

Exploring How to Use Groundwater Chemistry to Identify Migration of Methane near Shale Gas Wells in the Appalachian Basin

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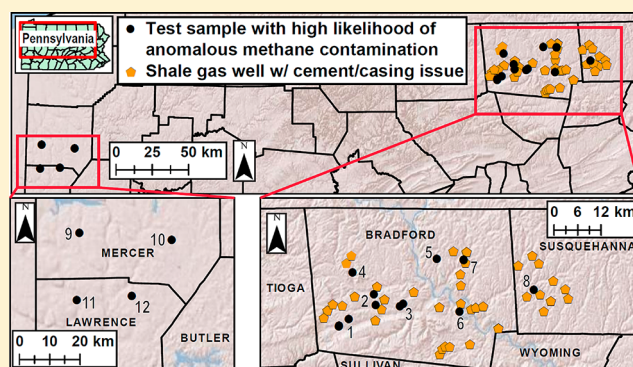
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Supporting Information

ABSTRACT: Methane (CH₄) enters waters in hydrocarbon-rich basins because of natural processes and problems related to oil and gas wells. As a redox-active greenhouse gas, CH₄ degrades water or emits to the atmosphere and contributes to climate change. To detect if methane migrated from hydrocarbon wells (i.e., anomalous methane), we examined 20 751 methane-containing groundwaters from the Upper Appalachian Basin (AB). We looked for concentrations (mg/L) that indicated AB brine salts (chloride concentrations ([Cl]) > 30; [Ca]/[Na] < 0.52) to detect natural methane, and we looked for concentrations of redox-active species ([SO₄] ≥ 6; [Fe] ≥ 0.3) to detect anomalous methane. These indicators highlight natural contamination by methane-containing brines or recent onset of microbial oxidation of methane coupled to iron- or sulfate-reduction. We hypothesized that only waters recently contaminated by methane still exhibit high iron and sulfate concentrations. Of the AB samples, 17 (0.08%) from 12 sites indicated potential contamination. All were located in areas with high densities of shale-gas or conventional oil/gas wells. In contrast, in southwestern Pennsylvania where brines are shallow and coal, oil, and gas all have been extracted extensively, no sites of recent methane migration were detectable. Such indicators may help screen for contamination in some areas even without predrill measurements.



INTRODUCTION

The ability to extract natural gas from “tight” reservoirs using horizontal drilling and hydraulic fracturing has revolutionized the world economy in the last two decades. For example, drilling and hydraulic fracturing of the Marcellus shale over the past 15 years has returned Pennsylvania (PA), a state with a long history of conventional oil/gas development as well as coal mining (Figure S1), back to one of the leading areas for hydrocarbon production in the U.S.A.¹ Like other hydrocarbon-rich regions, however, the recovery of shale gas has sometimes contaminated waters in the Marcellus shale area,^{2–5} and the well-publicized response of the public to these problems has created resistance to such hydrocarbon extraction in some locations around the world.

The best example of a contaminant that has created public pushback is methane (CH₄), the main constituent of natural gas. Methane has been measured in homeowner’s water wells at concentrations that can sometimes be ignited.⁶ Methane is also the most common contaminant documented during Marcellus development since 2004 by the Pennsylvania Department of Environmental Protection (PA DEP), the regulator of oil/gas production in PA.⁷ At the same time, many researchers have pointed out that most methane in PA

groundwaters is natural.^{8–11} Recently, a set of chemical indicators were identified that can accompany the new release of methane into an aquifer, perhaps allowing a distinction between new methane and long-standing natural methane.⁵ Woda et al.⁵ documented that these indicators successfully diagnosed new methane in groundwater samples from four sites that the U.S. Environmental Protection Agency (US EPA) had deemed as contaminated by oil and gas development and showed evidence of recent invasion into the sites based on the chemical indicators.¹² In this paper, we extend that effort by looking for evidence of these indicators in a much larger data set of groundwater quality in the Appalachian Basin (AB). We hypothesized that most of the methane in the AB waters is natural and that only a few sites should show chemical evidence of new methane. The data set allowed us to investigate the testing protocol in a state where the long complex history of energy extraction activities could have left behind myriad sites of contamination (Figure 1 and S1). In

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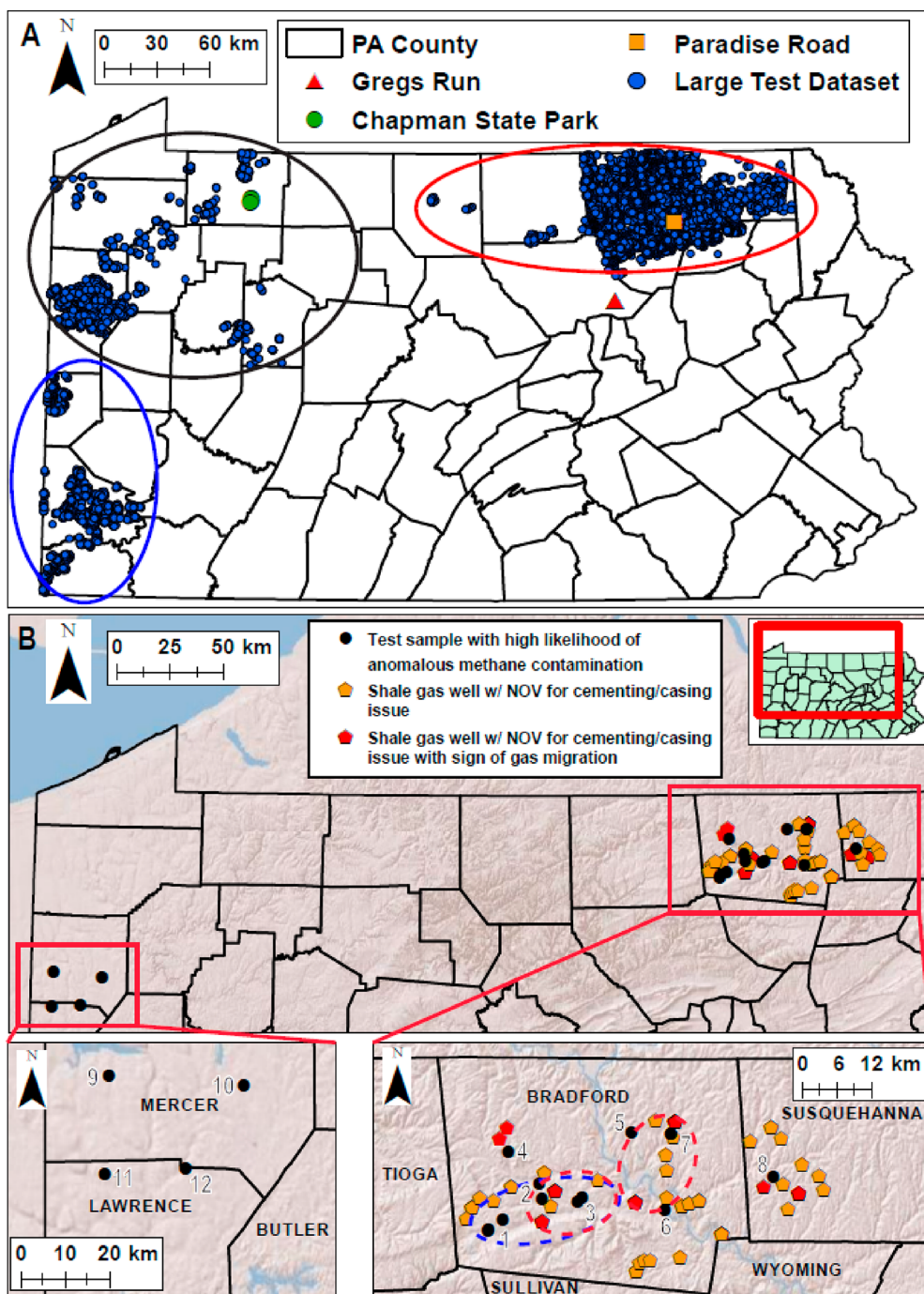


Figure 1. (A) Location of sites where waters were sampled as part of the validation ($n = 14$) and test (blue dots; $n = 20,751$) data sets. Test data are grouped into three regions: NE PA (red ellipse), SW PA (blue ellipse), and NW PA (black ellipse). The three regional data sets allow investigation of an area with a high density of unconventional gas wells (NE PA), a high density of conventional gas wells (NW PA), and a high density of conventional, unconventional, and coal mining (SW PA). Colored symbols show locations of validation data collected from three putatively contaminated sites in PA that were either compiled from other literature^{47–49} or collected and analyzed in this study. (B) Location of 17 water well samples from 12 sites (numbered from 1 to 12 in this figure; see also Table S5) that are type 4 ($n = 10$) and type 5 ($n = 7$) identified in the test data set. Type 4 and 5 samples are shown together as black dots. Areas circled with dashed red curves represent previously identified hotspots^{16,50,51} where methane was inferred to be potentially migrating from a few nearby unconventional gas wells where uncased or uncemented intervals of the boreholes may cross faults. The dashed blue curve coincides with the location of the Bridge Street and Towanda faults and Towanda anticline that may act as a natural pathway of methane into shallow aquifers.¹⁶

this respect, Pennsylvania is used as a testbed to yield insight for other areas of the country with different characteristics of hydrocarbon extraction.

We refer to methane that migrates from leaking gas wells as “anomalous” methane. Human-induced methane migration can

occur in settings where gas wells have experienced casing failures or blowouts or where wells lack adequate casing or cement across gas-producing zones. Landfill sites can also leak methane¹³ but we are not considering that phenomenon here. Identification of sites of leaking methane is important because

methane can cause deleterious effects in the groundwater such as the release of metals when concentrations increase rapidly in an aquifer.⁵ Methane can also degas, resulting in explosion hazards in confined areas such as basements.¹⁴ In addition, if it is released to the atmosphere, methane is a potent greenhouse gas that contributes to climate change.¹⁵

The identification of anomalous methane is complicated because of the following: (1) the presence of natural methane in shallow groundwater is common in many areas including the Marcellus shale footprint^{3,8–11,16,17} and (2) methane from natural and anthropogenic sources is often hard to geochemically distinguish even using isotopic measurements.¹⁸ Thus, the identification of groundwater that has been impacted by anomalous methane largely relies on a comparison of water quality data collected before (i.e., baseline or predrill data) and after oil/gas wells were drilled or completed. However, such baseline data have not always been collected, or if samples were collected, the data are often not accessible to the public.⁶

Woda et al.⁵ recognized that the deleterious chemical effects that they observed to accompany anomalous methane in groundwater samples could also be used to identify waters that had been recently contaminated by methane. Their work derived from investigating an aquifer and a stream (Sugar Run) in Lycoming County, PA that was putatively contaminated by nearby shale gas drilling.^{19,20} After identifying a few chemical indicators that changed most likely because of the invasion of anomalous methane into the aquifer, Woda et al.⁵ demonstrated that the indicators were also observed in some groundwater samples from other areas identified by regulators and US EPA as impacted by anomalous methane related to natural gas development. Similar evolution in water chemistry with respect to the same indicators was also identified in several other locations as well.^{5,12,21–25}

Specifically, Woda et al.⁵ observed that the presence of new methane in the contaminated aquifers was sometimes accompanied by an increase in dissolved iron for a transient period, and at the same time or shortly thereafter, a decrease in sulfate concentration. They inferred that this showed the onset of anaerobic oxidation of methane (AOM) coupled to iron reduction and, subsequently, coupled to sulfate reduction. They also pointed out that salt-related geochemical parameters were useful in distinguishing anomalous ($[Cl] \leq 30$ mg/L, $[Ca]/[Na] \geq 0.52$) from natural methane ($[Cl] > 30$ mg/L, $[Ca]/[Na] < 0.52$). These indicators documented salt concentrations that often accompany natural methane in the AB when AB brines (ABB) move upward with dissolved methane.^{4,5,20,26–28}

The threshold values identified by Woda et al.⁵ were derived from observations of a data set of groundwater from Lycoming County in central PA. They assumed that this data set of groundwater sampled predrill represented background, equilibrated concentrations that could be used as threshold indicators of anomalous methane.⁵ They tested the inferred background values by comparing to 5 sites that had been deemed contaminated by regulators. In this paper, we again explore the approach⁵ to identify groundwaters with anomalous methane versus those with naturally occurring methane in the AB where the Marcellus shale is located. We study waters with methane concentrations above 10 mg/L and seek to identify if they are likely to contain natural or anomalous methane. That concentration was used as a screening threshold because it has been identified as a level of concern in drinking waters and may thus need immediate

action.^{14,16,27,29–32} While waters with lower methane concentrations could still contain anomalous methane, such waters would not only be harder to identify, but would also not necessarily require immediate remediation. Furthermore, many researchers have shown that groundwater sampling for methane is difficult when methane concentrations are higher than about 10 mg/L because of ebullition of gas upon sampling,³³ so choosing a higher concentration as a screening level may not be defensible.

The specific goal of the research reported in this paper is to test how often the threshold indicators identified by Woda et al. (2018)⁵ are exceeded in a larger groundwater data set from the AB. We hypothesized that if these threshold indicators are indeed identifying methane contamination then we do not expect to see them exceeded frequently. We made that assumption because the rate of leakage of methane from shale gas wells reported by the PA regulator is very low, i.e., 0.24 to 3%, and each problematic well that is identified is then treated to solve the leak to the specification of the regulator.^{2,3} Where sites were identified by this screening approach to show indicators of anomalous methane, we investigated to see if there might be other evidence of contamination.

Ultimately, this testing protocol was designed to screen and to preliminarily diagnose groundwaters impacted by anomalous methane. We applied this protocol on a newly available, large data set of groundwater quality closely related to oil/gas development in PA (Figure 1 and S1). Most of the data in this study are released here to the public for the first time. The distribution of the data allowed us to use the geochemical tests to search for anomalous methane not only in areas of unconventional oil/gas development but also in areas with conventional oil/gas development and coal mining. The study thus also investigates whether the geochemical tests might be useful in other areas with varying histories of hydrocarbon extraction. In the following sections, we first examine the fundamentals behind the geochemical tests. We then exemplify the tests by using them in three sites that have been identified as contaminated. Finally, we apply the tests to the large groundwater data set.

■ GEOCHEMICAL RATIONALE FOR THE TESTING PROTOCOL

Salt-Related Tests for Methane Associated with ABB.

Deep brines are found at approximately 250 m depth in the AB³⁴ and are often accompanied by dissolved methane. These AB brines typically are enriched in Na and Cl.³⁵ In contrast, shallow aquifers in the AB, typically dominated by fresh recharge, are often low in concentration with respect to most brine components but relatively enriched in Ca and SO₄.^{17,36} However, solutes with the brine salt signature are occasionally found in shallow aquifers at low concentrations. Two hypotheses have been described for why this is naturally observed in PA: (1) deep brine may be migrating now into shallow aquifers along natural faults, fractures, or bedding pathways unrelated to drilling or (2) deep brine that previously migrated into shallow aquifers may have been partially but not entirely flushed out by circulating meteoric water.^{17,28,37,38} Either way, shallow groundwaters in the AB can be characterized as either Ca-rich (high Ca/Na mass ratio) waters that indicate little contribution of deep brine salts, or Na-rich (low Ca/Na mass ratio) waters that suggest some small contribution of deep brine. The latter waters are often found in valley areas³⁶ in PA.

These natural waters with brine salt signature in the AB are often associated with natural thermogenic methane.^{2,18,28,37,39,40} Thus, when methane is found as a dissolved component in ABB-contaminated shallow groundwater (i.e., low Ca/Na ratio and high Cl concentration), the methane is considered here to be likely of natural origin. Given these observations, Woda et al. (2018)⁵ used the large data set from one county in central PA to come up with a screening level and suggested that when waters containing methane above 10 mg/L also show a [Ca]/[Na] mass ratio ≥ 0.52 and [Cl] ≤ 30 mg/L, the methane is more likely to be anomalous methane. Here, we hypothesize elevated methane in groundwaters is mostly of thermogenic origin.

Redox Tests for Transient Dis-equilibrium. As methane enters an oxygenated aquifer, oxidation of the methane can consume dissolved oxygen. Once oxygen is depleted, AOM-bacteria can oxidize methane by coupling electron transfer to iron reduction, transiently causing a rise in ferrous iron concentration. Eventually, when the iron oxide is locally depleted or a surface coating of ferrous iron armors the ferric oxide,⁴¹ then sulfate reducers can outcompete iron reducers in oxidizing methane. The production of hydrogen sulfide is then accompanied by precipitation of metal sulfides so that iron concentrations that were transiently high drop to low levels in equilibrium with precipitated iron sulfide.^{23,41–43} Eventually, after a lag period, O₂, Fe, and SO₄ are all low in concentration while CH₄ concentration is high.

These considerations imply that, if the duration of time for the methane-water system is long enough to achieve equilibrium with respect to aquifer mineralogy and a high partial pressure of methane, the water will become not only enriched in methane but also depleted in aqueous O₂, Fe, and SO₄. In contrast, when methane newly invades into an aquifer, groundwater can be maintained out of equilibrium with respect to these species for a lag period because of the slow kinetics of these redox processes.⁴¹ Based on a small data set, Woda et al. (2018)⁵ suggested that the lag time for one aquifer for the iron and sulfate indicators was at least 7 months. This conceptual model requires that the methane influx be steady enough to maintain the new equilibrium. If the methane influx is seasonal such that O₂ and CH₄ alternately sweep the aquifer, equilibrium may never be obtained and the aquifer might switch back and forth between two Eh levels seasonally.

Geochemical Modeling of Redox Equilibration. These ideas about how water chemistry evolves during a methane invasion are exemplified here in a simple model run as a series of equilibrium calculations (with Geochemist's Workbench version 9.0 and thermo.dat). We simulated the impact of anomalous methane on groundwater chemistry averaged from the large groundwater data set (Table S1a, described further in the Materials and Methods section). All waters in the data set that contain high methane (≥ 10 mg/L), elevated sulfate (≥ 6 mg/L), and elevated iron (≥ 0.3 mg/L) concentrations were used to calculate an average composition. Equilibrium was then calculated for this composition in the presence of excess goethite, and then the partial pressure of methane was increased in the simulation from 1×10^{-6} to 1 atm (Figure S2). Simulations with hematite (not shown) differed by less than 5%. Given that the reduction of iron usually occurs before sulfate reduction in aquifers, the sulfur redox pair (HS⁻/SO₄) was not allowed to equilibrate until methane concentrations reached ~ 8 mg/L. Supersaturated minerals were allowed to precipitate. This geochemical model is discussed in detail in

the SI. The intent of the simulation is to explore equilibrium concentrations that represent the boundary conditions for aquifers with methane: micro-organisms catalyze reactions that are out of equilibrium and can maintain open systems close to equilibrium.

As shown in Figure S2, the values of [Fe²⁺] were observed to be equal to ~ 0.3 mg/L at pCH₄ = 10^{-4} atm (0.005 CH₄ mg/L) and [Fe²⁺] increased to values as high as 10 mg/L as they equilibrated with methane, as long as sulfate was not reduced to sulfide. This is roughly consistent with the highest iron concentrations reported in homeowner wells (3 mg/L) or in groundwater seeps (17 mg/L) in Sugar Run valley where anomalous methane is thought to have been present over 8 years up to this year.⁵ Once the sulfide concentration increases in the simulation by equilibration with CH₄ (i.e., once the sulfur redox couple is allowed to equilibrate), pyrite precipitates, depressing the concentration of Fe²⁺. The extent of drop in Fe²⁺ is controlled to some extent by how much sulfur is brought into the system in the water. This attribute was explored in another model described in the next paragraph.

To simulate the intrusion of new methane into groundwater and to observe the temporal change of groundwater chemistry in the presence of iron and sulfate reducing bacteria, we also explored a kinetic simulation for a well-mixed batch reactor model using CrunchFlow⁴⁴ for baseline groundwater chemistry from one impacted homeowner well (HO4) in Sugar Run⁵ (details in the SI). Two models were run for different initial sulfate concentrations: one with 0.0002 mol L⁻¹ (i.e., the measured sulfate concentration in the baseline chemistry from site HO4) and the other with 0.002 mol L⁻¹ (i.e., $10 \times$ the baseline value at site HO4). Modeling results are presented in Figure S3. We observe that sulfate concentration decreases as methane is oxidized and sulfide is formed (Figure S3A and S3B). Sulfide and iron concentrations increase and then decrease due to precipitation of FeS (am). The initial increase in Fe concentration is attributed to the reduction of ferric oxide to more soluble Fe(II) in the absence of reduced sulfur species while the subsequent decline is attributed to the eventual precipitation of iron-sulfide as sulfate is reduced to sulfide.⁴⁵ When we run the model with the increased initial sulfate concentration of 0.002 mol/L (Figure S3C and S3D), the decline of iron and sulfate concentrations occurs more rapidly (earlier) and the volume of the precipitated FeS (am) increases more rapidly. The differences between modeling results using different initial sulfate concentration is because of limitations in sulfate availability. With a higher concentration of initial sulfate, dissolved iron decreases earlier. In other words, the length of the transient period of high Fe concentration and elevated SO₄ concentration depends strongly on the relative concentrations of electron donors and acceptors which in turn depends upon the methane leak rate and the groundwater flow velocity, both of which affect the methane concentration, and the initial chemistry in aqueous and solid phases.⁴¹ Since most shallow aquifers may have abundant iron oxide minerals, the most pertinent variable may be the sulfate concentration in groundwater.

Applying the Geochemical Protocol. Woda et al.⁵ proposed that when groundwaters with [CH₄] ≥ 10 mg/L violated certain thresholds with respect to four parameters, the waters deserved further investigation to determine if they contain anomalous methane (threshold values shown in parentheses): chloride (≤ 30 mg/L), Ca/Na mass ratio

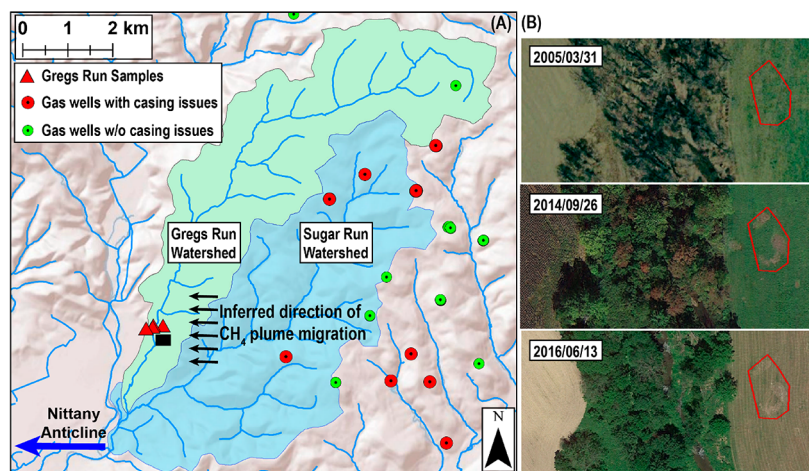


Figure 2. (A) Location of five Gregs Run samples (red triangles). Four groundwater samples were derived from the PA DEP database⁴⁹ and one groundwater sample was collected and analyzed in this study (Table S4). All of these five samples were collected from homeowner water wells. Watersheds for Sugar Run and Gregs Run are indicated by areas shaded in light blue and light green, respectively. The small black rectangle indicates a small zone in a farm field with dead vegetation where methane was detected in the soil gas.^{5,53} Woda et al.⁵ inferred that the methane plume identified under Sugar Run prior to 2018 might have migrated updip and westward into Sugar Run from leaking shale gas well(s) because of the local geologic structure, i.e., the orientation of the Nittany Anticline shown with a blue arrow pointing updip. The circles indicate shale gas well locations and the colors are related to casing issues identified by the state regulator, i.e., PA DEP, between 2008 and 2012. In most wells, the problems are thought to have been rectified. (B) Satellite images of the dead vegetation zone within the Gregs Run watershed in the years of 2005, 2014, and 2016. These images were accessed and downloaded from Google Earth on 2019/01/03. The dead vegetation zone has grown in size based on homeowner reports in the area and satellite images from different years as shown in panel (B).

(≥ 0.52), sulfate (≥ 6 mg/L), and iron (≥ 0.3 mg/L). For example, Woda et al.⁵ argued that a water with 12 mg/L methane, 20 mg/L Cl, 0.8 mass ratio of Cl/Na, 10 mg/L sulfate, and 1 mg/L iron would likely contain anomalous methane.

We investigate this here for a much larger data set by defining five water types: type 1 waters have low methane concentrations (i.e., < 10 mg/L); type 2 waters have high methane (i.e., ≥ 10 mg/L) and geochemical indicators suggesting they contain salts from ABB (i.e., Cl > 30 mg/L or Ca/Na < 0.52); type 3 waters have little indication of brine salt addition (i.e., Cl ≤ 30 mg/L and Ca/Na ≥ 0.52) and have high methane and appear to be equilibrated with respect to SO₄ concentrations (i.e., < 6 mg/L); type 4 freshwaters have high methane and appear dis-equilibrated with respect to SO₄ concentrations (i.e., ≥ 6 mg/L); and type 5 freshwaters have high methane with dis-equilibrated SO₄ concentrations (i.e., ≥ 6 mg/L) and evidence of transiently high Fe (i.e., ≥ 0.3 mg/L).

In the following sections, we demonstrate implementation of the protocol through analysis of a “validation data set” compiled from three putatively impacted sites (see also SI) that were not previously discussed by Woda et al. (2018).⁵ Second, we test the geochemical framework on a very large data set of groundwater quality, i.e., the “test data set”, to test the hypothesis that very few waters collected in predrill reconnaissance studies are indicated by the protocol as having been newly invaded by anomalous methane.

MATERIALS AND METHODS

Data described in this section include both validation and test data, for which we report six geochemical analytes including dissolved methane, Cl, Na, Ca, Fe, and SO₄. All groundwater samples were analyzed by accredited laboratories and details of sampling techniques and laboratory analyses have been described previously.^{10,16,30,46–51} Here, the terms “validation”

and “test” refer to the two steps in the proposed testing protocol that we used to identify groundwaters containing anomalous methane, and both are described below.

The validation data set includes water quality data ($n = 14$) collected from three presumably contaminated sites in PA including Gregs Run in Lycoming County,⁴⁹ Paradise Road in Bradford County,⁴⁷ and Chapman State Park in Warren County⁴⁸ (see Figure 1; Table S2 for the provenance of these data). We use these data as derived from contaminated sites to further validate the proposed testing protocol.

Test data include groundwater quality data ($n = 22,652$; only $n = 20,751$ samples have complete record of measurements)⁴⁶ collected by private consultants hired by oil and gas companies from sites near oil/gas wells in PA. These data were submitted to PA DEP and then shared with us. We cleaned, checked, and organized these test data. Test data are grouped into three subsets based on their location and proximity to different types of hydrocarbon extraction in the three areas: northeastern (NE), northwestern (NW), and southwestern (SW) PA (Tables S2 and S3 and Figure 1). Data values below reporting limit (RL) were assigned the associated RL.

The NE PA subset covers six counties including Bradford, Susquehanna, Wyoming, Sullivan, Tioga, and Potter counties, and represents one of the two most heavily drilled and hydraulically fractured areas in the AB. Within these six counties, the densities of unconventional and conventional wells are 0.32 and 0.17 per km², respectively, while only 0.01% of the area in NE PA are devoted to coal mining (Table S3). The NW PA subset spans 9 counties including Erie, Crawford, Mercer, Lawrence, Butler, Venango, Warren, Clarion, and Jefferson, while the SW PA subset only covers Beaver, Washington, and Greene counties (Table S2). NW PA has experienced minimal development of unconventional (shale) gas (0.05 per km²; Table S3) but was the center of the earliest known commercial oil well drilling (in the year of 1859) in the U.S. From the mid-1800s until today, NW PA has been an area

of intensive conventional oil/gas development (3.01 wells per km²; Table S3). SW PA differs from the other two regions because it is an area of both heavy unconventional gas development (0.58 per km²; Table S3) and coal mining where 35.12% of the area is devoted to coal mines (Table S3). Bradford, Mercer, and Washington counties, as the counties where most groundwater samples are located for the three regions, have 5%, 12.4%, and 14.9% of land categorized as “urban developed”, respectively.

The vast majority of groundwater samples in the test data set were collected after 2007 during the period of intense shale gas development in PA with the exception of a few samples ($n = 3187$) in the NW PA subset. A subset of the NE PA data ($n = 11156$) were discussed in a previous study¹⁶ where no evidence was found that indicated contamination for the majority of sites: only a few sites were highlighted as possibly contaminated by leaked methane. In that study, a few analytes showed evidence of possible improvement in water quality between the 1980s and the 2000s. A subset of the NW PA samples were also previously evaluated by Wen et al.³⁰ ($n = 1,863$). They found a slight but statistically significant increase in concentrations of some solutes (e.g., Cl) in groundwaters in central Mercer County since the 1980s. The rest of the test data are newly released here (<https://doi.org/10.26208/8ag3-b743>) and in the Shale Network database.⁴⁶

RESULTS AND DISCUSSION

Validation Data Set. In this section, we examine the approach of Woda et al. (2018)⁵ by using it for three new PA sites that are reputed to have been contaminated. In the previous work, Woda et al.⁵ compared groundwater quality data collected from five presumably contaminated sites in northcentral and northeastern PA^{5,12} to baseline water quality data ($n = 967$) from Lycoming County, PA.^{5,46} Of 33 groundwater samples reported by Woda et al.⁵ from several sites in the Sugar Run valley that were thought to be impacted by anomalous methane, 32 of 32 had $[\text{CH}_4] > 10$ mg/L, 18 of 18 had $[\text{Cl}] < 30$ mg/L, 0 of 19 had $[\text{Ca}]/[\text{Na}] > 0.52$, 12 of 20 had $[\text{SO}_4] > 6$ mg/L, and 8 of 21 had $[\text{Fe}] > 0.3$ mg/L. None of the waters displayed all the indicators. Below, we apply this same screening approach to the three new putatively contaminated sites (i.e., Gregs Run, Paradise Road, and Chapman State Park).

Only the results from Gregs Run are explicitly discussed here (results for Chapman State Park and Paradise Road are discussed further in SI). Gregs Run is a small stream valley that lies contiguous to and just west of the Sugar Run valley (Figure 2). Sugar Run is apparently impacted by anomalous methane that may be continuing to migrate from nearby shale gas well(s).^{5,19,20,52} Woda et al.⁵ and Heilweil et al.¹⁹ suggested that leakage may have started east of Sugar Run since 2011 and concluded that the observed high methane concentrations in groundwaters collected within the Sugar Run watershed were caused by updip and westward migration of a methane plume. Consistent with ongoing migration of the methane plume westward as described in the original publication,⁵ gas emissions have recently been noted in the neighboring valley of Gregs Run.

In this study, five groundwater samples (all collected from homeowner water wells) from Gregs Run watershed were either collected and analyzed by our team or compiled from the online database of the state regulator.⁴⁹ Four out of these five Gregs Run samples are categorized as type 4 or type 5

(Table S4) indicating the coexistence of methane concentrations >10 mg/L, and $\text{SO}_4 > 6$ mg/L, and/or $\text{Fe} > 0.3$ mg/L in fresh groundwater. The type 4 or type 5 categorization is considered consistent with anomalous methane.

The identification of type 4 and 5 waters in this site that has presumably been impacted by anomalous methane is consistent with other indications of the timing of methane migration. Specifically, satellite images show the appearance of zones of dead vegetation in farm fields at Gregs Run (Figure 2B) in 2014 and these dead zones were not observed in 2005. In addition, homeowners similarly report that the onset of the dead zones was recent. PA DEP inspections⁵³ also reported dead zones in farm fields within the Gregs Run watershed in 2015 and stated that soil gas in these dead zones contained 100% methane. Field observations and communication with the homeowner helped exclude the possibility of pests, disease, and/or herbicide usage that might cause the zones of dead vegetation. The presence of methane in soil gas was therefore inferred to have lowered the level of soil gas oxygen, leading to vegetation death.⁵⁴ In seven letters that were issued in early 2019 by PA DEP⁷ to homeowners in Gregs Run and Sugar Run area, PA DEP determined that these homeowners' waters were contaminated by nearby shale gas development. All of these letters noted the “surface expression” of gas as shown in Figure 2B in one farm in the Greg Run watershed.

When we combine the previous results from Woda et al.⁵ with the results for the three new sites discussed here (i.e., Gregs Run, Chapman, Paradise Road), we see that our proposed protocol is effective in identifying presumably impacted sites. Type 4 and 5 waters defined by the protocol are considered the most likely sites to be contaminated by anomalous methane. In the next section, we screen the large data set of AB groundwater quality from across PA, which we call the test data set, to look for additional sites that are likely to have anomalous methane.

Test Data Set. We applied the testing approach to a large compilation of water quality data across the upper AB in PA that included data sets from NE PA, NW PA, and SW PA (Figure 1). The goal was to identify previously unknown locations of anomalous methane contamination and to explore the distribution of locations identified by the protocol within regions of conventional and unconventional oil/gas development as well as regions of coal mining. Our hypothesis was that a very small number of sites would show the chemistry indicating anomalous methane.

Of all groundwater samples ($n = 20751$), 418 samples (2.0%) reported methane concentration above 10 mg/L. Among the high methane samples, the numbers of samples showing low Cl concentration (<30 mg/L) or high Ca/Na ratio are 141 and 103, respectively. Only 79 high methane samples show both low Cl concentration and a high Ca/Na ratio, as expected if they contained little evidence of brine salt signature. Among the high methane samples, 94 samples report sulfate ≥ 6 mg/L while 162 samples show iron ≥ 0.3 mg/L. Only 33 samples show both elevated sulfate and iron concentrations. For these results, 0.08% (17/20,751) were characterized as either type 4 ($n = 10$) or type 5 ($n = 7$) samples (Table S5). This number of identified sites is roughly consistent with the estimate that between 0.24 and 3% of shale gas wells have methane migration issues.^{2,3} Nonetheless, we have no way to determine if the identified sites were affected by anomalous methane. In the next sections, we inspect the data for different regions to both explore areas impacted by

different hydrocarbon extraction techniques and to seek evidence that some of the screened sites were contaminated.

The 17 groundwater samples that were identified as Type 4 or 5 were grouped into 12 sites (i.e., sites 1 to 12 in Figure 1). Specifically, if water samples were located within 5 km from each other they were treated as one “site”. The time period over which the 17 waters were sampled ranged from 1/16/1995 to 11/12/2012 (Table S5). Below we cross-check these water samples with inspection reports from the PA DEP database and previous research to ascertain if it is likely that the detected sites have been impacted by anomalous methane.

High Unconventional Well Density (NE PA). The majority of the NE PA samples are in Bradford and Susquehanna counties (Figure 1). Bradford and Susquehanna are the counties in PA with the second ($n = 1385$) and third ($n = 1384$) most unconventional wells drilled, respectively, and are only behind Washington County ($n = 1588$; Table S3).⁵⁵ Only 66 and 9 conventional gas wells have been drilled in Bradford and Susquehanna, respectively.⁵⁵

A total of 13 groundwater samples (including seven type 4 and six type 5 samples) from eight sites are found in these two counties: 12 samples from sites 1–7 in Bradford and one from site 8 in Susquehanna (Table S5; Figure 1). The water quality data set we have investigated is typically referred to as “pre-drill” data because the samples are collected before drilling a new well. However, given the large number of oil/gas wells in PA and the history of mineral extraction in the state, each of these water samples was collected in an area with many previously drilled wells. An investigation could ascertain if the sites are still impacted, and if so, could identify the input source and pathway of the methane. Such work is beyond the scope of this study; however, an active study of groundwater is ongoing in this area.⁵⁶ Nonetheless, below we provide several lines of evidence supporting the hypothesis that these sites might have been recently impacted by anomalous methane.

These eight sites in NE PA are located in areas either previously identified^{16,50,51} as likely to be contaminated by gas leaking from nearby unconventional wells using spatially resolved statistical techniques (sites 1–3 and 5–7), or surrounded by unconventional wells with cementing/casing violations according to PA DEP databases (sites 1–8).^{55,57} First we discuss the evidence from spatial statistical approaches. Some of the identified waters (sites 1–3 and 5–7) are located in two hotspots (i.e., red curves in Figure 1) identified by Wen et al.¹⁶ where elevated methane in groundwater cannot be attributed to natural sources related to faults or anticlines. These geological features were identified in that work to correlate with zones of high-methane groundwater that are often natural and geologically controlled (i.e., blue curves in Figure 1). Wen et al.¹⁶ assumed that high concentrations of methane in zones near faults and anticlines were always derived from natural sources when no evidence suggested otherwise. However, our refined geochemical protocol points out that seven samples at sites 1–3 are type 4 or 5 water show evidence of anomalous methane from anthropogenic activities even though they are aligned along geological features. One location, site 1 is a site of particular interest because it is located near the Bridge Street and Towanda faults and the Towanda anticline. The geological features might act as migration pathways for leaked methane into shallow aquifers if gas wells that are leaking also intersect pockets of stored methane in the anticline or faults at depth. Four samples from sites 2 and 3 (located within the left red

curve in Figure 1) are located within 5 km of previously identified potentially leaking gas wells (API numbers: 015-20116, 015-21353, and 015-20612).^{50,51} Sites 5–7 include four samples that are located in the other hotspot (red curve on the right side in Figure 1) where high-methane groundwater might have been caused by nearby leaking gas wells.¹⁶ In particular, sites 5, 6, and 7 are located within 5 or 6 km of four gas wells that might be problematic as previously implied (API numbers: 015–21181, 015-20960, 015-20871, and 015-21352).¹⁶ Sites 1, 4, and 8 are not associated with reportedly leaking gas wells.^{16,50,51} If leakage did occur during the sampling period (11/4/2010 to 11/12/2012), and if it is still occurring, time series data from continuous sampling and monitoring of groundwater chemistry at these sites would be needed to distinguish anomalous methane from natural methane.

To determine the likelihood that the anomalous methane identified in these water samples was caused by shale gas drilling, we have also reviewed violation reports issued by PA DEP for all unconventional wells within 10 km of water samples of types 4 and 5. All unconventional wells with cementing or casing issues, based on violation codes reported previously,^{2,5} are noted and shown as orange and red pentagons in Figure 1. Some of these inspection narratives summarize signs of gas migration (red pentagons in Figure 1). According to the PA Oil and Gas Act, oil and gas companies can be held responsible for the degradation of water quality within 2,500 feet (762 m) of unconventional wells following drilling if an investigation shows degradation. None of these 13 samples from the eight sites in NE PA are located within 762 m of any of the known problematic gas wells (Figure 1). On the other hand, 12 of the putatively contaminated groundwater samples (from seven sites in Bradford) are within 5 km of at least one problematic gas well reported by PA DEP to have been drilled before sampling. The final sample (site 8 in Susquehanna County; Figure 1) is likewise located within 10 km of two such PA DEP-reported problematic gas wells. If our protocol has successfully identified contamination by methane, then these findings could reflect that methane can migrate beyond 762 m from leaking gas wells or that leakage at some gas wells was never detected by the regulator. Previous studies have shown methane might migrate over 3 km in AB.^{47,58}

High Conventional Well Density (NW PA). In NW PA, no water samples collected in the 2010s are classified as type 4 or 5. In contrast, four groundwater samples from sites 9–12 collected in the 1990s from Mercer and Lawrence counties (Table S5; Figure 1) are identified as likely to be impacted by anomalous methane (i.e., types 4 and 5). In Mercer and Lawrence counties, less than 0.01% to 0.01% of the area is identified respectively as associated with coal mining (Table S3). In those counties, no unconventional wells were drilled before 2011 (Table S3).⁵⁵ Therefore, it is unlikely that unconventional drilling activities or coal mining itself caused the potentially anomalous methane that we infer may be migrating into these four type 4 and 5 water samples. On the other hand, many conventional wells ($n = 3888$) were drilled in the area of NW PA from which we derive the water quality data.⁵⁵ Conventional wells around these four type 4/5 groundwater samples are present in a much higher density than the average density in NE PA (Table S3; Figure S1). If the geochemical protocol has successfully identified anomalous methane, we conclude that conventional oil/gas wells are responsible for the migration in these samples. These

presumably impacted samples (all were collected in the 1990s) might be contaminated either by conventional wells that were drilled long before water sampling but started to leak recently (still in 1990s) or by conventional wells that were drilled in 1990s not long before sampling of these groundwaters.

We reviewed PA DEP compliance reports⁵⁷ in the four townships where these waters were sampled as well as nearby townships. However, no well inspections are available online for the conventional wells that were drilled prior to the sampling of these four samples. Nonetheless, we cannot completely exclude the possibility that undocumented violations associated with conventional wells could have caused the anomalous methane in these four water samples, especially because more than 1,500 oil/gas wells that are not even on the regulator's maps may be located in these two NW PA counties and these older undocumented legacy wells have higher tendency to leak.^{30,59,60} A lack of violations for documented conventional wells and the large number of pre-existing legacy wells implied that sites 9–12 might be more likely contaminated by conventional wells that were drilled long before water sampling but started to leak recently.

High Densities of Conventional and Unconventional Gas Wells and Coal Mining (SW PA). A total of 2502 groundwater samples were collected from Beaver, Washington, and Greene counties in SW PA from 2010 to 2016 (Table S2 and S3). Among these samples, only 43 samples show methane concentrations ≥ 10 mg/L (1.7%) and none of these high methane samples are classified as type 4 or 5. Among these 43 water samples with high methane, 38 samples reported Cl concentrations >30 mg/L, 42 samples had Ca/Na mass ratios <0.52 , 37 samples had SO_4 concentrations <6 mg/L, and 34 samples had Fe concentrations <0.3 mg/L. As discussed herein, the prevalence of the salt and low concentrations of the redox-sensitive analytes Fe and SO_4 are consistent with the conclusion that the high methane concentrations in these SW PA samples are pre-existing and not anomalous. In other words, where methane is present at high concentrations, it is likely derived from natural origins and is accompanied by brines and where Fe and SO_4 is low, methane's presence has been long-standing.

The absence of water samples of types 4 and 5 in SW PA could suggest that regional groundwater quality in SW PA has been well protected from perturbation by development of shale gas, as suggested in other studies.^{16,17}

Implications. In this study, we outline a geochemical approach using only commonly measured geochemical analytes including methane, Cl, Ca, Na, SO_4 , and Fe to detect groundwater samples likely impacted by anomalous methane. This geochemical testing protocol requires no baseline predrill data for water quality and is thus, a straightforward screening tool. When combining with other tools (e.g., satellite image/remote sensing, hydrocarbon dryness and wetness, methane isotope, groundwater dating, and noble gas data), this approach can be helpful to diagnose anomalous methane. This testing protocol could be readily applied in other areas within the Marcellus Shale footprint and in other shale plays around the world with similar hydrogeochemical characteristics.

The proposed approach could produce false negatives. For example, the depth of ABB is so shallow in SW PA¹⁷ that the prevalence of brine salts (with some natural methane) may simply be ubiquitous, and therefore, the salt signature could be present even in the presence of anomalous methane migration.

Furthermore, the prevalence of impacts from coal mining and acid mine drainage where high concentrations of Fe and SO_4 are common^{61–66} may also mask the evidence related to the geochemical protocol, making detection difficult. It is known, for example, that some new shale gas drilling in the area has intersected acid mine drainage,⁶⁷ coal mines,²² and shallow brines.²⁸ To distinguish new methane caused by shale gas drilling from the above-mentioned confounding factors, additional measurements of other geochemical tracers would be of use. In particular, noble gases that are inert and stable have been proven effective in determining the source and migration pathways of stray gas in shallow groundwaters in varying shale gas plays.^{4,20,26,27,29,68} In addition, the application of methane isotope and groundwater dating tools can help distinguish thermogenic methane from biogenic methane⁶⁹ that is not considered in this study.

On the other hand, when testing groundwater data collected from long-screened water wells (well with relatively long screen interval allowing the mixing of different types of waters from varying depths), the mixing of waters (e.g., briny water with high natural methane and freshwater with high sulfate but low methane) could lead to false positives. Thus, it is preferable to sample short-screened water wells when possible. In addition, if to-be-tested sampling sites are located along the edges of plumes of naturally occurring methane, the occurrence of methane in groundwater along the plume edges could be ephemeral and pulse-like that might lead to the redox dis-equilibrium in collected water. However, the presence of natural methane is likely accompanied by briny water, and thus our testing protocol will categorize such shallow groundwater as type 2.

When applying this protocol in shale plays with different geology/soil chemistry, land use, land cover, land management, topography, and/or climate pattern that define the regional baseline of groundwater chemistry,⁷⁰ the thresholds used in the protocol are best determined if large data sets of regional groundwater quality are available. If so, for a given test site, predrill baseline sample from this site is not necessary. The large data set of groundwater chemistry can teach us the geochemical characteristics of an aquifer with long-standing methane. The groundwater chemistry at a given site that deviates from the regional baseline warrants further investigation.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.9b02290](https://doi.org/10.1021/acs.est.9b02290).

Supporting Text S1–S2, Figures S1–S4, and Tables S1–S5 (PDF)

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