Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales

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Horizontal drilling and hydraulic fracturing have enhanced energy production but raised concerns about drinking-water contamination and other environmental impacts. Identifying the sources and mechanisms of contamination can help improve the environmental and economic sustainability of shale-gas extraction. We analyzed 113 and 20 samples from drinking-water wells overlying the Marcellus and Barnett Shales, respectively, examining hydrocarbon abundance and isotopic compositions (e.g., C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4}, δ\textsuperscript{13}C-CH\textsubscript{4}) and providing, to our knowledge, the first comprehensive analyses of noble gases and their isotopes (e.g., \(^{4}\)He, \(^{39}\)Ar) in groundwater near shale-gas wells. We addressed two questions. (i) Are elevated levels of hydrocarbon gases in drinking-water aquifers near gas wells natural or anthropogenic? (ii) If fugitive gas contamination exists, what mechanisms cause it? Against a backdrop of naturally occurring salt- and gas-rich groundwater, we identified eight discrete clusters of fugitive gas contamination, seven in Pennsylvania and one in Texas that showed increased contamination through time. Where fugitive gas contamination occurred, the relative proportions of thermogenic hydrocarbon gas (e.g., CH\textsubscript{4}, \(^{4}\)He) were significantly higher (\(P < 0.01\)) and the proportions of atmospheric gases (air-saturated water; e.g., N\textsubscript{2}, \(^{39}\)Ar) were significantly lower (\(P < 0.01\)) relative to background groundwater. Noble gas isotopic and hydrocarbon data link four contamination clusters to gas leakage from intermediate-depth strata through failures of annulus cement, three to target production gases that seem to implicate faulty production casings, and one to an underground gas well failure. Noble gas data appear to rule out gas contamination by upward migration from depth through overlying geological strata triggered by horizontal drilling or hydraulic fracturing.

Significance

Hydrocarbon production from unconventional sources is growing rapidly, accompanied by concerns about drinking-water contamination and other environmental risks. Using noble gas and hydrocarbon tracers, we distinguish natural sources of methane from anthropogenic contamination and evaluate the mechanisms that cause elevated hydrocarbon concentrations in drinking water near natural-gas wells. We document fugitive gases in eight clusters of domestic water wells overlying the Marcellus and Barnett Shales, including declining water quality through time over the Barnett. Gas geochemistry data implicate leaks through annulus cement (four cases), production casings (three cases), and underground well failure (one case) rather than gas migration induced by hydraulic fracturing deep underground. Determining the mechanisms of contamination will improve the safety and economics of shale-gas extraction.


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Previous efforts to resolve these questions identify the genetic fingerprint of hydrocarbon gases using the molecular (e.g., [C\textsubscript{2}H\textsubscript{6}], plus heavier aliphatic hydrocarbons) and stable isotopic [e.g., δ\textsuperscript{13}C-CH\textsubscript{4}, δ\textsuperscript{15}N-H-CH\textsubscript{4}] compositions of hydrocarbon gases (6–9, 13) (SI Text). These techniques resolve thermogenic and biogenic hydrocarbon contributions and differentiate between hydrocarbon sources of differing thermal maturity (e.g., Middle–Devonian (Marcellus)-produced gases vs. Upper Devonian (UD) gas pockets at intermediate depths). However, microbial activity and oxidation can alter the original geochemo signature (14) and obscure the sources or mechanisms of fluid migration (8, 9).

Noble gas elemental and isotopic tracers constitute an appropriate complement to hydrocarbon geochemistry. Their nonreactive nature (i.e., unaffected by chemical reactions or microbial activity) (14) and well-characterized isotopic compositions in the crust, hydrosphere, and atmosphere (SI Text) make noble gases ideal tracers of crustal fluid processes (14–17). In most aquifers, in aquifers overlying the Marcellus Shale is natural and unrelated to shale-gas development (8, 9, 13). This study addresses two critical questions: (i) are elevated levels of hydrocarbon gas in drinking-water aquifers near gas wells derived from natural or anthropogenic sources and (ii) if fugitive gas contamination exists, what mechanisms cause it?

Rising demands for domestic energy resources, mandates for cleaner burning fuels, and efforts to reduce greenhouse gas emissions are driving an energy transformation from coal toward hydrocarbon gases produced from unconventional resources (1, 2). Horizontal drilling and hydraulic fracturing have substantially increased hydrocarbon recovery from black shales and other unconventional resources (1, 2) (Fig. S1) to the extent that shale gas now accounts for more than one third of the total natural-gas production in the United States (3).

Public and political support for unconventional energy extraction is tempered by environmental concerns (4, 5), including the potential for compromised drinking-water quality near shale-gas development (6, 7). The presence of elevated methane and aliphatic hydrocarbons (ethane, propane, etc.) in drinking water, for instance, remains controversial and requires distinguishing between natural and anthropogenic sources (6–12). Some studies have suggested that shale-gas development results in fugitive gas contamination in a subset of wells near drill sites (6, 7), whereas others have suggested that the distribution of hydrocarbon gases. 

noble gas geochemistry | groundwater contamination | methane | water quality | isotopic tracers
the noble gas isotopic composition reflects a binary mixture of two sources: (i) air-saturated water (ASW), containing $^{21}$Ne, $^{36}$Ar, and $^{38}$Kr (and N$_2$) derived from solubility equilibrium with the atmosphere during groundwater recharge; and (ii) crustal rocks that release radiogenic noble gases such as $^4$He and $^{21}$Ne* (sourced from $^{36}$Cl + $^{238}$U + $^{232}$Th decay) and $^{36}$Ar* (sourced from $^{40}$K decay, where * indicates a radiogenic component) (18). Once noble gases incorporate into crustal fluids, they fractionate only by well-constrained physical mechanisms (e.g., diffusion, phase partitioning) (16, 18). Therefore, when paired with hydrocarbon composition and inorganic water chemistry, noble gases can help differentiate between natural geological migration of hydrocarbon gases and anthropogenic contamination. We also suggest that noble gas geochemistry can be used to determine the mechanisms by which anthropogenic gas contamination occur.

We envision seven scenarios that, alone or together, can account for the elevated hydrocarbon levels in shallow aquifers (Fig. 1): (i) in situ microbial methane production; (ii) natural in situ presence or tectonically driven migration over geological time of gas-rich brine from an underlying source formation [e.g., Marcellus or Barnett formation (Fm.)] or gas-bearing formation of intermediate depth (e.g., Lock Haven/Catskill Fm. or Strawn Fm.); (iii) exsolution of hydrocarbon gas already present in shallow aquifers following scenario 1 or 2, driven by vibrations or water level fluctuations from drilling activities; (iv) leakage from the target or intermediate-depth formations through a poorly cemented well annulus; (v) leakage from the target formation through faulty well casings (e.g., poorly joined or corroded casings); (vi) migration of hydrocarbon gas from the target or overlapping formations along natural deformation features (e.g., faults, joints, or fractures) or those initiated by drilling (e.g., faults or fractures created, reopened, or intersected by drilling or hydraulic fracturing activities); and (vii) migration of target or intermediate-depth gases through abandoned or legacy wells. In our study areas, other scenarios such as coal bed methane or leakage from pipelines or compressors into aquifers are unlikely (Figs. S2 and S3).

Here, we examine the noble gas (e.g., $^4$He, $^{21}$Ne, and $^{36}$Ar), hydrocarbon (e.g., $^{13}$C-$^8$CH$_4$, $^{13}$C-$^6$CH$_4$, and $^{12}$C-$^8$CH$_4$), and chloride (Cl$^-$) content of 113 domestic groundwater wells and one natural sandstone of the Lock Haven and Catskill Formations or outwash alluvium aquifers. The typical depth to drinking water in Texas is 60–75 m, sourced from the Upper Trinity limestone. More geological information is included in SI Text. To augment our previous studies (6, 7) that examined the relationship between methane and proximity to gas wells, in this study we intentionally targeted a subset of water wells known to have elevated CH$_4$ concentrations and surrounding water wells both near and far from drill sites. The reason for this approach was to distinguish among the mechanisms causing high gas concentrations naturally from those potentially associated with shale-gas development (Fig. 1).

### Results and Discussion

The occurrence, distribution, and composition of hydrocarbons in the Earth’s crust result from the interplay between tectonic and hydrologic cycles (14, 17). The remnants of these processes generate inorganic, hydrocarbon, and noble gas compositions with distinctive geochemical fingerprints (e.g., $^{13}$C-$^8$CH$_4$, $^4$He/$^8$CH$_4$, $^{20}$Ne/$^{36}$Ar, and Cl$^-$) that can help to distinguish hydrocarbons that migrated naturally from those that migrated as anthropogenic fugitive gases associated with shale-gas development. Our data show that in the aquifers overlying the MSA, the CH$_4$ levels in groundwater samples observed >1 km from shale-gas wells co-occurs with elevated concentrations of natural crustal brine components (e.g., Cl$^-$ and $^4$He) (triangles in Fig. 2 A and B). The composition of groundwater sampled <1 km from drill sites in the MSA shows clear evidence of two populations: (i) wells with compositions statistically indistinguishable from those collected >1 km from drill sites (circles in Fig. 2 A and B) and (ii) wells with low salt (Cl$^-$) concentrations but that are supersaturated with respect to methane and have distinct noble gas compositions (green-rimmed circles in Fig. 2 A and B).

Similar to the results for methane, the noble gas compositions from groundwater samples in the MSA >1 km from shale-gas wells (triangles), including the gas-rich saline spring at Salt Springs State Park north of Montrose, PA (square, Fig. 24), and some samples <1 km from drill sites (circles, Fig. 24) all had similar diagnostic noble gas compositions (Fig. 2 A and B). These samples have CH$_4$/Ar at or below CH$_4$ saturation [p(CH$_4$) < 1 atm, i.e., below the “bubble point”; SI Text] and show a corresponding increase in the ratio of thermogenic gas components to ASW (i.e., CH$_4$/Ar vs. [Cl$^-$]), $r^2 = 0.72$, $P < 0.01$; and $^{36}$Ar/Ne vs. [Cl$^-$], $r^2 = 0.59$, $P < 0.01$; Fig. 2 A and B). In fact, the regression of CH$_4$/Ar vs. [Cl$^-$] for all samples >1 km from gas wells (Fig. 2 A) is indistinguishable from a regression of the subset of points <1 km from drill sites, suggesting one continuous population ($P = 0.31$, Chow test); we define these samples as the “normal trend” for brevity. These data suggest that the natural salt- and gas-rich waters in the MSA have a groundwater chemistry derived from a deep gas-rich brine that migrated over geological time (typified by the Salt Spring) and then mixed with meteoric water of ASW composition ([Cl$^-$] = <10 mg/L; CH$_4$/Ar = 9; $^{36}$Ar/Ne = −0.3). The coexistence of elevated CH$_4$, Cl$^-$, and $^4$He is consistent with previous observations for brine migration that represents a natural hydrocarbon gas source in scenario 2 (Fig. 1) (20).

A subset of samples collected <1 km from drill sites, however, shows different relationships for CH$_4$/Ar and $^{36}$Ar/Ne vs. Cl$^-$; we define this subset as the “anomalous subset” for brevity. These samples show significantly higher levels of thermogenic gases ($P < 0.01$) relative to ASW gases (i.e., elevated CH$_4$/Ar and $^{36}$Ar/Ne independent of [Cl$^-$]) (green-rimmed circles in Fig. 2 A and B). Because CH$_4$ and $^{36}$Ar and $^4$He and $^{36}$Ne pairs have similar gas/liquid partition coefficient (1/solubility) ratios (SI Text), a lack of correlation between Cl$^-$ concentrations and either CH$_4$/Ar or $^{36}$Ar/Ne (P = 0.864 and 0.698, respectively) suggests that the anomalous subset (Fig. 2) represents a thermogenic

![Fig. 1. A diagram of seven scenarios that may account for the presence of elevated hydrocarbon gas levels in shallow aquifers (see discussion in text). The figure is a conceptualized stratigraphic section and is not drawn to scale. Additional scenarios (e.g., coal bed methane and natural-gas pipelines leaking into aquifers) are unlikely in our specific study areas (Figs. S2 and S3).](image-url)
increases of both CH$_4^{36}$Ar (24,782–722,534) and $^{4}$He$^{20}$Ne (267–263,242), whereas the other showed similar trends in CH$_4^{36}$Ar (750–81,163) and $^{4}$He$^{20}$Ne (42–569) during the same period (Fig. 2 C and D and SI Text). Because the [Cl$^-$] did not change in either well, we suggest that thermogenic hydrocarbon gas migrated into these wells in the gas phase accompanied by brine between December 2012 and August 2013.

The concentrations of dissolved ASW gases (i.e., $^{20}$Ne, $^{36}$Ar, and N$_2$) can further explain the interactions that occur between hydrocarbon gas and water (16, 22–25). In the MSA, all normal trend samples both >1 km and <1 km from drill sites had $^{36}$Ar and N$_2$ that varied within ~15% of the temperature-dependent ASW solubility curve (cyan line in Fig. 3 A–C) (25–28). Although some background groundwaters showed minor excess air entrainment common in pumped groundwater globally (SI Text) (23, 29), these ranges reflect equilibration between the atmospheric and meteoric water during groundwater recharge (26, 27).

In contrast, the anomalous subset of wells in the MSA (green-rimmed circles in Fig. 3 A and B) that have elevated methane and that departed from the brine-meteorite water mixing line were stripped of ASW gases compared with the expected solubility equilibriums ($P < 0.001$; Fig. 3 A and B).

Consistent with the results from the MSA, our data suggest that 5 water wells in the BSA display evidence of gas-phase migration associated with hydrocarbon gas extraction, whereas the remaining 15 samples appear to have acquired methane naturally. The initial December 2012 sampling identified three anomalous samples in Texas with supersaturated CH$_4$ that departed from the

hydrocarbon gas that has separated from the brine-meteoritic water mixture and migrated in the gas phase.

To test this geochemical framework in another shale-gas basin, we compared the MSA data to those from the BSA, where the source of elevated CH$_4$ concentrations reported in domestic water wells has been controversial (Fig. S3). Our initial sampling in December 2012 revealed that 9 of 12 BSA groundwater samples were similar to the normal trend samples from the MSA. For instance, [CH$_4$] and the ratios of thermogenic gas to meteoric water [i.e., CH$_4^{36}$Ar (r$^2$ = 0.59; P < 0.01) and $^{4}$He$^{20}$Ne (r$^2$ = 0.48; P < 0.01) (dashed lines in C and D). Five samples, including two that changed between the first and second sampling periods (Fig. S4), had substantially higher CH$_4^{36}$Ar and $^{4}$He$^{20}$Ne independent of [Cl$^-$]. The anomalous subset of samples from both locations with elevated CH$_4$ that do not fall along the normal trend (>1 km) regression lines are consistent with a flux of gas-phase thermogenic hydrocarbon gas into shallow aquifers.
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MSA, the hydrocarbon composition of the anomalous subset of
gas-phase migration or displace the ASW gases in the vadose zone
before recharge (22, 30). Even the naturally discharging gas-rich
Salt Spring in Pennsylvania has p(CH4) = ~1 atm and normal
ASW compositions, with minor bubble nucleation only occurring
near the well because hydrostatic pressure depressurization
(SI Text).
Stripped ASW composition in a subset of groundwater sam-
ple occurred exclusively <1 km from drill sites in the MSA and
BSA and indicate a rapid introduction of high pressure [i.e.,
p(CH4) > 1 atm] gas-phase hydrocarbons into shallow aquifers
at a rate that exceeds groundwater flow. There are no apparent
TECTONIC or hydrologic mechanisms to drive the migration of
hydrocarbon gas at sufficient rates to strip ASW gases within shallow
aquifers (<100 m) in either study area. Moreover, in both study
areas, samples with stripped ASW composition contain elevated
levels of aliphatic hydrocarbons (C2H6, C3H8, C4H10 < 0.01) and heavy
stable isotopic compositions (i.e., δ13C-C4H4 = −55‰) (δ9, 13
P < 0.01; Fig. 4B and Fig. S7), which preclude microbial pro-
duction as the source for elevated methane in shallow aquifers
(scenario 1) (6, 7). Note that three wells targeted for elevated
microbial methane levels in the MSA (e.g., landfills; diamond
symbols in Figs. 2–4) were easily distinguished by diagnostic noble
gas (e.g., low 36Ar/4He and 13He/CH4) and hydrocarbon isotopic
traces (light δ13C-C4H4, Figs. 4B and 4F), but still contained normal
ASW gas levels (Fig. 3A–C and Fig. S8). More importantly, in the
MSA, the hydrocarbon composition of the anomalous subset of
samples is consistent with either Marcellus-produced gases (black
box in Fig. 4A and B and SI Text) or overlying UD-produced gases
(pink box in Fig. 4A and B and SI Text; scenario 2), whereas BSA
samples require further consideration as discussed below.
The combined evidence of noble gas and hydrocarbon molecular
(C2H6/CH4) and stable isotopic (δ13C-C4H4) compositions for the
majority of anomalous subset samples is consistent with con-
tamination by fugitive gas migration.
By constraining the mechanisms that cause elevated hydro-
carbon concentrations in drinking water near natural-gas wells,
we can further distinguish the presence of fugitive gas contami-
nation. Gas-rich groundwater (>1 cm3 standard temperature
and pressure/L methane) samples that fall along the normal trends
for hydrocarbon levels, salts, and ASW gases (20Ar and N2) in
the MSA have 20Ar/36Ar far above ASW equilibrium (~0.156)
and 4He/CH4 well above any known thermogenic hydrocarbon
gases in the study area (Fig. 4A). We suggest that the enriched
20Ar/36Ar and excess 4He and 20Ne in these samples are rem-
nants of relatively low Vgas/Vwater conditions during the
geological migration of gas-rich brine from Marcellus source
rocks to conventional UD hydrocarbon traps and eventually
shallow aquifers as described by scenario 2 (Fig. 1).
We hypothesize that the geological migration of hy-
drocarbons by scenario 2 occurred in three successive steps. First,
hydrocarbon maturation in the Marcellus source rocks produced
sufficient methane to generate a free gas phase, which caused the
naturally present trace gases to partition from the formational
brine into the gas phase. As trace gases partition between the brine
and gas phases, the degree of fractionation between trace com-
ponents such as 20Ne and 36Ar (or other trace gases) is a function
of the respective partition coefficients between gas and water and
the relative volumes of gas and water (Vgas/Vwater; SI Text) (18).
Because Ne and He have higher partition coefficients (i.e., lower
solubilities in the fluid) than Ar or CH4, this initial stage of rela-
tively low Vgas/Vwater gas-phase separation causes the enrichment
of 20Ne and 4He in the migrating gas phase, whereas the residual
Marcellus fluid becomes relatively depleted in 20Ne,36Ar below
ASW (0.10–0.12), as reported in ref. 19. In the second stage, the
buoyant migration of relatively He- and Ne-enriched hydrocarbon
gas into overlying formations further increases the concentration
of less soluble trace gases (i.e., 4He and 20Ne) with respect to more
soluble gases (i.e., 36Ar and CH4) that will preferentially redis-
solve into the water-saturated crust. This redissolution process
would yield elevated 20Ne/36Ar and 4He/CH4 in the hydrocarbon
gases emplaced in the overlying UD reservoirs, which is sup-
ported by the observed 20Ne/36Ar composition of UD-produced
(gases up to 1.4) in the northern Appalachian Basin (Fig. 4A) as
reported in ref. 19. The final stage likely occurs at present, when
hydrocarbon gases that previously migrated into UD traps (e.g., in the Lock Haven/Catskill) diffuse into and equilibrate with overlying shallow aquifers.

In contrast to the normal trend samples that show extensive fractionation following a complex history of geological migration, all samples from the anomalous subset are located <1 km from drill sites in Pennsylvania and have noble gas compositions that are inconsistent with the geological migration of hydrocarbon gas through the water-saturated crust (scenario 2). Instead, the anomalous subset of samples has significantly lower $^{26}$Ne/$^{36}$Ar ($P < 0.01$) and $^4$He/CH$_4$ ($P < 0.01$) than background samples (Fig. 4A). These data likely suggest that hydrocarbon gases were emplaced into the shallow aquifer without significant fractionation of ASW $^{26}$Ne/$^{36}$Ar during transport through the water-saturated crust (green-rimmed circles in Figs. 3A–C and 4C). Consequently, for the anomalous subset of groundwater samples with stripped ASW compositions, five possible mechanisms for gas migration to shallow aquifers remain plausible (scenarios 3–7; Fig. 1), all of which implicate an anthropogenic mechanism related to gas drilling and extraction. Distinguishing among these mechanisms will further clarify the environmental implications of fugitive gas contamination and lead to engineering solutions.

Elevated CH$_4$ levels may result from the exsolution of hydrocarbon gas already present in shallow aquifers during drilling (scenario 3). This mechanism would release hydrocarbon gases that previously migrated into shallow aquifers by scenario 2 that later phase separated from brine-rich groundwater during drilling. However, this process would release hydrocarbon gases from shallow aquifers without altering the CH$_4$/$^4$He or $^4$He/$^{20}$Ne in either the migrated gas or the residual fluid because of the similar partition coefficients between the respective gases (SI Text). Because none of the data (specifically highly elevated CH$_4$/$^{26}$Ne, $^4$He/$^{20}$Ne, and $^{13}$C/CH$_4$) from the anomalous subset of samples are consistent with scenario 2 in the MSA or BSA, we suggest that scenario 3 is unlikely.

Gas-phase leakage through scenarios 4 (well annulus), 5 (faulty casing), and 7 (legacy/abandoned wells) would transmit thermogenic gases from depth to the shallow aquifers with minimal interactions between the deep, pressurized gas-phase and static water present in stratigraphic units in the crust. As a result, the hydrocarbon gas released by these mechanisms would have high ratios of thermogenic to ASW components (i.e., high CH$_4$/$^{26}$Ne and $^4$He/$^{20}$Ne), stripped ASW compositions and would undergo minimal fractionation of hydrocarbon gas during transport from each of the respective production intervals (e.g., Marcellus or UD formations) to shallow aquifers. As a result, the gases released through scenarios 4, 5, or 7 should also retain the composition of the gas-rich reservoir formation (i.e., $^4$He/CH$_4$, $^{20}$Ne/$^{36}$Ar, C$_2$H$_6$/CH$_4$, and $^{13}$C/CH$_4$).

The majority of anomalous subset samples (i.e., green-rimmed samples) in the MSA display minimal fractionation of gas compositions (e.g., low $^{26}$Ne/$^{36}$Ar and $^4$He/CH$_4$). These data are consistent with the anthropogenic release of a fugitive hydrocarbon gas by either scenario 4, 5, or 7 depending on location, although scenario 7 is unlikely based on the lack of legacy wells in the research area (Fig. 82). Importantly, all of these data are inconsistent with scenario 6 (direct migration of gases upward through the overlying strata following horizontal drilling or hydraulic fracturing) because in this scenario, gas/liquid partitioning would significantly fractionate the diagnostic gas isotope ratios during migration through the water-saturated crust.

In the MSA and many other basins, the molecular and isotopic fingerprints of the hydrocarbon gases can distinguish between scenarios 4 (annulus leakage) and 5 (faulty casing leakage) (31, 32). For example, UD-produced gases typically have lower $^{13}$C/CH$_4$ (−38% to −44%), normal $^{13}$C$_{1,2}$ = c0, and low ethane (C$_2$H$_6$/CH$_4$ = <0.01) (6, 7, 9) (pink box in Fig. 4B and SI Text). In contrast, Marcellus-produced gases have heavier $^{13}$C/CH$_4$ values (−29% to −35%), reversed stable isotopic composition (i.e., $^{13}$C$_{1,2}$ > 0), and a higher proportion of aliphatic hydrocarbons (C$_x$H$_{4x}$/CH$_4$ > 0.015; black box in Fig. 4B and SI Text) (7, 9, 13). By comparing $^4$He/CH$_4$, $^3$H$_4$/CH$_4$, and $^3$He/CH$_4$ vs. $^4$He/CH$_4$, the Marcellus-produced gases are consistent with these UD sources, whereas four clusters are consistent with a Marcellus composition (black box in Fig. 4A and B).

Similarly, in the BSA, the compositions of the five anomalous samples and the distance to legacy wells (Fig. S3) also preclude scenarios 1, 2, 3, 6, and 7. However, because the isotopic composition (δ$^{13}$C-CH$_4$) of both the Barnett Fm. and overlying Strawn Fm. are similar, routine analyses of hydrocarbon stable isotopic compositions do not easily distinguish between scenarios 4 and 5 in this setting (8). Here, additional fingerprinting techniques, such as noble gases (19) or the molecular composition of hydrocarbons, provide a complementary approach.

Noble gases are useful tracers because the ASW compositions ($^4$Ar, $^{20}$Ne) are generally consistent globally and the crustal components (e.g., $^4$He and $^{20}$Ar) are resolvable and unaffected by oxidation or microbial activity. The radiogenic gases (i.e., $^4$He and $^{20}$Ar) form by the time-integrated decay of U + Th and K in the crust and are released from different lithologies as a function of temperature (SI Text) (19). As a result, the $^4$He/$^4$Ar$^*$ ratio is a marker for the thermal maturity of thermogenic hydrocarbon gases (19). The similarity between C$_2$H$_6$/CH$_4$ vs. $^3$C/CH$_4$ and $^4$He/$^{40}$Ar$^*$ vs. $^4$He/$^{20}$Ne in the Strawn-produced gases and the anomalous subset of five groundwater samples in the BSA suggests that contamination likely results from the release of annulus-conducted gas sourced from the Strawn Fm. (scenario 4) rather than from the Barnett Shale (scenarios 5 or 6; Fig. 4C and D).

Unlike the seven discrete clusters of groundwater contamination discussed thus far, an eighth cluster of four groundwater samples (three water wells and one ephemeral spring) in the MSA displayed evidence of stripping and significantly elevated $^4$He/CH$_4$ and $^{20}$Ne/$^{36}$Ar (green-rimmed circles in the oval in Fig. 4I). This cluster includes the only samples consistent with significant fractionation during the migration of hydrocarbon gas from depth, through water-saturated strata in the crust, and finally into the shallow aquifers. We propose that the composition of these samples reflects a mixture between (i) residual water previously depleted in ASW components by a large flux of migrating gas similar to the mechanism observed for other stripped samples (green-filled circles) and (ii) a hydrocarbon gas that redissolved into groundwater within shallow aquifers following extensive fractionation during transport through water-saturated strata in the crust. A natural-gas production well near this sampling location experienced an “underground mechanical well failure” before our sampling (12, 33). Although our noble gas and hydrocarbon data cannot eliminate scenario 6 alone, the PA Department of Environmental Protection reports suggest that our data likely record a casing wall packer failure at depth (33), consistent with scenario 5, which permitted extensive fractionation of gas components during transport through the water-saturated crust. Thus, we find no unequivocal evidence for large-scale vertical migration of hydrocarbon gas from depth attributable to horizontal drilling or hydraulic fracturing (scenario 6).

In summary, our data demonstrate eight discrete clusters of groundwater wells (seven overlying the Marcellus and one overlying the Barnett) near shale-gas drill sites that exhibit evidence for fugitive gas contamination. Three clusters of groundwater wells in the MSA are consistent with hydrocarbon gas contamination from intermediate-depth UD sources and one cluster in the BSA is likely derived from an intermediate-depth Strawn source. The most likely cause for these four cases of fugitive gas contamination is the release of intermediate-depth hydrocarbon
gas along the well annulus, probably as a result of poor cem-
tation (i.e., scenario 4). Three of the remaining four groundwater
well clusters in the MSA are consistent with the release of Mar-
cellus-like hydrocarbon gas, presumably through poorly con-
structed wells (e.g., improper, faulty, or failing production casings),
whereas the fourth cluster, with modified Marcellus-like production
gases, surrounds the natural-gas well that experienced a docu-
tmented underground well failure.

In general, our data suggest that where fugitive gas contami-
nation occurs, well integrity problems are most likely associated
with casing or cementing issues. In contrast, our data do not sug-
uggest that horizontal drilling or hydraulic fracturing has provided
a conduit to connect deep Marcellus or Barnett Formations di-
rectly to surface aquifers. Well integrity has been recognized for
decades as an important factor in environmental stewardship
for conventional oil and gas production (34, 35). Future work
should evaluate whether the large volumes of water and high pressures
required for horizontal drilling and hydraulic fracturing influence
well integrity. In our opinion, optimizing well integrity is a critical,
feasible, and cost-effective way to reduce problems with drinking-
water contamination and to alleviate public concerns accompa-
nying shale-gas extraction.

Methods

All water samples in the MSA (n = 114) and the BSA (n = 20) were analyzed
for their major gas abundance (e.g., CH₄, C₂H₆, C₃H₈, N₂), stable isotopic
composition (e.g., δ¹³C-CH₄, δ¹⁸O-C₂H₆), chloride content, and noble gas ele-
mental and isotopic compositions of He, Ne, and Ar, following standard
methods reported previously (7, 19–21) (SI Text). The analytical errors in all data
plots reported here are smaller than the symbols.

Before sampling, water wells were pumped to remove stagnant water
until stable values for pH, electrical conductance, and temperature were
obtained. Water samples were collected before any treatment systems fol-
lowing standard methods (20).

A more complete review of noble gas background material and numerical
modeling is included in SI Text. Briefly, the anticipated fractionation-driven
changes in gas composition are calculated by modifying previously developed
GGS-R fractionation models (16). All Bunsen solubility constants (γ) are
calculated as a function of salinity and temperatures ranging between 15 °C
and 200 °C to represent present ambient groundwater temperatures and
hypothetical temperatures for the migration of a geological brine. Partition
coefficients (α = [g/μ]/[g]) were calculated as a function of temperature and sa-
linity according to refs. 26, 27, and 36.

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