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Research Article

Pathways and Environmental Impacts of Methane Migration: Case Studies in the Marcellus Shale, USA

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Gas migration incidents, particularly stream contamination cases, have been rarely investigated and gone through the peer review process, with the exception of three sites in northeast Pennsylvania (Dimock and two Sugar Runs in Lycoming and Bradford counties, respectively) where air emission surveys, dissolved methane measurements, and structural (hydro)geologic interpretations have been used to demonstrate potential environmental impacts due to shale gas operations. In addition to reviewing previously published work from these three sites, we report and analyze unpublished new data trying to determine if a direct relationship between methane migration, stream contamination, and air emissions exists at those sites. Our analysis indicates that subsurface methane migration, stream methane contamination, and air emissions might not be all present or detectable at a faulty/leaky shale gas well. Which of these signs of contamination, if any, exist is largely controlled by the local (hydro)geologic conditions. In each case, the most likely migration pathway was from gas charged zones up well annular spaces to confined permeable formations, then laterally to a direct discharge or by vertically controlled joints to streams, water wells, and the atmosphere. The confining units act as barriers to the buoyant movement of stray gases, allowing subsurface travel of gas for 1–4 km from a leaky gas well. The knowledge we learn from these three sites can guide the future investigations of methane contamination cases in other regions.

1. Introduction

The first hydraulic fracturing experiment occurred in a Kansas (USA) gas well in 1947, and horizontal wells were common by the late 1970s. While about 1,000,000 conventional "tight gas" wells have been hydraulically fractured since then, until the mid-2000s, few unconventional shale gas wells were completed by high-volume hydraulic fracturing (HVHF). Natural gas has been suggested as a bridge fuel before the world operates completely with renewable energy. Since natural gas is primarily methane, a potent greenhouse gas, losses of natural gas during production, processing, transmission, and distribution, could reduce its advantage in lowering CO_2 emissions. This has led to methane being one of the most widely reported contaminants related to shale gas production [1, 2]. The environmental impacts of methane on air and water resources occur mainly through three mechanisms: subsurface methane migration, air emission, and stream contamination.

Many papers (about 60,000) have been published on the technical aspects of horizontal drilling and hydraulic fracturing (e.g., [3]), while there have been relatively few studies on the environmental impacts of shale gas well activity. For example, Harrison [4] presented the first known peer-reviewed case study of a blow-out incident caused by an overpressurized, vertical, conventional, hydraulically fractured gas well in Shaws Corner, Pennsylvania. Two notable cases published in grey literature involved methane observed seeping into West Divide Creek, Garfield County, Colorado, during 2004 [5] and a 2007 gas well blowout in Bainbridge

Township, Ohio [6]. Osborn et al. [7] presented evidence that methane contamination of domestic wells was associated with shale gas extraction located within 1 km, with about 50% of samples collected near Dimock, Pennsylvania, which turns out to be an area known to be impacted by shale gas development activities. In the cases in Parker County, Texas, and Pavillion, Wyoming, there were conflicting studies as to whether methane concentrations in water wells were related to nearby gas well activity [8]. The early years of HVHF of shale gas wells were highly controversial, with much opposition by the public to the process and industry to governmental regulation. An example is the Sierra Club et al. brief filed in opposition to industry petitioner's motion of preliminary injunction of the Bureau of Land Management's (BLM) new hydraulic fracturing rule, 80 Fed. Reg. 16128 [9]. The brief included a review of public health, water quality, and air quality impacts of hydraulic fracturing. While extensive in nature, the few references to methane migration pathways were hypothetical and not supported by direct evidence. This was likely because there were an insufficient number of comprehensive early case studies completed at that time.

Among the few shale gas-related contamination sites reported in published peer-reviewed papers, three sites in the Marcellus Shale region of Northeastern Pennsylvania are most widely reported (Figure 1). The first is located near Dimock, Susquehanna County, where methane migration was demonstrated by Hammond [10], methane in Meshoppen Creek was measured by Heilweil et al. [11], and Payne et al. [12] recorded methane emitted downwind of the Herb Button Road (Teel) compressor station. The second site is along the Susquehanna River and Sugar Run, between Towanda and Wyalusing in Bradford County. Llewellyn et al. [13] indicated that methane migrating to nearby domestic wells and methane bubbling in the Susquehanna River were related to shale gas well activity. The present study indicates that the maximum distance of a contaminated water well was 4 km from the leaky gas well. Payne and Ackley [14] measured relatively low levels of methane emissions in the area during a survey using a cavity ring-down spectroscopy (CRDS) instrument. Heilweil et al. [11] measured methane concentrations and performed isotope analyses from samples taken in Sugar Run, Lycoming County (the third site). Two follow-on hydrogeological investigations were conducted at the Sugar Run, Lycoming County site; the first by Woda et al. [15] reported noble gas and isotopic evidence that free gas had migrated from a deep thermogenic source, likely a shale gas well, to domestic wells more than 1 km away. Methane emissions were measured along the stream and at outcrops using a Bell Surface Probe. The second investigation by Wen et al. [16] indicated that migration had continued up dip to Gregs Run, about 3 km from the shale gas well, where methane emissions were quantified near observed patches of dead vegetation and methane bubbling from the stream in a third investigation [17]. These three sites (Dimock and two Sugar Runs in Lycoming and Bradford counties) in Pennsylvania are selected and extensively discussed in this study because they are the only sites where sufficient public data have been reported and methane migration has a high chance of occurrence based on reported data. The United States is the largest shale gas producer among all countries while Marcellus Shale in Pennsylvania is one of the most prolific shale plays in the US and around the world. An assessment of the environmental impacts of shale gas production on groundwater, surface water, and air has important implications for other regions in the world where shale gas production is expanding or upcoming.

While only a limited number of case studies of shale methane migration have been reported in the United States, a lot more papers on numerical models have been published on the subject matter. Birdsell et al. [18] discussed permeable pathways that included wellbores, faults, joints, hydraulically induced fractures, or some combination of these features. Rice et al. [19] included similar pathways and added migration through abandoned oil and gas wells. Yudhowijoyo et al. [20] suggested that while hydraulic propagation of fractures connecting to naturally present subsurface faults may provide a pathway for methane leakage, the major cause of methane migration is through improperly sealed leaking gas wells, especially abandoned oil and gas wells.

To explain possible impacts of methane migration in northeast Pennsylvania (i.e., Dimock), Zhang and Soeder [21] performed a numerical simulation, based on a West Virginia incident, showing that high-pressure air from air hammer drilling produced bubbles from pre-existing methane at distances of 76 m and 179 m, but not at 464 m, from the drill site. Zhang et al. [22] developed a hypothetical model for a leaky gas well 170 m from a monitoring well using typical parameters for the Bradford Formation in Pennsylvania. Detectable tracer amounts were found in the monitoring well after 9.8 years. In the case where the leakage point was at the same depth as the perforation zone in the monitoring well and there were low permeability units above and below the perforation depth, then the arrival time at the monitoring well for the tracer was 81 days.

Cahill et al. [23] conducted a 72-day methane gas injection experiment into a shallow, flat-lying sand aquifer (9 m thick, underlain by a silty clay aquitard) at the Canadian Forces Base (CFB) Borden. Methane was injected into two 45°-angled drive-point wells over 72 days at 4.5 and 9 m below ground surface. Monitoring was performed for 245 days after start of injection across a network of monitoring points. Time-lapse ground-penetrating radar (GPR) and electrical resistivity tomography (ERT) were used to monitor the distribution and migration of the gas phase [24]. After 65 days, methane gas migrated >17 m down gradient. A conceptual model indicated that the methane migrated >100 m after 245 days. Klazinga et al. [25] carried out numerical simulations of the field experiments demonstrating that gas migrates vertically due to buoyancy, until reaching an aquitard with permeability 30% less than that of the aquifer, which can then lead to extensive lateral free gas migration.

Moortgat et al. [26] qualitatively simulated free gas methane migration through an aquifer system with highly permeable pathways to explain fast flowing lateral methane migration over long distances (~1 km). High-pressure pulses of gas leakage into sparsely fractured media were needed to

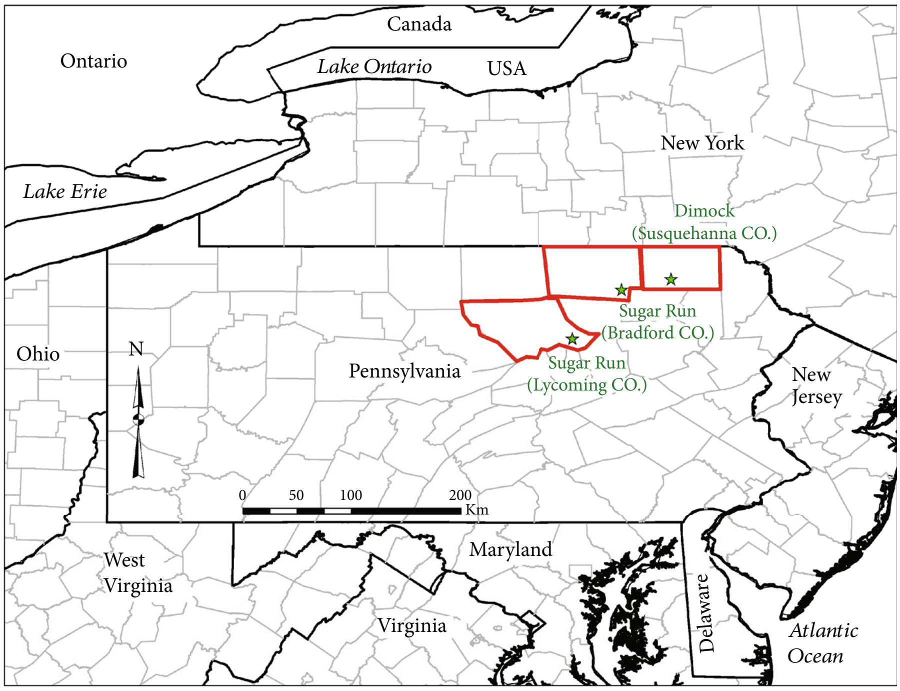

Figure 1: Location map. The three-county study area in northeast Pennsylvania is bordered in red. The sites for the case studies are indicated by green stars: Dimock (Susquehanna County), Sugar Run (Bradford County), and Sugar Run (Lycoming County).

produce the extensive rapid lateral spreading of free gas observed in field studies. Lower rates of methane leakage produce extensive lateral migration only in the aquifers with low vertical permeabilities, and fractures and bedding planes have sufficient tilt (~10°) to allow lateral buoyancy flow.

Taherdangkoo et al. [27] built a numerical model that consists of 171 m of shallow sediments, a 21 m thick claystone confining unit, and a 1608 m homogeneous, anisotropic over burden layer. There were measurement points at distances of 2000 m, 3000 m, and 4000 m from a leaky gas well, and simulations were conducted assuming tilt angles of 0°, 1°, and 3°, in horizontal and vertical directions. In this model, methane exists as free and dissolved-phase gas in the aqueous phase. In the base case (0° tilt), free and dissolved methane migrates upward predominantly by buoyancy and reaches the claystone after approximately 695 days. The diameter of the plume is about 320 m after 2 years and then remains constant. In a tilted formation, the claystone acts as an effective flow barrier which causes the methane plume to spread laterally. In the simulation where the formation has a 3° tilt, methane reaches the monitoring location 4000 m away from the gas wellbore within 7.2 years. If permeable pathways such as fractures, faults, and abandoned oil and gas wells are present, methane can migrate much faster at rates observed in case studies (1-3 months).

Rice et al. [28] conducted a numerical investigation of a dual-porosity reservoir that modelled fast, advective transport through fractures with slow, diffuse transport in a shale matrix. The result was that there was a bimodal gas phase breakthrough curve with maximum concentrations occurring decades after a 1-year methane leak pulse. However, Odeh [29], Carlson [30], and Hammond [31] have indicated that double porosity responses may be scale dependent and only reflect conditions near a wellbore. Schout et al. [32] constructed a flow and transport model to investigate methane migration in a 60 m thick unconsolidated sandy rock aquifer. They found that retention of methane by dissolution was significant even at a low (but not absent) groundwater flow velocity. With additional interbedded fine-grained sediments, simulations produced substantial lateral spreading of migrated methane gas. It was suggested that atmospheric methane emissions from such leaks could be delayed for decades, reduced, or prevented.

Targeted case studies following leakage events provide opportunities for evaluating possible natural gas migration in the subsurface. The multiple peer-reviewed papers presented above that reported field data at the three sites in Pennsylvania have often reached different conclusions, especially about the source of migrated methane and its migration pathway. This investigation will present a review of the results of each of those studies, including additional previously unpublished data, with independent interpretations of the data collected at each site. The purpose of the present study is to explore (1) what factors control the presence of methane in groundwater, surface water, and air and (2) if there is correlation among the presence of methane in these three zones.

2. Methods

To determine the origin and migration pathways of methane that were present in the shallow subsurface, surface water, and air at and in the vicinity of a hydrocarbon well, we compiled, reported, and interpreted geochemical data (i.e., stable carbon and hydrogen isotopic ratios) of natural gas and environmental samples as well as stratigraphic and geophysical data from hydrocarbon wells associated with three distinct case studies where gas migration was presumed from previous work. Among the data, unpublished methane concentrations and isotopic ratios (i.e., carbon and hydrogen) of stream water samples collected around the Dimock site (Susquehanna County, Pennsylvania) as well as from the Susquehanna River, near the Sugar Run site (Bradford County, Pennsylvania), were also reported and interpreted in this study. The data and information from all three sites were discussed and investigated to shed light on the lateral extent of methane migration around potentially leaky oil and gas wells. Our study suggested that a scenario considering only vertical movement driven by the gas buoyancy mechanism was not sufficient to explain the observations at these three sites. A review of the air emissions and stream data was conducted to differentiate between which emissions may be due to shale gas well operations as opposed to natural or other anthropogenic activities. A discussion of methods that have been used to generate these datasets is divided into two subsections: (1) application of geochemical tracers to detect leaky hydrocarbon wells and (2) geologic and hydrogeologic controls on fluid flow in fractured rock.

2.1. Application of Geochemical Tracers to Detect Leaky Hydrocarbon Wells. The use of the isotope ratios of $\delta^{13}C$-CH_4 ($\delta^{13}C_1$) in combination with the ratios of $\delta^{2}H$-CH_4 (δDC_1) can sometimes distinguish deep thermogenic methane and shallow biogenic methane [33]. In addition to these stable isotopes, alkane (methane, ethane, and propane) concentrations and ratios are also used to identify sources of methane that are present in shallow aquifers or surface water (i.e., stray gas). Baldassare et al. [34] indicated that the process can be complicated by the potential mixing of multiple sources of thermogenic natural gas of different maturity and additional sources of microbial methane. In addition, changes in hydrostatic head in the water table can also affect gas concentrations. Finally, anaerobic methane oxidation can also modify carbon isotopic values and relative concentrations of residual dissolved alkanes [15]. Another important note to address about the difference in the extent to which migrated methane could have been oxidized, between scenarios where dissolved methane concentration is high versus low, is that a higher concentration of dissolved methane in groundwater would lead to a smaller percentage of methane being oxidized. This was explained by Forde et al. [35]; i.e., a higher methane flux could result in an advection-dominated migration compared to the lower methane flux scenario where the diffusion is dominant. Due to this, even less methane oxidation will occur during the migration process when the methane flux is higher.

Concentrations and isotopic ratios of noble gases, which are largely unaffected by subsequent microbial processes or reaction with geologic substrate, have also been used to identify potential sources of stray gas [36].

Chemical characteristics of water are also investigated to illustrate the sources of water, which can be used to infer the potential source of dissolved methane. Certain hydrogeologic conditions are associated with two dominant water types: Ca-HCO_3 type water generally predominates in shallow units and/or groundwater with shorter residence time, while Na-HCO_3 or Na-Cl type water is commonly associated with deeper groundwater-bearing units and/or groundwater with longer residence times [37, 38].

2.2. Geologic and Hydrogeologic Controls on Fluid Flow in Fractured Rock. The two main factors controlling fluid flow in petroleum reservoirs or aquifers are permeability and porosity. Porosity can be further divided into two types: primary and secondary porosity. Primary porosity is the nonsolid part of a rock filled with fluids, which is developed during original sedimentation of granular rocks and usually range from 10% to 35% [39]. Secondary porosity is created by sediment compaction and other processes such as dissolving of limestones, fracturing, and dolomitization. Permeability reflects how easily fluids flow through a formation and depends on the size and shape of the formation, its fluid properties, the pressure exerted on the fluid, and the amount of fluid flow. Porosity is typically determined using data from neutron porosity and density porosity wireline logs in Marcellus Shale wells. Permeability can be determined by cross plots of water saturation derived from resistivity data and porosity [39] or from pressure testing with application of the Horner equation [40]. A useful indicator for the presence of gas is a decrease in neutron porosity and an increase in density porosity, which can cause the two curves to cross each other. In addition, gamma ray logs are useful in determining lithology and depositional environments [41].

Much of the early work describing groundwater flow in fractured rock terranes was conducted in New Jersey where well tests indicated that flow was controlled by directional rather than isotropic hydraulic behavior and that maximum and minimum directions of anisotropy were related to the structural strike and dip, respectively, of formation bedding planes [42–45]. More recent work introduced a system where flow in fractured rock structures and networks is primarily controlled by structure type, geometry, connectivity, and interactions within a network [46].

For Middle and Upper Devonian sediments (e.g., Catskill, Lock Haven and Trimmers Rock Formations, Tully Limestone, Mahantango Shale, and Marcellus Shale), Hancock and Engelder [47] indicate that near-vertical neotectonic joint systems are tension features formed during uplift and erosion. They generally occur within the upper 0.5 km of the crust on the New York Appalachian Plateau, or in the western portion of the Appalachian Plateau, at depths less than 1 km, with Devonian series burial depths of 2 km. Early joint sets were formed at close to or at the peak burial depth of >4.5 km [48]. Narr and Currie [49] indicate that for late-forming joints to develop more than 50% of the total overburden must be removed by erosion. The depths of the Marcellus Shale at the sites of the present study in Northeastern Pennsylvania are 1-2 km, indicating that shallow joints in that area may extend to depths of 0.5–1 km.

Most valleys in Western New York or Northeastern Pennsylvania, including the study area, have streams whose courses are oblique to the joint directions (joint-oblique valleys), but some well-developed valleys, however, have streams whose courses are parallel and perpendicular (joint-parallel valleys) to the nearly orthogonal joint sets [50].

Due to the low viscosity of free-phase gas and buoyancy effects, methane and other natural gases can move rapidly through an aquifer matrix, along high permeability bedding planes and fracture networks, and if not impeded by physical barriers or chemical reactions, some portion of the fugitive gas may reach the surface and vent to the atmosphere. This is most likely to occur in bedrock aquifers with steep dipping fracture networks and/or bedding planes, along areas of low hydrostatic pressure, such as valleys, groundwater discharge areas, and heads lowered by groundwater withdrawals, and can sometimes move significant distances (e.g., >1 mile or 1.6 km) away from the point of release. If there are significant barriers to the buoyant upward movement of free-phase gas, the gas will primarily spread laterally and remain in the subsurface [51].

3. Case Study in the Dimock Area, Susquehanna County

3.1. Previous Investigations. The area in Dimock, Pennsylvania (PA), has the most comprehensive set of literature concerning the impacts of methane migration on groundwater supplies and streamflow, as well as methane air emissions from shale gas infrastructure. Hammond [10] and Hammond et al. [8] describe the relationship of methane migration to gas well integrity for multiple shale gas wells in the area during the period 2009-2012. At the end of sampling in 2012 in the Meshoppen Creek Valley, methane was still migrating from well pad 8, while remediation at gas well GW-7 had eliminated the methane migration from that site (Figure 2). Heilweil et al. [11] published measurements of the methane concentrations just downstream of the Meshoppen Bog (MC US 2 (Meshoppen Creek upstream site 2)) in 2013. Grieve et al. [52], SRBC (Susquehanna River Basin Commission) in 2017, and PSU (Pennsylvania State University)/SRBC in 2018 (unpublished data; Table S1) also measured methane concentrations and isotopic compositions at MC US 2 between 2013 and 2018, details of which follow. Payne et al. [12] indicated that compressor stations were likely the source of elevated air methane concentrations in the southern and eastern portions of the Dimock Township, Pennsylvania. They noted that high concentrations of methane were measured at the Herb Button (Teel) compressor station, which produced a plume extending 3.2 km from the station up the Meshoppen Creek Valley. Peischl et al. [53] estimated the total CH_4 emission to the atmosphere using measurements taken aboard the chemically instrumented NOAA WP-3D aircraft in the summer of 2013, using a mass balance approach to calculate the horizontal flux of CH_4 through the planetary boundary layer (PBL) downwind of the Marcellus Shale region in Northeastern Pennsylvania. One area of the elevated methane emission concentrations that Peischl et al. [53] identified was in the Dimock area (Figure S1).

3.2. Reinterpretation of Published Data. Due to the coincidence of elevated methane levels, the timing of construction of a great deal of natural gas infrastructure, and the lack of other nearby methane sources, Payne et al. [12], using the results of a survey with a mobile cavity ring-down spectrometer (CRDS) and onboard GPS unit, suggested that three compressor stations in southern and eastern Dimock Township were the sources of the methane emissions. Of particular note in this regard was the compressor station on Herb Button Road, where methane levels were measured at their highest concentration (22.3 ppm by volume) 503 m from the compressor station and then dissipated downwind (Figures 2 and 3), with elevated methane levels measured up to 3.2 km from the compressor station. A follow-on survey in the nearby vicinity of the Herb Button (Teel) compressor station showed a reduced methane level of 7.4 ppm by volume (Figure 3); however, that track did not extend up the Meshoppen Creek Valley. Hammond [10] compiled and presented long-term records of methane chemistry in groundwater and related gas well operations for water wells WW-O, -P, -Q, and -R at gas well pad 8 (Figures S2, S3, and S4). Some predrill water samples were taken from nearby domestic wells, indicating that methane migration occurred after drilling, but prior to completion of HVHF. The final set of groundwater samples was taken from each water well between September 2010 and January 2012, with elevated methane concentration between 12 and 52 mg/L. Gas well GW-7, near the Teel Compressor, was completed on 7/21/2008, and HVHF was conducted on 8/9/2008. The first samples from water wells WW-M and WW-N were not taken until 10/25/2009 and 1/5/2010, with methane concentrations of 30 mg/L and 23 mg/L, respectively (Figure S5). After remediation of the gas and water wells, the methane concentrations were reduced to 0 mg/L on 2/24/2011 (WW-N) and 5/12/2011 (WW-M).

Prior to its construction in 2008, lower explosive limit (LEL) measurements were taken in two domestic water wells within 460 m of GW-2, which yielded negative results. Three domestic water wells were sampled in January 2009, two of which had methane levels less than 1 mg/L, and the third (WW-E) had a concentration of 17.9 mg/L. A sample collected from WW-E on 9/19/2010 had a methane concentration of 20.8 mg/L (Figure S6).

Figure 3 is a topographic map depicting the tracks in the Payne et al. [12] study and the locations of wetlands, especially the Meshoppen Bog, shale gas wells, and the Herb Button (Teel) compressor station. The methane concentration in air at the compressor station is a spike from a point source, with an extremely high concentration of 22,300 ppb by volume. The methane distribution immediately upwind in the Meshoppen Creek Valley is more diffuse and spread out and has a Gaussian shape, as expected from a nonpoint source. Payne et al. [12] indicated that this was a plume from the compressor station directed up the valley. A more likely explanation is that the methane emissions were caused by biological processes, especially since the highest methane concentration of 4,145 ppb was located in and had the same length as the Meshoppen Bog. The support for a natural origin for the methane emissions in the valley can be seen at MC US 3, where the concentrations are elevated on the east side of the north trending valley and at background levels on the west side of the valley, as shown by the red arrows,

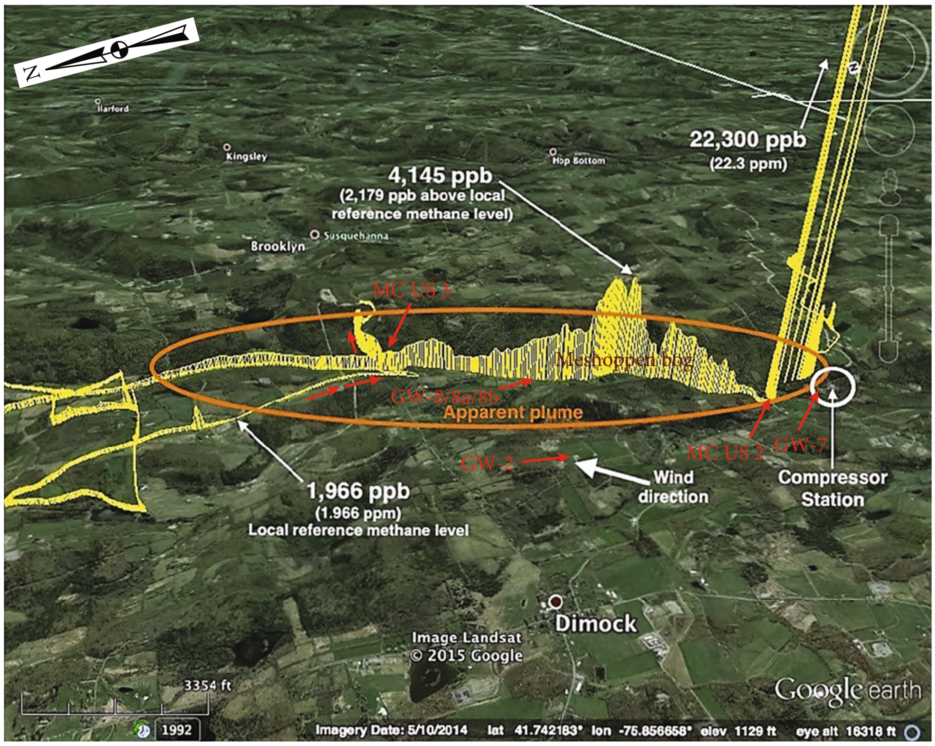

Figure 2: Adapted from Payne et al. [12]. Ambient CH_4 measurements collected from an area near Dimock, PA. Yellow lines are locations of CH_4 measurements. The vertical height of each line is proportional to the elevation of the CH_4 level at that location above the local reference level that day (1,966 ppb). The highest level (22,300 ppb) was emitted from the Herb Button (Teel) compressor station. Downwind was a diffuse emission (4,145 ppb) from the Meshoppen Bog. A minor plume is shown by the red lines near MC US3. Background levels occurred near MC US 2. Significant gas wells are GW-2, GW-7, and GW-8/8a/8b [10].

suggesting that a plume is oblique to the valley at or near MC US 3 and emanating from Meshoppen Creek. The track approaches near at least 10 gas shale wells without any clear evidence of methane emitting at those well sites, although only one known gas well at pad 8 was probably leaking in the subsurface at the time of the survey.

Figure 4 is a chart of isotopic compositions in the Dimock area of Marcellus production gases, shale gas well annular gases, water well gas samples, Mud Gas Log (MGL) data depicting geologic ages of gases, and samples from Meshoppen Creek at MC US 2. The data were used by Hammond [10] to show that annular space compositions were different from the production gas, but similar to the water well samples collected along Carter Road in 2009, prior to any mitigation measures. This suggested that the source of the migrated methane had a thermogenic origin from the formations above the Marcellus Shale. After mitigation, the samples with the lowest methane concentrations had significantly different compositions than those taken from the same water wells prior to mitigation. This suggested that the later samples had a natural origin. Later groundwater samples taken in the Meshoppen Creek Valley had a thermogenic origin. The results of isotopic analyses and methane/ethane (C1/C2) ratios of the early samples taken from WW-O and -Q indicate that the gases were immature thermogenic methane relative to the samples collected along Carter Road, suggesting a source from a younger and shallower formation. This is supported by a gas flow of 708 m^3/day reported from GW-8 at a depth of 475 m. For WW-P and -R, the isotopic analyses indicate a more mature thermogenic origin for the methane, but the C1/C2 ratios indicate that there is a biogenic component, possibly due to microbial alteration. A follow-on US EPA sample was collected from one of the water wells in 2012, which, due to the lack of exact locational data, could have been taken from either WW-Q or WW-R; however, the concentration and isotope data suggest that the sample was taken from WW-R. The data suggest that there were two separate sources in two individual sample clusters, one like that on Carter Road and the second of a much younger age. Several samples taken in the creek at MC US 2 had similar compositions to WW-O and WW-Q, but those and other samples collected at the site plotted along a trend indicating oxidation of naturally occurring methane of a biogenic origin. The most oxidized samples were taken in July 2017, suggesting that the degree of oxidation was temperature dependent.

3.3. Structural Geologic and Hydrogeologic Considerations.

Figure S7 is a segment of the geophysical log for GW-4 (Costello 1H) showing the top of the "Catskill Sandstone" on a transgressive sandstone over a delta-marine fringe, overlain by a 240 ft (73 m) low permeability confining unit. It is a local marker that carries well within the Dimock area. A map on top of the sandstone from 26 gas wells was prepared to demonstrate the structural relationships between the gas

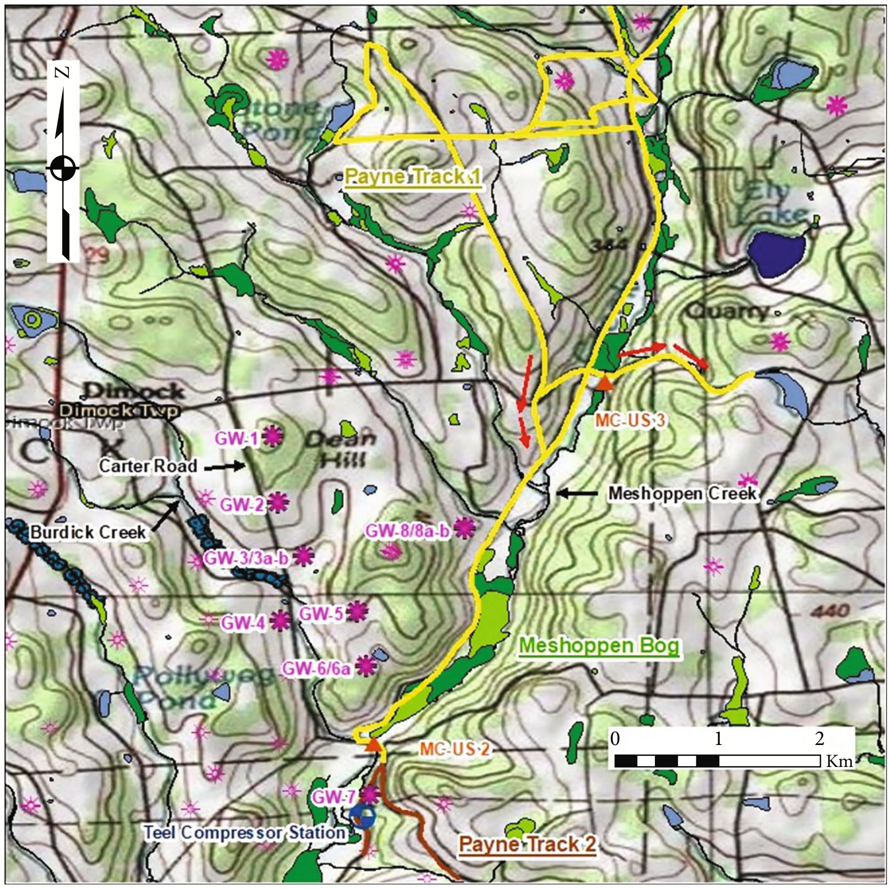

Figure 3: Topographic map of the Dimock area. From Payne et al. [12] are tracks (1) 11/22/2014 and (2) 11/14/2015. Freshwater wetlands are colored dark (forested) and medium (emergent) green, water bodies are medium (ponds) and dark (lakes) blue, and gas wells have magenta well symbols. All other features are as described in Figure 2.

and water wells in the area (Figure 5). At the GW-1, GW-2, GW-6, GW-7, and GW-8/8a/8b sites, the impacted homeowner wells were located along strike and/or updip of the gas wells. Along the middle of Carter Road (GW-3, GW-4, and GW-5), all the impacted homeowner wells were updip of GW-4, but downdip of GW-3 and along strike and updip from GW-5. Based on the temporal variations in methane concentrations in the water wells relative to gas shale operations, relative proximity of water wells to gas wells, and pressure testing of the gas wells, gas shows in GW-3a and GW-5 and the lack of gas shows in GW-4; Hammond [10] attributed the impacts to migration from gas wells GW-3 and GW-5. All that data was collected during the period 2009-2012; however, T. Engelder (Pennsylvania State University, personal communication, 2018) reported that the operator had a workover rig at the GW-4 site for a year between the spring of 2013 and 2014. A useful indicator for gas is a decrease in neutron porosity and an increase in density porosity, which can cause the two curves to cross each other, which occurs at 1843 ft and 1854 ft in the Catskill Sandstone on the geophysical (wireline) log for the Costello 1 (GW-4) well (Figure S7). The presence of gas indicates that Catskill Sandstone in the well is a permeable unit. Figure S7 also shows that a second crossover occurs at 3104 ft in a Bradford sandstone, in the Lock Haven Formation. The well log indicates that additional gas zones occur in a lower Bradford sandstone and the lower Marcellus and Onondaga formations, although none of the gas zones were listed on the well's drilling and completion report. There is also little agreement between the gas zones on the geophysical logs and completion reports of those wells for which both are available (Baker 1, Gesford 2, and Gesford 3) (Table S2). One possible reason is that the density/neutron combination works best in clean sandstone formations. If shale is present, then the density log responds as a reduced porosity, so the separation between the two curves is reduced. Also, if borehole pressure exceeds formation pressure and permeability exists, drilling fluid can be flushed into the formation. Where effective porosity is low, a zone which gives good gas shows when drilled will appear to be water-bearing when electric logged or tested. Conversely, flushing below the drill bit can have the most effect on a formation with high permeability and effective porosity, which during drilling will liberate little or no gas. Soon after drilling, however, the reservoir will return to its natural state and be logged or tested as a productive zone. If GW-4 was the source of the migrated gas, then the low annular pressures measured in 2010 and 2011 (0-23 psig or

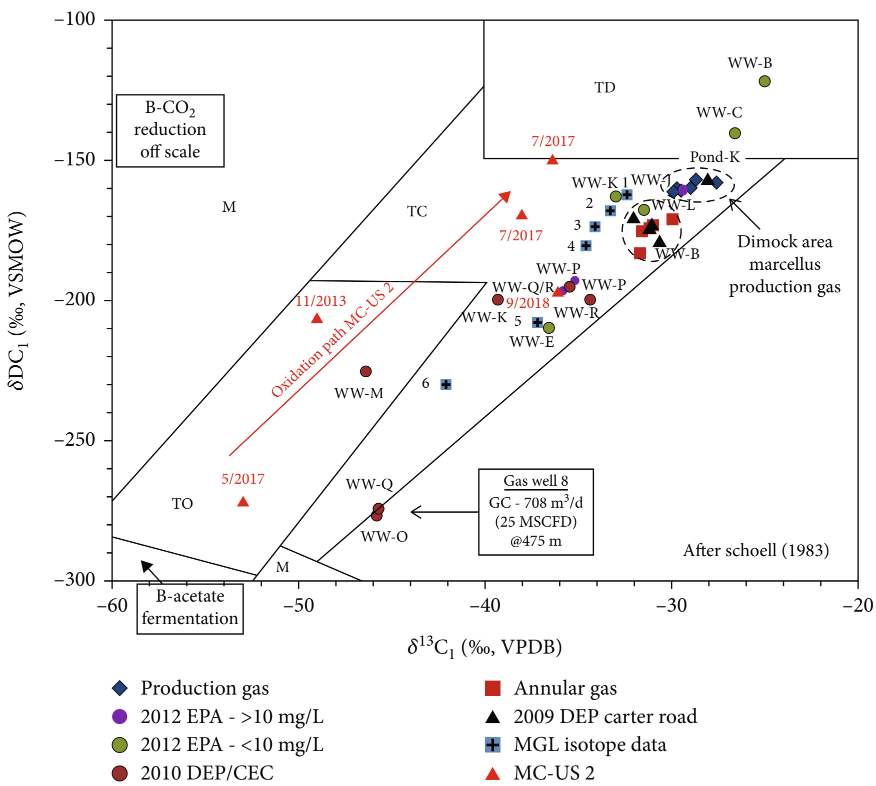

FIGURE 4: The Schoell diagram of methane gas samples in the Dimock study area analyzed by multiple researchers as described in the text. Adapted from Schoell [33]. B: bacterial gas; M: mixed gas; TO: oil associated thermogenic wet gas; TC: condensate associated thermogenic wet gas; TD: dry thermogenic gas. The figure is from Hammond [10] and modified to add stream samples collected at MC US2 and include Mud Gas Log (MGL) mean values from Baldassare et al. [34]: 1—Marcellus Shale; 2—Hamilton Group (Mahantango Shale); 3—Tully Limestone; 4—Geneseo Shale; 5—Brallier Formation; 6—Catskill/Lock Haven Formations.

$0\text{-}1.6 \times 10^5$ Pa) would indicate that remediation sealed the well annular space above the discharge point of the migrated methane.

Pohn [50] indicated that joint-parallel valleys erode by waterfall and plunge-pool formation; bedrock is undercut on the downstream side, and unstable blocks subsequently collapse into the plunge pool, while joint-oblique valleys tend to erode easily where the removal of joint-bounded blocks forms cascades that advance headward by apical erosion.

Meshoppen Falls, Slumber Valley Falls, Potts Falls, Meshoppen Bog, States Pond, Schooley Pond, and Sound Pond are all present in the Meshoppen Creek basin, suggesting that it is a joint-parallel valley. Burdick Creek is oriented at approximately 60-80° to Meshoppen Creek indicating that it is a joint-oblique valley.

A map (Figure S8) from Molofsky et al. [54] indicates that predrill methane concentrations are the highest in the stream valleys of the Susquehanna County study area, especially the major streams, oriented N-NE like Meshoppen Creek. Pohn [50] suggests a reason for this in that joint-parallel valleys could be due to a single deep, pervasive joint whose presence acts as a barrier to lateral expansion of the stream, or erosion along joint zones whose intense fracturing produces weak erosional resistance in the rocks. The Molofsky et al. [54] study also indicates that the predrill concentrations of methane in the Burdick Creek basin were very low (less than 1 mg/L). The oblique orientation of the joints may explain why not all of the impacted water wells along Carter Road are within the Burdick Creek valley.

The potential migration pathways in this area are leakage from noncommercial gas charged sands above the Marcellus Shale through uncased annular spaces to a high permeability confined sedimentary unit such as the likely "Catskill Sandstone" at a depth of 0.5-1 km, then laterally updip to joints parallel to Meshoppen Creek or to en echelon joints oblique to Burdick Creek, and then to the water wells in the shallow aquifer.

4. Case Study in Sugar Run, Bradford County

4.1. Previous Investigations. Another area of interest is Paradise Road along the north branch tributary of Sugar Run at Wyalusing in southeastern Bradford County, Pennsylvania, hereafter Sugar Run (Bradford County).

Llewellyn et al. [13] indicated that drilling of shale gas wells on the Welles series 2-5 pads was completed between September 2009 and May 2010 in the valley of the north branch of Sugar Run in Bradford County (Figure 6). All the gas wells on the five well pads were constructed with surface casings to 300 meters below ground surface (mbgs); there was no casing at intermediate depths, and production casing was completed through the zone of gas production

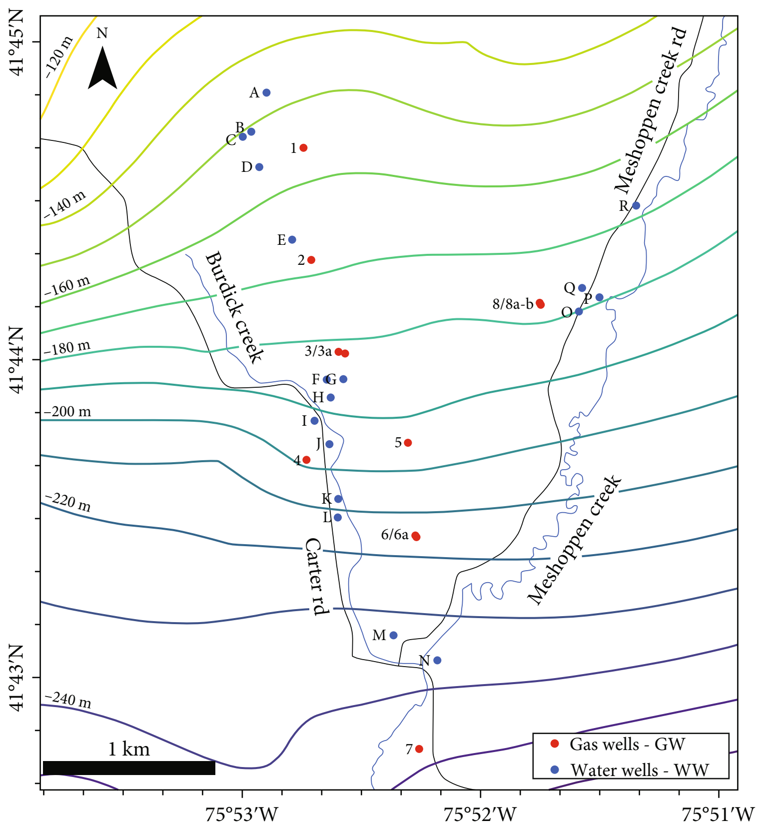

FIGURE 5: Structure contour map on the top of the Catskill Sandstone. Contours show depth in meters below sea level. Gas and water wells are numbered as in Hammond [10], without the WW-X or GW-X labels.

from 2100 to 2300 mbgs. High annular pressures (1500 to 6485 kPa) were measured in Welles 3-2H, 3-5H, 4-2H, 4-5H, 5-2H and 5-5H from May 2010 to June 2010 (Figure S9). Multiple gas shows were documented during drilling of the wells at intermediate depths where the boreholes were uncased. The one exception was the gas wells on well pad Welles 3, which may have had the gas shows suppressed due to overpressured drilling fluid used to suppress high formation pressures. These intermediate-depth gas shows may explain why the annular pressures of gas wells on well pads Welles 3 and 4 exceeded regulation values (2432 kPa). Contamination of six domestic water wells (i.e., 1–6) by natural gas and sediment along Paradise Road was reported in July 2010 after the completion of HVHF on Welles 1-3H and 1-5H in February 2010. An initial methane concentration of 0 mg/L was measured in domestic water well 2 in April 2010. It was unknown what the pressures, if any, were in Welles 1-3H, 1-5H, 2-2H, and 2-5H; however, no complications were reported during the drilling of those wells. Methane levels of 0–30 mg/L were measured in water wells 1–6 between July 2010 and October 2010. In addition to methane migrating to water wells 1-6 in the joint-parallel Sugar Run valley, bubbling of methane was observed in the Susquehanna River in September 2010 at numerous locations between the communities of Sugar Run and Wyalusing.

Remediation of Welles 3, 4, and 5 series gas wells occurred in October 2010 (Figure 7), while gas bubbling in the Susquehanna River continued until last reported on October 25, 2011, and water well methane levels were also reduced following the elevated levels measured from February 2011 to April 2012. No remediation of the Welles 1 and 2 series gas wells was recorded, which could indicate that there was no annular pressure in those wells. During May 2012, high methane concentrations were again measured in water wells 1, 3, 4, 5, and 6 (i.e., 5–48 mg/L). Elevated methane concentrations (4.5 to 20 mg/L) occurred in water wells 1 and 6 in October and November 2012, prior to HVHF of Welles 2-2H and 2-5H on November 11, 2012. Note, HVHF of Welles 3, 4, and 5 series gas wells were completed by September 2013.

Llewellyn et al. [13] concluded that the migration of stray gas from an intermediate to a shallow depth likely occurred (without excluding the possibility of contamination from surface sources, e.g., wastewater pit) based on multiple lines of evidence including, e.g., (1) high methane concentrations in domestic water wells following the drilling and completion of nearby gas wells, (2) the similarity in stable isotopic ratios of natural gas collected from domestic water wells and from the annular space of gas wells (Figure 8), (3) elevated pressures in the gas wells, and (4) detection of the shale gas drilling-related organic 2-n-butoxyethanol.

4.2. Reinterpretation of Published Data. Bedrock strata dip ~5–10 degrees to the southeast toward the Welles series gas wells, where bedding planes that outcrop near the river

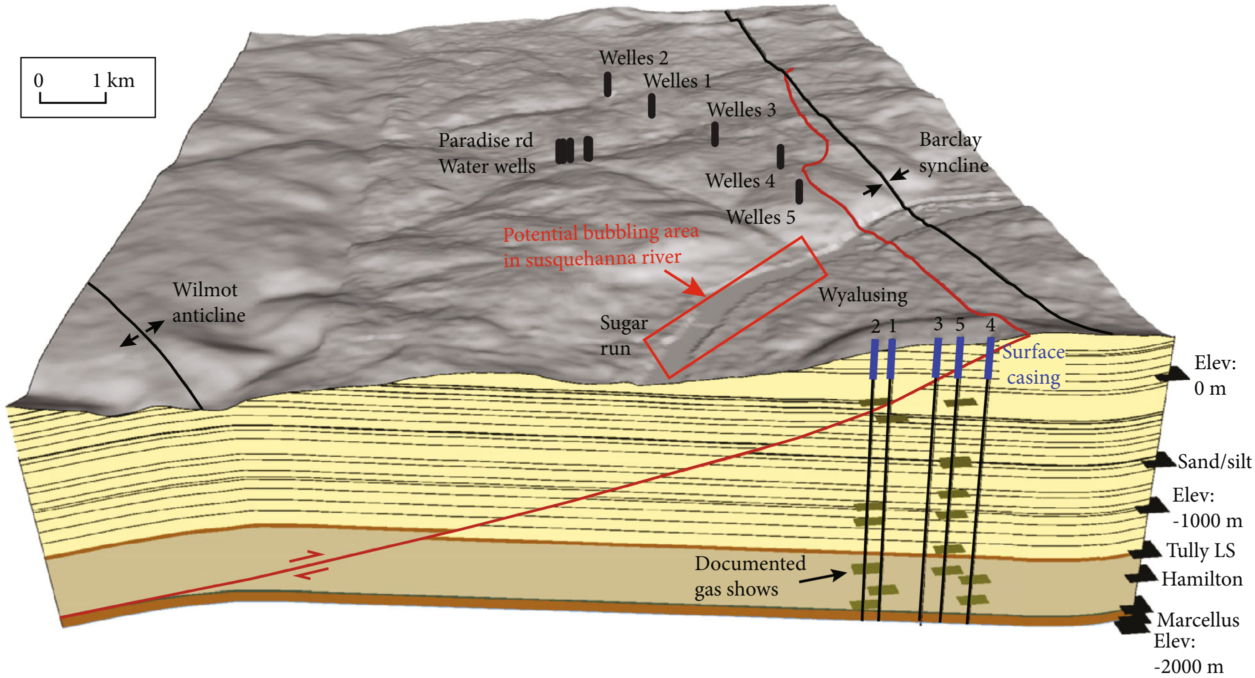

FIGURE 6: Block diagram illustrating shallow angle thrust fault, structural fold surficial traces, and bedding planes at Sugar Run in Bradford County. The positions of water wells 1-6 (Paradise Road) and gas wells Welles 1-5 series are shown with the gas wells projected to the front of the block. In September 2010, gas was observed bubbling from the Susquehanna River, between the Wyalusing and Sugar Run communities, which ceased after the completion of gas well remedial activities. Modified from Llewellyn et al. [13]. View is toward the west.

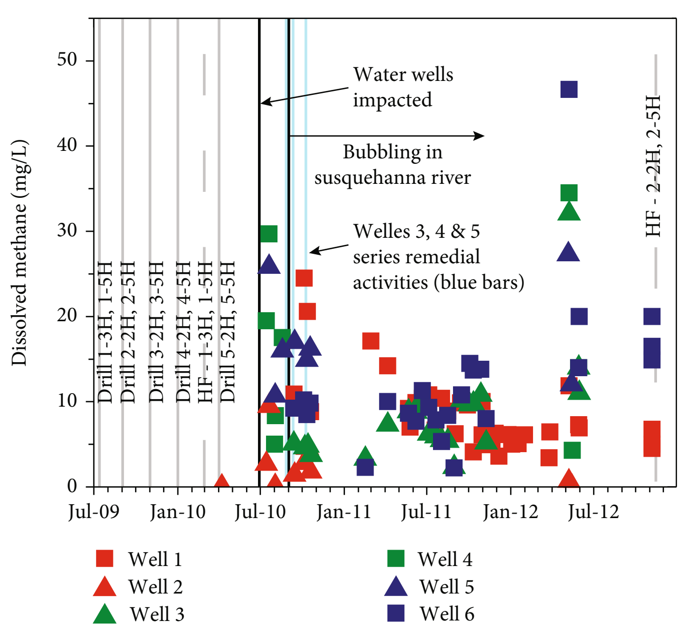

FIGURE 7: Time series plot of dissolved methane concentrations at the Sugar Run (Bradford) site with gas drilling and HVHF dates (dashed grey lines), gas well remedial activities, onset of impacts to water wells 1–6, and bubbling in the Susquehanna River (modified from [13], adding last date bubbling was observed in Susquehanna River).

(presumably facilitating methane migration) intersect the open bore holes at~400–600 m (1312-1967 ft) bgs. The neutron porosity and density porosity curves cross each other at 2028 ft (618 m) and 2040 ft (622 m) in the Catskill Sandstone on the geophysical (wireline) log for the Welles 1-5H well (Figure S10). As with the Dimock gas wells, there is little agreement between the gas zones on the geophysical logs and completion reports of those wells for which both are

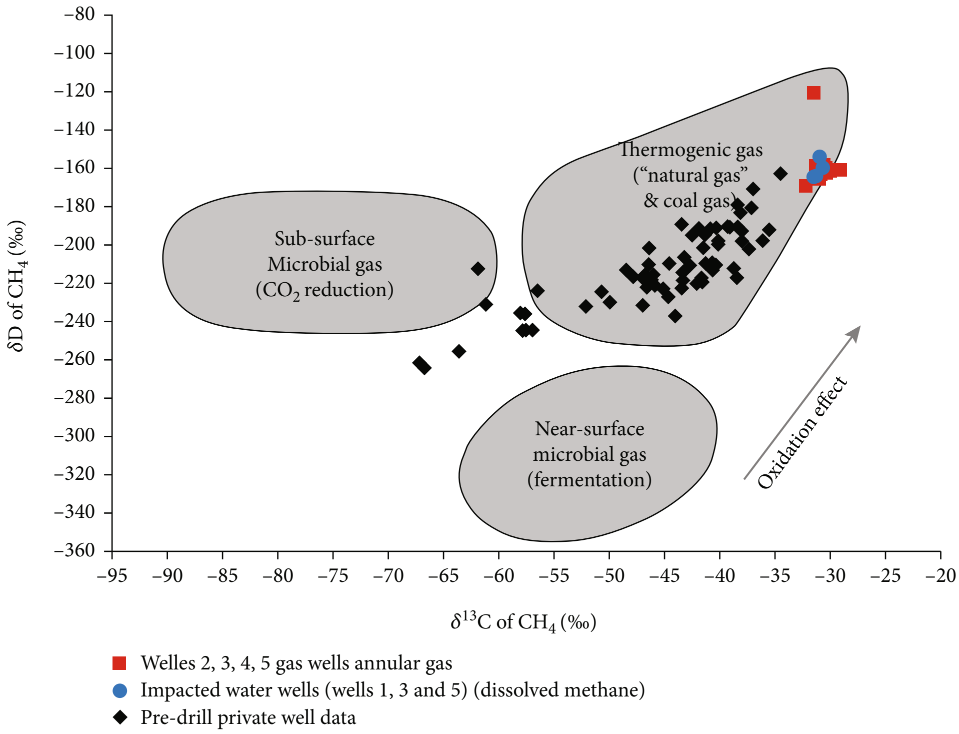

Figure 8: Plot of δD against δ^{13}C (per mil) for methane sampled from the annuli of gas wells (Welles 2, 3, 4, and 5 series) and impacted water wells (wells 1, 3, and 5). Isotopic data were not available for other impacted water wells. Predrill private well data were collected throughout Bradford, Sullivan, Susquehanna, and Tioga counties in NE Pennsylvania [34]. Reproduced from Llewellyn et al. [13].

available (Welles 2-2H, 3-5H, and 4-2H) (Table S3). Porosity log curve crossovers occur in the equivalent Catskill, Bradford, and Elk sandstone/siltstones, while the gas shows in the completion reports (mud logs) occur in the deeper Hamilton Group (Mahantango Shale or Marcellus Shale). The same explanation as given for the clean sandstones and shaley formations in the Dimock area gas wells applies in this case. The section between the Catskill Sandstone and Tully Limestone consists primarily of impermeable shales and secondary siltstones. Neither the geophysical logs nor the completion report provides evidence of gas shows in the Tully Limestone; however, the presence of shales in the limestone unit could make a gas response difficult to see. Well-developed vertical to near-vertical fractures (joints) are observed in outcrop to trend NNW–SSE in the study area, consistent with joint-controlled valley development. Llewellyn et al. [13] indicated that the combination of dipping strata and joints presumably facilitated methane migration. In addition to the jointing, a thrust fault plane, identified from seismic reflection data, dips ~16 degrees downward to the south away from the Welles gas wells: the fault plane intersects the Welles 1–5 series gas wells at depths between ~180 mbgs and 580 mbgs and likely intersects some uncased portions of boreholes at the Welles 1, 2, and 3 pads.

The Peischl et al. [53] 2013 research aircraft survey indicated that no enhanced methane levels were measured in the region of Sugar Run (Bradford County) (Figure S1).

Payne and Ackley [14] used a customized portable cavity ring-down laser spectrometer (CRDS) and combustible gas indicator (CGI) to measure ground-level methane emissions during a survey of the Wyalusing-Sugar Run-Paradise Road area. On January 31, 2013, winds were from the west at nearly 20 miles per hour. Under those conditions, Payne and Ackley [14] indicated that any methane emissions had been dispersed rapidly. During the follow-on 3-4 June 2013 field work, the wind was from the north-northwest at an average speed of 5 miles per hour. Under the more favorable conditions, the methane levels were slightly to moderately elevated over portions of the survey area (Figure S11). The average methane level was 1.86 ppm (by volume), with a minimum of 1.79 ppm, and 99% of the measurements were below 2.08 ppm. Payne et al. [12] indicated that typical background concentrations of methane are 1.7–2.1 ppm (by volume). Survey work was limited to publicly accessible roads; consequently, the impacts of methane emissions were measured at considerable distances from the potential methane emission sources (if any), except for the Welles series W-3 gas wells and water wells 1–6.

Payne and Ackley [14] indicated that the plumes of the agricultural and industrial sources in the area were not extensive and most of the methane emission sources were likely shale gas well pads and pipelines and that elevated methane levels were concentrated within the Paradise Road impact area. The 4-mile-long (i.e., 6.4 km) impact area (Figure S11) designated by the Pennsylvania Department of Environmental Protection (PA DEP) is much larger when compared to the Dimock site, where methane migration was confined to areas within 0.5 mile (800 m) of a shale gas well. The Payne and Ackley [14] tracks cross the thrust fault and joints parallel to stream valleys in the Sugar Run, Bradford County (Figure 9); however, there were no detected elevated methane levels in the air.

4.3. Structural Geologic and Hydrogeologic Considerations. Gas wells on well pad Welles 3 are a possible source of methane leakage and migration to Paradise Road, as they are closest to water wells 1–6 and may be open to the regional fault, local joints, and bedding planes, potentially connecting the gas wells to the water wells. Gas wells on well pad Welles 1 and 2 had no evidence of elevated annular pressures and required no remediation. While the thrust fault was cased off in gas wells from well pads Welles 4 and 5, those wells are open to the bedding planes potentially connecting those gas wells to the water wells and Susquehanna River. No evidence of methane emissions from the survey tracks was detected around Welles series W-3, near Welles series W-5, or the thrust fault and joints.

Sites A, A1, B, C, and D are all near wetlands features. The most prominent plume is downwind of the Crane Swamp at site A. Two gas wells are located in the same area; but no plumes were detected downwind of those wells. Site A1 is also near, but upwind of the Crane Swamp and downwind of a gas well. There are no methane plumes downwind of the impacted water wells, or the fault and joint features that might connect a gas well with the water wells. It appears that there is no clear evidence that the presumable methane migration in the subsurface is related to the slightly elevated methane air emissions in the Paradise Road impact area. Measured methane emissions in the region of Sugar Run (Bradford County) by Payne and Ackley [14] might be simply reflecting the background variability. The emitted methane from the surface expressions (if any) of subsurface methane migration may have been quickly diluted and dissipated, and the vehicle-mounted emission detector was too far from an emission source (if any) to detect any significant emissions.

Llewellyn et al. [13] also performed an aquifer test showing an asymmetrical trough of depression due to joints parallel to Sugar Run with alignment along the direction of the Welles gas well pads and impacted water wells. Off the flank of the Wilmot anticline, the bedrock dip was 5-10 degrees downward from the domestic wells to the Welles gas wells, intersecting the boreholes at 400-600 mbgs. Therefore, the presumable methane migration from the gas well to domestic water wells via bedding planes and fractures is driven by not only the fluid buoyancy but also along the anticline and bedding plane dipping directions.

In addition to methane migrating to water wells 1-6 in the joint-parallel valley along Paradise Road, methane was observed bubbling in the Susquehanna River in September 2010 and at numerous homeowner wells between the communities of Sugar Run and Wyalusing near or along PA Route 187 (Figure 9). With the exception of BH07 (2.16 mg/L), /the methane concentrations in the domestic wells varied from 15 mg/L to 55.8 mg/L (Table S4). Unlike the Llewellyn et al. [13] data, methane isotopes reported by Baldassare [55] for the domestic wells near PA Route 187 and the Susquehanna River (Figure S12) were depleted relative to the annular space samples of the shale gas wells. One exception is C-5, which has a lower concentration and different isotopic signature relative to the other samples. In addition, C3 (propane) is absent in the C-5 sample but present in all other gas and water well samples. These data suggest a separate, possibly, oxidized natural source for the methane in C-5. The depleted C-6, HO4, and HO8 water wells and Susquehanna River samples relative to the gas well signatures indicate that possible mixing of migrated gas with shallow biogenic gas occurred. Conversely, the similar isotopic Welles series gas well and Sugar Run water well signatures suggest a likely thermogenic source (possibly a Welles 3 series gas well) that is not mixed with any shallow biogenic gas. Higher order alkanes are present in all gas wells, except the Welles 5-5H well (Table S5). They are also absent in all PA Route 187 water well and Susquehanna River samples. This suggests that leakage from the Welles 5-5H gas well is the likely source of fugitive gas migrating to the domestic wells along PA Route 187 and the Susquehanna River.

5. Case Study in Sugar Run, Lycoming County

5.1. Previous Investigations. A gas migration incident into groundwater and streams was studied along Sugar Run in southeastern Lycoming County, Pennsylvania, hereafter Sugar Run (Lycoming County), near an abundance of shale gas wells with known casing or cementing related violations (Figure 10). The nearest shale gas well, Harman, Lewis Unit 1H (API# 081-20292), was cited by the PA DEP for impacting at least five domestic water wells. The Harman, Lewis Unit 1H well was drilled on 3/17/2011 and hydraulically fractured on 06/2011. The Marcellus Shale was intersected at a depth of 3,272 feet (~997 meters), and the well was intermediately cased to a depth of 2,039 feet (~621 meters). The production and intermediate casings were both cemented to land surface. On 1/9/2012, the PA DEP was notified of discolored water in a water supply well near the Harman, Lewis Unit 1H gas well, invoking an investigation into the cause of discoloration and subsequent elevated methane concentrations in nearby homeowner water wells. On 2/7/2012, the PA DEP found defective cement in the annulus of the Harman, Lewis Unit 1H well based on shut-in tests (352 psi or 2.4×10^6 Pa on the $5\ 1/2 \times 95/8$ in or 14×24 cm annular space) and the presence of microannular flow paths, based on a 5000 psi (3.4×10^7 Pa) test of the 5 1/2 in (14 cm) casing. Methane was detected outside the surface casing on 5/14/2012, and on 9/20/2013, the operator of the Harman, Lewis Unit 1H well was issued a notice of violation for failing to prevent migration of gas or other fluids into groundwater. Since 4/13/2015, the PA DEP has investigated complaints as far as 9,850 feet (3,000 m) from the Harman, Lewis Unit 1H well and observed dead vegetation and soil gases with as much as 100% methane by volume in a farm field in the adjacent stream valley—Gregs Run, which is to the west of the Sugar Run watershed.

Heilweil et al. [11, 56] observed elevated dissolved methane and bubbling in the stream body of Sugar Run and elevated dissolved methane and active bubbling in an off-channel spring during field campaigns in 2013. The authors

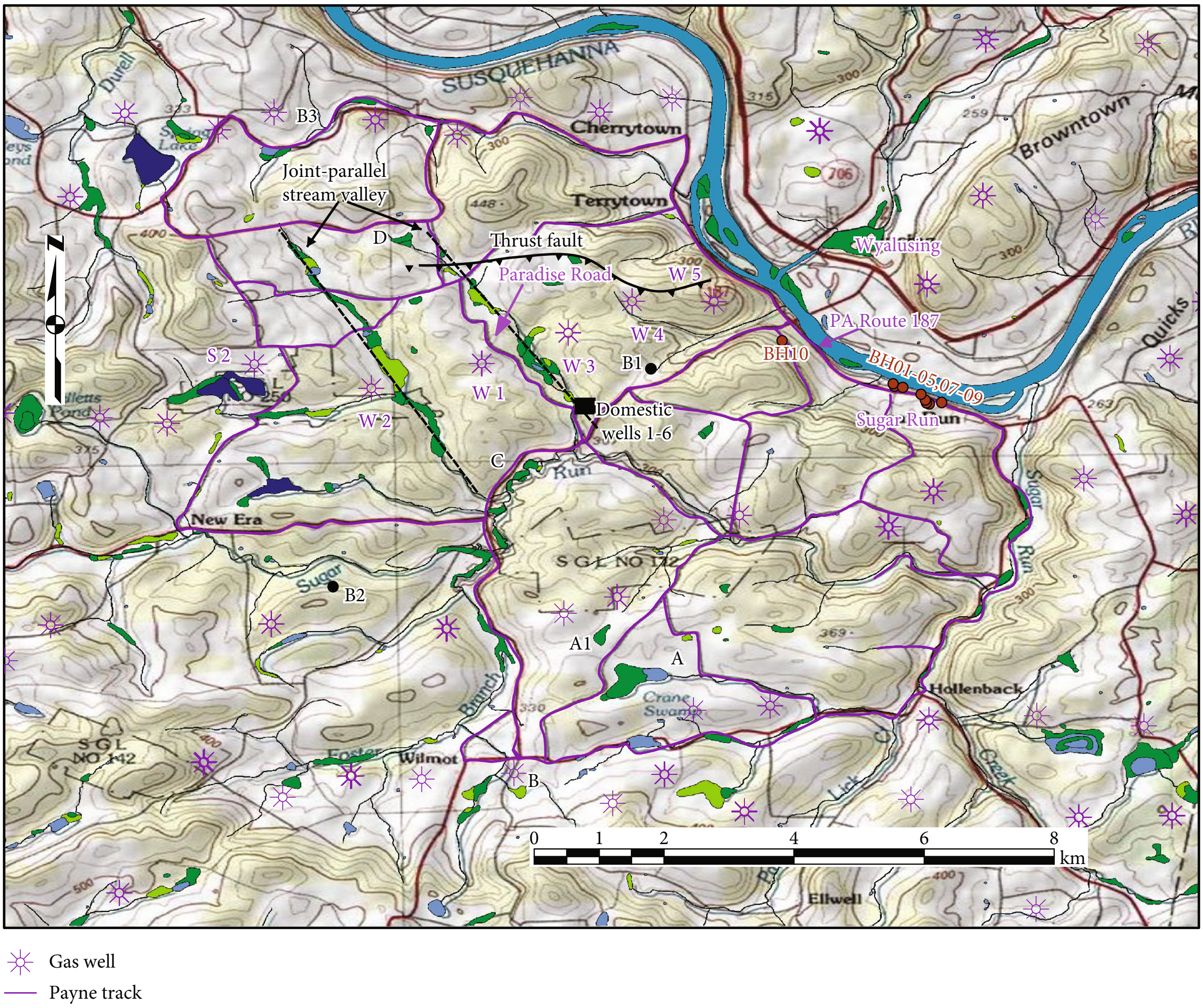

Figure 9: Topographic map with track from the 3-4 June 2013 Towanda-Wyalusing ambient air survey [14]. Sites A, A1, B, C, and D represent above background (1.9 ppm) levels (maximum 3.9 ppm at site B). Moderate (forested) and dark (emergent) green features are wetlands. Light (ponds) and dark (lakes) blue features are water bodies. W1-W5 and S2 are Welles series gas wells. Impacted domestic water wells 1-6 along Paradise Road are clustered in the black square symbol. There are two joint-parallel tributaries to Sugar Run, and a thrust fault identified from seismic data [13]. Water wells (BHX) along or near PA Route 187 were impacted, and bubbling of methane occurred in the Susquehanna River [55].

argued that isotopic compositions of carbon in methane and ethane ($\delta^{13}C$ in CH_4 and C_2H_6) from the spring were consistent with thermally mature black shales such as the Marcellus Shale. These sample locations were downstream of the Harman, Lewis Unit 1H gas well, but structurally up gradient of that well. Figure 11 provides examples of oxidation of migrated thermogenic methane in Sugar Run relative to natural methane oxidized in Meshoppen Creek. The authors suggested that because of the known methane release and a lack of correlation between methane and salinity, the elevated stream methane was best explained by the invasion of natural gas independent from brine migration rather than coupled (natural) migration of natural gas and deep brine. However, the authors did acknowledge that without baseline stream methane data, a definitive conclusion could not be reached.

Grieve et al. [52] compared stream methane and other tracers in Sugar Run (Lycoming County) to other streams with natural inputs of thermogenic CH_4. Grieve et al. [52] used multiple lines of evidence to argue that methane in Sugar Run was of anthropogenic origin. In particular, elevated methane in the stream and riparian groundwater, relatively high gas influxes to the stream channel, isotopic signatures of Marcellus gases in methane, isotopic signatures of Marcellus fluids using strontium (Sr) isotopes ($^{87}Sr/^{86}Sr$), noble gases (i.e., helium), and mass balance arguments were all used to support the claim that gas was migrating in an unnatural free gas phase.

Woda et al. [15] continued sampling at Sugar Run; however, the authors investigated the regional geology, local temporally extensive groundwater chemistry, and additional tracers (e.g., the full suite of noble gases including helium,

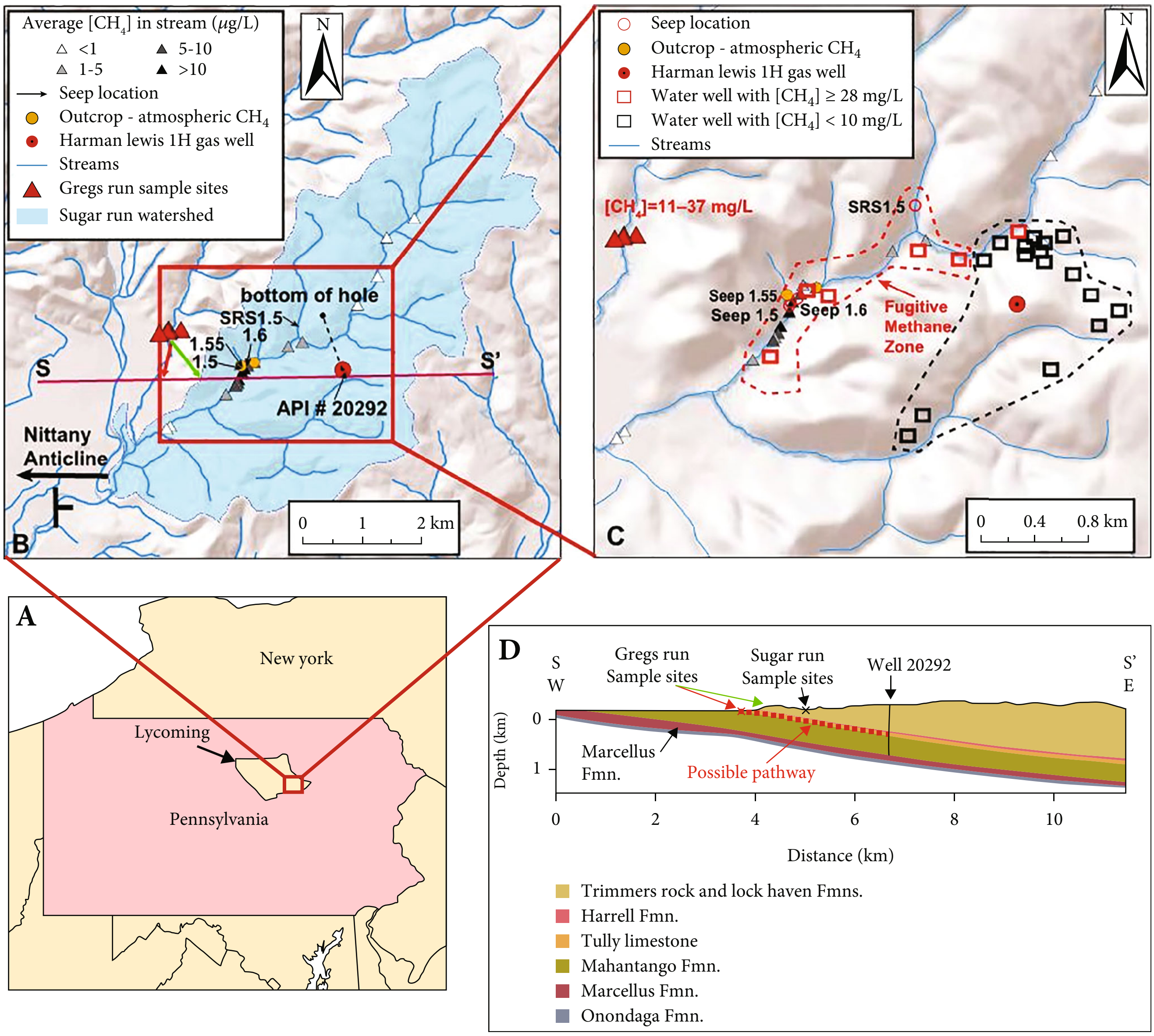

Figure 10: (A) Study area showing Lycoming County, Pennsylvania. (B) Expanded view of Sugar Run and Gregs Run sites. Shown are seep, outcrop and Harman, Lewis 1H gas well locations, and Gregs Run sample sites. (C) Expanded view of the study area showing homeowner water wells sampled and fugitive methane zone (CH4 ≥ 28 mg/L), sample locations in Sugar Run and Gregs Run, and outcrops. (D) Cross-section S-S′ defined in (B) roughly follows the plunge of the Nittany Anticlinorium to the east. Location of Gregs Run sample sites is projected along formation strike (green arrow) or along main joint direction (red arrow). One possible migration pathway (red dashed line) is up the gas wellbore, then laterally until intersecting vertical fractures connected to Sugar Run and a direct discharge to Gregs Run. Depths are measured relative to mean sea level. Fmn = formation.

neon, argon, krypton, and xenon) to determine the origin and effects of methane migration into the Sugar Run aquifer more conclusively.

Unlike previous studies, Woda et al. [15] interpreted groundwater data collected as part of the PA DEP and gas company's investigation into the alleged stray gas migration. Three homeowner water (HO4, HO5, and HO6) wells showed a clear increase in methane and ethane concentrations after completion of drilling and hydraulic fracturing in the nearest shale gas well, Harman, Lewis Unit 1H (Figure 12). One of these wells (HO4) still contained methane and ethane well above predrill values at least 7 years after the initial increase. Following the increase in hydrocarbons, a spike in iron concentration was followed by the subsequent decrease in both iron and sulfate, inferring these increases and decreases were controlled by redox reactions (Figure S13). In addition, predrill sampling of HO5 and HO6 found no ethane, while the postdrill concentrations were 0.1 to 2.5 mg/L. Water wells from the Sugar Run study region containing either high methane and high iron or high methane and high sulfate were then compared to other known impacted water wells in Northeastern Pennsylvania and a dataset of presumably unimpacted predrill water samples in Lycoming County, central Pennsylvania. Together,

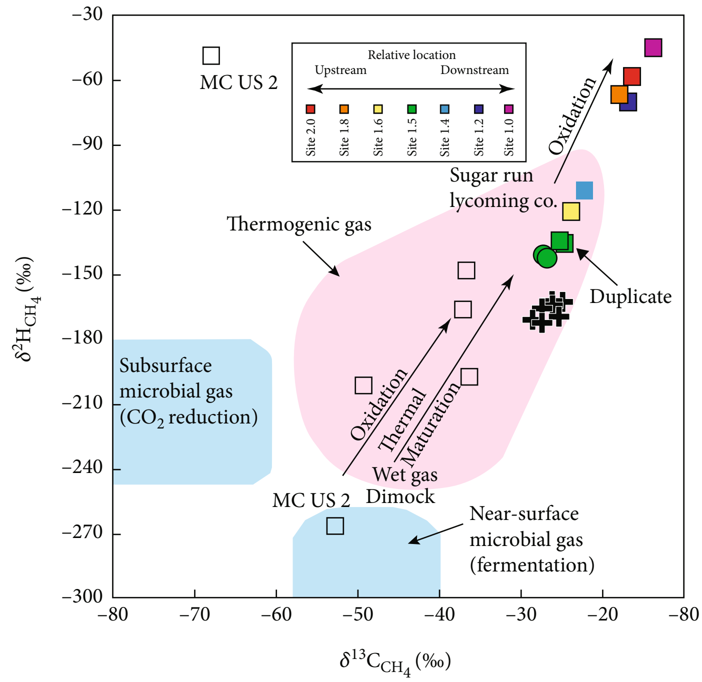

FIGURE 11: Plot of δD against δ^{13}C (per mil) for methane sampled from Sugar Run stream samples (colored squares) and groundwater near site 1.5 (green circles) [11], and Dimock Meshoppen Creek, US MC 2 (hollow squares), from the present study. Black crosses represent Marcellus gas well compositions in Lycoming County [57]. Regions of microbial and thermogenic type gases [58].

these impacted water wells stood out from the presumably unimpacted high methane and low iron or high methane and low sulfate background samples from Lycoming County.

Wen et al. [16] looked at groundwater chemistry across Pennsylvania to test for and identify water wells with "anomalous methane" (i.e., methane that had migrated from hydrocarbon wells relatively recently). Water wells from previous Sugar Run (Lycoming County) studies were used to help define geochemical tracers and their characteristics that are commonly observed in waters governed by the presence of anomalous methane versus the presence of naturally occurring methane or no methane. In addition, Wen et al. [16] considered water samples from homeowner wells in the Gregs Run watershed directly to the west of Sugar Run. Gregs Run similarly lies about 3 km updip from the Harman, Lewis Unit 1H gas well and was actively bubbling at the time of that study. Also, historic satellite images showed that dead vegetation zones can be spotted in a farm within the Gregs Run watershed in the years of 2014 and 2016 but not in the year of 2005 (note: the Harman, Lewis Unit 1H well was drilled and hydraulically fractured in early 2011), and the spotted dead vegetation zones were increasing in size over years. Dennis et al. [17] derived δ^{13}C and δD values of dissolved CH_4 in the groundwater collected from one homeowner well (HOGR-D, Figure 13) that is essentially identical to thermogenic production and annular space methane collected directly from the Harman Lewis Unit 1H gas well, suggesting that the Marcellus Shale was the source for the stray gas.

5.2. Reinterpretation of Published Data. The Marcellus Shale is about 0.8 km below Sugar Run and 0.5 km below Gregs Run and could have been intersected by near-vertical neotectonic joints. It, however, is unlikely to be a migration pathway, since the formation has a low permeability, the direction of the horizontal lateral of the Harman, Lewis Unit 1H gas well used for hydraulic fracturing is perpendicular to the migrated plume, and the expected mixing of gases did not occur at Gregs Run.

The Peischl et al. [53] 2013 research aircraft survey did not fly over the Sugar Run/Gregs Run (Lycoming County) study area (Figure S1).

5.3. Structural Geologic and Hydrogeologic Consideration. Woda et al. [15] analyzed the local geology to try to understand a possible mechanism for methane migration and the high percentage of casing-related violations in the study area. They concluded that a large anticline plunging east through the study region (with a dip of ~11 degrees), combined with the relatively shallow depth of the Marcellus Shale (~1 km at the Harman, Lewis Unit 1H well), could provide a mechanism for updip flow along bedding planes and joints to the study area to the west. Analysis of local curvature, which has been used as a proxy for fracture density, concluded that geology underneath both the study site and the Harman, Lewis Unit 1H gas well contained a much larger mean curvature than the surrounding area, supporting the theory of extensive fracturing in the region.

Indeed, reported high methane water wells impacted with recently introduced methane [15, 16] illustrate a plume with an anisotropic shape (roughly 1 km × 3 km). A simple explanation would be that methane is migrating updip along or near the crest of the regional anticline. This would limit

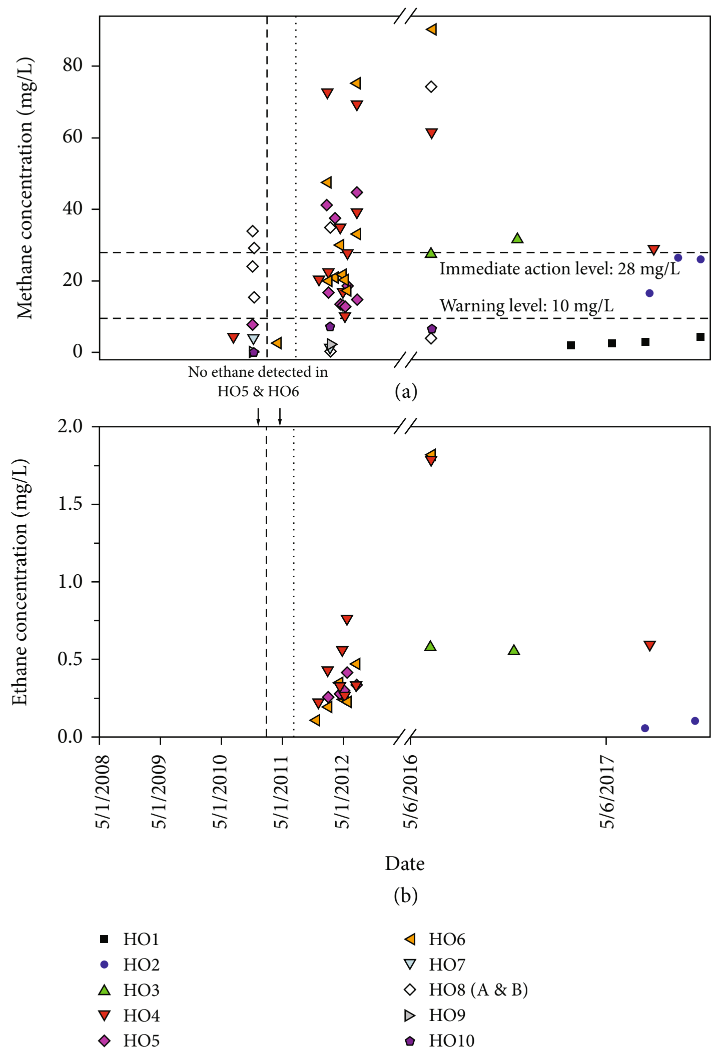

FIGURE 12: (a) A time series plot of dissolved CH_4 concentrations from homeowner (HO) water wells 1–10 sampled in the study region near Sugar Run in Lycoming County, PA. Plotted data for water well HO8 include two water wells (a, b) sampled on the same property. The vertical dashed and dotted lines indicate the spud date and hydraulic fracturing date, respectively, for gas well Harman Lewis 1H. Horizontal dashed lines represent Immediate Action and Warning Levels [59]. (b) A time series plot of dissolved C_2H_6 concentrations for wells HO6, HO5, HO4, HO3, and HO2 from data reported online (Range Resources LLC 2013), by the PA DEP (http://www.depgis.state.pa.us/emappa), or in Woda et al. [15].

the lateral distribution of the gas since the beds dip away from the axis of the anticline. Geophysical logs from the Harman, Lewis Unit 1H well were not available. The completion report for the well did not indicate that there were any gas shows, but as with the Dimock and Welles series wells, this does not mean that stray gas was not present. The Catskill Sandstone is not listed on the completion report, but using the ratios of the differences in depth between the Catskill, Tully Limestone, and Marcellus Shale at the Dimock and Sugar Run (Bradford) sites, the Catskill Sandstone in the Harman, Lewis 1H well is either very shallow or is missing, likely due to erosion. A more detailed plausible explanation is that fugitive methane leaks up the wellbore through microannuli until reaching a permeable formation such as the Tully Limestone or Mahantango Formation. It then moves updip until reaching fractures connecting to Sugar Run and its lower hydrostatic head and the immediately adjacent homeowner wells such as HO4, HO5, and HO6. This is supported with field observations where methane was detected emanating from horizontal bedding planes and fractures in outcrops alongside Sugar Run using a handheld Bascom-Turner Gas Rover methane detector (Figure S14).

The remaining methane continues updip until reaching Gregs Run and a shallower groundwater unit and lower hydrostatic head. The average Ca/Na ratio for the Gregs Run samples of 1.53 supports a shallow groundwater source. The average Ca/Na ratio for the samples taken from the Sugar Run wells HO4-6 is 0.25 and typical of a deep groundwater source. Along with the differing C-H isotopes between the Sugar Run and Gregs Run samples, this may suggest that unaltered free gas phase methane discharges directly or nearly directly to Gregs Run, while the methane in Sugar Run has to migrate through several hundred feet of overlying fractured

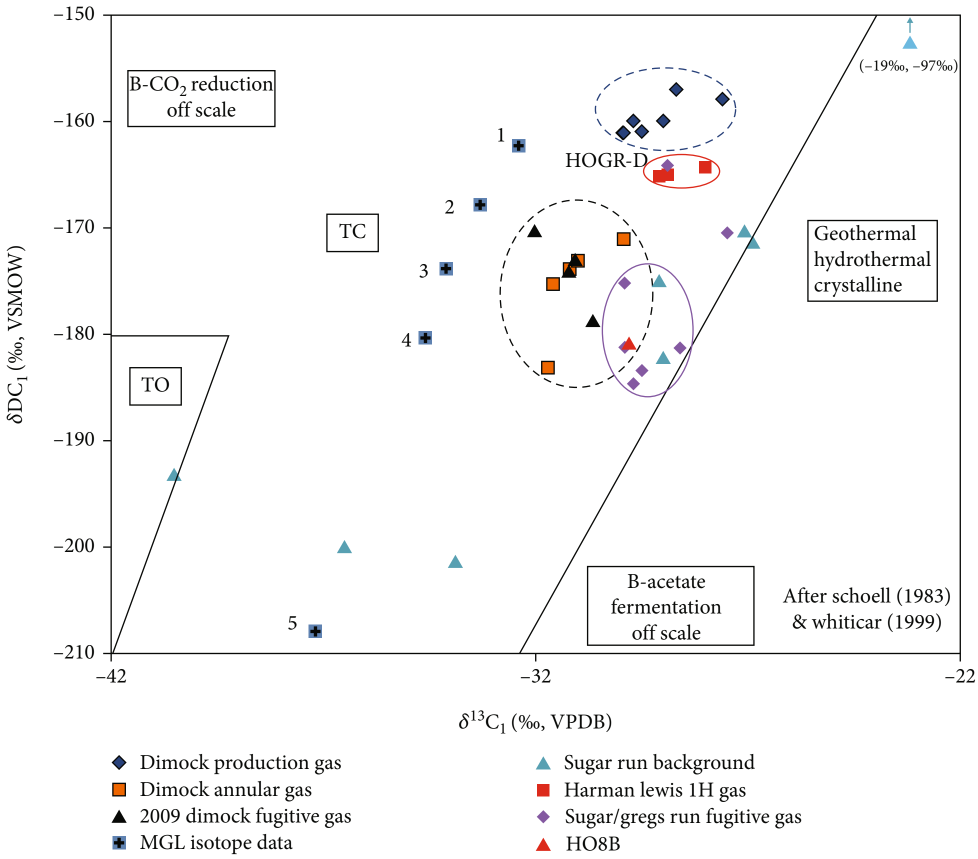

Figure 13: The Schoell diagram of methane gas samples in the Dimock, Sugar Run, and Gregs Run (HOGR-D) study areas. B: bacterial (microbial) gas; TO: oil associated thermogenic wet gas; TC: condensate associated thermogenic wet gas. Mud Gas Log (MGL) mean values from Baldassare et al. [34]: 1—Marcellus Shale; 2—Hamilton Group (Mahantango Shale); 3—Tully Limestone; 4—Geneseo Shale; 5—Brallier Formation; 6—Catskill/Lock Haven Formations. Water well HO8B had anomalous samples as explained in the text.

rock, allowing more time for mixing with lower concentrations of natural methane in shallower groundwater units. The likely migration pathway is shown in Figure 10(D).

6. Discussion

Key findings and results from the literature about the three case studies discussed in this work are listed in Table S6. A question that remains is why methane collected from homeowner wells in Sugar Run (Lycoming) has a different isotopic signature than that of the Harman, Lewis 1H natural gases (assuming these two gas samples have the same source), whereas the Sugar Run (Bradford County) and Carter Road Dimock homeowner wells had isotopic signatures similar to the annular gases (prior to remediation), and both were different from the Marcellus production gases. Another question is why the postdrill isotopes for HO8B in Sugar Run (Lycoming County), a water well with high predrill methane concentrations, are nearly identical to the homeowner well samples impacted by natural gas migration.

Two mechanisms are proposed to explain the differences between the Sugar Run (Lycoming) homeowner and annular gas isotopic signatures; one is oxidation of the migrated gases, and the other is mixing with shallower gas sources. Oxidation reduces the concentration of methane and "enriches" the gas in heavy isotopes, producing more positive (less negative) values of δDC_1 and $\delta^{13}C_1$. Examples are shown in Figure 11, where both biogenic gases in Meshoppen Creek (Dimock) and thermogenic gases in Sugar Run (Lycoming County) stream samples were oxidized. Mixing of gases would depend on the ratio of the concentrations of deep thermogenic gases and shallow biogenic gases. In Dimock, the similarity in δDC_1 and $\delta^{13}C_1$ values between methane samples collected from Carter Road homeowner wells and annular space of Marcellus gas well indicates that the dominant source of fugitive methane in the homeowner wells was annular gas (Figure 13). In Sugar Run (Lycoming County), the offset between the δDC_1 of the Harman, Lewis Unit 1H gases and that of homeowner well gases (16‰) and that of microbial gas (120‰) suggests a mixing of the two end members of methane gas in the homeowner wells at Sugar Run (Lycoming County).

One other observation of note is the composition of homeowner well water samples with low methane concentrations at Sugar Run (Lycoming County), shown by the Sugar Run background symbols in Figure 13. They are also widely scattered, but mostly lie on an approximate oxidation path originating from a shallow microbial source (i.e., about $-300‰ \geq \delta DC_1$ and $-50‰ \geq \delta^{13}C_1$), similar to the results contained in the Heilweil et al. [11] study for Sugar Run (Bradford County), indicating that those samples had been oxidized. When compared to the postdrill clustered homeowner and Harman, Lewis Unit 1H gas samples, this would indicate that those high concentrations of methane in the homeowner samples had not been oxidized.

The next question that needs to be addressed is why the pre- and postdrill methane concentrations in well HO8B are similar (assuming the nearby oil and gas production activities caused changes to groundwater and surface water chemistry), a factor used by the operator to indicate that the methane had a natural origin. As previously discussed, the isotopes of the low concentration house samples are widely scattered and likely from a shallow biogenic source. The isotopes and concentrations of HO8B indicate a deep thermogenic source, either the Marcellus Shale or a closely overlying formation. The Marcellus Shale appears to be at about the same depth (1 km) beneath well HO8B as in the Harman, Lewis Unit 1H well. With an overburden of 1 km, the maximum estimated depth of a natural joint is about 0.5 km, so it is unlikely that the Marcellus Shale is the natural source of methane in well HO8B. The isotopes for HO8B were taken after the drilling, and hydraulic fracturing of the Harman, Lewis Unit 1H well was completed. While the concentrations of that sample were like the predrill sample (30-35 mg/L), a later sample for HO8B had a much higher concentration (74 mg/L). When compared to the seasonal variations of methane concentrations in other homeowner wells (HO4, HO5, and HO6), it is possible than the early postdrill sample was an approximately coequal mixture of migrated gas and methane from a shallower thermogenic source.

Woda et al. [15] compiled and reported a dataset of 892 predrill methane measurements collected from Lycoming County from 1995 to 2012. These methane measurements range from below the detection limit ($n = 725$) to 33.91 mg/L with a mean value of 0.98 mg/L and a median of 0.02 mg/L (if assuming all below detection values are at the corresponding detection limit). Among these methane measurements, only one sample reports a high methane concentration > 28 mg/L (0.1% of all samples) while 1.7% ($n = 15$) and 3.5% ($n = 31$) of all these predrill samples present methane concentrations higher than 10 mg/L and 3 mg/L, respectively. The rarity of high methane concentration (i.e., >10 mg/L) in the Sugar Run (Lycoming County) predrill samples suggests that the high predrill methane concentrations of HO8A and HO8B are anomalous.

The impacted domestic wells at Sugar Run and Gregs Run (Lycoming County) and Sugar Run (Bradford County) are located in stream valleys. Also, 12 of the 17 impacted wells in the Dimock area are located in the Meshoppen Creek and Burdick Creek valleys. Meshoppen Creek is a joint-parallel stream, while Burdick Creek is a joint-oblique stream with possible joint directions parallel to Meshoppen Creek. Both Sugar Run streams are joint-parallel features, while Gregs Run is a joint-oblique stream. There were several gas wells in the Dimock area with high casing pressures but no evidence of fugitive gas migration impacts. Due to the low dip of the bedding planes in that area and the presence of impermeable barriers, methane that was potentially leaking from those gas wells may have migrated but remained in the subsurface.

There were clusters of δDC_1 and $\delta^{13}C_1$ isotopes in samples of highly concentrated migrated gases and a scattering of the isotopes in low concentration homeowner well samples, either in predrill samples or after gas well remediation, at Dimock and the two Sugar Run sites. The highest concentration of methane in streams occurred in Meshoppen Creek, but the C-H isotopes indicated that those samples were from a natural biogenic source that varied seasonally due to oxidation, giving the appearance of a thermogenic source. Conversely, the samples from Sugar Run (Lycoming County) were from migrated methane that had a thermogenic signature also changed by oxidation. While there were no stream samples available from Sugar Run (Bradford County), the timing of bubbling in the Susquehanna River and Sugar Run indicates that it was migrated methane.

There was no direct relationship between methane migration and stream contamination when compared to air emissions in the Dimock study area. The highest concentrations of methane in air were due to emissions from the Herb Button (Teel) compressor. Natural elevated methane levels were caused by biological processes in the Meshoppen Bog. There were only slightly elevated levels of methane in air at the Sugar Run (Bradford County) site that appear to have come from wetlands in the area. In most cases, the vehicle-mounted detectors may have been too far from the sources to detect any significant emissions, except for the impacted Paradise Road water wells and the potential gas well source of the migrated methane; however, only near background level emissions were detected at those sites. High levels of methane in air were measured in Sugar Run (Lycoming County), especially when a handheld gas monitor was set directly on rock outcrops near the stream. Where methane emissions were detected, the measurements taken with a handheld detector were more than an order of magnitude higher than those using a mobile, truck-mounted spectrometer, which were then greater than those from aircraft observations. The differences are likely due to the rapid dispersion of methane in air and proximity to the sources.

To evaluate the environmental impacts of shale gas development activities, the selection of methods, i.e., one or a combination of air emission survey, water quality measurement, and structural hydrogeologic interpretation, largely depends on the availability of time and resources, as well as the specific type of environmental impact in question. In the ideal scenario, a comprehensive study of data from all three methods will provide the most holistic evaluation of environmental impacts of shale gas development activities. Impacts to groundwater wells and streams are best determined by water quality measurements including the commonly used methane concentrations and stable C-H isotope analyses and alkane concentrations in water usually taken from gas wells, nearby domestic water wells, and streams. One problem is the potential mixing of multiple sources and anaerobic methane oxidation. Concentrations and isotopic ratios of noble gases, which are largely unaffected by microbial processes or chemical reactions with geologic substrate, can also be useful in many cases but are relatively expensive analyses. Air emissions are measured by handheld, vehicle mounted, or aerial methane detectors. This might be the best method for determining impacts to the atmosphere. However, rapid dispersion of methane in air might lead to below detection limit measurements. Stable isotope analyses are often needed to separate natural from anthropogenic sources for air contamination. A structural hydrogeologic survey will be particularly useful to determine the potential migration pathway of fugitive gas from source to the receiver. For example, in the northeast Pennsylvania cases, long sections (several thousand feet) of gas wells were open bore holes between the surface casing (Sugar Run, Bradford County) and intermediate casing (Dimock) and the production casing a few hundred feet above the production zone. The intermediate casing was set much deeper in the Sugar Run, Lycoming County, well, but the PADEP found defective cement in the annulus, based on the results of pressure testing and the presence of microannular flow paths. During our investigation, we were able to correlate through geophysical log interpretation the regionally extensive gas charged Catskill Sandstone in the Dimock area and Sugar Run (Bradford County) gas wells. As a result of about 1°-7° tilt in the bedding, the Catskill Sandstone could reach shallow enough depths to intersect measured or inferred (from geomorphological features) near-vertical neotectonic joints. With open gas well boreholes, a migration pathway could be inferred up a borehole annulus, then laterally along strike and updip in the Catskill Sandstone, intersecting vertical neotectonic joints, to finally reach water wells or streams. There were no available geophysical logs at the Sugar Run (Lycoming) gas well site; however, a previously published structural-stratigraphic cross-section and map supports a similar migration mechanism, except C-H isotope analysis indicated that there was a direct discharge of stray gas to Gregs Run, about 3 km from the gas well.

7. Conclusion

We looked for the possible factors that could control flow of fugitive natural gas from well annular spaces into the fractured Devonian formations of Northeastern Pennsylvania and how they were related to gas seepage in streams and methane air emissions. First, pressure and gas were noted within the annular spaces of wells within all three study areas. Second, impacted water wells and gas seepage locations are updip or along strike of potential source gas wells in all cases. For Sugar Run (Lycoming), structural geology analysis and measurements of atmospheric gas at fractures, within streams, along dead patches in farm fields, and water wells themselves support the migration mechanism of updip migration along fractures and bedding planes. At the Sugar Run (Bradford) site, wetlands appeared to be the source of methane emissions that were slightly above background levels. As with the Sugar Run (Lycoming) site, methane measured in water wells along Sugar Run and in the Susquehanna River supported updip migration of methane. In both cases, bedding dipped steeply (5-10°) and methane migration extended to a distance greater or equal to 3 km. At Dimock, beds dipped at a slight angle (1-2°); however, migration was still updip, but at distances less than 1 km. In all three studies, hydrocarbon movement is supported in a free gas phase, initially through bedding planes in confined units until reaching an outcrop and potentially venting to the atmosphere or intersecting vertical joint fractures at depths less than about 0.5-1 km, then to aquifers and streams. An initial lateral dispersion along strike may give the appearance of a broad plume which can change to a narrow linear feature that may extend for several kilometers. In addition, subsurface methane migration, stream methane contamination, and air emissions might not be all present or detectable around a leaky shale gas well. The presence of these three phenomena is largely controlled by local geologic and hydrogeologic conditions.

Data Availability

The data used to support the findings of this study are included within the article.

Additional Points

Article Impact Statement. Subsurface methane migration, stream methane contamination, and air emission might not be all present or detectable around a leaky shale gas well.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

The supplementary materials include 14 figures and 6 tables that provide additional information about the three sites discussed in this study. *(Supplementary Materials)*

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