivalent per day) in Ohio, Deighton et

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al.[23] observed mean emission rates for hexane, heptane, cyclohexane, and benzene at 21.6, 16.9, 5.9, and 1.2 g d^{-1}, respectively. Hence, the mean emission rate of benzene in marginal oil wells was ~55× higher than that observed in this investigation. Median values of emission rates of hexane, heptane, cyclohexane, and benzene in our investigation were less than mean values due to a small proportion of abandoned wells having high emission rates. Summary statistics for emission rates of other compounds were heavily left-censored (64.6−95.8%) and hence should be viewed with caution.

In this investigation, benzene emission rates could not be measured at 24 of 48 (50%) abandoned wells because gas flow was too low to be measured (10 wells), benzene was not detected (3 wells), or both conditions were present (11 wells) (Figure 3). Also, emission of methane did not necessarily correspond to the emission of benzene. For instance, the plugged well with the highest flow rate and methane emission rate (059-01162) (83 kg d^{-1}) had a non-measurable benzene emission rate. Hence, the emission of benzene cannot be assumed based on the presence of methane or a leakage flow rate from an abandoned well. Depending on the limit of flow and benzene detection at individual wells, the limits of measurement of benzene emission rates in this investigation varied from 3.0×10^{-6} to 8.5×10^{-3} g d^{-1}.

3.4. Proximity Analysis. Of 18,608 documented abandoned wells with coordinates in Pennsylvania, a proximity analysis indicated that there are 499 (2.68%), 4243 (22.8%), and 17,299 (93.0%) abandoned wells within 10 m, 100 m, and 1 km of a building, respectively (Figure 4a). Our accuracy check of 5% of surveyed abandoned wells (n = 213) found a total of 92.5% (n = 197) true positives, 7.0% (n = 15) false positives, and 0.5% (n = 1) demolished (Table S7). While 5% of the wells surveyed are a relatively small subset of our dataset, given the random selection of these wells and their distribution across the entirety of our study area, we expect a similar distribution of true and false positives within the entire dataset.

Of 430 documented abandoned wells with coordinates in densely populated Allegheny County, there are 42 (9.77%), 176 (40.9%), and 373 (86.7%) abandoned wells within 10 m, 100 m, and 1 km of a residence, respectively (Figure 4b). Since the actual number of abandoned wells likely exceeds the number of documented abandoned wells by almost an order of magnitude and the percentage of false positives in our proximity analysis is relatively low, the actual number of abandoned wells within 10 or 100 m of buildings in Pennsylvania and residences in Allegheny County is likely much larger than presented here.

Further evidence of concern regarding the proximity of abandoned wells to buildings and residences is provided by field observations. During this investigation, the PADEP initiated an emergency plug and abandon action at 003-00832 because of complaints of odor by residents in a new housing development over 1 km from the well. Gas from this unplugged abandoned well had a benzene concentration of 250 ppmv and a benzene emission rate of 0.74 g d^{-1}—the highest emission rate measured in this investigation. Acrid gas emissions at this well-made sampling were challenging, indicating that future field work should include respiratory protection. At one abandoned unplugged well (125-21260), we could not calculate a benzene emission rate due to high wind and difficulty enclosing leak locations. However, gas from this abandoned well had a benzene concentration of 212 ppmv and was located at the edge of a driveway adjacent to a house. At one location, an unplugged abandoned well was located in a backyard close (10−15 m) to a rented residence, where the renter was unaware that the pipe exiting the ground was an abandoned well. Although benzene was not detected in the gas from this well, 100% gas (i.e., 100% instrument response) was observed during screening, and methane was being emitted at a rate of 3.0 kg d^{-1} representing a potential fire hazard.

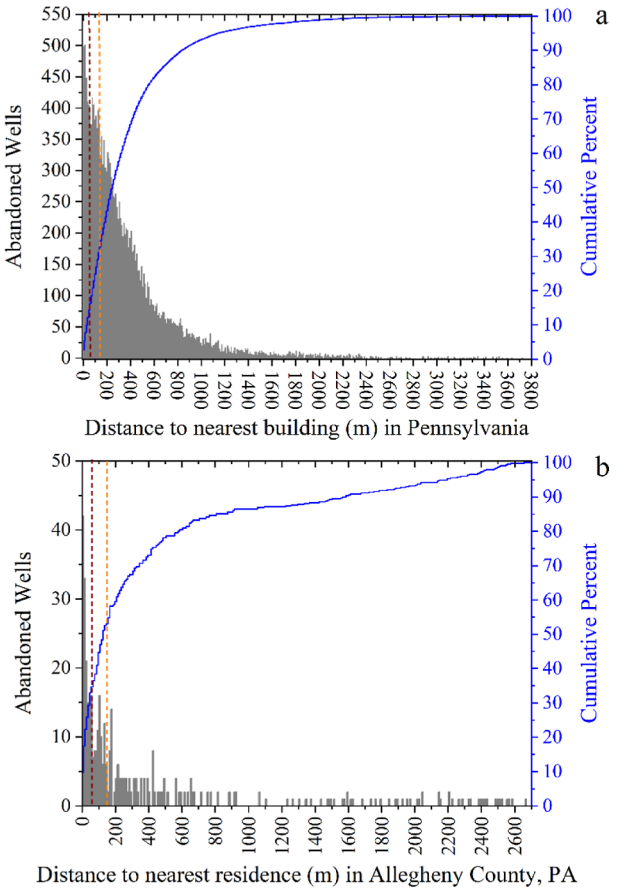

Figure 4. Histograms (bin size = 10 m) illustrating the proximity of documented abandoned wells (a) to the nearest building in Pennsylvania and (b) to the nearest residence in Allegheny County in western Pennsylvania. Wine and orange colored dashed lines represent setback distances from buildings in Pennsylvania for conventional (200 ft) and unconventional (500 ft) oil and gas wells (58 PA CS 3215).

4. CONCLUSIONS

Gas emissions from abandoned oil and gas wells have recently received considerable interest due to their potential impacts on the climate. However, these studies have been limited to methane. This is the first study in which VOC concentrations and associated emission rates have been measured in abandoned wells. In this investigation, we demonstrate that: (1) gas from abandoned wells contains VOCs, including benzene, a known human carcinogen; (2) VOCs are emitted from abandoned wells, the magnitude of which depends on the flow rate and concentration of VOCs in the gas stream; and (3) abandoned wells are located in proximity to buildings and residences in western Pennsylvania. Together, these observations indicate that further investigation is necessary to determine whether gas emissions pose an inhalation risk to people living, working, or congregating near abandoned wells.

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Also, benzene concentrations measured in active and abandoned wells in this investigation in western Pennsylvania were lower than those found in active wells in other parts of the United States. Hence, benzene emissions from abandoned wells at other locations could be higher than those observed in this investigation, necessitating further investigation in other geographic areas.

Finally, in this investigation, we had a dual objective of determining both the concentration and emission rate of VOCs in gas from abandoned wells. Moving forward, though, given the difficulty in sample collection (air intrusion) and low flow measurement, if the primary objective is the determination of VOC emission rates, a flux-based methodology employed by Kang et al.[26−28] and others[29−36] should be utilized and supplemented with VOC analysis and equipment blanks.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c00676.

Estimation of flowrates, sample locations, carbon-13 analysis, estimation of air intrusion into samples, proximity analysis, and VOCs in equipment blanks (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Dominic C. DiGiulio − *Department of Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, Colorado 80309, United States;* orcid.org/0000-0001-9880-5197; Email: dominic.digiuliojr@colorado.edu

Authors

Robert J. Rossi − *PSE Healthy Energy, Oakland, California 94612, United States;* orcid.org/0000-0002-7819-1068

Eric D. Lebel − *PSE Healthy Energy, Oakland, California 94612, United States;* orcid.org/0000-0001-5255-6893

Kelsey R. Bilsback − *PSE Healthy Energy, Oakland, California 94612, United States;* orcid.org/0000-0002-5996-1522

Drew R. Michanowicz − *PSE Healthy Energy, Oakland, California 94612, United States;* orcid.org/0000-0002-2538-4819

Seth B.C. Shonkoff − *PSE Healthy Energy, Oakland, California 94612, United States; Environmental Health Sciences, School of Public Health, University of California, Berkeley, California 94720, United States; Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States;* orcid.org/0000-0002-2696-0259

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c00676

Author Contributions

Research concept origination: S.B.C.S. and D.D. Field screening, sample collection, data interpretation, and manuscript preparation: D.D. and R.R. Proximity analysis: R.R. Carbon-13 analysis and manuscript review: E.L. Manuscript review: K.B., D.M., and S.B.C.S.

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Notes

The authors declare no competing financial interest.

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