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Scientist–Nonscientist Teams Explore Methane Sources in Streams Near Oil/Gas Development

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Abstract: New techniques are needed to distinguish between leakage of methane (CH_4) into surface waters from gas wells and natural sources. Here, scientists worked with >50 citizen scientists in a hydrocarbon-rich basin (Pennsylvania, U.S.A.) to measure methane concentrations ([CH_4]) in streams. These measurements were combined with published observations to form a reconnaissance dataset. The dataset was then used to categorize sites as background or as impacted by other sources of gas. For 479 samples at 131 sites, 470 were supersaturated with respect to the atmosphere ($\geq$0.08 μg/L). Sites with the lowest concentrations generally were located in low-productivity, sandstone-underlain upland streams, while other streams contained CH_4 from sources in addition to atmospheric. The median of 63 sites not located near wetland habitats and not affected by known thermogenic influxes yielded an estimate of background [CH_4] in the streams, 0.5 μg/L. The highest individual measurements (~70 μg/L) in the stream dataset were observed in one site near a wetland and one site near a putatively leaking gas well. Inspection of the dataset revealed that values of [CH_4] above a threshold for non-wetland sites, 4 μg/L, signals gas is likely deriving from sources such as leaking gas wells, shallow organic-rich shales, coal, or landfills. Using historical and local volunteer knowledge, we discovered 12 non-wetland sites above the threshold that are potentially contaminated by such sources. Although sources of CH_4 cannot be proven from such surveys of [CH_4], stream sampling with nonscientists nonetheless allows discovery of sites of potential contamination that can be further investigated.

Keywords: *water quality, shale gas, hydraulic fracturing, natural gas, citizen science*

Atmospheric methane (CH_4) concentrations are increasing at unprecedented rates to levels that have not been observed for the past 800,000 years (IPCC 2013). As CH_4 is currently the third most important greenhouse gas in the atmosphere, it is imperative to assess the various sources and sinks to predict future climate consequences. While we have learned a great deal about CH_4 sources over the years (Nisbet et al. 2016), estimating fugitive gas emissions from oil and gas extraction sites and pipelines is challenging. In addition, some leakage from oil and gas wells occurs below-ground where CH_4 can accumulate in aquifers and streams, be degraded by microbiota, or degas into the atmosphere (Vidic et al. 2013; U.S. EPA 2016). Such contamination of water resources by shale gas development – including lateral drilling and high-volume hydraulic fracturing (HVHF) – has spawned considerable public controversy over the last 15 years (Vidic et al. 2013; Brantley et al. 2014; Jackson et al. 2014). This paper explores a new method to survey for subsurface gas leakage.

CH_4 migration and accumulation in surface waters from active or abandoned wells is of concern because it occasionally leads to hazards related to combustion (Harrison 1983; Vidic et al. 2013). In addition, in some basins, CH_4 is the most commonly reported contaminant in water resources related to oil and gas development (Brantley et al. 2014). Monitoring for CH_4 leakage into water is difficult because there are many sources of both biogenic and thermogenic gas (produced and/or consumed at low temperature by bacteria, or at high temperature by thermal degradation of higher chain hydrocarbons in rocks, respectively). Gas from natural sources can mix with leaked fugitive gas (from oil and gas activity), making it difficult to identify leakage (Molofsky et al. 2011; Jackson et al. 2013; Molofsky et al. 2013; Molofsky et al. 2016; Grieve et al. 2018; Wen et al. 2018). One useful technique to distinguish biogenic and thermogenic gas is the measurement of the $^{13}C/^{12}C$ ratio in the CH_4, which is usually reported as $\delta^{13}C_{CH4}$ (Schoell 1980; Whiticar 1999). However, isotopes are generally an ambiguous fingerprint and multiple lines of evidence are always needed to distinguish the source of gas (Baldassare et al. 2014).

Typically, discovering leakage of CH_4 into aquifers relies on the time- and resource-intensive sampling of groundwater in individual water wells (Siegel et al. 2015). Many inadequacies have been noted with respect to such sampling (Jackson and Heagle 2016; Smith et al. 2016). Furthermore, where samples are taken before and after shale-gas development, the locations are generally not revealed because homeowners keep data confidential (Boyer et al. 2012; Brantley et al. 2018). Therefore, although the public needs better estimates of the location and quantity of CH_4 emanating from gas wells into water resources, accurate estimates are notoriously difficult to provide.

Recently, two new approaches were explored for identifying leaking oil and gas wells. The first entails the use of data mining tools to map CH_4 concentrations in groundwater using large datasets to identify concentration anomalies (Li et al. 2016; Li et al. 2017; Zheng et al. 2017a; Zheng et al. 2017b; Wen et al. 2018). The second technique targets publicly accessible streams in watersheds with upwelling groundwater (Heilweil et al. 2015). An added benefit of focusing on streams is that CH_4 emissions from fluvial systems to the atmosphere are globally significant but poorly constrained (estimated between 0.01 and 160 Tg/ CH_4 per year) (Stanley et al. 2016). To explore both approaches and learn more about natural and anthropogenic sources of CH_4, we developed a protocol for sampling, measuring, and categorizing CH_4 concentrations in streams ([CH_4]). Using the technique, we then discovered a few sites of potential leakage from oil or gas wells.

Stream sampling has benefits and drawbacks compared to groundwater sampling in households. First, by sampling public streams, no homeowner permissions are needed, and waters can be sampled repeatedly and easily. Second, in upland areas such as those where shale-gas drilling is prevalent in Pennsylvania, streams generally gain discharge from groundwater along their flowpath and therefore can be used to canvas broadly for areas of natural gas leakage (Heilweil et al. 2013; Heilweil et al. 2014; Heilweil et al. 2015). Such gaining streams can collect CH_4 in groundwater from gas-well leakage and from natural upward movement of either biogenic or thermogenic CH_4 (Heilweil et al. 2015).

However, new problems emerge when using streams to survey for gas well leakage: i) resources limit how many of the tens of thousands of kilometers of streams overlying the shale-gas play can be measured; ii) sampling must occur close to the leak before dilution and degassing occurs downstream; iii) leak detection in streams will vary in efficacy depending upon stream discharge level meaning that timing of sampling is important with respect to storms; and iv) influx of contamination can be limited to small stream reaches that are difficult to find without local knowledge of the landscape. To address these problems, we worked with local nonscientists who were taught to take samples and identify sites that might be impacted by leakage.

The intent of this paper is to describe what was learned about [CH_4] in streams from three datasets -- a reconnaissance dataset, a contamination-targeted dataset, and a wetland-lake dataset -- and what we learned about the stream-surveying approach itself. We first describe a reconnaissance dataset of [CH_4] in streams and we separate those data into categories based on the inferred sources of CH_4 (e.g., wetlands, natural thermogenic gas, and fugitive gas from putatively leaking gas wells). From inspection of the reconnaissance dataset, we propose a threshold value for non-wetland streams: when [CH_4] is above the threshold, some additional source of gas is likely to be contaminating the stream, for example, from a leaking well, a coal seam, a shallow shale, or a landfill. The threshold does not prove leakage but rather can be used to focus future research to confirm contamination. Finally, we test the reasonableness of the threshold by comparing it to "contamination-targeted" data near potentially leaking sources in streams. These sites were chosen based on i) data mining techniques developed to identify anomalies and outliers in large datasets of groundwater [CH_4] (Li et al. 2016; Li et al. 2017; Zheng et al. 2017a; Zheng et al. 2017b); ii) historical activity with respect to oil and gas development; and iii) information from nonscientist volunteers.

Methods

Working with Volunteers

Sites sampled for the reconnaissance dataset were chosen from knowledge of shale-gas well locations, accessibility, and the desires of volunteers or watershed group coordinators. Some data were included from volunteer sampling completed in each of two modes: "snapshot" sampling days where volunteers (see acknowledgements) fanned out over a watershed to collect a sampling of water quality on one day, or repetitive sampling of water quality at specific locations by volunteers. For the "snapshot" sampling, we worked with a coldwater fisheries conservation group (Trout Unlimited (TU)) that organized varying numbers of local volunteers (~20 to 30) to sample at 30–50 sites within one watershed during one day. Volunteers collected water samples for CH_4 analyses and measured turbidity using a 120cm Secchi tube, temperature and conductivity using a Lamotte Tracer Pocket Tester, and pH using pH strips at sites chosen by the TU coordinator (data hosted at www.citsci.org). Sites were chosen on the basis of safety, access, locations of current and projected shale gas development, the location of wild and native trout populations, and location within state-owned lands. In the second collaborative mode, Penn State teams worked with groups that were already monitoring a watershed, albeit not for CH_4. For these sites, we trained volunteers to sample water for CH_4 analyses at their own sites, and sites were sampled at multiple times.

Sampling for Reconnaissance Dataset

Two sites near State College, PA (U.S.A.) that are not in the shale-gas play and 129 sites throughout the play were sampled by our team or by watershed volunteers (see acknowledgements). A subset of these data have already been published (Grieve et al. 2018). When possible, samples were collected mid-stream in half liter polycarbonate bottles.

Bottles were transported to the field site filled with 18.2 MΩ·cm purified water to pre-condition the bottle. Initially, the bottle water was discarded downstream of the collection site. The bottles were then submerged with the volunteer and bottle facing upstream, and filled in the middle of the stream when possible. In all cases, bottles were rinsed with stream water three times and then the bottle was filled with stream water and capped with rubber septa underwater without air bubbles. Samples were returned to the laboratory for analysis within five days.

Contamination-Targeted and Wetland-Lake Datasets

For this dataset, stream samples were collected in the same way as described above, but from sites more likely to be contaminated by CH_4 through oil and gas development activity. This "targeted" dataset was sampled in i) the northwestern part of the state where many leaking orphaned and abandoned oil/gas wells have been identified (Kang et al. 2014), ii) New York where natural gas was first used in the U.S. commercially and where gas seepage was reported as early as the 1800s, and iii) sites in Pennsylvania (PA) where geospatial techniques have indicated anomalies in groundwater CH_4 (Li et al. 2016; Li et al. 2017; Zheng et al. 2017a; Zheng et al. 2017b). To identify these latter anomalies, the researchers first attributed much of the variation in CH_4 concentrations in groundwater to natural features such as geological faults or anticlines. The anomalies were then identified as locations away from those geological features where CH_4 was slightly higher in concentration.

Finally, 10 samples also were collected in a wetlands lake at Black Moshannon State Park (Pennsylvania). This site was chosen to determine an estimate of maximum concentrations of biogenic CH_4 in a Pennsylvania wetland. To seek the highest concentrations possible, 10 samples were collected in Black Moshannon Lake at varying locations on July 18, 2015. This date was chosen because this dammed wetland lake flows into Black Moshannon Creek and samples from that creek at the outflux (labelled as BlackMoshannonState - Park Site 1 in the reconnaissance dataset) were observed to have very high [CH_4] in summertime.

Samples taken from the lake were sampled as described for the reconnaissance dataset except using lake water rather than stream water for rinsing. Locations were either on- or off-shore and depths of sampling were about 20 cm.

Laboratory Analysis

Samples were analyzed at the Laboratory for Isotopes and Metals in the Environment, Pennsylvania State University. Helium (~60cc) was introduced into each sample bottle while removing the same volume of water to create a headspace. Bottles were then shaken to equilibrate the dissolved CH_4 into the headspace overnight. Once equilibrated, the headspace CH_4 concentration was measured using standard gas chromatographic (GC) techniques to determine the partial pressure of CH_4 in the headspace (Kampbell and Vandegrift 1998). [CH_4] in the water then was calculated using the Henry's law partition coefficient for the measured CH_4 partial pressure with respect to liquid water.

The technique reproducibly measures [CH_4] in stream waters down to 0.06 µg CH_4/L, lower than most commercial laboratories where detection limits have been reported as 1, 5, or 26 µg CH_4/L (Li et al. 2016). The low detection stems from the vacuum inlet system custom-designed for the GC for samples that have low concentrations and limited volume (Sowers et al. 1997; Sowers and Jubenville 2000). Our detection limit is lower than the equilibrium CH_4 concentration in water (0.08 µg CH_4/L) in contact with present day CH_4 concentrations in air, 1.87 ± 0.01 ppm.

We analyzed storage effects in various bottles (Isotech, VWR, glass), presence or absence of different biocides to inhibit bacterial reactions (Na azide, benzylkonium chloride, potassium hydroxide (KOH)), refrigeration, and the time between sampling and CH_4 analyses. To determine which biocide (if any) was needed in our bottles, we sampled four streams in triplicate and added KOH and benzalkonium chloride to two bottles, keeping the third bottle without preservative. In addition, we added preservative to six blank bottles containing 18.2 MΩ·cm purified water with three additional bottles containing only the purified water. All samples were measured together five days after collection. The mean value for the three process blanks + five identical bottles with either KOH or benzylkonium chloride and distilled water (0.093 ± 0.014 µg CH_4/L) was slightly above the atmosphere-equilibrated value (0.08 µg CH_4/L). Applying a T test to all these data showed that with 95% confidence, data from the "no treatment" samples were indistinguishable from those with biocide additives.

Reproducibility

We estimated overall uncertainty using samples with low CH_4 concentrations collected in triplicate every two to three weeks from two sites (Slab Cabin Run, Spring Creek) near State College, PA (Figure 1, Table S1). We calculated standard deviations around the mean for each of these 63 individual stream sampling events as a measure of the total error associated with the sampling and analyses. This is an overestimate because it incorporates short timescale temporal variability in stream [CH_4] over the period of sampling, typically less than 10 minutes. The average standard deviation for these 64 sample events was 7.5%, and this is considered representative of reproducibility that includes both sampling and analytical uncertainty, as well as in-stream variation for streams with low [CH_4] over short time periods.

To assess such reproducibility for sites with higher [CH_4], we collected consecutive samples within approximately 10 minutes of one another (Table S2) from i) the stream that originates at the wetland lake in Black Moshannon State Park in Centre County, Pennsylvania, thus containing biogenic gas; and ii) a seep close to Sugar Run that is near several putatively leaking shale gas well(s) in Lycoming County, Pennsylvania (Heilweil et al. 2015). For eight consecutive samples from the stream near the wetland ([CH_4] < 10 µg CH_4/L), the relative standard deviation was 11.6%. For seven consecutive samples from the Sugar Run site ([CH_4] ≈ 200 µg CH_4/L), the relative standard deviation equaled 10.8%. These data show that the overall reproducibility of our data, including natural variability over a short time period, sampling, and analysis is about 12%.

Isotopic Measurements

We measured $\delta^{13}C_{CH4}$ on headspace samples from eight sites within the "contamination-targeted" dataset to identify the CH_4 source using a slight modification of a published technique used for samples from ice cores (Sowers et al. 2005). For the modification, we exchanged the stainless steel sample tube from the ice core extraction device with a simple septa allowing injection of headspace gas from our sample bottles directly into the helium carrier stream. We sampled ~5 nmoles of CH_4 from a sample bottle headspace with a gas tight syringe and injected the sample into the helium carrier stream using a pre-concentration device (PreCon) connected to a Thermo Delta V isotope ratio mass spectrometer. The CH_4 was then cryogenically and chromatographically separated from the other headspace constituents before being converted to carbon dioxide for Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS). $\delta^{13}C_{CH4}$ results are reported on the VPDB scale. Air standards are run at the start of each day to correct for slight (<0.2‰) day-to-day instrument drift. The measured air standard value is always within 0.2‰ of the assigned value. Analytical uncertainty associated with $\delta^{13}C_{CH4}$ analyses based on replicate analyses of 1% CH_4 in a nitrogen (N_2) flask standard is better than 0.3‰.

Results

Reconnaissance Dataset

Given the difficulties of organizing volunteers and finding safe, public, and accessible sites that also met scientific or watershed group goals, our sampling sites were neither randomly selected nor distributed comprehensively across the Marcellus shale play. Table S1 summarizes all values of [CH_4] for samples collected by the authors and volunteers, as well as from a recent publication (Grieve et al. 2018). These latter values were collected by part of our team in i) two streams (Tunkhannock, Nine Partners) known to receive influxes of thermogenic as well as biogenic CH_4 from natural sources, and ii) two streams (Sugar Run, Meshoppen) that have relatively high [CH_4] and that drain areas with hydraulically fractured shale gas wells that are known to have had leakage problems. Sugar Run is located in Lycoming County near several shale-gas wells cited for leaking CH_4 by the state regulator (Heilweil et al. 2015). The other stream, Meshoppen Creek, is characterized by the presence of both problematic shale-gas wells and wetland habitats (Hammond 2016).

Data from Tunkhannock, Nine Partners, Sugar Run, and Meshoppen are incorporated for comparison in Table S1 because all four may be receiving gas from deep thermogenic sources that flow upward into groundwaters. For example, seep and piezometer waters sampled at Sugar Run revealed 2300 and 4600 µg CH_4/L, respectively (Heilweil et al. 2014) and a seep at Nine Partners Creek revealed 210 µg/L (Grieve et al. 2018). These three samples of upwelling groundwater are plotted on Figure 1 as a comparison with the stream water data. The influx of upwelling CH_4-containing groundwater into streams demonstrates why the stream-based approach may help to find leaking gas wells. Some of the same sites reported by Grieve et al. (2018) were originally sampled and analyzed by Heilweil et al. (2014).

All the data in Table S1 were combined with the streamwater data from Heilweil et al. (2014) for the same sites at Sugar Run to constitute the "reconnaissance dataset". This dataset includes 479 values of [CH_4] measured at 131 sites in Pennsylvania (Figure 1). For each site, individual data were reported along with site-aggregated means (i.e., for time series data). The distribution of values for the 131 site-aggregated means in the reconnaissance dataset is highly skewed (Figure 2); therefore, the best parameter to describe the data is the median, 1 µg/L (Table 1). The concentrations of individual samples range from <0.06 to 68.5 µg/L. In comparison, [CH_4] in some groundwaters in one county of Pennsylvania approach 100,000 µg/L (Li et al. 2016).

Nine sites were undersaturated with respect to the theoretical concentration (0.08 µg/L) in equilibrium with today's atmospheric CH_4: eight samples from Beech Creek watershed and

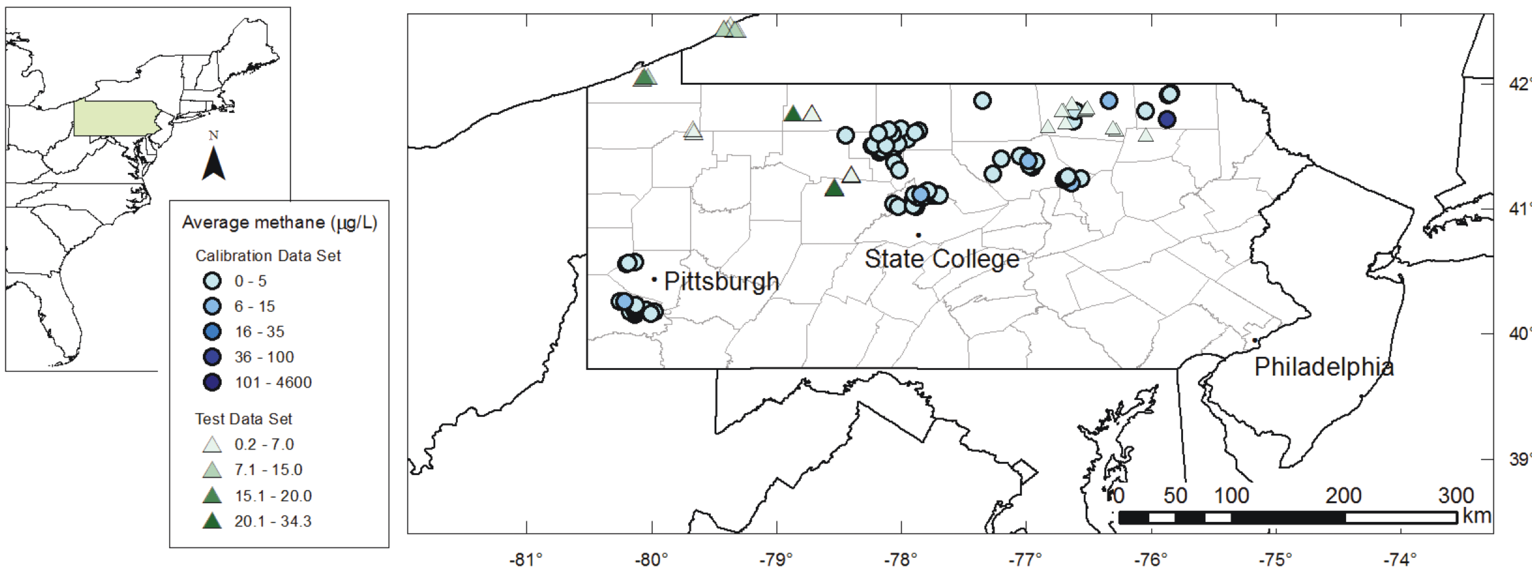

Figure 1. Locations and values of [CH_4] measured at sites in the reconnaissance (circles) and contamination-targetted (triangles) datasets. Blue shading indicates the range of [CH_4] as shown in the legend. Sites were sampled by the authors and watershed groups (Trout Unlimited, Chartiers Creek Watershed Association, Centre County Pennsylvania Senior Environmental Corps, State College Area High School TeenShale Network, and Fern Hollow Nature Center QV Creekers). The reconnaissance dataset also included published stream data at sites in Sugar Run near Hughesville, Meshoppen Creek, Tunkhannock Creek, and Nine Partners Creek (Heilweil et al. 2015; Grieve et al. 2018). For comparison, three groundwater concentrations are also shown from seeps and piezometers near Sugar Run: these are the three highest concentrations and are located near one or more gas wells cited by the state regulator for possible leakage (Heilweil et al. 2015). Samples in the reconnaissance dataset outside the Appalachian Basin at Slab Cabin and Spring Creek near State College, PA are listed in Table S1 but not plotted.

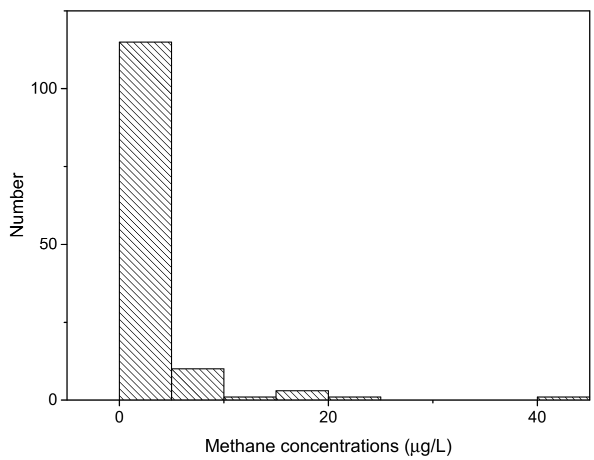

Figure 2. Histogram of the reconnaissance dataset of site-aggregated means for the 131 stream sites (see Figure 1).

one small tributary to Meshoppen Creek. Six of the samples from Beech Creek watershed were below detection (<0.06 μg/L), i.e., sites in or near Council Run, Hayes Run, Sandy Run, and Big Run. These sites as well as the other two below-equilibrium sites in Beech Creek watershed (Beauty Run, North Fork Beech Creek) were sampled by a volunteer group (Pennsylvania Centre County Senior Environmental Corps). All streams with low [CH_4] were underlain largely by sandstone formations; in addition, the Beech Creek streams were identified as relatively low productivity based on measurements of macroinvertebrates (Pennsylvania Centre County Senior Environmental Corps (PA CCSEC) 2017).

Contamination-Targeted and Wetland-Lake Datasets

The contamination-targeted dataset included 42 samples around sites thought to have a high potential for contamination (Figure 1, Table S3). In these sites, [CH_4] varied from 0.2 to 33.7 μg/L (Table S3). One site at Walnut Creek was inadvertently sampled near both an orphaned well and a wetland, but all other sites were far from mapped wetlands. One sample was taken in an area of oil and gas development but also was discovered to be located downstream from an active landfill. Twelve of the targeted non-wetland samples showed [CH_4] > 4 μg/L (Table S3). The eight samples measured for $\delta^{13}C_{CH4}$, also reported in Table S3, all appear to be mixtures of biogenic and thermogenic gas.

The wetland-lake dataset summarizes 10 data values from the lake at Black Moshannon State Park. [CH_4] for the 10 positions around the lake varied from 17.8 to 45.2 μg/L (Table S4).

Discussion

Site Categories

Extended geological and isotopic analysis to determine the source of CH_4 in each stream was beyond project scope. Instead, we explored what could be learned from the reconnaissance dataset using geographic and published information. Specifically, the data were binned into four categories: i) sites with no known or suspected sources of gas other than background; ii) sites with known or suspected inputs of biogenic gas from nearby wetlands; iii) sites with known or suspected inputs from natural sources of thermogenic gas; and iv) sites with inputs of gas hypothesized to derive from a nearby leaking shale-gas well or set of wells.

The four categories are referred to herein as i) other, ii) wetland-biogenic, iii) thermogenic, and iv) putatively anthropogenic. Although such binning of sources is necessarily ambiguous, it leads to some observations explored below. Overall, 63 of 131 sites were categorized as "other", 37 as "wetland biogenic", 20 as "thermogenic", and 11 as "putatively anthropogenic" (Table 1, Figure 3). These short-hand descriptors are not meant to imply that each site derives gas from only a single source. For example, "other" sites likely contain atmospheric gas and biogenic gas from the riparian zone; "wetland-biogenic" sites contain atmospheric CH_4 as well as CH_4 that originates from near-surface methanogen activity within a wetland; "thermogenic" sites contain small amounts of atmospheric and biogenic gas -- but the bulk is thermogenic gas naturally leaking upward from buried shale sources. The "putatively anthropogenic" classification was reserved only for those sites located within 2 km of a set of shale gas wells in the Sugar Run valley where gas well(s) are possibly leaking (Heilweil et al. 2015; Grieve et al. 2018). The point was to determine what can be learned about CH_4 in streams in the Appalachian Basin using such admittedly ambiguous categories. For watershed groups that can afford CH_4 analyses

Table 1. Summary of CH_4 concentrations (µg/L) in the reconnaissance dataset.

	All Data	Bin Type: Other	Wetland-Biogenic	Thermogenic	Putatively Anthropogenic
131 Site-Aggregated Means					
Median	1.0	0.5	2.2	1.0	9.8
Minimum	<0.06	<0.06	0.1	0.1	5.0
Maximum	40.1	6.3	40.1	5.3	20.4
N	131	63	37	20	11
479 Individual Measurements					
Minimum	<0.06	<0.06	0.06	0.1	5.0
Maximum	68.5	6.3	68.5	5.3	67

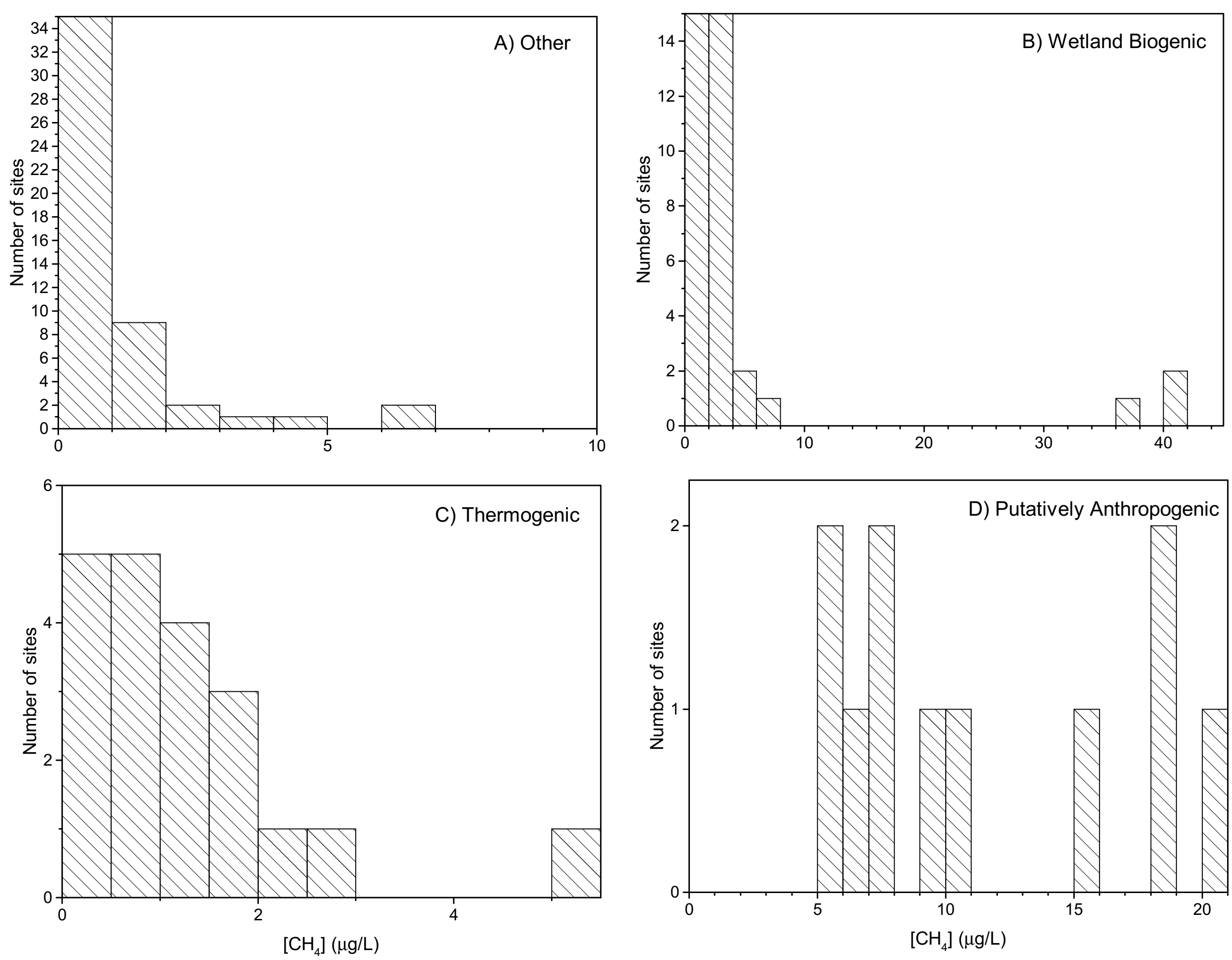

Figure 3. Histogram of site-aggregated average values of $[CH_4]$ for A) "other" sites; B) "wetland-biogenic" sites; C) "thermogenic" sites; and D) "putatively anthropogenic" sites. See text for how sites were categorized and for references. The proposed threshold that warrants more investigation for a non-wetland site is ~4 µg/L.

in streams, for example, could such data from reconnaissance sampling focus future work to highlight leakage from gas wells?

Categorizing Sites

Sites were put in the category "wetland-biogenic" if they were located within the zone of influence of a wetland as defined by the U.S. Fish and Wildlife Service for watershed planners (Castelle et al. 1994). The zone of influence was set equal to 30 meters.

Nine Partners Creek and Tunkhannock Creek in Susquehanna County were the only known sites in the reconnaissance dataset without associated leaking gas wells but with inputs from naturally derived biogenic and thermogenic CH_4. Most of the sites along those two creeks near their confluence were defined as "thermogenic" because i) they were located within 100 meters of natural lineaments (Llewellyn 2014), ii) when measured for isotopes, $\delta^{13}C_{CH4}$ values were heavier than -40 ‰, and iii) they were not located near reportedly leaking gas wells (Grieve et al. 2018) or features such as wetlands, coal seams, or landfills. Lineaments are straight segments of streams or valleys or other features that can be observed on a topographic map and that often represent the surface expressions of faults or joints in Pennsylvania (Llewellyn 2014). Along such faults, CH_4-containing groundwater often travels upward even in the absence of human activities (Llewellyn 2014; Siegel et al. 2015; Li et al. 2016; Wen et al. 2018).

Analyses for Sugar Run waters in Lycoming County from sites within 2 km of Marcellus shale-gas wells that are thought to be leaking into groundwater (Heilweil et al. 2015; Grieve et al. 2018) were all classified as "putatively anthropogenic". The presence of higher order hydrocarbons such as ethane in some of these samples and values of $\delta^{13}C_{CH4}$, $\delta^{13}C_{C2H6}$, and δD_{CH4} are consistent with a thermogenic source for at least some of the gas (Heilweil et al. 2014; Heilweil et al. 2015; Grieve et al. 2018). Sites SR1, SR1.1, SR1.15, SR1.2, SR1.4, SR1.45, SR1.5, SR1.55, SR1.6, SR1.8, and SR2 along Sugar Run were all within 2 km of a nearby gas well that was cited by the Pennsylvania Department of Environmental Protection (PA DEP) for failure to report defective, insufficient, or improperly cemented casing (http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewer.aspx?/Oil_Gas/OG_Compliance). These sites were thus binned into the putatively anthropogenic category. Reported values of stream [CH_4] were as high as 67 µg/L in Sugar Run (Heilweil et al. 2014; Heilweil et al. 2015).

After binning analyses into wetland-biogenic, thermogenic, and putatively anthropogenic, the rest of the sites were defined as "other". "Other" sites have no known inputs from wetlands, coal seams, acid mine drainage, landfills, or leaking oil and gas wells, and therefore are defined here as the best estimate of natural background in the north-northwestern half of Pennsylvania. Gas in these streams is thought to derive from the atmosphere and from production in the riparian zone.

Observations about Categories

A priori, we might expect that every category would include sites with low [CH_4] because of dilution effects or degassing. Indeed, the minima for site-aggregated means for the wetland-biogenic and thermogenic sites were the same (0.1 µg/L, Table 1). However, all the samples where [CH_4] values were less than detection fell into the "other" category, lending credence to the binning scheme. Furthermore, the minimum of the site-aggregated means for the putatively anthropogenic category was higher: 5.0 µg/L (Table 1).

The [CH_4] in individual samples categorized as "other" varied from <0.06 to 6.3 µg/L with a median of 0.5 µg/L. Of these site-aggregated means, only one was higher than 5 µg/L. The [CH_4] in individual wetland-biogenic samples varied from 0.06 to 68.5 µg/L with a median of 2.2 µg/L. The highest site-aggregated value (from Meshoppen Creek) was 40.1 µg/L (Heilweil et al. 2014). The [CH_4] in individual thermogenic samples varied from 0.1 to 5.3 µg/L, and the median of the site-aggregated thermogenic values was 1.0 µg/L (Table S1, Table 1). The highest value, 5.3 µg/L, derived from Nine Partners Creek (Grieve et al. 2018). In comparison, the groundwater sampled in groundwater upwelling at the seep near Nine Partners was 40 times higher (220 µg/L) (Grieve et al., 2018). The [CH_4] in individual samples in sites categorized as putatively anthropogenic (Sugar Run) ranged from 5.0 to 67 µg/L with a median value of 9.8 µg/L (the highest value, 67 µg/L, was reported by Heilweil et al. (2014)). Like the comparison of groundwater to stream water for Nine Partners Creek, the groundwater [CH_4] sampled at a piezometer in the bed of Sugar Run was much larger (4600 µg/L) (Heilweil et al. 2014), indicating CH_4-rich groundwater below the stream.

Estimated Background Concentration

Our best estimate of the background [CH_4] in non-wetland streams located in the western and north central parts of Pennsylvania (Figure 1) is the median value, 0.5 µg/L, of the "other" group. None of these samples measured >7 µg/L and all except nine had concentrations equal to or higher than water in equilibrium with today's atmosphere (0.08 µg/L). Many researchers have similarly observed that most stream waters are oversaturated with respect to atmospheric CH_4 concentrations, indicating that streams are a net source of CH_4 to the atmosphere (e.g., De Angelis and Lilley 1987; De Angelis and Scranton 1993; Jones and Mulholland 1998a, 1998b; Bastviken et al. 2011; Stanley et al. 2016). Even the two streams sampled outside the Appalachian Basin (Slab Cabin Run and Spring Creek) showed [CH_4] values above equilibrium (Table S1). Similar observations at other sites have been attributed to CH_4 generation in the riparian zone of streams (Jones and Mulholland 1998a, 1998b).

Comparison to Other Regions

Stanley et al. (2016) recently summarized measurements for stream [CH_4] worldwide. The PA values reported here are much lower than the highest measured values, ~6200 µg/L. Those values were generally found in highly polluted river systems (i.e., Adyar River, India). Stanley et al. (2016) concluded that no relationship was observed in the global dataset with respect to stream size or latitude. However, higher values were often observed in streams that were wetland- or human-impacted (agricultural or urban). In Table 2, the PA values are compared to a few example streams. The PA values are higher than values in Oregon and Tennessee but much lower than reported in Amazon River wetland habitats in Brazil (Bartlett et al. 1990).

Nine of the values reported here were undersaturated with respect to atmospheric CH_4 (<0.08 µg/L). Of these nine sites, it is notable that eight were from first order streams from the same watershed -- Beech Creek. Macroinvertebrate diversity has also been reported in four of these streams (PA CCSEC 2017). These biosurveys document fair (Hayes Run), good to fair (Council Run), and poor to fair (Big Run) macroinvertebrate populations and one site is completely dead (North Fork Beech Creek). The low biodiversity is presumably related to the upland nature of these streams, the low productivity of the sandstone lithologies, and the incidence of acid mine drainage from coal mining in the watershed. Perhaps, the low influx of organic matter and low dissolved organic carbon (DOC) in these upland streams explains both the low macroinvertebrate diversity and the low [CH_4]. Low DOC was observed to correlate with low [CH_4] in the global dataset of Stanley et al. (2016).

Can Stream Surveys Highlight Potential Leakage?

If we could identify a maximum value of [CH_4] in pristine (non-impacted) streams, surveys could be used to identify contamination from leaking wells or other sources directly. However, Heilweil et al. (2014) observed that the maximum [CH_4] within 30 meters of a wetland and within 2 km of a putatively leaking gas well were almost identical: 68.5 µg/L and 67 µg/L, respectively. These sites were included in our reconnaissance dataset and categorized as "wetland-biogenic" (Meshoppen Creek at Parkvale) and "putatively anthropogenic" (Sugar Run), respectively. The maximum [CH_4] therefore cannot easily be used to identify contamination versus wetland inputs.

On the other hand, a threshold value might be useful at least as a signal to highlight the possibility of contamination, even if other lines of evidence would be needed to make the conclusion definitive. For example, inspection of Figure 3A for "other" samples shows no samples above 7 µg/L, suggesting that value could be such a screening threshold.

The maximum value of [CH_4] of the "other" category overlaps with the minimum of the putatively anthropogenic category. We therefore

Table 2. Selected stream and river [CH_4] values.

Location	Range in [CH_4] (µg/L)	Reference
Eastern Tennessee (USA)	0.67 – 1.56	Jones and Mulholland (1998a)
Oregon rivers (USA)	0.08 – 27.8	De Angelis and Lilley (1987)
Peatland stream in United Kingdom	0.8 – 39	Dinsmore et al. (2013), as reviewed by Stanley et al. (2016)
Pennsylvania streams	<0.06 – 68.5	This work (including published data)
Amazon River (Brazil)	1 – 590	Bartlett et al. (1990)
Global compilation	0 – 6190	Stanley et al. (2016)

inspected the highest "other" site for the possibility of contamination. This site, with [CH_4] = 6.3 µg/L, was taken from a tributary to Rose Valley Lake (Lycoming County) on July 29, 2015 near several shale gas wells. Just prior to sampling (on July 16, 2013), the nearest well, API#081-20584 (Lundy North 1HOG well), was cited by the PA DEP for PA DEP 78.86*, "failure to report defective, insufficient, or improperly cemented casing w/in 24 hrs or submit a plan to correct w/in 30 days." The inspector included this comment: "the 13 3/8 in x 9 5/8 in annular space of the 1 H is showing 20 % methane". Based on this inspection, the relatively high [CH_4] value in Rose Lake tributary could represent contamination, and we therefore propose a lower screening threshold, 4 µg/L. Consistent with this threshold, none of the site-aggregated values from the putatively anthropogenic category had [CH_4] < 5 µg/L. In addition, only one sample in the "other" category has a value of [CH_4] at this threshold (Horton Run, 4.2 µg/L). But that site cannot be concluded to be contaminated because it is located 30.87 m from the nearest wetland, i.e., extremely close to our operational definition of a wetland (within 30 m). Therefore, [CH_4] ≈ 4 µg/L is proposed as a good screening threshold for focusing future investigations of sites not located within 30 m of wetland habitat.

Because the threshold value is defined for non-wetland sites, it obviously cannot help identify contamination of wetlands. For example, the highest [CH_4] in a stream, 68.5 µg/L, was measured at Meshoppen Creek sampled at Parkvale, PA in a wetland area, and was thus not considered to be indicative of contamination. However, isotopic data for that site point toward influxes from both biogenic and thermogenic gas (Heilweil et al. 2014; Grieve et al. 2018). Given that Meshoppen is located very close to the township of Dimock -- an area of a relatively large number of reported gas well-related problems that have been investigated by the PA DEP and the U.S. Environmental Protection Agency (U. S. Environmental Protection Agency 2015; Hammond 2016) – the high [CH_4] could also be consistent with an influx from unknown leaking gas well(s). Hammond (2016) concluded that 17 of 18 groundwater wells in the Dimock area, including wells in the Meshoppen Creek valley, were impacted by gas well development.

As a partial test of this ambiguity with respect to Meshoppen, we estimated the maximum [CH_4] values expected for wetlands in Pennsylvania by measuring [CH_4] in 10 locations during the summer in the lake at Black Moshannon State Park, a natural low-flow wetland in an area without shale gas development. Those values (Table S4) never exceeded 45.2 µg/L. These values are similar to measurements in a peatland in the United Kingdom over five years that varied up to 38.4 µg/L ((Dinsmore et al. 2013) as summarized by Stanley et al. (2016)). Such data may indicate that the attribution of dissolved CH_4 in Meshoppen Creek (sampled at Parkvale, PA) strictly to natural wetland influx is worthy of further investigation.

Inferences from the Contamination-Targeted Dataset

To explore if 4 µg/L is an appropriate threshold, we collected a contamination-targeted dataset that we predicted would have a high incidence of above-threshold values. Samples were collected at 42 sites targeted for the possibility of leakage (Figures 1, 4, Table S3). In choosing the sites, wetlands were avoided, although one site near an orphaned well was inadvertently sampled near a wetland (see Table S3). Consistent with our prediction, 13 of 42 targeted samples (12 of 41 non-wetland sites) showed $[CH_4] > 4$ µg/L (Figures 1, 4).

The above-threshold sites include several sites near active, plugged, orphaned, or abandoned oil or gas wells. Some sites were near wells not currently included in the database of orphaned and abandoned wells maintained by the PA DEP, as indicated in Table S3. One site with $[CH_4] = 7.3$ µg/L is located 3 km from three active oil and gas wells -- but is also downstream of a landfill.

Three sites sampled in New York state were above threshold near Fredonia on Lake Erie (Canadaway Creek, Van Buren Point). At Fredonia, gas was used in the early 1800s for the first time globally to power municipal gas lamps. Gas emits naturally into the creek bed and lake from an organic-rich shale located close to the land surface, and has been described for decades in local newspapers.

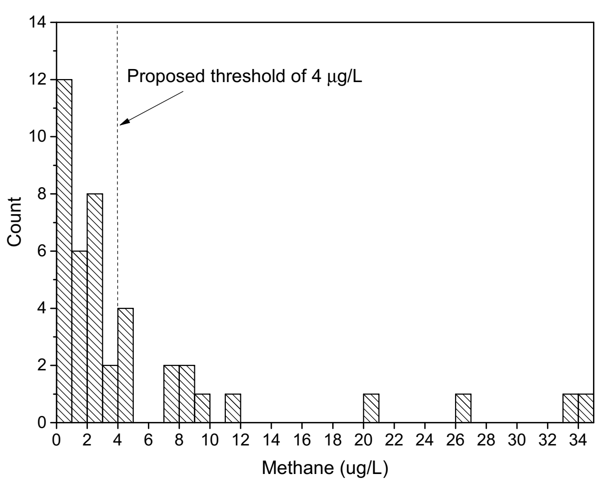

Figure 4. Histogram of the "contamination-targeted" dataset. These values of $[CH_4]$ were measured at sites targeted because of their potential for contamination. The proposed threshold that warrants more investigation for a non-wetland site is ~4 µg/L.

Some above-threshold sites ($[CH_4] = 8.5$, 9.2, 33.7 µg/L) were located near abandoned oil or gas wells that are listed as some of the highest emitters on a survey of atmospheric emissions from old Pennsylvania oil and gas wells (Kang et al. 2014; Kang et al. 2016). One site near a plugged gas well and near coal mining was particularly high in concentration, $[CH_4] = 34.3$ µg/L; possibly, this site is contaminated by coal CH_4 instead of, or in addition to, CH_4 from the well. One site near an abandoned well near Chappel Fork with $[CH_4] = 26.3$ µg/L was discovered by a volunteer (from a watershed group known as Save our Streams PA) working in collaboration with N. Meghani (marcellusmatters.psu.edu; Penn State) (pers. comm.).

Finally, three sites (Sugar Creek, Towanda, and Tomjack) were discovered using two geospatial techniques relying on data mining of groundwater chemistry (Li et al. 2016; Zheng et al. 2017a; Zheng et al. 2017b; Wen et al. 2018). The first technique (Li et al. 2016) mapped correlations between $[CH_4]$ in groundwater and distance to shale-gas wells for a large dataset of groundwater chemistry. The map showed a spot where CH_4 concentrations in groundwater increased slightly near gas wells near Towanda Creek, and Li et al. (2016) argued this might indicate well leakage. We therefore sampled in Towanda Creek as near that hotspot as possible and discovered one location with $[CH_4] > 4$ µg/L (Table S3).

The second geospatial technique (Zheng et al. 2017a; Zheng et al. 2017b) used the same large dataset of groundwater chemistry and identified sites that appeared to be outliers on the basis of features such as latitude, longitude, distance to conventional gas wells, distance to unconventional gas wells, and distance to faults. Sugar Creek and Tomjack Creek were sampled near the identified outliers on the map and were discovered to have $[CH_4] > 4$ µg/L (Table S3). Above-threshold values of $[CH_4]$ in the streams near the groundwater anomalies are consistent with the possibility of contamination related to gas wells (more investigation is warranted).

Isotopic Measurements in Targeted Dataset

Because some sites in the targeted dataset were discovered with $[CH_4]$ > threshold, a few isotopic measurements were completed to investigate the source of gas. The scope of the project limited the number of isotopic measurements: seven were completed at above-threshold sites and one at a below-threshold site ([CH_4] = 3.7 μg/L).

In PA, thermogenic gas generally has $\delta^{13}CH_4$ > -50 ‰ and biogenic gas < -60 ‰ (Revesz et al. 2010). Eight of the sites in the test dataset were measured for $\delta^{13}CH_4$. For these samples, all showed evidence of thermogenic gas ($\delta^{13}CH_4$ > -50 ‰) – even the below-threshold site. Some were in the range of biogenic + thermogenic (-60 ‰ < $\delta^{13}CH_4$ < -50 ‰), including the sample within 30 m of a wetland and near an active well. That sample had the most negative isotopic signature (-56.9 ‰), indicating a high biogenic contribution. The abandoned well discovered by a volunteer near Chappel Fork had the highest carbon (C) isotopic signature (-26.6 ‰, Table S3), consistent with a very high contribution from thermogenic gas, possibly documenting leakage from the well. Another interpretation is that bacteria-mediated oxidation of the gas has driven the $\delta^{13}CH_4$ to more positive values (Baldassare et al. 2014; Grieve et al. 2018).

One site that was sampled was located near three active oil/gas wells, but also was 400 m downstream of a landfill. At that site, [CH_4] = 7.3 μg/L (Table S3). CH_4 can advect with landfill leachate in groundwater flow (van Breukelen et al. 2003). The measured stream $\delta\,^{13}C_{CH4}$ values (-43.5 ± 0.2‰, Table S3) at that site were more characteristic of $\delta\,^{13}C_{CH4}$ values associated with the Marcellus Formation (-43 to -32‰ (Baldassare et al. 2014)) than with landfills (-54 ± 2‰, (Chanton et al. 1999; Bogner and Matthews 2003)). However, oxidation of the gas during transit as leachate could also have shifted the $\delta\,^{13}C_{CH4}$ to more positive values. In a nearby non-wetland tributary of Walnut Creek located near an orphaned well, the isotopic measurement (Table S3), -34.7 ‰, is consistent with a thermogenic source.

The 28 below-threshold, non-wetland sites included samples from Oil Creek near the location of the world's first commercial oil well (Titusville, PA). This area was heavily drilled in the 1800s before implementation of modern regulations but the Titusville sites all showed [CH_4] below 3 μg/L. This observation could mean that no leakage is occurring or that the discharge in Oil Creek dilutes the CH_4. In fact, one of the samples near Titusville, PA in the test dataset that had [CH_4] values below threshold (2.9 μg/L, Oil Creek) was also measured for C isotopic signature and the value summarized in Table S3 is consistent with thermogenic gas (-49.8 ‰). Thus, the threshold value does not flag all sites above background; hydrologic factors are also important determinants of the stream [CH_4]. In contrast to Oil Creek, lower-discharge streams in the Titusville area might show contamination.

Strategies for Finding Leakage

Twelve of 41 non-wetland sites in the targeted dataset were above threshold, consistent with our prediction that many of those targeted sites would be above background. The threshold value can therefore be used in a stream survey to find sites that warrant deeper investigation. However, designing a strategy to survey the tens of thousands of kilometers of streams above the Marcellus shale-gas play in Pennsylvania to find non-wetland streams with [CH_4] > 4 μg/L is daunting. Grieve et al. (2018) argued that to find contamination using a stream survey requires very close spacing of samples because seepage into a stream is commonly restricted to faults or fractures.

By collaborating with citizen scientists, we showed it is possible to increase the sampling density and frequency, while also focusing on areas of interest to the public. The drawbacks of incorporating volunteers into sampling include the requirements for significant organization, safety concerns, general inflexibility in scheduling or choice of location, the lack of volunteers in some locations, and the need for standardized sample handling coordinated with rapid analysis. In addition, sampling to detect CH_4 from leaking gas wells is best completed during dry periods when streams are dominated by baseflow and not diluted, and this can be difficult with volunteers because re-scheduling during storms is difficult.

Despite those problems, our stream survey revealed information about background levels and the overall distribution of [CH_4]. Collaboration with volunteers lead to discovery of sites with leaking wells (Table S3). Future surveys with volunteers should grow the dataset to clarify the distribution of [CH_4] in streams by emphasizing smaller streams under baseflow conditions.

Conclusions

This paper summarizes an approach that can incorporate volunteers in stream surveys designed to learn about CH_4 emissions and find leaking gas wells. Citizen scientists lowered the sampling time for the science team, increased spatial sampling density, and discovered leaking wells not reported on the map of the state regulator.

The reconnaissance dataset was tentatively categorized with respect to source using geographic and published information. The best estimate for background [CH_4] in Pennsylvania streams is 0.5 μg/L. Above a screening threshold of ~ 4 μg/L for non-wetland streams, further investigation is warranted to identify additional CH_4 entering from anthropogenic or natural thermogenic sources. Investigations could include frequent measurements of [CH_4], densely spaced stream and groundwater surveys, isotopic measurements, analysis of higher chain hydrocarbons, mapping with respect to gas wells, temporal analysis with respect to oil or gas development, and investigations of nearby gas wells.

Further work is needed to investigate the effects of seasonal variations in stream [CH_4] and the best ways to pick survey sites. One novel approach that showed some success herein is to mine groundwater chemistry data using new algorithms (Li et al. 2016; Li et al. 2017; Zheng et al. 2017a; Zheng et al. 2017b; Wen et al. 2018). Such identifications of anomalies in groundwater maps, when combined with stream chemistry, will elucidate the nature of natural and anthropogenic sources of CH_4 to freshwaters, and, in turn, to the atmosphere.

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Appendix: Summary of Measurements

Table S1. CH_4 concentrations in streams in Pennsylvania.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
9/26/2015	B	Bailey Run (lower)	41.512	-78.046	1.0	1.0		
9/26/2015	O	Bailey Run (upper)	41.524	-78.066	0.5	0.5		
1/14/2016	O	Barberry	40.576	-80.138	0.4	0.4		
1/14/2016		Barberry	40.576	-80.138	0.5			
9/16/2015	O	Beauty Run*	41.078	-77.907	0.5	0.3	12	4.2
3/1/2016		Beauty Run_Kato Rd	41.078	-77.907	0.4		8	4.9
5/5/2016		Beauty Run_Kato Rd	41.078	-77.907	0.06		9	5.7
11/10/2015	O	Beech Creek	41.108	-77.694	0.2	0.2		
8/10/2015	O	BeechCreek_Monument	41.113	-77.705	0.5	0.4	18	4.2
4/11/2016		BeechCreek_Monument	41.113	-77.705	0.2		5	4.1
9/26/2015	O	Berge Run	41.489	-78.052	0.1	0.1		
9/26/2015	O	Big Nelson Run	41.556	-78.034	0.3	0.3		
8/10/2015	O	BigRun	41.111	-77.732	0.5	0.5	16	5.4
9/16/2015		Big Run	41.111	-77.732	1.0		14	4.6
11/9/2015		LHU_Big_Run	41.111	-77.732	0.3		6	4.3
4/11/2016		BigRun	41.111	-77.732	0.1		5	5.2
9/26/2015	O	Billy Buck Run	41.587	-78.442	0.2	0.2		
9/26/2015	O	Birch Run	41.558	-77.951	0.8	0.8		
6/24/2015	O	Black Mo meets Red Mo - Site 3	41.036	-78.060	0.3	0.4	N/A	6.9
6/24/2015		Black Mo meets Red Mo - Site 3	41.036	-78.060	0.2		N/A	N/A
7/8/2015		Black Mo meets Red Mo - Site 3	41.036	-78.060	0.1		N/A	7.1
7/8/2015		Black Mo meets Red Mo - Site 3	41.036	-78.060	0.1		N/A	7.1
7/8/2015		Black Mo meets Red Mo - Site 3	41.036	-78.060	0.1		N/A	7.1
8/19/2015		Black Mo meets Red Mo - Site 3	41.036	-78.060	0.2		N/A	6.4
8/19/2015		Black Mo meets Red Mo - Site 3	41.036	-78.060	0.3		N/A	6.4
8/19/2015		Black Mo meets Red Mo - Site 3	41.036	-78.060	0.2		N/A	6.4
9/16/2015		Black Mo meets Red Mo - Site 3	41.036	-78.060	2.2		N/A	6.8
6/24/2015	O	BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.6	0.6	15.8	7.2
6/24/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.4		15.8	7.2
6/24/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.2		15.8	7.2
7/8/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.5		N/A	7.1
7/8/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.4		N/A	7.1
7/8/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.4		N/A	7.1
8/19/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.7		N/A	7.1
8/19/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.8		N/A	7.1
8/19/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.9		N/A	7.1
9/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.5		N/A	N/A
9/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.2		N/A	N/A
9/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.4		N/A	N/A
10/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.4		N/A	N/A

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
10/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.6		N/A	N/A
10/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.6		N/A	N/A
10/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.4		N/A	N/A
10/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.6		N/A	N/A
10/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.4		N/A	N/A
10/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.8		N/A	N/A
10/16/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	2.1		N/A	N/A
11/10/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.5		N/A	7.0
11/10/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.3		N/A	7.0
11/10/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.5		N/A	7.0
11/10/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.4		N/A	7.0
11/10/2015		BlackMoshannon at Bridge - Site 2	41.016	-78.022	0.3		N/A	7.0
6/24/2015	B	BlackMoshannonState Park- Site 1	40.919	-78.059	0.6	7.8	20.1	6.6
6/24/2015		BlackMoshannonState Park- Site 1	40.919	-78.059	0.2		20.1	6.6
6/24/2015		BlackMoshannonState Park- Site 1	40.919	-78.059	0.5		20.1	6.6
7/8/2015		BlackMoshannonState Park- Site 1	40.919	-78.059	7.9		17.6	6.3
7/8/2015		BlackMoshannonState Park- Site 1	40.919	-78.059	7.6		17.6	6.3
7/8/2015		BlackMoshannonState Park- Site 1	40.919	-78.059	8.8		17.6	6.3
8/19/2015		BlackMoshannonState Park- Site 1	40.919	-78.059	14.7		N/A	6.8
8/19/2015		BlackMoshannonState Park- Site 1	40.919	-78.059	15.2		N/A	6.8
8/19/2015		BlackMoshannonState Park- Site 1	41.016	-78.022	25.6		N/A	6.8
3/16/2016		BlackMoshannonState Park- Site 1	40.919	-78.059	6.2		N/A	6.2
3/16/2016		BlackMoshannonState Park- Site 1	40.919	-78.059	7.8		N/A	6.2
3/16/2016		BlackMoshannonState Park- Site 1	40.919	-78.059	6.7		N/A	6.2
3/16/2016		BlackMoshannonState Park- Site 1	40.919	-78.059	6.2		N/A	6.2
3/16/2016		BlackMoshannonState Park- Site 1	40.919	-78.059	7.4		N/A	6.2
3/16/2016		BlackMoshannonState Park- Site 1	40.919	-78.059	6.0		N/A	6.2
3/16/2016		BlackMoshannonState Park- Site 1	40.919	-78.059	7.0		N/A	6.2
3/16/2016		BlackMoshannonState Park- Site 1	40.919	-78.059	5.5		N/A	6.2
3/16/2016		BlackMoshannonState Park- Site 1	40.919	-78.059	6.0		N/A	6.2
7/29/2015	O	Caleb Run	41.336	-76.955	0.3	0.3		
6/22/2015	B	Chartiers Creek	40.250	-80.206	3.0	3.0		
6/22/2015	O	Chartiers Run	40.248	-80.212	2.6	2.5		
1/14/2016		Chartiers Run	40.248	-80.212	2.3			
6/22/2015	B	Chartiers Run	40.258	-80.257	2.1	2.1		
10/12/2015	O	Council Run	41.091	-77.819	0.3	0.2	8	7.5
8/10/2015		Council Run	41.091	-77.819	0.2		14	6.8
11/9/2015		Council Run	41.091	-77.819	0.2		6	5.7
5/5/2016		Council Run	41.091	-77.819	<0.06		10	5.4
9/26/2015	O	Driftwood Branch (Emporium)	41.508	-78.236	1.0	1.0		
9/26/2015	O	East Branch of Cowley Run	41.597	-78.183	0.6	0.6		
9/16/2015	B	Eddy Lick Run	41.114	-77.812	0.4	0.4	12	5.8
9/26/2015	O	Elklick Run	41.522	-78.026	1.0	1.0		

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
1/14/2016	B	Fern Hollow	40.573	-80.158	2.3	2.2		
1/14/2016		Fern Hollow	40.573	-80.158	2.2			
9/26/2015	B	First Fork Sinnemahoning Creek (@ SP)	41.451	-78.047	2.8	2.8		
9/26/2015	O	Freeman Run	41.601	-78.064	0.7	0.7		
7/29/2015	O	Hagerman Run	41.422	-77.049	0.1	0.1		
11/9/2015	O	Hayes Run	41.105	-77.759	0.2	0.1	6	5.7
5/5/2016		Hayes Run	41.105	-77.759	<0.06		10	6.2
9/26/2015	O	Horton Run	41.616	-77.875	4.2	4.2		
4/11/2016	O	Jonathan Run	41.020	-77.882	0.4	0.4	8	6.9
9/26/2015	O	Lick Island Run	41.373	-78.053	0.2	0.3		
9/26/2015		Lick Island Run	41.373	-78.053	0.4			
6/22/2015	O	Little Chartiers	40.228	-80.144	2.7	2.4		
8/6/2015		Little Chartiers	40.228	-80.144	2.1			
8/6/2015	B	Little Chartiers	40.157	-80.134	2.9	2.9		
8/6/2015	B	Little Chartiers	40.182	-80.146	2.6	2.6		
10/26/2015	B	Little Chartiers Creek	40.178	-80.136	4.2	4.1		
11/15/2015		Little Chartiers Creek	40.178	-80.136	4.1			
11/15/2015	B	Little Chartiers Creek	40.163	-80.134	2.6	2.6	6.9	5.9
11/15/2015	B	Little Chartiers Creek	40.178	-80.136	2.5	3.3		
11/15/2015		Little Chartiers Creek	40.178	-80.136	4.1			
11/15/2015	B	Little Chartiers Creek	40.195	-80.136	3.2	3.2		
9/26/2015	O	Little Moores Run	41.643	-78.002	0.4	0.4		
9/26/2015	O	Little Portage Creek	41.604	-78.067	0.6	0.6		
9/16/2015	B	Little Sandy Run	41.076	-77.961	1.3	0.8	14	5.4
11/10/2015		Little Sandy Run	41.076	-77.961	0.2		9	6.2
9/26/2015	O	Lower Hunts Run	41.453	-78.174	0.4	0.4		
1/14/2016	O	Marrow	40.558	-80.201	0.4	0.5		
1/14/2016		Marrow	40.558	-80.201	0.5			
9/26/2015	O	McKinnon Branch	41.464	-78.173	0.7	0.7		
11/14/2013	B	Meshoppen Creek (MC1)	41.717	-75.871	11.6	11.6	3	6.6
11/14/2013	B	Trib Meshoppen Creek (MC1 Trib)	41.718	-75.871	0.1	0.07	4	7.8
9/26/2015	O	Middle Hunts Run	41.474	-78.151	0.9	0.9		
7/29/2015	O	Mill Creek West	41.345	-76.972	0.2	0.2		
10/26/2015	O	Mingo Creek	40.195	-80.042	1.0	1.0		
9/26/2015	O	Montour Run	41.307	-78.017	0.2	0.2		
9/26/2015		Montour Run	41.307	-78.017	0.3			
10/12/2015	O	Monument Run	41.113	-77.704	0.3	0.2	9	6.3
4/11/2016		Monument Run	41.113	-77.704	0.1		6	6.3
8/10/2015	B	North Fork Beech Creek	41.05	-77.94	3.0	2.0	14	6.1
11/10/2015		North Fork Beech Creek	41.05	-77.94	3.5		9	5.8
5/5/2016		North Fork Beech Creek	41.05	-77.94	0.06		10	6.3
3/1/2016		North Fork Beech Creek_Clarence Rd	41.05	-77.94	1.2		7	5.8

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
11/10/2015	O	Panther Run	41.112	-77.842	5.7	2.0	9	6.6
8/10/2015		Panther	41.112	-77.842	0.2		13	7.1
4/11/2016		Panther	41.112	-77.842	0.1		7	6.4
1/14/2016	B	Pink House	40.571	-80.159	0.6	0.7		
1/14/2016		Pink House	40.571	-80.159	0.8			
6/22/2015	B	Plum Run	40.258	-80.219	5.3	2.9		
1/14/2016		Plum Run	40.258	-80.219	0.4			
1/14/2016	B	Plum Run (2)	40.255	-80.216	2.6	2.6		
7/31/2013	T	(SAH-13-10) Tunkhannock Creek	41.703	-75.671	1.3	1.3		
7/31/2013		(SAH-13-10) Tunkhannock Creek	41.703	-75.671	1.3			
5/30/2013	T	(SAH-13-9) Tunkhannock Creek	41.707	-75.672	1.6	1.4		
7/31/2013		(SAH-13-11) Tunkhannock Creek	41.707	-75.672	1.0			
7/31/2013		(SAH-13-11) Tunkhannock Creek	41.707	-75.672	1.5			
5/30/2013	T	(SAH-13-8) Tunkhannock Creek	41.710	-75.672	1.9	2.1		
7/31/2013		(SAH-13-12) Tunkhannock Creek	41.710	-75.672	2.2			
7/31/2013		(SAH-13-12) Tunkhannock Creek	41.710	-75.672	2.2			
7/31/2013		(SAH-13-12) Tunkhannock Creek	41.710	-75.672	2.2			
5/30/2013	T	(SAH-13-7) Tunkhannock Creek	41.711	-75.672	2.6	2.6		
5/30/2013	T	(SAH-13-13) 9 Partners Creek	41.712	-75.671	5.3	5.3		
7/31/2013	T	(SAH-13-14) Tunkhannock Creek	41.712	-75.67	0.4	0.3		
11/13/2013		(SAH-13-24) Tunkhannock Creek	41.712	-75.67	0.2			
11/13/2013	T	(SAH-13-25) 9 Partners	41.712	-75.671	1.6	1.6	1.8	6.9
11/13/2013	T	(SAH-13-26) 9 Partners	41.712	-75.671	1.6	1.6	2.1	7.4
11/13/2013	B	(SAH-13-27) 9 Partners	41.713	-75.672	1.3	1.3	2.3	7.3
11/13/2013	B	(SAH-13-28) 9 Partners	41.714	-75.673	1.4	1.4	2.5	7.2
11/13/2013	B	(SAH-13-29) 9 Partners	41.714	-75.674	1.5	1.5	2.6	7.4
11/13/2013	T	(SAH-13-30) 9 Partners	41.715	-75.675	1.5	1.5	2.9	7.5
9/1/2013	B	(SAH-13-19) 9 Partners	41.714	-75.673	2.5	2.5		
8/1/2013	T	(SAH-13-18) Tunkhannock Creek	41.715	-75.668	0.5	0.5		
8/1/2013		(SAH-13-18) Tunkhannock Creek	41.715	-75.668				
7/31/2013	T	(SAH-13-16) Tunkhannock Creek	41.717	-75.698	1.1	1.6		
8/1/2013		(SAH-13-17) Tunkhannock Creek	41.717	-75.664		0.9		
8/1/2013		(SAH-13-17) Tunkhannock Creek	41.717	-75.664				
7/31/2013	T	(SAH-13-15) TribTunkhannock Creek	41.718	-75.66	0.1	0.1		
5/30/2013	B	(SAH-13-6) Tunkhannock Creek	41.719	-75.65	0.7	0.7		
5/30/2013	T	(SAH-13-5) Tunkhannock Creek	41.720	-75.649	0.9	0.9		
5/30/2013	T	(SAH-13-4) Tunkhannock Creek	41.723	-75.646	0.7	0.7		
9/1/2013	T	(SAH-13-20) 9 Partners	41.729	-75.676	0.4	0.4		
9/1/2013	T	(SAH-13-21) 9 Partners	41.729	-75.677	0.4	0.4		
5/30/2013	T	(SAH-13-1) Tunkhannock Creek	41.733	-75.632	0.7	0.7		
5/30/2013	T	(SAH-13-2) Tunkhannock Creek	41.733	-75.630	0.6	0.6		
5/30/2013	T	(SAH-13-3) Tunkhannock Creek	41.733	-75.633	1.0	1.0		

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
9/1/2013	T	(SAH-13-22) 9 Partners	41.763	-75.687	0.2	0.2		
9/1/2013	B	(SAH-13-23) 9 Partners	41.787	-75.687	2.6	2.6		
10/12/2015	O	Salt Lick	41.105	-77.723	0.2	0.2	9.7	6.3
4/11/2016		Salt Lick	41.105	-77.723	0.1		6.9	6.1
9/26/2015	O	Salt Run	41.534	-78.195	0.5	0.5		
11/10/2015	B	Sandy Run*	41.078	-77.908	1.1	1.6	9	5.8
3/1/2016		Sandy Run_Kato Rd	41.078	-77.908	0.4		8	5.4
9/16/2015		SandyRun_Kato	41.078	-77.908	4.6		12	5.4
5/5/2016		SandyRun_Kato	41.078	-77.908	<0.06		9	5.3
9/26/2015	O	Sinnemahoning Portage Creek (Emporium)	41.513	-78.22	0.4	0.4		
6/11/2015	B	Slab Cabin	40.809	-77.826	1.2	0.8	18.3	8.3
6/11/2015		Slab Cabin	40.809	-77.826	1.2		18.3	8.3
6/11/2015		Slab Cabin	40.809	-77.826	1.2		18.3	8.3
6/11/2015		Slab Cabin	40.809	-77.826	1.2		18.3	8.3
6/18/2015		Slab Cabin	40.809	-77.826	0.9		15.3	7.9
6/18/2015		Slab Cabin	40.809	-77.826	0.8		15.3	7.9
6/18/2015		Slab Cabin	40.809	-77.826	1.4		15.3	7.9
6/18/2015		Slab Cabin	40.809	-77.826	1.1		15.3	7.9
6/25/2015		Slab Cabin	40.809	-77.826	0.6		15.3	8.0
6/25/2015		Slab Cabin	40.809	-77.826	0.6		15.3	8.0
6/25/2015		Slab Cabin	40.809	-77.826	0.6		15.3	8.0
6/25/2015		Slab Cabin	40.809	-77.826	0.7		15.3	8.0
6/29/2015		Slab Cabin	40.809	-77.826	1.0		13.5	7.8
6/29/2015		Slab Cabin	40.809	-77.826	0.9		13.5	7.8
6/29/2015		Slab Cabin	40.809	-77.826	0.8		13.5	7.8
6/29/2015		Slab Cabin	40.809	-77.826	0.8		13.5	7.8
7/1/2015		Slab Cabin	40.809	-77.826	0.8		14.0	7.8
7/1/2015		Slab Cabin	40.809	-77.826	1.2		14.0	7.8
7/1/2015		Slab Cabin	40.809	-77.826	1.2		14.0	7.8
7/1/2015		Slab Cabin	40.809	-77.826	1.2		14.0	7.8
7/6/2015		Slab Cabin	40.809	-77.826	1.2		N/A	N/A
7/6/2015		Slab Cabin	40.809	-77.826	1.1		N/A	N/A
7/6/2015		Slab Cabin	40.809	-77.826	0.9		N/A	N/A
7/6/2015		Slab Cabin	40.809	-77.826	1.0		N/A	N/A
7/15/2015		Slab Cabin	40.809	-77.826	0.9		16.3	8.2
7/15/2015		Slab Cabin	40.809	-77.826	1.0		16.3	8.2
7/15/2015		Slab Cabin	40.809	-77.826	1.0		16.3	8.2
7/15/2015		Slab Cabin	40.809	-77.826	1.0		16.3	8.2
7/29/2015		Slab Cabin	40.809	-77.826	0.6		14.3	8.1
7/29/2015		Slab Cabin	40.809	-77.826	0.7		14.3	8.1
7/29/2015		Slab Cabin	40.809	-77.826	0.6		14.3	8.1
7/29/2015		Slab Cabin	40.809	-77.826	0.6		14.3	8.1

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
8/12/2015		Slab Cabin	40.809	-77.826	0.6		14.9	8.2
8/12/2015		Slab Cabin	40.809	-77.826	0.6		14.9	8.2
8/12/2015		Slab Cabin	40.809	-77.826	0.8		14.9	8.2
8/25/2015		Slab Cabin	40.809	-77.826	0.7		17.9	8.4
8/25/2015		Slab Cabin	40.809	-77.826	0.5		17.9	8.4
8/25/2015		Slab Cabin	40.809	-77.826	0.7		17.9	8.4
9/11/2015		Slab Cabin	40.809	-77.826	0.9		18	8.3
9/11/2015		Slab Cabin	40.809	-77.826	0.9		18	8.3
9/11/2015		Slab Cabin	40.809	-77.826	0.5		18	8.3
10/5/2015		Slab Cabin	40.809	-77.826	0.5		N/A	N/A
10/5/2015		Slab Cabin	40.809	-77.826	0.5		N/A	N/A
10/5/2015		Slab Cabin	40.809	-77.826	0.5		N/A	N/A
10/19/2015		Slab Cabin	40.809	-77.826	0.3		8.8	7.9
10/19/2015		Slab Cabin	40.809	-77.826	0.3		8.8	7.9
10/19/2015		Slab Cabin	40.809	-77.826	0.7		8.8	7.9
11/9/2015		Slab Cabin	40.809	-77.826	0.6		8.8	7.9
11/9/2015		Slab Cabin	40.809	-77.826	0.7		8.8	7.9
11/9/2015		Slab Cabin	40.809	-77.826	0.4		8.8	7.9
11/21/2015		Slab Cabin	40.809	-77.826	0.3		8.4	8.3
11/21/2015		Slab Cabin	40.809	-77.826	0.3		8.4	8.3
11/21/2015		Slab Cabin	40.809	-77.826	0.3		8.4	8.3
12/12/2015		Slab Cabin	40.809	-77.826	0.4		10.4	8
12/12/2015		Slab Cabin	40.809	-77.826	0.3		10.4	8
12/12/2015		Slab Cabin	40.809	-77.826	0.3		10.4	8
1/8/2016		Slab Cabin	40.809	-77.826	0.2		4.8	8.0
1/8/2016		Slab Cabin	40.809	-77.826	0.2		4.8	8.0
1/8/2016		Slab Cabin	40.809	-77.826	0.2		4.8	8.0
2/3/2016		Slab Cabin	40.809	-77.826	0.7		4.1	7.5
2/3/2016		Slab Cabin	40.809	-77.826	0.7		4.1	7.5
2/3/2016		Slab Cabin	40.809	-77.826	0.7		4.1	7.5
3/18/2016		Slab Cabin	40.809	-77.826	0.3		9.7	8.0
3/18/2016		Slab Cabin	40.809	-77.826	0.3		9.7	8.0
3/18/2016		Slab Cabin	40.809	-77.826	0.3		9.7	8.0
4/13/2016		Slab Cabin	40.809	-77.826	0.3		14.3	8.4
4/13/2016		Slab Cabin	40.809	-77.826	0.3		14.3	8.4
4/13/2016		Slab Cabin	40.809	-77.826	0.3		14.3	8.4
5/1/2016		Slab Cabin	40.809	-77.826	1.0		11.5	8.0
5/1/2016		Slab Cabin	40.809	-77.826	1.0		11.5	8.0
5/1/2016		Slab Cabin	40.809	-77.826	1.0		11.5	8.0
5/16/2016		Slab Cabin	40.809	-77.826	0.4		16	8.5
5/16/2016		Slab Cabin	40.809	-77.826	0.4		16	8.5
6/8/2016		Slab Cabin	40.809	-77.826	1.0		15.7	8.3
6/8/2016		Slab Cabin	40.809	-77.826	1.0		15.7	8.3

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	[CH_4] µg/L	Mean [CH_4] µg/L	Water Temp °C	pH
6/8/2016		Slab Cabin	40.809	-77.826	1.0		15.7	8.3
6/23/2016		Slab Cabin	40.809	-77.826	0.9		19	8.2
6/23/2016		Slab Cabin	40.809	-77.826	0.9		19	8.2
6/23/2016		Slab Cabin	40.809	-77.826	0.8		19	8.2
6/30/2016		Slab Cabin	40.809	-77.826	1.1		19.5	8.1
6/30/2016		Slab Cabin	40.809	-77.826	0.7		19.5	8.1
6/30/2016		Slab Cabin	40.809	-77.826	0.8		19.5	8.1
7/13/2016		Slab Cabin	40.809	-77.826	1.1		N/A	N/A
7/13/2016		Slab Cabin	40.809	-77.826	1.0		N/A	N/A
7/13/2016		Slab Cabin	40.809	-77.826	1.0		N/A	N/A
7/27/2016		Slab Cabin	40.809	-77.826	1.2		N/A	N/A
7/27/2016		Slab Cabin	40.809	-77.826	1.2		N/A	N/A
7/27/2016		Slab Cabin	40.809	-77.826	1.3		N/A	N/A
8/15/2016		Slab Cabin	40.809	-77.826	0.8		N/A	N/A
8/15/2016		Slab Cabin	40.809	-77.826	0.8		N/A	N/A
8/15/2016		Slab Cabin	40.809	-77.826	0.8		N/A	N/A
8/28/2016		Slab Cabin	40.809	-77.826	0.7		21.7	8.1
8/28/2016		Slab Cabin	40.809	-77.826	0.9		21.7	8.1
8/28/2016		Slab Cabin	40.809	-77.826	0.8		21.7	8.1
9/21/2016		Slab Cabin	40.809	-77.826	1.0		19.1	8.1
9/21/2016		Slab Cabin	40.809	-77.826	1.0		19.1	8.1
9/21/2016		Slab Cabin	40.809	-77.826	1.0		19.1	8.1
10/9/2016		Slab Cabin	40.809	-77.826	0.7		12.2	7.9
10/9/2016		Slab Cabin	40.809	-77.826	0.7		12.2	7.9
10/9/2016		Slab Cabin	40.809	-77.826	0.7		12.2	7.9
10/23/2016		Slab Cabin	40.809	-77.826	0.7		10.7	7.4
10/23/2016		Slab Cabin	40.809	-77.826	0.6		10.7	7.4
9/16/2015	O	South Fork Beech Creek	41.024	-77.904	0.4	0.4	12	6.2
5/5/2016		South Fork Beech Creek	41.024	-77.904	0.3		10	6.5
9/16/2015	O	Spring above W. Branch of Big Run	41.146	-77.791	0.3	0.2	11	5.3
3/1/2016		Spring above West Branch-Big Run	41.146	-77.791	0.3		9	6.9
5/5/2016		Spring above West Branch-Big Run	41.146	-77.791	<0.06		9	6.0
6/11/2015	B	Spring Creek	40.82	-77.83	1.7	1.2	15.5	8.3
6/11/2015		Spring Creek	40.82	-77.83	1.6		15.5	8.3
6/11/2015		Spring Creek	40.82	-77.83	1.2		15.5	8.3
6/11/2015		Spring Creek	40.82	-77.83	1.6		15.5	8.3
6/11/2015		Spring Creek	40.82	-77.83	1.7		15.5	8.3
6/25/2015		Spring Creek	40.82	-77.83	1.1		13.8	8.0
6/25/2015		Spring Creek	40.82	-77.83	1.1		13.8	8.0
6/25/2015		Spring Creek	40.82	-77.83	1.0		13.8	8.0
6/25/2015		Spring Creek	40.82	-77.83	1.1		13.8	8.0
6/29/2015		Spring Creek	40.82	-77.83	1.3		13.1	7.8
6/29/2015		Spring Creek	40.82	-77.83	1.1		13.1	7.8

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
6/29/2015		Spring Creek	40.82	-77.83	1.3		13.1	7.8
6/29/2015		Spring Creek	40.82	-77.83	1.6		13.1	7.8
7/1/2015		Spring Creek	40.82	-77.83	1.4		13.6	7.8
7/1/2015		Spring Creek	40.82	-77.83	1.4		13.6	7.8
7/1/2015		Spring Creek	40.82	-77.83	1.3		13.6	7.8
7/6/2015		Spring Creek	40.82	-77.83	1.2		N/A	N/A
7/6/2015		Spring Creek	40.82	-77.83	1.7		N/A	N/A
7/6/2015		Spring Creek	40.82	-77.83	1.5		N/A	N/A
7/6/2015		Spring Creek	40.82	-77.83	1.5		N/A	N/A
7/15/2015		Spring Creek	40.82	-77.83	1.2		15.9	8.3
7/15/2015		Spring Creek	40.82	-77.83	1.2		15.9	8.3
7/15/2015		Spring Creek	40.82	-77.83	1.2		15.9	8.3
7/15/2015		Spring Creek	40.82	-77.83	1.1		15.9	8.3
7/29/2015		Spring Creek	40.82	-77.83	1.3		14	8.1
7/29/2015		Spring Creek	40.82	-77.83	1.2		14	8.1
7/29/2015		Spring Creek	40.82	-77.83	1.1		14	8.1
7/29/2015		Spring Creek	40.82	-77.83	1.3		14	8.1
8/12/2015		Spring Creek	40.82	-77.83	1.5		13.7	8.1
8/12/2015		Spring Creek	40.82	-77.83	1.5		13.7	8.1
8/12/2015		Spring Creek	40.82	-77.83	1.7		13.7	8.1
8/25/2015		Spring Creek	40.82	-77.83	1.8		15.8	8.3
8/25/2015		Spring Creek	40.82	-77.83	1.7		15.8	8.3
8/25/2015		Spring Creek	40.82	-77.83	1.8		15.8	8.3
9/11/2015		Spring Creek	40.82	-77.83	1.4		15.9	8.2
9/11/2015		Spring Creek	40.82	-77.83	1.0		15.9	8.2
9/11/2015		Spring Creek	40.82	-77.83	1.6		15.9	8.2
10/5/2015		Spring Creek	40.82	-77.83	1.1		N/A	N/A
10/5/2015		Spring Creek	40.82	-77.83	1.0		N/A	N/A
10/5/2015		Spring Creek	40.82	-77.83	1.0		N/A	N/A
10/19/2015		Spring Creek	40.82	-77.83	0.3		N/A	N/A
10/19/2015		Spring Creek	40.82	-77.83	0.7		N/A	N/A
10/19/2015		Spring Creek	40.82	-77.83	0.7		N/A	N/A
11/9/2015		Spring Creek	40.82	-77.83	0.4		8.4	8.2
11/9/2015		Spring Creek	40.82	-77.83	0.4		8.4	8.2
11/9/2015		Spring Creek	40.82	-77.83	0.3		8.4	8.2
11/21/2015		Spring Creek	40.82	-77.83	1.0		7.7	8.2
11/21/2015		Spring Creek	40.82	-77.83	0.9		7.7	8.2
11/21/2015		Spring Creek	40.82	-77.83	1.1		7.7	8.2
12/12/2015		Spring Creek	40.82	-77.83	0.7		10.1	8.1
12/12/2015		Spring Creek	40.82	-77.83	0.5		10.1	8.1
12/12/2015		Spring Creek	40.82	-77.83	0.6		10.1	8.1
1/8/2016		Spring Creek	40.82	-77.83	0.5		5.6	7.9
1/8/2016		Spring Creek	40.82	-77.83	0.5		5.6	7.9

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
1/8/2016		Spring Creek	40.82	-77.83	0.5		5.6	7.9
2/3/2016		Spring Creek	40.82	-77.83	1.0		5.2	7.5
2/3/2016		Spring Creek	40.82	-77.83	1.1		5.2	7.5
2/3/2016		Spring Creek	40.82	-77.83	0.9		5.2	7.5
3/18/2016		Spring Creek	40.82	-77.83	0.5		9.7	8.2
3/18/2016		Spring Creek	40.82	-77.83	0.5		9.7	8.2
3/18/2016		Spring Creek	40.82	-77.83	0.5		9.7	8.2
4/13/2016		Spring Creek	40.82	-77.83	0.6		12.5	8.5
4/13/2016		Spring Creek	40.82	-77.83	0.7		12.5	8.5
4/13/2016		Spring Creek	40.82	-77.83	0.6		12.5	8.5
5/1/2016		Spring Creek	40.82	-77.83	1.2		10.6	8.1
5/1/2016		Spring Creek	40.82	-77.83	1.2		10.6	8.1
5/1/2016		Spring Creek	40.82	-77.83	1.3		10.6	8.1
5/16/2016		Spring Creek	40.82	-77.83	0.9		13.5	8.4
5/16/2016		Spring Creek	40.82	-77.83	0.7		13.5	8.4
6/8/2016		Spring Creek	40.82	-77.83	1.4		13.8	8.2
6/8/2016		Spring Creek	40.82	-77.83	1.4		13.8	8.2
6/8/2016		Spring Creek	40.82	-77.83	1.4		13.8	8.2
6/23/2016		Spring Creek	40.82	-77.83	1.4		16.4	8.1
6/23/2016		Spring Creek	40.82	-77.83	1.4		16.4	8.1
6/23/2016		Spring Creek	40.82	-77.83	1.3		16.4	8.1
6/30/2016		Spring Creek	40.82	-77.83	1.2		17.1	7.9
6/30/2016		Spring Creek	40.82	-77.83	1.2		17.1	7.9
6/30/2016		Spring Creek	40.82	-77.83	1.1		17.1	7.9
7/13/2016		Spring Creek	40.82	-77.83	1.2		N/A	N/A
7/13/2016		Spring Creek	40.82	-77.83	1.3		N/A	N/A
7/13/2016		Spring Creek	40.82	-77.83	1.2		N/A	N/A
7/27/2016		Spring Creek	40.82	-77.83	1.3		N/A	N/A
7/27/2016		Spring Creek	40.82	-77.83	1.5		N/A	N/A
7/27/2016		Spring Creek	40.82	-77.83	1.4		N/A	N/A
8/15/2016		Spring Creek	40.82	-77.83	2.4		N/A	N/A
8/15/2016		Spring Creek	40.82	-77.83	2.4		N/A	N/A
8/15/2016		Spring Creek	40.82	-77.83	2.4		N/A	N/A
8/28/2016		Spring Creek	40.82	-77.83	2.3		19.4	7.97
8/28/2016		Spring Creek	40.82	-77.83	2.4		19.4	7.97
8/28/2016		Spring Creek	40.82	-77.83	2.6		19.4	7.97
9/21/2016		Spring Creek	40.82	-77.83	1.6		18.2	8.2
9/21/2016		Spring Creek	40.82	-77.83	1.6		18.2	8.2
9/21/2016		Spring Creek	40.82	-77.83	1.5		18.2	8.2
10/9/2016		Spring Creek	40.82	-77.83	1.3		11.1	8.0
10/9/2016		Spring Creek	40.82	-77.83	1.5		11.1	8.0
10/9/2016		Spring Creek	40.82	-77.83	1.4		11.1	8.0
10/23/2016		Spring Creek	40.82	-77.83	2.0		10	7.8

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
10/23/2016		Spring Creek	40.82	-77.83	1.8		10	7.8
10/23/2016		Spring Creek	40.82	-77.83	1.8		10	7.8
7/9/2015	A	SR 1 (Sugar Run)	41.236	-76.696	5.0	5.0	17.07	7.42
7/9/2015		SR 1 (Sugar Run)	41.236	-76.696	5.0			
6/13/2016	A	SR 1.1 (Sugar Run)			20.4	20.4		
7/9/2015	A	SR 1.15 (Sugar Run)	41.236	-76.694	5.4	5.4	16.99	7.25
7/9/2015		SR 1.15 (Sugar Run)	41.236	-76.694	5.4			
7/9/2015	A	SR 1.2 (Sugar Run)	41.237	-76.694	10.0	10.3	17.37	6.83
7/9/2015		SR 1.2 (Sugar Run)	41.237	-76.694	10.0			
6/13/2016		SR 1.2 (Sugar Run)			10.9			
7/9/2015	A	SR 1.4 (Sugar Run)	41.238	-76.693	13.3	15.1	16.42	7.27
7/9/2015		SR 1.4 (Sugar Run)	41.238	-76.693	13.3			
6/13/2016		SR 1.4 (Sugar Run)			18.6			
12/9/2014	A	SR 1.45 (Sugar Run)	41.239	-76.692	9.7	18.0		
7/9/2015		SR 1.45 (Sugar Run)	41.239	-76.692	17.5		16.47	7.08
7/9/2015		SR 1.45 (Sugar Run)	41.239	-76.692	17.5			
6/13/2016		SR 1.45 (Sugar Run)			27.4			
12/9/2014	A	SR 1.5 (Sugar Run)	41.239	-76.692	6.7	11.0		
12/9/2014		SR 1.5 (Sugar Run)	41.239	-76.692	10.1			
12/9/2014		SR 1.5 (Sugar Run)	41.239	-76.692	7.6			
12/9/2014		SR 1.5 (Sugar Run)	41.239	-76.692	9.0			
7/9/2015		SR 1.5 (Sugar Run)	41.239	-76.692	10.6		16.31	7.43
7/9/2015		SR 1.5 (Sugar Run)	41.239	-76.692	10.7			
7/9/2015		SR 1.5 (Sugar Run)	41.239	-76.692	10.4			
6/13/2016		SR 1.5 (Sugar Run)			22.9			
12/9/2014	A	SR 1.55 (Sugar Run)	41.24	-76.692	6.2	7.1		
7/9/2015		SR 1.55 (Sugar Run)	41.24	-76.692	7.5		15.57	7.43
7/9/2015		SR 1.55 (Sugar Run)	41.24	-76.692	7.5			
12/9/2014	A	SR 1.6 (Sugar Run)	41.24	-76.691	6.6	6.5		
12/9/2014		SR 1.6 (Sugar Run)	41.24	-76.691	6.5			
12/9/2014		SR 1.6 (Sugar Run)	41.24	-76.691	5.5			
12/9/2014		SR 1.6 (Sugar Run)	41.24	-76.691	6.2			
7/9/2015		SR 1.6 (Sugar Run)	41.24	-76.691	7.1		16.69	7.34
7/9/2015		SR 1.6 (Sugar Run)	41.24	-76.691	6.5			
7/9/2015		SR 1.6 (Sugar Run)	41.24	-76.691	7.8			
6/13/2016		SR 1.6 (Sugar Run)			5.8			
7/9/2015	A	SR 1.8 (Sugar Run)	41.241	-76.691	9.1	8.5	17.66	7.05
7/9/2015		SR 1.8 (Sugar Run)	41.241	-76.691	9.1			
6/13/2016		SR 1.8 (Sugar Run)			7.4			
7/9/2015	A	SR 2 (Sugar Run)	41.241	-76.69	9.3	8.6	19.1	6.08
7/9/2015		SR 2 (Sugar Run)	41.241	-76.69	9.3			
6/13/2016		SR 2 (Sugar Run)			7.1			
10/26/2015	B	Trib 36989 to Little Chartiers Creek	40.178	-80.166	2.2	2.2		
10/26/2015	O	Trib 39657 to Pigeon Creek	40.178	-79.979	3.1	3.1		

Table S1 Continued.

Date	Type	Site Name	Latitude	Longitude	$[CH_4]$ µg/L	Mean $[CH_4]$ µg/L	Water Temp °C	pH
10/26/2015	O	Trib 39670 to Pigeon Creek	40.163	-80.009	0.4	0.4		
5/21/2013	O	Trib 5.5	41.248	-76.668	0.2	0.2		
7/18/2015	B	Trib Black Moshannon Lake	40.891	-78.042	1.4	1.4		
7/18/2015	B	Trib Black Moshannon Lake	40.894	-78.043	4.3	4.3		
1/14/2016	B	Trib to Plum Run	40.258	-80.218	2.1	2.1		
8/10/2015	O	Trib_to_CouncilRun	41.091	-77.819	0.2	0.2	15	6.6
5/5/2016		Trib_to_CouncilRun	41.091	-77.819	<0.06		10	5.9
10/12/2015		Tributary to Council Run	41.091	-77.819	0.3		8	6.4
11/9/2015		LHU_Trib_to_CouncilRun	41.091	-77.819	0.2		7	5.8
10/12/2015	O	Twin Run	41.108	-77.694	0.3	0.2	9	6.1
4/11/2016		Twin Run	41.108	-77.694	0.1		5	6.4
8/10/2015		Twin Run	41.108	-77.694	0.3		13	5.7
3/1/2016	O	Two Rock Run	41.131	-77.804	0.4	0.4	7	6.9
9/16/2015	O	Two Rock Run	41.108	-77.694	0.8	0.8	13	5.8
8/6/2015	O	Unnamed Tributary (Chartiers)	40.178	-80.175	1.0	1.0		
8/6/2015	O	Unnamed Tributary (Chartiers)	40.183	-80.133	1.3	1.3		
8/6/2015	B	Unnamed Tributary (Chartiers)	40.200	-80.131	3.4	3.4		
8/6/2015	B	Unnamed Tributary (Chartiers)	40.217	-80.153	3.4	3.4		
8/6/2015	B	Unnamed Tributary Chartiers)	40.217	-80.141	1.4	1.4		
6/22/2015	B	Unnamed Tributary 1 (Chartiers)	40.223	-80.135	1.6	2.7		
8/6/2015		Unnamed Tributary 1 (Chartiers)	40.223	-80.135	3.7			
8/6/2015	O	Unnamed Tributary 2 (Chartiers)	40.229	-80.126	2.6	1.8		
6/22/2015		Unnamed Tributary 2 (Chartiers)	40.229	-80.126	1.0			
7/29/2015	O	UNT to Rose Valley Lake	41.384	-76.979	6.3	6.3		
9/26/2015	O	Upper East Fork Sinnemahoning	41.628	-77.86	0.7	0.7		
9/26/2015	O	Upper Hunts Run	41.503	-78.125	0.9	0.9		
1/14/2016	O	Walker	40.570	-80.190	0.5	0.5		
1/14/2016		Walker	40.570	-80.190	0.4			
7/29/2015	O	Wallis Run	41.379	-76.923	0.7	0.7		
9/26/2015	O	West Branch Freeman Run	41.634	-78.103	0.5	0.5		
9/16/2015	O	West Branch of Big Run	41.148	-77.781	0.3	0.2	12	6.5
3/1/2016		West Branch-Big Run	41.148	-77.781	0.3		7	7
5/5/2016		West Branch-Big Run	41.148	-77.781	<0.6		10	6.2
9/26/2015	O	Wildboy Run	41.61	-77.891	1.0	1.0		
9/26/2015	O	West Branch of Cowley Run	41.599	-78.186	0.5	0.5		
10/12/2015	O	Wolf Run	41.111	-77.897	0.4	0.3	11	6.4
4/11/2016		Wolf Run	41.111	-77.897	0.1		7	6.55
8/10/2015	O	LHU_WolfRun_Panther	41.090	-77.868	0.2	0.2	18	5.5
10/12/2015		Wolf Run – Panther Rd.	41.090	-77.868	0.2		12	6.7
4/11/2016		Wolf Run – Panther Rd.	41.090	-77.868	0.1		7	6.2
8/10/2015	O	Wolf Run - State Line	41.111	-77.897	1.2	1.2	15	6

*Type: O = other, B = biogenic, T = thermogenic, A = anthropogenic, N/A indicates data not available due to instrument unavailability.

Table S2. High CH_4 concentrations for samples collected on one day.

Date	Time	Stream ID	Latitude	Longitude	Total CH_4 (µg/L)	Average CH_4 (µg/L)
3/16/16	9:46 AM	Black Moshannon State Park (Site 1)	40.919	-78.059	6.95	6.6 ± 0.8
	9:48 AM				6.19	
	9:49 AM				7.39	
	9:51 AM				7.78	
	9:52 AM				6.66	
	9:53 AM				6.23	
	9:54 AM				6.03	
	9:55 AM				5.45	
6/13/16	12:05 PM	Sugar Run (SR 1.5 SEEP)	41.240	-76.692	231.4	216 ± 23
	12:07 PM				245.5	
	12:08 PM				230.6	
	12:09 PM				203.0	
	12:10 PM				218.9	
	12:11 PM				211.0	
	12:13 PM				173.7	

Table S3. Field data, concentrations, and isotopic data in the contamination-targeted dataset.

Sample Date	Stream ID	Lat	Long	$[CH_4]$ µg/L	T °C	pH	Sp. Cond. µS/cm	DO mg/L	Lat	Long	Comments	$\delta^{13}C_{CH4}$
3/9/16	Laurel Run	41.167	-78.539	0.4					41.167	-78.539	Plugged gas well in Moshannon Forest. SPUD Date: 4/17/1958 Date Plugged: 8/5/1998 Site is located in an area of historic coal mining. Sample sites are approximately 40 meters down gradient of well.	--
	Laurel Run	41.167	-78.539	0.4								
	Laurel Run	41.167	-78.539	0.3								
	Laurel Run	41.167	-78.539	0.4								
	Laurel Run	41.167	-78.539	8.1								
	Laurel Run	41.167	-78.539	34.3							This sample was collected near an outflow pipe. Rocks and sediment were coated with orange colored (Fe) precipitate.	
3/9/16	Elk Bar Run	41.766	-78.719	0.2					41.767	-78.718	Abandoned well in Allegheny State Forest, not part of the PADEP database. Location information obtained from S. Pelepko (PADEP). Gas had been observed bubbling in a wet area near the creek. It was thought there was communication between an abandoned well and a new shale gas well.	--
	Elk Bar Run	41.767	-78.718	2.1								
	Elk Bar Run	41.767	-78.718	2.0								
	Elk Bar Run	41.767	-78.718	2.1								
	Elk Bar Run	41.767	-78.719	2.5								

Table S3 Continued.

Sample Date	Stream ID	Lat	Long	$[CH_4]$ µg/L	T °C	pH	Sp. Cond. µS/cm	DO mg/L	Lat	Long	Comments	$\delta^{13}C_{CH4}$
3/9/16	Bennett Br.	41.276	-78.401	0.4					41.277	-78.401	Abandoned well not part of the PADEP database. Location information obtained from S. Pelepko (PADEP). Well discovered because a nearby camp, located within a cluster of old wells, observed ground catch on fire due to fireworks.	--
	Bennett Br.	41.276	-78.401	0.5								
	Bennett Br.	41.277	-78.401	0.3								
	Bennett Br.	41.277	-78.401	0.4								
5/30/16	Walnut Creek	42.062	-80.027	7.3					42.064	-80.018	Site located approximately 400 m down gradient of Waste Management - Erie, PA Landfill, but near three active oil and gas wells.	-43.6
5/30/16	Trib.1 Walnut Creek	42.061	-80.057	20.0					42.064	-80.053	Located downstream of an active well (dry hole) spudded in 1956, and two culverts. Located within 30 m of a wetland.	-56.9
5/30/16	Trib. 2 Walnut Creek	42.046	-80.071	3.7					42.042	-80.070	Site located downgradient of a PA DEP orphaned well, in an area of many active conventional wells.	-34.7
5/30/16	Oil Creek	41.639	-79.671	2.9					41.639	-79.671	Site located 0.10 mile downstream from active gas well, spud date 5/17/2005. Located upstream from two abandoned wells.	-49.8
7/3/16	Canadaway Creek	42.442	-79.392	1.5	22	8.3	910	6.93			Sampled middle of stream, just above waterfall at bridge (Rigley St.), upstream of bridge, and waterfall. On sandy shale, very flat lying planes of cleaved rock.	--
7/3/16	Canadaway Creek	42.438	-79.333	8.0	22	8.3	831	11.93			Sampled mid channel above Main St. Bridge behind fire station. Cobbly bottom.	
7/3/16	Canadaway Creek	42.476	-79.365	4.3							Sampled along bank near Tenmile Rd. at intersection with highway 5.	
7/3/16	Canadaway Creek	42.433	-79.314	0.8	21	8.3	853	13.25			Sampled along edge. Followed Liberty St. to Porta: dead end street off Porta with stream access.	
7/3/16	Canadaway Creek	42.438	-79.337	2.8							Just downstream of Forest Place. Shaley bed. Parts of creek cutting through thinly bedded black shale.	
7/3/16	East Van Buren point	42.446	-79.420	11.6	21	7.9	1010	11			Stream depth 30 cm, sampled above bridge along road. Steam doesn't reach to the beach/Lake Erie, may be flowing backwards or at a stand still.	
7/3/16	West Van Buren point	42.446	-79.420	1.3	19	7.9	1381	9.31			Sampled along very small stream draining into Lake Erie at edge. Location at end of Lakeshore Boulevard extension. Very shallow.	

Table S3 Continued.

Sample Date	Stream ID	Lat	Long	$[CH_4]$ µg/L	T °C	pH	Sp. Cond. µS/cm	DO mg/L	Lat	Long	Comments	$\delta^{13}C_{CH4}$
7/3/16	Oil Creek	41.615	-79.658	3.6							Sampled at Drake Well Road (Museum Rd) where it crosses Oil Creek. Sampled under bridge near parking lot near edge.	
7/18/16	West Branch Tomjac Creek	41.807	-76.632	4.52							Close to an outlier based on data mining of groundwater (Zheng et al. 2017) in Bradford County.	
7/18/16	Sugar Creek	41.763	-76.688	4.93							Kms downstream of an outlier based on data mining of groundwater (Zheng et al. 2017) in Bradford County.	
7/18/16	Sugar Creek	41.762	-76.699	1.78							Kms downstream of an outlier based on data mining of groundwater (Zheng et al. 2017) in Bradford County.	
7/18/16	Bailey Run	41.781	-76.534	2.70							Downstream of inferred groundwater hotspot (Li et al. 2016) and near an outlier based on data mining of groundwater (Zheng et al. 2017).	
7/19/16	Bailey Run	41.762	-76.550	0.27							Upstream of inferred groundwater hotspot (Li et al. 2016) and near an outlier based on data mining of groundwater (Zheng et al. 2017).	
7/19/16	Bailey Run	41.770	-76.544	2.47							Close upstream of inferred groundwater hotspot (Le et al. 2016) and near an outlier based on data mining of groundwater (Zheng et al. 2017).	
7/19/16	Towanda Creek	41.680	-76.677	4.87							Near inferred groundwater hotspot identified by Li et al. (2016).	
7/19/16	Towanda Creek	41.657	-76.790	2.99							Near inferred groundwater hotspot identified by Li et al. (2016).	
7/19/16	Sugar Run (Bradford Co.)	41.626	-76.274	1.17							Close to outliers based on data mining of groundwater (Zheng et al. 2017) and sites described by Llewellyn et al. (2015).	
7/19/16	Meshoppen Creek	41.614	-76.048	0.69							Near Dimock, PA	
7/19/16	North Branch of Sugar Run	41.640	-76.295	1.04							Close to an outlier based on data mining of groundwater (Zheng et al. 2017) and sites described by Llewellyn et al. (2015).	
7/13/16	Kinzua Creek	41.8	-78.7	33.7					41.770	-78.862	A top emitter, as described by M. Kang (pers. comm.) Well Status: DEP abandoned list (Combined oil and gas): SPUD Date: 1/1/1800. Sample located 0.07 mile down gradient of well. Allegheny State Forest.	-32.4‰

Table S3 Continued.

Sample Date	Stream ID	Lat	Long	$[CH_4]$ µg/L	T °C	pH	Sp. Cond. µS/cm	DO mg/L	Lat	Long	Comments	$\delta^{13}C_{CH4}$
7/13/16	Mud Run	41.8	-78.7	9.2 8.5					41.179	-78.529	A top emitter, as described by M. Kang (pers. comm.) Plugged gas well. SPUD Date: 3/3/1958 Date Plugged: 10/8/1991 Sampling site located 0.39 mile down gradient from well. Allegheny State Forest.	-34.8‰ -44.8‰
7/13/16	Chappel Fork	41.8	-78.7	26.3					41.809	-79.898	Well discovered by L. Barr of Save our Streams PA. Well not on the PADEP orphaned/abandoned well list. Allegheny State Forest.	-26.6‰

Table S4. Wetland-lake dataset (Black Moshannon Lake).

Date Sampled	Sample ID	Latitude	Longitude	$[CH_4]$ (µg/L)
7/18/2015	Black Moshannon Lake-1	40.9071	-78.0559	17.8
7/18/2015	Black Moshannon Lake-2	40.9059	-78.0549	22.7
7/18/2015	Black Moshannon Lake-3	40.9055	-78.0538	19.0
7/18/2015	Black Moshannon Lake-4	40.9017	-78.0568	45.2
7/18/2015	Black Moshannon Lake-5	40.8994	-78.0596	33.7
7/18/2015	Black Moshannon Lake-6	40.8953	-78.0619	26.6
7/18/2015	Black Moshannon Lake-7	40.8999	-78.0541	24.3
7/18/2015	Black Moshannon Lake-8	40.9010	-78.0555	11.1
7/18/2015	Black Moshannon Lake-9	40.9044	-78.0552	23.8
7/18/2015	Black Moshannon Lake-10	40.8943	-78.0434	20.9

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