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Leakage Detection of Marcellus Shale Natural Gas at an Upper Devonian Gas Monitoring Well: A 3-D Numerical Modeling Approach

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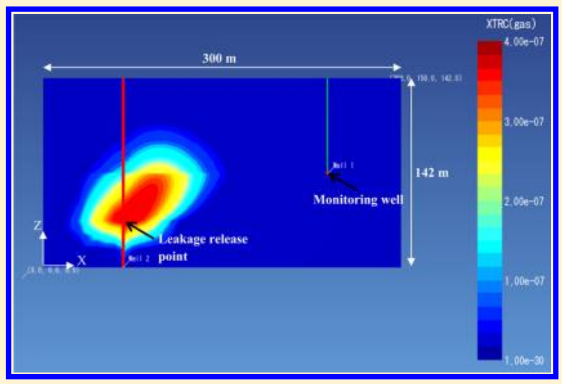
Supporting Information

ABSTRACT: Potential natural gas leakage into shallow, overlying formations and aquifers from Marcellus Shale gas drilling operations is a public concern. However, before natural gas could reach underground sources of drinking water (USDW), it must pass through several geologic formations. Tracer and pressure monitoring in formations overlying the Marcellus could help detect natural gas leakage at hydraulic fracturing sites before it reaches USDW. In this study, a numerical simulation code (TOUGH 2) was used to investigate the potential for detecting leaking natural gas in such an overlying geologic formation. The modeled zone was based on a gas field in Greene County, Pennsylvania, undergoing production activities. The model assumed, hypothetically, that methane (CH_4), the primary component of natural gas, with some tracer, was leaking around an existing well between the Marcellus Shale and the shallower and lower-pressure Bradford Formation. The leaky well was located 170 m away from a monitoring well, in the Bradford Formation. A simulation study was performed to determine how quickly the tracer monitoring could detect a leak of a known size. Using some typical parameters for the Bradford Formation, model results showed that a detectable tracer volume fraction of 2.0×10^{-15} would be noted at the monitoring well in 9.8 years. The most rapid detection of tracer for the leak rates simulated was 81 days, but this scenario required that the leakage release point was at the same depth as the perforation zone of the monitoring well and the zones above and below the perforation zone had low permeability, which created a preferred tracer migration pathway along the perforation zone. Sensitivity analysis indicated that the time needed to detect CH_4 leakage at the monitoring well was very sensitive to changes in the thickness of the high-permeability zone, CH_4 leaking rate, and production rate of the monitoring well.



■ INTRODUCTION

The development of unconventional natural gas resources has become economically viable in the 21st century because of advances in both directional drilling and reservoir simulation.[1,2] The Marcellus Shale, a sedimentary rock formation in the eastern United States, contains an estimated natural gas resource that may be as high as 4 trillion cubic meters (144 trillion cubic feet or TCF)[3] and is only one gas shale of several in the Appalachian Basin. Most of the natural gas production from Appalachian shales has been in Ohio, Pennsylvania, and West Virginia.[4]

The rapid expansion of unconventional natural gas production has raised public concerns regarding impacts to water resources[2,5] and possible risk of contaminating fresh groundwater as a result of upward migration of natural gas, hydraulic fracturing fluid, and/or brine from deep formations.[1] Recent publications have attempted to make a case that an increase in methane concentration in some NE Pennsylvania drinking water wells may be linked to drilling and hydraulic fracturing in active shale gas-extraction areas,[6] and modeling results suggest that brine from the Marcellus Shale may be able to migrate upward into shallow aquifers along fractures or other flow paths.[7]

In contrast, other researchers have found evidence of high concentrations of predrilling background levels of methane in NE Pennsylvania groundwater,[8,9] and some possible data interpretation errors in ref 6. More details about possible data interpretation errors can be found in ref 10. Thus, a definitive link between multistage hydraulic fracturing of the Marcellus Shale and the significant upward leakage of methane and liquids has not been unequivocally established.

To explore this issue further, the DOE National Energy Technology Laboratory (NETL) undertook a study in cooperation with an industrial partner at a Marcellus Shale production site in southwestern Pennsylvania to evaluate the performance of tracer monitoring for leakage associated with a

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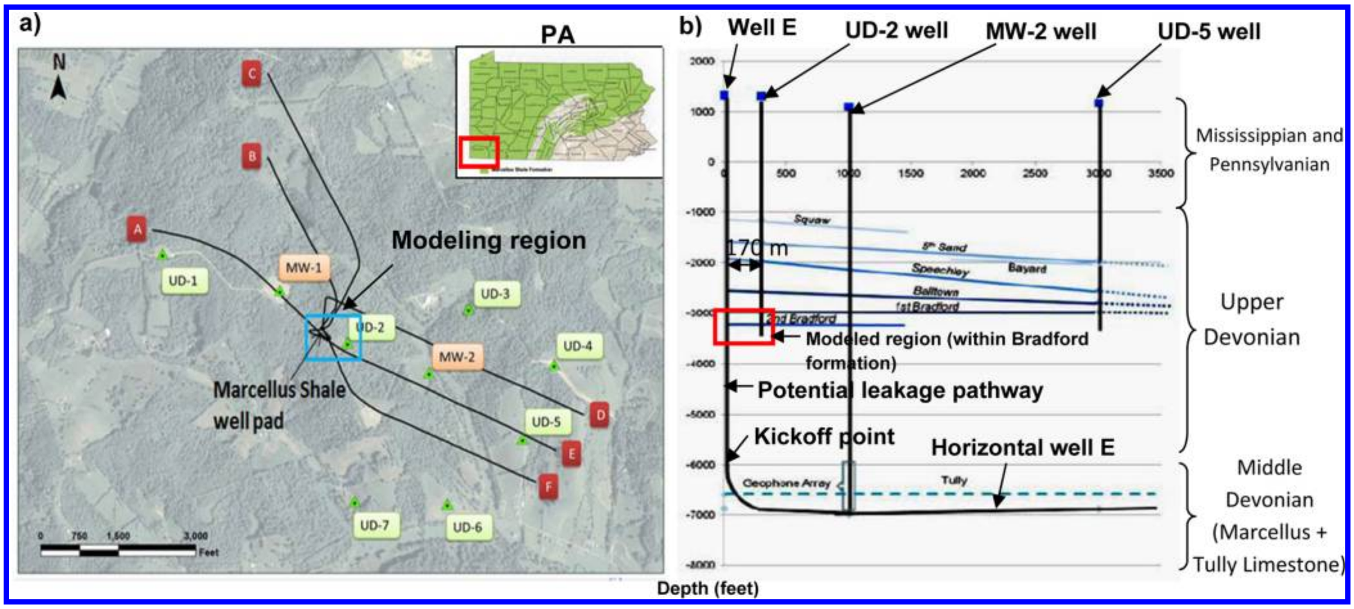

Figure 1. a) Locations of the Marcellus Shale well pad and seven Upper Devonian (UD) wells in the research site. A to F are six horizontal Marcellus Shale wells, and MW-1 and MW-2 are two vertical Marcellus Shale wells. b) Cross-section view at the horizontal well E. Both images are modified from Hammack et al. (2013).

hydraulic fracture. Tracers were added to the fracturing fluid that would partition into the natural gas in the Marcellus and could be transported with the gas, should it migrate in the subsurface. Pressure and gas chemistry were monitored periodically in a shallower gas sand above the shale to determine if any leakage occurred. A numerical transport model was developed to evaluate the performance of tracer monitoring and assess the length of time necessary for periodic sampling of the monitoring well to be certain of detecting the tracer.

Description of the Research Site and Tracer Field Monitoring Procedures. The region modeled is a shale gas well drilling site in Greene County, located within an area of intense drilling and production activity in the heart of the dry gas play area of the Marcellus Shale in southwestern Pennsylvania. The site includes seven vertical wells into the Upper Devonian Bradford gas sand, two vertical wells into the Middle Devonian Marcellus Shale, and six horizontal wells drilled from a single pad into the Marcellus Shale. All of these wells were in place before the NETL study began.[11]

The Upper Devonian Bradford Sandstone at the Greene County site occurs at depths ranging from 915 to 1220 m (3,000–4,000 ft) below the surface and at least 900 m (about 3,000 ft) below underground sources of drinking water.[11] The Bradford formation is a sandstone formation composed of fine sand particles. The Marcellus Shale is present at a depth of approximately 2438 m (8,000 ft) below the surface, significantly deeper than the Bradford Sandstone. Seven vertical wells were actively producing gas from the Upper Devonian interval at the site; these wells were completed at multiple depths between 730 and 1460 m (approximately 2400 to 4800 ft). The site has six horizontal Marcellus wells drilled from a single well pad and two vertical wells that extend down to the Marcellus. The closest Upper Devonian well to the Marcellus horizontal wells is designated UD 2 and located about 170 m (560 ft) from the well pad (Figure 1).

NETL was given access to the Upper Devonian wells to monitor pressure and tracer concentration in the produced gas. A chemical tracer consisting of a volatile perfluorocarbon (PFC) compound was added to the hydraulic fracturing fluid to tag the Marcellus Shale gas so that it could be detected if it migrated upward into the overlying Bradford Sandstone.[11] Data from this field experiment have been used to constrain the boundaries and cell parameters of the transport model used in this study.

Four different PFC tracers were injected with hydraulic fracturing fluid at different stages during a 14-stage hydraulic fracturing operation on one of the six horizontal Marcellus Shale gas wells:[11]

- perfluoromethylcyclohexane (PMCH) was injected for stages 5, 6, and 7;
- perfluorotrimethylcyclohexane (PTMCH) was injected for stages 8–10;
- perfluorodimethylcyclobutane (PDCB) was injected for stages 11–13;
- perfluoro-i-propylcyclohexane (P-i-PCH) was injected for stage 14.

In an idealized scenario, tracers are able to thoroughly mix with the natural gas in the Marcellus Shale after the hydraulic fracturing fluid is injected. Tracers then migrate with the Marcellus Shale natural gas and can be detected in overlying formations to which the Marcellus Shale natural gas may migrate. Figure S-1 in the Supporting Information provides a simplified schematic of the tracer monitoring configuration used for the detection of potential natural gas migration into an overlying, producing conventional natural gas formation from a hydraulically fractured, unconventional natural gas formation. For this particular study, the positive detection of a tracer in the production stream from the Upper Devonian natural gas wells would be a strong indicator of natural gas migration from the Marcellus Shale to the overlying Upper Devonian natural gas production interval.

Samples of produced gas were collected each month from the Upper Devonian and Marcellus wells and subsequently analyzed for gas composition using a gas chromatograph with mass spectrometry (GC/MS). The periodic samples were collected for six months. A concentration limit of 1.0×10^{-15} (volume fraction) was used as the practical cutoff for GC/MS detection of the PFC tracer.[11] During the six-month monitoring period, none of the PFC tracers that were injected with the fracturing fluids into horizontal Marcellus Shale well E have been detected in natural gas produced from the UD-2 well.[11] However, the site operators are not sure if they have monitored long enough to say in confidence that there is no leakage after 6 months of monitoring without detection of PFC tracer at the UD-2 well. The goal of this paper is to give operators of the research site an estimation of how long they need to monitor tracer concentration at the UD-2 well to determine if there is a leakage along the borehole of the Marcellus Shale well to the Bradford formation, and that is the connection between the field test and the numerical study. The field test provided the impetus for the numerical study, which is an attempt to develop estimates of the tracer appearance at the monitoring well under different conditions and involving some worst-case scenarios.

The Numerical Model. TOUGH2 (Transport of Unsaturated Groundwater and Heat, Version 2) coupled with the graphical user interface (GUI) code PetraSim was used as the modeling tool to develop the numerical transport model.[12] The reliability of TOUGH 2 has been established through comparison of realizations with many different analytical and numerical solutions, supported by results from laboratory experiments and field observations (e.g., refs 13−18). The code has been widely used in projects investigating the hydraulic fracturing process (coupled with FLAC3D geomechanical simulator), oil and gas production operations, geological CO_2 storage, and environmental remediation. To specify the components to be incorporated into the model, TOUGH 2 utilizes multiple equation-of-state (EOS) modules, which define phases and related thermophysical properties (such as density, viscosity, and enthalpy) of the fluid or mixture being considered. In this study, the module EOS7C was used to establish model parameters for the flow and transport of methane at a given temperature and pressure.[19]

■ METHODOLOGY

Design of the Model: General Description. A 3-D gas migration model was developed for the Greene County research site to help estimate the length of time it might take to detect a leak of a given size in a production well in the Upper Devonian unit. It is important to note that the leak we modeled is a hypothetical leak at the Upper Devonian formation and that hypothetical leak does not imply a high leakage potential from the Marcellus Shale to the Upper Devonian formation. This was done for the purpose of helping us improve our interpretation of monitoring data from the Upper Devonian wells and to plan future monitoring activities.

For simplicity, the model only simulated the migration of leaking gas from the vicinity of the six-well Marcellus pad to the closest Upper Devonian monitoring well (UD 2 - refer to Figure 1 for the modeling region within the blue rectangle). Again for simplicity, only the perfluoromethylcyclohexane (PMCH) tracer was modeled. The model yielded the tracer concentration change and pressure changes at the UD-2 well caused by a constant rate influx of leaking gas. A concentration of PMCH tracer higher than the detection limit indicates the presence of natural gas from the Marcellus Shale.

The model was constructed with five vertically stacked horizontal layers (Figure 2). Layer 1 at the base and Layer 5 at the top were boundary layers with relatively low permeability, and Layers 2, 3, and 4 were production layers within the formation having relatively high permeability. Layer 3 in the center of the model represented the location of the perforation zone of the UD-2 monitoring well. Based on field data, the production rate of the well was set in the model at 0.014 kg/s. The model had a total of 72,996 ($79 \times 22 \times 42$) active grid blocks, with 42,900 ($65 \times 22 \times 30$) of active grids in the producing zone between the leakage release point and the bottom of the monitoring well. The configuration of the grid blocks can be found in the Supporting Information. For each simulation, the model was run for 5×10^7 s before the application of the leakage, so as to allow enough time for the model to reach steady state before the occurrence of leakage.

There are three important leakage pathways (the annuli of imperfectly cemented gas wells, natural faults, and abandoned wells) that allow leaky natural gas to migrate from the deep shale to the shallower overlying formations.[1] For the Greene County research site, the Marcellus Shale (approximately 2438 m below the surface) is vertically intercepted by natural faults that extend upward through the Tully Limestone but do not intercept the shallower Bradford formation, which is the formation modeled in this study.[11] Moreover, there are no abandoned wells that intercept the Bradford formation at the Greene County research site.[11] Therefore, there are no natural faults or abandoned wells that can serve as the leakage pathways for leaky natural gas to migrate from the Marcellus Shale to the Bradford formation. As a result, only the leakage through the annuli of imperfectly cemented gas wells is modeled in this study. Specifically, the leakage release point is at the void between the face of the subsurface formation and the cement of the Marcellus Shale well E and is 35 m below the perforation zone of the UD-2 well (see Figure 2).

Important Assumptions of the Model. The following key modeling assumptions should be noted:

1) The model is a single-phase gas flow model with no liquid-phase leakage considered. Residual water saturation in the Bradford formation is assumed to be immobile and no water transport is modeled. This assumption is made because both methane and the PMCH tracer have very low solubility in water. In fact, the low solubility in water makes PMCH tracer well suited to trace the vapor/steam phase in two-phase geothermal systems.[20,21] Therefore, it is sufficient to assume that the PMCH tracer transport in aqueous phase can be ignored, and movement/production of aqueous phase may not have an impact on PMCH tracer transport in gaseous phase.

2) The model assumes uniform distribution of porosity, permeability, and mineral composition within each layer.

3) There is continuous imperfection (incomplete coverage) in the cement from one of the hydraulic fractures along the horizontal well all the way to the release point, which results in a leakage release point 35 m below the perforation zone of the UD-2 well. 35 m is an arbitrary chosen value, and a sensitivity analysis was conducted to study the impact of leakage point location change on the detection time. This assumption represents a worst-case leakage scenario that would result in the shortest tracer detection time. In a more realistic scenario, it is unlikely that the entire leakage rate could be applied at the leakage release point, and the tracer detection time at the monitoring well would be longer than that of the worst-case scenario.

4) Methane (CH_4) is considered sufficiently representative of natural gas in the model, and the leaking gas contains only methane and the PMCH tracer. This assumption is reasonable because other possible impurities in natural gas (e.g., CO_2 and H_2S) are not expected to affect PMCH tracer transport.

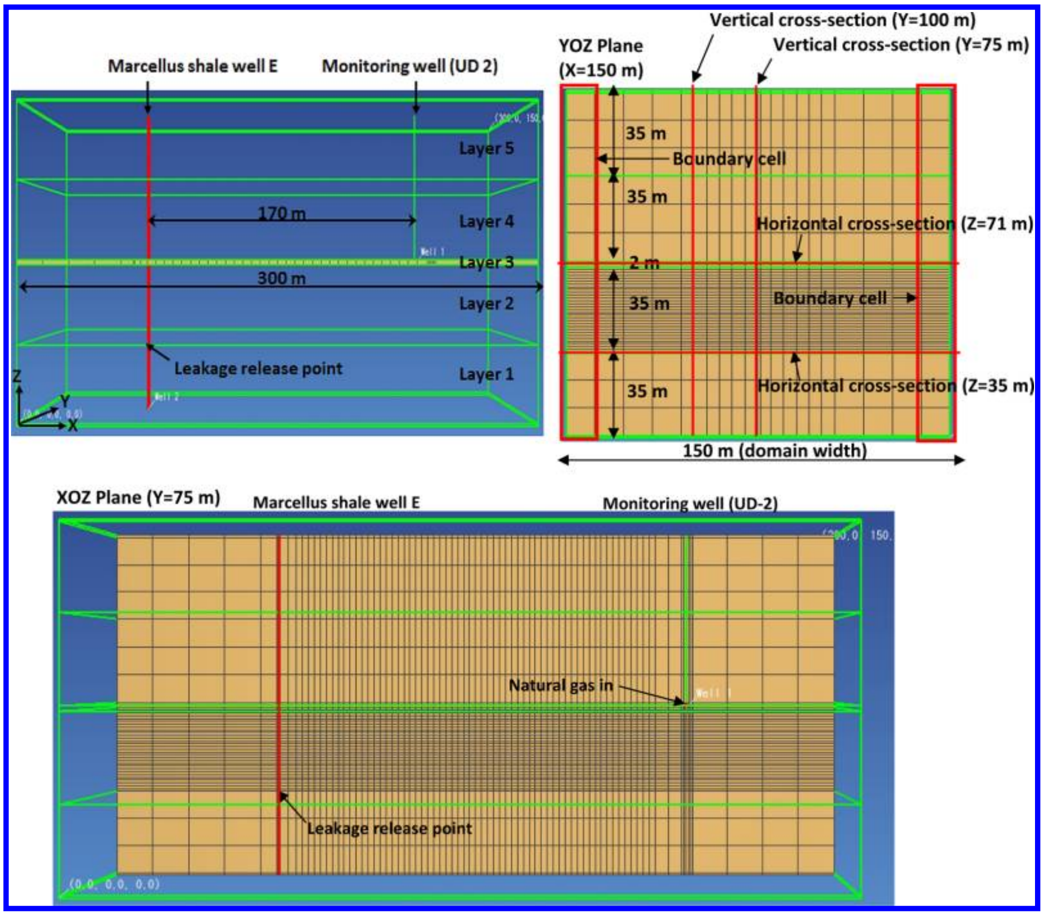

Figure 2. Set up of the model. Layers 1, 2, 4, and 5 have the same thickness of 35 m, and Layer 3 has a thickness of 2 m. The bottom of the monitoring well intersects with Layer 3. The depth at the middle of Layer 3 is 1380 m (Hammack et al., 2013). Boundary cells (in red rectangles) were assigned with 100 times larger volume than that of normal cells, so as to ensure 1) free passage of leaking gas and tracer out of the model domain; 2) minimization of size discrepancy between the model domain and the real Bradford formation. Very fine grid cells were applied in the region between the leakage release point and the bottom of the monitoring well, so as to ensure accuracy of simulation.

Table 1. Modeling Parameters Used for the Base Scenario

parameter	value	parameter	value
density of rock in Layers 1−5	2600 kg/m^3	production rate	0.014 kg/s
initial pressure in Layer 1	6.895 MPa	leaking rate	0.001 kg/s
temperature in Layer 3	29.4 °C	tracer mass fraction in leaking gas	4.0×10^{-7}
horizontal permeability (Layers 1 and 5)	10^{-16} m^2	layer thickness (1, 2, 4 and 5, each layer)	35 m
vertical permeability (Layers 1 and 5)	1×10^{-17} m^2	Layer 3 thickness	2 m
horizontal permeability (Layers 2−4)	3.6 × 10−15 m^2	depth at bottom of Layer 3	1380 m
vertical permeability (Layers 2−4)	3.6×10^{-16} m^2	porosity (Layers 1−5)	0.15
simulation time step	automatic adjustment (initial step =1000 s)	maximum simulation time	32 years
domain width (*Y* coordinate)	150 m		
detection limit (mass fraction)	4.38×10^{-14}		

5) Gas is assumed to leak at a constant rate. This assumption represents a worst-case leakage scenario that would result in the shortest tracer detection time. In a more realistic scenario, due to the exponential decline of natural gas production from shales (shales can lose over 50% of the production rate within 6 months from the inception of production), the leaking rate is expected to decrease with the increase of time.

6) Leakage is assumed to only occur along one Marcellus Shale well (Well E).

7) Production of the other Upper Devonian wells in this field (not included in the model) does not affect pressure and tracer monitoring at the target UD-2 Upper Devonian well. This assumption needs to be validated by a future investigation with all surrounding UD wells included in the model.

8) Heat transport is ignored in the model, and the simulation has been run isothermally (a vertical temperature gradient of 0.03 °C/m is applied in the model and the temperature does not change over time). Heat transport is ignored because the small leaking rate of natural gas from higher-temperature Marcellus Shale is not expected to have a significant impact on existing temperature gradient or tracer transport in the shallower Upper Devonian formation.

Important Modeling Parameters. Table 1shows important modeling parameters used in the base scenario. For the horizontal permeability of Layers 1 to 5, it is difficult to find site-specific permeability data. A literature survey suggests a permeability of less than 200 mD for Upper Devonian sand at Jacksonburg-Stringtown Oil Field, West Virginia.[22] The permeability of Upper Devonian sand is expected to be higher than that of Devonian shale, which has a permeability range of 0.2 to 19×10^{-8} mD but usually below 10^{-4} mD.[23,24] Nelson[25] suggests a permeability range of 3.6 mD to 10.1 mD for formations composed of very fine sand, which can be used to describe the permeability of Upper Devonian sand. In this work, we assume 0.1 mD permeability for sandstone in the low-production zone (e.g., sandstone with low permeability, Layers 1 and 5) and 3.6 mD permeability for sandstone in the high-production zone (e.g., sandstone with high permeability, Layers 2 to 4). Vertical permeability is assumed to be one-tenth of the horizontal permeability ($k_v/k_h = 0.1$). The theoretical detection limit for PMCH is around 1×10^{-15} (volume fraction, 11). However, due to the possible measurement error, background PMCH accumulation, and contamination, a safe detection limit that is higher than the theoretical limit is chosen for the model. Here we use a volume fraction of 2×10^{-15} (corresponding to 4.38×10^{-14} in mass fraction) as the safe detection limit. As to temperature, the temperature at Layer 3 is assumed to be 29.4 °C, and a temperature gradient of 0.03 °C/m[26] is applied in the model.

Based on the well production data, the average total production rate of the monitoring well from four and a half years of measurement is 0.028 kg/s. Here we assume that the production rate at the most bottom production zone (Layer 3) is 50% of the total production rate, and the value is 0.5×0.028 kg/s = 0.014 kg/s. The calculation is based on the average MCF per day and tubing ground pressure data for the monitoring well. The concentration of the PMCH tracer in the producing Marcellus wells was used as our base case value for tracer concentration in the leaking gas. The PMCH concentration in the leaking gas is 18.3 ppb (the average of 26 measurements of PMCH concentration in producing gas after PMCH injection into the Marcellus Shale formation, see Table S-1 in the Supporting Information for details), which corresponds to a mass fraction of 4.0×10^{-7}. As to porosity, the literature suggests a porosity range of 0.06 to 0.16 for Upper Devonian sandstone.[27] A value of 0.15 is chosen for this study.

Sensitivity Analysis. A sensitivity analysis was conducted to assess how the uncertainties associated with the modeling parameters may have affected the simulation results. Table 2 shows a summary of parameters tested for sensitivity analysis. A total of 19 scenarios were tested (including the base case). A model with slightly larger grid blocks (the grid block size in x direction was 5 m in the producing zone between the leakage release point and the bottom of the monitoring well, while the base case model had a grid block size of 2.5 m in x direction) was used to do sensitivity analysis, so as to avoid extremely long computation time.

Table 2. Parameters Used in a Total of 19 Scenarios (Including the Base Case) for Sensitivity Analysis[c]

parameter	low	base	high
production rate (kg/s)	0.0055	0.014	0.1
leaking rate (kg/s)	0.0001	0.001	0.01
horizontal perm (mD)	0.36	3.6	36
k_v/k_h	0.05	0.1	0.2
porosity	0.1	0.15	0.2
detection limit (mass fraction)	4.38×10^{-16}	4.38×10^{-14}	4.38×10^{-12}
tracer concentration in leaking gas (mass fraction)	4.0×10^{-9}	4.0×10^{-7}	4.0×10^{-5}
high-permeability zone thickness[a] (Layers 2–4, m)	2	72	119
location of the leaking point[b] (distance to the bottom of Layer 3, m)	0	35	58

[a]The leaking point is assumed to be at the bottom of the high-permeability zone. Therefore, the thinner the unit, the shorter the distance the tracer must travel to reach the monitoring well. [b]The thickness of the high-permeability zone is held constant. [c]Only one parameter is changed from the base case in one scenario, and all the other parameters remain the same as those in the base case.

RESULTS

Base Scenario Simulation Results. Figures 3a–3d show the migration of tracer with the increase of elapsed time. Because the horizontal permeability of the formation was set higher than the vertical permeability in the base case, the tracer migrated faster in the horizontal direction than in the vertical direction. When the elapsed time was relatively short (i.e., 0.8 years; Figures 3a and 3c), the preferential migration of the tracer toward the monitoring well was not obvious. When the elapsed time was long (i.e., 17.4 years; Figures 3b and 3d), the preferential migration of the tracer toward the monitoring well became apparent. There was a preferential migration toward the monitoring well because the monitoring well was producing natural gas, which created a low pressure at the bottom of the monitoring well. The pressure difference between the leaking point and the monitoring well was higher than the pressure difference in other directions, and that resulted in a preferential leakage flow toward the monitoring well.

Figure 4 shows the change in tracer concentration for a hypothetical sampling port at the bottom of the monitoring well as a function of elapsed time. The model realization shows that the tracer required 9.8 years to reach the detection limit of 2.0×10^{-15} (volume fraction) at the monitoring well.

Summary of Simulation ReSults for Sensitivity Analysis. Figure 5 shows the tracer detection times for all scenarios tested for sensitivity analysis. The vertical line down the center of this figure represents the base case detection time of 9.8 years, as described above. The horizontal bars represent how variations in the values of each parameter affect the detection time of the tracer. For example, changing the production rate of the monitoring well, the thickness of the high-permeability zone, and the leakage rate of the migrating natural gas resulted in the greatest variation in detection times. The simulation is most sensitive to these parameters. Another sensitive parameter is horizontal permeability; a moderate decrease caused detection time to increase from 9.8 years to 13.7 years. In contrast, the detection time was much less sensitive to vertical permeability change (represented by k_v/k_h). Detection time was moderately sensitive to the nominal detection limit of the tracer material, the tracer concentration in the leaking gas, and the porosity of the formation.

DISCUSSION

Based on sensitivity analysis results, the time needed to detect the tracer at the monitoring well was dependent on four main factors:

1. The thickness of the production zone and the vertical travel distance of the tracer from the leak point to the monitoring well (related to the location of the leak point);
2. Production rate of the monitoring well;

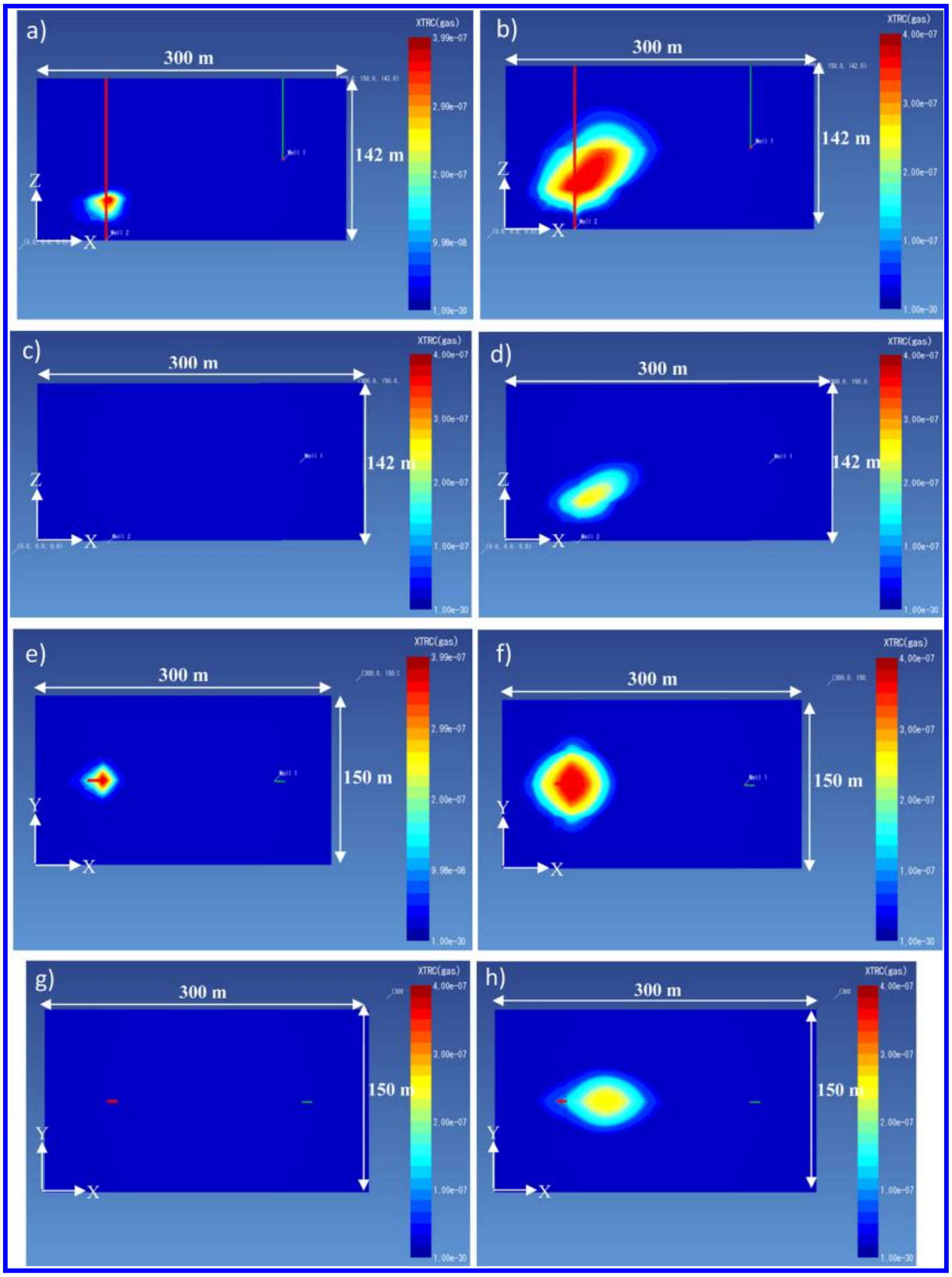

Figure 3. Tracer migration as a function of the elapsed time. "XTRC (gas)" in parts 3a−3h refers to mass fraction of the PMCH tracer in the gas phase. Different colors represent different mass fractions of the tracer in the gas flow. A red color represents the highest mass fraction of the tracer, and a dark blue color represents the background mass fraction of the tracer. a) Vertical cross-section view (plane location: Y = 75 m, see Figure 2) of tracer concentration distribution after 0.8 years of leakage; b) Vertical cross-section view (plane location: Y = 75 m, see Figure 2) of tracer concentration distribution after 17.4 years of leakage; c) Vertical cross-section view (plane location: Y = 100 m, see Figure 2) of tracer concentration distribution after 0.8 years of leakage; d) Vertical cross-section view (plane location: Y = 100 m, see Figure 2) of tracer concentration distribution after 17.4 years of leakage; e) Horizontal cross-section view (plane location: Z = 35 m, see Figure 2) of tracer concentration distribution after 0.8 years of leakage; f) Horizontal cross-section view (plane location: Z = 35 m, see Figure 2) of tracer concentration distribution after 17.4 years of leakage; g) Horizontal cross-section view (plane location: Z = 71 m, see Figure 2) of tracer concentration distribution after 0.8 years of leakage; h) Horizontal cross-section view (plane location: Z = 71 m, see Figure 2) of tracer concentration distribution after 17.4 years of leakage.

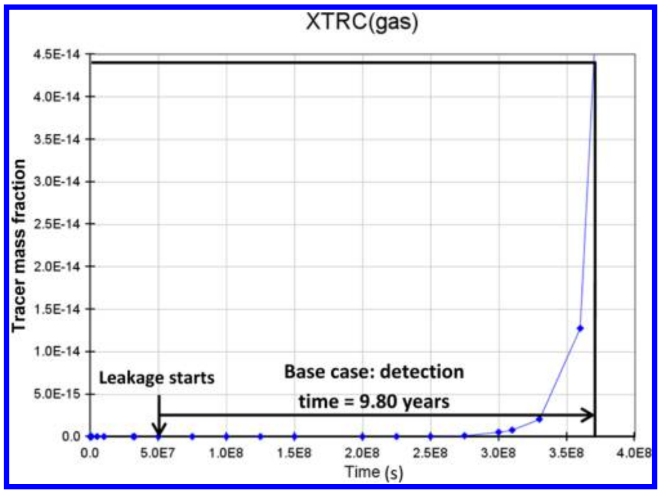

Figure 4. PMCH tracer concentration at the monitoring well (base case). Given a detection limit of 2×10^{-15} (corresponding to 4.38×10^{-14} in mass fraction), it would take 9.8 years to detect the leakage.

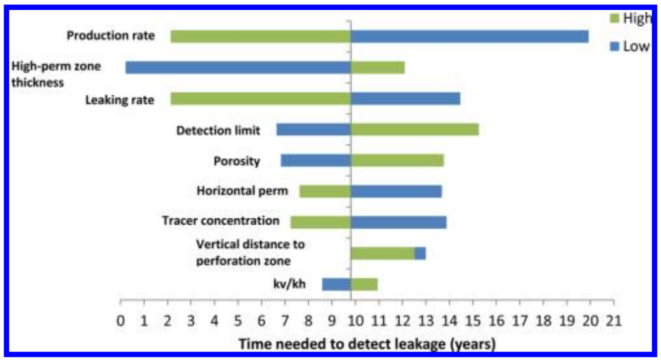

Figure 5. Tracer detection times for all scenarios tested for sensitivity analysis.

3. The amount of tracer entering the Upper Devonian gas reservoir (related to the volume of tracer injected and rate of the leak);

4. Permeability of the formation (primarily in the horizontal direction).

The well production rate can be measured and thus does not contribute significantly to the uncertainty of the detection time. However, estimating the spatial heterogeneous permeability and predicting the location of the leak point are far more uncertain. Using unconstrained estimates for these factors in the model leads to results with a wide range of possible detection times. The sensitivity analysis of the model provided an assessment of where uncertainty needed to be reduced on the input parameters.

An important observation shown in Figure 5 is that changing the vertical permeability of the high-permeability zone has little effect on the tracer detection time at the monitoring well. A possible explanation is that for the situation we studied, the gas and tracer migrate a much farther distance in horizontal direction than they do vertically (170 m vs 35−58 m); so, by the time the gas has migrated horizontally to the UD-2 well, it has had plenty of time to migrate vertically to the perforated zone. Therefore, lower vertical permeability does not necessarily result in longer tracer detection time at the monitoring well as the vertical traveling time is not a limiting factor for the total travel time.

Another important observation is that a thick production zone results in significant delay of tracer detection if a hypothetical leakage is located within the production zone. For example, given a leakage release point at the perforation zone of the monitoring well (Layer 3), if the thickness of the production zone is high, the tracer detection time would be much longer than the detection time of the scenario with a very thin production zone (13 years vs 81 days, corresponding to scenarios of low vertical distance to perforation zone and low high-perm zone thickness in Figure 5). The reason is that, for the scenario with low high-perm zone thickness, the zones above and below the perforation zone have low permeability, which creates a preferred tracer migration pathway along the perforation zone and results in very fast tracer detection at the monitoring well. However, for the scenario with high high-perm zone thickness, tracer would migrate upward with methane due to buoyancy effect, not toward the monitoring well. As a result, the leakage could only be detected at the monitoring well after very long time (see Figure S-2 in the Supporting Information).

Production rate of the monitoring well, tracer concentration in leaking natural gas (related to the amount of tracer injected during hydraulic fracturing), and the detection limit are the three parameters that the site operator can adjust to reduce the tracer detection time. The most effective way to reduce the tracer detection time is to simply increase the production rate of the monitoring well. Increasing the amount of tracer injected or replacing the current tracer with another material that has a lower detection limit is also possible, but these have to work their way through the "plumbing" and enter the Upper Devonian gas reservoir by way of the leak. Increasing the production rate of the monitoring well works on tracer that is already in the sandstone gas reservoir, moving it along more quickly to the monitoring point.

It should be noted that the model still has some limitations to be addressed in the future work. One problem with this model is that it does not take into account the production of other Upper Devonian wells in the vicinity of the well pad, even though the production of those wells may have an impact on tracer migration. It also does not consider leakage at places other than along the single set of wells in the well pad. A 3-D model incorporating a larger zone and including all of the producing Upper Devonian wells and more leakage sources would provide a more complete simulation of tracer movement through the shallower gas sand.

Another limitation of the simulation is that it used a single-phase CH_4 flow model that assumed no methane consumption reactions occurred during the transport process. As such, the model may not be appropriate for methane migration in formations where water flow may be involved or formations that contain abundant methanotrophic (methane-consuming) bacteria.

The model assumes that the formation is homogeneous and no transmissive natural fractures are present. This is probably reasonable for uniform, shallow sandstones, but the model should not be applied to describe CH_4 migration in heavily fractured formations or ones with significant permeability heterogeneity.

The model assumes that the PMCH tracer travels at the same rate as that of CH_4. However, the rate of gas transport (e.g., CO_2 and CH_4) in geologic formations is usually faster than the rate of PFC tracer transport due to the retention of PFC tracer.[28−30] For example, Zhong et al.[30] conducted a column test to study the transport of CO_2 and PMCH tracer in different sediments, and they found that CO_2 travels up to 2.7 times faster than PMCH tracer in a dry sand column, which is similar to the properties of the Upper Devonian sand formation. The slow transport of PMCH tracer is primarily due to the adsorption of PMCH tracer on the surface of sand particles in the column.[30] For our model, due to the retention of PMCH tracer in the formation, the time needed to detect the PMCH tracer at the monitoring well is actually longer than the time needed for leaky CH_4 to reach the monitoring well. As a result, a comprehensive model needs to be developed in the future to take account of tracer retention.

Implications. The findings of this study have important implications for future research related to risk assessment of natural gas leakage and monitoring at natural gas production sites. This model results demonstrate that a moderate subsurface leakage rate from a shale gas production well (i.e., 0.001 kg/s, or about 7% of the production rate of the monitoring well) will not be detected very quickly by monitoring for the tracer even at a relatively nearby well. In scenarios with the monitoring well located 170 m away, the detection occurred in less than 1 year only if the leakage point was at the same depth as the perforation zone of the monitoring well and the production zone of the monitoring well was very thin, which was a very extreme scenario. If the leakage rate is reduced to 10^{-4} kg/s or less, it will take longer than 10 years to detect the tracer at the monitoring well.

The model results suggest that monitoring tracer concentration from a monitoring well is only useful in a short time frame (<1 year) if the leaky location is very close to the monitoring well (well within 170 m) or if there is a fast path (such as an open fracture) between the leaky well and the monitoring well. Because it may take more than ten years to detect leakage in many of the scenarios tested in this study, the use of a tracer monitoring approach may not be appropriate to meet the requirements of industry to detect natural gas leakage from shales in a time-efficient manner. The time needed to detect leakage can be reduced by either increasing the amount of tracer injected with the hydraulic fracturing, replacing the current tracer with another having a much lower detection limit, or by locating the monitor much closer to the leak point.

■ ASSOCIATED CONTENT

Supporting Information

Figures S-1 and S-2 and Table S-1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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