Methane in groundwater before, during, and after hydraulic fracturing of the Marcellus Shale

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Concern persists over the potential for unconventional oil and gas development to contaminate groundwater with methane and other chemicals. These concerns motivated our 2-year prospective study of groundwater quality within the Marcellus Shale. We installed eight multilevel monitoring wells within bedrock aquifers of a 25-km^2 area targeted for shale gas development (SGD). Twenty-four isolated intervals within these wells were sampled monthly over 2 years and groundwater pressures were recorded before, during, and after seven shale gas wells were drilled, hydraulically fractured, and placed into production. Perturbations in groundwater pressures were detected at hilltop monitoring wells during drilling of nearby gas wells and during a gas well casing breach. In both instances, pressure changes were ephemeral (<24 hours) and no lasting impact on groundwater quality was observed. Overall, methane concentrations ([CH_4]) ranged from detection limit to 70 mg/L, increased with aquifer depth, and, at several sites, exhibited considerable temporal variability. Methane concentrations in valley monitoring wells located above gas well laterals increased in conjunction with SGD, but CH_4 isotopic composition and hydrocarbon composition (CH_4/C_2H_6) are inconsistent with Marcellus origins for this gas. Further, salinity increased concurrently with [CH_4], which rules out contamination by gas phase migration of fugitive methane from structurally compromised gas wells. Collectively, our observations suggest that SGD was an unlikely source of methane in our valley wells, and that naturally occurring methane in valley settings, where regional flow systems interact with local flow systems, is more variable in concentration and composition both temporally and spatially than previously understood.

methane | groundwater | hydraulic fracturing | shale gas | water quality

Directional drilling and high-volume hydraulic fracturing (HVHF) have altered the global energy landscape by increasing oil and gas production in North America. As more countries consider developing their tight oil and gas reserves, they, like the United States and Canada, are seeking clarification on the risks this extraction poses to groundwater resources (1). Incidences of drinking water contamination by methane (CH_4) and other contaminants emerged as resource development by HVHF spread from the US gulf coast states into other unconventional oil and gas (UOG) plays. As of the end of 2017, the Pennsylvania Department of Environmental Protection (PADEP) had issued 302 letters to homeowners documenting incidences of presumed groundwater contamination from oil and gas development (2), and in that time 10,908 unconventional wells were drilled in Pennsylvania (3). Disagreement over causes of water-quality impairments has persisted, suggesting that new approaches and observations are needed to better understand and resolve this contentious issue. Herein, we report a prospective study that coordinates time series sampling with the timing of shale gas development (SGD) operations to elucidate CH_4 origins and factors affecting its variability in groundwaters above the Marcellus Shale play.

Sources of aquifer methane are inferred through chemical and isotopic analysis of samples from drinking water wells (4–7) or from groundwater gaining streams (8). Research has demonstrated the natural occurrence of biogenic and thermogenic methane in aquifers that overlie UOG reservoirs (see *SI Appendix* for further details). It has also linked CH_4 contamination to SGD in a small number of cases (4, 8–10). Some studies implicating SGD in groundwater contamination have been challenged with critics characterizing the lack of predrill (baseline) measurements as a weakness and suggesting that CH_4 predated SGD (6, 11, 12). Partly in response to this debate, expert panels (13) and peer reviewed publications (4) have recommended prospective studies to assess the vulnerability of groundwater to HVHF and attendant activities. Prospective studies involve collection of baseline data and measurement of water quality over time and, especially, throughout key stages of UOG development (14). The value of prospective studies lies in their potential to reduce uncertainty in CH_4 source attribution, enable resolution of water-quality impacts to individual stages of SGD, and illuminate interactions between natural and SGD-related processes that affect [CH_4] variability. Recognizing this value, the US Environmental Protection Agency planned prospective studies of HVHF effects on freshwater, but were unable to identify locations that met their criteria and those of industry partners (13, 14).

We evaluate temporal and spatial changes in CH_4 isotopic composition and concentration in context of complementary hydrological and geochemical measurements and SGD operational

Significance

This study incorporates time series sampling of groundwater before, during, and after drilling, hydraulic fracturing, and initiation of shale gas production. Using monitoring wells installed next to gas well pads and above gas well laterals, previously undocumented responses to drilling and a gas well casing breach were observed, although groundwater impacts arising from the process of hydraulic fracturing were not detected. We discover considerable temporal variability in methane concentrations in deeper horizons of freshwater aquifers and attribute this to persistent shifts in aquifer recharge that influence mixing between shallow freshwater and comparatively saline and methane-rich deep groundwater. These results have implications for attribution of groundwater contamination to specific stages of shale gas development or natural processes and improving regulatory monitoring.

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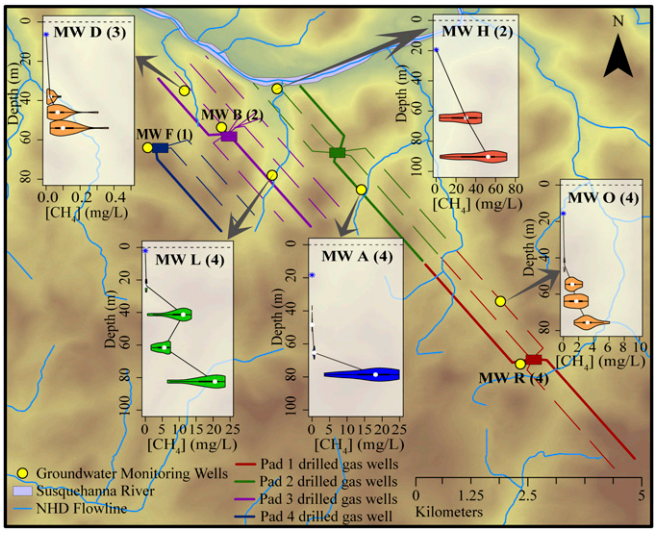

Fig. 1. Locations of four gas well pads, horizontal gas wells drilled from the well pads, and groundwater monitoring wells (MWs) A, B, D, F, H, L, O, and R. Colored rectangles represent well pads, and solid lines emanating from well pad locations delineate the seven gas wells drilled during the study. Two gas wells were drilled from well pads 2–4, while one gas well was drilled from well pad 1. Dashed lines delineate gas wells that were planned by the operator at the study outset, but have yet to be drilled. The number of sampling zones at a MW is indicated after the well label. Violin plots show variability of $[CH_4]$ in isolated zones of the MWs located in valleys. Depth to water table following borehole completion is denoted by the blue asterisk. Blue lines show locations of streams.

events. Through a formal agreement with a natural gas production company, we were given schedules for well pad construction, drilling, and HVHF for a portion of the company's leased acreage in Susquehanna County, PA. Based on this information, we sited eight multilevel groundwater monitoring wells (MWs) within undrilled lease units (blocks of leased properties with no existing shale gas wells). The MWs were configured for groundwater sampling and pressure measurements within one to four screened intervals isolated at different depths within zones of bedrock fracture (*SI Appendix*, Table S1). We collected groundwater from the MWs at 2- to 5-wk intervals over a period of 2 y, during which time seven horizontal gas wells, each with its own top hole (vertical section), were drilled from four well pads and completed within the Marcellus Shale (Fig. 1).

Results and Discussion

Groundwater Flow and CH_4 Occurrence Next to Well Pads. Monitoring wells B, F, and R were sited on hilltops at the edges of well pads 1, 3, and 4 to measure near-field hydrological and water-quality responses to top-hole drilling, lateral (horizontal) drilling, and HVHF of five gas wells that have now been in production for more than 1 y (Fig. 1 and *SI Appendix*, Table S2). (We were unable to secure landowner permission requisite for siting a MW on the edge of well pad 2, from which the remaining two gas wells in our study area were drilled.) The five top holes at well pads 1, 3, and 4 were drilled <100 m from MWs B, F, and R with an air-hammer bit, which relies on compressed air for cooling and lifting cuttings from the borehole. Within hours of the start of drilling, MW pressures dropped abruptly, then increased just as rapidly before falling back to predrill levels (Fig. 2 and *SI Appendix*, Fig. S1). Momentary release of groundwater from aquifer storage into the borehole followed by an immediate charging of the formation with air as the drill bit advanced may account for trough–peak pattern of the pressure response. This MW pressure cycle was consistently observed with a period of approximately 1 d, longer than the 6–10 h required to drill the borehole for the 200-m deep surface casings. The total change in pressure over a cycle (20–100 kPa) was comparable to the intra-annual variability in fluid pressures observed at the MWs (Fig. 2 and *SI Appendix*, Fig. S1), but orders of magnitude lower than air pressures exerted during top-hole drilling (2,400 kPa, based on operator drilling reports), indicating that the pressure surges dissipated sharply with distance from the gas well. Field-based observations and model results suggest that compressed air from drilling can penetrate hundreds of meters into fractured aquifers and create pressure gradients that extend over similar distances (15). While the pressure pulse propagates rapidly through the aquifer, the movement of groundwater and dissolved constituents is much slower and persists only as long as the pressure gradient is maintained. Published simulations show that groundwater surges caused by top-hole drilling could drive the transport of predrill, dissolved CH_4, initially present within 2 m of the borehole location, a distance of 11 m over a period of 1 d (16). Drilling-boosted transport of any dissolved CH_4 and other aqueous phase constituents may have been comparable at our sites, where drilling pressures were twofold lower and sustained half as long, and the hydraulic conductivities of the fractured bedrock at hilltop sites (K, *SI Appendix*, Table S1) were of the same order of magnitude as the model simulated K (10^{-6} m·s^{-1}). Pressure waves could propagate farther from the borehole at sites with more permeable aquifers or if drilling pressures were greater or sustained longer, possibly leading to farther afield changes in water quality, such as ephemeral increases in turbidity reported by homeowners living near newly drilled gas wells (2).

Methane concentrations in samples (n = 173) collected from seven ports of the three hilltop MWs averaged <0.05 mg/L at all ports and did not exceed 0.12 mg/L (Fig. 3 and *SI Appendix*, Fig. S2). In MWs B and R, $[CH_4]$ generally increased with depth. The jumps in $[CH_4]$ observed during the initial 6 mo of sampling at MW R, and the jump in June 2015 in the deep port at MW B, could have been induced by top-hole drilling either as pressure perturbations redistributed groundwater with low levels of dissolved CH_4 or as air migrating from the drilling location entrained preexisting pockets of gas-phase CH_4. The time for entrained gas-phase CH_4 to migrate, pore spaces to resaturate, and CH_4 to dissolve into aqueous phase may account for the lags between top-hole drilling and the small CH_4 peaks at MWs B and R (17).

Temporal trends in $[CH_4]$ were most evident at MW F, where $[CH_4]$ rose from 5×10^{-3} mg/L 2 mo after HVHF of the adjacent

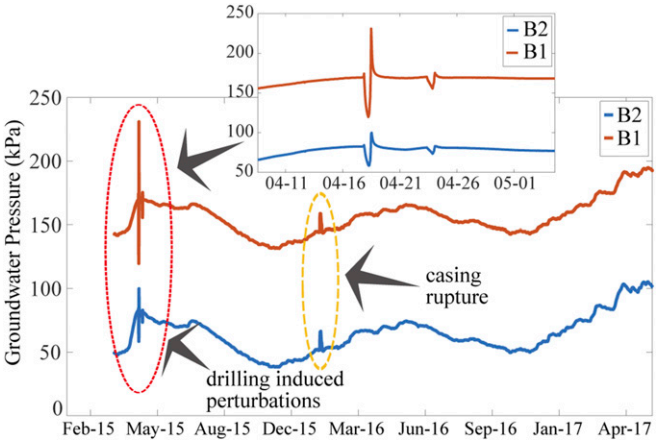

Fig. 2. Measurements of groundwater pressure at the deep port (B1) and more shallow port (B2) of MW B. See *SI Appendix*, Table S1 for port elevations. The *Inset* magnifies the pressure responses at site B in April 2015, when two gas wells were drilled 1 wk apart. A 9.81-kPa change in groundwater pressure corresponds to a 1-m change in hydraulic head.

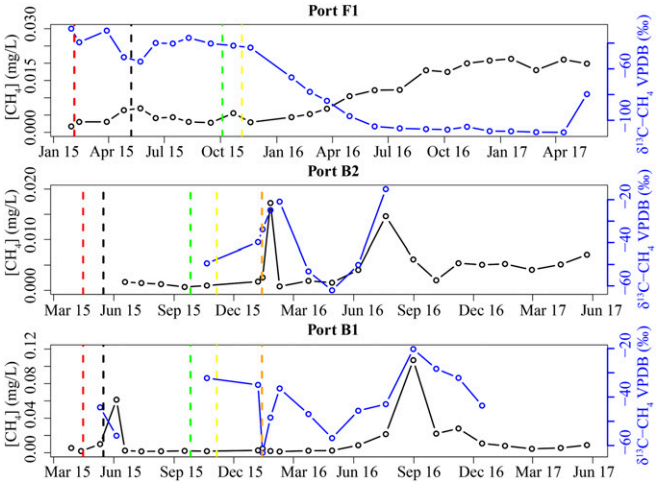

Fig. 3. Time series observations of $[CH_4]$ (black line) and $\delta^{13}C\text{-}CH_4$ (blue line) at the single sampling port of MW F and at the shallow (B2) and deep (B1) ports of MW B. The dashed red, black, and green lines, respectively, designate the times of top-hole drilling, horizontal drilling, and HVHF of the gas well, or the gas well drilled first, on the adjacent well pad. The dashed yellow line designates the start of production (*SI Appendix*, Table S2). For MW B the timing of the rupture in the production and intermediate casings is shown in orange. Methane concentrations ≥0.01 mg/L were analyzed for $\delta^{13}C\text{-}CH_4$. Samples of interest with lower $[CH_4]$ samples were also analyzed for $\delta^{13}C\text{-}CH_4$, but results could not always be obtained for these lower concentrations.

gas well to an asymptotic level of 2×10^{-2} mg/L 1 y later (Fig. 3). Samples collected before drilling of the gas well lateral could not contain Marcellus gas, so $\delta^{13}C\text{-}CH_4$ oscillations during this period (−29 to −52‰) likely reflect dynamical mixing between pools of biogenic gas, depleted in ^{13}C, and upper-Devonian thermogenic gas ($\delta^{13}C\text{-}CH_4$ = −50 to −38‰), further enriched in ^{13}C through anaerobic oxidation (Fig. 3). The decline in $\delta^{13}C\text{-}CH_4$ that occurred as $[CH_4]$ increased after HVHF appears to exclude compromised well integrity as a source of CH_4. Instead, it reflects an increasing influx of biogenic CH_4. As $[CH_4]$ neared its maximum, $\delta^{13}C\text{-}CH_4$ fell to −105‰, an extreme level of isotopic depletion outside the range typically observed for biogenic CH_4 in groundwater (−80 to −60‰) (4, 18), but within the range of biogenic CH_4 (19). The variability in $\delta^{13}C\text{-}CH_4$ at MW F, observed both before and after HVHF, likely stems from low $[CH_4]$ that renders the mixing ratio between CH_4 end members sensitive to small changes in the mass of one of the end members.

On January 13, 2016, bubbles were detected on the outside of the production and intermediate casing of a gas well on pad 3 (Fig. 1), 64 m from MW B. Both the production casing and intermediate casing developed small ruptures (~10 cm^2) at a depth of 20 m, which were likely caused by a flow control device that was being trialed on a small number of gas wells. Gas pressures in the open annulus between the ruptured production and intermediate casings rose enough (9,000 kPa) to displace the annular water, thereby removing a barrier to gas flow from the base of the intermediate casing (depth = 490 m) (20). Gas escape from the base of the surface casing (depth = 184 m) was also possible, but would have been impeded by 164 m of cement beneath the rupture that filled the annulus between the intermediate and surface casings. A cement plug was set at 1,740 m 4 d after the rupture occurred to seal off the well until repairs were completed in March 2016, whereupon the well was returned to production.

Groundwater pressures surged slightly (10 kPa) on the day of the rupture (Fig. 2), signaling transmission of a pressure anomaly away from the gas well and possible entry of gas into the groundwater system at depth. Methane concentrations in MW B exhibited small fluctuations (<0.01 mg/L) within 2 wk of the pressure surge (Fig. 3). Following a brief period of stability, $[CH_4]$ increased again, most appreciably at the deepest sampling port, B1, where concentrations peaked at 0.12 mg/L 7 mo after the casing rupture. Postrupture $\delta^{13}C\text{-}CH_4$ sometimes exceeded $\delta^{13}C\text{-}CH_4$ of Marcellus gas from the compromised gas well (−32‰) and varied proportionally with $[CH_4]$ during the second half of 2016, when $[CH_4]$ was most elevated (Fig. 3). Sporadic peaks in $[CH_4]$ also occurred at MW R (*SI Appendix*, Fig. S2), another hilltop well, but, in contrast to MW B, $\delta^{13}C\text{-}CH_4$ was uncorrelated with concentration and never exceeded −42‰. Moreover, ethane (C_2H_6) was not detected in MW R samples, but was detected in an August 2016 sample from MW B. The methane-to-ethane ratio (C_1/C_2 in mol/mol) equaled 213, the lowest value recorded at a hilltop well, but greater than that of Marcellus gas (C_1/C_2 = 53).

The postrupture correlation between $\delta^{13}C\text{-}CH_4$ and $[CH_4]$ and the intermittent occurrence of C_2H_6 is consistent with migration of Marcellus gas into the shallow aquifer. Oxidation reactions that enriched CH_4 in ^{13}C and preferentially degraded C_2H_6 during migration (21) could account for higher $\delta^{13}C\text{-}CH_4$ and C_1/C_2 in the groundwater samples relative to the Marcellus gas. Hydraulic heads decreased with depth at MW B (Fig. 2), indicating a downward component of groundwater flow, and inorganic chemistry was steady. Methane, then, likely migrated in the gas phase (18), dissolving into groundwater as it moved upward from the base of gas well surface or intermediate casing. Even at their peak, $[CH_4]$ at MW B was 65 times lower than the 7 mg/L action level set for homeowner wells by the Pennsylvania Oil and Gas Act (22). A signal attributable to the well casing rupture could not be detected at MW D, H, or L, three groundwater springs, ranging from 536 m to 826 m from the gas well pad, or a stream located within 1.3 km of the compromised well.

Methane Variability in Valleys Above Gas Well Laterals. Monitoring wells A, D, H, L, and O were installed in valleys, near streams and above five gas well laterals that were completed during the study (Fig. 1). (The offsets of MWs H and O from the underlying laterals reflect landowner-imposed constraints on MW siting.) Methane concentrations in 369 samples collected from the 15 ports of these multilevel wells spanned from <0.01 mg/L to 70 mg/L (Fig. 4 and *SI Appendix*, Fig. S3). Median $[CH_4]$ exceeded 20 mg/L at three sites (A, H, and L) and tended to increase with depth at a site, differing by as much as 25 mg/L between shallowest and deepest ports. Within-port trends in $[CH_4]$ were apparent. At MW O, $[CH_4]$ trended downward from 6 to 2 mg/L at the deepest port as $[CH_4]$ climbed to 3 mg/L before falling to less than 0.1 mg/L at ports 2 and 3 (*SI Appendix*, Fig. S3). Methane levels increased asymptotically and approximately concurrently at MWs A, L, and H. In the deepest ports, where $[CH_4]$ increases were greatest, concentrations stabilized at 15, 13, and 44 mg/L above predrill averages at A1, L1, and H1, respectively (Fig. 4). Although $[CH_4]$ at these sites began rising before top-hole drilling, most of the overall increase at these three ports occurred after SGD was initiated (Fig. 4). If the postdrill increases in $[CH_4]$ observed in MWs A, H, and L were to occur in water supply wells within 762 m (2,500 ft) of an active UOG well (our MWs lie beyond this threshold) (*SI Appendix*, Table S3), then, according to the PA Oil and Gas Act, the gas well operator would be presumed responsible for pollution of the water supply (22), regardless of the origins of the gas.

As $[CH_4]$ at A1 increased from 4 to 25 mg/L, $\delta^{13}C\text{-}CH_4$ and C_1/C_2 remained stable, averaging −69.1 ± 1.9‰ (mean ± SD) and 3,838 ± 426, respectively (Fig. 5). Dissolved gas at A1 was isotopically much lighter and drier than Marcellus and upper Devonian (UD) thermogenic gas (23), and, according to its $\delta^{13}C\text{-}CH_4$ and C_1/C_2, was largely methanogenic in origin (24, 25). Moreover, $\delta^{13}C$-DIC increased with $[CH_4]$ from −13 to −1‰, while SO_4 concentrations trended downward, signaling a shift from waters influenced by sulfate reduction toward waters

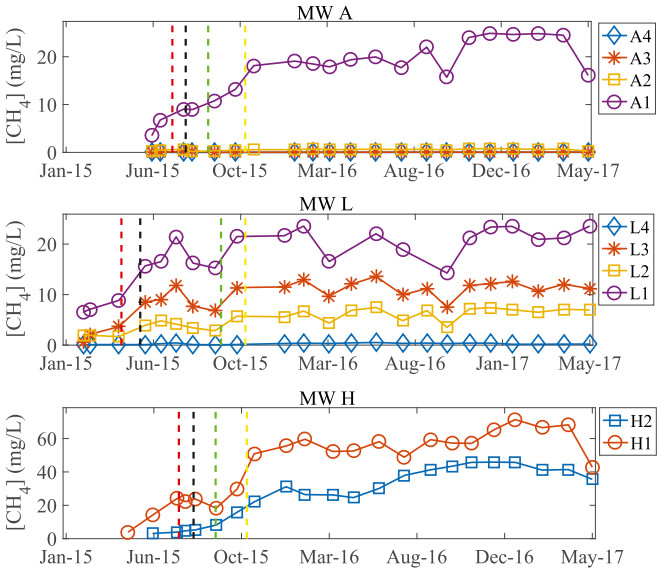

Fig. 4. Methane concentrations ([CH_4]) at valley monitoring wells A, L, and H. Each solid line represents [CH_4] measured in water samples collected from a particular port, numbered from deepest (e.g., A1) to shallowest (e.g., A4). The dashed red, black, and green lines, respectively, designate the times of top-hole drilling, horizontal drilling, and HVHF of the nearest underlying gas well lateral, while the dashed yellow line designates the start of production.

increasingly influenced by microbial methanogenesis (*SI Appendix*, Fig. S4) (19). The concomitant increase in [CH_4] and δ^{13}C-DIC, together with steady δ^{13}C-CH_4 and C_1/C_2, is consistent with a change in mixing ratios of end members comprising the A1 groundwater. The simplest conceptualization that accounts for this collective behavior involves mixing of CH_4-free water that is depleted in ^{13}C-DIC with increasing amounts of groundwater that is enriched in ^{13}C-DIC and in CH_4 of predominantly methanogenic origin.

Whereas CH_4 occurrence was restricted to the deepest sampling zone at site A, [CH_4] averaged >5 mg/L in the three deepest ports at site L (Fig. 4). Measurements of δ^{13}C-CH_4 at L1 averaged −55.1‰ and were nearly steady, declining from predrill levels by 5‰ as the nearest gas well was drilled and as [CH_4] rose and plateaued above 20 mg/L. Depth variations in δ^{13}C-CH_4 exceeded temporal variations at this site, with δ^{13}C-CH_4 at L2 averaging −68.5 ± 3.3‰, or 14‰ lower than in the surrounding L1 and L3 ports (*SI Appendix*, Fig. S5). Measurements of C_1/C_2 were stable at L1 (4,015 ± 154) and exhibited comparably low variability at L2 (3,841 ± 190) and L3 (7,419 ± 330) (*SI Appendix*, Fig. S5). The δ^{13}C of C_2H_6 in L1–L3 samples ranged from −40 to −29‰ (*SI Appendix*, Table S4), which lies above the range for bacteriogenic C_2H_6 (26) and within the thermogenic field (27, 28). Mixing of thermogenic and biogenic gases can account for the isotopic signatures of CH_4 and C_2H_6 at MW L; however, it is unlikely that [CH_4] increases at L1–L3 stemmed from introduction of Marcellus gas from SGD. Values of δ^{13}C-CH_4 trended downward, further away from the δ^{13}C of Marcellus CH_4, and the C_1/C_2 was too large to be attributable to mixing with more than very small amounts of Marcellus gas.

Methane levels were high at site H, paralleling the temporal increase observed at A1 and plateauing at 70 and 45 mg/L at H1 and H2, respectively (Fig. 4). Unlike A1, where δ^{13}C-CH_4 was stable and typical of biogenic gas (69.1 ± 1.9‰), δ^{13}C-CH_4 at site H trended upwards, leveling off at 9‰ higher than the predrill measurements at H1 (−55‰) and H2 (−58‰) (Fig. 5 and *SI Appendix*, Fig. S6). Oxidation of CH_4 was not responsible for this ^{13}C enrichment because it would also lower δ^{13}C-DIC and [CH_4], which is counter to our observations (*SI Appendix*, Fig. S7). Introduction of Marcellus gas would cause δ^{13}C-CH_4 to increase, but is similarly improbable because the corresponding reduction in C_1/C_2 was far too small (*SI Appendix*, Fig. S8) and an isotopic reversal (i.e., δ^{13}C-CH_4 > δ^{13}C-C_2H_6), which is indicative of Marcellus gas, did not occur at either H1 or H2.

The absence of a Marcellus gas signature at MW H, as well as at MWs A and L, does not exclude the possibility that SGD contributed in some way to the postdrill [CH_4] increases at these valley sites. Compromised gas well integrity, stemming from casing failure or faulty cement seals, may lead to a loss of zonal isolation, enabling vertical pressure gradients to drive CH_4 that enters the well annulus upward into freshwater aquifers (20, 29). In our study region (northeast Pennsylvania), where well integrity loss has been documented with relatively high frequency, CH_4-charged units of UD age that lie above the Marcellus Shale are possible sources of this stray gas (29–31). Excessive casing-annulus pressures have been linked to incidences of well integrity loss and stray gas migration (20, 29). For example, annular gas pressures in four gas wells in Bradford County, PA climbed to 3,300–6,500 kPa, leading to CH_4 migration to nearby drinking water wells (10). Measurements of annular pressures on the seven gas wells completed in our study area were made at least once a month, except during a 2-mo period at a well on pad 3 that was temporarily plugged for repairs, as described above. The gauge pressures averaged 27 kPa (4 psig) at one gas well and less than 0.7 kPa (0.1 psig) at the other six wells (*SI Appendix*, Fig. S9). These low annular pressures are indicative of gas wells that have thus far maintained their structural integrity. They are more than 50-fold smaller than critical pressures theorized to induce stray gas migration (20) and thresholds that would trigger a regulatory response (22).

If not gas well integrity, the process of HVHF itself could have indirectly affected [CH_4] in the valley MWs. The fastest change in [CH_4] at site H began after HVHF of the underlying gas well lateral, possibly reflecting a piston-type effect whereby propagation of excess fluid pressure drove UD (not Marcellus) gas toward the surface. Published calculations, although untested against actual measurements, suggest HVHF-induced pressure perturbations should be localized, dissipating in tens of meters of within low permeability siltstones and shales ($K = 10^{-13} - 10^{-8}$ m·s^{-1}) (32) above the Marcellus (33). Although not known to exist, natural fractures connecting the Marcellus to shallow aquifers could transmit pressures faster and with less dissipation; however, model predictions indicate that pressures would decline rapidly as the gas well was placed into production, leading to an ephemeral increase in [CH_4] (34), in contrast to the persistent increase

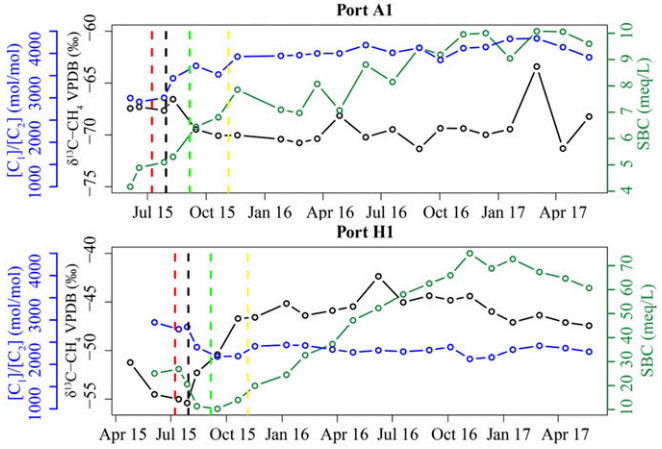

Fig. 5. Time series measurements of δ^{13}C-CH_4, C_1/C_2, and salinity [as sum of the base cations (SBC); Ca, Mg, Na, K]. See Fig. 3 caption for description of vertical dashed lines. The sum of base cations constituted ≥99% of positive charge in groundwater samples. meq, milliequivalent; VPDB, Vienna Pee Dee belemnite.

observed at sites A, H, and L. Groundwater pressures at site H, as well as the other valley sites, exhibited weak seasonal variation, showing no perturbations consistent with transmission of pressures away from the HVHF zone (*SI Appendix*, Fig. S10). It is possible that our monitoring network was too sparse to detect propagation of HVHF pressure waves into the shallow aquifer. Nevertheless, this mechanism of UD gas mobilization is not supported by our available observations or peer-reviewed model results.

Sources of Elevated Methane in Valley Wells. Based on the available chemical, isotopic, and hydrologic evidence, together with knowledge of gas well conditions, it appears improbable that changes in valley [CH_4] arise from gas well drilling, loss of integrity, or HVHF. Other anthropogenic activities that may contribute CH_4 to groundwater, such as coal mining or conventional oil and gas extraction, have not occurred in our study area. Therefore, natural processes likely account for the variability in [CH_4].

At H1 and H2, as well as the next three lowest elevation ports (A1, L1–L3), where [CH_4] exhibited the steepest increases from baseline levels, [CH_4] rose proportionately with salinity (Fig. 5 and *SI Appendix*, Figs. S5 and S6). This temporal covariation is inconsistent with gas-phase migration of CH_4 caused by gas well leakage, drilling, or HVHF, but it does suggest increases in CH_4 and salinity may be traceable to the same source. Surface releases, such as spills of flowback or produced waters (35), were unlikely sources because salinity changes were more pronounced in deeper sampling ports and concurrent across different sites. Measurements of δ^2H-H_2O, δ^{18}O-H_2O, ^{3}H, SF_6, and chlorofluorocarbons suggest these groundwaters are composed largely of meteoric water recharged after 1950. Nevertheless, Cl/Br mass ratios and linear relationships between concentrations of Cl and conservative cations (Na, Li) suggest that groundwater from lower ports of valley MWs is influenced by inputs of deep basin brines (*SI Appendix*, Figs. S11 and S12) (36, 37).

Others have observed higher salinities and elevated [CH_4] of mixed biogenic/thermogenic origin beneath lowlands of this area (23, 38) and elsewhere (28), leading to the interpretation that valley wells draw groundwater from a transitional zone (39). This zone separates shallow, dilute groundwater of local flow systems from highly saline groundwater that flows sluggishly through deeper formations of UD age. Methane in shallow groundwater is either absent or mainly biogenic, tending to increase in concentration closer to the transition zone once oxygen and other electron acceptors are consumed along flow paths. Gas beneath the transition zone is thermogenic, composed of gas generated in place and gas partially stripped of longer chained hydrocarbons (e.g., C_2H_6) by solubility and diffusive fractionation (18, 40, 41) during slow migration from even deeper formations (e.g., Marcellus). Shallow and deep groundwaters comingle within the transition zone. Here macrodispersive processes smear zonal interfaces and incompletely mix methanogenic and postgenetically altered thermogenic gas. In our study area, this vertical mixing may be enhanced by valley stress relief fractures and possibly faults (42), as well as by bedding planes that dip gently to the south and east (36), approximately parallel to the regional hydraulic gradient. According to this conceptualization, our hilltop MWs draw shallow groundwater from above the transition zone. In the lowlands, however, the transition zone lies closer to the surface, where it is penetrated by the deeper ports of our valley MWs.

The covarying [CH_4] and salinity in our valley MWs may reflect changes in the relative contributions of shallow and deep groundwaters to the transition zone. Measurements of $^{87}Sr/^{86}Sr$ and [Sr]/[Ca], which have been used to identify diluted Marcellus brines (36, 43), show little variation between pre- and post-HVHF groundwater (*SI Appendix*, Fig. S13); thus, the increases in salinity and [CH_4] cannot be attributed to migration of HVHF fluids from the Marcellus Formation. Fluctuations in [CH_4] measured previously in open-hole, drinking water wells have been linked to seasonal water table variations that change the proportions of shallow and deep groundwater entering the wells (44). Hydraulic heads (H) at our sites were uncorrelated with the monotonically increasing [CH_4]. Moreover, temporal variations in H were particularly small in the valley wells (SD < 0.5 m), signifying nearly steady flow typical of regional flow regimes (*SI Appendix*, Fig. S10). These observations demonstrate that variability in [CH_4] at depth can be uncoupled from contemporaneous fluctuations in H and saturated thickness. We hypothesize that the observed salinity and [CH_4] trends are a response to persistent shifts in aquifer recharge predating this study that altered mixing ratios and led to spatial gradients in [CH_4] and salinity along transition zone flow paths. The timing of [CH_4] increases was similar at four sites (A, D, H, and L), each in different headwater catchments, which suggests a larger scale-forcing mechanism consistent with meteorologically driven shifts in aquifer recharge.

Conclusions

During this ∼2 y study, SGD had perceptible effects on groundwater flow and [CH_4], although, based on observations taken from eight multilevel MWs and nearby springs, they appeared to be ephemeral, restricted to the proximity of the well pad, and too small to constitute a water-quality concern. The effects did not stem from HVHF or management of fluids associated with this process, but from top-hole drilling and a casing rupture caused by flow control that was being trialed. Hydrologic measurements pinpointed the timing of the casing rupture and revealed drilling-induced perturbations capable of remobilizing CH_4, which underscores the value of near-field hydrologic monitoring in aquifer protection during SGD.

High [CH_4] are known to occur beneath valleys of the Appalachian Basin. We find that [CH_4] in these settings can exhibit considerable temporal variability that is likely unrelated to SGD, particularly at depths where drinking water is commonly withdrawn and where biogenic and thermogenic CH_4 from shallow and regional flow systems mix. That [CH_4] unsteadiness can reflect SGD or can occur naturally complicates contaminant source attribution and suggests that regulatory monitoring programs may need to collect samples with higher frequency in locations with significant [CH_4]. In our case, reliable conclusions on CH_4 source attribution could not be made solely on the basis of [CH_4] changes relative to the timing of SGD operations, but required consideration of pre- and postdrill observations of hydrocarbon composition of dissolved gases from discrete-depth sampling, as well as hydrologic observations and access to indicators of gas well integrity.

The prospective study design, as implemented here, provides insight into the effects of SGD and natural processes on the temporal dynamics of water quality that is not otherwise possible, but it is not without limitations. One limitation of the prospective approach is that the comparatively high costs of MW installation and time series sampling place constraints on the number of gas wells that can be monitored. Consequently, prospective studies are not suitable for assessing regionwide rates of SGD-related water-quality impairment, which recent analyses of large publicly available datasets suggest are low (45). Another issue is that a cooperating oil and gas producer could introduce bias into a prospective study by deciding to exercise extraordinary precautions in the monitored portion of its operations. This did not appear to be the case in our experience, and the cooperating producer placed no restrictions on our selections of MW locations.

Prospective studies are a necessary complement to household water-quality studies (4, 7, 28, 46), as well as data-mining and geological approaches that identify areas where CH_4 migration may be of particular concern (42, 45). Future prospective studies should evaluate aquifer responses to drilling, which in this study were small but unambiguous, across different geologic terrains and under different UOG drilling methods. When considered collectively, prospective studies could help in assessment of the efficacy of state-dependent regulations for UOG well construction

in reducing the likelihood of leaking wells and stray gas migration. To maximize the benefits of their insights, prospective studies should be conducted in conjunction with larger scale studies of drinking water quality at the outset of the development of a UOG play.

Methods

A formal agreement with Southwestern Energy, a natural gas production company, provided authors with prior knowledge of locations of well pads and laterals and timing of development activities. According to the agreement, all data collected by the authors would be owned, analyzed, and interpreted by authors with no restrictions on publication of the findings. MWs were located in topographic highs (three wells) adjacent to shale gas well pads, and topographic lows (five wells) down gradient from well pads and above laterals. The MWs were drilled through bedrock to depths of 90–120 m, and borehole geophysical and straddle-packer measurements were used to identify one to four fracture zones in each borehole that were isolated by permanent packers and equipped with dedicated pressure transducers and sampling pumps. Additional field and laboratory methods are described in *SI Appendix*.

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