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Spatiotemporal Correlation Analysis of Hydraulic Fracturing and Stroke in the United States

Chuanbo Hu [1], Bin Liu [2], Shuo Wang [3], Zhenduo Zhu [4], Amelia Adcock [5], James Simpkins [6] and Xin Li [1,*]

[1] Lane Department of Computer Science and Electrical Engineering, West Virginia University, Morgantown, WV 26505, USA
[2] Department of Management Information Systems, West Virginia University, Morgantown, WV 26505, USA
[3] Department of Radiology, Washington University, St. Louis, MO 63110, USA
[4] Department of Civil, Structural and Environmental Engineering, University at Buffalo, Buffalo, NY 14260, USA
[5] Department of Neurology, West Virginia University, Morgantown, WV 26505, USA
[6] Department of Neuroscience, West Virginia University, Morgantown, WV 26505, USA
* Correspondence: xin.li@mail.wvu.edu

Abstract: Hydraulic fracturing or fracking has led to a rapid growth of oil and gas production in the United States, but the impact of fracking on public health is an important but underresearched topic. We designed a methodology to study spatiotemporal correlations between the risk of fracking and stroke mortality. An annualized loss expectancy (ALE) model is applied to quantify the risk of fracking. The geographically and temporally weighted regression (GTWR) model is used to analyze spatiotemporal correlations of stroke mortality, fracking ALE, and nine other socioeconomic- and health-related factors. The analysis shows that fracking ALE is moderately correlated with stroke mortality at ages over 65 in most states of fracking, in addition to cardiovascular disease and drug overdose being positively correlated with stroke mortality. Furthermore, the correlations between fracking ALE and stroke mortality in men appear to be higher than in women near the Marcellus Shale, including Ohio, Pennsylvania, West Virginia, and Virginia, while stroke mortality among women is concentrated in the Great Plains, including Montana, Wyoming, New Mexico, and Oklahoma. Lastly, within two kilometers of the fracking mining activity, the level of benzene in the air was found to be significantly correlated with the fracking activity in Colorado.

Keywords: fracking; stroke mortality; annualized loss expectancy (ALE); geographically and temporally weighted regression (GTWR); spatiotemporal analysis

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1. Introduction

Hydraulic fracturing [1], also known as fracking, is a geochemical engineering process by which large volumes of water combined with chemical and sand proppants are injected into tight formations with high pressure to fracture and facilitate recovery of unconventional reserves of oil and gas [2]. With the development of fracking technology in the United States, shale gas is becoming an increasingly important source of natural gas, and interest has spread to countries around the world with shale gas storage. The US Energy Information Administration (EIA) assessed 137 shale formations in 42 countries around the world [3], and the distribution of assessed shale gas and shale oil basins of the world is shown in Figure 1. They represent 10% of the world's crude oil and 32% of the world's natural gas. However, as of 2013, only three countries (United States, Canada, and China) have significant commercial shale gas production due to technical limitations and local laws.

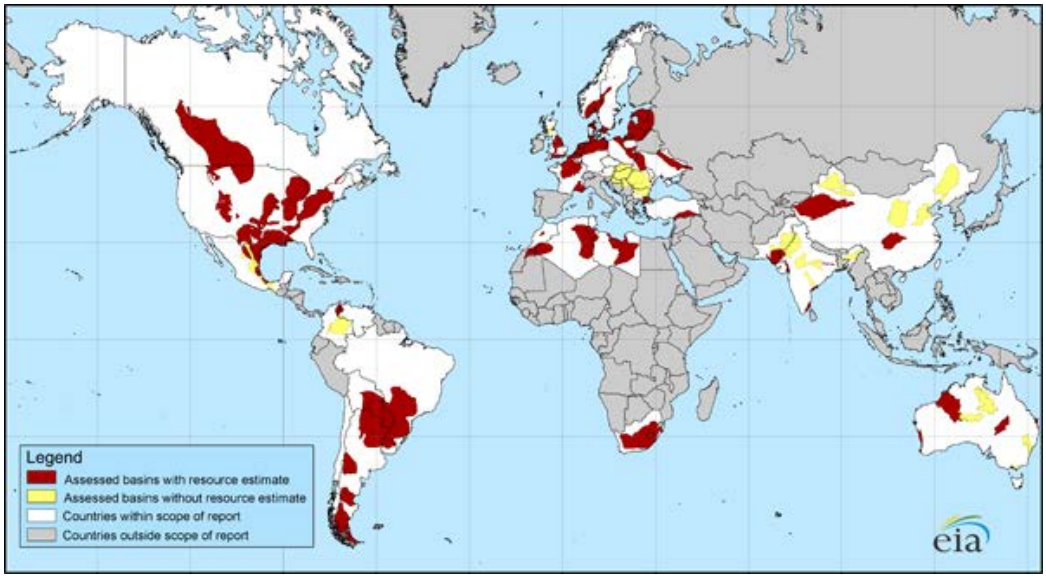

Figure 1. Mapping the distribution of assessed global shale gas and shale oil basins [3]. Source from United States Energy Information Administration (EIA) and United States Geological Survey.

Currently, the United States is the world's largest producer of both natural gas and crude oil. According to the US Energy Information Administration (EIA), there were approximately 23,000 fracking wells in the US in 2000. In 2015, the number of fracking wells increased rapidly to approximately 300,000, representing 67% of United States natural gas production and 51% of United States crude oil production [4]. Despite the economic benefits of fracking, this expansion has brought the industrial activities of oil and gas development closer to backyards and communities, increasing the risk of human exposure to new contaminants and threats [5,6].

The health implications and effects of fracking have not been adequately studied [7–12]. There is a growing body of research studies on the negative impact of fracking on air and water quality [13–17], as well as public health [18–22]. Although health discussions have focused on drinking water contamination, particularly in the eastern US, there is growing interest in studying a variety of health threats arising from air pollution [7,23]. Health threats from air pollution vary significantly across environments [24–27]. For example, research has attempted to link fracking pollution with unhealthy levels of smog and toxic air pollutants [28]. Exposure to this pollution can cause eye, nose, throat, respiratory disease, birth defects, cancer, or premature death [29]. However, little is known about whether fracking can cause life-threatening conditions such as stroke [8].

Stroke as a neurological disease is the leading cause of long-term adult disability and the fifth leading cause of death in the United States [30], with approximately 795,000 stroke events annually. Stroke belt refers to a consistent pattern of striking geographic variation in stroke mortality rates within the United States [31]. It covers 11 states in the southeast US with an unusually high incidence of stroke and other forms of cardiovascular disease. Factors that explain the prevalence of excessive stroke in the stroke belt include differences in socioeconomic status (e.g., employment rate and marital rate), risk factors (e.g., smoking and unhealthy diet), and prevalence of common chronic diseases (e.g., diabetes and heart disease) [32,33]. A recent study has shown that the highest contributors to the Stroke Belt include a higher burden of risk factors, higher levels of inflammation and infection, and lower socioeconomic status, while environmental exposures and lifestyle choices are considered lesser contributors [34].

Does fracking induce a higher risk of stroke? Although a potential connection between fracking and stroke has been mentioned in the literature (e.g., [35–37]), there is no systematic study to address this question. The closest research to this work is the study on the impact of fracking on water pollution [38] and air pollution [39], but its research data are limited

to the local area. Furthermore, the spatial extent of the public health impact of hydraulic fracturing is a question that existing research attempts to answer. For example, the distance to the nearest fracking well has been used as an important indicator to analyze the spatial correlation between fracking and infant health [40]. A spatial analysis method has been designed to quantify the environment at risk of Marcellus Shale fracking in the state of PA, USA [41]. The study [42] verified that people within 0.8 km of a fracking well are particularly at risk to their health. However, few studies have analyzed the spatiotemporal impacts of hydraulic fracturing on public health. The goal of this study is to address this question from a geographic information system (GIS) perspective using the extension of the geographically weighted regression (GWR) method [43]: geographically and temporally weighted regression (GTWR) [44]. We performed a detailed regression analysis of the stroke and fracking data using GTWR. We hope that this work can shed light on the relations between fracking and stroke risk and stimulate more quantitative studies on the health risk of fracking, which can better inform decision makers about energy and public health policy.

2. Methodology

2.1. Study Area and Data Collection

To study the spatiotemporal correlations of stroke mortality and fracking, the present study has chosen 49 states in the US as the study area. Alaska is not included due to its geographical isolation. Figure 2 shows the stroke death rate per 100,000 people over 65 years of age and all sites of fracking activity before 2018. To explore the impact of fracking on stroke mortality, we divide the 49 states into *fracking states* and *non-fracking states*. As a result, there are 24 fracking states that had fracking activities (including 19 states with active fracking and 5 states with little fracking) and 25 non-fracking states that did not have fracking activity by 2018.

Stroke is closely related to people's behavior habits (tobacco use, high cholesterol diet, and physical activity index), socioeconomic status (family mean income, marital rate, and employment rate), and other diseases (cardiovascular, overdose, and diabetes) [33,45]. Therefore, these variables have been selected for comparison with risk factors for fracking. Table 1 shows the details of the dependent and explanatory variables and their data sources. All data was collected in the US from 2010 to 2018. The scale of the data we collected is state-level except for fracking, because the county-level data contain a lot of missing data that can cause problems with the analysis. Furthermore, since stroke is a chronic disease, we processed the fracking data into the cumulative number of fracking wells. In other words, the number of fracking wells in any year includes all fracking wells before that year.

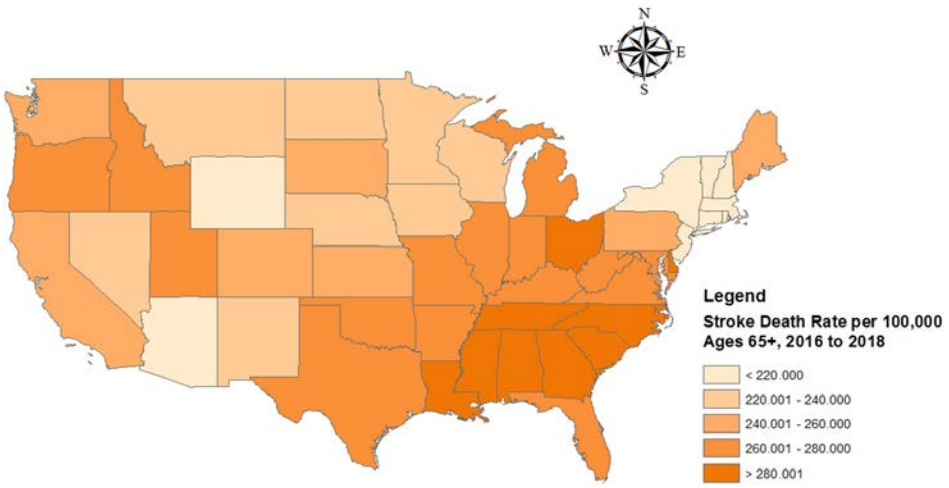

Figure 2. *Cont.*

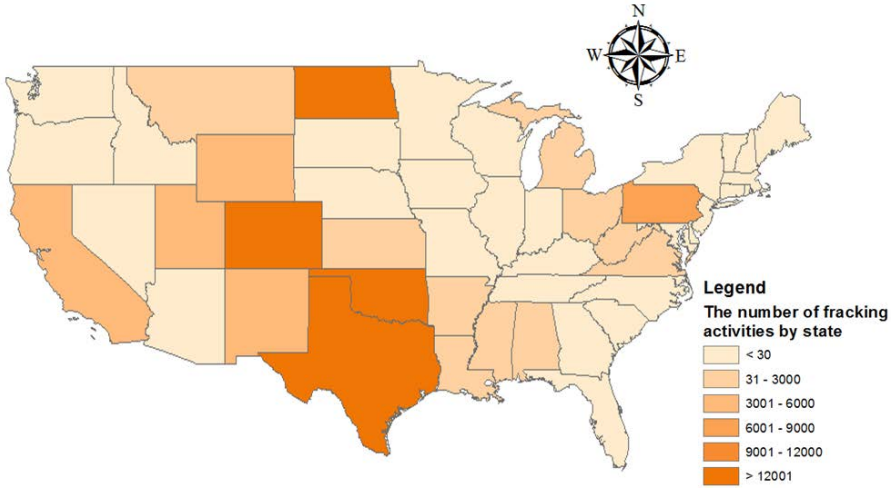

Figure 2. Map of the study area and the distribution of the stroke death rate per 100,000 population 65 years and older (**upper**) and US fracking activities by state prior to 2018 (**lower**).

Table 1. Description of the data used in this study (CDC: Centers for Disease Control and Prevention; USCB: The United States Census Bureau; FF: United States FracFocus; HAPs: Hazardous Air Pollutants; EPA: The United States Environmental Protection Agency).

Type	Variables	Description	Source
Fracking	Fracking activity	The location of Fracking wells	FF
Stroke mortality	65+ stroke mortality	Stroke deaths rate over 65 per 100,000	CDC
	Male stroke mortality	Male Stroke deaths rate per 100,000	CDC
	Female stroke mortality	Female Stroke deaths rate per 100,000	CDC
Disease	Diabetes	Proportion of diagnosed diabetes	CDC
	Cardiovascular	Cardiovascular deaths rate over 65 per 100,000	CDC
	Overdose	Drug overdose death rates	CDC
	Hypertension	High blood pressure deaths over 65 per 100,000	CDC
	Obesity	Adults with a BMI > 30	CDC
Behavior	Tobacco use	Current cigarette use by adults	CDC
	High cholesterol	High total cholesterol among adults	CDC
	Physical activity index	Physical Inactivity Prevalence	CDC
	Heavy Drink	8 or more drinks per week (female) or 15 or more drinks per week (male)	CDC
Socioeconomic	Mean income	Family income by number of workers	USCB
	Marital rate	Proportion of married population	USCB
	Employment rate	Proportion of employed population	USCB
	Education	Bachelor's degree or higher	USCB
HAPs	Butadiene	Concentration monitoring data for Butadiene	EPA
	Benzene	Concentration monitoring data for Benzene	EPA
	Formaldehyde	Concentration monitoring data for Formaldehyde	EPA
	Acetaldehyde	Concentration monitoring data for Acetaldehyde	EPA

2.2. Quantitative Risk Analysis: Annual Loss Expectancy of Fracking

Recent research illustrated that 2–16% of oil and gas wells spill liquids every year [46]. These accidents have caused fracking chemicals to contaminate drinking water and air, further raising serious public health risks [47–49]. To quantify the public health risk of fracking, the annualized loss expectancy (ALE) model [50] has been applied to assess the public health-related ALE caused by fracking by state, which is abbreviated as fracking ALE.

ALE is the product of the annual rate of occurrence (ARO) and the single loss expectancy (SLE) [51] caused by fracking, as shown in Equation (1).

$$\text{ALE} = \text{ARO} \times \text{SLE} \tag{1}$$

where fracking ARO is the annual occurrence of pollutant leakage due to fracking, which is equal to the Fracking Density per square kilometer (FD) multiplied by the annual rate of occurrence per fracking per square kilometer (AROF), ARO = FD × AROF.

Fracking SLE is defined as a population with negative health impacts expected from the occurrence of fracking accidents. For risk calculation, SLE is used to calculate a single loss when a specific event occurs. Fracking SLE is calculated by multiplying the Population Density per square kilometer (PD) by the fracking exposure factor (EF), SLE = PD × EF, as the higher the population density in fracking-active states, the greater the negative impact of fracking on public health.

Fracking ALE represents the product of AROF, FD, PD, and EF, which means the average loss per year of environmental pollution caused by fracking on public health. The FD and PD of the jth state in the ith year are FD_{ij} and PD_{ij}, respectively. As an important explanatory variable for the regression in Section 2.3.3, ALE is normalized as follows:

$$\textit{Normalized}\ \text{ALE}_{ij} = \frac{\text{ALE}_{ij} - \textit{Min}(\text{ALE})}{\textit{Max}(\text{ALE}) - \textit{Min}(\text{ALE})} \tag{2}$$

where $\textit{Normalized}\ \text{ALE}_{ij}$ is the normalized ALE in state j in year i. Since AROF and EF are constants, Equation (2) can be further formulated as

$$\textit{Normalized}\ \text{ALE}_{ij} = \frac{\text{FD}_{ij} \times \text{PD}_{ij} - \textit{Min}(\text{FD} \times \text{PD})}{\textit{Max}(\text{FD} \times \text{PD}) - \textit{Min}(\text{FD} \times \text{PD})} \tag{3}$$

2.3. Regression Model

2.3.1. Multicollinearity

We performed multicollinearity diagnostics before applying the regression model, since several explanatory variables could be highly correlated. Multicollinearity means that there is a high linear correlation between several specific explanatory variables, which could lead to bias in explaining the significance and associations of other variables. We adopted the variance inflation factor (VIF) [52], a metric of the severity of multicollinearity, to eliminate this problem. Explanatory variables with a VIF greater than 10 are considered to cause multicollinearity and should be excluded from the model [53].

2.3.2. Spatial Autocorrelation

As a commonly used spatial autocorrelation test, Moran's I test represents the spatial autocorrelation of a single explanatory variable and can be expressed as [54].

$$I = \frac{n}{\sum_{i=1}^{n}\sum_{j=1}^{n} w_{ij}} \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} w_{ij}(y_i - \bar{y})(y_j - \bar{y})}{\sum_{i=1}^{n}(y_i - \bar{y})^2} \tag{4}$$

Moran's I ranges from -1 to 1. A higher positive value indicates that closer observations have more similar attribute values, whereas farther observations have more distinct attribute values, indicating spatial aggregation. Negative values represent a spatially distributed distribution and a zero value represents a spatially random distribution. The null hypothesis of the Moran's I test indicates that the explanatory variables are spatially independent. It indicates that the Moran's I is close to zero. The Z-score is used as a significant indicator to measure Moran's I to verify the null hypothesis, whose formula is as follows [54].

$$Z(I) = \frac{I - E(I)}{\sqrt{Var(I)}} \tag{5}$$

where $E(I)$ and $Var(I)$ are the expectation and standard deviation of Moran's I, respectively. The significance level in this study is established as the p-value < 0.05.

2.3.3. Geographical and Temporal Weighted Regression (GTWR)

Spatiotemporal data analysis provides a series of important tools to solve problems such as correlation analysis of spatiotemporal data, spatiotemporal pattern analysis, and spatiotemporal prediction problems [44,55–59]. To analyze the spatio-temporal correlation between risk factors (see Table 1) and stroke mortality, the GTWR model was selected as the regression model. Compared to traditional Geographically Weighted Regression (GWR) [43], which only considers spatial features, the GTWR model [44] considers the non-stationary effect in space and time. Therefore, it was adopted to explore the spatiotemporal heterogeneity of the influence of fracking on different stroke mortality (i.e., age-based and gender-based) under the constraint of spatiotemporal differences. By establishing a three-dimensional elliptical coordinate system (including time, longitude, and latitude) in which the temporal dimension is the vertical dimension, in addition to the two horizontal spatial dimensions (longitude and latitude), the model can describe the spatio-temporal influence via the regression coefficients corresponding to explanatory variables. The GTWR model is described as

$$\mathbf{Y}_i = \beta_0(u_i, v_i, t_i) + \sum_k \beta_k(u_i, v_i, t_i) X_{ik} + \varepsilon_i \quad (6)$$

where u and v represent longitude and latitude, respectively. $\beta_0(u_i, v_i, t_i)$ represents the intercept item of state with centroid at (u_i, v_i) in year t_i; k is the number of explanatory variables; $\beta_k(u_i, v_i, t_i)$ is the regression coefficient of the kth explanatory variable in year t; X_{ik} is the kth explanatory variable. These explanatory variables are defined in Table 1.

The correctional values of the Akaike Information Criterion (AICc) [60] is an important metric and often used to select explanatory variables and determine the final model with the lowest AICc. In this study, the ArcGIS GTWR plugin was used to analyze the spatio-temporal correlation between stroke mortality and risk factors such as fracking ALE.

3. Results

3.1. Model Comparison

To solve the multicollinearity problem between multiple variables, the variables with a VIF greater than 10 (i.e., hypertension and obesity) were removed. The results of the VIF values of significant explanatory variables are given in Table A1 for stroke mortality over 65 years and Table A2 stroke mortality 45–64 in Appendix A. Additionally, Moran's I statistics were calculated to determine whether the explanatory variables in Tables A1 and A2 are spatially associated. The results of the Moran's I test are given in Table A3 in Appendix A. The 10 selected variables with a p-value below 0.05 were included in the regression model, indicating that all variables are spatially autocorrelated.

Furthermore, to increase the significance of the regression variable, two explanatory variables (i.e., heavy drink and education) have been removed using stepwise selection based on AICc. Furthermore, a comparison with three baseline models was implemented, including Ordinary Least Squares (OLS) [61], Temporally Weighted Regression (TWR) [44] and GWR [43]) to evaluate the performance of the GTWR model [44]. As shown in Table 2. GTWR outperforms OLS, TWR, and GWR in model fitting, demonstrating that it better explains dependent variable stroke mortality. Taking the fracking state model as an example, the values of R^2 increase from 0.757 in the OLS model, 0.768 in the TWR model, and 0.933 in the GWR model, to 0.970 in the GTWR model. The AICc reduces from −401.129 in the OLS, −399.780 in the TWR model and −534.502 in the GWR model, to −564.090 in the GTWR model (the lower, the better). The explanatory power increases significantly as spatial information and temporal information are considered in the model. In the rest of the paper, we will only analyze the results of the GTWR model.

Table 2. Comparison results of OLS, TWR, GWR, and GTWR models.

	Fracking States			Non-Fracking States		
	AICc	R^2	*Adjusted* R^2	*AICc*	R^2	*Adjusted* R^2
OLS [61]	−401.129	0.757	0.745	−293.313	0.601	0.584
TWR [44]	−399.780	0.768	0.757	−318.285	0.691	0.678
GWR [43]	−534.502	0.933	0.929	−481.016	0.897	0.892
GTWR [44]	**−564.090**	**0.970**	**0.968**	**−487.886**	**0.931**	**0.928**

Estimates of regression coefficients for 65+ stroke mortality in fracking states and non-fracking states are given in Tables 3 and 4. The results of both models showed the positive effect of cardiovascular and overdose on 65+ stroke mortality, and the negative effect of marital rate and employment rate on 65+ stroke mortality. These results share some similarities with other findings of previous work [62–64]. Furthermore, Table 3 shows that most fracking ALE coefficients are positively associated with stroke mortality at 65 years, although the correlation was much lower than for stroke mortality variables such as cardiovascular disease and overdose. Tables 3 and 4 show that there is no positive correlation between high cholesterol and stroke mortality. The result shares some similarities with other observations from previous work [33]. Furthermore, there is no correlation between tobacco use and 65+ stroke mortality, as its p-value > 0.1 (see Table A1).

Table 3. Estimation of the GTWR model for 65+ stroke mortality in fracking states.

Variables	MIN	LQ	MED	UQ	MAX	AVG
Related-disease risk factors						
Diabetes	−0.661	−0.316	−0.001	0.218	0.632	−0.018
Cardiovascular	−1.506	−0.070	0.269	0.524	1.141	0.232
Overdose	−0.861	−0.030	0.389	0.693	1.148	0.347
Behavior risk factors						
Tobacco use	−0.973	−0.342	−0.157	−0.035	0.351	−0.197
High cholesterol	−1.346	−0.325	−0.149	0.090	0.415	−0.139
PAI	−0.585	−0.161	−0.080	0.020	0.521	−0.056
Socioeconomic risk factors						
Mean income	−1.442	−0.215	0.147	0.367	0.623	0.039
Marital rate	−1.459	−0.984	−0.677	−0.409	0.720	−0.663
Employment rate	−2.106	−0.604	−0.014	0.128	0.627	−0.223
Fracking risk factor						
Fracking ALE	−0.327	0.041	0.116	0.154	0.394	0.094
Intercept	−0.009	0.487	0.669	0.792	3.747	0.715

Table 4. Estimation of the GTWR model for 65+ stroke mortality in non-fracking states.

Variables	MIN	LQ	MED	UQ	MAX	AVG
Related-disease risk factors						
Diabetes	−0.603	−0.085	0.227	0.314	0.467	0.109
Cardiovascular	−0.354	0.272	0.357	0.427	0.896	0.305
Overdose	−1.341	−0.189	0.166	0.286	0.805	0.037
Behavior risk factors						
Tobacco use	−0.577	−0.036	0.102	0.222	0.71	0.08
High cholesterol	−0.841	−0.539	−0.296	−0.165	0.175	−0.333
PAI	−0.493	−0.101	0.043	0.233	0.451	0.063
Socioeconomic risk factors						
Mean income	−2.403	−0.684	−0.412	−0.222	0.476	−0.479
Marital rate	−1.448	−0.651	−0.078	0.265	0.354	−0.221
Employment rate	−1.657	−1.07	−0.615	−0.144	1.122	−0.507

3.2. Spatiotemporal Features of Fracking ALE Coefficients

We analyze the temporal and spatial characteristics of fracking ALE using the average values of the regression coefficients, which help to explore the temporal trends and spatial differences of fracking ALE on stroke mortality at ages 65 and older.

3.2.1. Temporal Features of Fracking ALE Coefficients

The aforementioned improvement of GTWR is extended by incorporating the temporal dimension into the traditional GWR model. From the results of the GTWR model, we can obtain the time series of the yearly fracking ALE coefficients. Figure 3 presents the fluctuation of the average coefficients of the Fracking ALE variables over a 9-year period (from 2010 to 2018). Negative coefficients indicate the reverse correlation between the dependent and explanatory variables, and vice versa. 19 states with active fracking activity were discussed and 5 states with very few fracking activities were removed [65]. As Figure 3 shows, the positive correlation between fracking ALE and stroke mortality (65+) in California, Utah, Alabama, Louisiana, and Oklahoma decreased significantly year by year. In contrast, the positive correlation between fracking ALE and stroke mortality (65+) in North Dakota increased significantly. The coefficient of Fracking ALE in West Virginia, Ohio, Pennsylvania, Michigan, and Virginia slowly decreases. The ALE coefficient for fracking in Colorado and New Mexico first increases and then decreases.

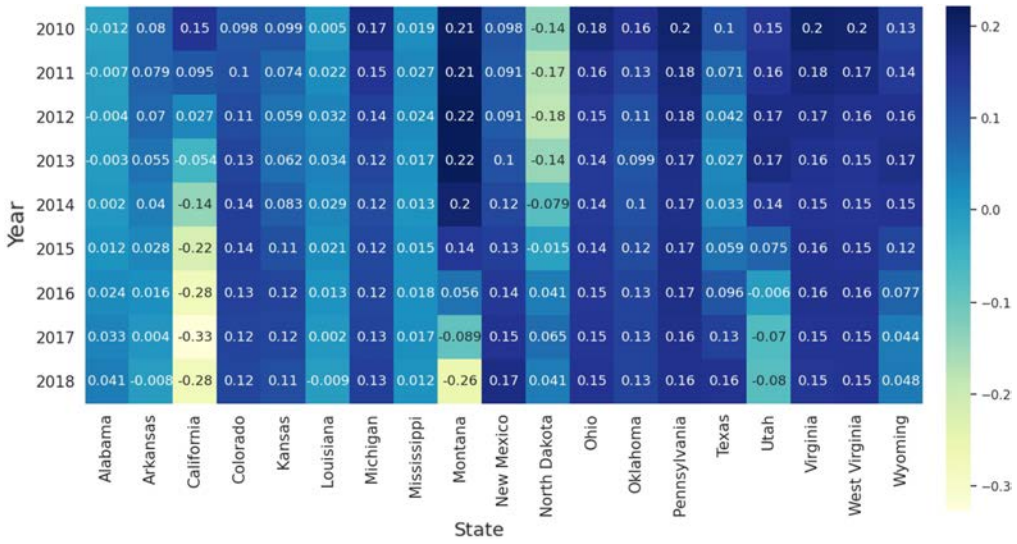

Figure 3. Temporal distribution of the average coefficients of the ALE of Fracking for 19 states with active fracking.

3.2.2. Spatial Features of Fracking ALE Coefficients

An important feature of the GTWR model is that the estimated coefficients are mappable for visual analysis. The spatial distributions of the effects of explanatory variables on ALE fracking are visualized in Figure 4. This study sets zero as a threshold to distinguish positive and negative effects. Darker states on the map have stronger positive correlations between fracking ALE and stroke mortality above 65. Figure 4 shows that the positive correlation between the ALE of fracking and stroke mortality (65+) in North Dakota, Ohio, Montana, Kansas, and Arkansas is stronger than in other states of fracking. Fracking has been active in North Dakota and Ohio [65]. Although fracking is generally active in Montana, Kansas, and Arkansas, fracking in their respective neighbors (e.g., North Dakota, Colorado, Texas) is always active. In contrast, the positive correlation in Virginia, Mississippi, and Oklahoma is weaker than in other states of fracking. Fracking is not active in the states of Virginia and Mississippi, according to the report by Environment America [4]. Additionally, Oklahoma, New Mexico, and Texas, where fracking is the most prevalent, have lower ALE coefficients for fracking than most states. The possible reason for this is

that Fracking ALE is positively correlated with some socioeconomic factors, such as family mean income and marital rate (see Figure A1), which are negatively correlated with stroke mortality over 65 years (see Figure A2).

Figure 4. Spatial distribution of the average coefficients of fracking ALE for 19 states related to fracking.

3.3. Comparative Analysis on the Effect of Fracking on Gender-Based Stroke Mortality

To explore spatio-temporal differences in the effect of hydraulic fracturing on gender-based stroke mortality, we performed spatio-temporal regressions on male and female stroke mortality separately using the selected explanatory variables. Based on the regression coefficients obtained for the two groups, the temporal and spatial characteristics of different sexes were compared and analyzed.

Figures 5 and 6 show, respectively, the regression coefficients of fracking ALE for different dependent variables (male stroke mortality and female stroke mortality). We found that the fracking ALE regression coefficients for males with stroke mortality and females with stroke mortality have similar temporal trends in Ohio, West Virginia, Virginia, and Pennsylvania. They slowly decreased from 2010 to 2018. The correlation coefficient between fracking ALE and stroke mortality (both men and women) in California decreased significantly year by year. The correlation coefficient between fracking ALE and stroke mortality (both male and female) in North Dakota increased significantly year by year. The correlation coefficients in the state of Colorado first increased and then decreased for male stroke mortality, but reversed for female stroke mortality. Additionally, the correlation coefficients between ALE from fracking and stroke mortality (both male and female) in California and some states (Arkansas, Louisiana, Mississippi, and Alabama) in the stroke belt are lower than those of other states from fracking.

In addition to the temporal characteristics of gender-based stroke mortality, the fracking ALE regression coefficients are spatially differentiated (see Figure 7). The ALE coefficients of fracking for male and female on stroke mortality around Marcellus shale (including Pennsylvania, West Virginia, and Ohio) and New Mexico and Oklahoma are higher than those of other states of fracking. In contrast, the ALE coefficients for fracking on female stroke mortality are higher in Montana and Wyoming, but its ALE coefficients for male are lower.

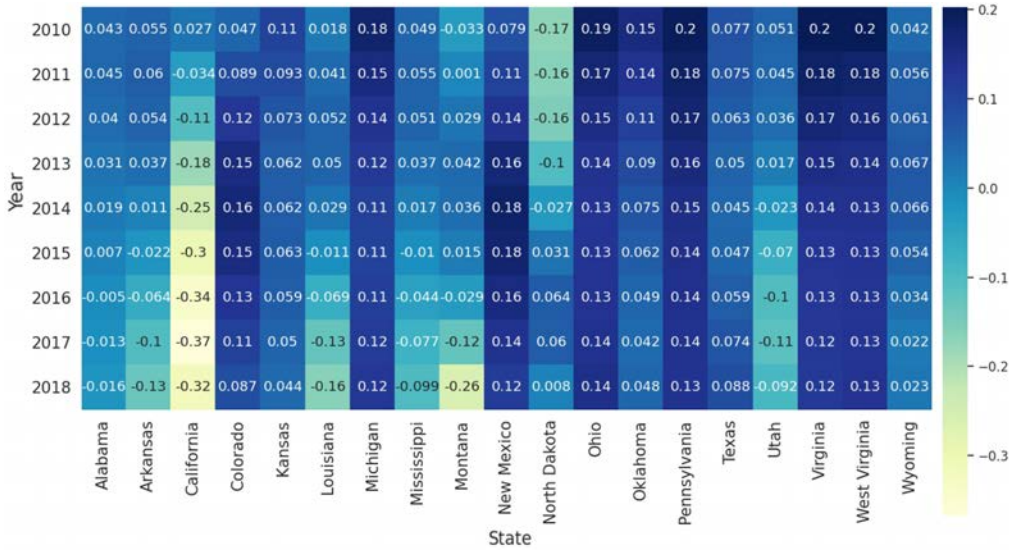

Figure 5. Temporal distribution of the average coefficients of the ALE of Fracking for 19 states related to fracking (Male).

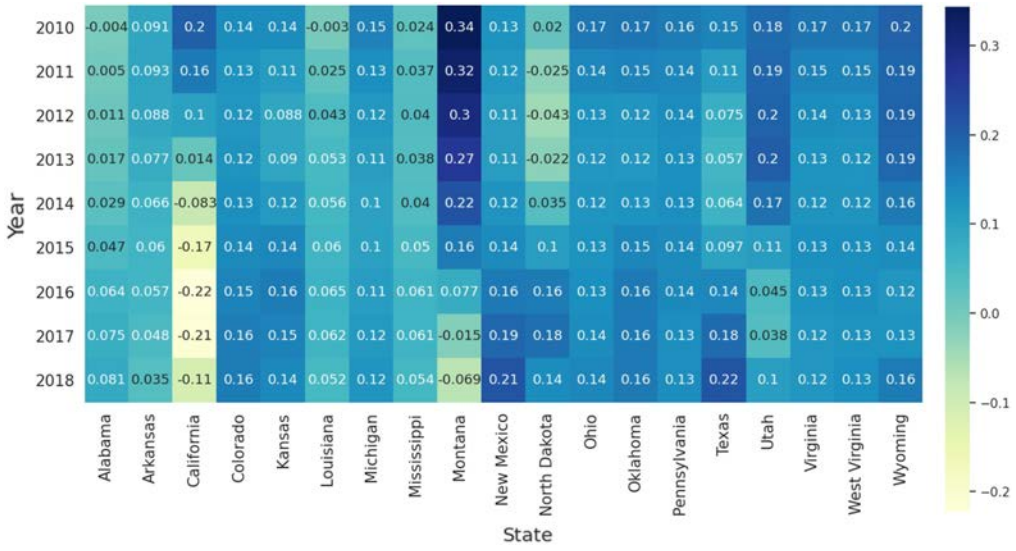

Figure 6. Temporal distribution of the average coefficients of ALE of fracking for 19 states related to fracking (Female).

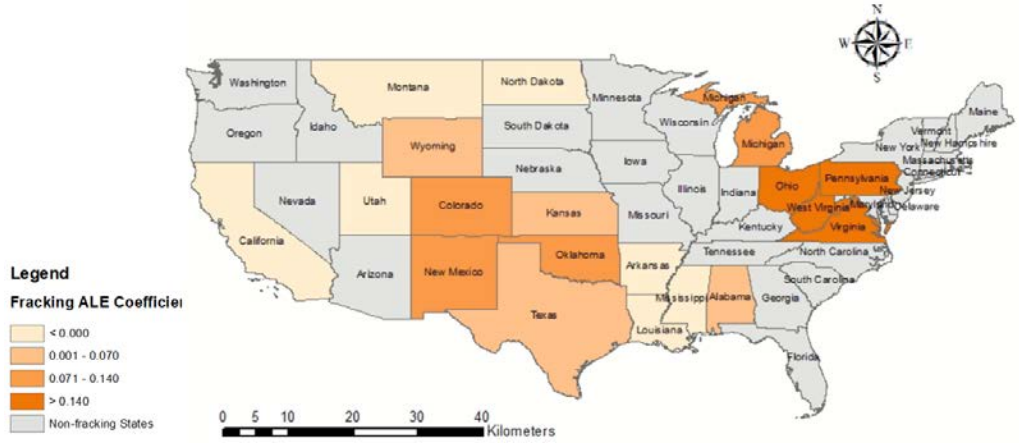

Figure 7. *Cont.*

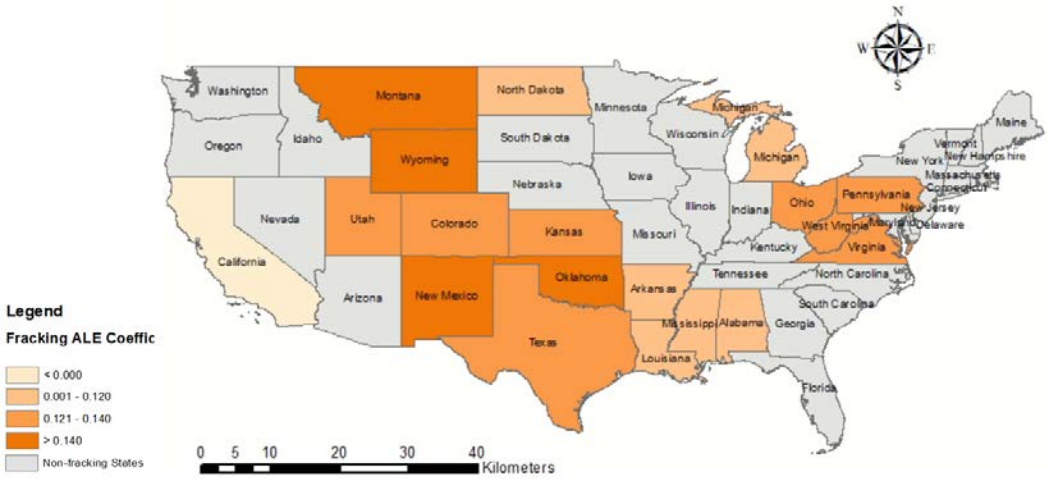

Figure 7. Spatial distribution of the average coefficients of fracking ALE for 19 states related to fracking for Male (**upper**) and Female (**lower**).

4. Discussion

4.1. Does Fracking Cause a Higher Risk of Stroke?

Despite the potential health risks associated with fracking, there have been several quantitative studies on how fracking can affect public health on a local scale [40,66], characterizing the risk of fracking as the distance from the patient's residence to the nearest well. However, these methods are based on privacy-protected clinical data that contain large amounts of patient personal information. They are not applicable to this study, since patient personal information is not included in the publicly available dataset from CDC. This study uses ALE to quantitatively study the possible connection between fracking and stroke using publicly available data. It can be observed from the results of the GTWR analysis that fracking has a non-negligible effect on stroke mortality above 65 in most areas with fracking prevalent, as shown in Table 3 and Figure 4. According to USCB, there were 40.3 M US residents 65 years and older in the 2010 Census and 54.1 M in the population estimates of 1 July 2019, (https://www.census.gov/topics/population/older-aging.html). With the aging of the United States and the increase in fracking activities, how to keep fracking activities away from communities with a high proportion of adults 65 years or older is a question that policy makers should consider. However, its impact is relatively minor compared to other more dominant factors, such as cardiovascular disease and overdose.

4.2. Spatiotemporal Differences in the Effect of Fracking on Age/Gender-Based Stroke Mortality

Deeper reasoning is needed to understand the geographic variations of cases of stroke mortality related to fracking based on the age and sex of the patients. As shown in Tables A1 and A2, the Fracking ALE variable for stroke mortality between 45–64 years is not considered statistically significant with a p-value > 0.1, but the Fracking ALE variable for stroke mortality over 65 years is considered statistically significant with a p-value < 0.01. For gender-based stroke mortality, the higher Fracking ALE coefficient for men than for women seems to suggest that men are at higher risk, at least in regions near Marcellus shale. Additionally, higher fracking ALE coefficients for women than for men suggest that women are at greater risk in some states, including Montana, Wyoming, Oklahoma, and New Mexico. Furthermore, the fracking ALE coefficients for both male and female stroke mortality are small in some states of the stroke belt (e.g., Arkansas, Louisiana, Mississippi, and Alabama), suggesting that fracking is not a major factor in stroke mortality compared to some major factors, such as cardiovascular disease.

4.3. Air Pollutant Emissions from Fracking

We examined a possible mechanism for how fracking threatens public health. An existing report indicates that fracking produces environmental pollution, including hazardous

water pollutants and hazardous air pollutants (HAPs) [67]. To explore which HAPs are associated with fracking activities, we collected air pollutants data from the HAP monitoring station in Colorado (longitude: −108.053259 and latitude: 39.453654). We have drawn a zone of interest with a radius of two kilometers around the HAP monitoring station and calculated the number of fracking wells. Four HAPs (Butadiene, Benzene, Formaldehyde, and Acetaldehyde) were monitored through this station, and we upsampled the four HAP monitoring data through linear interpolation to ensure that all four HAPs had the same time resolution. We then constructed a time series of fracking activities according to the start and end times of each fracking activity, and the overlapping fracking activities were aggregated. Finally, the four HAPs and the time series of the fracking activity were normalized, and then the fracking activities were analyzed for time series correlation with different HAPs using Pearson's correlation [68]. Pearson's r, which ranges from −1 to 1, was calculated to measure the degree of correlation between the two time series. When r > 0, a larger Pearson's r suggests a stronger positive correlation. Table 5 shows that the Pearson correlation (r) of benzene was higher than the other three HAPs and the correlation is statistically significant (p-value < 0.01). A study has shown the correlation between benzene exposure and the risk of cardiovascular disease due to the high level of trans, trans-muconic acid (t,t-MA) [69]. Although benzene exposure has also been found to be associated with high cholesterol [70], cardiovascular disease has a stronger correlation with stroke mortality at 65+ in our study than high cholesterol. The high density lipoprotein cholesterol was found to be more important for patients ≤65 years of age than older adults [71]. In addition, high cholesterol has been shown not to be associated with stroke mortality in some studies [33,72]. Therefore, the leakage of the chemical benzene due to fracking might contribute to cardiovascular disease thus stroke mortality but further study is needed and other processes such as water pollution might contribute as well.

Table 5. Pearson correlation significance test.

Air Pollutants	Pearson r	p-Value
Butadiene	0.119	0.083
Formaldehyde	0.093	0.175
Acetaldehyde	0.049	0.474
Benzene	0.245	0.000 *

* indicates $p < 0.01$.

4.4. What Is the Implication of This Study on Health Policy-Making?

With the increase in fracking activity, the socioeconomic environment, such as the employment rate and family income, continues to increase. At the same time, more and more people and communities in areas with many hydraulically fractured wells report health problems, such as cancer and harm to the nervous, respiratory, and immune systems. Macroscopically, we found that the effects of fracking and stroke mortality were not significant for the 19 active states of fracking in the US. This is likely due to the following reasons: (1) Fracking areas in the US are mainly distributed in the Great Plains and Marcellus Shale, which are often located in mountainous or suburban areas with low population density, which may lead to limited spatial impact. (2) The fracking process generally only lasts 3–5 days, which leads to a limited impact on time. (3) The development of fracking will promote local socioeconomic status (e.g., employment rate and marital rate), which is negatively related to stroke mortality. This may cause the effect of fracking on stroke mortality to be insignificant in some states (e.g., Texas) where fracking is active.

This study analyzed the correlation between fracking and different hazardous air pollutants based on the public air pollutant dataset from the US Environmental Protection Agency (EPA). We found that the concentration of benzene in the air was related to the calculated sequence of fracking activity in the buffer zone within a radius of 2 km (Pearson $r = 0.2452$ and the p-value < 0.01). To minimize health risk, this research suggests that there should be no public facilities with a high population density within 2 km of fracking

activities. Furthermore, the high concentration of benzene in the air may be due to fracking, which caused groundwater pollution due to the extremely high volatility of benzene. It may be important to identify and investigate domestic water wells that are within two kilometers of a fracking well. A more systematic study of the impact of fracking on water contamination [28] remains for future research.

5. Conclusions

This article provided a systematic study on the spatiotemporal correlation between fracking and stroke mortality using the GTWR model. The temporal trend of positive correlation between fracking ALE and stroke mortality shows a varying pattern from state to state. The spatial distribution appears to demonstrate that there is a gender difference between the Great Plains and the Marcellus Shale. Our regression results also show that disease-related risk factors, including cardiovascular and overdose, have a more significant correlation with stroke mortality over 65 years of age than those related to fracking. Finally, there appears to be a significant temporal dependency between fracking and air pollutant emissions, especially for benzene. Future studies may focus on developing county-level GWR/GTWR models, although missing data is a critical challenge to resolve.

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Appendix A

The VIF values of the explanatory variables are shown in Table A1 (for stroke mortality older than 65 years) and Table A2 (for stroke mortality from 45 to 64 years). Figure A1 shows the correlation coefficient between two explanatory variables. The correlation coefficient ranges from -1 to 1. The closer the coefficient is to 1, the stronger the positive correlation, the closer to -1, the stronger the negative correlation, and the closer to 0, the smaller the correlation. To avoid multicollinearity, explanatory variables (e.g., hypertension and obesity) with VIF values greater than 10 have been removed. Table A3 shows the results of the Moran's I test for explanatory variables. The VIF and Moran's I values were used to identify explanatory variables involved in the regression analysis. Regression analysis of the GWR model based on the selected explanatory variables obtains regression coefficients for several significant explanatory variables. Some important explanatory variables are visualized in the space for comparative analysis with the ALE regression coefficients of fracking, as shown in Figure A2. Additionally, to investigate whether air pollutant emissions from Fracking affects stroke mortality, monitoring data for benzene concentrations in Colorado are shown in Figure A3.

Table A1. VIF values of explanatory variables of the OLS model for 65+ stroke mortality.

Variables	Fracking States			Non-Fracking States		
	Coef.	*p*-Value	VIF	Coef.	*p*-Value	VIF
Related-disease risk factors						
Diabetes	0.126	0.043	3.550	0.242	0.002	1.847
Cardiovascular	0.351	0.000	5.168	0.377	0.000	1.847
Overdose	0.531	0.000	6.309	0.239	0.012	3.698
Behavior risk factors						
Tobacco use	−0.079	0.255	5.193	0.076	0.478	2.959
High cholesterol	−0.179	0.002	3.284	−0.257	0.000	2.210
PAI	−0.032	0.572	3.698	−0.109	0.132	1.853
Socioeconomic risk factors						
Mean income	0.290	0.002	5.236	−0.191	0.009	2.961
Marital rate	−0.918	0.000	2.880	−0.204	0.042	2.078
Employment rate	−0.076	0.232	2.072	−0.309	0.000	1.598
Fracking risk factors						
Fracking ALE	0.113	0.000	1.511			

Table A2. VIF values of the explanatory variables of the OLS model for 45–64 stroke mortality.

Variables	Fracking States			Non-Fracking States		
	Coef.	*p*-Value	VIF	Coef.	*p*-Value	VIF
Related-disease risk factors						
Diabetes	0.304	0.000	3.550	0.2220	0.000	1.847
Cardiovascular	0.637	0.000	5.168	0.7286	0.000	1.847
Overdose	0.048	0.435	6.309	0.0376	0.513	3.698
Behavior risk factors						
Tobacco use	−0.016	0.784	5.193	0.1970	0.003	2.959
High cholesterol	−0.027	0.568	3.284	−0.0377	0.364	2.210
PAI	0.0626	0.187	3.698	0.1752	0.000	1.853
Socioeconomic risk factors						
Mean income	−0.040	0.612	5.236	−0.0682	0.121	2.961
Marital rate	0.093	0.360	2.880	0.3925	0.000	2.078
Employment rate	−0.236	0.000	2.072	−0.1005	0.037	1.598
Fracking risk factors						
Fracking ALE	0.0337	0.128	1.511			

Table A3. Moran's I test result for explanatory variables.

Variables	Fracking States			Non-Fracking States		
	Moran's I	Z-Score	*p*-Value	Moran's I	Z-Score	*p*-Value
Related-disease risk factors						
Diabetes	0.799	24.055	0.000	0.659	20.274	0.000
Cardiovascular	0.955	28.695	0.000	0.924	28.348	0.000
Overdose	0.725	21.836	0.000	0.666	20.501	0.000
Behavior risk factors						
Tobacco use	0.854	25.731	0.000	0.589	18.140	0.000
High cholesterol	0.553	16.679	0.000	0.321	9.944	0.000
PAI	0.925	27.811	0.000	0.759	23.426	0.000
Socioeconomic risk factors						
Mean income	0.734	22.111	0.000	0.778	23.928	0.000
Marital rate	0.221	6.761	0.000	0.356	11.219	0.000
Employment rate	0.944	28.664	0.000	0.918	28.173	0.000
Fracking risk factor						
Fracking ALE	0.271	8.955	0.000			

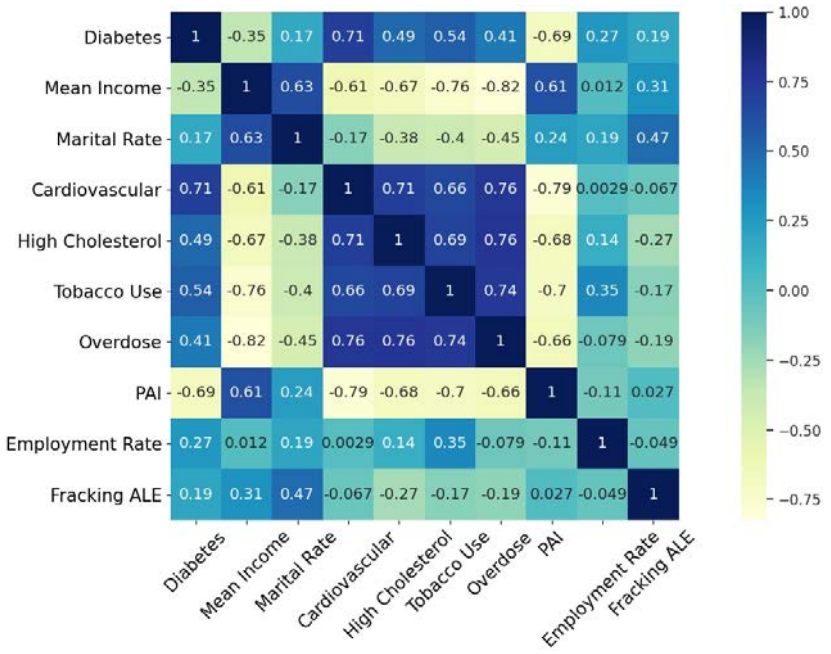

Figure A1. VIF between explanatory variables.

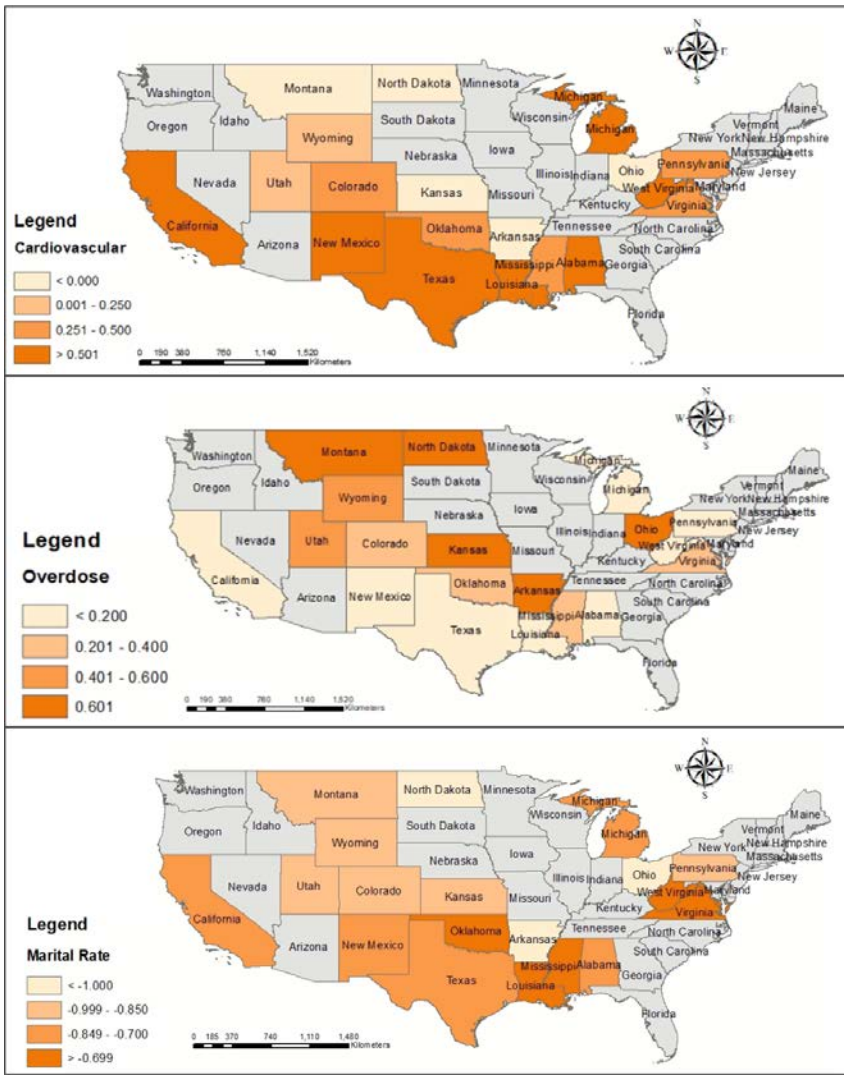

Figure A2. Spatial distribution of the significant coefficients for 19 states related to fracking.

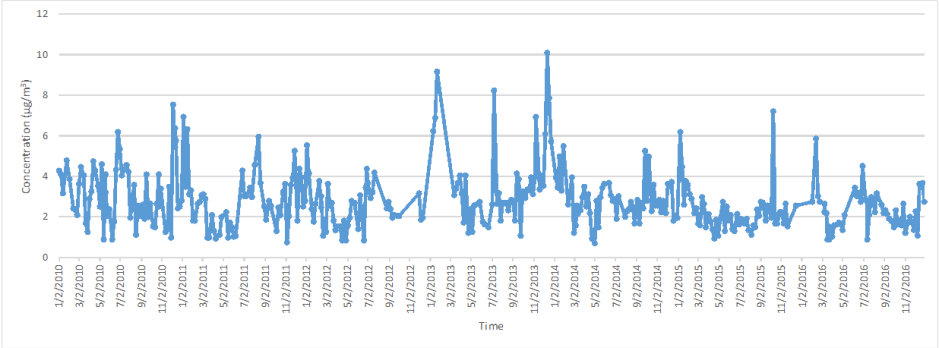

Figure A3. Benzene concentration monitoring data.

Reference

1. Gandossi, L.; Von Estorff, U. An overview of hydraulic fracturing and other formation stimulation technologies for shale gas production. *Eur. Commisison Jt. Res. Cent. Tech. Rep.* **2013**, *26347*.
2. Montgomery, C.T.; Smith, M.B. Hydraulic fracturing: History of an enduring technology. *J. Pet. Technol.* **2010**, *62*, 26–40. [CrossRef]
3. Kuuskraa, V.; Stevens, S.H.; Moodhe, K.D. *Technically Recoverable Shale Oil and Shale Gas Resources: An Assessment of 137 Shale Formations in 41 Countries Outside the United States*; US Energy Information Administration, US Department of Energy: Washington, DC, USA, 2013.
4. U.S. Energy Information Administration. *Hydraulic Fracturing Accounts for About Half of Current U.S. Crude Oil Production*; U.S. Energy Information Administration: Washington, DC, USA, 2016.
5. Finkel, M.L.; Hays, J. The implications of unconventional drilling for natural gas: A global public health concern. *Public Health* **2013**, *127*, 889–893. [CrossRef] [PubMed]
6. Meng, Q. Characterizing and modeling environmental emergency of unconventional oil and gas spills in the USA: Life-year versus spill factors. *J. Clean. Prod.* **2019**, *237*, 117794. [CrossRef]
7. Kovats, S.; Depledge, M.; Haines, A.; Fleming, L.E.; Wilkinson, P.; Shonkoff, S.B.; Scovronick, N. The health implications of fracking. *Lancet* **2014**, *383*, 757. [CrossRef]
8. Black, K.J.; Boslett, A.J.; Hill, E.L.; Ma, L.; McCoy, S.J. Economic, Environmental, and Health Impacts of the Fracking Boom. *Annu. Rev. Resour. Econ.* **2021**, *13*, 311–334. [CrossRef]
9. Soyer, M.; Kaminski, K.; Ziyanak, S. Socio-Psychological Impacts of Hydraulic Fracturing on Community Health and Well-Being. *Int. J. Environ. Res. Public Health* **2020**, *17*, 1186. [CrossRef]
10. Caron-Beaudoin, É.; Whyte, K.P.; Bouchard, M.F.; Chevrier, J.; Haddad, S.; Copes, R.; Frohlich, K.L.; Dokkie, D.; Juul, S.; Bouchard, M.; et al. Volatile organic compounds (VOCs) in indoor air and tap water samples in residences of pregnant women living in an area of unconventional natural gas operations: Findings from the EXPERIVA study. *Sci. Total. Environ.* **2022**, *805*, 150242. [CrossRef]
11. Ma, L.; Hurtado, A.; Eguilior, S.; Borrajo, J.F.L. Exposure risk assessment to organic compounds based on their concentrations in return water from shale gas developments. *Sci. Total. Environ.* **2022**, *822*, 153586. [CrossRef]
12. Meng, Q. The impacts of fracking on the environment: A total environmental study paradigm. *Sci. Total. Environ.* **2017**, *580*, 953–957. [CrossRef]
13. McKenzie, L.M.; Witter, R.Z.; Newman, L.S.; Adgate, J.L. Human health risk assessment of air emissions from development of unconventional natural gas resources. *Sci. Total. Environ.* **2012**, *424*, 79–87. [CrossRef]
14. Vengosh, A.; Jackson, R.B.; Warner, N.; Darrah, T.H.; Kondash, A. A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environ. Sci. Technol.* **2014**, *48*, 8334–8348. [CrossRef]
15. Deziel, N.C.; Brokovich, E.; Grotto, I.; Clark, C.J.; Barnett-Itzhaki, Z.; Broday, D.; Agay-Shay, K. Unconventional oil and gas development and health outcomes: A scoping review of the epidemiological research. *Environ. Res.* **2020**, *182*, 109124. [CrossRef]
16. Tao, Z.; Liu, C.; He, Q.; Chang, H.; Ma, J. Detection and treatment of organic matters in hydraulic fracturing wastewater from shale gas extraction: A critical review. *Sci. Total. Environ.* **2022**, *824*, 153887. [CrossRef]
17. Meng, Q. Rethink potential risks of toxic emissions from natural gas and oil mining. *Environ. Pollut.* **2018**, *240*, 848–857. [CrossRef]
18. Casey, J.A.; Savitz, D.A.; Rasmussen, S.G.; Ogburn, E.L.; Pollak, J.; Mercer, D.G.; Schwartz, B.S. Unconventional natural gas development and birth outcomes in Pennsylvania, USA. *Epidemiology* **2016**, *27*, 163. [CrossRef]
19. Rasmussen, S.G.; Ogburn, E.L.; McCormack, M.; Casey, J.A.; Bandeen-Roche, K.; Mercer, D.G.; Schwartz, B.S. Association between unconventional natural gas development in the Marcellus Shale and asthma exacerbations. *JAMA Intern. Med.* **2016**, *176*, 1334–1343. [CrossRef]

20. Tustin, A.W.; Hirsch, A.G.; Rasmussen, S.G.; Casey, J.A.; Bandeen-Roche, K.; Schwartz, B.S. Associations between unconventional natural gas development and nasal and sinus, migraine headache, and fatigue symptoms in Pennsylvania. *Environ. Health Perspect.* **2017**, *125*, 189–197. [CrossRef]
21. Casey, J.A.; Wilcox, H.C.; Hirsch, A.G.; Pollak, J.; Schwartz, B.S. Associations of unconventional natural gas development with depression symptoms and disordered sleep in Pennsylvania. *Sci. Rep.* **2018**, *8*, 11375. [CrossRef]
22. Marlin-Tackie, F.A.; Smith, J.M. Key characteristics influencing risk perceptions of unconventional energy development. *J. Clean. Prod.* **2020**, *251*, 119644. [CrossRef]
23. McDermott-Levy, R.; Kaktins, N.; Sattler, B. Fracking, the environment, and health. *AJN Am. J. Nurs.* **2013**, *113*, 45–51. [CrossRef]
24. Wong, C.M.; Vichit-Vadakan, N.; Kan, H.; Qian, Z. Public Health and Air Pollution in Asia (PAPA): a multicity study of short-term effects of air pollution on mortality. *Environ. Health Perspect.* **2008**, *116*, 1195–1202. [CrossRef]
25. Kelly, F.J.; Fussell, J.C. Air pollution and public health: emerging hazards and improved understanding of risk. *Environ. Geochem. Health* **2015**, *37*, 631–649. [CrossRef]
26. Hu, C.B.; Zhang, F.; Gong, F.Y.; Ratti, C.; Li, X. Classification and mapping of urban canyon geometry using Google Street View images and deep multitask learning. *Build. Environ.* **2020**, *167*, 106424. [CrossRef]
27. Turner, M.C.; Andersen, Z.J.; Baccarelli, A.; Diver, W.R.; Gapstur, S.M.; Pope, C.A., III; Prada, D.; Samet, J.; Thurston, G.; Cohen, A. Outdoor air pollution and cancer: An overview of the current evidence and public health recommendations. *CA Cancer J. Clin.* **2020**, *70*, 460–479. [CrossRef]
28. Jackson, R.B.; Vengosh, A.; Carey, J.W.; Davies, R.J.; Darrah, T.H.; O'sullivan, F.; Pétron, G. The environmental costs and benefits of fracking. *Annu. Rev. Environ. Resour.* **2014**, *39*, 327–362. [CrossRef]
29. Stacy, S.L. A review of the human health impacts of unconventional natural gas development. *Curr. Epidemiol. Rep.* **2017**, *4*, 38–45. [CrossRef]
30. Towfighi, A.; Saver, J.L. Stroke declines from third to fourth leading cause of death in the United States: Historical perspective and challenges ahead. *Stroke* **2011**, *42*, 2351–2355. [CrossRef] [PubMed]
31. Lanska, D.J.; Kuller, L.H. The geography of stroke mortality in the United States and the concept of a stroke belt. *Stroke* **1995**, *26*, 1145–1149. [CrossRef] [PubMed]
32. Liao, Y.; Greenlund, K.J.; Croft, J.B.; Keenan, N.L.; Giles, W.H. Factors explaining excess stroke prevalence in the US Stroke Belt. *Stroke* **2009**, *40*, 3336–3341. [CrossRef] [PubMed]
33. Feigin, V.L.; Roth, G.A.; Naghavi, M.; Parmar, P.; Krishnamurthi, R.; Chugh, S.; Mensah, G.A.; Norrving, B.; Shiue, I.; Ng, M.; et al. Global burden of stroke and risk factors in 188 countries, during 1990–2013: A systematic analysis for the Global Burden of Disease Study 2013. *Lancet Neurol.* **2016**, *15*, 913–924. [CrossRef]
34. Howard, G.; Howard, V.J. Twenty years of progress toward understanding the stroke belt. *Stroke* **2020**, *51*, 742–750. [CrossRef]
35. Srebotnjak, T.; Rotkin-Ellman, M. Fracking fumes: Air pollution from hydraulic fracturing threatens public health and communities. *Nat. Resour. Def. Counc.* **2014**. Available online: https://legacy-assets.eenews.net/open_files/assets/2014/12/16/document_cw_01.pdf (accessed on 25 August 2022).
36. Law, A.; Duff, D.; Saunders, P.; Middleton, J.; McCoy, D. Medical organisations must divest from fossil fuels. *BMJ* **2018**, *363*, k5163. [CrossRef]
37. Krajnak, K.; Kan, H.; Russ, K.A.; McKinney, W.; Waugh, S.; Zheng, W.; Kashon, M.L.; Johnson, C.; Cumpston, J.; Fedan, J.S. Biological effects of inhaled hydraulic fracturing sand dust. VI. Cardiovascular effects. *Toxicol. Appl. Pharmacol.* **2020**, *406*, 115242. [CrossRef]
38. Oikonomou, P.D.; Kallenberger, J.A.; Waskom, R.M.; Boone, K.K.; Plombon, E.N.; Ryan, J.N. Water acquisition and use during unconventional oil and gas development and the existing data challenges: Weld and Garfield counties, CO. *J. Environ. Manag.* **2016**, *181*, 36–47. [CrossRef]
39. Purvis, R.M.; Lewis, A.C.; Hopkins, J.R.; Wilde, S.E.; Dunmore, R.E.; Allen, G.; Pitt, J.; Ward, R.S. Effects of 'pre-fracking'operations on ambient air quality at a shale gas exploration site in rural North Yorkshire, England. *Sci. Total. Environ.* **2019**, *673*, 445–454. [CrossRef]
40. Currie, J.; Greenstone, M.; Meckel, K. Hydraulic fracturing and infant health: New evidence from Pennsylvania. *Sci. Adv.* **2017**, *3*, e1603021. [CrossRef]
41. Meng, Q. Spatial analysis of environment and population at risk of natural gas fracking in the state of Pennsylvania, USA. *Sci. Total. Environ.* **2015**, *515*, 198–206. [CrossRef]
42. Meng, Q.; Ashby, S. Distance: A critical aspect for environmental impact assessment of hydraulic fracking. *Extr. Ind. Soc.* **2014**, *1*, 124–126. [CrossRef]
43. Brunsdon, C.; Fotheringham, A.S.; Charlton, M.E. Geographically weighted regression: A method for exploring spatial nonstationarity. *Geogr. Anal.* **1996**, *28*, 281–298. [CrossRef]
44. Huang, B.; Wu, B.; Barry, M. Geographically and temporally weighted regression for modeling spatio-temporal variation in house prices. *Int. J. Geogr. Inf. Sci.* **2010**, *24*, 383–401. [CrossRef]
45. Feigin, V.L.; Forouzanfar, M.H.; Krishnamurthi, R.; Mensah, G.A.; Connor, M.; Bennett, D.A.; Moran, A.E.; Sacco, R.L.; Anderson, L.; Truelsen, T.; et al. Global and regional burden of stroke during 1990–2010: Findings from the Global Burden of Disease Study 2010. *Lancet* **2014**, *383*, 245–255. [CrossRef]

46. Patterson, L.A.; Konschnik, K.E.; Wiseman, H.; Fargione, J.; Maloney, K.O.; Kiesecker, J.; Nicot, J.P.; Baruch-Mordo, S.; Entrekin, S.; Trainor, A.; et al. Unconventional oil and gas spills: Risks, mitigation priorities, and state reporting requirements. *Environ. Sci. Technol.* **2017**, *51*, 2563–2573.
47. Korfmacher, K.S.; Jones, W.A.; Malone, S.L.; Vinci, L.F. Public health and high volume hydraulic fracturing. *New Solut. J. Environ. Occup. Health Policy* **2013**, *23*, 13–31.
48. Colborn, T.; Kwiatkowski, C.; Schultz, K.; Bachran, M. Natural gas operations from a public health perspective. *Hum. Ecol. Risk Assess. Int. J.* **2011**, *17*, 1039–1056.
49. Bamberger, M.; Oswald, R.E. Impacts of gas drilling on human and animal health. *New Solut. J. Environ. Occup. Health Policy* **2012**, *22*, 51–77. [CrossRef]
50. Bistarelli, S.; Fioravanti, F.; Peretti, P. Defense trees for economic evaluation of security investments. In Proceedings of the First International Conference on Availability, Reliability and Security (ARES'06), Vienna, Austria, 20–22 April 2006; p. 8.
51. Karabacak, B.; Sogukpinar, I. ISRAM: Information security risk analysis method. *Comput. Secur.* **2005**, *24*, 147–159.
52. Akinwande, M.O.; Dikko, H.G.; Samson, A. Variance inflation factor: As a condition for the inclusion of suppressor variable (s) in regression analysis. *Open J. Stat.* **2015**, *5*, 754. [CrossRef]
53. Kutner, M.H.; Nachtsheim, C.J.; Neter, J.; Wasserman, W. *Applied Linear Regression Models*; McGraw-Hill/Irwin: New York, NY, USA, 2004; Volume 4.
54. Moran, P.A. Notes on continuous stochastic phenomena. *Biometrika* **1950**, *37*, 17–23. [CrossRef]
55. Shekhar, S.; Jiang, Z.; Ali, R.Y.; Eftelioglu, E.; Tang, X.; Gunturi, V.M.; Zhou, X. Spatiotemporal data mining: A computational perspective. *ISPRS Int. J. Geo-Inf.* **2015**, *4*, 2306–2338. [CrossRef]
56. Wang, W.; Hu, C.; Chen, N.; Xiao, C.; Wang, C.; Chen, Z. Spatio-temporal enabled urban decision-making process modeling and visualization under the cyber-physical environment. *Sci. China Inf. Sci.* **2015**, *58*, 1–17. [CrossRef]
57. Xiao, C.; Chen, N.; Gong, J.; Wang, W.; Hu, C.; Chen, Z. Event-driven distributed information resource-focusing service for emergency response in smart city with cyber-physical infrastructures. *ISPRS Int. J. Geo-Inf.* **2017**, *6*, 251.
58. Chuanbo, H.; Lan, Y.; Hui, L. A Process-oriented Risk Monitoring and Assessment Modeling Approach in Urban Public Safety. *Acta Geod. Cartogr. Sin.* **2018**, *47*, 1062.
59. Wang, W.; Hu, C.; Chen, N.; Xiao, C.; Jia, S. Spatio-Temporal Risk Assessment Process Modeling for Urban Hazard Events in Sensor Web Environment. *ISPRS Int. J. Geo-Inf.* **2016**, *5*, 203. [CrossRef]
60. Cavanaugh, J.E. Unifying the derivations for the Akaike and corrected Akaike information criteria. *Stat. Probab. Lett.* **1997**, *33*, 201–208. [CrossRef]
61. Dismuke, C.; Lindrooth, R. Ordinary least squares. *Methods Des. Outcomes Res.* **2006**, *93*, 93–104.
62. Arboix, A. Cardiovascular risk factors for acute stroke: Risk profiles in the different subtypes of ischemic stroke. *World J. Clin. Cases WJCC* **2015**, *3*, 418.
63. Avan, A.; Digaleh, H.; Di Napoli, M.; Stranges, S.; Behrouz, R.; Shojaeianbabaei, G.; Amiri, A.; Tabrizi, R.; Mokhber, N.; Spence, J.D.; et al. Socioeconomic status and stroke incidence, prevalence, mortality, and worldwide burden: An ecological analysis from the Global Burden of Disease Study 2017. *BMC Med.* **2019**, *17*, 191. [CrossRef]
64. Addo, J.; Ayerbe, L.; Mohan, K.M.; Crichton, S.; Sheldenkar, A.; Chen, R.; Wolfe, C.D.; McKevitt, C. Socioeconomic status and stroke: An updated review. *Stroke* **2012**, *43*, 1186–1191.
65. Center, E.A.R..P. *Fracking by the Numbers The Damage to Our Water, Land and Climate from a Decade of Dirty Drilling*; Environment America Research and Policy Center: Washington, DC, USA, 2016.
66. Clark, C.J.; Xiong, B.; Soriano, M.A., Jr.; Gutchess, K.; Siegel, H.G.; Ryan, E.C.; Johnson, N.P.; Cassell, K.; Elliott, E.G.; Li, Y.; et al. Assessing unconventional oil and gas exposure in the Appalachian basin: Comparison of exposure surrogates and residential drinking water measurements. *Environ. Sci. Technol.* **2022**, *56*, 1091–1103. [CrossRef]
67. Windham, G.C.; Zhang, L.; Gunier, R.; Croen, L.A.; Grether, J.K. Autism spectrum disorders in relation to distribution of hazardous air pollutants in the San Francisco Bay area. *Environ. Health Perspect.* **2006**, *114*, 1438–1444. [CrossRef]
68. Benesty, J.; Chen, J.; Huang, Y.; Cohen, I. Pearson correlation coefficient. In *Noise Reduction in Speech Processing*; Springer: Berlin/Heidelberg, Germany, 2009; pp. 1–4.
69. Abplanalp, W.; DeJarnett, N.; Riggs, D.W.; Conklin, D.J.; McCracken, J.P.; Srivastava, S.; Xie, Z.; Rai, S.; Bhatnagar, A.; O'Toole, T.E. Benzene exposure is associated with cardiovascular disease risk. *PLoS ONE* **2017**, *12*, e0183602. [CrossRef]
70. Alshareef, A.; Ibrahim, M. Neurological and Biological Toxicity of Subchronic Exposure to Inhaled Benzene in Male Rats. *J. Biochem. Technol.* **2020**, *11*, 52–59.
71. Tirschwell, D.; Smith, N.; Heckbert, S.; Lemaitre, R.; Longstreth, W.; Psaty, B. Association of cholesterol with stroke risk varies in stroke subtypes and patient subgroups. *Neurology* **2004**, *63*, 1868–1875. [CrossRef]
72. Bowman, T.S.; Sesso, H.D.; Ma, J.; Kurth, T.; Kase, C.S.; Stampfer, M.J.; Gaziano, J.M. Cholesterol and the risk of ischemic stroke. *Stroke* **2003**, *34*, 2930–2934. [CrossRef]

ATTACHMENT C

STUDY 23

Human health risk assessment of air emissions from development of unconventional natural gas resources

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Human health risk assessment of air emissions from development of unconventional natural gas resources ☆,☆☆

Lisa M. McKenzie *, Roxana Z. Witter, Lee S. Newman, John L. Adgate

Colorado School of Public Health, University of Colorado, Anschutz Medical Campus, Aurora, Colorado, USA

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ABSTRACT

Background: Technological advances (e.g. directional drilling, hydraulic fracturing), have led to increases in unconventional natural gas development (NGD), raising questions about health impacts.
Objectives: We estimated health risks for exposures to air emissions from a NGD project in Garfield County, Colorado with the objective of supporting risk prevention recommendations in a health impact assessment (HIA).
Methods: We used EPA guidance to estimate chronic and subchronic non-cancer hazard indices and cancer risks from exposure to hydrocarbons for two populations: (1) residents living >½ mile from wells and (2) residents living ≤½ mile from wells.
Results: Residents living ≤½ mile from wells are at greater risk for health effects from NGD than are residents living >½ mile from wells. Subchronic exposures to air pollutants during well completion activities present the greatest potential for health effects. The subchronic non-cancer hazard index (HI) of 5 for residents ≤½ mile from wells was driven primarily by exposure to trimethylbenzenes, xylenes, and aliphatic hydrocarbons. Chronic HIs were 1 and 0.4. for residents ≤½ mile from wells and >½ mile from wells, respectively. Cumulative cancer risks were 10 in a million and 6 in a million for residents living ≤½ mile and >½ mile from wells, respectively, with benzene as the major contributor to the risk.
Conclusions: Risk assessment can be used in HIAs to direct health risk prevention strategies. Risk management approaches should focus on reducing exposures to emissions during well completions. These preliminary results indicate that health effects resulting from air emissions during unconventional NGD warrant further study. Prospective studies should focus on health effects associated with air pollution.

1. Introduction

The United States (US) holds large reserves of unconventional natural gas resources in coalbeds, shale, and tight sands. Technological advances, such as directional drilling and hydraulic fracturing, have led to a rapid increase in the development of these resources. For example, shale gas production had an average annual growth rate of 48% over the 2006 to 2010 period and is projected to grow almost fourfold from 2009 to 2035 (US EIA, 2011). The number of unconventional natural gas wells in the US rose from 18,485 in 2004 to 25,145 in 2007 and is expected to continue increasing through at least 2020 (Vidas and Hugman, 2008). With this expansion, it is becoming increasingly common for unconventional natural gas development (NGD) to occur near where people live, work, and play. People living near these development sites are raising public health concerns, as rapid NGD exposes more people to various potential stressors (COGCC, 2009a).

The process of unconventional NGD is typically divided into two phases: well development and production (US EPA, 2010a; US DOE, 2009). Well development involves pad preparation, well drilling, and well completion. The well completion process has three primary stages: 1) completion transitions (concrete well plugs are installed in wells to separate fracturing stages and then drilled out to release gas for production); 2) hydraulic fracturing ("fracking": the high pressure injection of water, chemicals, and propants into the drilled well to release the natural gas); and 3) flowback, the return of fracking and geologic fluids, liquid hydrocarbons ("condensate") and natural gas to the surface (US EPA, 2010a; US DOE, 2009). Once development is

Abbreviations: BTEX, benzene, toluene, ethylbenzene, and xylenes; COGCC, Colorado Oil and Gas Conservation Commission; HAP, hazardous air pollutant; HI, hazard index; HIA, health impact assessment; HQ, hazard quotient; NATA, National Air Toxics Assessment; NGD, natural gas development.

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☆☆ The authors declare they have no competing financial interests.

* Corresponding author at: Colorado School of Public Health, 13001 East 17th Place, Mail Stop B119, Aurora, CO 80045, USA. Tel.: +1 303 724 5557; fax: +1 303 724 4617.
E-mail address: lisa.mckenzie@ucdenver.edu (L.M. McKenzie).

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complete, the "salable" gas is collected, processed, and distributed. While methane is the primary constituent of natural gas, it contains many other chemicals, including alkanes, benzene, and other aromatic hydrocarbons (TERC, 2009).

As shown by ambient air studies in Colorado, Texas, and Wyoming, the NGD process results in direct and fugitive air emissions of a complex mixture of pollutants from the natural gas resource itself as well as diesel engines, tanks containing produced water, and on site materials used in production, such as drilling muds and fracking fluids (CDPHE, 2009; Frazier, 2009; Walther, 2011; Zielinska et al., 2011). The specific contribution of each of these potential NGD sources has yet to be ascertained and pollutants such as petroleum hydrocarbons are likely to be emitted from several of these NGD sources. This complex mixture of chemicals and resultant secondary air pollutants, such as ozone, can be transported to nearby residences and population centers (Walther, 2011; GCPH, 2010).

Multiple studies on inhalation exposure to petroleum hydrocarbons in occupational settings as well as residences near refineries, oil spills and petrol stations indicate an increased risk of eye irritation and headaches, asthma symptoms, acute childhood leukemia, acute myelogenous leukemia, and multiple myeloma (Glass et al., 2003; Kirkeleit et al., 2008; Brosselin et al., 2009; Kim et al., 2009; White et al., 2009). Many of the petroleum hydrocarbons observed in these studies are present in and around NGD sites (TERC, 2009). Some, such as benzene, ethylbenzene, toluene, and xylene (BTEX) have robust exposure and toxicity knowledge bases, while toxicity information for others, such as heptane, octane, and diethylbenzene, is more limited. Assessments in Colorado have concluded that ambient benzene levels demonstrate an increased potential risk of developing cancer as well as chronic and acute non-cancer health effects in areas of Garfield County Colorado where NGD is the only major industry other than agriculture (CDPHE, 2007; Coons and Walker, 2008; CDPHE, 2010). Health effects associated with benzene include acute and chronic nonlymphocytic leukemia, acute myeloid leukemia, chronic lymphocytic leukemia, anemia, and other blood disorders and immunological effects. (ATSDR, 2007a, IRIS, 2011). In addition, maternal exposure to ambient levels of benzene recently has been associated with an increase in birth prevalence of neural tube defects (Lupo et al., 2011). Health effects of xylene exposure include eye, nose, and throat irritation, difficulty in breathing, impaired lung function, and nervous system impairment (ATSDR, 2007b). In addition, inhalation of xylenes, benzene, and alkanes can adversely affect the nervous system (Carpenter et al., 1978; Nilsen et al., 1988; Galvin and Marashi, 1999; ATSDR, 2007a; ATSDR, 2007b).

Previous assessments are limited in that they were not able to distinguish between risks from ambient air pollution and specific NGD stages, such as well completions or risks between residents living near wells and residents living further from wells. We were able to isolate risks to residents living near wells during the flowback stage of well completions by using air quality data collected at the perimeter of the wells while flowback was occurring.

Battlement Mesa (population ~5000) located in rural Garfield County, Colorado is one community experiencing the rapid expansion of NGD in an unconventional tight sand resource. A NGD operator has proposed developing 200 gas wells on 9 well pads located as close as 500 ft from residences. Colorado Oil and Gas Commission (COGCC) rules allow natural gas wells to be placed as close as 150 ft from residences (COGCC, 2009b). Because of community concerns, as described elsewhere, we conducted a health impact assessment (HIA) to assess how the project may impact public health (Witter et al., 2011), working with a range of stakeholders to identify the potential public health risks and benefits.

In this article, we illustrate how a risk assessment was used to support elements of the HIA process and inform risk prevention recommendations by estimating chronic and subchronic non-cancer hazard indices (HIs) and lifetime excess cancer risks due to NGD air emissions.

2. Methods

We used standard United States Environmental Protection Agency (EPA) methodology to estimate non-cancer HIs and excess lifetime cancer risks for exposures to hydrocarbons (US EPA, 1989; US EPA, 2004) using residential exposure scenarios developed for the NGD project. We used air toxics data collected in Garfield County from January 2008 to November 2010 as part of a special study of short term exposures as well as on-going ambient air monitoring program data to estimate subchronic and chronic exposures and health risks (Frazier, 2009; GCPH, 2009; GCPH, 2010; GCPH, 2011; Antero, 2010).

2.1. Sample collection and analysis

All samples were collected and analyzed according to published EPA methods. Analyses were conducted by EPA certified laboratories. The Garfield County Department of Public Health (GCPH) and Olsson Associates, Inc. (Olsson) collected ambient air samples into evacuated SUMMA® passivated stainless-steel canisters over 24-hour intervals. The GCPH collected the samples from a fixed monitoring station and along the perimeters of four well pads and shipped samples to Eastern Research Group for analysis of 78 hydrocarbons using EPA's compendium method TO-12, Method for the Determination of Non-Methane Organic Compounds in Ambient Air Using Cyrogenic Preconcentration and Direct Flame Ionization Detection (US EPA, 1999). Olsson collected samples along the perimeter of one well pad and shipped samples to Atmospheric Analysis and Consulting, Inc. for analysis of 56 hydrocarbons (a subset of the 78 hydrocarbons determined by Eastern Research Group) using method TO-12. Per method TO-12, a fixed volume of sample was cryogenically concentrated and then desorbed onto a gas chromatography column equipped with a flame ionization detector. Chemicals were identified by retention time and reported in a concentration of parts per billion carbon (ppbC). The ppbC values were converted to micrograms per cubic meter ($\mu g/m^3$) at 01.325 kPa and 298.15 K.

Two different sets of samples were collected from rural (population < 50,000) areas in western Garfield County over varying time periods. The main economy, aside from the NGD industry, of western Garfield County is agricultural. There is no other major industry.

2.1.1. NGD area samples

The GCPH collected ambient air samples every six days between January 2008 and November 2010 (163 samples) from a fixed monitoring station located in the midst of rural home sites and ranches and NGD, during both well development and production. The site is located on top of a small hill and 4 miles upwind of other potential emission sources, such as a major highway (Interstate-70) and the town of Silt, CO (GCPH, 2009; GCPH, 2010; GCPH, 2011).

2.1.2. Well completion samples

The GCPH collected 16 ambient air samples at each cardinal direction along 4 well pad perimeters (130 to 500 ft from the well pad center) in rural Garfield County during well completion activities. The samples were collected on the perimeter of 4 well pads being developed by 4 different natural gas operators in summer 2008 (Frazier, 2009). The GCPH worked closely with the NGD operators to ensure these air samples were collected during the period while at least one well was on uncontrolled (emissions not controlled) flowback into collection tanks vented directly to the air. The number of wells on each pad and other activities occurring on the pad were not documented. Samples were collected over 24 to 27-hour intervals, and samples included emissions from both uncontrolled flowback and

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diesel engines (i.e., from. trucks and generators supporting completion activities). In addition, the GCPH collected a background sample 0.33 to 1 mile from each well pad (Frazier, 2009). The highest hydrocarbon levels corresponded to samples collected directly downwind of the tanks (Frazier, 2009; Antero, 2010). The lowest hydrocarbon levels corresponded either to background samples or samples collected upwind of the flowback tanks (Frazier, 2009; Antero, 2010).

Antero Resources Inc., a natural gas operator, contracted Olsson to collect eight 24-hour integrated ambient air samples at each cardinal direction at 350 and 500 ft from the well pad center during well completion activities conducted on one of their well pads in summer 2010 (Antero, 2010). Of the 12 wells on this pad, 8 were producing salable natural gas; 1 had been drilled but not completed; 2 were being hydraulically fractured during daytime hours, with ensuing uncontrolled flowback during nighttime hours; and 1 was on uncontrolled flowback during nighttime hours.

All five well pads are located in areas with active gas production, approximately 1 mile from Interstate-70.

2.2. Data assessment

We evaluated outliers and compared distributions of chemical concentrations from NGD area and well completion samples using Q–Q plots and the Mann–Whitney *U* test, respectively, in EPA's ProUCL version 4.00.05 software (US EPA, 2010b). The Mann–Whitney *U* test was used because the measurement data were not normally distributed. Distributions were considered as significantly different at an alpha of 0.05. Per EPA guidance, we assigned the exposure concentration as either the 95% upper confidence limit (UCL) of the mean concentration for compounds found in 10 or more samples or the maximum detected concentration for compounds found in more than 1 but fewer than 10 samples. This latter category included three compounds: 1,3-butadiene, 2,2,4-trimethylpentane, and styrene in the well completion samples. EPA's ProUCL software was used to select appropriate methods based on sample distributions and detection frequency for computing 95% UCLs of the mean concentration (US EPA, 2010b).

2.3. Exposure assessment

Risks were estimated for two populations: (1) residents >½ mile from wells; and (2) residents ≤½ mile from wells. We defined residents ≤½ mile from wells as living near wells, based on residents reporting odor complaints attributed to gas wells in the summer of 2010 (COGCC, 2011).

Exposure scenarios were developed for chronic non-cancer HIs and cancer risks. For both populations, we assumed a 30-year project duration based on an estimated 5-year well development period for all well pads, followed by 20 to 30 years of production. We assumed a resident lives, works, and otherwise remains within the town 24 h/day, 350 days/year and that lifetime of a resident is 70 years, based on standard EPA reasonable maximum exposure (RME) defaults (US EPA, 1989).

2.3.1. Residents >½ mile from well pads

As illustrated in Fig. 1, data from the NGD area samples were used to estimate chronic and subchronic risks for residents >½ mile from well development and production throughout the project. The exposure concentrations for this population were the 95% UCL on the mean concentration and median concentration from the 163 NGD samples.

2.3.2. Residents ≤½ mile from well pads

To evaluate subchronic non-cancer HIs from well completion emissions, we estimated that a resident lives ≤½ mile from two well pads resulting a 20-month exposure duration based on 2 weeks per well for completion and 20 wells per pad, assuming some overlap in between activities. The subchronic exposure concentrations for this population were the 95% UCL on the mean concentration and the median concentration from the 24 well completion samples. To evaluate chronic risks to residents ≤½ mile from wells throughout the NGD project, we calculated a time-weighted exposure concentration (C_{S+c}) to account for exposure to emissions from well completions for 20-months followed by 340 months of exposure to emissions from the NGD area using the following formula:

$$C_{S+c} = (C_c \times ED_c/ED) + (C_S \times ED_S/ED)$$

where:

C_c Chronic exposure point concentration ($\mu g/m^3$) based on the 95% UCL of the mean concentration or median concentration from the 163 NGD area samples

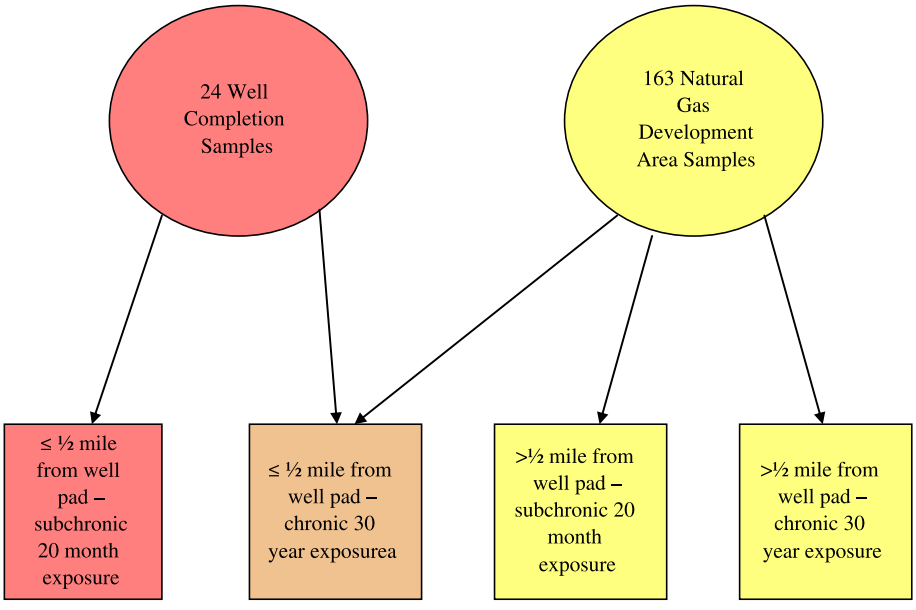

Fig. 1. Relationship between completion samples and natural gas development area samples and residents living ≤½ mile and >½ mile from wells. [a]Time weighted average based on 20-month contribution from well completion samples and 340-month contribution from natural gas development samples.

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ED_c Chronic exposure duration
C_S Subchronic exposure point concentration (μg/m^3) based on the 95% UCL of the mean concentration or median concentration from the 24 well completion samples
ED_S Subchronic exposure duration
ED Total exposure duration

2.4. Toxicity assessment and risk characterization

For non-carcinogens, we expressed inhalation toxicity measurements as a reference concentration (RfC in units of μg/m^3 air). We used chronic RfCs to evaluate long-term exposures of 30 years and subchronic RfCs to evaluate subchronic exposures of 20-months. If a subchronic RfC was not available, we used the chronic RfC. We obtained RfCs from (in order of preference) EPA's Integrated Risk Information System (IRIS) (US EPA, 2011), California Environmental Protection Agency (CalEPA) (CalEPA, 2003), EPA's Provisional Peer-Reviewed Toxicity Values (ORNL, 2009), and Health Effects Assessment Summary Tables (US EPA, 1997). We used surrogate RfCs according to EPA guidance for C_5 to C_{18} aliphatic and C_6 to C_{18} aromatic hydrocarbons which did not have a chemical-specific toxicity value (US EPA, 2009a). We derived semi-quantitative hazards, in terms of the hazard quotient (HQ), defined as the ratio between an estimated exposure concentration and RfC. We summed HQs for individual compounds to estimate the total cumulative HI. We then separated HQs specific to neurological, respiratory, hematological, and developmental effects and calculated a cumulative HI for each of these specific effects.

For carcinogens, we expressed inhalation toxicity measurements as inhalation unit risk (IUR) in units of risk per μg/m^3. We used IURs from EPA's IRIS (US EPA, 2011) when available or the CalEPA (CalEPA, 2003). The lifetime cancer risk for each compound was derived by multiplying estimated exposure concentration by the IUR. We summed cancer risks for individual compounds to estimate the cumulative cancer risk. Risks are expressed as excess cancers per 1 million population based on exposure over 30 years.

Toxicity values (i.e., RfCs or IURs) or a surrogate toxicity value were available for 45 out of 78 hydrocarbons measured. We performed a quantitative risk assessment for these hydrocarbons. The remaining 33 hydrocarbons were considered qualitatively in the risk assessment.

3. Results

3.1. Data assessment

Evaluation of potential outliers revealed no sampling, analytical, or other anomalies were associated with the outliers. In addition, removal of potential outliers from the NGD area samples did not change the final HIs and cancer risks. Potential outliers in the well completion samples were associated with samples collected downwind from flowback tanks and are representative of emissions during flowback. Therefore, no data was removed from either data set.

Descriptive statistics for concentrations of the hydrocarbons used in the quantitative risk assessment are presented in Table 1. A list of the hydrocarbons detected in the samples that were considered qualitatively in the risk assessment because toxicity values were not available is presented in Table 2. Descriptive statistics for all hydrocarbons are available in Supplemental Table 1. Two thirds more hydrocarbons were detected at a frequency of 100% in the well completion samples (38 hydrocarbons) than in the NGD area samples (23 hydrocarbons). Generally, the highest alkane and aromatic hydrocarbon median concentrations were observed in the well completion samples, while the highest median concentrations of several alkenes were observed in the NGD area samples. Median concentrations of benzene, ethylbenzene, toluene, and m-xylene/p-xlyene were 2.7, 4.5, 4.3, and 9 times higher in the well completion samples than in the NGD area samples, respectively. Wilcoxon–Mann–Whitney test results indicate that

Table 1
Descriptive statistics for hydrocarbon concentrations with toxicity values in 24-hour integrated samples collected in NGD area and samples collected during well completions.

Hydrocarbon (μg/m^3)	NGD area sample results[a]							Well completion sample results[b]						
	No.	% > MDL	Med	SD	95% UCL[c]	Min	Max	No.	% > MDL	Med	SD	95% UCL[c]	Min	Max
1,2,3-Trimethylbenzene	163	39	0.11	0.095	0.099	0.022	0.85	24	83	0.84	2.3	3.2	0.055	12
1,2,4-Trimethylbenzene	163	96	0.18	0.34	0.31	0.063	3.1	24	100	1.7	17	21	0.44	83
1,3,5-Trimethylbenzene	163	83	0.12	0.13	0.175	0.024	1.2	24	100	1.3	16	19.5	0.33	78
1,3-Butadiene	163	7	0.11	0.020	0.0465	0.025	0.15	16	56	0.11	0.021	NC	0.068	0.17
Benzene	163	100	0.95	1.3	1.7	0.096	14	24	100	2.6	14	20	0.94	69
Cyclohexane	163	100	2.1	8.3	6.2	0.11	105	24	100	5.3	43	58	2.21	200
Ethylbenzene	163	95	0.17	0.73	0.415	0.056	8.1	24	100	0.77	47	54	0.25	230
Isopropylbenzene	163	38	0.15	0.053	0.074	0.020	0.33	24	67	0.33	1.0	1.0	0.0	4.8
Methylcyclohexane	163	100	3.7	4.0	6.3	0.15	24	24	100	14	149	190	3.1	720
m-Xylene/p-Xylene	163	100	0.87	1.2	1.3	0.16	9.9	24	100	7.8	194	240	2.0	880
n-Hexane	163	100	4.0	4.2	6.7	0.13	25	24	100	7.7	57	80	1.7	255
n-Nonane	163	99	0.44	0.49	0.66	0.064	3.1	24	100	3.6	61	76	1.2	300
n-Pentane	163	100	9.1	9.8	14	0.23	62	24	100	11	156	210	3.9	550
n-Propylbenzene	163	66	0.10	0.068	0.10	0.032	0.71	24	88	0.64	2.4	3.3	0.098	12
o-Xylene	163	97	0.22	0.33	0.33	0.064	3.6	24	100	1.2	40	48.5	0.38	190
Propylene	163	100	0.34	0.23	0.40	0.11	2.5	24	100	0.41	0.34	0.60	0.16	1.9
Styrene	163	15	0.15	0.26	0.13	0.017	3.4	24	21	0.13	1.2	NC	0.23	5.9
Toluene	163	100	1.8	6.2	4.8	0.11	79	24	100	7.8	67	92	2.7	320
Aliphatic hydrocarbons C_5–C_8[d]	163	NC	29	NA	44	1.7	220	24	NC	56	NA	780	24	2700
Aliphatic hydrocarbons C_9–C_{18}[e]	163	NC	1.3	NA	14	0.18	400	24	NC	7.9	NA	100	1.4	390
Aromatic hydrocarbons C_9–C_{18}[f]	163	NC	0.57	NA	0.695	0.17	5.6	24	NC	3.7	NA	27	0.71	120

Abbreviations: Max, maximum detected concentration; Med, median; Min, minimum detected concentration; NGD, natural gas development; NC, not calculated; No., number of samples; SD, standard deviation; % > MDL, percent greater than method detection limit; μg/m^3 micrograms per cubic meter; 95% UCL 95% upper confidence limit on the mean.

[a] Samples collected at one site every 6 six days between 2008 and 2010.

[b] Samples collected at four separate sites in summer 2008 and one site in summer 2010.

[c] Calculated using EPA's ProUCL version 4.00.05 software (US EPA, 2010b).

[d] Sum of 2,2,2-trimethylpentane, 2,2,4-trimethylpentane, 2,2-dimethylbutane, 2,3,4-trimethylpentane, 2,3-dimethylbutane, 2,3-dimethylpentane, 2,4-dimethylpentane, 2-methylheptane, 2-methylhexane, 2-methylpentane, 3-methylheptane, 3-methylhexane, 3-methylpentane, cyclopentane, isopentane, methylcyclopentane, n-heptane, n-octane.

[e] Sum of n-decane, n-dodecane, n-tridecane, n-undecane.

[f] Sum of m-diethylbenzene, m-ethyltoluene, o-ethyltoluene, p-diethylbenzene, p-ethyltoluene.

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Table 2
Detection frequencies of hydrocarbons without toxicity values detected in NGD area or well completion samples.

Hydrocarbon	NGD area sample[a] detection frequency (%)	Well completion sample[b] detection frequency (%)
1-Dodecene	36	81
1-Heptene	94	100
1-Hexene	63	79
1-Nonene	52	94
1-Octene	29	75
1-Pentene	98	79
1-Tridecene	7	38
1-Undecene	28	81
2-Ethyl-1-butene	1	0
2-Methyl-1-butene	29	44
2-Methyl-1-pentene	1	6
2-Methyl-2-butene	36	69
3-Methyl-1-butene	6	6
4-Methyl-1-pentene	16	69
Acetylene	100	92
a-Pinene	63	100
b-Pinene	10	44
cis-2-Butene	58	75
cis-2-Hexene	13	81
cis-2-Pentene	38	54
Cyclopentene	44	94
Ethane	100	100
Ethylene	100	100
Isobutane	100	100
Isobutene/1-Butene	73	44
Isoprene	71	96
n-Butane	98	100
Propane	100	100
Propyne	1	0
trans-2-Butene	80	75
trans-2-Hexene	1	6
trans-2-Pentene	55	83

Abbreviations: NGD, natural gas development.
[a] Samples collected at one site every 6 six days between 2008 and 2010.
[b] Samples collected at four separate sites in summer 2008 and one site in summer 2010.

concentrations of hydrocarbons from well completion samples were significantly higher than concentrations from NGD area samples ($p<0.05$) with the exception of 1,2,3-trimethylbenzene, n-pentane, 1,3-butadiene, isopropylbenzene, n-propylbenzene, propylene, and styrene (Supplemental Table 2).

3.2. Non-cancer hazard indices

Table 3 presents chronic and subchronic RfCs used in calculating non-cancer HIs, as well critical effects and other effects. Chronic non-cancer HQ and HI estimates based on ambient air concentrations are presented in Table 4. The total chronic HIs based on the 95% UCL of the mean concentration were 0.4 for residents >½ mile from wells and 1 for residents ≤½ mile from wells. Most of the chronic non-cancer hazard is attributed to neurological effects with neurological HIs of 0.3 for residents >½ mile from wells and 0.9 for residents ≤½ mile from wells.

Total subchronic non-cancer HQs and HI estimates are presented in Table 5. The total subchronic HIs based on the 95% UCL of the mean concentration were 0.2 for residents >½ mile from wells and 5 for residents ≤½ mile from wells. The subchronic non-cancer hazard for residents >½ mile from wells is attributed mostly to respiratory effects (HI = 0.2), while the subchronic hazard for residents ≤½ mile from wells is attributed to neurological (HI = 4), respiratory (HI = 2), hematologic (HI = 3), and developmental (HI = 1) effects.

For residents >½ mile from wells, aliphatic hydrocarbons (51%), trimethylbenzenes (22%), and benzene (14%) are primary contributors to the chronic non-cancer HI. For residents ≤½ mile from wells, trimethylbenzenes (45%), aliphatic hydrocarbons (32%), and xylenes (17%) are primary contributors to the chronic non-cancer HI, and trimethylbenzenes (46%), aliphatic hydrocarbons (21%) and xylenes (15%) also are primary contributors to the subchronic HI.

3.3. Cancer risks

Cancer risk estimates calculated based on measured ambient air concentrations are presented in Table 6. The cumulative cancer risks based on the 95% UCL of the mean concentration were 6 in a million for residents >½ from wells and 10 in a million for residents ≤½ mile from wells. Benzene (84%) and 1,3-butadiene (9%) were the primary contributors to cumulative cancer risk for residents >½ mile from wells. Benzene (67%) and ethylbenzene (27%) were the primary contributors to cumulative cancer risk for residents ≤½ mile from wells.

4. Discussion

Our results show that the non-cancer HI from air emissions due to natural gas development is greater for residents living closer to wells. Our greatest HI corresponds to the relatively short-term (i.e., subchronic), but high emission, well completion period. This HI is driven principally by exposure to trimethylbenzenes, aliphatic hydrocarbons, and xylenes, all of which have neurological and/or respiratory effects. We also calculated higher cancer risks for residents living nearer to wells as compared to residents residing further from wells. Benzene is the major contributor to lifetime excess cancer risk for both scenarios. It also is notable that these increased risk metrics are seen in an air shed that has elevated ambient levels of several measured air toxics, such as benzene (CDPHE, 2009; GCPH, 2010).

4.1. Representation of exposures from NGD

It is likely that NGD is the major source of the hydrocarbons observed in the NGD area samples used in this risk assessment. The NGD area monitoring site is located in the midst of multi-acre rural home sites and ranches. Natural gas is the only industry in the area other than agriculture. Furthermore, the site is at least 4 miles upwind from any other major emission source, including Interstate 70 and the town of Silt, Colorado. Interestingly, levels of benzene, m,p-xylene, and 1,3,5-trimethylbenzene measured at this rural monitoring site in 2009 were higher than levels measured at 27 out of 37 EPA air toxics monitoring sites where SNMOCs were measured, including urban sites such as Elizabeth, NJ, Dearborn, MI, and Tulsa, OK (GCPH, 2010; US EPA, 2009b). In addition, the 2007 Garfield County emission inventory attributes the bulk of benzene, xylene, toluene, and ethylbenzene emissions in the county to NGD, with NGD point and non-point sources contributing five times more benzene than any other emission source, including on-road vehicles, wildfires, and wood burning. The emission inventory also indicates that NGD sources (e.g. condensate tanks, drill rigs, venting during completions, fugitive emissions from wells and pipes, and compressor engines) contributed ten times more VOC emissions than any source, other than biogenic sources (e.g. plants, animals, marshes, and the earth) (CDPHE, 2009).

Emissions from flowback operations, which may include emissions from various sources on the pads such as wells and diesel engines, are likely the major source of the hydrocarbons observed in the well completion samples. These samples were collected very near (130 to 500 ft from the center) well pads during uncontrolled flowback into tanks venting directly to the air. As for the NGD area samples, no sources other than those associated with NGD were in the vicinity of the sampling locations.

Subchronic health effects, such as headaches and throat and eye irritation reported by residents during well completion activities

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Table 3
Chronic and subchronic reference concentrations, critical effects, and major effects for hydrocarbons in quantitative risk assessment.

Hydrocarbon	Chronic		Subchronic		Critical effect/ target organ	Other effects
	RfC (μg/m^3)	Source	RfC (μg/m^3)	Source		
1,2,3-Trimethylbenzene	5.00E+00	PPTRV	5.00E+01	PPTRV	Neurological	Respiratory, hematological
1,3,5-Trimethylbenzene	6.00E+00	PPTRV	1.00E+01	PPTRV	Neurological	Hematological
Isopropylbenzene	4.00E+02	IRIS	9.00E+01	HEAST	Renal	Neurological, respiratory
n-Hexane	7.00E+02	IRIS	2.00E+03	PPTRV	Neurological	–
n-Nonane	2.00E+02	PPTRV	2.00E+03	PPTRV	Neurological	Respiratory
n-Pentane	1.00E+03	PPTRV	1.00E+04	PPTRV	Neurological	–
Styrene	1.00E+03	IRIS	3.00E+03	HEAST	Neurological	–
Toluene	5.00E+03	IRIS	5.00E+03	PPTRV	Neurological	Developmental, respiratory
Xylenes, total	1.00E+02	IRIS	4.00E+02	PPTRV	Neurological	Developmental, respiratory
n-propylbenzene	1.00E+03	PPTRV	1.00E+03	Chronic RfC PPTRV	Developmental	Neurological
1,2,4-Trimethylbenzene	7.00E+00	PPTRV	7.00E+01	PPTRV	Decrease in blood clotting time	Neurological, respiratory
1,3-Butadiene	2.00E+00	IRIS	2.00E+00	Chronic RfC IRIS	Reproductive	Neurological, respiratory
Propylene	3.00E+03	CalEPA	1.00E+03	Chronic RfC CalEPA	Respiratory	–
Benzene	3.00E+01	ATSDR	8.00E+01	PPTRV	Decreased lymphocyte count	Neurological, developmental, reproductive
Ethylbenzene	1.00E+03	ATSDR	9.00E+03	PPTRV	Auditory	Neurological, respiratory, renal
Cyclohexane	6.00E+03	IRIS	1.80E+04	PPTRV	Developmental	Neurological
Methylcyclohexane	3.00E+03	HEAST	3.00E+03	HEAST	Renal	–
Aliphatic hydrocarbons C_5–C_8[a]	6E+02	PPTRV	2.7E+04	PPTRV	Neurological	–
Aliphatic hydrocarbons C_9–C_{18}	1E+02	PPTRV	1E+02	PPTRV	Respiratory	–
Aromatic hydrocarbons C_9–C_{18}[b]	1E+02	PPTRV	1E+03	PPRTV	Decreased maternal body weight	Respiratory

Abbreviations: 95%UCL, 95% upper confidence limit; CalEPA, California Environmental Protection Agency; HEAST, EPA Health Effects Assessment Summary Tables 1997; HQ, hazard quotient; IRIS, Integrated Risk Information System; Max, maximum; PPTRV, EPA Provisional Peer-Reviewed Toxicity Value; RfC, reference concentration; μg/m^3, micrograms per cubic meter. Data from CalEPA 2011; IRIS (US EPA, 2011); ORNL 2011.

[a] Based on PPTRV for commercial hexane.

[b] Based on PPTRV for high flash naphtha.

occurring in Garfield County, are consistent with known health effects of many of the hydrocarbons evaluated in this analysis (COGCC, 2011; Witter et al., 2011). Inhalation of trimethylbenzenes and xylenes can irritate the respiratory system and mucous membranes with effects ranging from eye, nose, and throat irritation to difficulty in breathing and impaired lung function (ATSDR, 2007a;

Table 4
Chronic hazard quotients and hazard indices for residents living >½ mile from wells and residents living ≤½ mile from wells.

Hydrocarbon	>½ mile		≤½ mile	
	Chronic HQ based on median concentration	Chronic HQ based on 95% UCL of mean concentration	Chronic HQ based on median concentration	Chronic HQ based on 95% UCL of mean concentration
1,2,3-Trimethylbenzene	2.09E−02	1.90E−02	2.87E−02	5.21E−02
1,2,4-Trimethylbenzene	2.51E−02	4.22E−02	3.64E−02	2.01E−01
1,3,5-Trimethylbenzene	1.96E−02	2.80E−02	3.00E−02	1.99E−01
1,3-Butadiene	5.05E−02	2.23E−02	5.05E−02	2.25E−02
Benzene	3.03E−02	5.40E−02	3.32E−02	8.70E−02
Cyclohexane	3.40E−04	9.98E−04	3.67E−04	1.46E−03
Ethylbenzene	1.63E−04	3.98E−04	1.95E−04	3.23E−03
Isopropylbenzene	3.68E−04	1.78E−04	3.90E−04	3.05E−04
Methylcyclohexane	1.18E−03	2.00E−03	1.36E−03	5.32E−03
n-Hexane	5.49E−03	9.23E−03	5.76E−03	1.47E−02
n-Nonane	2.11E−03	3.14E−03	2.95E−03	2.31E−02
n-Pentane	8.71E−03	1.32E−02	8.79E−03	2.39E−02
n-propylbenzene	9.95E−05	9.59E−05	1.28E−04	2.64E−04
Propylene	1.09E−04	1.27E−04	1.10E−04	1.30E−04
Styrene	1.43E−04	1.25E−04	1.42E−04	4.32E−04
Toluene	3.40E−04	9.28E−04	4.06E−04	1.86E−03
Xylenes, total	1.16E−02	1.57E−02	1.54E−02	1.71E−01
Aliphatic hydrocarbons C_5–C_8	4.63E−02	7.02E−02	4.87E−02	1.36E−01
Aliphatic hydrocarbons C_9–C_{18}	1.22E−02	1.35E−01	1.58E−02	1.83E−01
Aromatic hydrocarbons C_9–C_{18}	5.44E−03	6.67E−03	7.12E−03	2.04E−02
Total Hazard Index	2E−01	4E−01	3E−01	1E+00
Neuorological Effects Hazard Index[a]	2E−01	3E−01	3E−01	9E−01
Respiratory Effects Hazard Index[b]	1E−01	2E−02	2E−02	7E−01
Hematogical Effects Hazard Index[c]	1E−01	1E−01	1E−01	5E−01
Developmental Effects Hazard Index[d]	4E−02	7E−02	5E−02	3E−01

Abbreviations: 95%UCL, 95% upper confidence limit; HQ, hazard quotient.

[a] Sum of HQs for hydrocarbons with neurological effects: 1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,3,5-Trimethylbenzene, 1,3-butadiene, benzene, cyclohexane, ethylbenzene, isopropylbenzene, n-hexane, n-nonane, n-pentane, n-propylbenzene, styrene, toluene, xylenes, aliphatic C_5–C_8 hydrocarbons.

[b] Sum of HQs for hydrocarbons with respiratory effects: 1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,3-butadiene, ethylbenzene, isopropylbenzene, n-nonane, propylene, toluene, xylenes, aliphatic C_9–C_{18} hydrocarbons, aromatic C_9–C_{18} hydrocarbons.

[c] Sum of HQs for hydrocarbons with hematological effects: 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, benzene.

[d] Sum of HQs for hydrocarbons with developmental effects: benzene, cyclohexane, toluene, and xylenes.

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Table 5
Subchronic hazard quotients and hazard indices residents living >½ mile from wells and residents living ≤½ mile from wells.

Hydrocarbon (μg/m^3)	>½ mile		≤½ mile	
	Subchronic HQ based on median concentration	Subchronic HQ based on 95% UCL of mean concentration	Subchronic HQ based on median concentration	Subchronic HQ based on 95% UCL of mean concentration
1,2,3-Trimethylbenzene	2.09E−03	1.90E−03	1.67E−02	6.40E−02
1,2,4-Trimethylbenzene	2.51E−03	4.22E−03	2.38E−02	3.02E−01
1,3,5-Trimethylbenzene	1.18E−02	1.68E−02	1.29E−01	1.95E+00
1,3-Butadiene	5.04E−02	2.23E−02	5.25E−02	8.30E−02
Benzene	1.14E−02	2.02E−02	3.25E−02	2.55E−01
Cyclohexane	1.13E−04	3.33E−04	2.93E−04	3.24E−03
Ethylbenzene	1.81E−05	4.42E−05	8.56E−05	5.96E−03
Isopropylbenzene	1.63E−03	7.92E−04	3.62E−03	1.14E−02
Methylcyclohexane	1.18E−03	2.01E−03	4.67E−03	6.47E−02
n-Hexane	1.92E−03	3.23E−03	3.86E−03	3.98E−02
n-Nonane	2.11E−04	3.14E−04	1.80E−03	3.78E−02
n-Pentane	8.71E−04	1.32E−03	1.05E−03	2.13E−02
n-propylbenzene	9.95E−05	9.57E−05	6.36E−04	3.26E−03
Propylene	1.43E−04	3.80E−04	4.12E−04	6.02E−04
Styrene	5.68E−04	4.16E−05	4.00E−06	1.97E−03
Toluene	4.18E−05	9.28E−04	2.46E−04	1.84E−02
Xylenes, total	2.91E−03	3.93E−03	2.05E−02	7.21E−01
Aliphatic hydrocarbons C_5–C_8	1.07E−03	1.63E−03	2.07E−03	2.89E−02
Aliphatic hydrocarbons C_9–C_{18}	1.3E−02	1.41E−01	7.9E−02	1.03E−00
Aromatic hydrocarbons C_9–C_{18}	6.00E−04	6.95E−04	3.7E−03	2.64E−02
Total Hazard Index	1E−01	2E−01	4E−01	5E+00
Neuorological Effects Hazard Index[a]	9E−02	8E−02	3E−01	4E+00
Respiratory Effects Hazard Index[b]	7E−02	2E−01	2E−01	2E+00
Hematogical Effects Hazard Index[c]	3E−02	4E−02	2E−01	3E+00
Developmental Effects Hazard Index[d]	1E−02	3E−02	5E−02	1E+00

Abbreviations: 95%UCL, 95% upper confidence limit; HQ, hazard quotient.
[a] Sum of HQs for hydrocarbons with neurological effects: 1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,3,5-Trimethylbenzene, 1,3-butadiene, benzene, cyclohexane, ethylbenzene, isopropylbenzene, n-hexane, n-nonane, n-pentane, n-propylbenzene, styrene, toluene, xylenes, aliphatic C_5–C_8 hydrocarbons.
[b] Sum of HQs for hydrocarbons with respiratory effects: 1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,3-butadiene, ethylbenzene, isopropylbenzene, n-nonane, propylene, toluene, xylenes, aliphatic C_9–C_{18} hydrocarbons, aromatic C_9–C_{18} hydrocarbons.
[c] Sum of HQs for hydrocarbons with hematological effects: 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, benzene.
[d] Sum of HQs for hydrocarbons with developmental effects: benzene, cyclohexane, toluene, and xylenes.

ATSDR, 2007b; US EPA, 1994). Inhalation of trimethylbenzenes, xylenes, benzene, and alkanes can adversely affect the nervous system with effects ranging from dizziness, headaches, fatigue at lower exposures to numbness in the limbs, incoordination, tremors, temporary limb paralysis, and unconsciousness at higher exposures (Carpenter et al., 1978; Nilsen et al., 1988; US EPA, 1994; Galvin and Marashi, 1999; ATSDR, 2007a; ATSDR, 2007b).

4.2. Risk assessment as a tool for health impact assessment

HIA is a policy tool used internationally that is being increasingly used in the United States to assess multiple complex hazards and exposures in communities. Comparison of risks between residents based on proximity to wells illustrates how the risk assessment process can be used to support the HIA process. An important component of the HIA process is to identify where and when public health is most likely to be impacted and to recommend mitigations to reduce or eliminate the potential impact (Collins and Koplan, 2009). This risk assessment indicates that public health most likely would be impacted by well completion activities, particularly for residents living nearest the wells. Based on this information, suggested risk prevention strategies in the HIA are directed at minimizing exposures for those living closet to the well pads, especially during well completion activities when emissions are the highest. The HIA includes recommendations to (1) control and monitor emissions during completion transitions and flowback; (2) capture and reduce emissions through use of low or no emission flowback tanks; and (3) establish and maintain communications regarding well pad activities with the community (Witter et al., 2011).

4.3. Comparisons to other risk estimates

This risk assessment is one of the first studies in the peer-reviewed literature to provide a scientific perspective to the potential health risks associated with development of unconventional natural

Table 6
Excess cancer risks for residents living >½ mile from wells and residents living ≤½ mile from wells.

Hydrocarbon	WOE		Unit Risk (μg/m^3)	Source	>½ mile		≤½ mile	
	IRIS	IARC			Cancer risk based on median concentration	Cancer risk based on 95% UCL of mean concentration	Cancer risk based on median concentration	Cancer risk based on 95% UCL of mean concentration
1,3-Butadiene	B2	1	3.00E−05	IRIS	1.30E−06	5.73E−07	1.30E−06	6.54E−07
Benzene	A	1	7.80E−06	IRIS	3.03E−06	5.40E−06	3.33E−06	8.74E−06
Ethylbenzene	NC	2B	2.50E−06	CalEPA	1.75E−07	4.26E−07	2.09E−07	3.48E−06
Styrene	NC	2B	5.00E−07	CEP	3.10E−08	2.70E−08	3.00E−08	9.30E−08
Cumulative cancer risk					5E−06	6E−06	5E−06	1E−05

Abbreviations: 95%UCL, 95% upper confidence limit; CalEPA, California Environmental Protection Agency; CEP, (Caldwell et al., 1998); IARC, International Agency for Research on Cancer; IRIS, Integrated Risk Information System; Max, maximum; NC, not calculated; WOE, weight of evidence; μg/m^3, micrograms per cubic meter. Data from CalEPA 2011; IRIS (US EPA, 2011).

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gas resources. Our results for chronic non-cancer HIs and cancer risks for residents >than ½ mile from wells are similar to those reported for NGD areas in the relatively few previous risk assessments in the non-peer reviewed literature that have addressed this issue (CDPHE, 2010; Coons and Walker, 2008; CDPHE, 2007; Walther, 2011). Our risk assessment differs from these previous risk assessments in that it is the first to separately examine residential populations nearer versus further from wells and to report health impact of emissions resulting from well completions. It also adds information on exposure to air emissions from development of these resources. These data show that it is important to include air pollution in the national dialogue on unconventional NGD that, to date, has largely focused on water exposures to hydraulic fracturing chemicals.

4.4. Limitations

As with all risk assessments, scientific limitations may lead to an over- or underestimation of the actual risks. Factors that may lead to overestimation of risk include use of: 1) 95% UCL on the mean exposure concentrations; 2) maximum detected values for 1,3-butadiene, 2,2,4-trimethylpentane, and styrene because of a low number of detectable measurements; 3) default RME exposure assumptions, such as an exposure time of 24 h per day and exposure frequency of 350 days per year; and 4) upper bound cancer risk and non-cancer toxicity values for some of our major risk drivers. The benzene IUR, for example, is based on the high end of a range of maximum likelihood values and includes uncertainty factors to account for limitations in the epidemiological studies for the dose–response and exposure data (US EPA, 2011). Similiarly, the xylene chronic RfC is adjusted by a factor of 300 to account for uncertainties in extrapolating from animal studies, variability of sensitivity in humans, and extrapolating from subchronic studies (US EPA, 2011). Our use of chronic RfCs values when subchronic RfCs were not available may also have overestimated 1,3-butadiene, n-propylbenzene, and propylene subchronic HQs. None of these three chemicals, however, were primary contributors to the subchronic HI, so their overall effect on the HI is relatively small.

Several factors may have lead to an underestimation of risk in our study results. We were not able to completely characterize exposures because several criteria or hazardous air pollutants directly associated with the NGD process via emissions from wells or equipment used to develop wells, including formaldehyde, acetaldehyde, crotonaldehyde, naphthalene, particulate matter, and polycyclic aromatic hydrocarbons, were not measured. No toxicity values appropriate for quantitative risk assessment were available for assessing the risk to several alkenes and low molecular weight alkanes (particularly $<C_5$ aliphatic hydrocarbons). While at low concentrations the toxicity of alkanes and alkenes is generally considered to be minimal (Sandmeyer, 1981), the maximum concentrations of several low molecular weight alkanes measured in the well completion samples exceeded the 200–1000 $\mu g/m^3$ range of the RfCs for the three alkanes with toxicity values: n-hexane, n-pentane, and n-nonane (US EPA, 2011; ORNL, 2009). We did not consider health effects from acute (i.e., less than 1 h) exposures to peak hydrocarbon emissions because there were no appropriate measurements. Previous risk assessments have estimated an acute HQ of 6 from benzene in grab samples collected when residents noticed odors they attributed to NGD (CDPHE, 2007). We did not include ozone or other potentially relevant exposure pathways such as ingestion of water and inhalation of dust in this risk assessment because of a lack of available data. Elevated concentrations of ozone precursors (specifically, VOCs and nitrogen oxides) have been observed in Garfield County's NGD area and the 8-h average ozone concentration has periodically approached the 75 ppb National Ambient Air Quality Standard (NAAQS) (CDPHE, 2009; GCPH, 2010).

This risk assessment also was limited by the spatial and temporal scope of available monitoring data. For the estimated chronic exposure, we used 3 years of monitoring data to estimate exposures over a 30 year exposure period and a relatively small database of 24 samples collected at varying distances up to 500 ft from a well head (which also were used to estimate shorter-term non-cancer hazard index). Our estimated 20-month subchronic exposure was limited to samples collected in the summer, which may have not have captured temporal variation in well completion emissions. Our ½ mile cut point for defining the two different exposed populations in our exposure scenarios was based on complaint reports from residents living within ½ mile of existing NGD, which were the only data available. The actual distance at which residents may experience greater exposures from air emissions may be less than or greater than a ½ mile, depending on dispersion and local topography and meteorology. This lack of spatially and temporally appropriate data increases the uncertainty associated with the results.

Lastly, this risk assessment was limited in that appropriate data were not available for apportionment to specific sources within NGD (e.g. diesel emissions, the natural gas resource itself, emissions from tanks, etc.). This increases the uncertainty in the potential effectiveness of risk mitigation options.

These limitations and uncertainties in our risk assessment highlight the preliminary nature of our results. However, there is more certainty in the comparison of the risks between the populations and in the comparison of subchronic to chronic exposures because the limitations and uncertainties similarly affected the risk estimates.

4.5. Next steps

Further studies are warranted, in order to reduce the uncertainties in the health effects of exposures to NGD air emissions, to better direct efforts to prevent exposures, and thus address the limitations of this risk assessment. Next steps should include the modeling of short- and longer-term exposures as well as collection of area, residential, and personal exposure data, particularly for peak short-term emissions. Furthermore, studies should examine the toxicity of hydrocarbons, such as alkanes, including health effects of mixtures of HAPs and other air pollutants associated with NGD. Emissions from specific emission sources should be characterized and include development of dispersion profiles of HAPs. This emissions data, when coupled with information on local meteorological conditions and topography, can help provide guidance on minimum distances needed to protect occupant health in nearby homes, schools, and businesses. Studies that incorporate all relevant pathways and exposure scenarios, including occupational exposures, are needed to better understand the impacts of NGD of unconventional resources, such as tight sands and shale, on public health. Prospective medical monitoring and surveillance for potential air pollution-related health effects is needed for populations living in areas near the development of unconventional natural gas resources.

5. Conclusions

Risk assessment can be used as a tool in HIAs to identify where and when public health is most likely to be impacted and to inform risk prevention strategies directed towards efficient reduction of negative health impacts. These preliminary results indicate that health effects resulting from air emissions during development of unconventional natural gas resources are most likely to occur in residents living nearest to the well pads and warrant further study. Risk prevention efforts should be directed towards reducing air emission exposures for persons living and working near wells during well completions.

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References

Antero. Air Quality Sampling Summary Report Well Completion and Flowback Development Scenario Watson Ranch Pad Garfield County Colorado December 22, 2010. Denver, CO: Antero Resources; 2010.
ATSDR. Toxicological Profile for Benzene. Atlanta, GA: Agency for Toxic Substances and Disease Registry, US Deparment of Health and Human Services; 2007a.
ATSDR. Toxicological Profile for Xylenes. Atlanta, GA: Agency for Toxic Substances and Disease Registry, US Deparment of Health and Human Services; 2007b.
Brosselin P, Rudant J, Orsi L, Leverger G, Baruchel A, Bertrand Y, et al. Acute Childhood Leukaemia and Residence Next to Petrol Stations and Automotive Repair Garages: the ESCALE study (SFCE). Occup Environ Med 2009;66(9):598–606.
Caldwell JC, Woodruff TJ, Morello-Frosch R, Axelrad DA. Application of health information to hazardous air pollutants modeled in EPA's Cumulative Exposure Project. Toxicol Ind Health 1998;14(3):429–54.
CalEPA. Toxicity Criteria Database. California Environmental Protection Agency, Office of Environmental Health Hazard Assessment; 2003. Available: http://oehha.ca.gov/risk/chemicalDB/index.asp [Accessed May 2011].
Carpenter CP, Geary DL, Myers RC, Nachreiner DJ, Sullivan LJ, King JM. Petroleum Hydrocarbons Toxicity Studies XVII. Animal Responses to n-Nonane Vapor. Toxicol Appl Pharmacol 1978;44:53–61.
CDPHE. Garfield County Air Toxics Inhalation: Screening Level Human Health Risk Assessment: Inhalation of Volatile organic Compounds Measured in Rural, Urban, and Oil &Gas Areas in Ambient Air Study (June 2005–May 2007). Denver, CO: Environmental Epidemiology Division, Colorado Department of Public Health and Environment; 2007. Available: http://www.garfieldcountyaq.net/default_new.aspx.
CDPHE. Garfield County Emissions Inventory. Denver, CO: Air Pollution Control Division, Colorado Department of Public Health and Environment; 2009. Available: http://www.garfieldcountyaq.net/default_new.aspx.
CDPHE. Garfield County Air Toxics Inhalation: Screening Level Human Health Risk Assessment: Inhalation of Volatile Organic Compounds Measured In 2008 Air Quality Monitoring Study. Denver, CO: Environmental Epidemiology Division, Colorado Department of Public Health and Environment; 2010. Available: http://www.garfieldcountyaq.net/default_new.aspx.
COGCC. Statement of Basis, Specific Statutory Authority, and Purpose: New Rules and Amendments to Current Rules of the Colorado Oil and Gas Conservation Commission, 2 CCR 404–1. Colorado Oil and Gas Conservation Commission; 2009a. Available: http://cogcc.state.co.us/.
COGCC. Rules and Regulations, 2 CCR 404–1. Colorado Oil and Gas Conservation Commission; 2009b. Available: http://cogcc.state.co.us/.
COGCC. Inspection/Incident Database. Denver, CO: Colorado Oil and Gas Information System, Colorado Oil and Gas Conservation Commission; 2011. Available: http://cogcc.state.co.us/.
Collins J, Koplan JP. Health impact assessment: a step toward health in all policies. JAMA 2009;302(3):315–7.
Coons T, Walker R. Community Health Risk Analysis of Oil and Gas Industry in Garfield County. Grand Junction, CO: Saccommano Research Institute; 2008. Available: http://www.garfieldcountyaq.net/default_new.aspx.
Frazier A. Analysis of Data Obtained for the Garfield County Air Toxics Study Summer 2008. Rifle Denver, CO: Air Pollution Control Division, Colorado Department of Public Health and Environment; 2009. Available: http://www.garfieldcountyaq.net/default_new.aspx.
Galvin JB, Marashi F. n-Pentane. J Toxicol Environ Health 1999;1(58):35–56.
GCPH. Garfield County 2008 Air Quality Monitoring Summary Report. Rifle CO: Garfield County Public Health Department; 2009. Available: http://www.garfieldcountyaq.net/default_new.aspx.
GCPH. Garfield County 2009 Air Quality Monitoring Summary Report. Rifle CO: Garfield County Public Health Department; 2010. Available: http://www.garfieldcountyaq.net/default_new.aspx.
GCPH. Garfield County Quarterly Monitoring Report. Fourth Quarter October 1 through December 31, 2010. Rifle CO: Garfield County Public Health Department; 2011. Available: http://www.garfieldcountyaq.net/default_new.aspx.
Glass DC, Gray CN, Jolley DJ, Gibbons C, Sim MR, Fritschi L, et al. Leukemia Risk Associated with Low-Level Benzene Exposure. Epidemiology 2003;14(5):569–77.
Kim BM, Park EK, LeeAn SY, Ha M, Kim EJ, Kwon H, et al. BTEX exposure and its health effects in pregnant women following the Hebei spirit oil spill. J Prev Med Public Health Yebang Uihakhoe Chi 2009;42(2):96-103.
Kirkeleit J, Riise T, Bråtveit M, Moen B. Increased risk of acute myelogenous leukemia and multiple myeloma in a historical cohort of upstream petroleum workers exposed to crude oil. Cancer Causes Control 2008;19(1):13–23.
Lupo P, Symanski E, Waller D, Chan W, Langlosi P, Canfield M, et al. Maternal Exposure to Ambient Levels of Benzene and Neural Tube Defects among Offspring, Texas 1999–2004. Environ Health Perspect 2011;119(3):397–402.
Nilsen OG, Haugen OA, Zahisen K, Halgunset J, Helseth A, Aarset A, et al. Toxicity of n-C9 to n-C13 alkanes in the rat on short term inhalation. Pharmacol Toxicol 1988;62:259–66.
ORNL. The Risk Assessment Information System. Oak Ridge National Laboratory, TN: US Department of Energy; 2009. Available: http://rais.ornl.gov/ [Accessed May 2011].
Sandmeyer EE. Aliphatic Hydrocarbons. Patty's Industrial Hygeine and Toxicology, Third Edition, Volume IIB. New York: John Wiley; 1981. p. 3175–220.
TERC. VOC Emissions from Oil and Condensate Storage Tanks. Texas Environmental Research Consortium; 2009. p. 1-34. Available online at: http://files.harc.edu/Projects/AirQuality/Projects/H051C/H051CFinalReport.pdf. The Woodlands, TX.
US DOE. "Modern Shale Gas Development in the United States: A Primer," Office of Fossil Energy and National Energy Technology Laboratory, United States Department of Energy; 2009. http://www.netl.doe.gov/technologies/oil-gas/publications/EPreports/Shale_Gas_Primer_2009.pdf (accessed January 2012).
US EIA. Annual Energy Outlook 2011 with Projections to 2035. Washington DC: Energy Information Administration, United States Department of Energy; 2011.
US EPA. Risk Assessment Guidance for Superfund (Part A). Washington, DC: Office of Emergency and Remedial Response, US Environmental Protection Agency; 1989.
US EPA. Chemicals in the Environment: 1,2,4-trimethylbenzene (C.A.S. No. 95-63-6). Washington, DC: Office of Pollution Prevention and Toxics, US Environmental Protection Agency; 1994.
US EPA. Health Effects Assessment Summary Tables. Washington, DC: US Environmental Protection Agency; 1997.
US EPA. Method for the Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentrations and Direct Flame Ionization Detection (PDFID). Cincinnati OH: Office of Research and Development, US Environmental Protection Agency; 1999.
US EPA. The OAQPS Air Toxic Risk Assessment Library. US Environmental Protection Agency; 2004. Available: http://www.epa.gov/ttn/fera/risk_atra_main.html.
US EPA. Provisional Peer Reviewed Toxicity Values for Complex Mixtures of Aliphatic and Aromatic Hydrocarbons. Cinninati Ohio: Superfund Health Risk Technical Support Center National Center for Environmental Assessment: Office of Reasearch and Development., US Environmental Protection Agency; 2009a.
US EPA. Technology Transfer Network Air Quality System. Washington DC: Office of Air and Radiation, US Environmental Protection Agency; 2009b. Available: http://www.epa.gov/ttn/airs/airsaqs/.
US EPA. Greenhouse Gas Emissions Reporting from the Petroleum and Natural Gas Industry Background Technical Support Documtent. Washington DC: Climate Change Division, US Environmental Protection Agency; 2010a.
US EPA. ProUCL Version 4.00.05 Technical Guide Statistical Software for Environmental Applications for Data Sets With and Without Nondetect Observations(Draft). Washington DC: Office of Research and Development, US Environmental Protection Agency; 2010b.
US EPA. Integrated Risk Information System (IRIS). Washington DC: US Environmental Protection Agency; 2011. Available: http://www.epa.gov/IRIS/ [Accessed May 2011].
Vidas H, Hugman B. ICF International. Availability, Economics, and Production Potential of North American Unconventional Natural Gas SuppliesPrepared for The INGAA Foundation, Inc. by: ICF International; 2008.
Walther E. Screening Health Risk Assessment Sublette County, Wyoming. Pinedale WY: Sierra Research, Inc.; 2011. Available: http://www.sublettewyo.com/DocumentView.aspx?DID=438.
White N, teWaterNaude J, van der Walt A, Ravenscroft G, Roberts W, Ehrlich R. Meteorologically estimated exposure but not distance predicts asthma symptoms in school children in the environs of a petrochemical refinery: a cross-sectional study. Environ Health 2009;8(1):45.
Witter R, McKenzie L, Towle M, Stinson K, Scott K, Newman L, et al. Draft Health Impact Assessment for Battlement Mesa, Garfield County, Colorado. Colorado School of Public Health; 2011. Available: http://www.garfield-county.com/index.aspx?page=1408.
Zielinska B, Fujita E, Campbell D. Monitoring of Emissions from Barnett Shale Natural Gas Production Facilities for Population Exposure Assessment. Houston TX: Desert Research Institute; 2011. Available: http://www.sph.uth.tmc.edu/mleland/attachments/Barnett%20Shale%20Study%20Final%20Report.pdf.

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ATTACHMENT C

STUDY 24

Air Quality Impacts of Shale Gas Development in Pennsylvania

Ruohao Zhang, Huan Li, Neha Khanna, Alan J. Krupnick, Elaine L. Hill, Daniel M. Sullivan

Abstract: We estimate the impact of shale gas development on particulate matter pollution using a quasi-experimental setting in Pennsylvania where some wells were developed to produce natural gas whereas other wells were permitted but not drilled. In doing so, we utilize a novel empirical approach drawing upon insights from atmospheric chemistry to account for windblown pollution spillovers in a difference-in-differences framework. Utilizing a high frequency, high resolution satellite-based measure of PM pollution between 2000 and 2018, we identify causal increases in $PM_{2.5}$ concentration ranging from 0.017 $\mu g/m^3$ to 0.062 $\mu g/m^3$ in the vicinity of over 20,000 wells, resulting in approximately 20 additional deaths between 2010 and 2017.

JEL Codes: I15, I18, Q51, Q53, R11, R12

Keywords: shale gas, fracking, air pollution, particulate matter, aerosol optical depth, difference-in-differences, spillovers, mortality

Efficient environmental regulation presumes knowledge of the relationship between (local) pollutant concentrations, damages, and the sources of pollution. However, in many cases, this relationship, even if understood, is difficult to model accurately

Ruohao Zhang is at the department of Data Science, Centre College, Danville, KY. Huan Li is at the Department of Economics, North Carolina A&T State University, Greensboro, NC. Neha Khanna (corresponding author) is at the Department of Economics, Binghamton University, 4400 Vestal Pkwy E, Binghamton, NY 13902 (nkhanna@binghamton.edu). Alan J. Krupnick is at Resource for the Future, Washington DC. Elaine L. Hill is at the Department of Public Health Sciences and the Department of Economics, University of Rochester, Rochester, NY. Daniel M. Sullivan is at the J. P. Morgan Chase Institute, Washington DC. We would like to *Dataverse data:* https://doi.org/10.7910/DVN/WQZQBT

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because pollutants can disperse widely and cause damage in areas far from the original source.[1] We utilize an empirical model for air pollution that is informed by a standard air dispersion model to assess the change in particulate matter (PM) pollution due to the explosive growth of the shale gas industry in Pennsylvania between 2000 and 2018. Our model accounts for the interaction between potential outcomes in a difference-in-differences (DID) context and allows us to separately identify not only the local air pollution impact of a marginal well but also the impact due to airborne spillovers from other wells.

Overlaying the massive Marcellus shale formation, Pennsylvania is the largest producer of shale gas in the United States, accounting for almost 30% of total shale gas produced in the country (https://www.eia.gov/dnav/ng/ng_prod_shalegas_s1_a.htm). Unlike other major shale formations in the United States, including the Bakken, Barnett, and Eagle Ford formations, the geological properties and location of the Marcellus formation have led to shale gas activity in relatively densely populated areas, especially in southwest Pennsylvania (see fig. A7; figs. A1–A10 are available online), with correspondingly acute concerns regarding the environmental impacts from hydraulic fracturing and unconventional shale gas development.

Our particular focus on PM rather than the other types of air pollutants is important for two reasons. First, there is documented public concern that shale gas drilling activities contribute to local PM pollution (Litovitz et al. 2013), yet there is little causal evidence linking the two. Furthermore, while the literature has documented health effects on populations living close to unconventional wells (Currie et al. 2017; Hill 2018; Willis et al. 2021), the channels explaining these effects are uncertain.[2] PM pollution has known

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1. For example, Miller et al. (2019) show that wildfire smoke plumes can be detected hundreds of miles away from the original source, crossing local, regional, and national jurisdictions.

2. A notable exception is Hill and Ma (2017), which identifies an association between shale gas activity within 1 kilometer (km) of a public water system source and the birth weight of infants born to mothers it serves. Although not specifically related to hydraulic fracturing, Blundell and Kokoza (2022) show that upwind natural gas flaring causes increases in respiratory health related hospital visitation rates. Likewise, Cushing et al. (2020) establishes that pregnant mothers living within 5 km of flaring activity were more likely to give birth to premature babies and babies with lower birth weight; Willis et al. (2020) links flaring and natural gas production to childhood asthma in Texas.

adverse health impacts (Dominici et al. 2006; Atkinson et al. 2014), so understanding the causal effects of shale gas development on local PM pollution is relevant to policy.

We expect that PM pollution will increase during two phases in the life cycle of a shale gas well: well preparation and production. Well preparation activities, such as drilling and the associated commercial vehicle traffic, bring dust and diesel combustion, known sources of PM pollution (Roy et al. 2014; Graham et al. 2015), to well sites and nearby areas. Similarly, the production of natural gas is associated with on-site diesel combustion (Litovitz et al. 2013) and fugitive emissions.[3] We estimate the causal effects of the two treatments (well preparation and production, respectively) on local PM pollution in the vicinity of hydraulically fractured wells, accounting for airborne spillovers to/from nearby areas. To construct the counterfactual, we exploit the fact that not every well that is permitted eventually gets spudded and drilled (Pennsylvania Department of Environmental Protection 2020). According to Hill (2018), drilling of permitted wells is primarily correlated with shale depth rather than community characteristics or leasing behavior of local residents. We define our study unit (which we name "pollution area" or P-area) as a circular area of 3 km radius around every unconventional well and assign these areas to the treatment group if their centroid well has ever been in either the well preparation or production treatment, while the control group includes P-areas with centroid wells that were permitted but did not experience significant well preparation activities (i.e., not spudded).[4]

Our novel empirical contribution lies in estimating the causal effect of shale gas activity on local air pollution while explicitly accounting for the spillovers from one well's activities on other areas. Our model of the airborne pollution spillovers is based on a standard Gaussian point source air dispersion model in which the aerosol travels along the downwind direction and diffuses along the crosswind direction.[5] This model

3. Fugitive emissions include benzene, toluene, ethyl-benzene, xylene, and other toxic hydrocarbons (Srebotnjak and Rotkin-Ellman 2014). These aerosols can interact with sunlight and water vapor to form liquid particles and are a secondary source of PM pollution.

4. In table A1 (tables A1–A16 are available online), we compare four socioeconomic variables for the census block groups where treatment and control P-areas are located. As expected, because of the large sample size ($N = 20{,}677$), the group differences are statistically significant except for the 2000 population and 2018 education. Nonetheless, the differences are economically negligible in magnitude, suggesting reasonably well balanced socioeconomic profiles between the treatment and control groups.

5. Air pollution spillovers may arise from two channels. First, because PM pollution is airborne and travels with wind, well preparation and production operations may increase PM pollution in downwind areas, including control group areas with no wells. Second, a cluster of wells may share infrastructure, such as road access to the fracking site, pipelines, waste pits, and other facilities, thereby lowering the marginal change in PM pollution in the vicinity of a new well. We account for the second channel by including the number of wells in the well preparation period, in production, or plugged and inactive in the 20 km radius around every well as control variables in our regression.

reflects the fact that the magnitude of the airborne spillovers changes daily with wind direction.

We find statistically detectable changes in daily aerosol optical depth (AOD), our satellite-based measure of $PM_{2.5}$ pollution, during both the well preparation and production phases of a marginal unconventional well. Not surprisingly, the marginal increase is quite a bit higher during well preparation (2.19% relative to the baseline AOD) than during production (1.35% of baseline). Furthermore, while the airborne treatment effect declines with distance from a centroid well, it can be detected as far as 10 km downwind from the pollution source. These results are robust across multiple subsamples selected using different selection-on-observables strategies, alternative definitions of the treatment period, and falsification tests using placebo treatments. Accounting for airborne spillovers, on average, fracking increases daily AOD by 1.27% for the whole sample (which includes areas with no wells), and by 5.67% for the subsample of P-areas with a treated well. Based on Lee et al. (2011), these overall increases in AOD imply that daily $PM_{2.5}$ concentrations increased by 0.017 micrograms per cubic meter ($\mu g/m^3$) and 0.062 $\mu g/m^3$, respectively, in the average P-area.[6] Using the concentration response functions in Lepeule et al. (2012) and Fowlie et al. (2019), we estimate that this resulted in an additional 20 deaths between 2010 and 2017 in 671 census block groups across 40 counties that contain at least one shale gas well, with a total population of about 840,000 and an annual average death rate of 12 per 1,000.[7]

We join a growing body of literature in economics that utilizes satellite data to estimate air quality (see, e.g., Donaldson and Storeygard 2016; Currie et al. 2020) when traditional monitor-based data are inadequate or unavailable. In doing so, we build on a literature that uses quasi-experimental research designs to quantify the effects of economic activity on air quality and human health.[8] Our work is relevant to policy makers who seek to understand the welfare effect of shale gas development. It is also relevant to communities located close to shale gas wells for whom the local air quality impact is a direct concern. In a broader context, we provide a prototype for empirical analyses of airborne pollution from stationary or point sources where spillovers are expected.

6. These daily increases are equivalent to 0.14% and 0.5%, respectively, of the current National Ambient Air Quality Standard of 12 $\mu g/m^3$.

7. As a comparison, Fowlie et al. (2019) estimate that the inaccurate $PM_{2.5}$ attainment designation in the United States is associated with 23–335 deaths nationwide every year.

8. For example, Deryugina et al. (2019) use wind direction, air quality data from the Environmental Protection Agency (EPA), and Medicare claims to estimate the costs of air pollution on mortality and health-care costs.

1. LOCAL AIR POLLUTION FROM SHALE GAS DEVELOPMENT IN PENNSYLVANIA

The innovation of hydraulic fracturing and horizontal drilling technology decreased the production cost of shale gas significantly, making unconventional production economically feasible. The rapid development of shale gas increased the supply of natural gas and lowered the prices relative to the scenario without hydraulic fracturing (Newell and Raimi 2014). In turn, this facilitated the displacement of coal by natural gas in power generation, leading to air quality improvement. At the same time, lower prices encourage energy consumption. Newell and Raimi (2014) show that the retirement of coal-fired power plants has dominated the increase in energy consumption, thus lowering US greenhouse gas emissions.

1.1. The Link between Shale Gas Development and Local Air Pollution

Despite the positive global and regional environmental externality, the shale gas boom has raised concerns regarding local air quality. Most fracking activities come with diesel combustion and dust, increasing emissions of ambient pollutants like CO, NO, hydrocarbons, and PM. It usually takes several months to complete well preparation (Hill 2018). Activities include building roads, clearing sites, and transporting heavy equipment, such as drilling rigs, high-volume fracking pumps, and large storage tanks. According to Graham et al. (2015), it takes roughly 1,500 heavy-truck trips to deliver equipment and materials to a site and to remove the construction and drilling wastes from the site. In addition, off-road heavy-duty engines are used to operate drill rigs and hydraulic fracturing pumps (Roy et al. 2014). When the construction is completed, a completion venting is performed for cleaning and bringing the well to production (Roy et al. 2014). Venting occurs multiple times during the life cycle of a well and is a major source of volatile organic compounds (VOCs) emissions.

During the production period, on-site equipment, including compressors to maintain the pressure of produced natural gas and other diesel machinery for well maintenance, results in diesel and natural gas combustion and air pollution. Additionally, toxic air pollutants and VOCs, including benzene, toluene, ethyl-benzene, xylene, and other toxic hydrocarbons, are released when gas is flared, vented, or accidentally leaked during production as well as from associated infrastructure such as condensate tanks (to store liquid separated from produced natural gases), dehydrators (to remove water from the produced natural gas), waste water impoundment pits, and pipelines (Srebotnjak and Rotkin-Ellman 2014). Many of these aerosols interact with sunlight and water vapor to form liquid particles and are a secondary source of PM pollution. In fact, secondary aerosols contribute a large portion of total PM and are the dominating source of PM in many cases (Lewandowski et al. 2008; Heo et al. 2009; Larsen et al. 2012; Huang et al. 2014).

1.2. Local Air Pollution Measurements

Since many of the pollutants emitted during the well's preparation and production period are either primary or secondary sources of PM, we assess the impact of shale gas development on local air quality through PM concentration. PM measurements are available from multiple sources, including the EPA's ground-based monitoring, network stations, aircraft measurements, and satellite platforms as summarized in Field et al. (2014). The commonly used ground-based monitoring data from EPA are not useful for this study because the monitors are mostly located in urban areas of Pennsylvania such as Philadelphia and Pittsburgh, whereas shale wells are concentrated in rural areas in the northeast and southwest parts of the state (see fig. A1). On the other hand, the satellite platform provides a local, daily measurement of PM with widespread geographic coverage. We therefore take advantage of NASA's satellite-based measurements of aerosal optical depth (AOD), which is a high-frequency and high resolution (3 km × 3 km) measure and is known to be one of the most robust aerosol parameters retrieved by the Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA's satellites (Streets et al. 2013).[9] The literature has shown that AOD is a good predictor of PM of different sizes: $PM_{2.5}$ (diameter < 2.5 μm) and PM_{10} (diameter $<$ 10 μm) (Liu et al. 2004; Van Donkelaar et al. 2016). Higher AOD indicates worse air quality and higher PM pollution.

Our use of AOD as a measure of air quality is not unique in the economics literature. Zou (2021) studies the current EPA policy of intermittent monitoring of environmental standards and uses AOD to measure air quality when ground monitoring is off. His study finds that air quality is significantly worse on unmonitored days. Foster et al. (2009) studies the air pollution impact of a voluntary pollution reduction program in Mexico and its beneficial consequences on infant health. Sullivan and Krupnick (2019) uses AOD to measure air quality in individual counties across the United States and argues that due to the limited number of ground monitors, many counties are mistakenly assigned as being in "attainment" with the 2015 National Ambient Air Quality Standards for PM. A similar result is also found by Fowlie et al. (2019).

The spatial scale of air pollution from shale gas wells is small. Companies conduct the drilling process on about a 3-acre pad of land, with a number of trucks that become part of an oil and gas drilling process. Given that the sources of air pollution are from truck traffic and on-site construction and production processes, we focus on a 3 km circular area (the P-area) around each permitted well (which we refer to as the centroid well).

9. AOD is generated by the following method: remote sensors record the interaction between electromagnetic radiation and aerosols, including solid and liquid particles in the atmosphere, then convert the recorded results to AOD by applying radioactive transfer models (Remer et al. 2005). There are two NASA satellites with MODIS instruments: Aqua and Terra. We use Terra because it has a longer observation period starting from February 2000, whereas Aqua starts from May 2002.

1.3. Empirical Issues

One challenge in identifying the causal air pollution due to shale gas development is that treatment is not randomly assigned because the location of shale gas is highly correlated with various geological and socioeconomic characteristics.[10] To overcome this challenge, we employ a control group of P-areas with a permitted centroid well that is not spud during our sample period (i.e., although the well was permitted it was not drilled so there is no centroid well in these P-areas). These control P-areas should provide a credible counterfactual for PM pollution in the absence of shale gas development because they share many of the same geological and socioeconomic characteristics as the treatment group (i.e., P-areas with a centroid well that is spud or produces gas during our sample period).

Figure 1 shows the location of all wells in the treatment and control groups of our study. It is clear that there is a strong geographic overlap between the two groups of wells. However, as shown in figure A2, there is systematic temporal variation in well preparation and production periods in the sample. For example, there is a cluster of wells in the northeastern part of Pennsylvania permitted during 2012–15 and a cluster of wells in the southwestern part permitted after 2015. As wells that are permitted earlier tend to be spudded and produce earlier, this implies a nonrandom temporal variation in the airborne pollution spillovers.

2. MODELING $PM_{2.5}$ POLLUTION

Our empirical model of $PM_{2.5}$ pollution due to shale gas activities is based on a standard DID framework that identifies the average treatment effects of well preparation and shale gas production on air quality. The outcome variable is particulate matter pollution in each P-area, a circular area of 3 km radius around each permitted well.[11] The treatment group contains P-areas with a centroid well that is spud and/or produces shale gas within our sample period, and the control group is defined as P-areas with a permitted well at its centroid that is not spud during our sample period.

We start from the following baseline standard DID model:

$$q_{id} = \eta T_{id} + \boldsymbol{Z}'_{id}\zeta + \mu_i + \sigma_d + u_{id}. \quad (1)$$

Here, q_{id} represents the air quality of P-area i on day d. The term T_{id} is a binary variable indicating air pollution treatment from the well that is located at the centroid of the P-area, with $T_{id} = 1$ when the well is generating pollution and zero otherwise. We consider $PM_{2.5}$ pollution treatments generated by two different activities: well preparation and shale gas production. Therefore, in our case, P-areas can enter/exit treatment periods on different days. The term $\boldsymbol{Z}'_{id}$ is a vector of time varying covariates

10. For example, shale gas wells are more likely to locate in rural areas with lower than average population density.

11. We also use 5 km and 10 km as alternative radii for the P-areas: see table A13.

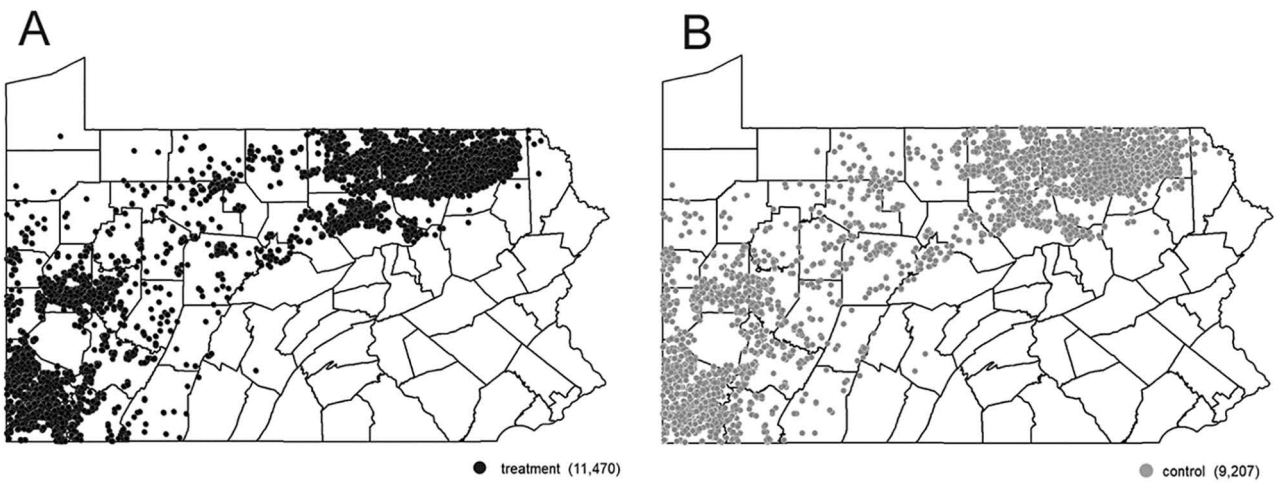

Figure 1. Wells location by groups. *A*, Wells in treatment group. *B*, Wells in control group

that are correlated with particulate matter pollution. The two-way fixed effects are the P-area fixed effect μ_i and day fixed effect σ_d; thus in the DID framework, η estimates the average treatment effect of air pollution from the well. The term u_{id} is the error term, assumed to be independently and identically distributed.

2.1. Airborne Pollution Spillovers

Air pollution can travel with wind, and the air quality of a P-area can be affected by the pollution not only from its own centroid well but also from wells located in other P-areas in close geographical proximity. This holds true for both the treatment and control P-areas. For example, a P-area in the control group that does not have a spud centroid well may receive windblown pollution from a neighboring P-area in the treatment group where the centroid well is generating pollution. Furthermore, systematic patterns in wind direction and temporal variation in treatments implies that the windblown pollution spillovers are nonrandom.

The systematic temporal variation in shale gas development in Pennsylvania means that wells located close to each other tend to be drilled and produce shale gas at the same time. Therefore, we expect that P-areas in the treatment period receive greater windblown spillovers, on average, than both P-areas in the pretreatment period and P-areas in the control group (the summary statistics in table 1 align with our expectation). This has an important implication for our empirical analysis since the systematic differences in pollution spillovers will lead to an overestimation of the treatment effect if not accounted for. In figure 2, we illustrate the rationale behind the overestimation by the simple DID model that does not account for the spillover: T denotes the treatment group P-areas with drilled centroid wells and C denotes the control group

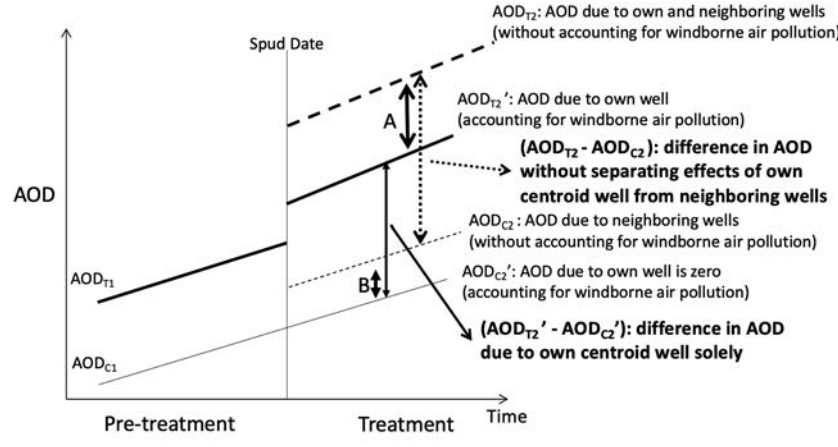

Figure 2. Spillovers in treatment and DID

P-areas with permitted but not drilled centroid wells, 1 and 2 refer to the pretreatment and treatment periods, respectively. The solid lines represent the model that accounts for the airborne spillover of pollution from neighboring wells; the dashed lines represent the model that assumes that all the pollution in a P-area is generated by centroid well and ignores windblown spillovers.

In the model that accounts for airborne spillovers from neighboring wells, we separate the pollution from the P-area's own centroid well and airborne air pollution from neighboring wells. In this case, the average treatment effect (ATE) of the own centroid well is $\text{ATE} = (\text{AOD}'_{T2} - \text{AOD}'_{C2}) - (\text{AOD}_{T1} - \text{AOD}_{C1})$. On the other hand, in the model without airborne spillovers, the estimated ATE of the own centroid well reflects pollution from the centroid well as well as spillover effects from neighboring wells: $\text{ATE}' = (\text{AOD}_{T2} - \text{AOD}_{C2}) - (\text{AOD}_{T1} - \text{AOD}_{C1})$. The error in estimating the ATE using a simple DID without accounting for the pollution spillovers from neighboring areas is given by $\text{ATE}' - \text{ATE} = (\text{AOD}_{T2} - \text{AOD}_{C2}) - (\text{AOD}'_{T2} - \text{AOD}'_{C2}) = \text{A} - \text{B}$, where A is the airborne spillovers to P-areas in the treatment group, while B is the airborne spillovers to P-areas in the control group. A priori, we do not know the sign of $A - B$. However, given the systematic temporal variation in shale gas development shown in our data, we expect $A - B > 0$.

We address the potential bias by explicitly modeling the treatment spillovers, which enables us to "partial out" the windblown pollution in both treatment and control P-areas. Similar to Butts (2021), our model separates the direct local effect, which is the effect on a P-area of the centroid well entering the well preparation or production phase, from the spillover effects, which is the airborne spillover of pollution from neighboring upwind wells.[12]

We expect the pollution spillovers through wind to attenuate nonlinearly with distance, so we arbitrarily distinguish three distance bins—0–2 km, 2–5 km, and 5–10 km—and allow the spillover effects from upwind $PM_{2.5}$ pollution to differ by bin. In addition to distance, wind direction matters too. The closer the wind direction to the geographic direction between the centroid of the P-area and the external emission source, the greater the spillover effects, conditional on distance. This can be captured by the angle between the geographic direction (from the external emission source to the P-area) and the wind direction. Therefore, in our framework, the spillover matrix is continuous and varies by date because the wind direction is different every day.

We define $\boldsymbol{w}^B_{id}$ as a $1 \times N$ vector of weights for P-area i on day d, where N is the total number of P-areas in the sample. The jth element in $\boldsymbol{w}^B_{id}$, indicated by w^B_{ijd}, measures the

12. It is possible that pollution may spill over from commercial vehicle traffic along roads. We expect that the spillover due to this channel is small since (1) traffic-related air pollution travels only a short distance (about 600 meters) by wind (Anderson 2020), which is unlikely to affect neighboring P-areas; (2) moving traffic is reported to create much less pollution compared to standing vehicles at/near a well pad (Kumar and Goel 2016).

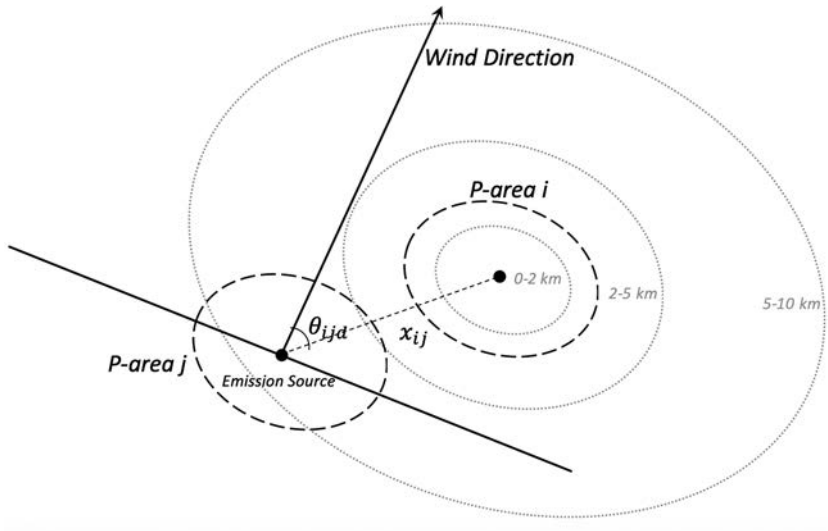

Figure 3. Pollution transportation by wind. This is an example of upwind pollution spillovers coming from an active well (emission source) at the centroid of P-area *j* that is located within the 5–10 km ring of P-area *i*.

magnitude of the spillovers that P-area *i* receives from a well located at the centroid of P-area *j* on day *d*, under the condition that the well is in bin *B* of P-area *i*. The element w_{ijd}^{B} will vary over time depending on whether P-area *i* is located downwind from *j*'s emission source. To quantify w_{ijd}^{B}, we use the geographical locations and wind direction on day *d*. As shown in figure 3, suppose θ_{ijd} is the angle between the wind direction on day *d* and the geographical direction from a well in P-area *j* to the centroid of P-area *i*, and x_{ij} is the distance between the two wells. Then w_{ijd}^{B} is defined as:

$$w_{ijd}^{0-2} = \cos(\theta_{ijd}) \text{ if } \theta_{ijd} \leq \pi \text{ and } 0 < x_{ij} \leq 2, \quad w_{ijd}^{0-2} = 0 \text{ otherwise,}$$

$$w_{ijd}^{2-5} = \cos(\theta_{ijd}) \text{ if } \theta_{ijd} \leq \pi \text{ and } 2 < x_{ij} \leq 5, \quad w_{ijd}^{2-5} = 0 \text{ otherwise,}$$

$$w_{ijd}^{5-10} = \cos(\theta_{ijd}) \text{ if } \theta_{ijd} \leq \pi \text{ and } 5 < x_{ij} \leq 10, \quad w_{ijd}^{5-10} = 0 \text{ otherwise.}$$

The design of our spillover weight matrix follows the spirit of the Gaussian point source dispersion model,[13] in which the aerosol travels along the downwind direction and diffuses along the crosswind direction. The definition of w_{ijd}^{B} implies that the weight is zero if P-area *j*'s centroid well is downwind from P-area *i*, and the weight

13. The Gaussian point source dispersion model is a fundamental atmospheric dispersion model. See https://en.wikipedia.org/wiki/Atmospheric_dispersion_modeling.

is positive if *j*'s centroid well is located upwind from P-area *i*. The smaller the angle between the wind direction and the geographical direction from *j*'s centroid well to P-area *i*, the larger the spillover effect on P-area *i*.

Imbens and Rubin (2015) warn against the possibility of "hidden variation in treatment," which leads to a violation of the stable unit treatment value assumption (SUTVA). By incorporating the daily variation in wind direction in our spillover matrix we mitigate this potential bias.

2.2. Model Specification

We use the following DID model as our preferred specification:

$$q_{id} = \eta T_{id} + \sum_B \beta^B \boldsymbol{w}_{id}^B \boldsymbol{H}_d^B + \boldsymbol{Z}_{id}'\zeta + \mu_i + \sigma_d + u_{id}, \tag{2}$$

where q_{id}, T_{id}, and $\boldsymbol{Z}_{id}'$ have the same definitions as the baseline model in equation (1). The summation term represents the aggregate magnitude of windblown pollution spillovers from centroid wells in other P-areas. The term $\boldsymbol{H}_d^B$ is a vector of dummies for all centroid wells, in which an element is equal to 1 if and only if P-area *j*'s centroid well is in P-area *i*'s distance bin B and the emission source is generating $PM_{2.5}$ on day d. In matrix notion, $\boldsymbol{w}_{id}^B \boldsymbol{H}_d^B$ is the weighted sum of all airborne spillovers from bin B received by P-area i on day d.[14]

The coefficient η is the average effect of local treatment, which represents the additional air pollution in P-area i generated by its own centroid well. The β^B terms capture the effects due to the combined spillovers of air pollution generated by neighboring wells located in different distance bins. That is, η measures the average AOD difference between treated P-areas (with an active centroid well) and control P-areas (without an active centroid well), conditional on the pollution spillovers from nearby wells in each distance bin. The total air pollution a P-area i receives on date d is the sum of the pollution generated by its centroid well and the spillovers from neighboring wells and can be represented by $\eta T_{id} + \Sigma_B \beta^B \boldsymbol{w}_{id}^B \boldsymbol{H}_d^B$.

Similar to Butts (2021), in our model the "total treatment effect" of a centroid well entering well preparation or production is the local effect on its own P-area plus the spillovers to neighboring areas. But our model is more complicated than the models in Butts (2021) because the pollution spillovers and therefore the "total treatment effect" vary across wells and time, depending on the number and location of neighboring P-areas and the wind direction. For example, suppose for an active well at the centroid of P-area i on date d, there are only two neighboring P-areas a and b located in its downwind direction that receive its pollution spillovers. Let x_{ia} and x_{ib} be the distance

14. See also Delgado and Florax (2015), which accounts for spatial treatment spillovers through a binary time-invariant spatial weight matrix.

from the centroid of P-area i (the location of the active well) to the centroid of P-areas a and b, let θ_{iad} and θ_{ibd} be the angles between the downwind direction and the relative geographical locations of P-areas a and b on date d. Suppose $x_{ia} < 2$ km, 5 km $< x_{ib} <$ 10 km, $\theta_{iad} < \pi$, $\theta_{ibd} < \pi$, then the "total treatment effect" of the centroid well in P-area i on date d can be calculated as $\text{TE}_{id} = \eta + \beta^{0-2}\cos(\theta_{iad}) + \beta^{2-5}\cos(\theta_{ibd})$.[15]

It is worth noting that our model identifies the average effect on $PM_{2.5}$ pollution due to on-site construction and production activities for a typical shale gas well, and we assume that, conditional on our specification, the $PM_{2.5}$ pollution generated is the same across all marginal wells. However, we recognize that an isolated well is likely to generate a different magnitude of $PM_{2.5}$ pollution than a well located among a cluster of wells because of differences in the level of related economic activities, such as access road development and pipeline construction. Empirically, we account for such variation in emissions due to related activities by including the density of shale gas wells in the area as control variables in the regression.

3. DATA

3.1. Data Source

We create a comprehensive data set that includes every well that was permitted in Pennsylvania between February 24, 2000, and September 20, 2018.[16] Our data set includes detailed information on each well and daily information on air pollution and weather from multiple data sources.

3.1.1. Pennsylvania Shale Gas Data

Our well data are compiled from two sources published by the Pennsylvania Department of Environmental Protection (PA DEP): Oil Gas Locations—Unconventional (https://gis.dep.pa.gov/PaOilAndGasMapping/OilGasWellsStrayGasMap.html?) and Oil and Gas Well Production Report (http://www.depreportingservices.state.pa.us/ReportServer). These sources include information submitted by well operators, as required by PA DEP (Regulation Code sec. 78a.121) and contain a unique well identifier and well coordinates, allowing us to merge information across these sources.

15. Given the tremendous variation in the "total treatment effect" across P-area locations and dates, it is not very meaningful to compute an average of the "total treatment effect" for our sample. In addition, although the "total treatment effect" captures the spillovers of pollution from a given P-area, our empirical computation of it ignores the spillovers on downwind areas that do not have a permitted or spud well and are therefore excluded from our sample. For these reasons, we do not report numerical estimates of the spillover treatment effect from a typical well in our sample.

16. February 24, 2000, is the first day that the AOD data are available. September 20, 2018, is the date we accessed the data.

We have information on each well's geographic coordinates and permit date, regardless of whether the well is spudded or not. For wells that were drilled, we have current well status, along with the spud date, production period, and completion date if already plugged.[17] This allows us to determine each well's activities on any given day. Given our focus on air quality, we consider three periods in the life cycle of a well: permitted but not yet spud, well preparation period, and production period.

In total, we obtained information on 20,677 unconventional wells that were permitted over our study period. As shown in figure A1, most of these permitted wells are located in Pennsylvania's northeastern corner (Susquehanna and Bradford counties) and southwestern corner (Washington and Greene counties). This is because the depth of the Marcellus Shale base in these regions ranges from 5,000 to 8,500 feet, higher than other parts of Pennsylvania, suggesting that these areas are especially productive (https://marcellus.psu.edu/resources/maps-graphics-and-videos/).

3.1.2. Local Air Quality: MODIS AOD

There are two NASA satellites with MODIS instruments: Aqua and Terra. We use the data provided by Terra because it has a longer observation period (starting from February 2000, whereas Aqua starts from May 2002). There are four levels of MODIS data available: L0 to L3, with the higher level referring to data that are more preprocessed but with lower spatial resolution. We use L2 data, which provide daily AOD observations at a 3 km × 3 km pixel resolution.[18]

With the prior that well preparation and production activities primarily affect air quality in the immediate vicinity of a well, we define P-areas as the circular area of 3 km radius surrounding a well. There are two difficulties in measuring a P-area's AOD (i) L2 AOD data are for 3 km × 3 km square pixels, whereas P-areas are 3 km radius circles. (ii) The pixels in the L2 data change every day with the orbit of the satellite. We overcome these difficulties as follows. First, we overlap all pixels with P-areas to find the square-circle intersections between pixels and every P-area for each day separately. Second, we assign every pixel a daily weight based on the daily intersection area to calculate the daily weighted average AOD for each P-area.

For example, suppose on day d, a P-area overlaps with pixel 1 and pixel 2 only. Pixel 1 has x_{1d} km^2 intersection area with the P-area on day d and has AOD equal to q_{1d}. Pixel 2 has x_{2d} km^2 intersection area and AOD of q_{2d}. Then on day d the weights of pixels 1 and

17. Spud date is the day when the main drill bit begins drilling into the ground.

18. We use version 6.1 MOD04_3K HDF data file. We choose the "Corrected_Optical_Depth_Land" layer. The level 2 data are also available at 5 km × 5 km resolution. L0 is the raw spectral channel, and L1 is calibrated and geolocated radiance. Neither of them can be directly used. L3 also provides AOD, but the resolution is 1° × 1° global grid, and the data frequency is either eight days or one month.

2 are $x_{1d}/(x_{1d} + x_{2d})$ and $x_{2d}/(x_{1d} + x_{2d})$, respectively. The weighted average AOD for the P-area on day d becomes $[q_{1d}x_{1d}/(x_{1d} + x_{2d})] + [q_{2d}x_{2d}/(x_{1d} + x_{2d})]$. In general, where a P-area overlaps with J pixels on day d, the weighted average AOD for P-area i is:

$$\mathrm{AOD}_{id} = q_{1d}\left(\frac{x_{1d}}{x_{1d} + x_{2d} + \ldots + x_{Jd}}\right) + \ldots + q_{jd}\left(\frac{x_{jd}}{x_{1d} + x_{2d} + \ldots + x_{Jd}}\right) + \ldots + q_{Jd}\left(\frac{x_{Jd}}{x_{1d} + x_{2d} + \ldots + x_{Jd}}\right).$$

3.1.3. Weather

We include daily information on local weather as our key control variables. We do so for three reasons. First, the weather variables account for the possible correlation between weather conditions and the choice of spud date. Second, weather is an important confounder of the strong association between AOD and $PM_{2.5}$ (Kumar et al. 2007; Foster et al. 2009), and both well preparation and production activities affect AOD through $PM_{2.5}$. Third, wind information helps us address the air pollution spillovers.

The weather data are from the Parameter-Elevation Regressions on Independent Slopes Model (PRISM), a spatial climate database. PRISM provides daily information on precipitation, mean temperature, and mean dew point temperature. One advantage of PRISM is that it is based on a spatial resolution of 4 km^2 pixels, which is comparable in size to a well's P-area and the spatial resolution of the AOD data. We process the daily precipitation, temperature, and dew point data in a manner similar to the AOD data. That is, we overlay the 4 km^2 grid of weather data with P-areas and calculate the weighted average for each P-area using the (time-invariant) intersection areas as weights.

Daily information on wind speed and direction is from the National Centers for Environmental Prediction (NCEP)–US Department of Energy Reanalysis II (NCEPRII). These data are available at a resolution of 2.5 degree in latitude and longitude. We assign wind information to each P-area based on the 2.5 degree square that the centroid well is located in. Wind speed serves as an additional control variable, and wind direction is used to address the airborne spillovers of pollution.[19]

19. Wind speed is decomposed into two components: U wind speed and V wind speed. U wind is the east-west component of wind. Positive U wind means the wind is from west to east, and negative U wind implies it is from east to west. V wind is the north-south component of wind. Positive V wind means the wind is from south to north, and negative V wind means it is from north to south. The combination of U wind and V wind provides the wind direction and wind speed.

3.2. Defining the Well Preparation and Production Treatments

Each well has a unique duration for the well preparation and production periods. We use each well's permit date, spud date, drilling and production period, and plug date to define the different periods in its life cycle. Since the data do not report the end of the well preparation period, we assume that the well preparation period ends immediately prior to the start of production. Accordingly, we divide the life cycle of an unconventional well into three periods that are defined as follows:[20]

- Pre-spud (pretreatment) period: before the well spud date;
- well preparation period: well spud date to one day before production commences;
- production period: first production date to last production date/plug date.[21]

Appendix A.1 (appendix is available online) provides details on how we use the well production reports to determine the lengths of the well preparation and production treatments.

When estimating our regression models, we cluster standard errors by well pads. A well pad, typically 3 acres in size, may consist of multiple wells with overlapping P-areas. Out of 20,677 unconventional wells in our sample, 7,884 do not have well pad information. We assume that wells close to each other are located on the same well pad and artificially assign a well pad ID to every individual well. In particular, we designate any well that is less than 63 meters from any other well to be on the same well pad (Muehlenbachs et al. 2015). Comparing our artificially designated well pad IDs to the sample of original well pad IDs, only 1.9% of wells are mistakenly assigned to a different artificial well pad.

3.3. Descriptive Statistics

The final sample is an unbalanced panel consisting of 20,677 wells on 4,691 days, from February 24, 2000 to September 20, 2018.[22] Out of the 20,677 permitted wells, 11,470 wells experienced well preparation or/and production periods and are included in the treatment group; the remaining 9,207 wells were not spudded and are in the

20. We acknowledge that we conflate truck-related pollution with own well preparation and production treatments for P-areas with active wells; for areas with no active wells, we are not able to estimate the air pollution due to truck traffic from upwind areas.

21. We do not consider postproduction activities, i.e., the pollution from on-site activities at abandoned/plugged wells. So we drop observations after production ends.

22. The original data contain 20,680 unconventional wells. Based on the production reports, three of these wells do not have unconventional gas extraction activities. We exclude these three wells from the sample.

control group.[23] The majority of the wells in our sample were permitted after 2007 and are located in the southwestern and northeastern corners of Pennsylvania. For wells that have been spudded (i.e., wells in the treatment group), the well preparation period lasts 406 days, on average. Once the well preparation period ends, wells immediately go into production and, on average, gas is extracted for 1,805 days (five years) until production is completed.

Table 1 presents summary statistics for our main analysis sample. We compare the mean statistics from the full sample and subsamples with treatment group observations in the pre-spud period, well preparation period, production period, and control group observations separately. The mean daily AOD is 0.23, with a standard deviation of 0.26. While the treated P-areas have a pre-spud average AOD that is slightly higher than that for the control P-areas, their average AOD is smaller. This might be explained by the fact that (i) the majority of wells in our sample were constructed and producing in the later years of our sample and (ii) there is a downward trend in AOD over time as shown in the first panel of figure A3.[24] The weather variables are relatively stable across the full sample and various subsamples.

In panel 2 of table 1, we summarize the magnitude of the aggregate air pollution spillovers received by an individual P-area across the different distance bins ($\boldsymbol{w}_{id}^{B}\boldsymbol{H}_{d}^{B}$). The subsample of observations with centroid wells in the well preparation phase has the largest mean values for aggregate spillovers received from upwind well preparation activities across all three distance bins as well as the highest density of wells in the well preparation phase in a 20 km radius around the centroid well. This suggests that a P-area with a centroid well in the well preparation phase is more likely to be located near other wells in the same phase. Likewise, the subsample of observations with centroid wells in the production phase has the largest mean value for aggregate spillovers received due to upwind shale gas production activities across all three distance bins as well as the highest density of wells in the production phase in a 20 km radius around the centroid well. These statistics suggest the existence of systematic spatial and temporal air pollution spillovers.

3.4. Assessing the Reliability of the Control Group

The validity of our DID estimates depends on the ability of our control group P-areas to provide a reliable counterfactual. We utilize an event study to illustrate

23. In our data set, out of the 11,470 wells in the treatment group, 2,184 wells are associated with a well preparation period only, 94 wells have information only for the production period, and 9,192 wells have information for both periods.

24. The yearly AOD trend is consistent with the yearly $PM_{2.5}$ trend of the United States. See the EPA website: https://epa.maps.arcgis.com/apps/Cascade/index.html?appid=6656472ac1d7492b87a826a921e2d81d. The rest of fig. A3 describes the yearly trend in the weather variables.

Table 1. Descriptive Statistics

	1. Key Variables				
		Treatment			
	Full Sample	Pre-spud	Well Preparation	Production	Control
AOD (unitless)	.23	.24	.20	.19	.23
	(.26)	(.27)	(.22)	(.22)	(.26)
Precipitation (mm)	1.22	1.21	1.204	1.23	1.22
	(4.43)	(4.49)	(4.09)	(4.23)	(4.45)
Temperature (Celsius)	12.32	12.35	12.03	12.41	12.29
	(7.99)	(7.87)	(8.31)	(8.31)	(7.98)
Dew point (Celsius)	5.50	5.44	5.28	5.76	5.50
	(8.53)	(8.42)	(8.75)	(8.85)	(8.53)
Wind speed (m/s)	3.98	3.97	4.00	3.98	3.99
	(2.12)	(2.12)	(2.13)	(2.12)	(2.12)
	2. Spillover Received by P-Area and Well Densities				
		Treatment Group			
	Full Sample	Untreated Period	Well Preparation Period	Production Period	Control Group
Magnitude of spillover:					
Well preparation in 0–2 km ring	.22	.11	1.88	.34	.18
	(.98)	(.67)	(2.50)	(1.23)	(.83)
Well preparation in 2–5 km ring	.79	.51	2.71	1.65	.68
	(2.35)	(1.93)	(4.13)	(3.29)	(2.10)

Well preparation in 5–10 km ring	2.22	1.48	6.06	4.61	2.00
	(5.21)	(4.39)	(7.87)	(6.83)	(4.87)
Production in 0–2 km ring	.86	.23	1.17	3.87	.64
	(2.29)	(1.13)	(2.40)	(3.93)	(1.87)
Production in 2–5 km ring	3.09	1.15	5.89	11.53	2.51
	(7.23)	(4.28)	(8.85)	(11.41)	(6.24)
Production in 5–10 km ring	8.22	3.40	16.18	27.57	7.11
	(18.59)	(11.58)	(23.07)	(28.61)	(16.79)
Number of wells:					
In well preparation, 20 km ring	30.85	20.23	87.13	62.12	28.55
	(50.60)	(42.48)	(63.81)	(56.68)	(48.92)
In production, 20 km ring	113.80	47.50	223.14	363.20	103.05
	(203.37)	(121.70)	(226.04)	(262.67)	(192.55)
Inactive, 20 km ring	17.54	7.41	30.17	54.21	16.52
	(35.14)	(24.41)	(36.28)	(49.17)	(32.56)
No. of observations	31,531,987	12,894,727	1,004,184	3,607,236	14,025,840
Total no. of wells	20,677	11,470	11,376	9,286	9,207

Note. This table reports the mean statistics for the full sample and four subsamples. The numbers in parentheses are standard deviations. 107 wells in the sample are transformed from conventional to unconventional, so they do not have preproduction phases. The *t*-test statistics for the differences in means between the treatment and control groups (pre-spud, i.e., untreated period, vs. control, well preparation vs. control, and production vs. control) are always significant; we expect the significance is driven by the large sample size.

pretreatment differences between the treatment and control groups by estimating the conditional daily differences between these two groups using the following regression:

$$q_{id} = \sum_{a \neq 0} \eta_a I_{\{i \in \text{Treatment Group},\, d - d^s = a\}} + \boldsymbol{Z}'_{id}\zeta + \sum_B \beta^B \boldsymbol{w}^B_{id} \boldsymbol{H}^B_d + \mu_i + \sigma_d + u_{id}, \quad (3)$$

where d^s is the spud date, a is the difference in days between date d and the spud date. $I_{\{i \in \text{Treatment Group},\, d - d^s = a\}}$ is the indicator function, which equals 1 if the condition in the subscript is satisfied and 0 otherwise. η_a captures the conditional daily gap between the treatment and control groups, conditional on weather and pollution spillovers from upwind areas.

Most of the estimated $\hat{\eta}_a$ coefficients are centered at zero (3.5% are significant at 99%, 12.1% are significant at 95%: see fig. A4, which plots the estimated coefficients and the 95% confidence intervals constructed using standard errors that are clustered by well pad). Nonetheless, there is an obvious cluster of significant coefficients before $t = 0$ (highlighted in red in fig. A4). We expect that this is due to preparation activities before the spud date (which is the date the drill bit hits the ground). As noted by Srebotnjak and Rotkin-Ellman (2014), the length of time between the permit and spud dates is quite variable, ranging from two days to one year, depending on the availability of preexisting infrastructure such as access roads and pipelines. Unfortunately, we do not have additional information prior to the spud date to capture activities before the well preparation treatment, but we can test whether and to what extent these activities affect our ATE estimates. We do so in section 5, where we extend the well preparation treatment period to begin from one month/year before the spud date. We conclude that although there is a small fraction of days with significant differences between the treatment and control groups in the pretreatment period due to unobserved activities before the well preparation treatment, the corresponding bias in our estimated ATE is negligible.

In addition, we use two alternative analyses to assess pretreatment differences between the treatment and control groups. First, we estimate the conditional daily differences between treatment and control groups during the pretreatment period to reaffirm the pretreatment common trend. In this analysis, we exclude all treated observations so that we do not need to normalize dates with respect to treatment time, thus avoiding the potential bias of staggered treatments. The details of this analysis are described in appendix A.3, and the results are plotted in figure A5. Second, we explicitly account for staggered treatments and follow Gardner (2021) to estimate residualized daily differences between the treatment and control groups. The coefficients from this analysis are plotted in figure A6. Results from both supplementary analyses are generally consistent with the event study results obtained by estimating equation (3) and are consistent with the common trend assumption.

4. EMPIRICAL RESULTS

4.1. Main Results

Table 2 summarizes the average treatment effect of a P-area's own centroid well. Our baseline DID model shows that, on average, a P-area's AOD increases significantly when its centroid well is in the well preparation and production phases. However, the estimates are confounded with the effect of windblown pollution from upwind wells. Hence, our preferred estimate is based on the DID model that specifically accounts for pollution spillovers. Similar to the baseline DID model, the DID model with spillovers also shows that well preparation and production activities significantly increase daily AOD in the centroid well's P-area: well preparation activity increases a treated P-area's AOD by 0.00429, which is 2.19% relative to the average AOD in our sample, whereas a well's production activities increase AOD in its P-area by 1.35%. These results are similar in magnitude to Zou (2021), who found a 1.6%–1.8% increase in AOD when the EPA's ground PM monitors are off.

Table 2. Average Treatment Effects: Main Results

	DID		DID with Spillovers	
Treatments	Coefficient	SE	Coefficient	SE
Own treatment effects:				
Well preparation treatment	.00624***	(.00040)	.00429***	(.00039)
Production treatment	.00463***	(.00040)	.00258***	(.00036)
Pollution spillovers:				
Well preparation treatments in 0–2 km ring			.00101***	(.00010)
Well preparation treatments in 2–5 km ring			.00050***	(.00004)
Well preparation treatments in 5–10 km ring			.00008***	(.00002)
Production treatments in 0–2 km ring			.00066***	(.00008)
Production treatments in 2–5 km ring			.00026***	(.00003)
Production treatments in 5–10 km ring			.00002**	(.00001)
Control variables:				
Weather, well densities in 20 km				
Circular area, two-way fixed effects	Y		Y	
Adjusted R^2	.76		.76	
Sample size	31,531,987		31,531,987	

Note. The full results are reported in table A4. The daily weather controls are mean precipitation, mean dew point, mean temperature, and wind speed. The well density in the 20 km circular area includes wells that are under preparation, in production, and inactive. Standard errors are clustered by well pads. In table A14, we confirm that the statistical significance is insensitive to different clusters of standard errors.

* $p < .1$.

** $p < .05$.

*** $p < .01$.

The coefficients on the pollution spillovers (β^B) confirm that the airborne spillovers from wells in upwind areas increase local AOD. Furthermore, while this effect attenuates by distance, both for well preparation and production treatments, it is statistically detectable as far as 10 km from its emission source. Additionally, well preparation activities from upwind wells have a much larger spillover treatment effect than production activities in all the three distance rings.

Shale gas is not produced at a constant rate over the entire production phase of the well. In fact, production is relatively high in the first several years after production commences, but then it declines rapidly to a relatively stable level (Considine et al. 2010). We find corresponding differences in the magnitude of the production treatment effects. As shown in table A15 (tables A1–A16 are available online), the production treatment effect is highest during the first three years of production and declines thereafter. In fact, nearly the entire production treatment effect can be traced to the first three years of the well's life when the effect of the marginal well is as high as the effect during the well preparation phase.[25]

4.2. Overall AOD Impact of the Shale Gas Industry

We use the coefficients reported in table 2 to estimate the overall increase in AOD in each P-area due to unconventional shale gas development. Let the overall AOD increases in P-area i on date d be s_{id}, then

$$\hat{s}_{id} = \hat{\eta}_c T^c_{id} + \hat{\eta}_p T^p_{id} + \sum_B \hat{\beta}^{B,c} \boldsymbol{w}^B_{id} \boldsymbol{H}^{B,c}_d + \sum_B \hat{\beta}^{B,p} \boldsymbol{w}^B_{id} \boldsymbol{H}^{B,p}_d. \quad (4)$$

The terms $\hat{\eta}_c$, $\hat{\eta}_p$, $\hat{\beta}^{B,c}$, and $\hat{\beta}^{B,p}$ are the estimated coefficients from our benchmark model shown in the last column of table 2. Overall, fracking increases AOD by 0.00276 for the whole sample, and 0.01031 for the subsample of observations under treatment.[26] This represents a 1.27% and 5.67% increase in AOD, respectively, above the counterfactual level which we estimate as, $\hat{b}_{id}$ which equals $q_{id} - \hat{s}_{id}$, where q_{id} is the observed AOD level.[27]

25. In col. 2 of table A15, the coefficient on production treatment from a centroid well that has produced for four years or more is statistically insignificant. However, the corresponding spillover treatments from the 0–2 km and 2–5 km rings are significant but with smaller magnitude. This reflects the fact that the spillover is received from multiple neighboring wells while the production treatment is the own effect of a marginal well.

26. The overall increase in AOD (0.00276) represents the predicted average effect of fracking activities from both the centroid well and neighboring wells using the whole sample, while 0.01031 represents the predicated average effect of fracking activities from the centroid well plus neighboring wells using the treated sample.

27. The percentage is calculated as $\hat{s}_{id}/\hat{b}_{id}$.

4.3. Staggered Treatment

The wells in our data set enter/exit well preparation and production at different points in time. As Goodman-Bacon (2021) points out, in this setting the two-way fixed effects model used here yields biased estimates of the treatment effects. A recent literature has proposed ways to address the bias, such as separating the treatment group into several subgroups based on treatment starting times, and estimating the ATE as a weighted average of ATEs for each treatment subgroup; see, for example, Callaway and Sant'Anna (2021). However, the empirical examples provided in the literature usually have a single treatment starting in a handful of different years. In our case, it is extraordinarily challenging to execute the suggested computations because we have a large data set (more than 31.5 million observations) with two treatments (well preparation and production) whose timing varies at a daily frequency over multiple years and across individual wells. Even if we are able to execute the computation, estimating tens of thousands of daily-subgroup ATEs of the type suggested by Callaway and Sant'Anna (2021) for a small number of wells in each treatment subgroup will not be meaningful.

To assess how our benchmark results are affected by the staggered treatments, we artificially decrease the sample variation in treatment by comparing P-areas that receive late centroid well treatment (i.e., after 2010) with the control group. We estimate the models separately for the well preparation and production treatments, where we drop observations under production treatment when analyzing the well preparation treatment and vice versa, so that we can prevent the sample variation in one treatment from contaminating the other. We also drop all posttreatment observations after the treatment ends. Table A5 reports the results, which are qualitatively similar to the results in table 2: the coefficients on both treatments are positive and significant, and the coefficient on well preparation is greater than the coefficient on production. These results suggest that our analysis is not plagued by the issue of negative weights noted by Goodman-Bacon (2021).[28]

4.4. Discussion

The estimated coefficients on the well preparation treatment and its pollution spillovers reported in table 2 are almost double the coefficients on the production treatment and its pollution spillovers. This suggests that the $PM_{2.5}$ pollution from well preparation activities is considerably more severe than from shale gas production activities. Furthermore, the average treatment effect due to the production treatment is mainly driven by the $PM_{2.5}$ pollution in the early years of production. Therefore, we conclude that the $PM_{2.5}$ pollution from shale gas development is mostly short-run, concentrated within

28. In additional analysis, we further limit the variation in treatment start dates by comparing treatment group P-areas that receive treatment between 2010–12, 2013–15, and 2016–18, with the control group, respectively. Table A6 reports the results, which are also qualitatively similar to the benchmark results.

the well preparation period and the first few years of production. We also find that the pollution spillovers decline quickly as the distance from a fracked well increases, so that the $PM_{2.5}$ pollution is localized and affects downwind residents within about 10 km.

Importantly, our findings that $PM_{2.5}$ pollution generated during preproduction is approximately twice that during production and that the $PM_{2.5}$ pollution dissipates within a few years of the spud date have important policy implications. These results imply that regulating particulate matter emissions during preproduction, including truck traffic and on-site diesel combustion activities, could reduce $PM_{2.5}$ emissions from shale gas development quite significantly. Furthermore, flaring and venting occur during this phase (Agerton et al. 2020; Lade and Rudik 2020; Boslett et al. 2021), which may be an additional source of PM, including black carbon and volatile organic compounds (Ezani et al. 2018). Regulations of preproduction $PM_{2.5}$ may lead to retrofitting diesel trucks or using liquid natural gas for trucks and drilling rigs, targeting air emissions leakages from on-site equipment, taxing flaring and venting or increased innovation to reduce emissions (USFS 2011; Cai et al. 2017; Agerton et al. 2020; Lade and Rudik 2020). To support these policies, ambient air monitors near sites (Carlton et al. 2014) or process-specific emissions inventories would inform the specific shale gas processes throughout the life cycle of development that are contributing to the $PM_{2.5}$ pollution that we observe.

5. ROBUSTNESS CHECKS

To evaluate the validity and robustness of the causal effects identified in our benchmark results, we conduct several additional analyses. First, we consider the fact that unobserved confounders such as local community preferences and bargaining power in leasing land to the shale gas industry may correlate with both well location and socioeconomic conditions, leading to nonrandom sorting of wells into treatment and control groups. To reduce the possible endogeneity from these unobserved confounders, we draw three different subsamples based on observable characteristics: one includes wells from the treatment group only, and the others use two different matching criteria. Second, considering the uncertainty regarding the start and end of the well preparation period due to data limitations, we use two alternative definitions of the well preparation period. In addition, we also test the sensitivity of our results with different P-area definitions, where the radius of the P-area is set alternatively at 5 km and 10 km (rather than 3 km as in the original setting), and report the results in table A13. Finally, we conduct two falsification tests. All of these additional analyses yield results that are consistent with ATEs identified in our main analysis.

5.1. Treatment Group Observations Only

Each well in the treatment group experienced well preparation or production activities at a different point in time, staggering the treatments in our sample. As Goodman-Bacon

(2021) and Athey and Imbens (2018) have discussed, not only observations in the control group but also treatment group observations during the pre-spud period and posttreatment period can provide a valid counterfactual. For the sake of eliminating any unobserved factors that lead to nonrandom assignment between the treatment and control groups, we reestimate our DID models using a subsample of P-areas from the treatment group only.

The ATEs are reported in table 3 and are consistent with the benchmark results: well preparation and production increase AOD significantly, well preparation increases AOD by a larger magnitude than production activities, and the pollution spillover effects from upwind well preparation and production operations are statistically significant and attenuate with distance. The magnitudes of the estimated coefficients are comparable to those in table 2.

5.2. Matched Samples

Figure A2 suggests nonrandomness in treatment across location and permit issue dates. For example, there is a cluster of wells in the northeastern part of Pennsylvania permitted

Table 3. Robustness Check: Using Treatment Group P-Areas Only

	DID		DID with Spillovers	
Treatments	Coefficient	SE	Coefficient	SE
Own treatment effects:				
Well preparation treatment	.00651***	(.00040)	.00475***	(.00040)
Production treatment	.00488***	(.00060)	.00281***	(.00059)
Pollution spillovers:				
Well preparation treatments in 0–2 km ring			.00086***	(.00010)
Well preparation treatments in 2–5 km ring			.00048***	(.00004)
Well preparation treatments in 5–10 km ring			.00008***	(.00002)
Production treatments in 0–2 km ring			.00060***	(.00009)
Production treatments in 2–5 km ring			.00025***	(.00003)
Production treatments in 5–10 km ring			.00003**	(.00001)
Control variables:				
Weather, well densities in 20 km				
Circular area, two-way fixed effects	Y		Y	
Adjusted R^2	.76		.76	
Sample size	17,506,147		17,506,147	

Note. The full results are reported in table A7. The daily weather controls are mean precipitation, mean dew point, mean temperature, and wind speed. The well density in the 20 km circular area includes wells that are under preparation, in production, and inactive. Standard errors are clustered by well pads.

* $p < .1$.

** $p < .05$.

*** $p < .01$.

during 2012–15 and another cluster of wells in the southwestern part permitted after 2015. In fact, wells are permitted and spudded sequentially, not only because of geological conditions but also because of other unobserved factors such as differences in regulatory cost and lease timing, and challenges in accessing well sites (Timmins and Vissing 2015; Vissing 2017). To address the potential bias arising due to such unobserved economic factors, we use the "selection on observables" method and trim our sample to eliminate possible systematic differences between treated and control P-areas. The first strategy uses one-to-one matching by distance, permit year, and permit month. That is, each P-area in the treatment group is matched with the closest P-area in the control group, such that the centroid wells from the two P-areas are permitted in the same month and same year. The second strategy is one-to-one matching by distance, permit year, and county. In this case, each P-area in the treatment group is matched with its closest P-area in the control group from the same county, and the centroid wells of the two P-areas were permitted in the same year. The third strategy utilizes propensity score matching and selects P-areas from the control group with permitted wells that have a similar probability of being spudded as the wells in the treatment group. The probability is estimated using a logit regression that includes population, income per capita, education, and house value at the block group level, and well spud year as control variables. In the first two matching methods, wells in the control group are used repeatedly; in the propensity score matching, every treated P-area is matched with a unique control P-area. These three matching strategies allow us to exclude control group observations from P-areas that are temporally, geographically, and economically distant from the regional clusters in the treatment group, thus mitigating the effects of unobserved socioeconomic factors that are associated with permit time.

The first matching strategy gives us 11,368 wells in the treatment group and 3,000 wells in the control group. The average distance between a matched treatment P-area and a control P-area is 16.43 km. The second matching strategy gives us 11,293 wells in the treatment group and 2,833 wells in the control group. The average distance between the matched treatment P-area and control P-area is 3.45 km.[29] The propensity score matching strategy gives us 9,207 pairs of treated-control P-areas. For all subsamples, we find that the balance between the treatment and control arms is improved, with the difference in the average AOD between the pre-spud treatment observations and control observations reduced from 0.013 to about 0.011 for the first and second matched subsample, and reduced to about 0.001 for propensity score matching subsample. Figures A8–A10 demonstrate the locations of the wells in the three matched subsamples. Using these subsamples, we reestimate the two DID models, with the results reported in table 4. The coefficients are remarkably consistent with the main findings reported in table 2, in terms of their magnitudes and statistical significance, suggesting

29. The average distance between treatment and control P-areas in the full sample is 194.01 km.

Table 4. Robustness Check, Using Matched Samples

	Matched Sample 1 (1)	Matched Sample 2 (2)	Matched Sample 3 (3)
	1. Standard DID		
Well preparation	.00609***	.00624***	.00547***
	(.00039)	(.00039)	(.00043)
Production	.00449***	.00475***	.00449***
	(.00051)	(.00051)	(.00052)
Weather, well densities in 20 km circular area, two-way fixed effects	Y	Y	Y
Adjusted R^2	.76340	.76349	.76305
Sample size	21,949,389	21,583,079	28,052,033
	2. DID with Spillovers		
Well preparation	.00436***	.00452***	.00377***
	(.00038)	(.00038)	(.00042)
Production	.00262***	.00291***	.00257***
	(.00048)	(.00049)	(.00049)
Well preparation (0–2 km)	.00093***	.00093***	.00092***
	(.00010)	(.00010)	(.00010)
Well preparation (2–5 km)	.00043***	.00048***	.00048***
	(.00004)	(.00004)	(.00004)
Well preparation (5–10 km)	.00008***	.00008***	.00007***
	(.00002)	(.00002)	(.00002)
Production (0–2 km)	.00061***	.00060***	.0065***
	(.00008)	(.00009)	(.00008)
Production (2–5 km)	.00026***	.00027***	.00030***
	(.00003)	(.00003)	(.00001)
Production (5–10 km)	.00002**	.00002**	.00003***
	(.00001)	(.00001)	(.00001)
Weather, well densities in 20 km circular area, two-way fixed effects	Y	Y	Y
Adjusted R^2	.76350	.76389	.76314
Sample size	21,949,389	21,583,079	28,052,033

Note. Matched sample 1 is matched by distance, permit year, and permit month; matched sample 2 is matched by distance, permit year, and county; matched sample 3 is matched by propensity scores. The full results are reported in tables A8 and A9. The weather controls are daily mean precipitation, daily mean dew point, daily mean temperature, and wind speed. The well density in the 20 km circular area includes wells that are under preparation, in production, and inactive. Standard errors are clustered by well pads.

* $p < .1$.

** $p < .05$.

*** $p < .01$.

that our benchmark results are not biased by unobserved nonrandomness due to the temporal clusters.

5.3. Extended Well Preparation Period

We assume that well preparation operations start on the spud date, that is, the date when the drill bit hits the ground. But, it is possible that well preparation activities begin before the spud date. For example, building access roads and delivering equipment to the well site take several weeks (Hill 2018) and usually take place before spudding a well. As shown by the event study (fig. A4), there is a short period of about one year before the spud date when AOD in the treatment group is significantly larger than the control group. Taking this into consideration, in table 5, we extend the well preparation period by one month and one year before the spud date, respectively, and reestimate our model under these new definitions of the well preparation treatment.[30] The results for both the baseline DID and the preferred DID model with spillovers are not sensitive to a change in the length of well preparation period.

5.4. Falsification Tests

To validate the causal nature of our estimates, we implement falsification tests by excluding observations with true treatments and assigning two alternative placebo treatments. In the first placebo treatment, we assign a hypothetical treatment from 1,080 days (about three years) before the well preparation period to 720 days (about two years) before the well preparation period. In the second placebo test, we assign a placebo treatment from 1,440 days (about four years) before the well preparation period to 1,080 days (about three years) before the well preparation period. In both cases, we assign a single placebo treatment and do not distinguish between well preparation and production. We include the true airborne pollution spillovers in the regressions so as to avoid contaminating the placebo treatment effects.[31]

The results are reported in table 6: the coefficients on the placebo treatments are statistically insignificant, while the true spillover treatment effects remain positive and significant. Thus, our results survive the two falsification tests, showing little evidence that the true treatment effects are distorted by AOD trends in the pre-spud period.

In addition to using placebo treatments for the centroid well, we also estimate a model in which we substitute the true pollution spillovers by fake spillovers, where the fake spillovers are constructed using the true wind direction and a placebo treatment

30. We extend the well preparation periods for the centroid wells only but not the upwind neighboring wells so as to correctly capture the true pollution spillovers.

31. P-areas are not affected by the true treatment from their centroid well, but they may still receive pollution spillovers from neighboring wells. By including the true pollution spillover variables in our regression model we avoid the bias noted by Butts (2021).

Table 5. Robustness Check: Extended Well Preparation Phase

	Extended by 30 Days		Extended by 365 Days	
	DID	DID with Spillovers	DID	DID with Spillovers
Own treatment effects:				
Extended well preparation treatment	.00620***	.00433***	.00571***	.00446***
	(.00039)	(.00038)	(.00035)	(.00033)
Production treatment	.00470***	.00264***	.00531***	.00321***
	(.00049)	(.00046)	(.00050)	(.00048)
Pollution spillovers:				
Well preparation treatments in 0–2 km ring		.00101***		.00101***
		(.00010)		(.00009)
Well preparation treatments in 2–5 km ring		.00050***		.00049***
		(.00004)		(.00004)
Well preparation treatments in 5–10 km ring		.00008***		.00007***
		(.00002)		(.00002)
Production treatments in 0–2 km ring		.00066***		.00066***
		(.00008)		(.00008)
Production treatments in 2–5 km ring		.00026***		.00026***
		(.00003)		(.00003)
Production treatments in 5–10 km ring		.00002**		.00002**
		(.00001)		(.00001)
Control variables:				
Weather, well densities in 20 km circular area, two-way fixed effects	Y	Y	Y	Y
Adjusted R^2	.76	.76	.76	.76
Sample size	31,531,987	31,531,987	31,531,987	31,531,987

Note. The full results are reported in table A10. The weather controls are daily mean precipitation, daily mean dew point, daily mean temperature, and wind speed. The well density in the 20 km circular area includes wells that are under preparation, in production, and inactive. Standard errors are clustered by well pads.

* $p < .1$.

** $p < .05$.

*** $p < .01$.

on upwind neighboring wells. All the estimated fake spillover coefficients are insignificant (see table A12).

6. MORTALITY ANALYSIS

Is the estimated increase in AOD due to shale gas development economically meaningful? To answer this question, we use a concentration response function to estimate the

Table 6. Placebo Test for Centroid Well (Own) Treatments

	Placebo Test 1		Placebo Test 2	
	DID	DID with Spillovers	DID	DID with Spillovers
Placebo own treatment effects	.00019	.00036	–.00015	.00008
	(.00034)	(.00033)	(.00034)	(.00034)
True pollution spillovers:				
Well preparation treatments in 0–2 km ring		.00120***		.00119***
		(.00012)		(.00012)
Well preparation treatments in 2–5 km ring		.00055***		.00055***
		(.00005)		(.00005)
Well preparation treatments in 5–10 km ring		.00013***		.00013***
		(.00002)		(.00002)
Production treatments in 0–2 km ring		.00070***		.00070***
		(.00010)		(.00010)
Production treatments in 2–5 km ring		.00029***		.00029***
		(.00004)		(.00004)
Production treatments in 5–10 km ring		.00002*		.00002*
		(.00001)		(.00001)
Control variables:				
Weather, well densities in 20 km circular area, two-way fixed effects	Y	Y	Y	Y
Adjusted R^2	.76	.76	.76	.76
Sample size	26,920,567	26,920,567	26,920,567	26,920,567

Note. The full results are reported in table A11. The weather controls are daily mean precipitation, daily mean dew point, daily mean temperature, and wind speed. The well density in the 20 km circular area includes wells that are under preparation, in production, and inactive. Standard errors are clustered by well pads.

* $p < .1$.

** $p < .05$.

*** $p < .01$.

increase in mortality due to the increase in local $PM_{2.5}$ pollution associated with the overall increase in AOD due to shale gas development.

6.1. AOD-$PM_{2.5}$ Relationship

Epidemiological concentration response functions describe the magnitude of a population-level health response from exposure to pollution. In our setting, the first step in applying a concentration response function is to translate the change in AOD to a change in $PM_{2.5}$ concentration. For this, we utilize the random coefficient model proposed by Lee et al. (2011), which, though simpler than the popular model by

Van Donkelaar et al. (2015) and Van Donkelaar et al. (2016), is intuitively appealing to economists. We predict the daily relationship between AOD and the $PM_{2.5}$ concentration for each P-area using $PM_{2.5}$ concentration data from all 73 EPA ground monitors in Pennsylvania to estimate the random coefficient model and then use the estimated coefficients to predict the daily change in $PM_{2.5}$ concentration for each P-area due to fracking activities. Specifically, we estimate the following regression:

$$PM_{md} = (\alpha + u_d) + (\beta + v_d)q_{md} + b_m + \epsilon_{mt}, \quad (5)$$

where m denotes the monitor site, and d denotes the date. The term q_{md} is the average AOD value in a 3 km radius area surrounding each $PM_{2.5}$ monitor. The term b_m is the monitor-specific random intercept, u_d is the date-specific random intercept, and v_d is the daily random component in the slope of the AOD-$PM_{2.5}$ relationship. We assume $b_m \sim N(0, \sigma_b^2)$, $(u_d, v_d) \sim N((0, 0), \sum)$, and

$$\sum = \begin{bmatrix} \sigma_u^2 & \sigma_u\sigma_v \\ \sigma_u\sigma_v & \sigma_v^2 \end{bmatrix},$$

and estimate equation (5) using maximum likelihood.[32]

Figure 4 shows that the predicted $PM_{2.5}$ concentration fits the true $PM_{2.5}$ concentration in the vicinity of ground monitors with $R^2 = 0.78$, which is similar in magnitude to Van Donkelaar et al. (2016).[33] Nonetheless, the plot follows a concave pattern that is especially obvious at relatively high $PM_{2.5}$ concentrations where its slope is smaller than the 45 degree line. It implies that our model leads to a downward bias when predicting the value of $PM_{2.5}$ and that the bias increases with the concentration of $PM_{2.5}$. This also implies that the changes in AOD-predicted $PM_{2.5}$ are smaller than the true changes in areas with high $PM_{2.5}$ concentrations and that our model underpredicts the $PM_{2.5}$ impact of shale gas development. This is especially true for areas with relatively poor air quality with $PM_{2.5}$ concentration well above the National Ambient Air Quality Standard of 12 $\mu g/m^3$ (the concave shape becomes more pronounced when the true $PM_{2.5}$ reaches around 15 $\mu g/m^3$).

Let $\hat{\alpha}$ and $\hat{\beta}$ be the estimated coefficients, let $\hat{u}_d$ and $\hat{v}_d$ be the daily value of the random components. Recall that the overall increase in AOD in each P-area due to unconventional shale gas development is given by $\hat{s}_{id}$ (eq [4]). Then, from equation (5), the

32. The estimated slope coefficient $\beta + v_d$ follows a normal distribution $N(6.54, 8.59^2)$, where $v_d \sim N(0, 8.59^2)$; while the estimated intercept coefficient $\alpha + u_d + m_j$ follows a normal distribution $N(10.19, 5.92^2)$, where $u_d \sim N(0, 2.01^2)$ and $m_j \sim N(0, 5.57^2)$. These results can be interpreted as follows: for an average day in Pennsylvania, one additional unit of AOD implies a 6.54 $\mu g/m^3$ increase in $PM_{2.5}$.

33. We estimate the relationship specifically for Pennsylvania, so that we obtain a regionally consistent relationship between AOD and $PM_{2.5}$ (Li et al. 2015).

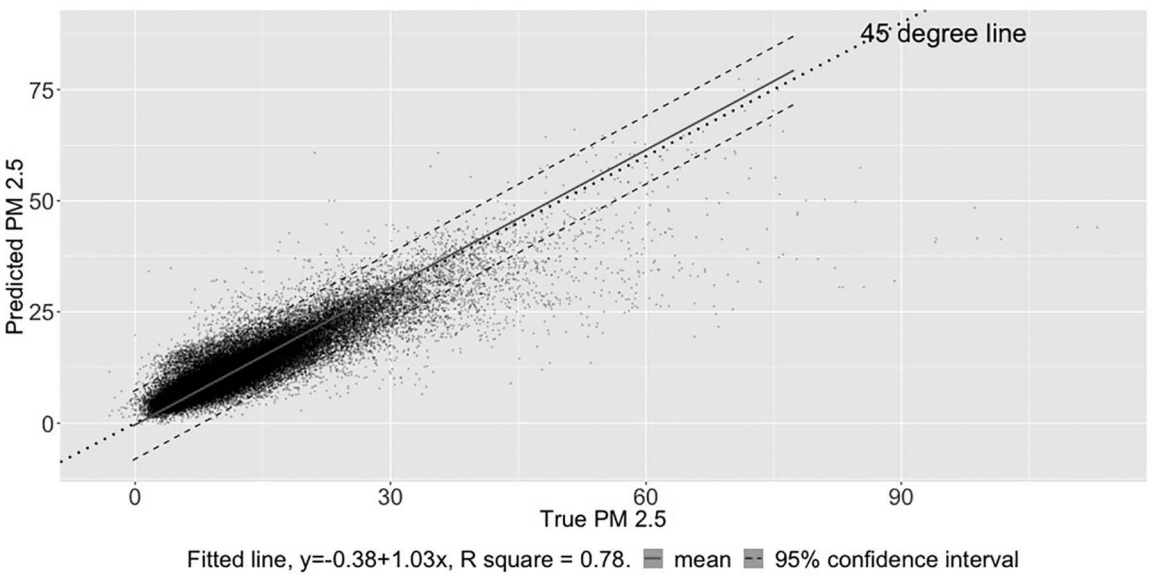

Figure 4. $PM_{2.5}$ prediction, $PM_{2.5}$ monitors in Pennsylvania ($\mu g/m^3$)

daily change in $PM_{2.5}$ concentration in P-area i due to shale gas development, Δ_{id}, is estimated as

$$\Delta_{id} = (\hat{\beta} + \hat{v}_d)\hat{s}_{id}. \tag{6}$$

We find that, on average, shale gas development increases the daily PM concentration by 0.017 $\mu g/m^3$ for the whole sample, and 0.062 $\mu g/m^3$ for P-areas in the treatment group.[34]

6.2. Mortality Estimates

We estimate the change in mortality due to the estimated change in $PM_{2.5}$ concentration at the census block group level for each year in our sample. We obtain county-level mortality data from CDC WONDER, the finest spatial resolution at which mortality data are publicly available, and census block group level population data from the American Community Survey. Let the mortality rate for census block group k in year t be λ_{kt}. We assume that the mortality rate is uniformly distributed across census block groups within a county. Let the average annual change in $PM_{2.5}$ concentration in census block group k due to shale gas development be $\Delta\overline{PM2.5}_{kt}$. To estimate $\Delta\overline{PM2.5}_{kt}$ we first determine the average annual change in $PM_{2.5}$ concentrations for each P-area in our sample for each year separately by aggregating daily estimates from equation (6). We then determine the yearly change in $PM_{2.5}$ for each census block as the average of the annual change in $PM_{2.5}$ concentrations of P-areas whose centroid wells are located in census block group k. That is $\Delta\overline{PM2.5}_{kt} = (1/N_k)\Sigma_{i\in I_k}\widehat{\Delta PM2.5_{it}}$, where N_k is the total number of centroid wells in census block k ($i \in I_k$) and $\widehat{\Delta PM2.5_{it}} = \Sigma_{d\in t}\Delta_{id}/N_t$ is the annual average change in $PM_{2.5}$ for individual P-area i (when date d is in year t, N_t is the number of days in year t for which we have AOD data for P-area i).

Krewski et al. (2009) and Lepeule et al. (2012) estimate mortality concentration-response functions for $PM_{2.5}$. They utilize a Cox proportional-hazard model with a log-linear functional form, which is also used by the EPA for its regulatory impact analysis (Fowlie et al. 2019). Appendix A.9 shows the detailed derivation of equation (7). We use the same method and estimate the change in mortality as follows:

$$\Delta\text{Deaths}_{kt} = \text{Pop}_{kt}\lambda_{kt}(1 - \exp(-\hat{\gamma}\Delta\overline{PM2.5}_{kt})), \tag{7}$$

where $\hat{\gamma}$ is the proportional hazard coefficient, and Pop_{kt} is block group k's population in year t. We use the values of $\hat{\gamma}$ estimated by Lepeule et al. (2012) and estimate mortality due to all causes (All), cardiovascular disease (Card), and chronic obstructive pulmonary disease (COPD). Lepeule et al. (2012) suggest that for every 1 $\mu g/m^3$ increment in $PM_{2.5}$ concentration, $\hat{\gamma}_{\text{All}} = 0.0131$, $\hat{\gamma}_{\text{Card}} = 0.0231$, and $\hat{\gamma}_{\text{COPD}} = 0.0157$.

34. As a comparison, Levy et al. (2002) find that coal-fired power plants in Illinois increase primary $PM_{2.5}$ concentrations in the area between 38°N and 44°N and between 84°W and 93°W by 0.04 $\mu g/m^3$.

Table 7. Mortality Estimates, 671 Census Block Groups

Year	Cardio	COPD	All Causes	Population
2010	.69[.39, 1.00]	.09[−.09, .28]	1.22[.63, 1.85]	841,848
	(3,104.83)	(555.43)	(9,522.19)	
2011	1.16[.66, 1.68]	.15[−.16, .47]	2.10[1.09, 3.19]	845,607
	(3,084.53)	(568.97)	(9,765.50)	
2012	1.32[.75, 1.92]	.17[−.18, .52]	2.42[1.25, 3.68]	843,169
	(3,022.89)	(543.39)	(9,670.84)	
2013	1.11[.63, 1.61]	.15[−.16, .46]	2.04[1.05, 3.09]	845,133
	(3,090.76)	(579.48)	(9,912.32)	
2014	1.35[.77, 1.98]	.18[−.19, .56]	2.53[1.31, 3.84]	843,801
	(3,053.58)	(555.91)	(9,866.78)	
2015	1.96[1.11, 2.85]	.28[−.29, .85]	3.70[1.91, 5.62]	838,444
	(3,122.42)	(589.06)	(10,159.49)	
2016	1.48[.84, 2.15]	.19[−.19, .58]	2.73[1.41, 4.14]	833,749
	(3,111.75)	(553.01)	(10,074.72)	
2017	1.78[1.01, 2.59]	.23[−.24, .72]	3.36[1.74, 5.10]	828,150
	(3,133.03)	(592.83)	(10,488.52)	
Total	10.85[6.15, 15.80]	1.44[−1.50, 4.43]	20.11[10.39, 30.52]	
	(24,723.80)	(4,538.08)	(79,420)	

Note. Numbers in brackets are confidence bounds calculated using eq. (7) by plugging the 95% confidence interval hazard coefficients reported in Lepeule et al. (2012) as the value of coefficient $\hat{\gamma}$. Numbers in parentheses are the true death counts due to each cause.

In table 7, we report the total estimated increase in the number of deaths due to shale gas related $PM_{2.5}$ pollution for 671 census block groups in Pennsylvania where permitted unconventional wells (both spud and not spud) are located. Table A16 reports the corresponding estimates in the top four counties in terms of the number of active shale gas wells. Our results show that from 2010 to 2017, shale gas development caused an additional 20.11 deaths in a population of 840,000 through an increase $PM_{2.5}$ concentration. Washington county is the most affected, with an additional 4.26 deaths between 2010 and 2017.[35] Using a value of statistical life of $7.4 million (2006 dollars) (https://www.epa.gov/environmental-economics/mortality-risk-valuation), the additional 20.11 deaths represent an economic loss of $148.814 million. This is a lower bound for the total economic loss given the downward bias in our estimate of the increase in $PM_{2.5}$ concentration and the fact that we do not consider other types of pollution associated with shale gas development.

35. Washington county is a $PM_{2.5}$ attainment county. From 2010 to 2017, the annual average $PM_{2.5}$ concentration for Washington county is between 9.4 $\mu g/m^3$ and 13.4 $\mu g/m^3$. Source: https://www.epa.gov/outdoor-air-quality-data/air-quality-statistics-report.

7. CONCLUSION

The US shale gas industry has developed rapidly in the past decades, growing from 1.6% of total natural gas production in 2000 to 69% in 2018 (Sieminski 2014). This growth has brought an unprecedented economic opportunity for many rural communities, combined with greater energy security for the nation. The boom in shale gas production is largely due to the application of a relatively new and controversial technology known as hydraulic fracturing: the massive deployment of this technology has been shown to impact local environmental conditions, including groundwater (Osborn et al. 2011; Jackson et al. 2013; Hill and Ma 2017) and surface water (Olmstead et al. 2013). In addition, various air pollutants, including carbon monoxide, nitrogen oxides, sulfur oxides, particulate matter, and volatile organic compounds are released to the air from fracking operations (Litovitz et al. 2013; Allen et al. 2014).

Analysis of the environmental impacts of a fracked well is complicated by the fact that pollutants can travel long distances through the air, water, and soil. Consequently, incorporating the potential dispersion of pollutants is an essential part of policy design. We incorporate insights from an atmospheric dispersion model to account for the transportation of airborne $PM_{2.5}$ pollution associated with unconventional well preparation and production activities in Pennsylvania. Building on a DID framework, we estimate the marginal air pollution impact from a local well, as well as the aggregate impact from neighboring wells located further upwind.

We utilize data on AOD obtained from specialized monitoring instruments on NASA's Terra satellite. These data provide a unique opportunity to study daily changes in air quality on a small geographical scale (3×3 km^2 grid). By linking the pollution information from the satellite data to well locations in Pennsylvania, we identify causal changes in local PM pollution over the life cycle of the wells. We find that the marginal deterioration in air quality is the highest during the well preparation and drilling phase and during the first three years after the well goes into production. While the air pollution from a more mature well is smaller in magnitude, it remains detectable throughout its life span. Furthermore, our results suggest that PM pollution from shale gas wells can travel through the wind for up to 10 km, but the pollution disperses and the impact decreases with distance. Accounting for airborne transportation of pollution, we find that, on average, the daily $PM_{2.5}$ concentration increased by 0.062 μg/m^3 in the 3 km radius around a fracked well and by 0.017 μg/m^3 in a broader area that includes all permitted wells regardless of whether they were drilled or not. We estimate that this increase in PM pollution is large enough to be associated with an additional 20 deaths in communities across 40 Pennsylvania counties with shale gas activity and a total population of about 840,000.

Our paper provides new evidence of the impact of shale gas development on $PM_{2.5}$ pollution. $PM_{2.5}$ can contain multiple emissions species, including VOCs, nitrogen oxide, sulfur dioxide, and black carbon. According to the EPA, the industry is a significant source of emissions of methane and the largest industrial source of

VOC emissions and air toxics (benzene, ethylbenzene, and n-hexane). VOCs lead to ground-level ozone, which is linked to a wide range of health effects, including aggravated asthma, increased emergency room visits and hospital admissions, and premature death. Prior work has reported associations between shale gas development and increased childhood asthma hospitalizations (Willis et al. 2020; Blundell and Kokoza 2022), increased pneumonia hospitalizations in the elderly (Peng et al. 2018), and increased risk of heart attacks and heart attack–related mortality (Denham et al. 2021). Our estimates provide robust evidence that shale gas development is increasing $PM_{2.5}$ in the vicinity of fracked wells, providing new evidence on the mechanism underlying these prior health studies.

Still, the shale revolution has undoubtedly yielded benefits. Hausman and Kellogg (2015) estimate that welfare increased by $48 billion annually between 2007 and 2013. Feyrer et al. (2017) estimated that a million dollars worth of shale gas yields an increase of $80,000 wage income and $132,000 royalty and business income within a county. According to Energy Information Administration reported shale gas production data (https://www.eia.gov/dnav/ng/hist/res_epg0_r5302_spa_bcfa.htm) and annual natural gas price data (https://www.eia.gov/dnav/ng/hist/n3035us3a.htm), the total shale gas production value in Pennsylvania from 2010 to 2017 is $110 billion, which translates to an estimated benefit of $8.8 billion increase in wage income and $145 billion increase in royalty and business income within fracking counties.

Our estimated local air pollution costs alone are clearly unlikely to negate the benefits from shale gas development. However, while shale gas development may have positive net benefits overall, the population exposed to the environmental impacts of shale gas development may not be the same population that benefits from the development of unconventional shale gas resources, and the exposed population may experience a net loss. From a public health standpoint, assessing PM emissions from shale gas development is critical as both short-term (hours, days) and long-term (months, years) exposure to $PM_{2.5}$ can be harmful, especially among vulnerable populations such as pregnant women, infants, and the elderly. Identifying the stages of well development and production that are most likely to cause increases in PM emissions will directly help regulators mitigate air emission risks. We have demonstrated that the PM pollution from shale gas development and extraction is of a serious enough magnitude to be associated with increases in mortality in the general population. Establishing a robust link between air emissions related to shale gas development and detailed health outcomes such as low birth weight among infants, childhood asthma, and cardiovascular disease among the elderly in local populations will inform policy makers and other stakeholders about the need to protect vulnerable populations residing near these operations.

REFERENCES

Agerton, Mark, Ben Gilbert, and Gregory B. Upton Jr. 2020. The economics of natural gas flaring in U.S. shale: An agenda for research and policy. PhD diss., Rice University.

Allen, David T., Vincent M. Torres, James Thomas, David W. Sullivan, Matthew Harrison, Al Hendler, Scott C. Herndon, et al. 2014. Measurements of methane emissions at natural gas production sites in the United States. *Proceedings of the National Academy of Sciences* 110 (44): 17768–73.

Anderson, Michael. 2020. As the wind blows: The effect of long-term exposure to air pollution on mortality. *Journal of the European Economic Association* 18 (4): 1886–1927.

Athey, Susan, and Guido W. Imbens. 2018. Design-based analysis in difference-in-differences setting with staggered adoption. NBER Working paper no. 24963, National Bureau of Economic Research, Cambridge, MA.

Atkinson, R. W., S. Kang, H. R. Anderson, I. C. Mills, and H. A. Walton. 2014. Epidemiological time series studies of $PM_{2.5}$ and daily mortality and hospital admissions: A systematic review and meta-analysis. *Respiratory Epidemiology* 69:650–62.

Blundell, Wesley, and Anatolii Kokoza. 2022. Natural gas flaring, respiratory health, and distributional effects. *Journal of Public Economics* 208 (1): 104601.

Boslett, Andrew, Elaine Hill, Lala Ma, and Lujia Zhang. 2021. Rural light pollution from shale gas development and associated sleep and subjective well-being. *Resource and Energy Economics* 64:101220.

Butts, Kyle. 2021. Differences-in-differences with spatial interference. Working paper. https://arxiv.org/abs/2105.03737.

Cai, Hao, Andrew Burnham, Rui Chen, and Michael Wang. 2017. Wells to wheels: Environmental implications of natural gas as a transportation fuel. *Energy Policy* 109:565–78.

Callaway, Brantly, and Pedro H. C. Sant'Anna. 2021. Difference-in-differences with multiple time periods. *Journal of Econometrics* 225 (2): 200–230.

Carlton, Annmarie G., Eleana Little, Michael Moeller, Stella Odoyo, and Paul B. Shepson. 2014. The data gap: Can a lack of monitors obscure loss of Clean Air Act benefits in fracking areas? *Environmental Science Technology* 48 (2): 893–94.

Considine, Timothy J., Robert Watson, and Seth Blumsack. 2010. The economic impacts of the Pennsylvania Marcellus Shale natural gas play: An update. Report, Pennsylvania State University.

Currie, Janet, Michael Greenstone, and Katherine Meckel. 2017. Hydraulic fracturing and infant health: New evidence from Pennsylvania. *Science Advances* 3 (12).

Currie, Janet, John Voorheis, and Reed Walker. 2020. What caused racial disparities in particulate exposure to fall? New evidence from the Clean Air Act and satellite-based measures of air quality. NBER Working paper no. 26659, National Bureau of Economic Research, Cambridge, MA.

Cushing, Lara J., Kate Vavra-Musser, Khang Chau, Meredith Franklin, and Jill E. Johnston. 2020. Flaring from unconventional oil and gas development and birth outcomes in the Eagle Ford Shale in South Texas. *Environmental Health Perspectives* 128 (7): 077003.

Delgado, Michael S., and Raymond J. G. M. Florax. 2015. Difference-in-differences techniques for spatial data: Local autocorrelation and spatial interaction. *Economics Letters* 137:123–26.

Denham, Alina, Mary D. Willis, Daniel P. Croft, Linxi Liu, and Elaine L. Hill. 2021. Acute myocardial infarction associated with unconventional natural gas development: A natural experiment. *Environmental Research* 195:110872.

Deryugina, Tatyana, Garth Heutel, Nolan H. Miller, David Molitor, and Julian Reif. 2019. The mortality and medical costs of air pollution: Evidence from changes in wind direction. *American Economic Review* 109 (12): 4178–4219.

Dominici, Francesca, Roger D. Peng, Michelle L. Bell, Luu Pham, Aidan McDermott, Scott L. Zeger, and Jonathan M. Samet. 2006. Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases. *JAMA* 295 (10): 1127–34.

Donaldson, Dave, and Adam Storeygard. 2016. The view from above: Applications of satellite data in economics. *Journal of Economic Perspectives* 30 (4): 171–98.

Ezani, Eliani, Nicola Masey, Jonathan Gillespie, Tara K. Beattie, Zoe K. Shipton, and Iain J. Beverland. 2018. Measurement of diesel combustion-related air pollution downwind of an experimental unconventional natural gas operations site. *Atmospheric Environment* 189:30–40.

Feyrer, James, Erin T. Mansur, and Bruce Sacerdote. 2017. Geographic dispersion of economic shocks: Evidence from the fracking revolution. *American Economic Review* 107 (4): 1313–34.

Field, R. A., J. Soltis, and S. Murphy. 2014. Air quality concerns of unconventional oil and natural gas production. *Environmental Science Processes and Impact* 16:954–69.

Foster, Andrew, Emilio Gutierrez, and Naresh Kumar. 2009. Voluntary compliance, pollution levels, and infant mortality in Mexico. *American Economic Review* 99 (2): 191–97.

Fowlie, Meredith, Edward A. Rubin, and Reed Walker. 2019. Bringing satellite-based air quality estimates down to earth. *AEA Papers and Proceedings* 109 (1): 283–88.

Gardner, John. 2021. Two-stage differences in differences. Working paper. https://jrgcmu.github.io/2sdd_current.pdf.

Goodman-Bacon, Andrew. 2021. Difference-in-differences with variation in treatment timing. *Journal of Econometrics* 225 (2): 254–77.

Graham, Jove, Jennifer Irving, Xiaoqin Tang, Stephen Sellers, Joshua Crisp, Daniel Horwitz, Lucija Muehlenbachs, Alan Krupnick, and David Carey. 2015. Increased traffic accident rates associated with shale gas drilling in Pennsylvania. *Accident Analysis and Prevention* 74:203–9.

Hausman, Catherine, and Ryan Kellogg. 2015. Welfare and distributional implications of shale gas. NBER Working paper no. 21115, National Bureau of Economic Research, Cambridge, MA.

Heo, J. B., P. K. Hopke, and S. M. Yi. 2009. Source apportionment of $PM_{2.5}$ in Seoul, Korea. *Atmospheric Chemistry and Physics* 9:4957–71.

Hill, Elaine L. 2018. Shale gas development and infant health: Evidence from Pennsylvania. *Journal of Health Economics* 61:134–50.

Hill, Elaine L., and Lala Ma. 2017. Shale as development and drinking water quality. *American Economic Review* 107 (5): 522–25.

Huang, Ru-Jin, Yanlin Zhang, Carlo Bozzetti, Kin-Fai Ho, Jun-Ji Cao, Yongming Han, Kaspar R. Daellenbach, et al. 2014. High secondary aerosol contribution to particulate pollution during haze events in China. *Nature* 514:218–22.

Imbens, Guido, and Donald Rubin. 2015. Causal inference in statistics, social, and biomedical sciences. Cambridge: Cambridge University Press.

Jackson, Robert B., Avner Vengosh, Thomas H. Darrah, Nathaniel Warner, Adrian Down, Robert J. Poreda, Stephen G. Osborn, Kaiguang Zhao, and Jonathan D. Karr. 2013. Increased stray gas abundance in a subset of drinking water wells near Marcellus Shale gas extraction. *Proceedings of the National Academy of Sciences* 110 (28): 11250–55.

Krewski, Daniel, Michael Jerrett, Richard T. Burnett, Renjun Ma, Edward Hughes, Yuanli Shi, Michelle C. Turner, et al. 2009. Extended follow-up and spatial analysis of the American Cancer Society study linking particulate air pollution and mortality. Health Effects Institute, Boston.

Kumar, Naresh, Allen Chu, and Andrew Foster. 2007. An empirical relationship between $PM_{2.5}$ and aerosol optical depth in Delhi Metropolitan. *Atmospheric Environment* 41:4492–4503.

Kumar, Prashant, and Anju Goel. 2016. Concentration dynamics of coarse and fine particulate matter at and around signalised traffic intersections. *Environmental Science; Processes and Impact* 18:1220.

Lade, Gabriel E., and Ivan Rudik. 2020. Costs of inefficient regulation: Evidence from the Bakken. *Journal of Environmental Economics and Management* 102:102336.

Larsen, B. R., S. Gilardoni, K. Stenström, J. Niedzialek, J. Jimenez, and C. A. Belis. 2012. Sources for PM air pollution in the Po Plain, Italy: II. Probabilistic uncertainty characterization and sensitivity analysis of secondary and primary sources. *Atmospheric Environment* 50:203–13.

Lee, H. J., Y. Liu, B. A. Coull, J. Schwartz, and P. Koutrakis. 2011. A novel calibration approach of MODIS AOD data to predict $PM_{2.5}$ concentrations. *Atmospheric Chemistry and Physics* 11 (15): 7991–8002.

Lepeule, Johanna, Francine Laden, Douglas Dockery, and Joel Schwartz. 2012. Chronic exposure to fine particles and mortality: An extended follow-up of the Harvard Six Cities study from 1974 to 2009. *Environmental Health Perspectives* 120 (7): 965.

Levy, Jonathan I., John D. Spengler, Dennis Hlinka, David Sullivan, and Dennis Moon. 2002. Using CALPUFF to evaluate the impacts of power plant emissions in Illinois: Model sensitivity and implications. *Atmospheric Environment* 36 (6): 1063–75.

Lewandowski, Michael, Mohammed Jaoui, John H. Offenberg, Tadeusz E. Kleindienst, Edward O. Edney, Rebecca J. Sheesley, and James J. Schauer. 2008. Primary and secondary contributions to ambient PM in the midwestern United States. *Environmental Science Technology* 42 (9): 3303–9.

Li, Jing, Barbara E. Carlson, and Andrew A. Lacis. 2015. How well do satellite AOD observations represent the spatial and temporal variability of $PM_{2.5}$ concentration for the United States? *Atmospheric Environment* 102:260–73.

Litovitz, Aviva, Aimee Curtright, Shmuel Abramzon, Nicholas Burger, and Constantine Samaras. 2013. Estimation of regional air-quality damages from Marcellus Shale natural gas extraction in Pennsylvania. *Environmental Research Letters* 8 (1): 014017.

Liu, Yang, Rokjin J. Park, Daniel J. Jacob, Qinbin Li, Vasu Kilaru, and Jeremy A. Sarnat. 2004. Mapping annual mean ground-level $PM_{2.5}$ concentrations using multiangle imaging spectroradiometer aerosol optical thickness over the contiguous United States. *Journal of Geophysical Research* 109 (D12): D22206.

Miller, Nolan, David Molitor, and Eric Zou. 2019. Blowing smoke: Health impacts of wildfire plume dynamics. Working paper.

Muehlenbachs, Lucija, Elisheba Spiller, and Christopher Timmins. 2015. The housing market impacts of shale gas development. *American Economic Review* 105 (12): 3633–59.

Newell, Richard G., and Daniel Raimi. 2014. Implications of shale gas development for climate change. *Environmental Science and Technology* 48 (15): 8360–68.

Olmstead, Sheila M., Lucija A. Muehlenbachs, Jhih-Shyang Shih, Ziyan Chu, and Alan J. Krupnick. 2013. Shale gas development impacts on surface water quality in Pennsylvania. *Proceedings of the National Academy of Sciences* 110 (13): 4962.

Osborn, Stephen, Avner Vengosh, Nathaniel Warner, and Robert Jackson. 2011. Methane contamination of drinking water accompanying gas well drilling and hydraulic fracturing. *Proceedings of the National Academy of Sciences* 108 (20): 8172–76.

Peng, Lizhong, Chad Meyerhoefer, and Shin-Yi Chou. 2018. The health implications of unconventional natural gas development in Pennsylvania. *Health Economics* 27 (6): 956–83.

Pennsylvania Department of Environmental Protection. 2020. All permits issued and wells drilled. http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/OilGasReports/2012/2009Wellspermitte-drilled.pdf (accessed July 2020).

Remer, L. A., S. Mattoo, R. C. Levy, and L. A. Munchak. 2005. MODIS 3km aerosol product: Algorithm and global perspective. *Journal of the Atmospheric Sciences* 62 (4): 947–73.

Roy, Anirban A., Peter J. Adams, and Allen L. Robinson. 2014. Air pollutant emissions from the development, production, and processing of Marcellus Shale natural gas. *Journal of the Air and Waste Management Association* 64 (1): 19–37.

Sieminski, Adam. 2014. Implications of the U.S. shale revolution. EIA US-Canada Energy Summit, Chicago.

Srebotnjak, Tanja, and Miriam Rotkin-Ellman. 2014. Fracking fumes: Air pollution from hydraulic fracturing threatens public health and communities. NRDC Issue brief 14-10-A, National Resources Defense Council, New York.

Streets, David G., Timothy Canty, Gregory R. Carmichael, Benjamin de Foy, Russell R. Dickerson, Bryan N. Duncan, et al. 2013. Emissions estimation from satellite retrievals: A review of current capability. *Atmospheric Environment* 77:1011–42.

Sullivan, Daniel M., and Alan Krupnick. 2019. Using satellite data to fill the gaps in the US air pollution monitoring network. RFF working paper no. 18–21, Resources for the Future, Washington, DC.

Timmins, Christopher, and Ashley Vissing. 2015. Environmental justice and Coasian bargaining: The role of race and income in lease negotiations for shale gas. NBER Working paper no. 294873, National Bureau of Economic Research, Cambridge, MA.

USFS (US Forest Service). 2011. Emission reduction techniques for oil and gas activities. USFS Document.

Van Donkelaar, Aaron, Randall V. Martin, Michael Brauer, N. Christina Hsu, Ralph A. Kahn, Robert C. Levy, Alexei Lyapustin, Andrew M. Sayer, and David M. Winker. 2016. Global estimates of fine particulate matter using a combined geophysical-statistical method with information from satellites, models, and monitors. *Environmental Science and Technology* 50:3762–72.

Van Donkelaar, Aaron, Randall V. Martin, Robert J. D. Spurr, and Richard T. Burnett. 2015. High-resolution satellite-derived $PM_{2.5}$ from optimal estimation and geographically weighted regression over North America. *Environmental Science and Technology* 49:10482–91.

Vissing, Ashley. 2017. Forced cooperation vs. competitive holdouts: Efficient land use policies in the oil and natural gas industry. Working paper.

Willis, Mary D., Elaine L. Hill, Andrew Boslett, Molly L. Kile, Susan E. Carozza, and Perry Hystad. 2021. Associations between residential proximity to oil and gas drilling and term birth weight and small-for-gestational-age infants in Texas: A difference-in-differences analysis. *Environmental Health Perspective* 129 (7): 077002.

Willis, Mary D., Perry Hystad, Alina Denham, and Elaine Hill. 2020. Natural gas development, flaring practices and paediatric asthma hospitalizations in Texas. *International Journal of Epidemiology* 49 (6): 1883–96.

Zou, Eric. 2021. Unwatched pollution: The effect of intermittent monitoring on air quality. *American Economic Review* 111 (7): 2101–26.

ATTACHMENT C

STUDY 25

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Unconventional natural gas development and pediatric asthma hospitalizations in Pennsylvania

Mary D. Willis[a], Todd A. Jusko[b,c], Jill S. Halterman[d], Elaine L. Hill[a,b,*]

[a] School of Biological and Population Health Sciences, College of Public Health and Human Sciences, Oregon State University, Corvallis, OR, USA
[b] Department of Public Health Sciences, University of Rochester School of Medicine and Dentistry, Rochester, NY, USA
[c] Department of Environmental Medicine, University of Rochester School of Medicine and Dentistry, Rochester, NY, USA
[d] Department of Pediatrics, University of Rochester School of Medicine and Dentistry, Rochester, NY, USA

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ABSTRACT

Background: Pediatric asthma is a common chronic condition that can be exacerbated by environmental exposures, and unconventional natural gas development (UNGD) has been associated with decreased community air quality. This study aims to quantify the association between UNGD and pediatric asthma hospitalizations.
Methods: We compare pediatric asthma hospitalizations among zip codes with and without exposure to UNGD between 2003 and 2014 using a difference-in-differences panel analysis. Our UNGD exposure metrics include cumulative and contemporaneous drilling as well as reported air emissions by site.
Results: We observed consistently elevated odds of hospitalizations in the top tertile of pediatric patients exposed to unconventional drilling compared with their unexposed peers. During the same quarter a well was drilled, we find a 25% increase (95% CI: 1.07, 1.47) in the odds of being hospitalized for asthma. Ever-establishment of an UNGD well within a zip code was associated with a 1.19 (95% CI: 1.04, 1.36) increased odds of a pediatric asthma hospitalization. Our results further demonstrate that increasing specific air emissions from UNGD sites are associated with increased risks of pediatric asthma hospitalizations (e.g. 2,2,4-trimethylpentane, formaldehyde, x-hexane). These results hold across multiple age groups and sensitivity analyses.
Conclusions: Community-level UNGD exposure metrics were associated with increased odds of pediatric asthma-related hospitalization among young children and adolescents. This study provides evidence that additional regulations may be necessary to protect children's respiratory health from UNGD activities.

1. Background

Unconventional natural gas development (UNGD) industry has exponentially grown throughout the United States (US) to accommodate growing domestic energy requirements, increasing from under 26,000 drilling sites in 2000 to over 300,000 drilling sites in 2015 (U.S. Energy Information Administration, 2017b). Recent estimates indicate that 17.6 million Americans now live within one mile of an active drilling site, which includes UNGD, thus there is a clear need to ascertain the children's health effects of living in a community with UNGD emissions (Czolowski et al., 2017).

Drilling for fossil fuel resources can be categorized in two ways: conventional (CONGD) and unconventional (UNGD) (U.S. Energy Information Administration, 2017a). CONGD involves drilling vertically to pump natural gas out of a pocket found within geological formations. However, natural gas can sometimes be trapped within layers of shale, necessitating UNGD techniques such as hydraulic fracturing with high volumes of high pressure fluids and horizontal drilling parallel to the surface to extract natural gas. This new advance in UNGD technology has allowed communities with no previous drilling activity to be inundated by the industry. UNGD technology enabled increased shale gas production worldwide in countries such as the United States, Canada, China, Argentina, Algeria, and Mexico (U.S. Energy Information Administration (EIA), 2016). Within the United States, one of the most productive geological formations is the Marcellus Shale in rural Pennsylvania, yielding about 18% of total domestic natural gas production (U.S. Energy Information Administration, 2017a).

Throughout UNGD processes, numerous toxic air pollutants are

Abbreviations: UNGD, unconventional natural gas development; CONGD, conventional natural gas development; US, United States; PHC4, Pennsylvania Healthcare Cost Containment Council; NATA, National Air Toxics Assessment; RHI, respiratory hazard index

* Corresponding author at: Department of Public Health Sciences, University of Rochester School of Medicine and Dentistry, 265 Crittenden Blvd Box 420644, Rochester, NY 14642, USA.
E-mail address: elaine_hill@urmc.rochester.edu (E.L. Hill).

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emitted that may cause adverse respiratory health outcomes. Existing environmental monitoring studies demonstrate air pollution above background levels in communities with UNGD sites for chemicals associated with UNGD processes, many of which are known respiratory irritants (McKenzie et al., 2012; Colborn et al., 2014; Macey et al., 2014; Swarthout et al., 2015; Webb et al., 2016). Specific toxicants that have been previously associated with air pollution from UNGD emissions include particulate matter (diesel PM, PM_{10}); volatile organic compounds (benzene, ethylbenzene, formaldehyde, n-hexane, toluene, and xylene); polycyclic aromatic hydrocarbons (naphthalene, chlorobenzene, phenol); and other pollutants (ethylene glycol, methanol) (Colborn et al., 2010, 2014; Adgate et al., 2014; Elliott et al., 2017; Paulik et al., 2016; Macey et al., 2014; McKenzie et al., 2012; Korfmacher et al., 2013). Children are especially sensitive to environmental toxicants and associated adverse health outcomes (Faustman et al., 1999).

Asthma is a common chronic illness that currently affects 8.4% of children and adolescents under eighteen in the US, or about six million children (CDC, 2017). This condition is characterized by recurrent episodes of cough and wheeze related to the narrowing of the airways and inflammation of the lungs (US Department of Health and Human Services National Institutes of Health National Heart, Lung, and Blood Institute, 2014). Pediatric asthma has a substantial impact on functional outcomes, as it is a key contributor to school absenteeism, lower quality of life, and limitation of physical activity (Stridsman et al., 2017). Patients under 18 years old with asthma cost 1.99 billion dollars per year in the United States, so this outcome represents a substantial burden to communities (CDC, 2005). Asthma prevalence varies by age group at 9.6% for children between 5 and 11, 10.3% for young teenagers between ages 12 and 14, and 9.8% for older teenagers between 15 and 17 (CDC, 2017). Asthma outcomes for children are typically considered within different age groups because the course of asthma can change over time, and a child's response to exposures and treatments may vary by age. The national guidelines for asthma management includes recommendations for control assessments and stepwise treatments based on child age category (NHLBI, 2007).

Although there are numerous triggers for asthma exacerbations, some types of outdoor environmental air pollution are known respiratory irritants (Adams et al., 2011; Pennsylvania Department of Health, 2016). Many chemicals that have been found at increased levels in areas located close to UNGD sites have also been implicated as environmental asthma triggers (Marrero et al., 2016; McKenzie et al., 2012; Pennsylvania Department of Health, 2016; Swarthout et al., 2015). It remains unclear what aspects of UNGD may be most associated with pediatric asthma such as the initial drilling of a new site or the ongoing activities as the site produces natural gas (Adgate et al., 2014; Czolowski et al., 2017).

Only one previous study exists on UNGD and respiratory health outcomes and it utilizes a Pennsylvania sample between ages 5 and 90 (Rasmussen et al., 2016). Their analyses find odds ratios ranging from 1.10 (95% CI: 0.92, 1.30) to 1.74 (95% CI: 1.45, 2.09) depending upon exposure metric. Additional community concern regarding the health effects of UNGD-related air pollution have also been raised, but no studies to date have examined specific components of UNGD air pollution and linked this information to population health effects (Macey et al., 2014; Maskrey et al., 2016; Paulik et al., 2016; Rabinowitz et al., 2015).

Our study demonstrates how age groups within the pediatric population may be at differing risks from exposure to UNGD-related air pollution and examining specific UNGD pollutants from reported site air emissions. We take into account potential co-exposures for our population such as pre-existing respiratory irritants and conventional oil and natural gas development (CONGD). Our results add to the body of literature on how UNGD is associated with asthma exacerbations among a vulnerable population of children.

2. Methods

2.1. Study population

We obtained data on individual inpatient hospitalization for the entire state of Pennsylvania (67 total counties) from the Pennsylvania Health Care Cost Containment Council (Pennsylvania Healthcare Cost Containment Council Inpatient Discharge Data). Each record contains the patient's residential zip code, which we used to assign exposure status. We included the zip codes in counties fully located on the Marcellus Shale, as zip codes not located on the Marcellus Shale have no potential for UNGD and may be inherently different than areas located on the Marcellus Shale. Furthermore, we excluded counties designated as urban by the Pennsylvania Department of Health's Asthma Prevalence report due to the large differences in urban versus rural air quality and other co-exposures (Pennsylvania Department of Health, 2016; Strosnider, 2017). By limiting our sample population to rural counties located on the Marcellus Shale, we are reducing the potential for residual confounding in our final risk estimates.

2.2. Study design

We use a difference-in-differences design to account for pre-existing time trends in pediatric asthma hospitalizations that may be present prior to the introduction of UNGD. This study design permits the comparison of trends in the outcome before and after the introduction of UNGD in a zip code, as well as contrast the trends to zip codes unexposed to UNGD over the entire study period.

2.3. Exposure metric

We obtained complete drilling wells dataset from the Pennsylvania Department of Environmental Protection (PADEP) and assigned wells' coordinates to specific zip codes and counties (PADEP, 2016b). Unlike residential-specific proximity exposure metrics, zip code and county exposures can consider how macroeconomic changes from UNGD may benefit the local area (e.g. decreased unemployment, increased private insurance), so these derived exposure metrics represent an effective community-level estimate of UNGD exposure. The database contains a field that indicates if a well site is permitted as unconventional as well as the exact date that drilling began, the combination of which we use to determine exposure status.

To assess exposure to UNGD within a zip code, we examined the number of wells drilled in the zip code in a specific quarter of a calendar year. We hypothesize that the immediate effect of a newly drilled well is more likely to affect local air quality and cause an asthma exacerbation than the long term cumulative effect of wells. However, the effect of an increasing amount of drilling activity in the zip code may create more air pollution for a longer period. Both exposure metrics have been used in previous epidemiologic work (Jemielita et al., 2015; Rasmussen et al., 2016; Tustin et al., 2016). Since there is little literature supporting either framework, we chose to create three metrics of UNGD exposure by zip code for each quarter and year observation: a binary contemporaneous variable for a newly spudded (initially drilled) well, a binary cumulative variable for ever-spudded wells, and tertiles of cumulative count of the wells ever drilled. We also incorporate similar exposure metrics for conventional oil and natural gas development (CONGD) to account for known co-occurrence of CONGD and UNGD.

We also leverage the Pennsylvania Unconventional Natural Gas Emission Inventory to assess the association between specific reported UNGD air pollutants and our pediatric asthma outcomes (PADEP, 2016a). This database contains annualized emissions data from all UNGD sites from 2011 through 2014 reported by companies for a number of pollutants: 2,2,4-trimethylpentane, benzene, carbon monoxide, carbon dioxide, ethylbenzene, formaldehyde, methane, nitrous

oxide, nitrogen oxides, $PM_{2.5}$, PM_{10}, toluene, volatile organic compounds, x-hexane, and xylenes. Although individual volatile organic compounds are in the emissions data, Pennsylvania regulates volatile organic compounds as a heterogeneous category and requires emissions to be reported as specific volatile organic compounds as well, thus we evaluate this category in both ways. All pollutants are reported in tons emitted per year. This database is one of the only ones that contains pollution by site from the UNGD process since UNGD sites are not subject to the national Toxic Release Inventory during our study period (US EPA, 2016). For all reporting UNGD sites, we linked our spud data from DrillingInfo to the emissions data by matching on company names, site names, and counties by year and determine how much pollution is being reported per zip code on an annual basis. This allows us to assess the annual sum of pollution in tons by chemical at the zip code level as an additional exposure metric in separate models. Our main models explore pollution in a log-sum framework to ascertain how different levels of emissions may affect our pediatric population.

2.4. Other respiratory hazards

We control for pre-existing respiratory hazards via the 2011 National Air Toxics Assessment (NATA) respiratory hazard index (RHI), a composite index of over 180 hazardous air pollutants from mobile and stationary sources (US Environmental Protection Agency, 2015). This data is available for the entire nation by census tract centroid, so we applied inverse distance interpolation to estimate NATA RHI for each zip code centroid in our analysis. To our knowledge, no other studies on respiratory health effects of UNGD have incorporated a composite metric for non-UNGD respiratory hazards.

2.5. Outcome metric

The Pennsylvania Healthcare Cost Containment Council (PHC4) hospitalization data include the diagnostic codes assigned to each patient upon discharge in Pennsylvania. Our analysis includes patients between the ages of 2 and 18 years with a 493.X ICD-9 code, which indicates acute asthma exacerbations. We excluded children under the age of 2 years from this analysis because an asthma hospitalization in this age group may be reflective of a viral illness, not a typical asthma case (Adams et al., 2011). Our outcome is a binary indicator of whether there is a pediatric asthma hospitalization in a specific zip code-quarter-year observation.

We stratified asthma-related hospitalizations into three age-specific categories (2–6, 7–12, and 13–18 years) to better examine the differences in asthma exacerbations throughout childhood and adolescence. These categorizations somewhat align with the age stratification scheme that the Center for Disease Control uses to report asthma incidence, but we categorize them into tertiles due to the exclusion of the children under 2 years (CDC, 2017). Hospitalizations were analyzed by year and quarter per zip code, thus considering spatiotemporal patterns. We also extracted patient sex, race, ethnicity, and insurance status for inclusion in our models.

2.6. Statistical analysis

The maximum number of observations in this analysis is fixed at the quantity of *(Number of years of data) * (Number of quarters per year) * (Number of zip codes)*. To account for the hierarchical nature of the data, we fit mixed effects logistic regression models with a random intercept for zip code and fixed effects for year and quarter. While a similar study used fixed effects Poisson regression due to the count nature of hospitalizations, we hypothesize that a mixed effects logistic regression model is more appropriate due to our rare outcome and has been previously used to study associations between UNGD and asthma (Jemielita et al., 2015; Rasmussen et al., 2016). We assume that absence of an ICD-indicated asthma hospitalization within the zip code during a specific quarterly timeframe indicates that a contemporaneous event did not occur.

For our analysis of reported emissions, we subset our hospitalizations to only 2011 through 2014, which aligns with the only available years of emissions data. We substitute our UNGD exposure metric for each annualized pollutant available in these four years of data but maintain the same models in all other regards, including the quarterly temporality to account for seasonal variation within a year.

Covariates in all of our asthma models include annual proportion of hospitalizations for sex, race, ethnicity, and insurance type by zip code derived from the individual-level PHC4 hospitalization data; zip code-level population density from the 2010 US Census and background respiratory hazard index from the 2011 National Air Toxics Assessment; and annual county-level unemployment, poverty for children under 18 years of age, and median household income from the US Census Small Area Income and Poverty Estimates (Surveillance, Epidemiology, and End Results Program, 2017, IPUMS NHGIS, 2016; US Environmental Protection Agency, 2015). Additional analyses stratify by pediatric age groups (2–6, 7–12, and 13–18 years) to examine potential heterogeneity across different stages of development. Our pollutant-specific models follow the same specifications.

In addition to assessing our results in calendar time, we also developed models to examine our results in terms of event time, which allows us to examine how the asthma hospitalization risk may change after the initial UNGD activity began. We collapse our data to the annual level and convert our data into years before and after UNGD started in each zip code. Our reference year is four quarters prior to the first UNGD site is spudded in the zip code. We limit this analysis to only eight years of before and after spudding since very few zip codes experience UNGD activity for greater than eight years of time in our study period.

2.7. Sensitivity analysis

First, we include a covariate for conventional oil and gas development (CONGD) to adjust for potential co-exposure effects. Second, we fit models using conditional likelihood logistic regression to confirm that the random intercept did not influence our effect estimates. Third, we examine cumulative count of UNGD wells within the zip code prior to hospitalization to estimate the effect of each additional well on asthma hospitalization. Fourth, we examine the relationship between the number of reporting UNGD sites regressed on the sum of emissions in each zip code by pollutant, which helps us ensure that these reported emissions are indicative of the number of sites in the zip code. Finally, we fit regressions for the quintile framework (lowest vs. highest quintiles) of specific pollutants to explore the association between our UNGD pollution and pediatric asthma hospitalizations for our most and least exposed communities.

3. Results

3.1. Descriptive statistics

Our inclusion criteria yield 29 counties containing 571 zip codes in Pennsylvania, which generates 27,296 observations by zip code, quarter, and year. In Pennsylvania between 2003 and 2014, new UNGD wells annually increases from 3 to 1372 with spuds drilled in 274 zip codes per year at its peak in 2011 (Fig. 1). In total, 5649 UNGD wells are drilled in our sample area between 2003 and 2014, with CONGD wells co-occurring within many zip codes across our study period (Fig. 2).

In total, 15,837 pediatric asthma-related hospitalizations are included. Our exposure distribution yields 1070 hospitalizations in 532 zip codes exposed to UNGD compared with 14,767 unexposed hospitalizations in 6794 zip codes, and most demographic information is similar among patients exposed and unexposed to UNGD activity

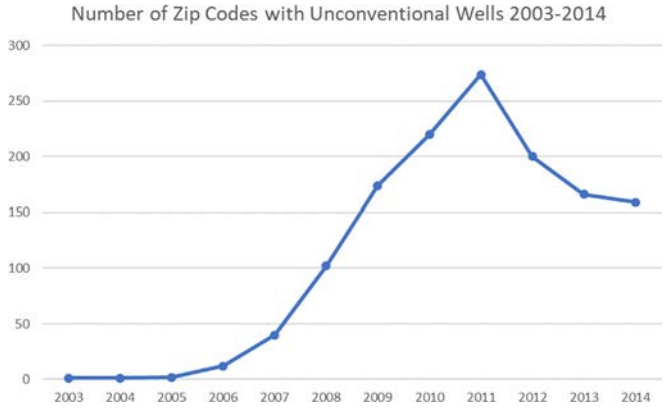

Fig. 1. Newly spudded UNGD sites by zip code 2003–2014.

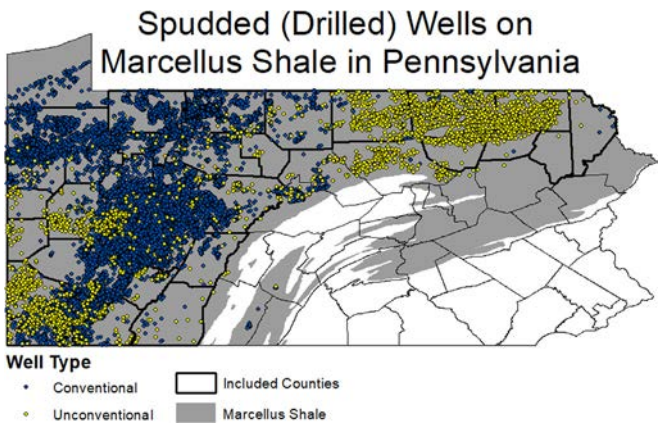

Fig. 2. Spatial distribution of UNGD and CONGD in Pennsylvania 2003–2014.

(Table 1). We note that patients exposed to UNGD tended to live in areas with slightly lower population densities.

3.2. Association of UNGD with pediatric asthma hospitalizations

We first determine that a logistic model is appropriate by graphing our hospitalizations counts means per quarter and zip code in a histogram (eFig. 1). After adjusting for secular time trends, children and adolescents exposed to newly spudded UNGD wells within their zip code have 1.25 (95% CI: 1.07, 1.47) times the odds of experiencing an asthma-related hospitalization compared with children who did not live in these communities (Table 2). When stratified by patient age, those between 2 and 6 years have the greatest odds of an asthma-related hospitalization (OR = 1.44; 95% CI: 1.18, 1.75) followed by ages 13–18 (OR = 1.34, 95% CI: 1.13, 1.60).

In the binary cumulative exposure framework, we observe similar results to the contemporaneous analysis (Table 2). Children and adolescents residing in a zip code with any current or previous drilling activity have 1.19 (95% CI: 1.04, 1.36) times the odds of experiencing an asthma-related hospitalization compared with children who do not live in these communities. Children between the ages of 2 and 6 have the most elevated odds ratio (OR = 1.35; 95% CI: 1.14, 1.60) followed by children ages 13–18 (OR = 1.29, 95% CI: 1.11, 1.49).

We conduct additional analyses using the number of UNGD sites ever drilled within a zip code to examine the effect of additional wells on pediatric asthma-related hospitalizations. The tertiles of exposure by number of wells ever drilled in the zip code is 1–2, 3–10, and > 11. The highest tertile of exposure is associated with increased odds of pediatric asthma hospitalizations for all age groups (OR = 1.39, 95% CI: 1.14, 1.71), while middle and lowest tertiles of exposure did not demonstrate clear dose-response (Table 2). Results for children between ages of 2 and 6 show the strongest evidence of dose-response, and in the highest tertile of exposure, UNGD is associated with a 1.73 higher odds (95% CI: 1.34, 2.23) of an asthma-related hospitalization compared with the no UNGD exposure group. Finally, we observe increases in the odds of an asthma-related hospitalization for years after the initial drilling begins (Fig. 3).

Table 1
Individual, zip code, and county demographic information for participants by exposure status.

	Unexposed[a]	Exposed
Individual		
Total Asthma Patients	14,767	1070
Age Group		
2–6	31%	30%
7–12	25%	20%
13–18	44%	50%
Zip Code[b]		
Female (%)	42%	42%
Race/Ethnicity (%)		
White	88%	90%
Black	6%	4%
Hispanic	2%	1%
Other	4%	5%
Insurance (%)		
Medicaid	51%	52%
Private	46%	45%
Uninsured	2%	2%
Other or Missing	1%	1%
Hospitalization Quarter		
1 (Jan, Mar)	25%	23%
2 (Apr, Jun)	25%	25%
3 (Jul, Sep)	25%	27%
4 (Oct, Dec)	25%	26%
Hospitalization Type (%)		
Emergency	50%	44%
Urgent	38%	45%
Elective	12%	11%
Respiratory Hazard Index[b]	1.1	1.2
County		
Median Income ($)[c]	41,059	43,596
Population Density[d]	48.0	34.5
Poverty Under 18 (%)[c]	20%	21%
Unemployment Rate (%)[e]	7%	8%

[a] Exposure status determined by any UNGD well drilled in a zip code contemporaneously with the asthma hospitalization.
[b] Zip code demographics determined using all pediatric hospitalizations in each zip code over the course of the study period.
[c] Derived from annual U.S. Census Small Area Income & Poverty Estimates.
[d] Derived from annual U.S. Intercensal County Population Data.
[e] Derived from annual U.S. Bureau of Labor Statistics.

3.3. Association of UNGD site emissions with pediatric asthma hospitalizations

Our pollutant-specific emissions models demonstrate consistent increased risks of pediatric asthma hospitalizations across most of our models when we compare the lowest to highest quintiles of exposure (Table 3). Full descriptions of the pollutant distributions are available in our Supplementary material data (eTable 1). Briefly, we find odds ratios ranging from 1.08 (95% CI: 0.93, 1.26) for carbon dioxide to 1.42 (95% CI: 1.22, 1.66) for VOCs. Specific reported pollutants with associations across our all-ages models include 2,2,4-trimethylpentane, carbon dioxide, formaldehyde, nitrous oxide, VOCs, and x-hexane. Ages 2–6 hospitalizations are also associated with exposure to carbon monoxide, methane, nitrogen oxides, $PM_{2.5}$, PM_{10}, toluene, and xylenes while hospitalizations among children ages 7–12 and adolescents 13–18 are associated with no additional pollutants.

Table 2
Associations between UNGD and pediatric asthma hospitalizations by exposure metric.[a]

	Binary exposure metrics		Tertile exposure metrics[de]			
Age group	**Contemporaneous[b]**	**Cumulative[c]**	**No UNGD**	**Low**	**Medium**	**High**
All	1.25 (1.07, 1.47)	1.19 (1.04, 1.36)	REF	1.15 (0.97, 1.36)	1.12 (0.94, 1.34)	1.39 (1.14, 1.71)
2–6	1.44 (1.18, 1.75)	1.35 (1.14, 1.60)	REF	1.24 (1.00, 1.54)	1.27 (1.01, 1.59)	1.73 (1.34, 2.23)
7–12	1.03 (0.83, 1.29)	1.05 (0.88, 1.25)	REF	1.06 (0.84, 1.34)	1.00 (0.79, 1.27)	1.11 (0.84, 1.47)
13–18	1.34 (1.13, 1.60)	1.29 (1.11, 1.49)	REF	1.28 (1.06, 1.55)	1.25 (1.03, 1.53)	1.35 (1.08, 1.70)

[a] Multilevel logistic models with a random intercept for zip code adjusted for sex, race, year, quarter, insurance status, zip code respiratory hazard index, county median household income quartile, county unemployment, county poverty under 18 years old, and county log population density.
[b] Exposure metric is whether any UNGD wells were drilled in the same zip code, quarter, and year as the hospitalization.
[c] Exposure metric is whether any UNGD wells were ever drilled in the same zip code, quarter, and year as the hospitalization.
[d] Reference group is zip codes with no UNGD activity in study period.
[e] Exposure metric is tertile of UNGD site count in a zip code through the quarter that the hospitalization occurred.

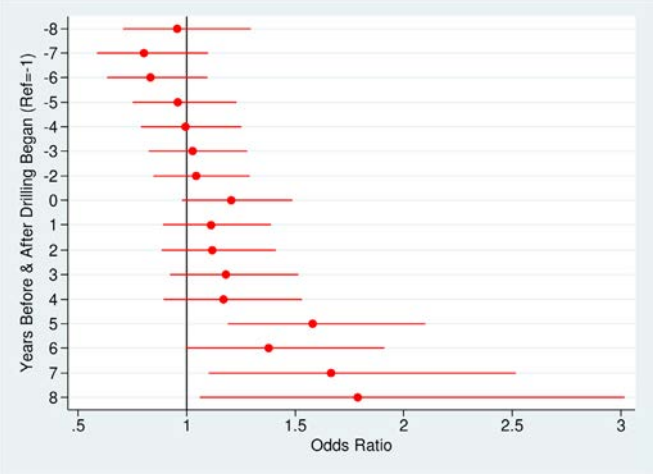

Fig. 3. Odds ratios for pediatric asthma hospitalizations by years before and after first spudded UNGD site in zip code.

3.4. Sensitivity analyses

Given the high quantity of conventional drilling occurring within our study time frame across our study area (Fig. 2), we adjust for CONGD exposure within the zip code in an additional set of analyses. For the binary exposure analysis, results remain similar in both analyses after adjusting for CONGD (Online Supplementary material eTable 2). For the tertile analysis, all results maintain similar, if slightly attenuated, risk estimates after controlling for CONGD. Our results likewise remain qualitatively similar when we use a fixed effects logistic regression instead of a mixed effects framework (Online Supplementary material eTable 3). We also find similar effect sizes for our cumulative UNGD metric for each additional well among the 2–6 age group but not others (Online Supplementary material eTable 4). In regressions of the sum of pollution on the number of reporting UNGD sites in a zip code, we find consistent positive associations, which demonstrates that the number of UNGD sites is sufficiently correlated with the self-reported emissions data (Online Supplementary material eTable 5). Our regression results for specific emissions in a quintile exposure framework also demonstrate similar, if higher, associations with wider confidence intervals between each pollutant and our pediatric asthma outcome (Online Supplementary material eTable 6).

4. Discussion

We conducted a difference-in-differences analysis of pediatric asthma-related hospitalizations in Pennsylvania using an administrative database from 2003 through 2014, which corresponds to the rapid development of the Marcellus Shale. This study examines the relationship between pediatric asthma hospitalizations and UNGD. In addition, this study shows how specific UNGD emissions may be linked to respiratory health outcomes. We are able to break down pediatric asthma hospitalizations by age group to examine the effects of UNGD

Table 3
Associations between log-sum UNGD emissions and pediatric asthma hospitalizations by pollutant.

Pollutants[a]	**All ages**	**2–6**	**7–12**	**13–18**
2,2,4-Trimethylpentane	1.29 (1.01, 1.64)	1.30 (1.07, 1.58)	1.04 (0.83, 1.30)	1.41 (1.12, 1.77)
Benzene	1.12 (0.99, 1.27)	1.09 (0.98, 1.21)	1.08 (0.96, 1.23)	1.04 (0.92, 1.17)
Carbon Monoxide	1.08 (0.93, 1.26)	1.20 (1.05, 1.37)	1.07 (0.93, 1.25)	1.03 (0.90, 1.19)
Carbon Dioxide	1.16 (1.02, 1.33)	1.20 (1.05, 1.36)	1.17 (1.01, 1.37)	1.11 (0.97, 1.28)
Ethylbenzene	1.11 (0.95, 1.30)	0.94 (0.82, 1.08)	1.01 (0.87, 1.17)	1.07 (0.93, 1.23)
Formaldehyde	1.20 (1.06, 1.36)	1.18 (1.06, 1.31)	1.06 (0.94, 1.20)	1.12 (1.00, 1.25)
Methane	1.10 (0.96, 1.26)	1.17 (1.04, 1.31)	1.05 (0.92, 1.19)	1.04 (0.92, 1.18)
Nitrous Oxide	1.17 (1.02, 1.33)	1.19 (1.06, 1.34)	1.16 (1.00, 1.34)	1.07 (0.94, 1.22)
NO_x	1.21 (0.98, 1.48)	1.23 (1.05, 1.45)	1.088 (0.90, 1.32)	1.20 (0.99, 1.45)
$PM_{2.5}$	1.06 (0.92, 1.22)	1.18 (1.04, 1.34)	1.04 (0.90, 1.20)	1.02 (0.89, 1.16)
PM_{10}	1.08 (0.94, 1.24)	1.23 (1.09, 1.40)	1.03 (0.90, 1.19)	1.04 (0.91, 1.18)
Toluene	1.09 (0.97, 1.24)	1.14 (1.03, 1.26)	0.99 (0.88, 1.12)	1.05 (0.94, 1.18)
SO_x	1.09 (0.96, 1.24)	1.08 (0.98, 1.21)	1.05 (0.93, 1.19)	1.11 (0.99, 1.25)
Volatile Organic Compounds	1.42 (1.22, 1.66)	1.34 (1.17, 1.54)	1.12 (0.97, 1.29)	1.32 (1.15, 1.52)
x-Hexane	1.23 (1.05, 1.43)	1.13 (0.99, 1.30)	1.129 (0.97, 1.32)	1.25 (1.08, 1.44)
Xylenes (Isomers & Mixtures)	1.16 (0.98, 1.36)	1.18 (1.03, 1.35)	1.09 (0.94, 1.27)	1.13 (0.98, 1.31)

[a] Models only include data 2011 through 2014. Multilevel logistic regression models with a random intercept for zip code adjusted for sex, race, year, quarter, insurance status, zip code respiratory hazard index, county median household income quartile, county unemployment, county poverty under 18 years old, and county log population density.

across the child developmental stages and demonstrate that specific pediatric age groups respond differently to UNGD in their community. Pediatric asthma hospitalization rates may be changing in our study period for reasons unrelated to UNGD, thus our analysis ensures that these secular trends are not influencing the results. Furthermore, we restrict our analysis to a relatively homogenous rural population in counties that are located on the Marcellus Shale, so our analysis reduces external confounding factors. We control for pre-existing respiratory health risks, which we adjust for via the National Air Toxics Assessment (NATA) respiratory hazard index (RHI). This method is more effective than controlling for individual ambient pollutants since the NATA RHI considers over 180 hazardous air pollutants from stationary and mobile sources at the local level. Our results appear to be driven by the highest exposure tertile, which insinuates that the intensity of pollution from UNGD is more important than the initial introduction of UNGD into a community.

Our results remain consistent with the existing literature on UNGD and respiratory health, though we observed attenuated estimates across all age groups and exposure levels (Rasmussen et al., 2016; Rabinowitz et al., 2015). The results presented in this study build upon the associations found in Rasmussen et al., 2016 by using the population of inpatient pediatric asthma hospitalizations between 2003 and 2014. We also show that the risk of a pediatric asthma hospitalization remains increased for years after the introduction of UNGD. Our findings further demonstrate that children between 2 and 6 years old are more susceptible to experiencing an asthma-related hospitalization in a UNGD zip code. After controlling for co-occurrence of CONGD, we continue to find an elevated risk of asthma-related hospitalizations with exposure to UNGD, which has not been previously shown. These results provide support that increased drilling activity may be associated with an increased risk of pediatric asthma hospitalizations.

In our analysis of individual pollutants from the emissions reports, we find evidence of specific pollutants from UNGD processes that may be driving increases in pediatric asthma hospitalization, including several known respiratory irritants such as volatile organic compounds and formaldehyde (Gordian et al., 2010; Kampa and Castanas, 2008; Webb et al., 2016). These results imply that the pollution from the UNGD sites themselves, as opposed to only UNGD-related traffic, may be contributing to pediatric asthma hospitalizations. Although this data is self-reported by the UNGD companies themselves, this data likely represents an underreporting of true UNGD site emissions, thus our results may be underreporting the risk of pediatric asthma from specific UNGD pollutants. We interpret these results with caution due to the self-reported nature of the emissions data; however, these results provide preliminary insights into the effects of specific UNGD pollutants on pediatric asthma hospitalizations.

Shale gas development has previously been implicated in decreased air quality, but these assessments have focused on UNGD and did not assess the CONGD co-exposure (Czolowski et al., 2017; Marrero et al., 2016; McKenzie et al., 2012; Swarthout et al., 2015; Walters et al., 2015). Any reductions in air quality are likely to be adversely experienced by the most vulnerable asthmatic patients in the local population, whom we captured in our study via their hospitalization records. Pediatric patients experiencing breathing difficulties are usually taken to the hospital, even in rural settings. The administrative nature of our data allows us to capture exacerbations among young patients, who are hard to access otherwise. Importantly, these episodes represent not only a significant event for the patient and his or her family, but also are associated with missed days of school and work, and substantial healthcare cost.

The present study has some limitations. Exposure and outcome were examined at the zip code level, which contributes to potential exposure misclassification. Our tertiles of drilling exposure by zip code attempt to examine the dose response relationship, but this imprecise exposure metric is not ideal for individual exposures since we cannot assess exactly where the patients reside in relation to the UNGD sites. However, our results indicate that community-level UNGD is associated with decreased respiratory health, which can be more easily translated into local policy decisions. Our results are further bolstered by our use of the UNGD emissions data in addition to accounting for background respiratory hazards, where we demonstrate that specific pollutants are more likely to be associated with pediatric asthma hospitalizations. Additionally, the reliance on hospitalization data did not permit the investigation of how patients with less severe asthma may be affected, which previous literature has shown to be susceptible to UNGD-related air pollution (Rasmussen et al., 2016).

Our analysis focuses on asthma-related hospitalizations among children and adolocents while adequately controling for pre-existing outcome trends that occurred prior to the introduction of UNGD. We also leverage a unique database of UNGD pollution to examine specific chemicals with respect to respiratory health outcomes, which has not been done in the UNGD and human health literature to date. Difference-in-differences designs can take these time trends into account, so future analyses of other outcomes should incorporate pre-existing outcome trends into their models to minimize spatiotemporal confounding. We supplement our results with models that demonstrate specific UNGD pollutants that may be creating the higher risks of pediatric asthma hospitalizations associated with community UNGD exposures. We also assess CONGD co-exposures with respect to a health outcome. Our populations of patients were relatively homogenous in terms of socio-demographic factors, and all had to be at risk for UNGD, which should reduce potential unmeasured confounding. Furthermore, our outcome data come from a standardized source and we focus on the children most vulnerable to air pollution increases. Finally, the zip code nature of our exposure allows for a community-level assessment of UNGD and demonstrate that community-level exposures to UNGD are associated with increased risk of pediatric asthma hospitalizations, which may better measure the amount of drilling exposure for policy implications.

5. Conclusions

Previous studies observe associations between UNGD and poorer local air quality. This study examines the associations between community-level UNGD activity and pediatric asthma while considering pre-existing time trends, co-occurrence of CONGD, and UNGD site-specific emissions reports. Additional work is needed to understand how UNGD air pollution may affect respiratory health, which could include detailed exposure assessments for UNGD and CONGD sites.

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Data provider disclaimer

The Pennsylvania Health Care Cost Containment Council (PHC4) is an independent state agency responsible for addressing the problem of escalating health costs, ensuring the quality of health care, and increasing access to health care for all citizens regardless of ability to pay. PHC4 has provided data to this entity to further PHC4's mission of educating the public and containing health care costs in Pennsylvania. PHC4, its agents, and staff, have made no representation, guarantee, or warranty, express or implied, that the data, – financial, patient, payor, and physician specific information, – provided to this entity, are error-free, or that the use of the data will avoid differences of opinion or interpretation. This analysis was not prepared by PHC4. This analysis was done by Dr. Hill and her collaborators. PHC4, its agents and staff, bear no responsibility or liability for the results of the analysis, which are solely the opinion of this entity.

Human subjects protection

This research was approved by University of Rochester Research Subjects Review Board (RSRB).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.envres.2018.06.022.

References

Adams, J., Sutter, M., Alberton, T., 2011. The patient with asthma in the emergency department. Clin. Rev. Allerg. Immunol. 43, 14–29.

Adgate, J.L., Goldstein, B.D., McKenzie, L.M., 2014. Potential public health hazards, exposures and health effects from unconventional natural gas development. Environ. Sci. Technol. 48, 8307–8320. http://dx.doi.org/10.1021/es404621d.

CDC, 2005. Preventing Chronic Disease. Centers for Disease Control and Prevention. Available: ⟨https://www.cdc.gov/pcd/issues/2005/jan/04_0053.htm⟩ (Accessed 5 May 2018).

CDC, 2017. Most Recent Asthma Data.

Colborn, T., Kwiatkowski, C.F., Schultz, K., Bachran, M., 2010. Natural gas operations from a public health perspective. Hum. Ecol. Risk Assess. Int. J. 17, 1040–1056.

Colborn, T., Schultz, K., Herrick, L., Kwiatkowski, C., 2014. An exploratory study of air quality near natural gas operations. Hum. Ecol. Risk Assess. Int. J. 20, 86–105. http://dx.doi.org/10.1080/10807039.2012.749447.

Czolowski, E., Santoro, R., Srebotnjak, T., Shonkoff, S., 2017. Toward consistent methodology to quantify populations in proximity to oil and gas development: a national spatial analysis and review. Environ. Health Perspect. 125.

Elliott, E.G., Trinh, P., Ma, X., Leaderer, B.P., Ward, M.H., Deziel, N.C., 2017. Unconventional oil and gas development and risk of childhood leukemia: assessing the evidence. Sci. Total Environ. 576, 138–147. http://dx.doi.org/10.1016/j.scitotenv.2016.10.072.

Faustman, E., Silbernagel, S., Fenske, R., Burbacher, T., Ponce, R., 1999. Mechanisms underlying children's susceptibility to environmental toxicants. Environ. Health Perspect. 108, 13–21.

Gordian, M.E., Stewart, A.W., Morris, S.S., 2010. Evaporative gasoline emissions and asthma symptoms. Int. J. Environ. Res. Public Health 7, 3051–3062. http://dx.doi.org/10.3390/ijerph7083051.

IPUMS NHGIS, 2016. National Historical Geographic Information System. Available: ⟨https://www.nhgis.org/⟩ (Accessed 12 January 2018).

Jemielita, T., Gerton, G.L., Neidell, M., Chillrud, S., Yan, B., Stute, M., et al., 2015. Unconventional gas and oil drilling is associated with increased hospital utilization rates. PLoS ONE 10, e0131093. http://dx.doi.org/10.1371/journal.pone.0131093.

Kampa, M., Castanas, E., 2008. Human health effects of air pollution. Environ. Pollut. 151, 362–367. http://dx.doi.org/10.1016/j.envpol.2007.06.012.

Korfmacher, K.S., Jones, W.A., Malone, S.L., Vinci, L.F., 2013. Public health and high volume hydraulic fracturing. New Solut. J. Environ. Occup. Health Policy NS 23, 13–31. http://dx.doi.org/10.2190/NS.23.1.c.

Macey, G.P., Breech, R., Chernaik, M., Cox, C., Larson, D., Thomas, D., et al., 2014. Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study. Environ. Health 13, 82. http://dx.doi.org/10.1186/1476-069X−13-82.

Marrero, J.E., Townsend-Small, A., Lyon, D.R., Tsai, T., Meinardi, S., Blake, D.R., 2016. Estimating emissions of toxic hydrocarbons from natural gas production sites in the barnett shale region of Northern Texas. Environ. Sci. Technol. 50, 10756–10764. http://dx.doi.org/10.1021/acs.est.6b02827.

Maskrey, J.R., Insley, A.L., Hynds, E.S., Panko, J.M., 2016. Air monitoring of volatile organic compounds at relevant receptors during hydraulic fracturing operations in Washington County, Pennsylvania. Environ. Monit. Assess. 188, 1–12. http://dx.doi.org/10.1007/s10661-016-5410-4.

McKenzie, L.M., Witter, R.Z., Newman, L.S., Adgate, J.L., 2012. Human health risk assessment of air emissions from development of unconventional natural gas resources. Sci. Total Environ. 424, 79–87. http://dx.doi.org/10.1016/j.scitotenv.2012.02.018.

NHLBI, 2007. Guidelines for the Diagnosis and Management of Asthma (EPR-3). National Heart, Lung, and Blood Institute. Available: ⟨https://www.nhlbi.nih.gov/health-topics/guidelines-for-diagnosis-management-of-asthma⟩ (Accessed 14 May 2018).

PADEP, 2016a. Instructions for Completing Air Quality Emission Inventory Forms.

PADEP, 2016b. Oil and Gas Reports.

Paulik, L.B., Donald, C.E., Smith, B.W., Tidwell, L.G., Hobbie, K.A., Kincl, L., et al., 2016. Emissions of polycyclic aromatic hydrocarbons from natural gas extraction into air. Environ. Sci. Technol. 50, 7921–7929. http://dx.doi.org/10.1021/acs.est.6b02762.

Pennsylvania Department of Health, 2016. 2015 Pennsylvania Asthma Prevalence Report.

Pennsylvania Healthcare Cost Containment Council Inpatient Discharge Data.

Rabinowitz, P.M., Slizovskiy, I.B., Lamers, V., Trufan, S.J., Holford, T.R., Dziura, J.D., et al., 2015. Proximity to natural gas wells and reported health status: results of a household survey in Washington County, Pennsylvania. Environ. Health Perspect. 123, 21–26. http://dx.doi.org/10.1289/ehp.1307732.

Rasmussen, S., Ogburn, E., McCormack, M., Casey, J., Bandeen-Roche, K., Mercer, et al., 2016. Association between unconventional natural gas development in the Marcellus Shale and asthma exacerbations. JAMA Intern. Med. 176, 1334–1343. http://dx.doi.org/10.1001/jamainternmed.2016.2436.

Stridsman, C., Dahlberg, E., Zandrén, K., Hedman, L., 2017. Asthma in Adolescence Affects Daily Life and School Attendance –Two Cross-sectional Population-based Studies 10 Years Apart.

Strosnider, H., 2017. Rural and urban differences in air quality, 2008–2012, and community drinking water quality, 2010–2015 — United States. MMWR Surveill. Summ. 66. http://dx.doi.org/10.15585/mmwr.ss6613a1.

Surveillance, Epidemiology, and End Results Program, 2017. National Cancer Institute. Available: ⟨https://seer.cancer.gov/⟩ (Accessed 12 January 2018).

Swarthout, R.F., Russo, R.S., Zhou, Y., Miller, B.M., Mitchell, B., Horsman, E., et al., 2015. Impact of marcellus shale natural gas development in Southwest Pennsylvania on volatile organic compound emissions and regional air quality. Environ. Sci. Technol. 49, 3175–3184. http://dx.doi.org/10.1021/es504315f.

Tustin, A.W., Hirsch, A.G., Rasmussen, S.G., Casey, J.A., Bandeen-Roche, K., Schwartz, B.S., 2016. Associations between unconventional natural gas development and nasal and sinus, migraine headache, and fatigue symptoms in Pennsylvania. Environ. Health Perspect. http://dx.doi.org/10.1289/EHP281.

U.S. Energy Information Administration (EIA), 2016. Shale Gas Production Drives World Natural Gas Production Growth. Available: ⟨https://www.eia.gov/todayinenergy/detail.php?id=27512⟩ (Accessed 10 January 2018).

U.S. Energy Information Administration, 2017a. Natural Gas Explained: Where Our Natural Gas Comes From.

U.S. Energy Information Administration, 2017b. U.S. Energy Information Administration Annual Energy Outlook 2017.

US Department of Health and Human Services; National Institutes of Health; National Heart, Lung, and Blood Institute, 2014. What Is Asthma?.

US Environmental Protection Agency, 2015. National Air Toxics Assessment. US EPA. Available: ⟨https://www.epa.gov/national-air-toxics-assessment⟩ (Accessed 12 January 2018).

US EPA, 2016. Addition of Natural Gas Processing Facilities to the Toxics Release Inventory Proposed Rule. US EPA. Available: ⟨https://www.epa.gov/toxics-release-inventory-tri-program/addition-natural-gas-processing-facilities-toxics-release⟩ (Accessed 7 May 2018).

Walters, K., Jacobson, J., Kroening, Z., Pierce, C., 2015. PM2.5 airborne particulates near frac sand operations. J. Environ. Health 78, 8–12.

Webb, E., Hays, J., Dyrszka, L., Rodriguez, B., Cox, C., Huffling, K., et al., 2016. Potential hazards of air pollutant emissions from unconventional oil and natural gas operations on the respiratory health of children and infants. Rev. Environ. Health. http://dx.doi.org/10.1515/reveh-2014-0070.

ATTACHMENT C

STUDY 26

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Adequacy of Current State Setbacks for Directional High-Volume Hydraulic Fracturing in the Marcellus, Barnett, and Niobrara Shale Plays

Marsha Haley,[1] Michael McCawley,[2] Anne C. Epstein,[3] Bob Arrington,[4] and Elizabeth Ferrell Bjerke[5]

[1]Department of Radiation Oncology, University of Pittsburgh Cancer Institute, Pittsburgh, Pennsylvania, USA; [2]School of Public Health, West Virginia University, Morgantown, West Virginia, USA; [3]Department of Internal Medicine, Texas Tech University Health Sciences Center School of Medicine, Lubbock, Texas, USA; [4]Parachute, Colorado, USA; [5]Graduate School of Public Health, Department of Health Policy and Management, University of Pittsburgh School of Law, Pittsburgh, Pennsylvania, USA

Background: There is an increasing awareness of the multiple potential pathways leading to human health risks from hydraulic fracturing. Setback distances are a legislative method to mitigate potential risks.

Objectives: We attempted to determine whether legal setback distances between well-pad sites and the public are adequate in three shale plays.

Methods: We reviewed geography, current statutes and regulations, evacuations, thermal modeling, air pollution studies, and vapor cloud modeling within the Marcellus, Barnett, and Niobrara Shale Plays.

Discussion: The evidence suggests that presently utilized setbacks may leave the public vulnerable to explosions, radiant heat, toxic gas clouds, and air pollution from hydraulic fracturing activities.

Conclusions: Our results suggest that setbacks may not be sufficient to reduce potential threats to human health in areas where hydraulic fracturing occurs. It is more likely that a combination of reasonable setbacks with controls for other sources of pollution associated with the process will be required.

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Introduction

Hydraulic fracturing, also referred to as "fracking," is a relatively recent well-stimulation technique used in some forms of oil and gas development. The method entails injecting pressurized liquids into rock formations of low permeability (e.g., shale) to mobilize oil or gas to the wellbore (Gandossi 2013). Hydraulic fracturing is used with other novel technologies, such as directional drilling, to access previously inaccessible resources such as shale gas, which has become an increasingly large portion of the overall energy supply in the United States (Pless 2012). Directional drilling increased from 6% of new hydraulically fractured wells drilled in the United States in 2000 to 42% of new wells drilled in 2010 (Gallegos and Varela 2015). This number is rising and the trajectory is expected to continue. A decade ago, shale gas production accounted for 2% of total U.S. output. In 2014, that figure was 37%, and an Information Handling Services study projects that natural gas developed through the use of hydraulic fracturing will rise to more than 75% of the domestic supply by 2035 (API 2014).

As a result of the proliferation of hydraulic fracturing, there is an increasing awareness of the multiple potential pathways leading to human health risks from this practice. Air pollution is a significant pathway: From volatile organic compounds (VOCs) found naturally in shale gas released during the drilling process, during blowdowns and venting (Macey et al. 2014), and through leaks at multiple connection points (U.S. EPA 2014); heavy diesel equipment used in the drilling process (Macey et al. 2014); chemical mixtures used to facilitate extraction (Goldstein et al. 2014); and silica sand as proppant (American Public Health Association 2012). Vapor dispersion is another health concern (Center for Chemical Process Safety 2015); in addition, natural gas well sites have experienced blowouts and other types of explosions (Hoffman 2015).

What constitutes a judicious setback distance between natural gas industrial activities and natural or anthropogenic structures is a debatable issue in more densely populated areas (Begos 2014). The literature is currently lacking concerning which particular setbacks are adequate to protect the health and safety of the public. In this paper we examine setback distances in three states located in three major shale plays—the Barnett, the Marcellus, and the Niobrara—and attempt to determine whether these legal setbacks are adequate.

Methods

We chose three of the largest and most heavily drilled areas of technically recoverable natural gas resources (natural gas plays) in the United States: the Barnett, Marcellus, and Niobrara (U.S. EIA 2011a), and confined our study to gas wells within three states in these regions of interest. Texas, Pennsylvania, and Colorado were selected to allow a comparison between state setback laws. We used the definition of "gas well" as defined by the International Association of Oil and Gas Producers (OGP) as one which has an estimated gas:oil ratio of > 1,000 (OGP 2010). We first reviewed the intended purpose of setbacks and the distances utilized. We then conducted an analysis of federal and state laws in Texas, Pennsylvania, and Colorado. In addition, Texas had municipal ordinances in place that were preempted by state law in 2015, and these were examined as well.

To determine whether current setbacks provide adequate distance in the case of a well blowout, we compiled historical blowout incidents and evacuations within the Texas Barnett Shale, the Pennsylvania Marcellus Shale, and the Colorado Niobrara Shale. Measurable evacuation zones in adjacent states within the target shale plays were included if available. We used the definition of "blowout" from the OGP as "an incident where formation fluid flows out of the well or between formation layers after

Address correspondence to M. Haley, Magee-Women's Hospital of UPMC, 300 Halket St., Pittsburgh, PA 15213 USA. Telephone: (412) 641-4600. E-mail: haleym@upmc.edu

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The other author (E.F.B) declares she has no actual or potential competing financial interests.

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all the predefined technical well barriers or the activation of the same has failed" (OGP 2010). In our analysis, we included Level 3 blowout events, which are defined as those that present serious and immediate risks to personnel, equipment, and the environment, and warrant the immediate activation of an emergency response plan. Surface blowouts and underground blowouts with insufficient casing fall into this category (Wild Well Control, Inc., and Travelers Indemnity Company 2012). We compiled the data using state agency reports, literature sources, incident reports, and media reports from 1997 to 2015. Wherever possible, we reviewed multiple reports of the same event to determine consistency and veracity. This search revealed 16 relevant sources, which are referenced in the Results section. We recorded the number of homes/families displaced, using these terms interchangeably. Evacuation zones were reported in feet and/or miles (Table 1). We did not use individual evacuees or well workers in our mathematical data, but discussed them where appropriate.

Since natural gas is composed primarily of methane hydrocarbon, it is flammable within a certain range in air (Cashdollar et al. 1996). An ignition source at a natural gas well site has the potential to set off an explosion (Nguyen 2010). Hazard assessment studies from liquefied natural gas fires indicate the potential for thermal injury to humans from radiant heat (Raj 2008). At a well site, if the combustion process occurs in the open air, the gas will burn at a constant pressure, allowing the gas to expand during the process (Arrington 2014). To estimate the radiant heat effects on humans from a natural gas well fire, we applied thermal modeling to a typical gas well. Allowing for a constant pressure and changing volume, the adiabatic flame temperature of methane is 1,950°C (3,452°F). We applied the Stefan-Boltzmann Law to a typical gas well producing 5.8 million ft^3/day with a pipe diameter up to 6 in. An average well is producing 549 times the fuel needed to supply a 1 ft^2 flux area. This assumes a flame ball of 549 ft^2, metric conversion of 51 m^2, with reduction of 1 m^2 to allow for a standard industry claim of 98% efficiency decline for a flare (Arrington 2014).

In addition to blowouts and radiant heat, potential hazards from hydraulic fracturing include vapor and toxic gas clouds. Shale gas often contains tens or hundreds of parts per million (ppm) of hydrogen sulfide (H_2S) (Weiland and Hatcher 2012), a flammable gas with known adverse respiratory and nervous systems effects [Agency for Toxic Substances and Disease Registry (ATSDR) 2014]. We included one recent (2014) reference each from Texas, Pennsylvania, and Colorado on H_2S measured in proximity to natural gas wells. We reviewed a 2005 report that was prepared for the U.S. Department of Transportation (DOT), Office of Pipeline Safety detailing the potential impact radius (PIR), which can be obtained to determine the possible impact on people or property in the case of failure of natural gas infrastructure (U.S. DOT 2005). A series of best-fit equations were used to relate release rate to distance to toxic end points based on information presented in the U.S. Environmental Protection Agency (EPA) Risk Management guidance document (U.S. EPA 2015b), assuming a 10-min peak-release period (U.S. DOT 2005). We also reviewed a 2011 report by the Fort Worth League of Neighborhoods. The League convened a committee of scientific and health professionals to review air testing data in the vicinity of gas drilling activities in the Barnett Shale. Their report included data from private tests by GD Air Testing Inc., Texas Commission on Environmental Quality (TCEQ 2010), and the Barnett Shale Energy Education Council's industry-funded study conducted by Titan Engineering (Barnett Shale Energy Education Council 2010). Dispersion modeling was performed to predict the way pollutants might travel from their source (Fort Worth League of Neighborhoods 2011). We used the results from these two studies to determine whether current setback distances provide adequate distance from clinically significant sulfide exposure, based on OSHA and NIOSH adult short-term exposure regulatory and recommended limits (U.S. Department of Labor 2015). Hydrogen sulfide levels are reported in ppm and carbon disulfide levels are reported in milligrams per cubic meter (mg/m^3) (Table 1).

Air pollution sources from shale gas extraction and its related activities include emissions from engines powering the drilling and hydraulic fracturing operations, equipment used to capture and transport the gas on site, venting, blowdowns, and flaring. Air pollutants include particulate matter, carbon monoxide, nitrogen dioxide, methane, and VOCs (Lattanzio 2013). Notable among the list of VOCs are the BTEX (Benzene, Toluene, Ethyl benzene and isomers of Xylene) compounds, which tend to be found ubiquitously at drill sites (Leusch and Bartlow 2010). In an exploratory study, benzene was the most common BTEX to exceed health-based risk levels (Macey et al. 2014). In addition, benzene is well-studied with regard to deleterious effects on humans (CDC 2013). We therefore focused on benzene for our air pollution analysis. Benzene levels are reported in both parts per billion (ppb) and micrograms per cubic meter ($\mu g/m^3$) to allow comparison between studies (Table 1).

We did not include data from predominantly oil sites, pipeline explosions, or compressor stations. Although we used Occupational Safety & Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH) data (U.S. Department of Labor 2015), we did not include studies of occupational safety and exposure. We did not address drinking well, aquifer, and natural water contamination by formation fluids and hydraulic fracturing fluid.

Results

Geography and Production

The Barnett Shale, the largest natural gas play in Texas (Airhart 2015), is located in the north-central part of the state, extending over a total area of 5,000 mi^2. It lies below the surface of 25 counties in Texas, 4 of these being core counties with the highest gas production (Railroad Commission of Texas 2015a). The Barnett shale produces primarily methane, and the producing gas-oil ratio in the core areas of the Barnett shale is above 100,000 standard ft^3/stock tank barrels (Holme 2013). There are approximately 18,000 to 19,000 producing gas wells in the Barnett Shale (Barnett Shale Energy Education Council 2012); the majority of these are horizontal wells that employ hydraulic fracturing (U.S. EIA 2011b).

The Marcellus Shale covers 95,000 mi^2 and stretches across eight states: New York (which currently has a hydraulic fracturing ban) (Klopott 2015); Pennsylvania (which has the most drilling in the Marcellus Shale) (Penn State Public Broadcasting 2014); West Virginia, Ohio, Maryland, and smaller portions of Virginia, Tennessee, and Kentucky. The shale play covers an estimated 64% of Pennsylvania (Curtis 2011), approximately 29,500 mi^2. The Marcellus is a predominantly methane-producing shale play (Holme 2013). By 2012, Marcellus Shale drilling had affected 0.07% of the total land area of the state (Penn State Public Broadcasting 2014). In 2013, Pennsylvania had over 57,000 producing gas wells; the

Table 1. Analysis parameters, methods, and units of measurement.

Parameter	Methods	Units
Thermal exposure	Modeling	kW/m^2
Vapor dispersion (hydrogen sulfide)	Measurements and modeling (literature review)	Concentration (ppm) and distance
Vapor dispersion (carbon disulfide)	Measurements (literature review)	Concentration (mg/m^3) and distance
Air pollution (benzene)	Measurements (literature review)	Concentration ($\mu g/m^3$ and ppb)

majority of new wells drilled in Pennsylvania are directional (U.S. EIA 2015).

The Niobrara Shale is situated in Northeastern and Northwestern Colorado and also covers portions of adjacent Wyoming, Nebraska, and Kansas. Natural gas is produced primarily from the Piceance Basin and gas and oil from the Denver-Julesburg (D-J) Basin (Higley and Cox 2007); it is one of the top 10 sources of natural gas in the United States (U.S. EIA 2009). There are approximately 15,000 gas wells in the Colorado Niobrara (Colorado Geological Survey 2011). Over 90% of new gas wells in Colorado use hydraulic fracturing (Weiner 2014).

Policies and Oversight

Natural gas well setbacks are determined at the state and, in some cases, municipality level (the exception to this is when drilling occurs near public work projects, such as dams and critical structures; in these cases federal regulation applies) (Fry 2013). In general, the source for a setback distance is considered to be the well bore, although this is not specifically indicated in all statutes. As discussed below, setback distances vary among the three states we studied (Table 2), and all three have variances which can shorten the distance.

Within the Barnett Shale of Texas, setbacks are designed to protect the health, safety, and welfare of residents; protect the rights of property owners; safeguard environmental quality; and promote efficient gas extraction. The Railroad Commission of Texas (RRC) is responsible for activities associated with oil and gas, including exploration, extraction, production, and transport (Fry 2013). The RRC does not directly determine setback distances; per Texas State Legislature Section 253.005c, a well "may not be drilled in the thickly settled part of the municipality or within 200 feet of a private residence" (Texas State Legislature 2009). In Texas, variances are granted "to prevent waste or to prevent the confiscation of property" (RRC 2015c). The majority of applications for gas drilling in the Dallas/Fort Worth Metroplex area contain a distance setback variance request (Welch 2015). Many municipalities consider the minimum setback to be too close and have established local setback distances. For example, setback rules vary among the 26 municipalities in heavily drilled Denton County, with a range of 300–1,500 ft, mode of 1,000 ft. With variance, the range is 150–1,125 ft, mode of 300 ft (Fry 2013). Recently, the state of Texas passed into law H.B. No. 40, which preempts regulation of oil and gas operations by municipalities (Texas State Legislature 2015); therefore all sites will presumably be required to conform to state law—even those such as the city of Denton, which had previously banned hydraulic fracturing entirely.

In Pennsylvania, setback distances are determined by the state legislature and enforced primarily by the Pennsylvania Department of Environmental Protection (PA DEP 2014b). In February of 2012, the Pennsylvania General Assembly enacted the Omnibus Amendment to the Oil and Gas Act (commonly known as Act 13), intended to strengthen environmental standards for unconventional shale gas extraction (Pennsylvania General Assembly 2012). According to Title 58, Section 3215 of the Pennsylvania Legislature, the current setback distance to buildings is 500 ft, unless the owner of the structure consents to a shorter distance (Pennsylvania General Assembly 2016). PA DEP may grant a variance from these distance restrictions if the well operator submits a plan identifying additional measures. Also, existing active well sites are "grandfathered" in and new wells can be drilled closer than 500 ft from a dwelling at such sites (PA DEP 2014b).

In Colorado, setbacks are determined by the Colorado Oil and Gas Conservation Commission (COGCC). The stated purpose of setbacks is to "protect the safety and welfare of the general public from environmental and nuisance impacts resulting from oil and gas development in Colorado, including spills, odors, noise, dust, and lighting" (COGCC 2013). In 2013, 2 CCR 404-1 Cause No. 1R Docket No. 1211-RM-04 established new rules for statewide setbacks (COGCC 2013). The distance is 500 ft from buildings (such as homes and commercial facilities), 1,000 ft from high-occupancy buildings (schools, day care centers, hospitals, nursing homes, and correctional facilities), 350 ft from outdoor recreational areas (playgrounds and sports fields), and 150 ft from a surface property line. Energy companies are also expected to employ mitigation measures to reduce the impact of their operations upon the public. Variances may be granted for existing wells, if the operator employs mitigation reassures, or if alternate locations are technically or economically impractical (COGCC 2013).

Federal laws provide for clean air (U.S. EPA 2015d); however, with few exceptions, natural gas extraction activities are exempt from these laws (NRDC 2013). Under federal law, gas well operators must comply with Title 40 of the Code of Federal Regulations, which outline emission standards and compliance schedules for the control of VOCs and sulfur dioxide (SO_2) emissions (U.S. EPA 2012b). The United States Environmental Protection Agency (EPA) requires gas well operators to utilize green completions (capturing of excess gas instead of releasing it into the atmosphere) to reduce air pollution from VOCs (U.S. EPA 2012a). According to Title 40 Subpart 0000 §60.5375, if state rules are more stringent and do not otherwise conflict with federal regulations, state law will prevail (U.S. EPA 2012b). In Texas, air quality is managed by TCEQ (RRC 2015a). In Pennsylvania, the PA DEP has the authority to regulate air quality, and operators are required to utilize detection and repair methods to control volatile organic compounds and associated hazardous air pollutants (PA DEP 2014a). In Colorado, emissions are overseen by the Colorado Department of Public Health and Environment (2013).

Thermal exposure criteria are regulated on a national basis. The National Fire Protection Association (NFPA; see http://www.nfpa.org/about-nfpa) is a global nonprofit organization which sets standards to eliminate death, injury, property and economic loss due to fire, electrical and related hazards. Liquid Natural Gas (LNG) Standard, NFPA 59A, sets limits in terms of maximum heat flux. For human outdoor exposure the limiting heat flux is 5 kW/m^2 (kilowatt per square meter) (NFPA 2015). The thermal radiation protection requirements in the U.S. Department of Transportation Regulations in 49 CFR, part 193 (U.S. GPO 2015) specify essentially the same requirements as NFPA 59A. The U.S. Department of Housing and Urban Development (HUD) regulations, which are applicable to HUD-assisted residential projects, have a much lower threshold of 1.4 kW/m^2 (HUD 1982).

Raw natural gas contains hydrogen sulfide (H_2S), which is classified by the EPA as a hazardous air pollutant (U.S. EPA 2015d). Due to its toxicity, flammability, and corrosive properties, H_2S is an important component to control at all stages of natural gas handling. H_2S has destructive effects on natural gas extraction and transportation equipment; there is also a threat to personnel working at natural gas sites (Ratner and Tiemann 2015). The U.S. Department of Labor recommends well-site management based on potential exposure to H_2S. OSHA set a ceiling limit of 20 ppm for hydrogen sulfide in workplace air, which is a 15-min time-weighted average that cannot be exceeded at any time during the working day. NIOSH recommends a 10-min ceiling level of 10 ppm for workers; 100 ppm is immediately dangerous to life

Table 2. Legal setback distances by state.

State	Minimum setback distance from buildings without variance
Texas	200 ft
Pennsylvania	500 ft
Colorado	500 ft (1,000 ft high occupancy)

or health of workers (U.S. Department of Labor 2015). A Minimal Risk Level of 0.07 ppm has been recommended by the ATSDR for acute-duration inhalation exposure to hydrogen sulfide, and a Minimal Risk Level of 0.02 ppm has been derived for intermediate-duration inhalation. Death has occurred after acute exposure to high concentrations (≥ 500 ppm) of hydrogen sulfide gas (ATSDR 2014). Carbon disulfide is another sulfide compound with neurotoxicological properties. OSHA 15-min exposure limit is 36 mg/m^3, and NIOSH 15-min limit is 30 mg/m^3 (ATSDR 1996).

Blowouts and Evacuations

Within the Barnett Shale between 1997 and 2006, there were 18 well blowouts—14 blowouts in Wise County and 4 in Denton County (Nguyen 2010). Since 2006, 16 blowouts have been reported by operators (RRC 2015b). A blowout in 2002 forced the evacuation of 30 homes in Haslet, TX (Nguyen 2010). In December 2005, an operator lost control of a Barnett Shale gas well in Palo Pinto County. The ensuing explosion blew a 750-ft-wide crater in the ground, and the fire burned uncontrollably for several days (Heinkel-Wolfe 2013; Nguyen 2010). On 22 April 2006, a blowout in Fort Worth required evacuation of 500 homes in a ½-mi radius. One worker was killed (Korosec 2006; Nguyen 2010). On 19 April 2013, a gas well blowout required evacuation of four homes and diversion of flights from the Denton Enterprise Airport (Heinkel-Wolfe 2013). On 11 April 2015, uncontrolled pressurized flowback required the evacuation of 100 homes and an evacuation zone of ⅛ mi (Arlington Voice 2015). On 7 May, lightning struck a gas well in Denton, resulting in an explosion and fire. No evacuation was ordered, but residents self-evacuated due to overwhelming smoke and fumes (Sakelaris 2015).

In June of 2010, a blowout in the Marcellus Shale of Clearfield County, Pennsylvania, spewed gas and drilling fluid 75 ft into the air, requiring closure of roads and a no-fly zone over the area. No evacuations were needed as there were no homes within 1 mi (Hurdle 2010; Nguyen 2010). On 7 June 2010, an explosion at a Moundsville, West Virginia, Marcellus shale well required burn unit hospitalization for seven people and closure of a highway (Nguyen 2010; Templeton and Hopey 2010). In April of 2011, a well blowout in Bradford County required evacuation of seven families (Casselman 2011). In June of 2012, a blowout in Tioga County required a 1-mi evacuation zone, with contingent plans for a 2-mi zone in case the well could not be brought under control (Detrow 2012). In March of 2013, a blowout in Wyoming County required a 1,500 ft evacuation zone and evacuation of three families (Legere 2013). On 11 February 2014, three gas wells exploded at a gas well site in Dunkard Township, Green County, Pa. The fire burned for 5 days, and well control was not regained until 2 weeks after the explosion. The accident killed one gas well worker and injured another. A ½-mi safety perimeter was established around the pad (RKR Hess 2014). At this rural site, no homes or businesses required evacuation (Santoni 2014). In September 2014, a blowout in Mercer County caused an evacuation of homes within a 1-mi radius of the well pad (CBS Pittsburgh 2014). In October 2014, a well rupture in adjacent Jefferson County, Ohio, Marcellus required evacuation of 400 families (Arenschield 2014).

In April of 2012, the operator lost control of a gas well in the Niobrara Shale of Wyoming, requiring evacuation of 67 residents within a 2.5 mi radius (Gebrekidan and Schneyer 2012).

Thermal Modeling

Damage from well-pad fires is a function of time and energy flux intensity and, in general, damage increases the longer a fire burns. In addition, the interval between blowout and gas ignition can affect the size of the resulting fireball and the extent of explosive damage. At a well site, if the combustion process occurs in the open air, the gas will burn at a constant pressure, allowing the gas to expand during the process (Arrington 2014). The risks to people and objects outside a vapor cloud fire arise primarily from radiant heat emitted by the fire (Raj 2007).

Applying the Stefan-Boltzmann Law to a typical gas well as described in the Methods section, at 500 ft the thermal exposure would be 2.98 kW/m^2; at 350 ft the thermal exposure would be 6 kW/m^2 (Arrington 2014).

Vapor Dispersion

Measurements of H_2S in four core counties in the Barnett Shale showed that 8.0% of wells had hydrogen sulfide concentrations > 4.7 ppb (0.0047 ppm) beyond the fence line (Eapi et al. 2014). PA DEP has designated 19 wells as "Special Caution Areas" due to elevated levels of H_2S encountered during drilling, defined as > 20 ppm (PA DEP 2014b), which is above the 15-min OSHA ceiling limit (U.S. Department of Labor 2015). In a community–based grab sample study, one in five samples in Colorado contained H_2S that exceeded ATSDR intermediate minimal risk levels (Macey et al. 2014).

PIR calculations presented in the U.S. DOT report resulted in a hydrogen sulfide toxic gas cloud radius of 0.27 mi (1,426 ft) for urban conditions and 0.37 mi (1,954 ft) for rural conditions (U.S. DOT 2005).

In the report by the Fort Worth League of Neighborhoods (2011) described in the Methods section, various sulfur compounds were detected at extremely high levels. The neurotoxin carbon disulfide was found at levels 300 times the norm for ambient urban air. Based on the testing results, dispersion modeling was performed for a drill site near an elementary school. The carbon disulfide plume extended 1 mi from the source; the full extent of plume was in excess of 2 mi. The model predicted up to 1,000 times the short term health benchmark for carbon disulfide, based on OSHA and NIOSH adult short-term exposure regulatory and recommended limits (ATSDR 1996). A second model on carbonyl sulfide was performed based on a site near three elementary schools and one high school. The plume extended in excess of 1 mi, with levels six times the health benchmark for carbonyl sulfide (Fort Worth League of Neighborhoods 2011).

Air Pollution

Within the Barnett Shale, air quality canister sampling identified 70 individual volatile organic compounds in the vicinity of gas wells and associated transport operation. The most abundant non-methane VOCs, accounting for approximately 90% of emissions, were ethane, propane, butane, and pentanes (Kibble et al. 2013). In 2009, TCEQ used infrared cameras to survey 94 natural gas sites in the Dallas-Fort Worth area in order to identify potential sources of emissions (Whiteley and Doty 2010). Air samples were collected at 73 of the sites; at 21 of those sites, benzene levels exceeded the U.S. EPA level for long-term health effects (ATSDR 2007), and 2 sites required immediate action for benzene levels high enough to pose an immediate threat to health and safety (Ethridge 2010). In 2010, testing by TCEQ confirmed that toluene and carbon disulfide, in addition to other chemicals, were being emitted by gas facilities in the Barnett Shale. Their report concluded that "gas production facilities can, and in some cases do, emit contaminants in amounts that could be deemed unsafe" and that "35 chemicals were detected above appropriate short term comparisons" (TCEQ 2010; Fort Worth League of Neighborhoods 2011).

In a community-based study in Susquehanna County, Pennsylvania, 25% of grab samples from well pads and associated infrastructure contained benzene levels that exceeded the 1/100,000 U.S. EPA cancer risk level (Macey et al. 2014; U.S. EPA 2015c). McCawley, working for the West Virginia Department of Environmental Protection in May 2013, obtained air samples 625 ft from the well pad center at seven unconventional drilling sites in the West Virginia Marcellus,

specifically for the purpose of determining if the 625 ft setback established for West Virginia was adequate to protect public health (McCawley 2013). Five of the sites were locations of active drilling and completion activities, and two sites involved only site preparation work. There were 22 data points provided, 15 of which came from the five active sites, and 7 of which came from the two well-pad preparation sites, all located 625 ft away from the well pad center. Benzene was found at the highest concentration of any of the VOCs, although toluene was the single VOC found most frequently (Figure 1) (McCawley 2015). Benzene levels exceeded the ATSDR minimum risk level for acute exposure—9 ppb (28.7 μg/m^3) for exposure of 14 days or less—in 5 out of 15 samples, and at 3 out of the 5 active drilling sites. The two highest benzene values, 85 ppb (270 μg/m^3) and 49 ppb (160 μg/m^3), were found at a single site during hydraulic fracturing and flowback activities. Well-pad preparation was not associated with elevated benzene levels (McCawley 2013).

In Colorado, daily air samples collected by the National Oceanic and Atmospheric Administration Boulder Atmospheric Observatory revealed that oil and gas activities, including shale gas extraction, were strongly associated with alkane and benzene levels in the atmosphere (Pétron et al. 2012). McKenzie et al. (2012) performed a health risk assessment by analyzing samples collected by the Garfield County Department of Public Health and Antero Resources. In 2008, the Garfield County Department of Public Health collected ambient air well completion samples, including emissions from both uncontrolled flowback and supporting completion equipment such as trucks and generators. Samples were taken 130–500 ft from the well pad. In 2010, Antero Resources Inc. collected ambient air samples 350 and 500 ft from the well pad center during completion activities. No other hydrocarbon sources were in the vicinity of the sampling locations. These samples were compared with 163 samples taken from a fixed monitor in a rural natural gas development area 2,500 ft away from the nearest well pad. The median air level of benzene in the well completion samples was 2.6 μg/m^3 (0.82 ppb), which is below level of concern, but benzene samples were found to be highly variable: the 95% level of benzene was 20 μg/m^3 (6.26 ppb), which is right at the 6 ppb Minimal Risk Level for intermediate exposure (ATSDR 2007), and the maximum benzene level was 69 μg/m^3 (21.6 ppb), which is more than twice the 9 ppb minimal risk level for acute exposure (ATSDR 2007). The benzene levels in the natural gas development area, by contrast, never reached levels of concern for health impacts. Residents living within ½ mi of an unconventional gas well were found to have an increased risk of neurological and respiratory health effects than residents living greater than ½ mi away. The risk of cancer was increased in these residents as well, with benzene and ethylbenzene as the primary hydrocarbon contributors (McKenzie et al. 2012).

Discussion

In the 155 years since the first modern oil well was drilled in Pennsylvania, technology has evolved from the spring pole to modern rotary rigs that can drill miles into the earth (American Oil & Gas Historical Society 2015). The more recent technological advancement of horizontal hydraulic fracturing has changed the landscape of gas and oil production.

Natural gas has the potential for a smaller carbon footprint than historical fossil fuel sources; for instance, there are substantially lower emissions of nitrous oxides and carbon dioxide per Btu of energy produced compared to coal (U.S. EIA 2015). As a result of the ability to access unconventional formations, the United States is less dependent on foreign natural gas; the United States has now surpassed Russia as the world's largest natural gas producer (Ratner and Tiemann 2015). While the influx of wells and related natural gas infrastructure has advanced the economics of some individuals and communities (API 2014), questions remain about public health and safety when a heavy industrial process is placed close to the public. The consequence of these concerns is that public support for hydraulic fracturing is declining, and the industry realizes the need to minimize risks to communities and the environment (Dittrick 2015). Setbacks are an attempt to address this need. Our paper attempts to address whether the current setback laws in three heavily drilled states within the Barnett, Marcellus, and Niobrara shale plays are sufficient to protect public health and safety.

The majority of setback distances in the areas we studied are not derived from peer-reviewed data, data driven analysis, or historical events (Fry 2013)—they are a compromise between governments, the regulated community, environmental and citizen interest groups, and landowners (COGCC 2013). In part to address the issue of setbacks, the University of Maryland School of Public Health performed an in-depth analysis of the current data, and prepared a report for the Maryland Department of the Environment and the Department of Health & Mental Hygiene. The authors recommended a minimum setback distance of 2,000 ft from well pads (Maryland Institute for Applied Environmental Health 2014). Also in 2014, the New York State Department of Health (NY DOH) published the results of a Public Health Review process. In preparing the report, the NY DOH reviewed and evaluated scientific literature, obtained input from outside public health expert consultants, engaged in field visits and discussions with health and environmental authorities in states with hydraulic fracturing activity, and communicated with multiple local, state, federal, international, academic, environmental, and public health stakeholders. The DOH report concluded that hydraulic fracturing activity has resulted in environmental impacts that are potentially adverse to public health (NY DOH 2014). As a result of this study, the Concerned Health Professionals of New York recommended a moratorium on hydraulic fracturing in New York State until it could be determined whether the potential risks could be managed (Concerned Health Professionals of New York 2014); the state subsequently banned the practice altogether (Klopott 2015). Citing similar concerns of environmental contamination, some countries, including France, Bulgaria, and Scotland have current bans and moratoria on hydraulic fracturing (Patel 2015).

In the geographic areas we studied, the most common setback distances from buildings were 300 and 500 ft with a range of 150–1,500 ft. Based on historical catastrophic events, thermal modeling, vapor cloud modeling, and air pollution data, these distances do not appear sufficient to protect public health and safety. We address each of these subsections below.

Blowouts and Evacuations/ Thermal Modeling

Blowouts can cause drill pipe, mud, cement, fracking fluids, and produced water (water that has been used in the hydraulic fracturing process) to be ejected from the bore and expelled at high pressure. These drilling

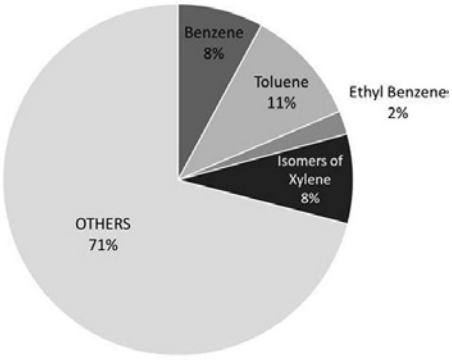

Figure 1. Distribution of chemical species of VOCs around Marcellus Shale drill sites.
Michael McCawley. Air Contaminants Associated with Potential Respiratory Effects from Unconventional Resource Development Activities. Seminars in Respiratory and Critical Care Med 2015;36:379–387, Thieme Publishers, www.thieme.com (printed by permission).

materials can be followed by production waters, gases and/or petroleum. Gas well blowouts can be very dangerous since a spark can set off an explosion (Nguyen 2010). Fires can involve other equipment on the well pad, releasing additional fumes, smoke, and volatiles (Arrington 2014). If members of the public are located in the vicinity, evacuations may be required, with a safety perimeter established around the well (Wild Well Control, Inc., and Travelers Indemnity Company 2012). Historical data indicate that blowout frequency is approximately 1 per 10,000 wells (OGP 2010). Published data from the Marcellus Shale indicates a blowout risk of 0.17%, with a well barrier or integrity failure rate of 6.3% for the years 2005–2013 (Davies et al. 2014); this is consistent with the historical numbers. Well blowout preventers are intended to control the internal well pressure; however, these blowout preventers are not failsafe (Nguyen 2010).

The Federal Emergency Management Agency (FEMA) Emergency Management Institute provides recommendations for emergency planning and response (Appendix 1) (FEMA 2015). During a level 3 event within the suburban setting, special consideration must be given to gas plume concentration/dispersion, smoke, hydrogen sulfide gas, explosions, heat radiation, and effects on buildings, homes, power lines, and nearby well and gas pipelines. Once the decision to evacuate is made, it should be done quickly and efficiently, with ongoing communication and assistance to evacuees (Wild Well Control, Inc., and Travelers Indemnity Company 2012). Based on thermal modeling, at 500 ft, the thermal exposure to those evacuating would be below the NFPA standard of 5 kW/m^2 (NFPA 2015). 2.7 kW/m^2 at 500 ft is what firefighters encounter and up to second degree burns will occur after 30 min or less of unprotected exposure, as indicated by sunburn type at 1.4 kW/m^2 at 30 min (Arrington 2014). API proposes a level of 6.3 kW/m^2 for situations in which emergency actions lasting up to 30 sec may be required by people without shielding but wearing clothing (API 2007). At the common Texas setback distance of 300 ft and the Colorado outdoor recreational distance of 350 ft, based on the calculation of radiant heat flux, second degree burn blisters would be expected to form after approximately 16 sec and 22 sec, respectively (Figure 2).

In the evacuation data we collected, the average evacuation zone was 0.8 mi (range of 660–13,200 ft) and the average number of homes/families displaced was 149 (range of 3–500 per event). Two incidents required aircraft diversion, one in the Barnett Shale (Heinkel-Wolfe 2013) and one in the Marcellus Shale (Nguyen 2010). An explosion in the Barnett Shale produced a 750 ft burn crater (Heinkel-Wolfe 2013; Nguyen 2010). The sizes of the evacuation zones, the number of families displaced, and the presence of a measurable burn crater, along with the thermal modeling data above, raise several questions: Does current unconventional gas well preplanning take into account *a*) the number of people to be evacuated from an area, *b*) the time it would take to evacuate, and *c*) the route needed for evacuation? Unfortunately, this does not appear to uniformly be the case. Wolverton (2010) published an Applied Research Project for the city of Shreveport, Louisiana, focusing on the hazards, challenges, and concerns regarding emergency response and public safety in relation to natural gas wells. For this study, a literature review was performed through the National Fire Academy's Learning Resource Center (U.S. Fire Administration 2016), search engines from the web, and published articles. Wolverton concluded that there was minimal research done on the topic of emergency response preplanning. In the Barnett shale area, some individual municipalities and gas companies develop and mail brochures to residents near gas wells, but this is not a uniform practice. Among the major challenges to responding to gas well hazards, Wolverton identified a lack of preplanning, inadequate resources, proximity to high-occupancy facilities, size of fires, and lack of training and equipment (Wolverton 2010).

During a level 3 event involving a gas well, officials should have a clear plan of notification, transportation, and evacuation routes for high-occupancy buildings. The COGCC appears to be considering this concept with the increased setback requirement for high-occupancy buildings, including schools (COGCC 2013). School evacuation protocols vary among states and districts; in general, in ideal circumstances, a fire drill evacuation is accomplished in several minutes. In an actual emergency, however, the evacuation time may be longer. For instance, after a school shooting in Connecticut, once the shelter in place was lifted, it took over 30 min to evacuate Sandy Hook Elementary School (Connecticut State Police 2013). Historical evacuation data, as well as the potential for thermal injury during an evacuation, should be taken into consideration when planning the location of a well.

Air Pollution/Vapor Dispersion

With variable frequency, benzene levels are elevated at multiple locations in close proximity to some gas development sites (Epstein 2016). This is not unexpected, considering that benzene occurs naturally in crude petroleum in levels up to 4 g/L (WHO 2010). At issue is that the frequency of elevated levels is sufficient to present a public health risk. Benzene is released from a number of natural gas extraction processes, and has the potential for adverse human health outcomes through inhalation exposure (Finkel et al. 2013).

In 2014, Bunch et al. (2014) published results of air monitoring from 4.6 million data points (representing data from seven monitors at six locations). Using a qualitative risk-based approach, the authors concluded that shale gas production activities have not resulted in exposures to VOCs, including benzene, at levels that would pose a health concern (Bunch et al. 2014). As discussed previously in this paper, however, other air monitoring studies have found benzene exceeding recommended

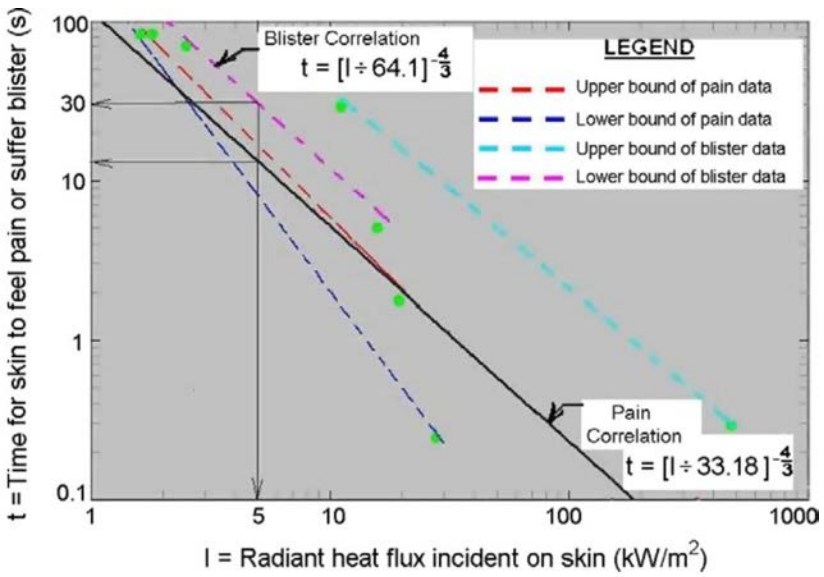

Figure 2. Range of experimental data on skin pain and skin burns and correlations of time for injury vs. incident radiant flux. (From Raj PK. A review of the criteria for people exposure to radiant heat flux from fires. *J Hazard Mater* 2008;159:61–71, with permission from Elsevier.)

health-based risk levels (McCawley 2013; McKenzie et al. 2012). Also notable is that multiple studies have found an association between proximity to natural gas well sites and adverse health outcomes, including congenital defects (McKenzie et al. 2014), decreased birth weight (Stacy et al. 2015), and increased hospitalization rates (Jemielita et al. 2015). These findings lend weight to the possibility that pollution from shale gas activities could potentially precipitate adverse health effects.

Hydrogen sulfide modeling has shown toxic gas cloud dispersion beyond even the most generous setback in our states of interest (U.S. DOT 2005). Dispersion modeling has also shown carbon dioxide and carbonyl sulfide plumes extending in excess of 1 mi from drill sites (Fort Worth League of Neighborhoods 2011). H_2S has an odor threshold of 0.01–1.5 ppm, whereupon people will begin to notice the unpleasant characteristic "rotten egg" smell. The odor becomes offensive at 3–5 ppm (U.S. Department of Labor 2015). Levels at which odor can be detected have been associated with mucosal irritation, respiratory symptoms, and need for anti-asthma drugs (ATSDR 2014). In a controlled setting, adults exposed to a range of H_2S from 0.05 to 5 ppm experienced anxiety and compromised verbal learning performance (Fiedler et al. 2008). At the basic science level, laboratory studies have shown genotoxicity and DNA damage from H_2S. Odor exposure is also associated with negative mood, stress, and annoyance for those living near H_2S-producing facilities (ATSDR 2014). Combined with the VOCs, this produces a potentially new set of exposures, possibly at distances of 2 km, which have not yet been well characterized nor well studied for their accompanying health effects. For example, there are recurring reports of nose bleeds and a metallic taste in populations living near drilling activity (McCawley 2015). A survey-based ambient health effects study showed that prevalence of dermal and respiratory complaints increased with proximity to drilling activities (Rabinowitz et al. 2015) (Table 3).

Air pollution from inadequate setbacks is of particular concern for vulnerable populations. The economically disadvantaged, people > 65 years old, and younger people with disabilities are most likely to have chronic health conditions which require institutional care (American Hospital Association 2011). In Pennsylvania, those living below the poverty line are significantly more likely to be exposed to pollution from unconventional gas wells (Ogneva-Himmelberger and Huang 2015). Children are a group that deserves special consideration, as physical vulnerabilities increase children and youth's susceptibility to illnesses, including asthma and other respiratory ailments (USDA 2012). Children are also more vulnerable to pollutants by nature of their developmental status (Pediatric Environmental Health Specialty Units 2011). These facts bring into particular question the wisdom of granting permits for unconventional gas wells in close proximity to schools and health care facilities, where a significant number of vulnerable individuals would be expected to be located.

With regard to air pollution associated with hydraulic fracturing, current setbacks do not appear to be fully protective. Although appropriately set distances may provide some measure of safety, setbacks do not necessarily reduce risk associated with potentially hazardous air emissions. Not all emissions emanate from the point of drilling and many may originate from distances as far away from the well pad as the setback distance itself, or even beyond. For example, when measured at the same setback distance for all the processes in an active drilling operation in the West Virginia study, the benzene concentration fluctuated substantially due to the proximity of the source to the setback distance (McCawley 2013). At the highest concentration, the source (a flare) was immediately adjacent to the samplers, even though the samplers were 625 ft from the center of the well pad. In this scenario, a setback does nothing to control the location or strength of the multiple possible sources at a well site and so it cannot be considered a control at all.

Given the advantages of domestic natural gas development, the question arises as to whether the risks of hydraulic fracturing are acceptable, particularly in close proximity to the public. There are many accepted definitions and permutations of acceptable risk, depending on one's point of view. From a business standpoint, acceptable risk is generally considered to be injury or loss from an industrial process that is considered tolerable by a society in view of the political, social, and economic cost-benefit analysis. From a scientific standpoint, the Precautionary Principle, which is endorsed by multiple national and international agencies, states that in cases of serious or irreversible threats to the health of humans or ecosystems, acknowledged scientific uncertainty should not be used as a reason to postpone preventive measures (WHO 2004). The U.S. EPA calculates both non-cancer and cancer risks from chemical exposure. Non-cancer risk is calculated by comparing the estimated daily intake of the chemical over a specific time period with the reference dose for that chemical derived for a similar period of exposure. Cancer risk is the probability that an exposed individual will develop cancer due to that exposure by age 70. For each chemical of concern, this value is calculated from the daily intake of the chemical from the site averaged over a lifetime, including a slope factor. In general, the U.S. EPA considers excess cancer risks that are below about 1 chance in 1,000,000 to be so small as to be negligible, and risks above 1 in 10,000 to be sufficiently large that some sort of remediation is preferred. The level of total cancer risk that is of concern, however, is a matter of personal, community, and regulatory judgment (U.S. EPA 2015c). Our findings represent an important case study for the science of risk assessment and public policy decisions of risk management. In the United States, risk management strategies for gas development vary widely by state, including acceptance of large-scale development (Texas, Pennsylvania, Colorado); more cautious consideration with extended controls and protections (Maryland); and outright bans (New York). The question remains as to whether society will continue to accept the level of risk associated with shale gas development given its potential benefits.

There are at least some additional actions to help to mitigate risk. The report by Wolverton (2010) highlighted the need for comprehensive planning prior to drilling. For detection of air pollution, air monitors could be placed at sensitive locations, and the sites connected to a central monitoring station by cellular phone or Wi-Fi to record air emission levels 24 hr a day. When the desired levels are exceeded, engineers would investigate to seek the source and report not only the cause, but also the steps taken to prevent a recurrence. Monitoring of all pertinent hazards could be considered for future regulations in conjunction with setbacks (Ziemkiewicz et al. 2014). In addition, the standard method of measuring air quality, using periodic 24-hr averages, does not accurately reflect the intensity, frequency or duration of meaningful exposure to the pollutants associated with the hydraulic fracturing process (Brown et al. 2014). Another factor to consider is well density. Risk calculations for environmental hazards are often based on measurements from a single source (U.S. EPA 2015a). In today's hydraulic fracturing environment, however, public exposure can come from multiple sources–either from multiwell pads or single well pads in proximity to one another. Simultaneous operations can introduce multiple hazards carrying additional

Table 3. Prevalences of reported respiratory disease in areas near drill sites (Rabinowitz et al. 2015).

Respiratory symptoms	< 1 km (N = 150)	1–2 km (N = 150)	> 2 km (N = 192)
Upper respiratory [n (%)]	58 (39)	46 (31)	35 (18)
Lower respiratory [n (%)]	29 (19)	29 (19)	27 (14)

risks (Boquist 2014). Applying accurate and comprehensive measurement techniques, along with mitigation factors, could allow selection of a setback based on the level of control exercised and maintained rather than on arbitrary distances set by legislative compromise.

Limitations

Our present study has some limitations. There are over 20 shale plays in the lower 48 United States (U.S. EIA 2011a); by confining our study to 3 shale plays, the scope of data was narrowed. We also limited our study to well sites. Excluding pipelines limited data on explosions and evacuations (Riordan Seville 2014), and excluding compressor stations restricted air pollution results (Shogren 2011). An inclusive study of the outcomes outlined in this study would include the wells and the potential contribution from necessary accompanying infrastructure.

Some of the evacuation data and noise complaint cases were gathered from media reports, which can introduce reporting errors and/or bias. Whenever possible, we evaluated information from multiple sources to determine consistency. Not all well blowouts required evacuations or had evacuation data available; for our analysis, we focused on those blowouts for which we could report an evacuation distance and/or number of families displaced.

Our air pollution analysis is by no means comprehensive. In the past several years, more data have emerged regarding air pollution related to hydraulic fracturing. Studies have varied in methods of collection and analysis; however, multiple studies show air pollutants at levels which raise health concerns (Shonkoff et al. 2014). We focused on those studies which raised concern regarding benzene and H_2S levels; a more thorough air pollution analysis would include nitrogen oxides, ozone, particulate matter, and the spectrum of VOCs (Shonkoff et al. 2014). In addition, benzene levels are characterized by high variability, which can result in inconsistencies within and between studies. Compounding the difficulty is the fact that air pollution varies widely, and there is an unmet need to study the episodic nature of air pollutant emissions.

Our thermal modeling was based on an average gas well. At each site, it is crucial to take into account the local geography, weather patterns, engineering specifics of each particular well, and nearby structures, which was not feasible for the purposes of this study.

Conclusion

Current natural gas well setbacks in the Barnett Shale of Texas, the Marcellus Shale of Pennsylvania, and the Niobrara Shale of Colorado cannot be considered sufficient in all cases to protect public health and safety. Based on historical evacuations and thermal modeling, people within these setback distances are potentially vulnerable to thermal injury during a well blowout. According to air measurements and vapor dispersion modeling, the same populations are susceptible to benzene and hydrogen sulfide exposure above health-based risk levels. Texas, Pennsylvania, and Colorado should consider adopting more generous setback distances, particularly in reference to vulnerable populations; however, distance is not an absolute measure of protection. Unfortunately, there is no defined setback distance that assures safety. As mitigation technology advances, current setback distances may eventually be sufficient to protect the public. Unfortunately, current mitigations are not fail-safe, and each has its limitations (U.S. Forest Service 2011). The results of our analysis based on three states suggest that assuming the threat posed to health originates from either the center of the drill pad or some small distance surrounding it requires reevaluation. A combination of a reasonable setback with accompanying controls on all aspects of the process is the best method for reducing the potential threats to public health.

Appendix 1. FEMA EMI recommendations for emergency planning and response (FEMA 2015).

Emergency planners should anticipate both active and passive resistance to the planning process and develop strategies to manage these obstacles.
Preimpact planning should address all hazards to which the community is exposed.
Preimpact planning should elicit participation, commitment, and clearly defined agreement among all response organizations.
Preimpact planning should be based upon accurate assumptions about the threat, typical human behavior in disasters, and likely support from external sources such as state and federal agencies.
EOPs should identify the types of emergency response actions that are most likely to be appropriate, but encourage improvisation based on continuing emergency assessment.
Emergency planning should address the linkage of emergency response to disaster recovery and hazard mitigation.
Preimpact planning should provide for training and evaluating the emergency response organization at all levels—individual, team, department, and community.
Emergency planning should be recognized as a continuing process.

References

Airhart M. 2015. The Barnett Shale Gas Boom: Igniting a Hunt for Unconventional Natural Gas Resources. Jackson School of Geosciences, University of Texas at Austin. Available: http://geology.com/research/barnett-shale-gas.shtml [accessed 15 June 2015].

American Hospital Association. 2011. Caring for Vulnerable Populations. Chicago, IL:American Hospital Association. Available: http://www.aha.org/research/cor/content/caring_vulnerable_populations_report.pdf [accessed 27 July 2015].

American Oil & Gas Historical Society. 2015. Making Hole – Drilling Technology. Available: http://aoghs.org/technology/oil-well-drilling-technology/ [accessed 17 June 2015].

American Public Health Association. 2012. The Environmental and Occupational Health Impacts of High-Volume Hydraulic Fracturing of Unconventional Gas Reserves. Available: https://www.apha.org/policies-and-advocacy/public-health-policy-statements/policy-database/2014/10/02/15/37/hydraulic-fracturing [accessed 28 January 2016].

API (American Petroleum Institute). 2007. Pressure-relieving and Depressuring Systems: ANSI/API Standard 521: ISO 23251 (Identical), Petroleum and Natural Gas Industries, Pressure-relieving and Depressuring Systems. 5th ed. Washington, DC:API.

API. 2014. Hydraulic Fracturing: Unlocking America's Natural Gas Resources. Available: http://www.api.org/~/media/Files/Oil-and-Natural-Gas/Hydraulic-Fracturing-primer/Hydraulic-Fracturing-Primer-2015-highres.pdf?la=en [accessed 27 July 2015].

Arenschield L. 2014. Most allowed back home after fracking-well blowout in eastern Ohio. *Columbus Dispatch*, Columbus, OH. 30 October 2014. Available: http://www.dispatch.com/content/stories/local/2014/10/29/well_explosion.html [accessed 27 July 2015].

Arlington Voice. 2015. Evacuation lifted in Arlington as gas well situation resolves [news story]. Arlington Voice, Arlington, TX. 11 April 2015. Available: http://www.arlingtonvoice.com/crime-emergency/story/apr/11/2015/west-arlington-residents-evacuated-report-gas-leak [accessed 15 June 2015].

Arrington B. 2014. Ring of Safety. Available: http://cogccuat.state.co.us/RR_HF2012/setbacks/CommentDocs/Public/Arrington_Comment.pdf [accessed 17 June 2015].

ATSDR (Agency for Toxic Substances and Disease Registry). 1996. Toxicological Profile for Carbon Disulfide. Available: http://www.atsdr.cdc.gov/toxprofiles/tp82.pdf [accessed 2 February 2016].

ATSDR. 2007. Toxicological Profile for Benzene. Available: http://www.atsdr.cdc.gov/toxprofiles/tp3.pdf [accessed 1 February 2016].

ATSDR. 2014. Toxicological Profile for Hydrogen Sulfide and Carbonyl Sulfide. Available: http://www.atsdr.cdc.gov/toxprofiles/tp114.pdf [accessed 2 February 2016].

Barnett Shale Energy Education Council. 2010. At-A-Glance: Air Quality Study Facts. Available: http://www.bseec.org/at_a_glance_air_quality_study_facts [accessed 2 February 2016].

Barnett Shale Energy Education Council. 2012. Barnett

Shale Natural Gas Wells Are Very Productive. Available: http://www.bseec.org/barnett_shale_natural_gas_wells_are_very_productive [accessed 15 June 2015].

Begos K. 2014. Fracking for Natural Gas Still Controversial, But Bringing Windfall of Revenue to Some Rural Areas. Associated Press. Available: http://www.oregonlive.com/business/index.ssf/2014/01/fracking_for_natural_gas_still.html [accessed 28 January 2016].

Boquist E. 2014. Multiwell Pad Drilling, Simultaneous Operations Introduce Unique Risks. The American Oil and Gas Reporter. Available: https://www.travelers.com/business-insurance/specialized-industries/oil-gas/docs/American-Oil-Gas-Reporter-12-14.pdf [accessed 11 September 2015].

Brown D, Weinberger B, Lewis C, Bonaparte H. 2014. Understanding exposure from natural gas drilling puts current air standards to the test. Rev Environ Health 29:277–292.

Bunch AG, Perry CS, Abraham L, Wikoff DS, Tachovsky JA, Hixon JG, et al. 2014. Evaluation of impact of shale gas operations in the Barnett Shale region on volatile organic compounds in air and potential human health risks. Sci Total Environ 468–469:832–842.

Cashdollar KL, Zlochower IA, Green GM, Thomas RA, Hertzberg M. 1996. Flammability of methane, propane, and hydrogen gases. Centers for Disease Control and Prevention. Available: http://www.cdc.gov/niosh/mining/UserFiles/works/pdfs/fompa.pdf [accessed 24 June 2015].

Casselman B. 2011. Pennsylvania gas-well blowout forces evacuation [news story]. Wall Street Journal. New York, NY. 20 April 2011. Available: http://www.wsj.com/articles/SB10001424052748704570704576275353686652670 [accessed 27 July 2015].

CBS Pittsburgh. 2014. Gas Well Fire Prompts Early Morning Evacuations In Mercer Co. Available: http://pittsburgh.cbslocal.com/2014/09/06/gas-well-fire-prompts-early-morning-evacuations-in-mercer-co/ [accessed 15 June 2015].

CDC (Centers for Disease Control and Prevention). 2013. Facts About Benzene. Available: http://www.bt.cdc.gov/agent/benzene/basics/facts.asp [accessed 15 June 2015].

Center for Chemical Process Safety. 2015. Mitigation Effect of High Expansion Foam on LNG Vapor Hazard. Available: http://www.aiche.org/academy/videos/conference-presentations/mitigation-effect-high-expansion-foam-on-lng-vapor-hazard [accessed 28 January 2016].

COGCC (Colorado Oil and Gas Conservation Commission). 2013. Exhibit C: Statement of Basis, Specific Statutory Authority, and Purpose: New Rules and Amendments to Current Rules of the Colorado Oil and Gas Conservation Commission, 2 CCR 404-1. Cause No. 1R. Docket No. 1211-RM-04: Setbacks. Order No. 1R-117. Available: http://cogcc.state.co.us/orders/orders/1R/117.html [accessed 2 February 2016].

Colorado Department of Public Health and Environment. 2013. Emissions Requirements for Oil and Gas Industry. State of Colorado. Available: https://www.colorado.gov/pacific/cdphe/emissions-requirements-oil-and-gas-industry [accessed 1 February 2016].

Colorado Geological Survey. 2011. Colorado's New Oil Boom—the Niobrara. Colorado Geological Survey Rocktalk 13(1):1–12.

Concerned Health Professionals of New York. 2014. Compendium of Scientific, Medical, and Media Findings Demonstrating Risks and Harms of Fracking (Unconventional Gas and Oil Extraction). Available: http://concernedhealthny.org/compendium/ [accessed 17 June 2015].

Connecticut State Police. 2013. Connecticut State Police-Western District Major Crime Squad. Available: https://assets.documentcloud.org/documents/841945/redacted-timeline-of-dec-14-2012.pdf [accessed 9 September 2015].

Curtis R. 2011. Where is Marcellus Shale Located in Pennsylvania? Institute for Energy and Environmental Research of Northeastern Pennsylvania, Marcellus Shale Information Clearinghouse. Available: http://energy.wilkes.edu/pages/153.asp [accessed 15 June 2015].

Davies RJ, Almond S, Ward RS, Jackson RB, Adams C, Worrall F, et al. 2014. Oil and gas wells and their integrity: implications for shale and unconventional resource exploitation. Mar Pet Geol 56:239–254.

Detrow S. 2012. Tioga County Methane Migration: Onetime Geyser Being Brought Under Control. NPR StateImpact. Available: https://stateimpact.npr.org/pennsylvania/2012/06/22/tioga-county-methane-migration-onetime-geyser-being-brought-under-conrol/ [accessed 27 July 2015].

Dittrick P. 2015. Study outlines policy strategy for unconventional development. Oil & Gas Journal Digital Edition. Tulsa, OK. 22 June 2015. Available: http://digital.ogj.com/ogjournal/20150622?sub_id=DKpr9MU3iH9cH&folio=23#pg24 [accessed 28 January 2016].

Eapi GR, Sabnis SS, Sattler ML. 2014. Mobile measurement of methane and hydrogen sulfide at natural gas production site fence lines in the Texas Barnett Shale. J Air Waste Manage Assoc 64(8):927–944.

Epstein AC. 2016. Health and environment risks from oil and gas development. In: Hydraulic Fracturing Impacts and Technologies: A Multidisciplinary Perspective (Uddameri V, Morse A, Tindle KJ, eds). Boca Raton, FL:CRC Press, 101–114.

Ethridge S. 2010. Texas Commission on Environmental Quality. Interoffice Memorandum. Subject: Health Effects Review of Barnett Shale Formation Area Monitoring Projects, including Phase I (August 24–28, 2009), Phase II (October 9–16, 2009), and Phase III (November 16–20, 2009); Volatile Organic Compound (VOCs), Reduced Sulfur Compounds (RSC), Oxides of Nitrogen (NOx), and Infrared (IR) Camera Monitoring, Document Number BS0912-FR. Available: http://www.tceq.state.tx.us/assets/public/implementation/barnett_shale/2010.01.27-healthEffects-BarnettShale.pdf [accessed 9 July 2015].

FEMA (Federal Emergency Management Agency). 2015. Emergency Management Institute. Preparedness for Emergency Response. Available: https://training.fema.gov/hiedu/docs/fem/chapter%209%20-%20preparedness%20for%20emergency%20response.doc [accessed 23 June 2015].

Fiedler N, Kipen H, Ohman-Strickland P, Zhang J, Weisel C, Laumbach R, et al. 2008. Sensory and cognitive effects of acute exposure to hydrogen sulfide. Environ Health Perspect 116:78–85, doi: 10.1289/ehp.10531.

Finkel ML, Hays J, Law A 2013. Modern natural gas development and harm to health: the need for proactive public health policies. ISRN Public Health 2013:408658, doi: 10.1155/2013/408658.

Fort Worth League of Neighborhoods. 2011. Recommendations for Policy Changes for Gas Drilling Near Schools. Report to ISD. Available: http://www.barnettshalenews.com/documents/ntxairstudy/FWLNA%20Report%20For%20FWISD%20Recommendations%20For%20Drilling%20Near%20Schools%20Feb%2022%202011.pdf [accessed 15 June 2015].

Fry M. 2013. Urban gas drilling and distance ordinances in the Texas Barnett Shale. Energy Policy 62:79–89.

Gallegos TJ, Varela BA. 2015. Trends in Hydraulic Fracturing Distributions and Treatment Fluids, Additives, Proppants, and Water Volumes Applied to Wells Drilled in the United States from 1947 Through 2010—Data Analysis and Comparison to the Literature. U.S. Geological Survey Scientific Investigations Report 2014–5131. Reston, VA: U.S. Geological Survey.

Gandossi L. 2013. An Overview of Hydraulic Fracturing and Other Formation Stimulation Technologies for Shale Gas Production. European Commission, Joint Research Centre, Institute for Energy and Transport. Available: http://publications.jrc.ec.europa.eu/repository/bitstream/111111111/30129/1/an%20overview%20of%20hydraulic%20fracturing%20and%20other%20stimulation%20technologies%20%282%29.pdf [accessed 27 January 2016].

Gebrekidan S, Schneyer J. 2012. Chesapeake well leaks in Wyoming, residents evacuate [news story]. Reuters U.S. Edition. New York, NY. 25 April 2012. Available: http://www.reuters.com/article/2012/04/25/us-chesapeake-natgas-blowout-idUSBRE83O18F20120425 [accessed 27 July 2015].

Goldstein BD, Broosk BW, Cohen SD, Gates AE, Honeycutt ME, Morris JB, et al. 2014. The role of toxicological science in meeting the challenges and opportunities of hydraulic fracturing. Toxicol Sci 139(2):271–283.

Heinkel-Wolfe P. 2013. Few answers in April gas well Blowout [news story]. Denton Record-Chronicle. Denton, TX. 27 July 2013. Available: http://www.dentonrc.com/local-news/local-news-headlines/20130727-few-answers-in-april-gas-well-blowout.ece [accessed 15 June 2015].

Higley DK, Cox DO. 2007. Oil and gas exploration and development along the front range in the Denver Basin of Colorado, Nebraska, and Wyoming. In: Petroleum Systems and Assessment of Undiscovered Oil and Gas in the Denver Basin Province, Colorado, Kansas, Nebraska, South Dakota, and Wyoming—USGS Province 39 (Higley DK, compiler). U.S. Geological Survey Digital Data Series DDS–69–P. Reston, VA:U.S. Geological Survey. Available: http://pubs.usgs.gov/dds/dds-069/dds-069-p/REPORTS/69_P_CH_2.pdf [accessed 15 June 2015].

Hoffman J. 2015. Potential Health and Environmental Effects of Hydrofracking in the Williston Basin, Montana. Geology and Human Health. Available: https://serc.carleton.edu/NAGTWorkshops/health/case_studies/hydrofracking_w.html [accessed 24 June 2015].

Holme A. 2013. Optimization of Liquid-Rich Shale Wells [Master's Thesis]. Trondheim, Norway:Norwegian University of Science and Technology, Department of Petroleum Engineering and Applied Geophysics.

HUD (U.S. Department of Housing and Urban Development). 1982. Urban Development Siting with Respect to Hazardous Commercial/Industrial Facilities. HUD Report HUD-777-CPD. Available: https://portal.hud.gov/hudportal/documents/huddoc?id=HUD-Guidebook.pdf [accessed 2 February 2016].

Hurdle J. 2010. RPT-Update 1 – Pennsylvania nat gas well capped after blowout [news story]. Reuters U.S. Edition. New York, NY. 4 June 2010. Available: http://www.reuters.com/article/idUSN0414919620100604 [accessed 15 June 2015].

Jemielita T, Gerton GL, Neidell M, Chillrud S, Yan B, Stute M, et al. 2015. Unconventional gas and oil drilling is associated with increased hospital utilization rates. Plos One 10:e0131093, doi: 10.1371/journal.pone.0131093.

Kibble A, Cabianca T, Daraktchieva Z, Gooding T, Smithard J, Kowalczyk G, et al. 2013. Review of the Potential Public Health Impacts of Exposures to Chemical and Radioactive Pollutants as a Result of Shale Gas Extraction. Public Health England, Centre for Radiation, Chemical, and Environmental Hazards. London, UK:Crown Copyright.

Klopott F. 2015. N.Y. officially bans fracking with release of seven-year study [news story]. Bloomberg Business. New York, NY. 29 June 2015. Available: http://www.bloomberg.com/news/articles/2015-06-29/n-y-officially-bans-fracking-with-release-of-seven-year-study [accessed 28 January 2016].

Korosec T. 2006. Gas-well issue gains urgency in Ft. Worth: worker's death puts residents on edge. Houston Chronicle, Knight Ridder/Chicago Tribune. Chicago, IL. 13 May 2006. Available: http://articles.chicagotribune.com/2006-05-13/news/0605130180_1_natural-gas-drilling-barnett-shale-city-task-force [accessed 15 June 2015].

Lattanzio RK. 2013. Air Quality Issues in Natural Gas Systems. Congressional Research Service #R42833. Available: http://www.civil.northwestern.edu/docs/Tight-Shale-Gas-2013/Air-Quality-Issues-Natural-Gas-Ratner-2013.pdf [accessed 15 June 2015].

Legere L. 2013. Wyoming County well malfunction causes spill, evacuation [news story]. Times-Tribune. Scranton, PA. 15 March 2013.

Leusch F, Bartkow M. 2010. A Short Primer on Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) in the Environment and in Hydraulic Fracturing Fluids. Southport, Queensland, Australia:Griffith University–Smart Water Research Centre, Department of Environment and Heritage Protection.

Macey GP, Breech R, Chernaik M, Cox C, Larson D, Thomas D, et al. 2014. Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study. Environ Health 13:82, doi: 10.1186/1476-069X-13-82.

Maryland Institute for Applied Environmental Health, School of Public Health, University of Maryland. 2014. Potential Public Health Impacts of Natural Gas Development and Production in the Marcellus Shale in Western Maryland. College Park MD:University of Maryland. Available: http://www.marcellushealth.org/uploads/2/4/0/8/24086586/final_report_08.15.2014.pdf [accessed 15 June 2015].

McCawley M. 2013. Air, Noise, and Light Monitoring Results for Assessing Environmental Impacts of Horizontal Gas Well Drilling Operations (ETD-10 Project). Morgantown, WV:West Virginia University School of Public Health. Available: http://wvwri.org/wp-content/uploads/2013/10/A-N-L-Final-Report-FOR-WEB.pdf [accessed 27 July 2015].

McCawley M. 2015. Air contaminants associated with potential respiratory effects from unconventional resource development activities. Semin Respir Crit Care Med 36(3):379–387.

McKenzie LM, Guo R, Witter RZ, Savtiz DA, Newman LS, Adgate JL. 2014 Birth outcomes and maternal residential proximity to natural gas development in rural Colorado. Environ Health Perspect 122:412–417, doi: 10.1289/ehp.1306722.

McKenzie LM, Witter RZ, Newman LS, Adgate JL. 2012. Human health risk assessment of air emissions from development of unconventional natural gas resources. Sci Total Environ 424:79–87.

NFPA. 2015. NFPA 59A: Standard for the Production, Storage, and Handling of Liquefied Natural Gas (LNG). Available: http://www.nfpa.org/codes-and-standards/document-information-pages?mode=code&code=59A [accessed 29 January 2016].

Nguyen P. 2010. Regulatory Options & Challenges in Hydraulic Fracturing. Washington Internships for Students of Engineering (WISE) and American Society of Mechanical Engineers (ASME): 5–248. Available: http://www.wise-intern.org/journal/2010/phinguyenwise2010.pdf [accessed 15 June 2015].

NRDC (National Resource Defense Council). 2013. NRDC Policy Basics: Fracking. Available: http://www.nrdc.org/legislation/policy-basics/files/policy-basics-fracking-FS.pdf [accessed 21 July 2015].

NY DOH (New York State Department of Health). 2014. A Public Health Review of High Volume Hydraulic Fracturing for Shale Gas Development. Available: http://www.health.ny.gov/press/reports/docs/high_volume_hydraulic_fracturing.pdf [accessed 2 February 2016].

Ogneva-Himmelberger Y, Huang L. 2015. Spatial distribution of unconventional gas wells and human populations in the Marcellus Shale in the United States: vulnerability analysis. Appl Geogr 60:165–174.

OGP (International Association of Oil and Gas Producers). 2010. OGP Risk Assessment and Data Directory: Blowout Frequencies. Report No. 434 – 2. Available: http://documents.mx/documents/ogp434-2blowoutfrequency.html [accessed 15 June 2015].

PA DEP (Pennsylvania Department of Environmental Protection). 2014a. Bureau of Air Quality, Commonwealth of Pennsylvania. Available: http://www.dep.pa.gov/Business/Air/Pages/default.aspx [accessed 2 February 2016].

PA DEP. 2014b. Office of Oil and Gas Management, Conservation Law Public Hearing. Available: http://www.dep.pa.gov/business/energy/oilandgasprograms/oilandgasmgmt/Pages/default.aspx [accessed 2 February 2016].

Patel T. 2015. Fracking in Europe: Fighting the revolution [news story]. Bloomberg Quick Take. Updated 19 May 2015. Available: http://www.bloombergview.com/quicktake/fracking-europe [accessed 1 February 2016].

Pediatric Environmental Health Specialty Units, American Academy of Pediatrics. 2011. PEHSU Information on Natural Gas Extraction and Hydraulic Fracturing for Health Professionals. Available: http://doa.alaska.gov/ogc/frac/fraccomments/HF29/HF29-17_PEHSU,%20Information%20on%20Natural%20Gas%20Extraction%20and%20Hydraulic%20Fracturing%20(Aug.%202011).pdf [accessed 27 July 2015].

Penn State Public Broadcasting. 2014. Public Media for Public Understanding: EXPLORE SHALE. Available: http://exploreshale.org/ [accessed 15 June 2015].

Pennsylvania General Assembly. 2012. Oil and Gas (58 PA.C.S.) – Omnibus Amendments. Act of Feb. 14, 2012. P.L. 87, No. 13. Available: http://www.legis.state.pa.us/WU01/LI/LI/US/HTM/2012/0/0013..HTM [accessed 2 February 2016].

Pennsylvania General Assembly. 2016. Title 58. Available: http://www.legis.state.pa.us/cfdocs/legis/LI/consCheck.cfm?txtType=HTM&ttl=58&div=0&chpt=23&sctn=15&subsctn=0 [accessed 2 February 2016].

Pétron G, Frost G, Miller BR, Hirsch AI, Montzka SA, Karion A, et al. 2012. Hydrocarbon emissions characterization in the Colorado Front Range: a pilot study. J Geophys Res 117:D04304, doi: 10.1029/2011JD016360.

Pless J. 2012. Natural Gas Development and Hydraulic Fracturing: A Policymaker's Guide. National Conference of State Legislatures. Available: http://www.ncsl.org/documents/energy/frackingguide_060512.pdf [accessed 15 June 2015].

Rabinowitz PM, Slizovskiy IB, Lamers V, Trufan SJ, Holford TR, Dziura JD, et al. 2015. Proximity to natural gas wells and reported health status: results of a household survey in Washington County, Pennsylvania. Environ Health Perspect 123:21–26, doi: 10.1289/ehp.1307732.

Raj PK. 2007. LNG fires: a review of experimental results, models and hazard prediction challenges. J Hazard Mater 140:444–464.

Raj PK. 2008. A review of the criteria for people exposure to radiant heat flux from fires. J Hazard Mater 159:61–71.

Ratner M, Tiemann M. 2015. An Overview of Unconventional Oil and Natural Gas: Resources and Federal Actions. Congressional Research Service: R43148. Available: https://www.fas.org/sgp/crs/misc/R43148.pdf [accessed 2 February 2016].

Riordan Seville L. 2014. Danger beneath: 'fracking' gas, oil pipes threaten rural residents [news story]. NBC News Investigations. 25 August 2014. Available: http://www.nbcnews.com/news/investigations/danger-beneath-fracking-gas-oil-pipes-threaten-rural-residents-n187021 [accessed 27 July 2015].

RKR Hess. 2014. Report on Chevron well explosion in Greene County, Pa [news story]. East Stroudsburg, PA. RKR HESS/UTRS, Inc. Available: http://www.rkrhess.com/report-on-chevron-well-explosion-in-greene-county-pa/ [accessed 15 June 2015].

RRC (Railroad Commission of Texas). 2015a. Barnett Shale Information. Available: http://www.rrc.state.tx.us/oil-gas/major-oil-gas-formations/barnett-shale-information/ [accessed 15 June 2015].

RRC. 2015b. Blowouts and Well Control Problems. Available: http://www.rrc.state.tx.us/oil-gas/compliance-enforcement/blowouts-and-well-control-problems/blowouts-and-well-control-problems-06-10/ [accessed 3 February 2016].

RRC. 2015c. Texas Administrative Code. Title 16: Economic Regulation, Part 1: Railroad Commission Of Texas, Chapter 3: Oil And Gas Division, Rule §3.37: Statewide Spacing Rule. Available: https://texreg.sos.state.tx.us/public/readtac$ext.TacPage?sl=R&app=9&p_dir=&p_rloc=&p_tloc=&p_ploc=&pg=1&p_tac=&ti=16&pt=1&ch=3&rl=37 [accessed 29 January 2016].

Sakelaris N. 2015. Gas well explodes in Denton after lightning strike [news story]. Dallas Business Journal. Dallas, TX. 8 May 2015. Available: http://www.bizjournals.com/dallas/news/2015/05/08/gas-well-explodes-in-denton-after-lightning-strike.html [accessed 15 June 2015].

Santoni M. 2014. Crews removing charred equipment, vehicles from well fire in Greene County [news story]. Pittsburgh Trib LIVE. Pittsburgh, PA.13 February 2014. Available: http://triblive.com/news/adminpage/5589207-74/gas-chevron-officials#axzz3h6VcWs5E [accessed 27 July 2015].

Shogren E. 2011. Air quality concerns threaten natural gas's Image [news story]. North Carolina Public Radio (Around the Nation). 21 June 2011. Available: http://www.npr.org/2011/06/21/137197991/air-quality-concerns-threaten-natural-gas-image [accessed 27 July 2015].

Shonkoff S, Hays J, Finkel ML. 2014. Environmental public health dimensions of shale and tight gas development. Environ Health Perspect 122:787–795, doi: 10.1289/ehp.1307866.

Stacy SL, Brink LL, Larkin JC, Sadovsky Y, Goldstein BD, Pitt BR, et al. 2015. Perinatal outcomes and unconventional natural gas operations in Southwest Pennsylvania. PLoS One 10:e0126425, doi: 10.1371/journal.pone.0126425.

TCEQ (Texas Commission on Environmental Quality). 2010. Barnett Shale Area Formation Monitoring Projects. Available: http://www.tceq.state.tx.us/assets/public/implementation/barnett_shale/2010.01.27-BarnettShaleMonitoringReport.pdf [accessed 2 February 2016].

Templeton D, Hopey D. 2010. 7 hurt in W.Va. gas well explosion. Pittsburgh Post-Gazette (Pittsburgh, PA) 7 June. Available: http://www.post-gazette.com/breaking/2010/06/07/7-hurt-in-W-Va-gas-well-explosion/stories/201006070145 [accessed 27 July 2015].

Texas State Legislature. 2009. Local Government Code. Title 8. Acquisition, Sale, or Lease of Property. Subtitle A. Municipal Acquisition, Sale, or Lease of Property. Chapter 253. Sale or Lease of Property by Municipalities. Lease of Oil, Gas, or Mineral Land. H.B. 2333, Sec. 253.005. Available: http://www.statutes.legis.state.tx.us/Docs/LG/htm/LG.253.htm#253.005 [accessed 2 February 2016].

Texas State Legislature. 2015. Relating to the exclusive jurisdiction of this state to regulate oil and gas operations in this state and the express preemption of local regulation of those operations. Texas H.B. No. 40, 2015-2016, 84R14474 T. Available: https://legiscan.com/TX/text/HB40/id/1160578 [accessed 2 February 2016].

USDA (U.S. Department of Agriculture). 2012. 4-H National Headquarters Fact Sheet: Vulnerable Populations. Available: https://nifa.usda.gov/sites/default/files/resource/Vulnerable%20Populations.pdf [accessed 23 June 2015].

U.S. Department of Labor. 2015. Occupational Safety & Health Administration. Safety and Health Topics: Hydrogen Sulfide. Available https://www.osha.gov/SLTC/hydrogensulfide/standards.html [accessed 23 June 2015].

U.S. DOT (U.S. Department of Transportation, Research and Special Programs Administration, Office of Pipeline Safety). 2005. TTO No. 14. Integrity Management Program: Delivery Order DTRS56-02-D-70036. Derivation of Potential Impact Radius Formulae for Vapor Cloud Dispersion Subject to 49 CFR 192. Final Report (OPS TTO14). Available: http://primis.phmsa.dot.gov/gasimp/docs/tto14_finalreport_january2005.pdf [accessed 27 July 2015].

U.S. EIA (U.S. Energy Information Administration). 2009. Top 100 Oil and Gas Fields. Available: http://www.eia.gov/oil_gas/rpd/topfields.pdf [accessed 15 June 2015].

U.S. EIA. 2011a. Review of Emerging Resources: U.S. Shale Gas and Shale Oil Plays. Available: http://www.eia.gov/analysis/studies/usshalegas/pdf/usshaleplays.pdf [access 15 June 2015].

U.S. EIA. 2011b. Technology Drives Natural Gas Production Growth from Shale Gas Formations. Available: http://www.eia.gov/todayinenergy/detail.cfm?id=2170 [accessed 28 July 2015].

U.S. EIA. 2015. Natural Gas. Available: http://www.eia.gov/naturalgas/ [accessed 28 July 2015].

U.S. EPA (U.S. Environmental Protection Agency). 2012a. EPA's Air Rules for the Oil & Natural Gas Industry. Summary of Requirements for Processes and Equipment at Natural Gas Well Sites. Available: http://www.epa.gov/airquality/oilandgas/pdfs/20120417summarywellsites.pdf [accessed 7 September 2015].

U.S. EPA. 2012b. Standards of Performance for Crude Oil and Natural Gas Production, Transmission and Distribution. Fed Reg 77(159):49542. Available: https://www.gpo.gov/fdsys/pkg/FR-2012-08-16/pdf/2012-16806.pdf [accessed 23 June 2015].

U.S. EPA. 2014. Oil and Natural Gas Sector Leaks. Available: http://www3.epa.gov/airquality/oilandgas/2014papers/20140415leaks.pdf [accessed 28 January 2016].

U.S. EPA. 2015a. Conducting a Human Health Risk Assessment. Available: http://www.epa.gov/risk/conducting-human-health-risk-assessment [accessed 1 February 2016].

U.S. EPA. 2015b. Guidance for Facilities on Risk Management Programs (RMP). Available: http://www.epa.gov/rmp/guidance-facilities-risk-management-programs-rmp [accessed 2 February 2016].

U.S. EPA. 2015c. HH: Risk Characterization. Available: https://www.epa.gov/risk/risk-characterization-handbook [accessed 1 February 2016].

U.S. EPA. 2015d. Summary of the Clean Air Act. Available: http://www.epa.gov/laws-regulations/summary-clean-air-act [accessed 29 January 2016].

U.S. Fire Administration. 2016. National Fire Academy. Available: https://www.usfa.fema.gov/training/nfa/index.html [accessed 1 February 2016].

U.S. Forest Service. 2011. Emission Reduction Techniques for Oil and Gas Activities. Available: http://www.fs.fed.us/air/documents/EmissionReduction-072011x.pdf [accessed 15 June 2015].

U.S. GPO (U.S. Government Publishing Office). 2015. Liquefied Natural Gas Facilities: Federal Safety Standards. 49 CFR § 193. Available: https://www.gpo.gov/fdsys/granule/CFR-2011-title49-vol3/CFR-2011-title49-vol3-part193 [accessed 29 January 2016].

Weiland RH, Hatcher NA. 2012. Approach Uses Tray Design to Optimize Treating Shale Gas Containing H2S and CO2. American Oil & Gas Reporter. Available: http://www.aogr.com/magazine/cover-story/approach-uses-tray-design-to-optimize-treating-shale-gas-containing-h2s-and [accessed 27 July 2015].

Weiner C. 2014. Oil and Gas Development in Colorado. Colorado State University. Available: http://extension.colostate.edu/topic-areas/family-home-consumer/oil-and-gas-development-in-colorado-10-639/ [accessed 15 June 2015].

Welch TS. 2015. Natural Gas Drilling and Its Effect on Property Values: A Municipal Perspective. American Bar Association 38:2. Available: http://www.americanbar.org/publications/state_local_law_news/2014-15/winter/natural_gas_drilling_and_its_effect_property_values_municipal_perspective.html [accessed 29 January 2016].

Whiteley T, Doty T. 2010. Texas Commission on Environmental Quality Barnett Shale Formation Area Monitoring Projects: Phase I- August 24–28, 2009, Phase II- October 9–16, 2009, Phase III- November 16–20, 2009 TCEQ Document Number B20912-FR. Available: http://www.tceq.state.tx.us/assets/public/implementation/barnett_shale/2010.01.27-BarnettShaleMonitoringReport.pdf [accessed 3 February 2016].

WHO (World Health Organization). 2004. The Precautionary Principle: Protecting Public Health, the Environment and the Future of Our Children. Available: http://www.euro.who.int/__data/assets/pdf_file/0003/91173/E83079.pdf [accessed 11 September 2015].

WHO. 2010. Exposure to Benzene: A Major Public Health Concern. Available: http://www.who.int/ipcs/features/benzene.pdf [accessed 23 June 2015].

Wild Well Control, Inc., Travelers Indemnity Company. 2012. Well Control Emergency Response Plan: U.S. Oil and Gas Land Operations. CP-7529. Houston,TX:Travelers Indemnity Company. Available: https://www.travelers.com/business-insurance/specialized-industries/oil-gas/docs/CP-7529%20OG%20Well%20Control%20Emergency%20Response%20Plan_6%205%2012.pdf [accessed 15 June 2015].

Wolverton ES. 2010. Pre-Planning Gas Well Sites in the City of Shreveport. Shreveport Fire Department and United States Fire Administration. Available: https://www.pdffiller.com/10313813-efo44974pdf-Scott-wolverton-shreveport-natural-gas-form-Various-Fillable-Forms-usfa-fema [accessed 23 June 2015].

Ziemkiewicz P, Quaranta JD, McCawley M. 2014. Practical measures for reducing the risk of environmental contamination in shale energy production. Environ Sci Process Impacts 16(7):1692–1699.

ATTACHMENT C

STUDY 27

ENVIRONMENTAL HEALTH

RESEARCH Open Access

Air concentrations of volatile compounds near oil and gas production: a community-based exploratory study

Gregg P Macey[1], Ruth Breech[2], Mark Chernaik[3], Caroline Cox[4], Denny Larson[2], Deb Thomas[5] and David O Carpenter[6*]

Abstract

Background: Horizontal drilling, hydraulic fracturing, and other drilling and well stimulation technologies are now used widely in the United States and increasingly in other countries. They enable increases in oil and gas production, but there has been inadequate attention to human health impacts. Air quality near oil and gas operations is an underexplored human health concern for five reasons: (1) prior focus on threats to water quality; (2) an evolving understanding of contributions of certain oil and gas production processes to air quality; (3) limited state air quality monitoring networks; (4) significant variability in air emissions and concentrations; and (5) air quality research that misses impacts important to residents. Preliminary research suggests that volatile compounds, including hazardous air pollutants, are of potential concern. This study differs from prior research in its use of a community-based process to identify sampling locations. Through this approach, we determine concentrations of volatile compounds in air near operations that reflect community concerns and point to the need for more fine-grained and frequent monitoring at points along the production life cycle.

Methods: Grab and passive air samples were collected by trained volunteers at locations identified through systematic observation of industrial operations and air impacts over the course of resident daily routines. A total of 75 volatile organics were measured using EPA Method TO-15 or TO-3 by gas chromatography/mass spectrometry. Formaldehyde levels were determined using UMEx 100 Passive Samplers.

Results: Levels of eight volatile chemicals exceeded federal guidelines under several operational circumstances. Benzene, formaldehyde, and hydrogen sulfide were the most common compounds to exceed acute and other health-based risk levels.

Conclusions: Air concentrations of potentially dangerous compounds and chemical mixtures are frequently present near oil and gas production sites. Community-based research can provide an important supplement to state air quality monitoring programs.

Keywords: Benzene, Community monitoring, Formaldehyde, Grab and passive samples, Hydraulic fracturing, Hydrogen sulfide, Oil and gas

* Correspondence: dcarpenter@albany.edu
[6]Institute for Health and the Environment, University at Albany, Rensselaer, New York, USA
Full list of author information is available at the end of the article

Background

New drilling and well stimulation technologies have led to dramatic shifts in the energy market. The Energy Information Administration forecasts that by the 2030s, the United States will become a net exporter of petroleum liquids such as shale oil [1]. Already an exporter of natural gas, the U.S. will retrieve nearly half of its gas from shale formations by that time [2]. Reserves such as shale oil and gas are referred to as "unconventional" because fuels within them do not readily flow to the surface [3]. Instead, they are distributed among tight sandstone, shale, and other geologic strata. Intensive practices are used to retrieve them, such as directional drilling (many kilometres underground and one or more kilometres horizontally through a formation) and hydraulic fracturing to break up the formation and ensure movement through source rock (using millions of gallons of water mixed with chemicals and sand, or "proppants") [4]. These technologies present public health challenges, including threats to air quality [5-7].

Unconventional oil and gas (hereinafter "UOG") development and production involve multiple sources of physical stressors (e.g., noise, light, and vibrations) [6], toxicants (e.g., benzene, constituents in drilling and hydraulic fracturing fluids) [8], and radiological materials (e.g., technologically-enhanced, naturally-occurring radioactive material) [9], including air emissions [10,11]. Air quality near UOG sites is an underexplored human health concern for several reasons. For a time, environmental scientists and regulators were primarily interested in potential impacts to surface and groundwater quality. High-profile impacts and the subsurface nature of technologies (e.g., hydraulic fracturing) encouraged this research trajectory [12]. This was true despite the fact that UOG development brings to the surface, in the case of natural gas, methane (78.3%), non-methane hydrocarbons (17.8%), nitrogen (1.8%), carbon dioxide (1.5%), and hydrogen sulfide (0.5%) [13]. These constituents, as well as emissions from combustion processes at the surface, are released to the air throughout the life cycle of a productive well [14].

Air emissions from UOG operations have been generally understood for some time – volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and criteria air pollutants such as NOx and $PM_{2.5}$ can be released at the wellhead, in controlled burns (flaring), from produced water storage pits and tanks, and by diesel-powered equipment and trucks, among other sources [15]. Yet the full range of emissions from drilling, well completion, and other activities remains elusive. New source categories are discovered, emissions from life cycle stages such as transmission and well abandonment have yet to be determined, and even stages such as drilling continue to present uncertainty [16]. We do not understand the extent of drilling-related air emissions as pockets of methane, propane, and other constituents in the subsurface are disturbed and released to the atmosphere [17]. Emissions measurements during flowback vary by orders of magnitude [18]. These and other data gaps limit the accuracy of state and federal emissions inventories, which compile and track known emissions sources. Inventories are also limited by self-reporting and data collection, and rely in some cases on outmoded emissions factors [15]. Flawed inventories constrain human health risk assessment and other research [7] and slow the identification of phenomena such as photochemical ozone production during winter months [19].

State pollution monitoring networks also constrain research on the air impacts of UOG development. Historically, air quality monitoring targeted urban areas, and criteria air pollutants such as particulate matter and ozone precursors were the primary chemicals of concern [10]. Monitoring stations were designed to ensure compliance with National Ambient Air Quality Standards (NAAQS) for a half-dozen pollutants. Even networks that focus on oil and gas emissions, such as one operated by public health officials in Garfield County, Colorado, do not target individual well pads. The Garfield County network encompasses five sites to monitor a suite of VOCs and (at three sites) particulate matter, in a jurisdiction that covers nearly 3,000 square miles of complex terrain [20]. The Texas Commission on Environmental Quality has arguably the most extensive monitoring network for UOG air emissions in oil and gas regions. Its monitors were sited to minimize urban source impacts and target locations where the public might be exposed to air emissions [21]. Still, its networks can be sparse; there are five permanent monitoring stations in the Eagle Ford Shale region, where 7,000 oil and gas wells have been drilled since 2008 [22]. These and other limited networks potentially mask local hot spots, the effects of unique topography, and fugitive emissions at certain well pads.

Even a denser monitoring network taking continuous samples may be unable to capture the full range of air impacts of UOG operations. Sources of variability of air emissions and concentrations of VOCs and other pollutants near UOG sites include: (1) the spatial variability of UOG operations; (2) the discontinuous use of equipment such as diesel trucks, glycol dehydrators, separators, and compressors during preparation, drilling, hydraulic fracturing, well completion, and other stages; (3) the composition of shale and other formations and the specific constituents of the drilling and hydraulic fracturing fluids used on-site (which can influence the makeup of produced or flowback water stored in pits and tanks); (4) intermittent emissions from venting, flaring, and leaks; (5) the shifting location, spacing, and intensity of well pads in response to market conditions,

improvements in technology, and regulatory changes; (6) the effects of wind, complex terrain, and microclimates; and (7) considerable differences among states in permitting, leak detection and repair, and other requirements [10,16,23-25]. Wind, for example, can influence outdoor and indoor concentrations of air pollutants. Brown et al. found that local air movement and mixing depth contribute to peak exposure to VOCs one mile from a compressor station [25]. Colborn et al. noted the role of wind and topography in higher VOC concentrations during winter months, when inversions trap air near ground level [10]. Fuller et al. identified wind speed and wind direction as significant predictors of indoor particulate matter levels near highways [26]. Similar variation can be found within and across geologic formations. Unconventional wells in the Barnett Shale play, for example, differ considerably in terms of reservoir quality, production rates, and recoverable gas [27]. Domestic shale gas plays exhibit even greater diversity, including depth and thickness of recoverable resources, the amount and range of chemicals present in produced water, and the presence of constituents such as bromide, naturally occurring radioactive material, hydrogen sulfide, and other toxic elements [23,28].

These and other sources of variability, and the adaptive drilling and well completion techniques they encourage, complicate the design of setback and well spacing rules that are protective of the public. They also explain why air quality studies carried out in UOG regions yield conflicting results. For example, McKenzie et al. [11] found greater cumulative cancer risks and higher non-cancer hazard indices for residents living less than 0.5 miles from certain well pads in Colorado, while Bunch et al. [21] analyzed data from monitors focused on regional atmospheric concentrations in the Barnett Shale region and found no exceedance of health-based comparison values. Colborn et al. [10] gathered weekly, 24-hour samples 0.7 miles from a well pad in Garfield County, and noted a "great deal of variability across sampling dates in the numbers and concentrations of chemicals detected." Eapi et al. [29] found substantial variation in fenceline concentrations of methane and hydrogen sulfide, which could not be explained by production volume, number of wells, or condensate volume at natural gas development sites.

Institutional factors also influence research on ambient air quality near UOG sites. Congressional exemption of oil and gas operations from provisions of the Clean Air Act, Clean Water Act, Safe Drinking Water Act, Emergency Planning and Community Right-to-Know Act, and other statutes limits data collection on the impacts of oil and gas development [30,31]. In addition, the peer-reviewed literature is divided between "top-down" and "bottom-up" treatments of air quality. The first set of studies explores the impact of UOG operations on regional air quality, with a concern for methane emissions and ozone precursors in regions such as the Green River Basin in Wyoming [32], the Uintah Basin in northeastern Utah [33], and the Denver-Julesburg Basin, home of the Wattenberg Field in northeastern Colorado [34]. These studies rely on airborne and tower measurements, and are at times supplemented by ground measurements such as mobile monitoring.

For example, Petron et al. [35] found a strong alkane signature downwind from the Denver-Julesburg Basin, based on samples taken at a 300-m tall tower (the National Oceanic and Atmospheric Administration Boulder Atmospheric Observatory) and a mobile monitoring unit. In the Uintah Basin, where winter ozone levels exceeded the NAAQS 68 times in 2010, Helmig et al. [36] carried out vertical profiling of ozone precursors at a tower at the northern edge of a gas field. They found levels of atmospheric alkanes during temperature inversion events in 2013 that were 200–300 times greater than regional background. These and other "top-down" studies are also used to estimate methane leakage, which is helpful in comparing the climate-forcing impact of UOG to the use of coal-fired power plants. Loss rate estimates for methane and other hydrocarbons vary considerably by study, from 17% [37] (Los Angeles Basin) to 8.9% [38] (Uintah Basin) (6.2-11.7%, 95% C.I.) to 4% [35] (Denver-Julesburg Basin) (2.3-7.7%, 95% C.I.). A number of studies share the finding that EPA underestimates methane leakage rates across the life cycle (their estimate was 1.65% in 2013) [16], but others, extrapolating from emissions factors and/or direct measurement, produce estimates as low as 0.42% [18]. None of these studies attempts to characterize air concentrations within residential or publicly-accessible areas near UOG operations.

Other studies follow a "bottom-up" approach to air quality, which is limited by access to well pads and other infrastructure, the availability of a power source for monitoring equipment, the stage of operation underway, scheduled or unscheduled flashing, flaring, and fugitive releases, or movement of truck traffic and equipment at or near a well pad during a given sampling period. Thus, bottom-up studies vary in terms of distance to site, sample frequency, and chemicals targeted. This helps explain the range of findings in the published literature. Nevertheless, existing research gives support to resident reports of acute and long-term health symptoms and other reductions in quality of life. Even as they offer conflicting evidence of the relative importance of one stage of production or another to air emissions [10,11], or differ in their ultimate conclusion regarding the existence [10,11,14,35,36,39] or lack [21,40,41] of human health threats from air emissions, they find VOC concentrations in ambient air considerable distances from well pads, including in residential areas and public spaces.

The research questions that guide existing studies create a final barrier to our ability to characterize air emissions in UOG regions. Top-down studies are motivated by questions such as identifying sources of regional nonattainment of ozone standards, or estimating methane and other hydrocarbon leakage rates from UOG operations. Bottom-up research gathers data from one or a limited number of well pads, chosen for reasons such as access or cooperation by owners and operators. The data are used to discuss general exposure conditions for an often-hypothetical community, or used to derive a risk factor. In either mode of study, resident exposure does not directly motivate the sampling protocol. Rather, it is considered obliquely in a study's choice of sample location (e.g., a one that is "near a small community"), assumed in measurements of concentrations within a certain distance of UOG activity, or ignored. What are missing from these studies are protocols grounded in a community's experience of air quality impacts of UOG operations.

Our multi-state air quality monitoring study uses a community-based, participatory research (CBPR) design to explore conditions near UOG operations [42]. Its sampling protocol is based not on access to a well pad, data needs conditioned by an existing averaging standard, or regional policy concerns. Rather, we partnered with residents in UOG regions to measure air quality under circumstances that, given local knowledge of operations (e.g., emissions from particular equipment or intermittent practices) gained through daily routines (e.g., regular observation of well pads) and use of public and private spaces nearby (e.g., livestock movement, farming) were viewed by community members as potential threats to human health. Existing studies often lack a data set suitable for statistical analysis. When such analyses are occasionally imposed on bottom-up data sets, they explain only a fraction of the variance in air quality outcomes. For example, the highest R^2 values in a study of 66 sites, which, due to the study's broad spatial range was limited to measurements of methane and hydrogen sulfide, were 0.26 (H_2S concentration vs. condensate volume nearby) and 0.17 (H_2S and number of wells nearby) [29]. CBPR studies, by comparison, are place-based – they begin with the experience of a population in order to identify environmental stressors and explore the heterogeneity of circumstances under which they arise [43,44]. Rather than discount these circumstances for lack of statistical power, they can be used to define the scope of confirmatory studies, tailor air quality monitoring networks and studies, or suggest novel pollution control measures and best management practices.

Methods

We explore air quality at a previously neglected scale: near a range of UOG development and production sites that are the focus of community concern. Residents conducted sampling in response to operational conditions, odor events, and a history of the onset of acute symptoms. Residents selected sampling sites after they completed a training program run by Global Community Monitor (GCM), an organization that has developed and modified community-based sampling protocols for more than twenty years. Sampling is designed to obtain accurate readings of public exposure near UOG development in the part-per-billion range [45]. Training sessions followed a written manual on proper sampling protocol and included instruction by experienced members of GCM in a classroom setting for five hours. In addition, samplers were trained in the field to properly demonstrate Quality Assurance/Quality Control (QA/QC) methods, such as use of data sheets and chain of custody records, sampling procedures including not taking samples in the presence of vehicle traffic or other sources of VOCs, and protocols for storage and delivery to an analytic laboratory [45]. Chain of Custody forms provided by the laboratory were explained and filled out in exercises in which each sampler participated. The trainings for community-based air sampling and related QA/QC measures were developed in conjunction with the Environmental Protection Agency under the federal Environmental Monitoring for Public Access and Community Tracking (EMPACT) program, and refined in cooperation with agencies including the Health Services Department of Contra Costa County, California and the Delaware Department of Natural Resources [46,47]. Any sample that did not meet QA/QC criteria was not included in the final data set.

Community monitors gauged industrial activity using field log sheets ("pollution logs") that allow each resident to record what they see, hear, feel, smell, and taste in areas downwind of industrial activity as they go about their daily routines. Each community monitor participated voluntarily in data collection for this study. They provided consent to use data gathered with questionnaires that they co-designed as well as grab and passive samplers. Residents documented activity including: (a) visible emissions drifting off-site; (b) odors that appear to derive from a site; (c) acute health symptoms that occur while in proximity to a site or during a specific industrial activity; (d) audible sounds of particular equipment in use within the boundaries of an operating well pad or related infrastructure; and (e) visible activity on-site, including the number and types of heavy trucks and tanks, vehicle traffic, workers present and job categories, and physical changes such as noise and vibrations near certain equipment. Similar to a neighborhood police watch, each resident determined locations that they would continue to observe and potentially return to for sampling.

Sampling for volatile compounds other than formaldehyde was carried out using methods described in

O'Rourke and Macey [48] and Larson et al. [49] using an evacuated sampling ("bucket") vessel modelled after the Summa canister [50]. The bucket is inexpensive, portable, and consists of a 10-liter Tedlar bag and vacuum to take a grab sample of air for two to three minutes (Figure 1). Air is collected using a battery-operated pump that forces air out of the bucket. Negative pressure created inside the sealed bucket by the external vacuum pump opens the bag when a stainless steel bulkhead is opened. After taking the sample, the Tedlar bag is sealed and sent to an analytical laboratory. The bucket sampler operates on the same principle that Summa canisters employ. Rather than collect a sample in a stainless steel can, the bucket contains a special bag made of Tedlar to hold the sample. Bags are obtained from the laboratory that processes the sample and purged three times with pure nitrogen by the laboratory prior to use. GCM's founder developed the sampling program under a project for Communities for a Better Environment, a non-profit organization founded in 1978 that provides legal, scientific, and technical assistance to heavily polluted communities. The device has been subjected to numerous validation tests organized by government agencies and independent laboratories [51-54]. Refinements include the use of field duplicates, which demonstrate no significant variation in results across comparison studies [45].

Residents collected 35 grab samples at locations of community concern, under conditions that would lead them to register a complaint with relevant authorities such as a county public health department or state oil and gas commission. Health symptoms contributed to the decision to take a grab sample on 29 occasions. The most common symptoms reported by samplers were headaches (17 reports), dizziness or light-headedness (13 reports), irritated, burning, or running nose (12 reports), nausea (11 reports), and sore or irritated throat (11 reports). Further details regarding each sample are provided in Additional file 1 (Tables S1 through S5).

In addition to grab samples, 41 formaldehyde badges were deployed in the five states targeting production facilities and compressor stations based on the results of pollution patrols. UMEx100 Passive Samplers for Formaldehyde are manufactured by SKC Inc. Samplers were placed near operating compressor stations and production facilities for a minimum of eight hours.

Samples were ultimately collected near production pads, compressor stations, condensate tank farms, gas

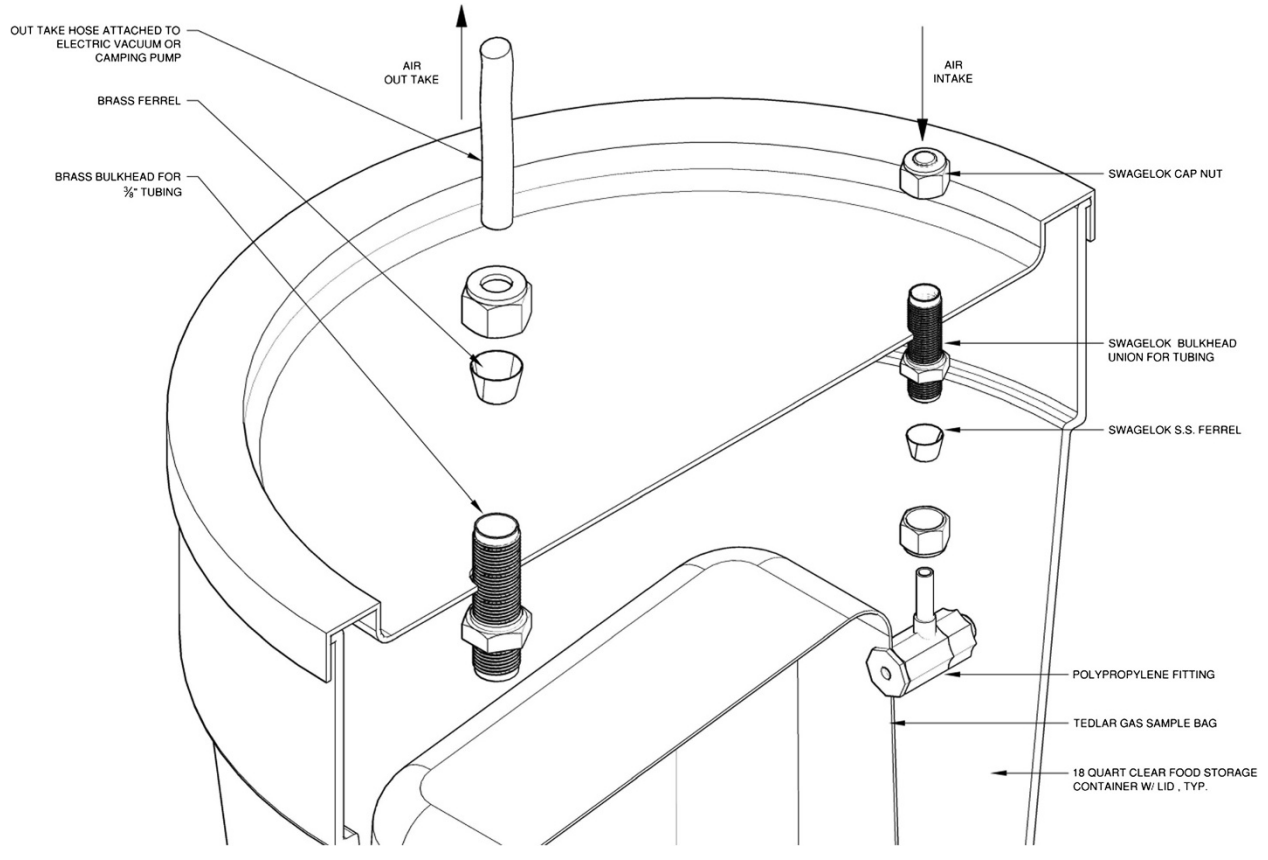

Figure 1 Design of bucket grab sampling device.

processing stations, and wastewater and produced water impoundments in five states (Arkansas, Colorado, Ohio, Pennsylvania, and Wyoming). The states were chosen to reflect a diverse range of urban and rural communities, operations (e.g., number of wells permitted and developed), history of development, and stages of production (see Table 1).

Air samples were analyzed for 75 volatile organic compounds (VOCs), including benzene, ethylbenzene, acrylonitrile, methylene chloride, toluene, hexane, heptane, and xylene by ALS Laboratories (Simi Valley, CA 93065) using EPA Method TO-15 or TO-3 (methane) by gas chromatograph/mass spectrometer interface to a whole air preconcentrator. Formaldehyde samples were analyzed using EPA Method TO-11A, modified for the sampling device by high performance liquid chromatography with UV detection. Samples were also analyzed for 20 sulfur compounds by ASTM D 5504–08 using a gas chromatograph equipped with a sulfur chemiluminescence detector. All compounds with the exception of hydrogen sulfide and carbonyl sulfide were quantitated against the initial calibration curve for methyl mercaptan. Chemicals of concern were compared to U.S. Agency for Toxic Substances and Disease Registry (ATSDR) minimal risk levels (MRLs) and EPA Integrated Risk Information System (IRIS) cancer risk levels. MRLs are estimates of daily human exposure that can occur without appreciable risk of human health effects. They are derived for acute (1–14 days), intermediate (15–364 days), or chronic (365 days or longer) periods of exposure. The laboratory is certified by ten state departments of health or environment, the American Industrial Hygiene Association, and the U.S. Department of Defense.

Results

Table 1 shows the diverse range of operation, including number of wells permitted and developed and setbacks from housing and other occupied structures, in UOG regions where grab and passive air samples were collected through partnership with community-based organizations.

Air contaminants

We identified unique chemical mixtures at each sample location (see Tables S1 through S5 in Additional file 1). In addition, we identified eight volatile compounds at concentrations that exceeded ATSDR minimal risk levels (MRLs) or EPA Integrated Risk Information System (IRIS) cancer risk levels (see Table 2). Although our samples represent a single point in time, we compared concentrations to acute as well as chronic risk levels as many of the activities that generate volatile compounds near UOG operations are long-duration (the life cycle of an unconventional natural gas well can span several decades) [16]. Residents chose sample locations where odors and symptoms were the "norm" for the area, not a one-time event. In addition, a growing body of research suggests that peak (e.g., 1-hr. maximum), rather than average exposure to air emissions may better capture certain risks to human health [55-57].

Sixteen of the 35 grab samples, and 14 of the 41 passive samples, had concentrations of volatiles that exceeded ATSDR and/or EPA IRIS levels. ATSDR MRLs and EPA IRIS levels for chemicals of concern are provided in Table 2. The chemicals that most commonly exceeded these levels were hydrogen sulfide, formaldehyde, and benzene. Background levels for these chemicals are 0.15 $\mu g/m^3$ for hydrogen sulfide, 0.25 $\mu g/m^3$ for formaldehyde, and 0.15 $\mu g/m^3$ for benzene [58-60]. Our samples that exceeded health-based risk levels were 90–66,000× background levels for hydrogen sulfide, 30-240× background levels for formaldehyde, and 35–770,000× background levels for benzene. Details of our results are presented in Tables 3, 4, and 5 and in Figures 2, 3, and 4 (greater detail is provided in Additional file 1). A state-by-state summary follows.

Wyoming (Park County)

Nine of the ten grab samples contained volatiles above ATSDR MRLs or EPA IRIS risk levels. Seven contained high concentrations of hydrogen sulfide (one was over 600× the ATSDR acute MRL) and three contained high levels of benzene, including one over 12,000× the ATSDR acute MRL. The sample with the highest benzene concentrations also contained 480,000 micrograms per cubic meter of heptane, 3,100,000 micrograms per cubic meter of pentane, and 4,100,000 micrograms per cubic meter of butane, all hydrocarbons that are frequently associated with methane. These hydrocarbon concentrations exceeded occupational health standards (NIOSH recommended exposure limits). Four of the seven samples with high levels of hydrogen sulfide were taken in northeast Park County (near Deaver), and three of the four samples with high benzene levels were taken in northwest Park County (near Clark). One of the five passive samples contained formaldehyde at levels that exceeded ATSDR MRLs and the 1/10,000 cancer risk level (Table 3, Figure 2).

Wyoming (Fremont County)

Four of the five grab samples contained volatiles at concentrations that exceeded ATSDR MRLs or EPA IRIS risk levels. One sample contained six volatiles exceeding these levels, including benzene at 75× the ATSDR acute MRL and 22× the EPA IRIS 1/10,000 cancer risk level. A second sample contained three volatiles exceeding ATSDR or EPA IRIS levels and also contained 4,167,000 micrograms per cubic meter of methane, an amount that exceeds its occupational health standard (Threshold Limit Value). None of the passive samples contained

Table 1 Oil and gas operations by state

State	Drilling permits issued (year)	Wells		Production		Setback requirements (dwellings and occupied structures)	Ambient air quality standards
		Drilled (year)	Producing (year)	Gas (Tcf) (year)	Oil (MMbbl) (year)		
AR	~ 890 (2012)[a]	–	8,538 (gas) (2012)[b]	1.15 (2012)[b]	6.59 (2012)[a]	200 ft. (from produced fluids storage tanks to habitable dwelling)	20 ppm (5 min.); 80 ppb (8-hr.) (H_2S)[c]
	~ 1,090 (2011)[a]					300 ft. (from produced fluids storage tanks to school, hospital, or other public use building)	
CO	4,025 (2013)[a]	–	46,697 (2014)[d]	1.71 (2012)[b]	64.88 (2013)[a]	500 ft. (from well to home or building, absent waiver)	–[c, e]
	3,775 (2012)[a]					1,000 ft. (from well to high occupancy building, absent hearing and approval)	
OH	903 (2012)[a]	553 (2012)[a]	51,739 (2012)[a]	.084 (2012)[b]	4.97 (2012)[a]	150 ft. (occupied dwelling in urbanized area, absent consent)	–[c, e]
	690 (2011)[a]					150 ft. (occupied or public dwelling, non-urban area)	
						200 ft. (occupied dwelling w/in drilling unit due to mandatory pooling)	
PA	4,617 (2013)[a]	2,174 (2013)[a]	55,812 (2011)[f]	2.26 (2012)[b]	2.7 (2011)[a]	500 ft. (from well bore to building or water well)	0.1 ppm (1-hr.); 0.005 ppm (24-hr.) (H_2S)[c, e]
	4,090 (2012)[a]						
WY	3,230 (Sept. 2013-Aug. 2014)[a]	–	37,301 (2012)[a]	2.23 (2012)[b]	57.5 (2012)[a]	350 ft. (from wellhead, pumping unit, pit, production tank, and/or production equipment to residence, school, or hospital)	40 μg/m^3 (half-hr. ave., 2x w/in 5 days) (H_2S)[c, e]

[a]State agency data.
[b]U.S. Energy Information Administration data.
[c]In addition to National Ambient Air Quality Standards for criteria air pollutants and federal emissions standards – new source performance standards (40 C.F.R. §§ 60.5360 - 60.5430) and national emission standards for hazardous air pollutants (40 C.F.R. §§ 63.760 - 63.777) – applicable to the oil and gas industry.
[d]Personal communication with state agency.
[e]In addition to state emissions standards (e.g., VOC emissions from glycol dehydrators; green completions; valve requirements for pneumatic devices). See, for example, Colorado Department of Public Health and Environment's revised Air Quality Control Commission Regulation Numbers 3, 6, and 7 (adopted 23 February 2014).
[f]Earthworks data.

Table 2 ATSDR minimal risk levels and EPA IRIS cancer risk levels for chemicals of concern (all data in μg/m^3)

Chemical	ATSDR MRLs			IRIS cancer risk levels		
	Acute	Intermediate	Chronic	1/1,000,000	1/100,000	1/10,000
Benzene	29	20	10	.45	4.5	45
1,3 butadiene				0.03	0.3	3
Ethylbenzene	21,700	8,680	260			
Formaldehyde	49	37	10	0.08	0.8	8
N-hexane			2,115			
Hydrogen sulfide	98	28				
Toluene	3,750		300			
Xylenes	8,680	2,604	217			

Table 3 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Wyoming

State/ID	County	Nearest infrastructure	Chemical	Concentration (μg/m^3)	ATSDR MRLs exceeded	EPA IRIS cancer risk exceeded
WY-4586	Fremont	5 m from separator	Hydrogen sulfide	590	I, A	n/a
WY-4586	Fremont	5 m from separator	Benzene	2,200	C, I, A	1/10,000
WY-4586	Fremont	5 m from separator	Toluene	1,400	C	n/a
WY-4586	Fremont	5 m from separator	Ethylbenzene	1,200	C	n/a
WY-4586	Fremont	5 m from separator	Mixed xylenes	4,100	C, I	n/a
WY-4586	Fremont	5 m from separator	n-hexane	22,000	C	n/a
WY-1103	Fremont	20 m from separator	benzene	31	C, I, A	1/100,000
WY-2069	Fremont	110 m from work-over rig[a]	Hydrogen sulfide	30	I	n/a
WY-4861	Fremont	5 m from separator	Benzene	230	C, I, A	1/10,000
WY-4861	Fremont	5 m from separator	Mixed xylenes	317	C	n/a
WY-4861	Fremont	5 m from separator	n-hexane	2,500	C	n/a
WY-4478	Park	25 m from separator	Hydrogen sulfide	91	I	n/a
WY-4478	Park	25 m from separator	Benzene	110,000	C, I, A	1/10,000
WY-4478	Park	25 m from separator	Toluene	270,000	C, A	n/a
WY-4478	Park	25 m from separator	Mixed xylenes	135,000	C, I, A	n/a
WY-4478	Park	25 m from separator	n-hexane	1,200,000	C	n/a
WY-129	Park	55 m from separator	benzene	100	C, I, A	1/10,000
WY-3321	Park	5 m from compressor	benzene	35	C, I, A	1/100,000
WY-4883-005	Park	5 m from compressor	Formaldehyde	46	C, I	1/10,000
WY-4864	Park	5 m from discharge canal	Hydrogen sulfide	210	I, A	n/a
WY-4865	Park	10 m from discharge canal	Hydrogen sulfide	1,200	I, A	n/a
WY-4496	Park	20 m from well pad	Hydrogen sulfide	6,100	I, A	n/a
WY-106	Park	Adjacent to discharge canal	Hydrogen sulfide	5,600	I, A	n/a
WY-184	Park	15 m from discharge canal	Hydrogen sulfide	240	I, A	n/a
WY-187	Park	15 m from discharge canal	Hydrogen sulfide	66,000	I, A	n/a
WY-187	Park	15 m from discharge canal	Benzene	23	C, I	1/100,000

C = chronic; A = acute; I = intermediate.
[a]Infrastructure used to pull and replace a well completion.

Table 4 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Arkansas

State/ID	County	Nearest infrastructure	Chemical	Concentration (μg/m^3)	ATSDR MRLs exceeded	EPA IRIS cancer risk exceeded
AR-3136-003	Faulkner	355 m from compressor	Formaldehyde	36	C	1/10,000
AR-3136-001	Cleburne	42 m from compressor	Formaldehyde	34	C	1/10,000
AR-3561	Cleburne	30 m from compressor	Formaldehyde	27	C	1/10,000
AR-3562	Faulkner	355 m from compressor	Formaldehyde	28	C	1/10,000
AR-4331	Faulkner	42 m from compressor	Formaldehyde	23	C	1/10,000
AR-4333	Faulkner	237 m from compressor	Formaldehyde	44	C, I	1/10,000
AR-4724	Van Buren	42 m from compressor	1,3-butadiene	8.5	n/a	1/10,000
AR-4924	Faulkner	254 m from compressor	Formaldehyde	48	C, I	1/10,000

C = chronic; I = intermediate.

volatiles at concentrations that exceeded ATSDR MRLs or EPA IRIS cancer risk levels (Table 3, Figure 2).

Arkansas (Cleburne, Faulkner, and Van Buren Counties)

One of the 8 grab samples, and 7 of the 13 passive samples, contained volatiles above ATSDR MRLs or EPA IRIS risk levels. One of the passive samples (taken at a residence) had formaldehyde levels that were close to the ATSDR MRL and exceeded EPA's 1/10,000 cancer risk level (Table 4, Figure 3).

Pennsylvania (Susquehanna County)

One of the four grab samples contained benzene at concentrations that exceeded the EPA 1/100,000 cancer risk level. Six of the ten passive samples contained formaldehyde at levels that exceeded ATSDR MRLs or EPA IRIS risk levels. Two of the samples exceeded both the acute MRL and the 1/10,000 cancer risk level (Table 5, Figure 4).

Colorado (Boulder and Weld Counties)

One of the five grab samples contained 41 micrograms per cubic meter of hydrogen sulfide and exceeded the ATSDR intermediate MRL. None of the passive samples had volatiles exceeding the ATSDR MRLs or EPA IRIS risk levels.

Ohio (Athens, Carroll, and Trumbull Counties)

None of the four grab samples or five passive samples contained volatiles at concentrations that exceeded the ATSDR MRLs or EPA IRIS risk levels.

State air quality monitoring survey

We reviewed air quality monitoring by state agencies in the five states covered by our sampling. We reviewed one study in Arkansas, seven in Colorado, one in Ohio, four in Pennsylvania, and one in Wyoming. Most of the studies measured VOC levels, two included hydrogen sulfide, and seven included methane and/or other hydrocarbons. Sampling durations ranged from four hours to 24 months; five of the studies lasted more than four weeks. Target compounds were detected in all studies that have been completed, including mixtures of 42 non-methane VOCs. None of the studies concluded that detected compounds posed significant human health risk (Table 6).

Table 5 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Pennsylvania

State/ID	County	Nearest infrastructure	Chemical	Concentration (μg/m^3)	ATSDR MRLs exceeded	EPA IRIS cancer risk exceeded
PA-4083-003	Susquehanna	420 m from compressor	Formaldehyde	8.3		1/10,000
PA-4083-004	Susquehanna	370 m from compressor	Formaldehyde	7.6		1/100,000
PA-4136	Washington	270 m from PIG launch[a]	Benzene	5.7		1/100,000
PA-4259-002	Susquehanna	790 m from compressor	Formaldehyde	61	C, I, A	1/10,000
PA-4259-003	Susquehanna	420 m from compressor	Formaldehyde	59	C, I, A	1/10,000
PA-4259-004	Susquehanna	230 m from compressor	Formaldehyde	32	C	1/10,000
PA-4259-005	Susquehanna	460 m from compressor	Formaldehyde	34	C	1/10,000

C = chronic; A = acute; I = intermediate.
[a]Launching station for pipeline cleaning or inspection tool.

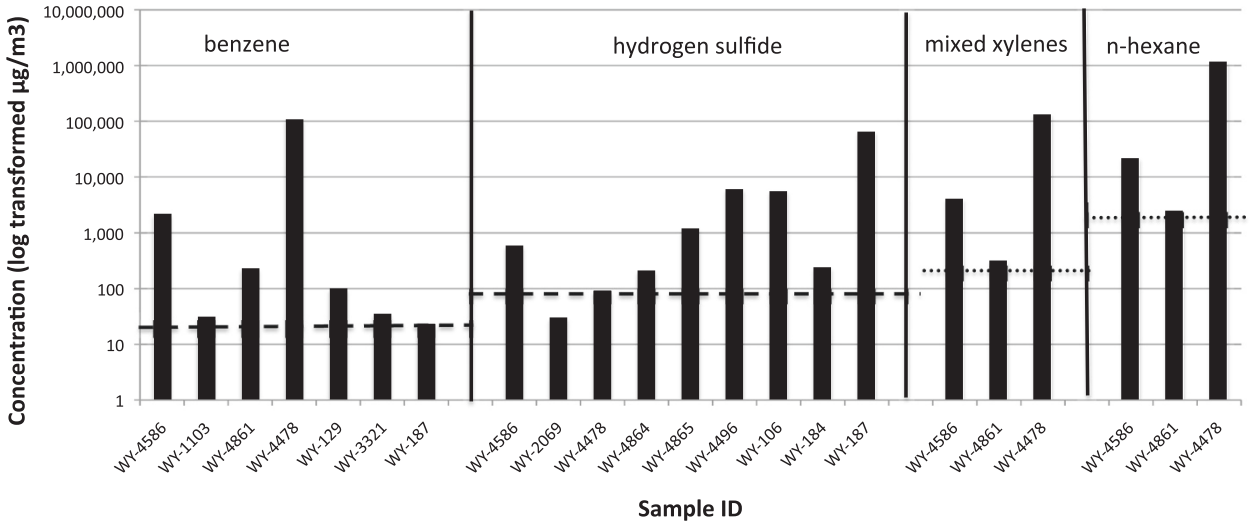

Figure 2 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Wyoming. Note log scale on y-axis. Dashed lines represent ATSDR intermediate-term MRLs. Dotted lines represent ATSDR chronic MRLs (not displayed: toluene, ethylbenzene, and formaldehyde).

Discussion

We identified significant concentrations of four well-characterized chemicals: benzene, formaldehyde, hexane, and hydrogen sulfide. Benzene was detected at sample locations in Pennsylvania and Wyoming. Concentrations exceeded health-based risk levels by as many as several orders of magnitude. Previous studies similarly found benzene concentrations near oil and gas development [10,11]. Our monitors detected benzene at higher concentrations (5.7 – 110,000 µg/m^3) than those found in the published literature. The results are of concern given their proximity to subdivisions, homes, and farms. In Wyoming, multiple samples with high benzene concentrations were taken on residential property 30–350 yards from the nearest well, or on farmland along the perimeter of a well pad. Equipment included separators, compressor stations, discharge canals, and pipeline cleaning operations. The results suggest that existing regulatory setback distances from wells to

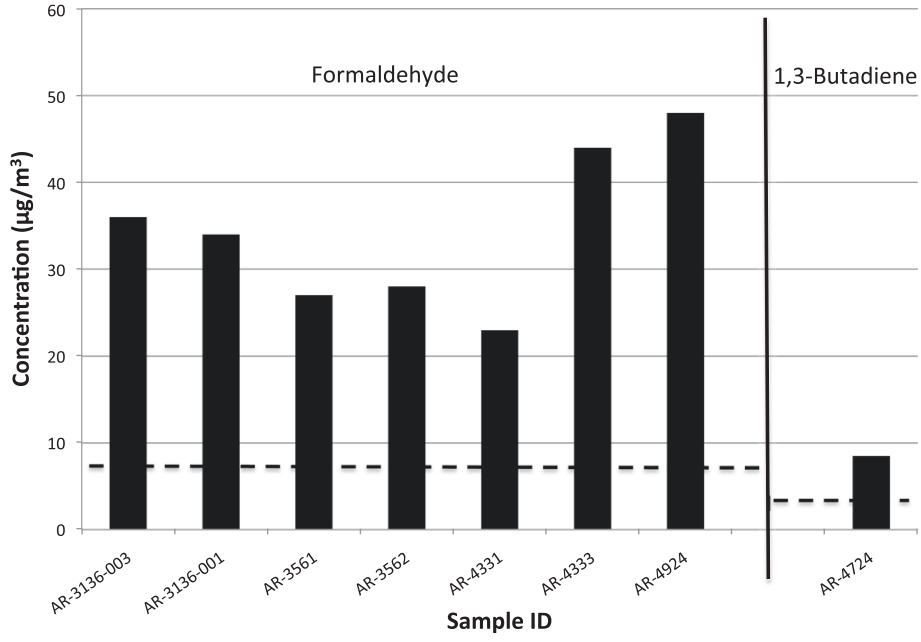

Figure 3 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Arkansas. Dashed lines represent EPA IRIS 1/10,000 cancer risk for formaldehyde and 1,3 butadiene.

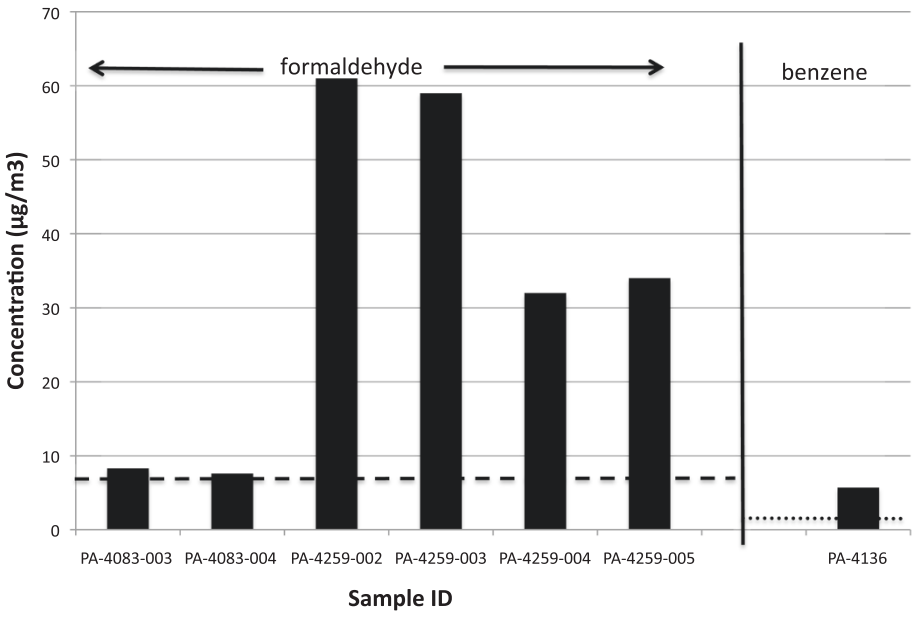

Figure 4 Concentrations of volatile compounds exceeding health-based risk levels in samples collected in Pennsylvania. Dashed line represents EPA IRIS 1/10,000 cancer risk for formaldehyde. Dotted line represents EPA IRIS 1/100,000 cancer risk for benzene.

residences may not be adequate to reduce human health risks [61]. Setbacks from wellheads to homes and other occupied structures cluster around the 150 to 500 feet range in the five states (see Table 1). We found high concentrations of volatile compounds at greater distances, including formaldehyde (up to 2,591 feet) and benzene (up to 885 feet). High levels of benzene near oil production wells indicate that EPA should revisit the extent to which oil wells are addressed in its new source performance standards [62].

Benzene is a known human carcinogen. Chronic exposure to benzene increases the risk of leukemia [63]. The increased risk occurs at low levels of exposure with no evidence of threshold level [64]. Benzene exposure increases risk of birth defects [65], including neural tube and other defects found near natural gas development [24]. Respiratory effects include pulmonary edema, acute granular tracheitis, laryngitis, and bronchitis [60].

UOG fields present multiple sources and exposure routes for benzene. Benzene occurs naturally in shale and other hydrocarbon deposits, and is vented, flared, or released as fugitive emissions along numerous points of production, such as wells, production tanks, compressors, and pipelines [6]. It can volatize and disperse from flowback and produced water at drilling sites and remain in the air for several days [66]. It was among the first pollutants found in air samples near shale gas operations [67]. Previous studies found benzene to be the largest contributor to excess lifetime cancer risk near gas fields [12]. Residents exposed to VOCs including benzene experience immediate health symptoms and illness. Within days after a flaring event at a Texas City refinery, children exhibited altered blood profiles, liver enzymes, and somatic symptoms [68]. Future research is needed to determine whether the concentrations of benzene we measured are due to continuous releases or flaring, fugitive emissions, or facility upsets.

Formaldehyde is another volatile compound that exceeded health-based risk levels near compressor stations in Arkansas, Pennsylvania, and Wyoming. As with benzene, there are known sources of formaldehyde emissions along the production chain. Formaldehyde is a product of incomplete combustion emitted by natural gas-fired reciprocating engines at compressor stations [69]. Formaldehyde is also formed from methane in the presence of sunlight, which may be an important source given significant amounts of methane that are known to escape from UOG sites [70]. But air monitoring studies, particularly in shale gas regions, either do not measure for formaldehyde [12,14] or find it at lower concentrations. For example, the Barnett Shale Energy Education Council [71] found levels that did not pose a risk to human health. Colborn et al. [10] found formaldehyde and acetaldehyde in each of 46 samples with a mean of 1.0 part per billion by volume. In contrast, our CBPR framework resulted in the targeting of compressor stations for passive sampling, where diesel emissions likely account for the higher levels that we found. Our results are similar to the Fort Worth Natural Gas Air Quality Study, which found formaldehyde concentrations in areas with multiple large compressor engines [72]. We found high concentrations of formaldehyde near fourteen compressor stations in three states.

Table 6 Five-state survey of air quality monitoring studies, unconventional oil and gas operations

Agency (year)	Target compound	Sampling equipment	Sample sites	Duration	Representative findings
ADEQ (2011)	VOCs (total) NO NO_2	PID (fixed) PID (handheld)	4 compressor stations 6 drilling sites 3 well sites (fracking) 1 upwind	1 d (4–6 hrs.)	VOCs "almost always below or near detection limits" VOCs at drilling sites elevated (ave. 38–678 ppb; max. 350–5,321 ppb) NO/NO_2 rarely exceed detection limits
CDPHE (2012)	NMOCs (78) Methane	Canister	1 well pad (Erie)	3 wks.	Detects = 42 of 78 compounds in >75% of samples Benzene "well within EPA's acceptable cancer risk range" Acute and chronic HQs "well below" 1
CDPHE (2009)	NMOCs (78) VOCs $PM_{2.5}$	Canister PID (handheld) Filter (handheld)	8 wells (4 drilling, 4 completion)	1 d	Total NMOC ave. 273 – 8,761 ppb at 8 sites Total VOC ave. 6–3,023 ppb at 8 sites $PM_{2.5}$ ave. 7.3 - 16.7 μg/m^3 at 8 sites
CDPHE, GCPHD (2007)	VOCs (43) PM_{10}	Canister Filter	14 sites 7 sites	24 mos.	Detects = 15 of 43 compounds Benzene ave. 28.2 μg/m^3, max 180 μg/m^3 (grab) Toluene ave. 91.4 μg/m^3, max 540 μg/m^3 (grab)
CDPHE (2003–2012)	NMOCs Carbonyls	Canister	5 sites (2003) 6 sites (2006) 3+ sites (2012)	2 mos.	Methane ave. 2,535 ppb (Platteville) vs. (1,780 ppb Denver) Top NMOCs in Platteville = ethane, propane, butane Benzene, toluene higher in Platteville
CDPHE (2002)	VOCs (42) SO_2 NO, NO_2	Canister Continuous	2 well sites 1 residential 1 active flare 2 up-, down-valley 1 background	1 mo.	Detects = 6 of 42 VOCs Benzene in 6 of 20 (2.2-6.5 μg/m^3) Toluene in 18 of 20 (1.5-17 μg/m^3)
OEPA (2014)	VOCs (69) VOCs $PM_{10}/PM_{2.5}$ H_2S CO	Canister GC/MS Filter	1 well site 1 remote site	12 mos.	Ongoing; data update provided in February 2014 Detects include BTEX, alkanes (e.g., ethane, hexane), H_2S Second site planned near processing plant
PA DEP (2010)	VOCs (48) Alkanes Leak detection	Canister OP-FTIR GC/MS FLIR	2 compressor stations 1 condensate tank 1 wastewater impoundment 1 background	5 wks.	Detects include methane, ethane, propane, benzene (max. 758 ppb) No conc.'s "that would likely trigger air-related health issues" Fugitive gas stream emissions
PA DEP (2011)	VOCs (48) Alkanes Leak detection	Canister OP-FTIR GC/MS FLIR	2 compressor stations 1 completed well 1 well site (fracking) 1 well (tanks, separator) 1 background	4 wks.	Detects include BTEX (benzene max. 400 ppb), methylbenzenes No conc.'s "that would likely trigger air-related health issues" Fugitive emissions from condensate tanks, piping
PA DEP (2011)	VOCs (48) Alkanes	Canister OP-FTIR GC/MS	2 compressor stations 1 well site (flaring) 1 well site (drilling) 1 background	4 wks.	Detects include benzene (max. 400 ppb), toluene, ethylbenzene Natural gas constituent detects near compressor stations Conc.'s "do not indicate a potential for major air-related health issues"
PA DEP (2012)	Criteria VOCs/HAPs Methane H_2S	"Full suite"	1 gas processing 2 large compressor stations 1 background	12 mos.	Ongoing; report due in 2014

Table 6 Five-state survey of air quality monitoring studies, unconventional oil and gas operations *(Continued)*

WDEQ (2013)	VOCs/NMHCs Ozone Methane NO, NO_2 $PM_{10}/PM_{2.5}$	Canister UV Photometric FID Chemiluminescence Beta Attenuation	7 permanent stations (e.g., Boulder, Juel Spring, Moxa) 3 mesonet stations (Mesa, Paradise Warbonnet) 2 mobile trailer locations (Big Piney, Jonah Field)	Ongoing	WDEQ mobile monitors placed at locations w/ oil & gas development Mini-SODAR also placed adjacent to Boulder permanent station "Relatively low concentrations" of VOCs found in canister samples VOCs "consistently higher" at Paradise site (near oil & gas sources)

BTEX = benzene, toluene, ethylbenzene, and xylenes; FID = flame ionization detector; FLIR = forward looking infrared; GC/MS = gas chromatography/mass spectrometry; HAP = hazardous air pollutant; NAAQS = National Ambient Air Quality Standard; NMHC = non-methane hydrocarbon; NMOC = non-methane organic compound; OP-FTIR = open-path Fourier transform infrared; PID = photoionization detector; VOC = volatile organic compound.

Formaldehyde is a suspected human carcinogen [73]. It can affect nearly every tissue in the human body, leading to acute (dermal allergies, asthma) and chronic (neuro-, reproductive, hematopoietic, genetic and pulmonary toxicity and cellular damage) health effects [74]. The science of childhood exposure to formaldehyde is progressing rapidly [75]. State agencies and international organizations continue to lower exposure limit values and guidelines for formaldehyde [76]. Our results exceed those guidelines. Symptoms reported by community members mirror the effects of acute formaldehyde exposure, which causes irritation of the eyes, nose, throat, and skin.

Other volatiles of concern included hexane and hydrogen sulfide. Hexane detects were most prevalent near oil and gas operations in Wyoming near well pads, compressor stations, separators, and produced water discharges. Other studies in oil and gas regions found hexane, but at low concentrations [10,12]. The circumstances under which high concentrations of hexane were found in Wyoming suggest a combination of leaks, spills, and fugitive emissions as potential causes. Acute exposure to hexane affects the central nervous system, causing dizziness, nausea, and headache. Chronic effects include neurotoxicity [77].

We also found elevated levels of hydrogen sulfide in Wyoming along the chain of production (pump jacks, produced water discharge impoundments, discharge canals) and near a well pad in Colorado. Hydrogen sulfide is a broad-spectrum toxicant that can impact most organ systems [78]. As such, it contributes to a range of short- and long-term neurological, upper respiratory, and blood-related symptoms, including those that were prevalent among community samplers in Wyoming (headaches, dizziness, eye irritation, fatigue) [79]. Hydrogen sulfide is a natural component of crude oil and natural gas [5] and is released during many industrial processes. In addition, five samples from Wyoming exceeded ATSDR health-based risk levels for toluene and xylenes.

Health-based risk levels provide only a limited sense of potential human health impacts from air emissions. They do not fully account for vulnerable subpopulations, and toxicity values are available for a comparatively small number of compounds. The levels that we found for the above chemicals of concern suggest that state monitoring studies are incomplete. Recent state-funded projects found air volatiles at UOG sites that were either near detection limits or within acceptable limits to protect the public [80-82]. One area of agreement between our community-based and state monitoring studies concerns the presence of complex chemical mixtures. These mixtures demonstrate the contingent nature of ambient air quality near UOG infrastructure.

For example, one sample, taken midday in early winter near a well pad in Wyoming with clicking pneumatic pumps, found high concentrations of hydrogen sulfide, hexane, benzene, and xylenes. It also captured cyclohexane, heptane, octane, ethylbenzene, nonane, 1,2,4-trimethylbenzene, and 15 tentatively identified compounds (TICs). TICs are compounds that a device or analytic process is not designed to measure. Total VOC concentrations in the sample exceeded 1.6 million $\mu g/m^3$, excluding methane. While toxicity values are not available for every TIC in our samples, they exceeded reference concentrations available for related compounds such as hexane [77]. Another sample taken in Arkansas, during autumn in the afternoon near a compressor station, captured 17 volatile compounds and five TICs. A third sample, near a separator shed in Wyoming in late autumn at midday, showed spikes in hydrogen sulfide, benzene, and hexane, 19 additional VOCs, and 15 TICs, with total VOC concentrations exceeding 25 million $\mu g/m^3$, excluding methane. These and other complex mixtures are provided in Additional file 1.

The mixtures that we identified are related to sources commonly used in well pad preparation, drilling, well completion, and production, such as produced water tanks, glycol dehydrators, phase separators, compressors, pipelines, and diesel trucks [14]. They can be released during normal operating conditions and persist near ground level, especially in regions where topography encourages air inversions [83]. The toxicity of some constituents is well known, while others have little or no toxicity information available. Our findings of chemical mixtures are of clinical significance, even absent spikes in chemicals of concern. The chemical mixtures that we identified should be further investigated for their primary emissions sources as well as their potential cumulative and synergistic effects [84]. Clinical and subclinical effects of hydrocarbons such as benzene are increasingly found at low doses [85]. Chronic and subchronic exposure to chemical mixtures is of particular concern to vulnerable subpopulations, including children, pregnant women, and senior citizens [86].

Apart from chemicals of concern (including known and suspected human carcinogens) and chronic exposure to complex mixtures, our findings point to the value of community-based research to inform state testing protocols. Air quality near the diverse range of equipment and stages of UOG development is inherently complex. While states sometimes rely on state-of-the-art technologies such as wireless sensors to characterize local air quality, they continue to collect only a “snapshot” of near-field conditions. For example, Arkansas carried out a technologically ambitious program, placing multi-sensor gas monitors on five-foot tripods along each perimeter of a well pad at several sites. AreaRAEs (the trade name for a wireless monitor produced by RAE Systems) use electrochemical sensors to measure nitrous oxides and a photoionization detector to determine VOC concentration.

The continuous monitors wirelessly transmitted data at five-second intervals over a four- to six-hour period (see Table 6). In addition, Arkansas Department of Environmental Quality (ADEQ) personnel carried handheld versions of the AreaRAE along the perimeter of the sites every one or two hours. While the study did not identify individual VOCs, it found that total VOC emissions at the edge of a well pad fluctuate wildly over a five-hour period. The agency concluded, "The spatial and temporal distribution of VOC concentrations at most drilling sites was significantly affected by monitor location, wind, and the interaction between location and wind direction" [81]. Other studies noted similar variation, although the extent to which short-term spikes and unique chemical mixtures might pose a risk to human health was not considered.

Community-based research can improve the spatial and temporal resolution of air quality data [87] while adhering to established methods. Our findings can inform and calibrate state monitoring and research programs. Additional file 1: Table S6 gives a more in-depth overview of community monitoring in action, including sample site selection factors, sources of public health concern at each site, and the range of infrastructure present and life cycle stage when samples were taken. For example, grab samples in Wyoming with some of the highest VOC concentrations were collected during production, as opposed to well completion (see Table S6, Additional file 1). The timing and location of our samples were driven by two primary factors: local knowledge gleaned from daily routines, and a history of chronic or subchronic symptoms reported by nearby residents. For example, a separator shed was targeted because of subchronic symptoms (dizziness, nausea, tight chest, nose and throat problems, metallic taste, and sweet smell) and loud sounds nearby ("hissing, clicking, and whooshing"). Well pads were selected based on impacts to livestock, pasture degradation from produced water, and observations of residents and farmers. Other samples were driven by observations of fugitive emissions, including vapor clouds, deposition, discoloration, and sounds (see Table S6 in Additional file 1).

Community-based research can identify mixtures, and their potential emissions sources, to prioritize for study of their additive, cumulative, and synergistic effects [88]. The mixtures can be used to determine source signatures [14] and isolate well pads for more intensive monitoring. Symptom-driven samples can define the proper length of a sampling period, which is often limited to days or weeks. They can inform equipment placement for continuous monitoring and facilitate a transition from exploratory to more purposive sampling. Testing informed by human health impacts, and more precise knowledge of the mix and spacing of sources that may contribute to them, contrasts with state efforts, which are limited by access to property, sources of electrical power, fixed monitoring sites, and the cooperation of well pad owners and operators. In these ways, community-based monitoring can extend the reach of limited public resources.

Conclusions

Community-based monitoring near unconventional oil and gas operations demonstrates elevations in concentrations of hazardous air pollutants under a range of circumstances. Of special concern are high concentrations of benzene, hydrogen sulfide, and formaldehyde, as well as chemical mixtures linked to operations with observed impacts to resident quality of life.

Additional file

Additional file 1: Contains six tables, including complete results from grab and passive sampling (Tables S1 through S5) and data on sample location selection in Wyoming (Table S6).

Abbreviations

ADEQ: Arkansas Department of Environmental Quality; ATSDR: Agency for Toxic Substances and Disease Registry; BTEX: benzene, toluene, ethylbenzene, and xylenes; CBPR: community-based participatory research; CDPHE: Colorado Department of Public Health and Environment; EMPACT: Environmental Monitoring for Public Access and Community Tracking; EPA: Environmental Protection Agency; FID: flame ionization detector; FLIR: forward looking infrared; GCM: Global Community Monitor; GC/MS: gas chromatography/mass spectrometry; GCPHD: Garfield County Public Health Department; HAP: hazardous air pollutant; IRIS: Integrated Risk Information System; MRL: minimal risk level; NAAQS: National Ambient Air Quality Standard; NIOSH: National Institute for Occupational Safety and Health; NMHC: non-methane hydrocarbon; NMOC: non-methane organic compound; OEPA: Ohio Environmental Protection Agency; OP-FTIR: open path Fourier transform infrared; PA DEP: Pennsylvania Department of Environmental Protection; PAH: polycyclic aromatic hydrocarbon; PID: photoionization detector; QA/QC: Quality Assurance/Quality Control; TIC: tentatively identified compound; UOG: unconventional oil and gas; VOC: volatile organic compound; WDEQ: Wyoming Department of Environmental Quality.

Competing interests

The authors declare they have no competing financial interest. Ruth Breech, Mark Chernaik, Caroline Cox, Denny Larson, and Deb Thomas are employed by non-profit organizations whose mission is to reduce exposure to toxic chemicals.

Authors' contributions

GPM provided study design and project management, a survey of state-sponsored air quality monitoring studies, data analysis, and initial drafts of the Background, Methods, Discussion, and Tables 1 and 6, and Additional file 1: Tables S1 through S6. RB managed air quality monitoring teams and provided an initial draft of the Methods. MC provided data analysis and interpretation of grab and passive samples. CC provided data analysis and interpretation of grab and passive samples and initial drafts of the Results, Tables 2, 3, 4, 5 and Figures 2, 3 and 4. DL developed the protocol for community-based air sampling and provided an initial draft of the Methods. DT managed air quality monitoring teams in Wyoming and provided an initial draft of Additional file 1: Table S6. DOC provided study design and guidance, data analysis, and initial drafts of the Background and Discussion. All authors participated in the study design, data analysis and interpretation, and drafting of the manuscript. All authors read and approved the final manuscript.

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Author details
[1]Center for Health, Science, and Public Policy, Brooklyn Law School, Brooklyn, New York, USA. [2]Global Community Monitor, Richmond, California, USA. [3]Environmental Law Alliance Worldwide, Eugene, Oregon, USA. [4]Center for Environmental Health, Oakland, California, USA. [5]Powder River Basin Resource Council, Clark, Wyoming, USA. [6]Institute for Health and the Environment, University at Albany, Rensselaer, New York, USA.

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References

1. USEIA: *Annual Energy Outlook 2013.* Washington, DC: United States Energy Information Administration; 2013 [http://www.eia.gov/forecasts/aeo/pdf/0383 (2013).pdf]
2. USEIA: *Annual Energy Outlook 2012.* Washington, DC: United States Energy Information Administration; 2012 [http://www.eia.gov/forecasts/aeo/pdf/0383 (2012).pdf]
3. USEIA: *Glossary of Terms.* Washington, DC: United States Energy Information Administration; 2014 [http://www.eia.gov/tools/glossary/]
4. Finkel ML, Law A: **The rush to drill for natural gas: a public health cautionary tale.** *Am J Public Health* 2011, **101:**784–785.
5. Colborn T, Kwiatkowski C, Schultz K, Bachran M: **Natural gas operations from a public health perspective.** *Hum Ecol Risk Assess Int J* 2011, **17:**1039–1056.
6. Witter RZ, McKenzie L, Stinson KE, Scott K, Newman LS, Adgate J: **The use of health impact assessment for a community undergoing natural gas development.** *Am J Public Health* 2013, **103:**1002–1010.
7. Adgate JL, Goldstein BD, McKenzie LM: **Potential public health hazards, exposures and health effects from unconventional natural gas development.** *Environ Sci Technol*. in press.
8. Jackson RB, Vengosh V, Darrah TH, Warner NR, Down A, Poreda RJ, Osborn SG, Zhao K, Karr JD: **Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction.** *Proc Nat Acad Sci* 2013, **110:**11250–11255.
9. Brown VJ: **Radionuclides in fracking wastewater: managing a toxic blend.** *Environ Health Perspect* 2014, **122:**A50–A55.
10. Colborn T, Schultz K, Herrick L, Kwiatkowski C: **An exploratory study of air quality near natural gas operations.** *Hum Ecol Risk Assess Int J* 2013, **20:**86–105.
11. McKenzie LM, Witter RZ, Newman LS, Adgate JL: **Human health risk assessment of air emissions from development of unconventional natural gas resources.** *Sci Total Environ* 2012, **424:**79–87.
12. Shonkoff SB, Hays J, Finkel ML: **Environmental public health dimensions of shale and tight gas development.** *Environ Health Perspect*. in press.
13. Skone TJ, Littlefield J, Marriott J: *Life Cycle Greenhouse Gas Inventory of Natural Gas Extraction, Delivery and Electricity Production.* Pittsburgh, PA: United States Department of Energy, National Energy Technology Laboratory; 2011.
14. Gilman JB, Lerner BM, Kuster WC, Gouw JA: **Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado.** *Environ Sci Technol* 2013, **47:**1297–1305.
15. Field RA, Soltis J, Murphy S: **Air quality concerns of unconventional oil and natural gas production.** *Environ Sci Process Impacts* 2014, **16:**954–969.
16. Moore CW, Zielinska B, Petron G, Jackson RB: **Air impacts of increased natural gas acquisition, processing, and use: a critical review.** *Environ Sci Technol*. in press.
17. Jiang M, Griffin WM, Hendrickson C, Jaramillo P, VanBriesen J, Venkatesh A: **Life cycle greenhouse gas emissions of Marcellus shale gas.** *Environ Res Lett* 2011, **6:**034014.
18. Allen DT, Torres VM, Thomas J, Sullivan DW, Harrison M, Hendler A, Herndon SC, Kolb CE, Fraser MP, Hill AD, Lamb BK, Miskimins J, Sawyer RF, Seinfeld JH: **Measurements of methane emissions at natural gas production sites in the United States.** *Proc Nat Acad Sci* 2013, **110:**17768–17773.
19. Schnell RC, Oltmans SJ, Neely RR, Endres MS, Molenar JV, White AB: **Rapid photochemical production of ozone at high concentrations in a rural site during winter.** *Nat Geosci* 2009, **2:**120–122.
20. Witter R, McKenzie L, Towle M, Stonson K, Scott K, Newman L, Adgate J: *Health Impact Assessment for Battlement Mesa, Garfield County Colorado.* Aurora, CO: Colorado School of Public Health; 2010.
21. Bunch AG, Perry CS, Abraham L, Wikoff DS, Tachovsky JA, Hixon JG, Urban JD, Harris MA, Haws LC: **Evaluation of impact of shale gas operations in the Barnett Shale region on volatile organic compounds in air and potential human health risks.** *Sci Total Environ* 2013, **468:**832–842.
22. Morris J, Song L, Hasemyer D: *Big Oil, Bad Air: Fracking the Eagle Ford Shale of South Texas.* Washington, DC: Center for Public Integrity; 2014.
23. Goldstein BD, Brooks BW, Cohen SD, Gates AE, Honeycutt ME, Morris JB, Orme-Zavaleta J, Snawder J: **The role of toxicological science in meeting the challenges and opportunities of hydraulic fracturing.** *Toxicol Sci* 2014, **139:**271–283.
24. McKenzie LM, Guo R, Witter RZ, Savitz DA, Newman LS, Adgate JL: **Birth outcomes and maternal residential proximity to natural gas development in rural Colorado.** *Environ Health Perspect*. in press.
25. Brown D, Weinberger B, Lewis C, Bonaparte H: **Understanding exposure from natural gas drilling puts current air standards to the test.** *Rev Environ Health*. in press.
26. Fuller CH, Brugge D, Williams PL, Mittleman MA, Lane K, Durant JL, Spengler JD: **Indoor and outdoor measurements of particle number concentration in near-highway homes.** *J Expo Sci Environ Epidemiol* 2013, **23:**506–512.
27. Rogers H: **Shale gas-the unfolding story.** *Oxford Rev Econ Pol'y* 2011, **27:**117–143.
28. Steinzor N, Subra W, Sumi L: **Investigating links between shale gas development and health impacts through a community survey project in Pennsylvania.** *New Solutions* 2013, **23:**55–83.
29. Eapi GR, Sabnis MS, Sattler ML: **Mobile measurement of methane and hydrogen sulfide at natural gas production site fence lines in the Texas Barnett Shale.** *J Air Waste Manag Assoc*. in press.
30. Kargbo DM, Wilhelm RG, Campbell DJ: **Natural gas plays in the Marcellus Shale: challenges and potential opportunities.** *Environ Sci Technol* 2010, **44:**5679–5684.
31. Beusse R, Dunlap C, Good K, Hauck E, McGhee-Lenart R, Narimatsu J: *EPA Needs to Improve Air Emissions Data for the Oil and Natural Gas Production Sector.* Washington, DC: Office of the Inspector General of the United States, Environmental Protection Agency, Report 13-P-0161; 2013.
32. Rappenglueck B, Ackermann L, Alvarez S, Golovko J, Buhr M, Field R, Slotis J, Montague DC, Hauze B, Adamson S, Risch D, Wilkerson G, Bush D, Stoeckenius R, Keslar C: **Strong wintertime ozone events in the Upper Green River Basin, Wyoming.** *Atmos Chem Phys* 2014, **14:**4909–4934.
33. Oltmans S, Schnell RC, Johnson B, Petron G, Mefford T, Nelly RN: **Anatomy of wintertime ozone associated with oil and natural gas extraction activity in Wyoming and Utah.** *Elementa* 2014. in press.
34. Swarthout RF, Russo RS, Zhou Y, Hart AH, Sive BC: **Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: influence of urban and natural gas sources.** *J Geophys Res-Atmos* 2013, **118:**10614–10637.
35. Petron G, Frost G, Miller BR, Hirsch AI, Montzka SA, Karion A, Trainer M, Sweeney C, Andrews AE, Miller L, Kofler J, Bar-Ilan A, Dlugokencky EJ, Patrick L, Moore CT Jr, Ryerson TB, Siso C, Kolodzey W, Lang PM, Conway T, Novelli P, Masarie K, Hall B, Guenther D, Kitzis D, Miller J, Wlesh D, Wolfe D, Neff W, Tans P: **Hydrocarbon emissions characterization in the Colorado Front Range: a pilot study.** *J Geophys Res-Atmos* 2012, **117:**1–19.
36. Helmig D, Thompson CR, Evans J, Boylan P, Hueber J, Park JH: **Highly elevated atmospheric levels of volatile organic compounds in the Uintah Basin, Utah.** *Environ Sci Technol*. in press.
37. Peischl J, Ryerson TB, Brioude J, Aikin KC, Andrews AE, Atlas E: **Quantifying sources of methane using light alkanes in the Los Angeles basin, California.** *J Geophys Res-Atmos* 2013, **118:**4974–4990.

38. Karion A, Sweeney C, Petron G, Frost G, Hardesty R, Kofler J, Miller BR, Newberger T, Wolter S, Banta R, Brewer A, Dlugokencky E, Lang P, Montzka SA, Schnell R, Tans P, Trainer M, Zamora R, Conley S: **Methane emissions estimate from airborne measurements over a western United States natural gas field.** *Geophys Res Lett* 2013, **40:**4393–4397.
39. Litovitz A, Curtright A, Abramzon S, Burger N, Samaras C: **Estimation of regional air-quality damages from Marcellus Shale natural gas extraction in Pennsylvania.** *Environ Res Lett* 2013, **8:**014017.
40. Zielinska B, Fujita E, Campbell D: *Monitoring of Emissions from Barnett Shale Natural Gas Production Facilities for Population Exposure Assessment.* Reno, NV: Desert Research Institute; 2010.
41. Levi MA: **Comment on "Hydrocarbon emissions characterization in the Colorado Front Range: a pilot study" by Gabrielle Petron et al.** *J Geophys Res Atmos* 2012, **117:**D21203.
42. Shepard PM, Northridge ME, Parkesh S, Stover G: **Advancing environmental justice through community-based participatory research.** *Environ Health Perspect* 2002, **110:**139.
43. Minkler M: **Linking science and policy through community-based participatory research to study and address health disparities.** *Am J Public Health* 2010, **100:**81–87.
44. Keeler GJ, Dvonch T, Yip FY, Parker EA, Israel BA, Marsik FJ, Morishita M, Barres JA, Robins TG, Brakefield-Caldwell W, Sam M: **Assessment of personal and community-level exposures to particulate matter among children with asthma in Detroit, Michigan.** *Environ Health Perspect* 2002, **110:**173–181.
45. Hobson J, Fishman S: *Quality Assurance Program Plan for the "Bucket Brigade" Community Air Sampling Pilot Project*, Approved by EPA Region IX and Contra Costa County Health Services; 1998.
46. Plate MC: *Region 9 Summary of Quality Assurance Planning for the "Bucket Brigade" Community Air Sampling Project, Contra Costa County, California.* San Francisco, CA: United States Environmental Protection Agency Region Nine; 2001.
47. Hobson J, Fishman S: *In Kind Donation of Analysis to the Contra Costa Bucket Brigade.* San Francisco, CA: Letter from Project Coordinator, Contra Costa County Health Services to Brenda Bettencourt, Lab Director, EPA Region IX Laboratory; 1998.
48. O'Rourke D, Macey GP: **Community environmental policing: assessing new strategies for public participation in environmental regulation.** *J Pol'y Analysis Manag* 2003, **22:**383–414.
49. Larson D, Breech R, Hendricks J, Chernaik M, Mall A, Smith F: *Gassed: Citizen Investigation of Toxic Air Pollution from Natural Gas Development.* El Cerrito, CA: Global Community Monitor; 2011.
50. NDEP: *Summa Canister Sampling.* Carson City, NV: State of Nevada Division of Environmental Protection; 2011 [http://www.ndep.nv.gov/fallon/summa/pdf]
51. USEPA: *Laboratory Case Narrative, Case Number R98X02.* Richmond, CA: United States Environmental Protection Agency Region IX; Nov. 1998.
52. USEPA: *Laboratory Case Narrative, Case Number R99X02.* Richmond, CA: United States Environmental Protection Agency Region IX; Jan. 1999.
53. USEPA: *Laboratory Case Narrative, Case Number R99X02.* Richmond, CA: United States Environmental Protection Agency Region IX; May 1999.
54. USEPA: *Laboratory Case Narrative, Case Number R99X02.* Richmond, CA: United States Environmental Protection Agency Region IX; Jun. 1999.
55. Darrow LA, Klein M, Sarnat JA, Mulholland JA, Strickland MJ, Sarnat SE, Russell AG, Tolbert PE: **The use of alternative pollutant metrics in time-series studies of ambient air pollution and respiratory emergency department visits.** *J Exp Sci Environ Epi* 2011, **21:**10–19.
56. Delfino R, Zeiger RS, Seltzer JM, Street DH, McLaren CE: **Association of asthma symptoms with peak particulate air pollution and effect modification by anti-inflammatory medication use.** *Environ Health Perspect* 2002, **110:**A607–A617.
57. Mills NL, Tornqvist H, Gonzalez MC, Vink E, Robinson SD, Soderberg S, Boon NA, Donaldson K, Sandstrom T, Blomberg A, Newby DE: **Ischemic and thrombotic effects of dilute diesel-exhaust inhalation in men with coronary heart disease.** *N Engl J Med* 2007, **357:**1075–1082.
58. USATSDR: *Toxicological Profile for Hydrogen Sulfide.* Atlanta, GA: United States Agency for Toxic Substances and Disease Registry Division of Toxicology and Environmental Medicine/Applied Toxicology Branch; 2006.
59. USATSDR: *Toxicological Profile for Formaldehyde.* Atlanta, GA: United States Agency for Toxic Substances and Disease Registry Division of Toxicology and Environmental Medicine/Applied Toxicology Branch; 1999.
60. USATSDR: *Toxicological Profile for Benzene.* Atlanta, GA: United States Agency for Toxic Substances and Disease Registry Division of Toxicology and Environmental Medicine/Applied Toxicology Branch; 2007.
61. Testa BM: **Home on the shales.** *Mech Eng* 2013, **135:**30–35.
62. USEPA: **Oil and natural gas sector: new source performance standards and national emission standards for hazardous air pollutants reviews.** *Fed Reg* 2014, **77:**49490–49600. Washington, DC: United States Environmental Protection Agency.
63. Vlaanderen J, Lan Q, Kromhout H, Rothman N, Vermeulen R: **Occupational benzene exposure and the risk of lymphoma subtypes: a meta-analysis of cohort studies incorporating three study quality dimensions.** *Environ Health Perspect* 2011, **119:**159–167.
64. Smith MT: **Advances in understanding benzene health effects and susceptibility.** *Ann Rev Public Health* 2010, **31:**133–148.
65. Lupo PJ, Symanski E, Waller DK, Chan W, Langlois PH, Canfield MA, Mitchell LE: **Maternal exposure to ambient levels of benzene and neural tube defects among offspring: Texas, 1999–2004.** *Environ Health Perspect* 2011, **119:**397–402.
66. Gross SA, Avens HJ, Banducci AM, Sahmel J, Panko JM, Tvermoes BE: **Analysis of BTEX groundwater concentrations from surface spills associated with hydraulic fracturing operations.** *J Air Waste Manag Assoc* 2013, **63:**424–432.
67. Wolf Eagle Environmental: *Town of Dish, Texas Ambient Air Monitoring Analysis Final Report.* Flower Mound, TX: Wolf Eagle Environmental; 2009 [http://townofdish.com/objects/DISH_-_final_report_revised.pdf].
68. D'Andrea MA, FACRO, Reddy GK: **Health effects of benzene exposure among children following a flaring incident at the British Petroleum refinery in Texas City.** *Pediatr Hematol Oncol* 2014, **31:**1–10.
69. USEPA: *Natural Gas-Fired Reciprocating Engines*, Volume AP-42 Section 3.2. Washington, DC: United States Environmental Protection Agency; 2000. [http://www.epa.gov/ttn/chief/ap42/ch03/final/c03s02.pdf]
70. Ingraffea AR, Wells MT, Santoro RL, Shonkoff SBC: **Assessment and risk analysis of casing and cement impairment in oil and gas wells in Pennsylvania, 2000–2012.** *Proc Nat Acad Sci.* in press.
71. Barnett Shale Energy Education Council: *Air Quality and the Barnett Shale.* Fort Worth, TX; 2011 [http://www.bseec.org/content/air-quality-and-barnett-shale]
72. Eastern Research Group: *City of Fort Worth Natural Gas Air Quality Study.* Morrisville, NC; 2011 [http://fortworthtexas.gov/uploadedFiles/Gas_Wells/AirQualityStudy_final.pdf]
73. USATSDR: *Report on Carcinogens, Twelfth Edition.* Research Triangle Park, NC: United States Agency for Toxic Substances and Disease Registry, National Toxicology Program; 2011.
74. Kim K, Jahan SA, Lee J: **Exposure to formaldehyde and its potential human health hazards.** *J Environ Sci Health Part C Environ Carcinog Ecotoxicol Rev* 2011, **29:**277–299.
75. McGwin G, Lienert J, Kennedy JI: **Formaldehyde exposure and asthma in children: a systematic review.** *Environ Health Perspect* 2010, **118**(3):313–317.
76. Wolkoff P, Nielsen GD: **Organic compounds in indoor air—their relevance for perceived indoor air quality.** *Atmos Environ* 2001, **35:**4407–4417.
77. USEPA: *Integrated Risk Information System, n-Hexane.* Washington, DC: United States Environmental Protection Agency; 2005.
78. Legator MS, Morris DL, Philips DL, Singleton CR: **Health effects from chronic low-level exposure to hydrogen sulfide.** *Arch Environ Health* 2001, **56:**123–131.
79. USATSDR: *Addendum to the Toxicological Profile for Hydrogen Sulfide.* Atlanta, GA: United States Agency for Toxic Substances and Disease Registry, Division of Toxicology and Environmental Medicine/Applied Toxicology Branch; 2012.
80. CDPHE: *Air Emissions Case Study Related to Oil and Gas Development in Erie.* Denver, CO: Colorado Department of Public Health and Environment; 2012.
81. ADEQ: *Emissions Inventory and Ambient Air Monitoring of Natural Gas Production in the Fayetteville Shale Region.* North Little Rock, AR: Arkansas Department of Environmental Quality; 2011.
82. PADEP: *Southwestern Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling.* Harrisburg, PA: Pennsylvania Department of Environmental Protection, Bureau of Air Quality; 2010.
83. Sexton K, Westberg H: **Nonmethane hydrocarbon composition of urban and rural atmospheres.** *Atmos Environ* 1984, **18:**1125–1132.
84. Carpenter DO, Arcaro K, Spink DC: **Understanding the human health effects of chemical mixtures.** *Environ Health Perspect* 2002, **110:**25–42.
85. Lan Q, Zhang L, Li G, Vermeulen R, Weinberg RS, Dosemeci M, Rappaport SM, Shen M, Alter BP, Wu Y, Kopp W, Waidyanatha S, Rabkin C, Guo W, Chanock S, Hayes RB, Linet M, Kim S, Yin S, Rotham N, Smith MT: **Hematotoxicity in workers exposed to low levels of benzene.** *Sci* 2004, **306:**1774–1776.

86. Vandenberg LN, Colborn T, Hayes TB, Heindel JJ, Jacobs DR, Lee DH, Shioda T, Soto AM, vom Saal FS, Welshons WV, Zoeller RT, Myers JP: **Hormones and endocrine-disrupting chemicals: low-dose effects and nonmonotonic dose responses.** *Endocrinol Rev* 2012, **33**:378–455.
87. Macey GP: **The architecture of ignorance.** *Utah L Rev* 2013, **2013**:1627–1685.
88. Carlin DJ, Rider CV, Woychik R, Birnbaum LS: **Unraveling the health effects of environmental mixtures: an NIEHS priority.** *Environ Health Perspect* 2013, **121**:6–8.

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ATTACHMENT C

STUDY 28

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ARTICLE

Health-based evaluation of ambient air measurements of $PM_{2.5}$ and volatile organic compounds near a Marcellus Shale unconventional natural gas well pad site and a school campus

Christopher M. Long[1] · Nicole L. Briggs[2] · Brian A. Cochran[3] · Destiny M. Mims[2]

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Abstract

Background Limited air monitoring studies with long-term measurements during all phases of development and production of natural gas and natural gas liquids have been conducted in close proximity to unconventional natural gas well pads.

Objective Conducted in an area of Washington County, Pennsylvania, with extensive Marcellus Shale development, this study investigated whether operations at an unconventional natural gas well pad may contribute to ambient air concentrations of potential health concern at a nearby school campus.

Methods Almost 2 years of air monitoring for fine particulate matter ($PM_{2.5}$) and volatile organic compounds (VOCs) was performed at three locations between 1000 and 2800 feet from the study well pad from December 2016 to October 2018. $PM_{2.5}$ was measured continuously at one of the three sites using a beta attenuation monitor, while 24-h stainless steel canister samples were collected every 6 days at all sites for analysis of 58 VOCs.

Results Mean $PM_{2.5}$ concentrations measured during the different well activity periods ranged from 5.4 to 9.5 $\mu g/m^3$, with similar levels and temporal changes as $PM_{2.5}$ concentrations measured at a regional background location. The majority of VOCs were either detected infrequently or not at all, with measurements for a limited number of VOCs indicating the well pad to be a source of small and transient contributions.

Significance All measurement data of $PM_{2.5}$ and 58 VOCs, which reflect the cumulative contributions of emissions from the study well pad and other local/regional air pollutant sources (e.g., other well pads), were below health-based air comparison values, and thus do not provide evidence of either 24-hour or long-term air quality impacts of potential health concern at the school.

Keywords $PM_{2.5}$ · VOCs · Natural gas · Marcellus Shale · Air monitoring · Public health

Introduction

There has been a proliferation of air monitoring data collected at major U.S. shale gas plays to understand the potential air quality impacts of the recent expansion of unconventional natural gas development (UNGD) activities, including horizontal drilling and hydraulic fracturing. Air measurement studies have been conducted by academic researchers [1–4], governmental agencies [5–9], industry scientists and industry-funded consultants [10–12], and environmental advocates and non-profit groups [13, 14]. Air pollutants that have been commonly measured in these studies include both US Environmental Protection Agency (US EPA) criteria air pollutants (e.g., fine particulate matter [$PM_{2.5}$], nitrogen dioxide [NO_2]), and volatile organic compounds (VOCs) classified by US EPA as air toxics (e.g., benzene, ethylbenzene, formaldehyde, n-hexane, toluene, and xylenes).

The Health Effects Institute (HEI)- Energy Research Committee [15] recently published a review of published air quality studies relevant to potential UNGD-related

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✉ Christopher M. Long
clong@gradientcorp.com

[1] Gradient, Boston, MA, USA

[2] Gradient, Seattle, WA, USA

[3] Spectrum Environmental Solutions, Austin, TX, USA

human exposures, identifying the need for additional studies to address important gaps in knowledge. In particular, the HEI-Energy report [15] highlighted the need for more research to characterize the spatial and temporal variability in airborne exposure levels and the conditions contributing to this variability, including more air monitoring data representing a range of geographic locales, meteorological conditions, UNGD operational conditions, and exposure durations (e.g., from acute durations of hours to weeks to chronic durations of a year and longer). In our review of air quality data available for the Marcellus Shale region [16], we observed that the majority of datasets consist of short-term measurements collected over time periods of days to weeks, thus providing insufficient data to evaluate long-term exposure conditions for the full life cycle of well pad development. In addition, most of the available measurement data are for monitoring locations between 0.2 and 1 miles from the nearest UNGD site, with fewer data for closer monitoring locations.

Pennsylvania's Washington County is one area in the Marcellus Shale region that has experienced rapid unconventional natural gas development in the last 10–15 years. In Washington County alone, nearly 1700 unconventional wells have been drilled in the last decade, the most of any Pennsylvania county [17]. Public concerns have been raised regarding potential health risks posed by the proliferation of well pads and other associated natural gas infrastructure (e.g., compressor stations and processing facilities) in Washington County, with air emissions and exposures being particular concerns [7–9].

This air monitoring study was conducted in a part of Washington County with extensive Marcellus Shale development [18] (Figure S.1). The primary objective of the study was to investigate whether development activities and production operations at an unconventional natural gas well pad site may be contributing to ambient air concentrations of potential health concern at a nearby school campus. Almost 2 years of measurements for both $PM_{2.5}$ and individual VOC species were made at three monitoring locations, including two locations between the well pad and the school campus and all between 1000 and 2800 feet from the well pad site (Fig. 1), during all phases of development and production of natural gas and natural gas liquids. Wind data (direction and speed) were also continuously collected at two of the monitoring sites. Thus, this dataset is notable for the lengthy duration of air quality measurements in close proximity to a well pad during all phases of development and production, and the collection of local wind data for assessing the contribution of the well pad to measured air concentrations.

We conducted a public health evaluation of this air monitoring dataset by comparing short-term (24-h) and long-term (>1 year) average $PM_{2.5}$ and VOC concentrations to acute and chronic health-based air comparison values developed by public health agencies to serve as conservative and health-protective benchmarks. In addition, we compared $PM_{2.5}$ and VOC measurements to air

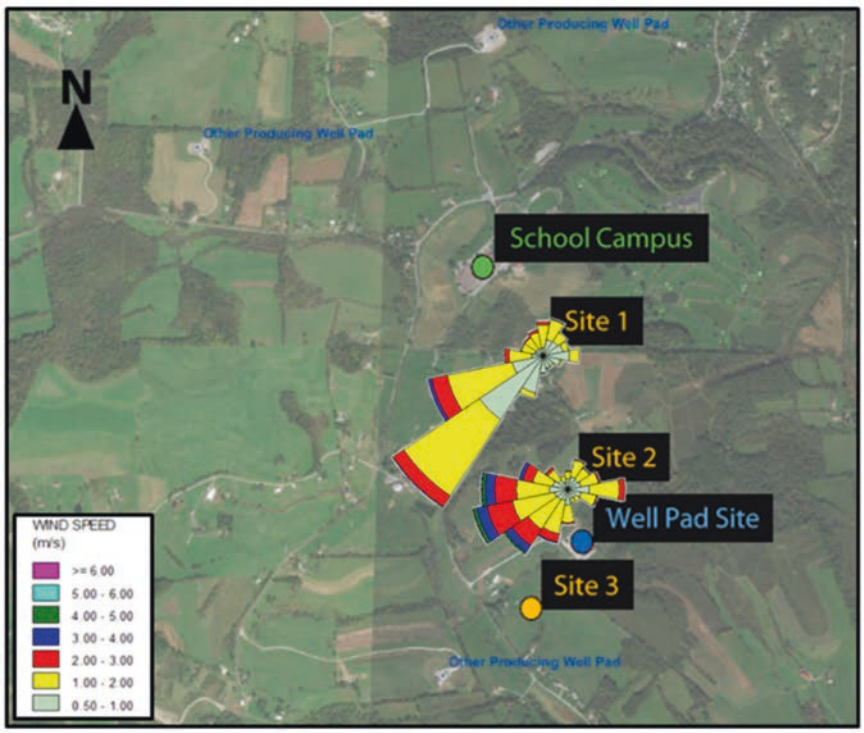

Fig. 1 Map of the three air monitoring sites relative to the study well pad site, the school campus, and other local producing well pads. Wind roses are also shown for Sites 1 and 2 where meteorological stations were operated.

concentrations measured at a background Washington County site more distant from oil and gas development activities and considered to be representative of regional background air quality. Although the study was designed to identify potential air quality impacts at the nearby school campus associated with operations at the study well pad site, the collected dataset reflects the cumulative contributions of air emissions from both the study well pad site and other local and regional sources.

Methods

Ambient air measurements

Three air monitoring sites were selected to address the primary study objective of evaluating air quality impacts at a nearby school campus associated with the development and operation of a UNGD well pad. Air monitoring sites 1 and 2 were located at distances of ≈2800 and 1000 feet, respectively, from the study well pad in the direction of the school campus (Fig. 1). Site 1 was the closest to the school campus (≈1500 feet to the southeast). The third monitoring site (site 3) was located about 1000 feet to the southwest of the well pad —i.e., upwind of the well pad for winds blowing in the direction of the school— to help evaluate whether other local sources, including the large number of other UNGD wells in the area (Figure S.1), may be important contributors to the site 1 and 2 measurements. Although an initial evaluation of the wind direction in the area indicated that winds were predominantly from the southwest, a monitoring site was not established to the northeast of the well pad because the area is wooded and inaccessible.

The monitoring program began in December 2016 during the site construction and set-up period of the study well pad and continued through October 2018 and after a full year of measurements were collected with all wells (six in total) in production. Table 1 shows the study air monitoring period relative to the different well pad activity periods, which included each of the typical well pad development phases, periods of lesser activity between the development phases that we have termed interlude periods, and the period when all wells were in production.

Ambient air measurements were made for $PM_{2.5}$ and 58 VOC species (see Table 1 for numbers of $PM_{2.5}$ measurement hours and VOC canister samples collected during each well pad activity period). Monitoring site 1 was chosen for the $PM_{2.5}$ measurements given that it was between the study well pad site and the school campus and in closer proximity to the school campus than site 2. Hourly average $PM_{2.5}$ measurements were collected continuously from February 2017 to October 2018 using a Met One Instruments Model

Table 1 Sampling dates and numbers of $PM_{2.5}$ measurement hours and VOC canister samples collected per study well pad activity period.

Study well pad activity period	Sampling dates	Number of monitoring site 1 $PM_{2.5}$ measurement hours in the period	Percentage of total sampling hours	# of VOC canister samples for study monitoring sites		
				# 1	# 2	# 3
Site construction and set-up	December 16, 2016–January 5, 2017	N/A	N/A	0	4	4
Vertical air drilling	January 5–February 18, 2017	177	1.2%	0	7	7
Interlude I	February 19–March 2, 2017	240	1.7%	2	2	2
Horizontal drilling	March 3–May 7, 2017	1546	10.9%	11	11	11
Interlude II	May 8–June 17, 2017	964	6.8%	6	6	6
Hydraulic fracturing	June 18–August 13, 2017	1302	9.2%	10	10	10
Interlude III	August 14–September 7, 2017	439	3.1%	4	4	4
Flowback	September 8–October 23, 2017	883	6.2%	8	8	8
Production	October 23, 2017–October 31, 2018	8618	60.8%	61	61	61

N/A Not Applicable, *$PM_{2.5}$* fine particulate matter less than 2.5 micrometers in diameter, *VOC* volatile organic compound.

BAM-1020 per the US EPA Federal Equivalent Method (FEM). Beginning on December 16, 2016, at sites 2 and 3, and February 15, 2018, at site 1, 24-h stainless steel canisters were collected for VOC analysis every 6 days through October 2018. Samples were analyzed using US EPA Method TO-15, focusing on 58 VOC species selected to match the set of TO-15 VOC species typically monitored by Pennsylvania Department of Environmental Protection (PADEP) at its air toxics sampling sites across the state. This expanded set of VOC analytes was selected based on prior experience of the well pad operator regarding typical air emission sources at its well pads. VOCs not known to be associated with UNGD activities (e.g., chlorinated solvents like carbon tetrachloride and methylene chloride) were retained as analytes. Acrolein was one of the 58 target VOCs, but we have not reported or evaluated the acrolein measurements based on determinations by both PADEP and US EPA that acrolein measurements obtained using this method are unreliable [8, 19, 20]. Wind speed and direction were also measured at both sites 1 and 2 using solar-powered portable met stations from February 8, 2017 to October 31, 2018, and December 16, 2016 to October 31, 2018, respectively; additional meteorological parameters (e.g., relative humidity, barometric pressure, and temperature) were also collected at site 1.

Data analysis

Microsoft Excel 2013 (Microsoft Corporation, Redmond, WA, USA), SigmaPlot (Systat Software, Inc., San Jose, CA, USA), R (R Core Team, Vienna, Austria), and ProUCL version 5.1 (US EPA, Washington, DC, USA) were used for statistical and graphical data analysis. For $PM_{2.5}$, we analyzed the hourly data, and also calculated 24-h daily average concentrations for days with 18 or more monitoring hours. For VOCs detected at least once, we substituted one-half the limit of detection (LOD) for non-detects (LODs were typically 0.06 parts per billion). The 95% upper confidence limits (UCLs) of mean concentrations were calculated for VOCs detected at least twice using US EPA's ProUCL software, with reporting of UCLs for the methods recommended by the software.

Correlations between measured concentrations at each site were examined using Spearman rank correlations. We conducted statistical testing to compare concentrations between sites, well activity periods, and wind directions using non-parametric tests that included the Kruskal–Wallis *H* Test and the Mann–Whitney rank sum test. Statistical significance was defined as a p value less than 0.05. For VOCs, we focused statistical testing on a subset of 14 of the 58 target VOCs that were consistently detected (i.e., detection frequencies >75%) at each of the monitoring sites.

The wind direction data collected at sites 1 and 2 were evaluated in several ways. Wind roses were prepared using WRPLOT View (Lakes Environmental, Waterloo, Ontario). To allow for the evaluation of wind directions on a daily basis corresponding to the VOC sampling periods, average daily wind directions were calculated, categorized according to an 8-point compass, and the percent of days in which the winds arrived from each of these directions was calculated. Given the hourly averaging time of the $PM_{2.5}$ measurements, the percent of hourly wind measurements in each of the eight directions was also calculated.

The $PM_{2.5}$ and VOC measurements were also compared to air concentrations measured at a monitoring site ≈10 miles away in Florence, PA, which has been used by PADEP as a background Washington County comparison site [8]. PADEP has described this rural monitoring site as being impacted primarily by regional transport [8]. $PM_{2.5}$ data for the study monitoring period were obtained for the Florence site from US EPA's Air Quality System (AQS). No VOC data are available from the Florence site for the study monitoring period, but maximum 24-h and mean VOC concentrations for 24-h canister samples collected every sixth day between October 2012 and December 2013 at the Florence monitoring site were obtained from PADEP [8] data summaries.

Health-based evaluation of ambient air measurements

We identified acute and chronic health-based air comparisons values (HBACVs) for this evaluation that are health-protective benchmarks developed by public health agencies. The US EPA $PM_{2.5}$ primary National Ambient Air Quality Standards (NAAQS), which are developed to be protective of the health of the general public as well as sensitive populations such as asthmatics, children, and the elderly, were used as $PM_{2.5}$ acute and chronic benchmarks. We compared the maximum 24-h daily average concentration to the level of the NAAQS (35 $\mu g/m^3$), a conservative comparison given that the standard is intended to be compared to a 3-year average of the 98th percentile of 24-h measurements at a site. The annual $PM_{2.5}$ NAAQS requires that the mean annual $PM_{2.5}$ concentration at a site, averaged over 3 years, remains below 12.0 $\mu g/m^3$. Given that $PM_{2.5}$ measurements were not available for a 3-year period, the mean concentration from the entire $PM_{2.5}$ sampling period was calculated and compared to the annual NAAQS.

The maximum 24-h measurement of each VOC detected at the three air monitoring sites was compared to acute HBACVs. We employed a tiered approach to identify acute HBACVs because there was not a single HBACV source inclusive of all measured VOCs. Agency for Toxic Substances and Disease Registry (ATSDR) acute inhalation

Minimal Risk Levels (MRLs) were considered to be the preferred source of HBACVs because they are developed to be protective of 24-h exposure durations according to a well-documented and conservative process based on the most sensitive substance-induced end point of relevance to humans [21]. ATSDR acute inhalation MRLs are derived for 1–14 day exposure durations, and therefore comparison to the 24-h air monitoring site measurements is conservative. If an ATSDR acute inhalation MRL was not available for a VOC, acute inhalation reference concentrations (RfCs) from the Department of Energy Oak Ridge National Laboratory (ORNL) Risk Assessment Information System (RAIS) were used. When neither a ATSDR MRL nor a RAIS RfC was available, we derived an acute HBACV by multiplying a US EPA chronic reference concentration (RfC) by 10 [22]. For ethanol, the US National Institute for Occupational Safety and Health (NIOSH) time-weighted average recommended exposure limit (REL) was selected as the acute HBACV. We were not able to identify acute HBACVs for 11 VOCs, however, the majority of these were not detected in any samples.

We evaluated chronic health risks by comparing 95% UCLs of mean VOC concentrations (or for VOCs detected just once, mean concentrations that were calculated using half of the LOD for non-detects) at each site to chronic HBACVs. We consider 95% UCLs to represent conservative estimates of chronic air exposure levels at the monitoring sites given not only the likelihood that they are overestimates of true long-term average concentrations, but also due to the transient nature of the well pad development phases. For non-carcinogenic VOCs, US EPA non-cancer RfCs were used as chronic HBACVs, and for known or suspected human carcinogens, the lower value of either the non-cancer US EPA RfC or the cancer-based estimated continuous lifetime concentration was used. Using US EPA inhalation unit risk (IUR) estimates, we calculated the cancer-based estimated continuous lifetime concentrations for a 1-in-10,000 excess lifetime cancer risk, consistent with the US EPA residual risk program and with long-term comparison levels developed as part of US EPA's School Air Toxics Initiative [22, 23].

Results

Wind measurement data

Wind roses constructed from wind data collected at monitoring sites 1 and 2 indicate that the prevailing local winds were from the west and southwest (Fig. 1), and thus did not generally blow emissions from the well pad towards the monitoring sites and the school campus. However, it is expected that winds blowing from the southerly and southeasterly directions would have transported study well pad air emissions to monitoring sites 1 and 2, and a detailed evaluation of wind directions at these sites confirmed that winds blowing from southeasterly and southerly directions were relatively common during each of the well pad activity periods (Table S.1).

Summary of $PM_{2.5}$ measurement data

Table 2 provides a summary of the hourly $PM_{2.5}$ measurement data collected from February 2017 to October 2018 at monitoring site 1, showing an overall mean $PM_{2.5}$ concentration of 7.1 μg/m^3 and mean concentrations for the different well activity periods that ranged from a low of 5.4 μg/m^3 for the vertical air drilling phase to a high of 9.5 μg/m^3 for the interlude III phase. Kruskal–Wallis H Tests identified statistically significant differences in hourly $PM_{2.5}$ concentrations between some of the well activity periods, including statistically higher concentrations for the interlude III and hydraulic fracturing periods and statistically lower concentrations for the vertical air drilling and production periods. When data were stratified by hours with winds from the south and southeast (i.e., from the direction of the study well pad site) versus winds from other directions, we observed statistically significant increased hourly $PM_{2.5}$ concentrations for the hours with southerly and southeasterly wind directions for all well activity periods except the interlude II and interlude III periods (Figure S.2); however, as illustrated by Fig. 2 which compares 24-h average $PM_{2.5}$ concentrations measured at monitoring site 1 with the corresponding 24-h average $PM_{2.5}$ concentrations measured at the PADEP Florence background site, highly similar $PM_{2.5}$ levels and temporal changes were observed as for a regional background site. Statistical testing showed no statistical difference between the two datasets (Mann–Whitney rank sum test, p value = 0.82).

Summary of VOC measurement data

Table S.2 provides a comprehensive set of summary statistics for the VOC measurement data by monitoring site, showing that the majority of the target VOC species were either detected infrequently or not at all. Only 14 VOCs were consistently detected (i.e., detection frequencies >75%) at each of the three monitoring sites—acetone, benzene, 2-butanone, carbon tetrachloride, chloromethane, dichlorodifluoromethane, ethanol, Freon 113, methanol, methylene chloride, n-hexane, propylene, toluene, and trichlorofluoromethane. While median concentrations for these VOCs were frequently less than 1 ppb and all were less than 10 ppb, maximum detected 24-h concentrations exceeded 100 ppb for a few of the VOCs (acetone, ethanol, and methanol). As shown in Table S.2, there were no

Table 2 Summary of hourly $PM_{2.5}$ measurements for monitoring site 1.

Study well pad activity period	Median hourly $PM_{2.5}$ conc. ($\mu g/m^3$)	Mean hourly $PM_{2.5}$ conc. ($\mu g/m^3$)	Standard deviation hourly $PM_{2.5}$ conc. ($\mu g/m^3$)	Maximum 1-h $PM_{2.5}$ conc. ($\mu g/m^3$)	Maximum 24-h $PM_{2.5}$ conc. ($\mu g/m^3$)
Site construction and set-up	N/A	N/A	N/A	N/A	N/A
Vertical air drilling	4.0	5.4	4.3	24.0	7.1
Interlude I	6.0	6.6	4.8	37.0	13.6
Horizontal drilling	6.0	6.8	4.4	54.0	14.4
Interlude II	6.0	6.8	4.0	29.0	14.2
Hydraulic fracturing	7.0	7.8	4.3	24.0	17.6
Interlude III	9.0	9.5	4.3	24.0	13.1
Flowback	6.0	7.0	4.9	41.0	14.4
Production	6.0	7.1	4.8	141.0	24.6
Total	6.0	7.1	4.7	141.0	24.6

The maximum 24-h $PM_{2.5}$ concentration was calculated for only days in which there were at least 18 hours of $PM_{2.5}$ data available.

N/A signifies that no data were collected for the period.

Conc concentration, *$PM_{2.5}$* fine particulate matter less than 2.5 micrometers in diameter

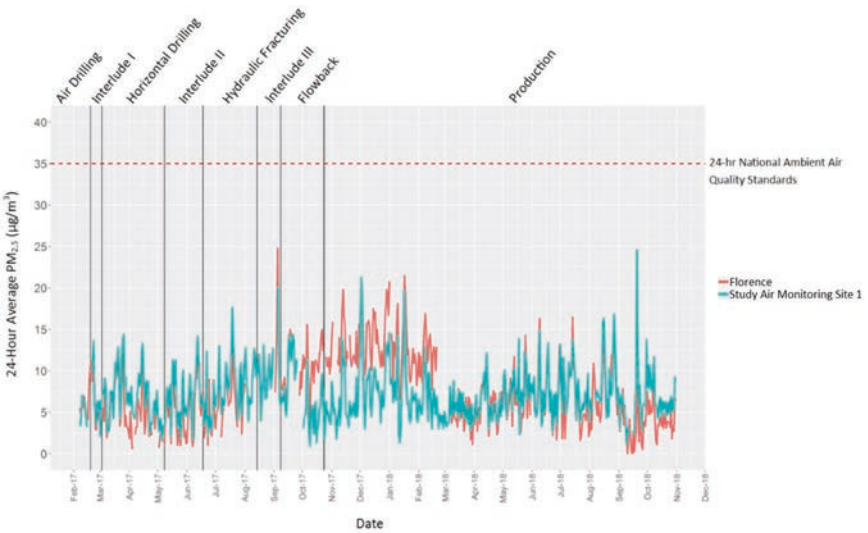

Fig. 2 Time series of 24-h $PM_{2.5}$ measurements at study monitoring site 1 and the PADEP background Florence site. PADEP Pennsylvania Department of Environmental Protection, $PM_{2.5}$ fine particulate matter less than 2.5 micrometers in diameter.

consistent patterns with respect to when maximum VOC concentrations were detected across VOCs and monitoring sites. For example, maximum detected concentrations for both acetone and methanol occurred in the interlude II, production, and interlude III periods for monitoring sites 1, 2, and 3, respectively; for toluene, maximum detected concentrations occurred in the horizontal drilling, production, and interlude II periods for monitoring sites 1, 2, and 3, respectively. For a limited number of VOCs, maximum concentrations occurred within the same well activity period for either all three sites or two out of three sites (e.g., benzene: site construction and set-up period for two sites; n-hexane: flowback period for all three sites; ethanol: production period for two sites; propylene: flowback period for two sites).

Correlational analysis revealed consistent moderate to strong correlations (Spearman's rank correlation coefficients r_s between 0.36 and 0.90) across the three monitoring sites between several groups of VOCs, suggesting that they may have common sources (Tables S. 3a, b, and c). These groupings included 2-butanone, acetone, ethanol, methanol, and toluene (for 2 of the 3 sites, also methylene chloride); chloromethane, dichlorodifluoromethane, and Freon 113; n-hexane and propylene (for 2 of the 3 sites, also toluene); and carbon tetrachloride and trichlorofluoromethane. Benzene exhibited statistically significant weak to moderate

correlations (r_s between 0.31 and 0.44) with propylene and toluene for all sites and with n-hexane for 2 of the 3 sites. For site 1, we also examined correlations between 24-h daily-average $PM_{2.5}$ concentrations and VOC concentrations, finding statistically significant weak correlations (r_s between 0.23 and 0.37) with benzene, carbon tetrachloride, methanol, n-hexane, and toluene. Although suggestive of possible common sources, the correlational analysis do not allow for the identification and apportionment of sources, such as any contributions from the study well pad site relative to other local well pads and area air emission sources (e.g., industrial sources and traffic).

Statistical testing using the Kruskal–Wallis *H* Test demonstrated no statistically significant differences in measured concentrations across the three monitoring sites for 9 of the 14 consistently detected VOCs. For the five VOCs where statistically significant differences by site were found (acetone, ethanol, methanol, methylene chloride, and toluene), multiple comparisons conducted using Dunn's Method consistently showed statistically significantly higher concentrations at monitoring sites 2 and 3 versus monitoring site 1, but no statistically significant differences between the site 2 and site 3 concentrations.

Focusing on sites 1 and 2 where there were concurrent wind direction measurements, Tables S.4 and S.5 compare summary statistics for the 14 consistently detected VOCs for sampling days with frequent winds from the southerly or southeasterly direction (i.e., from the study well pad site in the direction of the monitoring sites and the school campus) versus for other wind directions. These tables show relatively small difference in concentrations for the two sets of wind conditions (i.e., typical <1 ppb differences in median concentrations). For a limited number of the 14 VOCs, statistically significant increased concentrations were observed for sampling days with frequent winds from south and southeasterly directions versus other wind directions, including for acetone (site 1), benzene (site 2), 2-butanone (site 2), ethanol (site 1), n-hexane (sites 1 and 2), propylene (site 2), and toluene (sites 1 and 2). However, for site 3 (which is to the southwest of the study well pad), most of the same VOCs (all but ethanol and 2-butanone) were found to have statistically significantly higher concentrations for days with frequent southerly and southeasterly winds versus other wind directions, suggesting that other local/regional sources rather than the study well pad site may be responsible for the higher concentrations at monitoring sites 1 and 2 with southerly and southeasterly winds (the wind data for monitoring site 2 were used in this analysis due to the lack of site-specific wind data for monitoring site 3).

Additional statistical testing was conducted on the VOC data to investigate whether measured VOC concentrations were related to study well pad activity period. Given the small number of samples for some of the shorter duration well activity periods, well development and interlude periods were grouped together to form three broader activity periods—active well development periods (encompassing the site construction and set-up, vertical air drilling, horizontal drilling, hydraulic fracturing, and flowback periods), interlude periods (encompassing the three interlude periods), and the production period. This statistical analysis identified some statistically significant differences in VOC concentrations for these activity periods, although the results were not consistent across VOCs and monitoring sites and are thus difficult to interpret. For example, no statistically significant differences across the three activity periods were observed in the Kruskal–Wallis *H* Test for benzene (*p* values of 0.562, 0.379, 0.086), ethanol (*p* values of 0.061, 0.551, 0.347), or n-hexane (*p* values of 0.396, 0.170, 0.464). However, for both methanol and propylene, statistically significant differences were observed for the activity period factor for each of the three sites, with pairwise multiple comparisons on ranks (Dunn's Method) showing statistically significant lower methanol concentrations for the production period relative to the interlude periods for each site and to the active well pad development periods for one of the three sites, and statistically significant lower propylene concentrations for the production period relative to the active well pad development periods for all three sites.

Table S.6 compares summary statistics for VOCs measured at the three study monitoring sites with the corresponding values for 2012–2013 sampling conducted at the PADEP Florence background site [8]. As shown in this table, the same set of 12 VOCs was consistently detected at the Florence background site as at the study monitoring sites (note that neither ethanol nor methanol was monitored at the Florence site). Summary statistics were very similar between the two datasets for seven of the 12 VOCs, including benzene, 2-butanone, carbon tetrachloride, chloromethane, dichlorodifluoromethane, Freon 113, and trichlorofluoromethane. Six of these 7 VOCs are not well established to be associated with UNGD activities; although benzene is known to be present in UNGD site emissions, both mean and maximum benzene measurements for the study monitoring sites were generally lower than the Florence background site measurements. The 24-h maximum measurements for at least one of the three study monitoring sites were noticeably higher than the maximum measured Florence site concentrations for acetone, methylene chloride, n-hexane, propylene, and toluene. Although the study well pad site may have contributed to some of these maximum 24-h concentrations, an examination of the wind measurement data indicated that some of the maximum measurement days had few, if any, winds from the direction of the study

well pad site, suggesting the role of other sources unrelated to the study well pad site.

Comparison with health-based air comparison values (HBACVs)

The maximum 24-h $PM_{2.5}$ concentration for the entire $PM_{2.5}$ dataset was 24.6 μg/m^3 (based on data from 587 days with at least 18 hours of $PM_{2.5}$ data), which is well below the acute $PM_{2.5}$ HBACV of 35 μg/m^3. The overall mean $PM_{2.5}$ concentration plus or minus one standard deviation was 7.1 ± 4.7 μg/m^3, which is below the chronic $PM_{2.5}$ HBACV of 12 μg/m^3, even when including one standard deviation. Therefore, measured $PM_{2.5}$ concentrations near the study well pad are below established regulatory levels of both acute and chronic health concern.

For VOCs, Tables S.7 and S.8 provide the full set of comparisons to acute and chronic HBACVs. As shown in these tables, maximum measured 24-h VOC concentrations for each site were consistently below the acute HBACVs, while 95% UCLs of mean VOC concentrations calculated from all measurements and from only the production phase at each site were all below chronic HBACVs. Figures 3 and 4 illustrate the large differences that are typical between the measured VOC concentrations and the acute and chronic HBACVs for the BTEX compounds (benzene, toluene, ethylbenzene, and xylenes). There were four compounds detected at one or more of the air monitoring sites, but for which no appropriate acute or chronic benchmarks were identified: hexachloro-1,3-butadiene, m-dichlorobenzene, p-ethyltoluene, and trichlorofluoromethane. These VOCs are not expected to present either acute or chronic health risks due to the infrequent detections (for all but trichlorofluoromethane) and the low, sub-ppb detected concentrations (all).

Discussion

Given the long duration of air monitoring, our study provided a dataset that reflects a range of well pad development phases and operating conditions, meteorological conditions, and exposure durations in the Marcellus Shale region. For $PM_{2.5}$, the similar levels and diurnal trends between the study monitoring site and Florence background site indicate local/regional air quality as the dominant contributor to measured concentrations. Our analysis of $PM_{2.5}$ measurements across the different well activity periods suggest possible small $PM_{2.5}$ contributions at the measurement site from emissions at the study well pad site, such as for the hydraulic fracturing period; however, it bears mentioning that seasonal $PM_{2.5}$ trends are a likely confounder for data comparisons between well activity periods, and our analysis of $PM_{2.5}$ concentrations stratified by wind direction cannot differentiate between contributions from the study well pad and other local PM sources to the south and southeast. Both period-average and maximum 24-h concentrations for the well pad activity periods remained well below the US EPA NAAQS, indicating that if there were any $PM_{2.5}$ air quality impacts from development activities at the study well pad site, they did not contribute to NAAQS exceedances at the monitoring site. Given the location of the monitoring site between the study well pad site and the school campus, it is thus unlikely that the study well pad site caused any $PM_{2.5}$ NAAQS exceedances at the school campus.

Of the 14 consistently detected VOCs, seven (acetone, benzene, ethanol, methanol, n-hexane, propylene, toluene) have been associated with UNGD activities [9, 19, 24–26]. Of these seven VOCs, there were known sources of all but ethanol and methanol at the study well pad. Some of our study findings, including statistically significantly higher VOC concentrations (e.g., acetone, ethanol, methanol, methylene chloride, toluene) at the two monitoring sites closest to the study well pad site (sites 2 and 3) relative to the third site (1) and higher maximum 24-h VOC comparisons (e.g., acetone, methylene chloride, n-hexane, propylene, and toluene) at the study monitoring sites relative to data for the PADEP Florence background site, may indicate small and transient VOC contributions from the study well pad site at the monitoring sites. However, overall, there was significant variability in measured concentrations across different VOCs, sites, and sampling periods, and other findings suggest contributions from other local and regional sources. These findings include the measurement of maximum 24-h concentrations for a number of VOCs (e.g., acetone and methanol) during the nonactivity interlude periods at the study well pad site, and the similar statistically significant differences in VOC concentrations at monitoring site 3 with southerly and southeasterly winds as for monitoring sites 1 and 2. Half of the consistently detected VOCs (2-butanone, carbon tetrachloride, chloromethane, dichlorodifluoromethane, Freon 113, methylene chloride, trichlorofluoromethane) were frequently detected by PADEP during its short-term air monitoring studies conducted at UNGD sites in southwestern, northeastern, and north-central PA, and attributed to either regional or global air quality rather than Marcellus Shale development activities [19, 24, 25]. Other target VOCs reported to be associated with well development activities (e.g., 1,3-butadiene, ethylbenzene, xylenes, trimethylbenzenes) were infrequently detected despite the use of sensitive detection limits.

Regardless of VOC sources, the measured concentrations, which reflect the cumulative contributions of both air emissions from the study well pad site and from other local and regional air pollutant sources including other area well

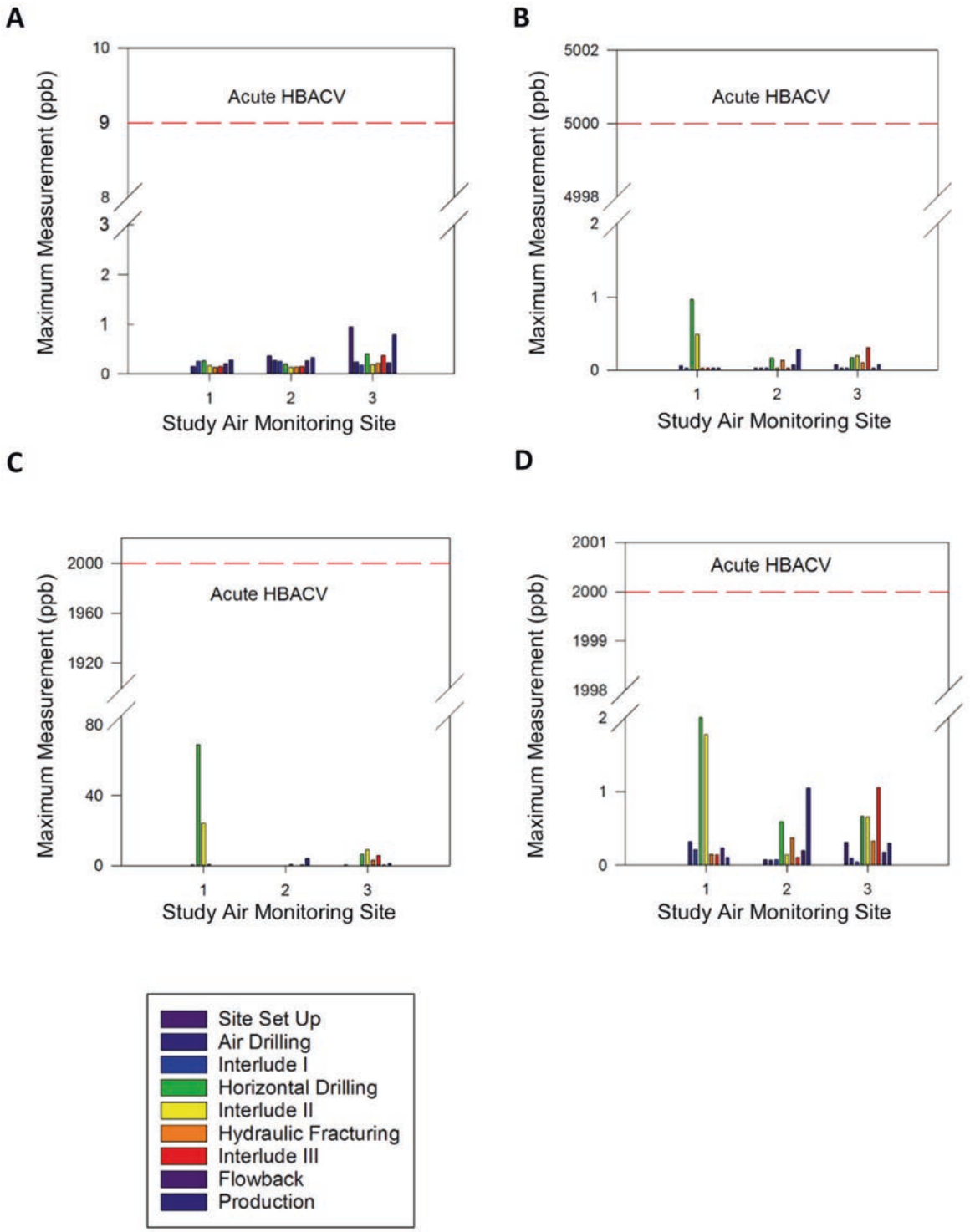

Fig. 3 Summary of maximum measured 24-h VOC concentrations by monitoring site and study well pad site development phase. **A** benzene, **B** ethylbenzene, **C** toluene, and **D** xylenes. Acute health-based air comparison values (HBACVs) are shown in red dashed lines. ppb parts per billion, VOC volatile organic compound. Measurements for m-, p-, and o-xylenes are summed in this figure because the applicable acute HBACV is for mixed xylenes.

pad sites, are consistently below levels of acute and chronic health concern. Given that two of the air monitoring sites are located between the study well pad site and the school campus, the VOC and $PM_{2.5}$ measurement data do not provide evidence of either 24-h or long-term average concentrations of potential health concern at the nearby school

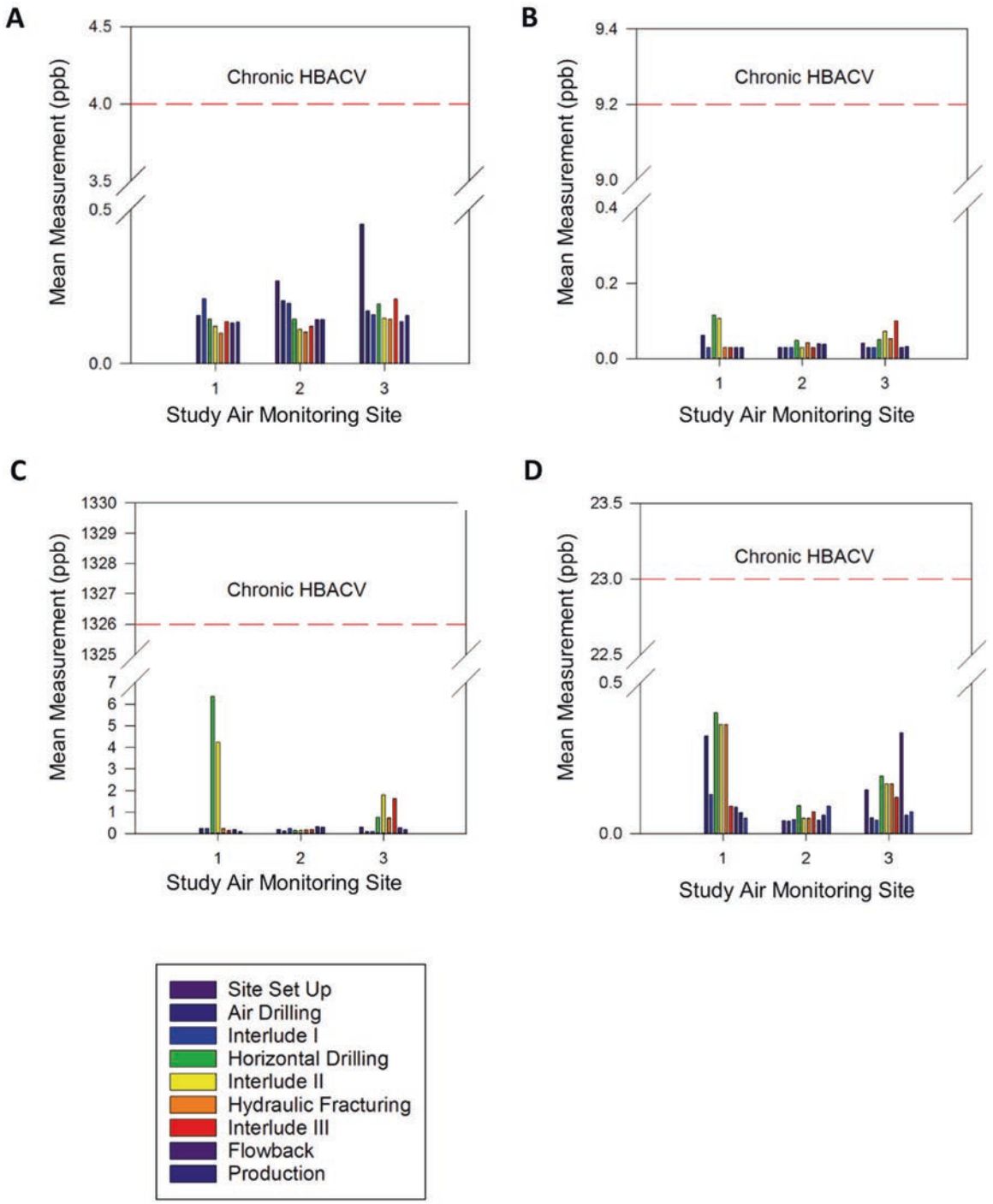

Fig. 4 Summary of mean VOC concentrations by monitoring site and study well pad site development phase. **A** benzene, **B** ethylbenzene, **C** toluene, and **D** xylenes. Chronic health-based air comparison values (HBACVs) are shown in red dashed lines. ppb parts per billion, VOC volatile organic compound. Measurements for m-, p-, and o-xylenes are summed in this figure because the applicable chronic HBACV is for mixed xylenes. Mean concentrations, and not 95% UCLs of the means, are shown due to the small number of samples and high fraction of non-detects for some development phases.

campus. More study is needed to confirm their broader generalizability, but these study findings supporting the lack of elevated chronic exposure levels when $PM_{2.5}$ and VOC concentrations were averaged across measurements made during all phases of well pad development may apply to other locales in the Marcellus Shale region with similar types of UNGD sites and operations.

These findings are consistent with operator efforts to control air emissions through continued refinement of best practices, as well as evolving governmental regulations

focused on air emissions. Operators have made continuous improvements to improve drilling performance, completion design, and production efficiency [27]. For example, during drilling, VOC emission rates are kept relatively low since hydrocarbon zones have not been stimulated, and emissions are combusted as required for safety. Range Resources has developed an enhanced flowback process using updated equipment and processes that is estimated to reduce air emissions during flowback by more than 80% [27]. Design changes, including a transition from flare stacks and enclosed burner units to vapor recovery compression and closed-loop systems, and upgrades to thief hatches on tank batteries [27], have been implemented to eliminate episodic high emission rates. In addition, operators such as Range Resources have deployed advanced technologies, including supervisory control and data acquisition software, remote telemetry monitoring systems, and infrared optical methane cameras, in order to oversee production and quickly respond to potential problems [27]. As discussed in Seguljic and Martin [28], both federal and Pennsylvania state regulations have evolved in recent years to target air emissions from well pad development and production operations.

Other recent studies in the Marcellus Shale region have similarly reported measured air pollutant concentrations to be generally below levels of human health concern for air sampling conducted in proximity to UNGD sites [4, 8, 9, 16, 19, 24, 25, 29, 30]. In particular, the Maskrey et al. [30] study was conducted in the same community as this study to investigate air quality impacts of development activities at another local UNGD well pad at the same school campus. Conducted on behalf of the local school board, this study made continuous measurements of total volatile organic compound (TVOC) concentrations and collected canister samples for individual VOC analysis at two monitoring sites (on the high school campus and at a private residence) over an ≈3-month period during four well pad activity periods: a baseline period before hydraulic fracturing commenced, the hydraulic fracturing period, the flaring period, and an inactive period following flaring. None of the VOC concentrations measured at either the high school or the private residence exceeded health-based benchmarks, and therefore the study investigators concluded that there was no measurable health impact from the well pad at either site.

The Allegheny County Health Department (ACHD) collected one of the few other long-term datasets for the Marcellus Shale region that included monitoring during all phases of development at nearby well pads. ACHD installed the Deer Lakes and Imperial Pointe temporary monitors in 2014 ≈0.85 and 0.3 miles, respectively, from the nearest well pads. The 4 years of VOC data available for each of these sites prior to their decommissioning in May 2017 have been categorized by ACHD according to activity time periods (baseline, site construction, drilling, fracking, and production) at the nearest well pads [5, 6]. All measured VOC concentrations are consistently low and below health-based benchmarks; for example, the highest 24-h benzene concentration measured during the ACHD monitoring was 0.8 ppb, while study-average benzene concentrations of 0.17 and 0.26 ppb were measured at the two sites [16].

Some studies have reported findings of elevated episodic air pollutant concentrations near UNGD sites during specific phases of development [31, 32]. As part of the West Virginia University (WVU) Air, Noise, and Light Monitoring Study, McCawley [31] reported elevated maximum 72-h benzene concentrations ranging from 8.2 to 85 ppb at four UNGD sites during drilling (horizontal or vertical) or hydraulic fracturing/flowback activities. In comparison, maximum 24-h benzene concentrations for this study ranged from 0.29 to 0.95 ppb and were either lower than or only slightly above measured benzene concentrations for the PADEP Florence background site (Table S.6). Differences in these findings may be due in part to the closer proximity (between 492 and 1312 feet [33]) of the monitoring sites to well pads in the WVU study, as well as differences in well pad design and operations and processes. In addition, as mentioned previously, our study did not have a monitoring site in the prevailing wind direction, and it is thus not possible to rule out the presence of higher benzene (or other VOC) concentrations associated with the study well pad site at other non-monitored locations.

While we did not identify any clear, consistent patterns in short-term $PM_{2.5}$ and VOC concentrations across the study well pad development phases, we acknowledge some important study limitations that have bearing on future studies investigating the temporal and spatial variability of air quality nearby to UNGD activity. Measurements in this study were focused on $PM_{2.5}$ and VOCs, which are important classes of air pollutants that have been associated with UNGD. However, there are a number of other air pollutants that have also been associated with UNGD via primary emissions or secondary atmospheric formation, including other criteria air pollutants (NO_2, carbon monoxide [CO], sulfur dioxide [SO_2], ozone [O_3]), and air toxics (e.g., acetaldehyde, formaldehyde, and hydrogen sulfide) [15, 16]. Hydrogen sulfide was not measured in this study based on prior analysis conducted by the site operator that indicated that this is not a sour gas region with significant hydrogen sulfide emissions. While it is thus not expected that hydrogen sulfide emissions at the well pad would have posed potential health risks at the school, this study did not address other air pollutants besides $PM_{2.5}$ and VOCs.

Similar to other air monitoring studies, this study was limited by the small number of air monitoring sites, and for VOCs, by the 24-h sample averaging time and every 6th

day sampling frequency. The $PM_{2.5}$ and VOC measurement data provide estimates of air exposure levels at the monitoring sites themselves and may not be representative of other locations or time periods. For example, the limited number of air monitoring sites did not allow for the characterization of the full range of potential air exposure levels associated with the well pad development. However, for the primary study objective of evaluating air quality impacts of the study well pad at the school campus, the study design, and specifically the location of two of the monitoring sites between the study well pad site and the school campus, provided reliable evidence that air quality impacts of potential health concern were unlikely at the school. It is possible that higher VOC concentrations may have occurred on non-sampling days, however, it bears mentioning that the collection of 24-h samples every 6th day is the standard US EPA sampling design for air toxics [34]. Moreover, with greater than 1 year of air sampling during the production phase, there were more than 60 air samples collected for VOC analysis at each of the three air monitoring sites, and thus a sizable dataset to represent both 24-h peak and long-term average VOC concentrations during the production phase of the study well pad.

It is recommended that future air monitoring studies conducted in proximity to UNGD well pads include higher resolution sampling (e.g., 1-h) for VOCs, as the standard 24-h sample duration does not allow for the characterization of episodic peak air pollutant events. These data are needed to assess whether brief, intermittent exposures (i.e., 1-h or less) may pose acute health risks. Only a small number of studies conducted in the Marcellus Shale region have measured VOC concentrations for sampling frequencies of 1-h or less [1, 2, 31, 34, 35]. Given the difficulty of disentangling the contributions of a specific local well pad site from other area oil & gas development sites, it is also recommended that studies be designed to facilitate source apportionment modeling.

Our study results indicated some higher $PM_{2.5}$ concentrations during the hydraulic fracturing phase when ≈100 temporary diesel-powered combustion sources (e.g., generators, light towers, pumps, pressure washers, heaters, and air compressors) are typically utilized at well pad sites. Although mean and maximum 24-h $PM_{2.5}$ concentrations remained below the corresponding NAAQS during this time period, our findings indicate a need for additional $PM_{2.5}$ monitoring during well completion activities to investigate possible off-site impacts of the combustion emissions. It bears mentioning that the industry has transitioned to greater direct use of natural gas in place of diesel fuel, or co-firing of natural gas with diesel fuel, for both drilling and well completion equipment [27, 36–38]. Flowback is generally recognized as a source of hydrocarbon emissions, and the high concentrations of some hydrocarbons (e.g., hexane and propylene) were detected during the flowback phase of the study well pad. Recognizing the recent transition to reduced emissions completions, our findings suggest that additional VOC monitoring during the flowback phase could be helpful to confirm the efficacy of reduced emissions completions for mitigating off-site VOC impacts.

In conclusion, this air quality and public health evaluation, which was designed to identify air quality impacts of potential health concern at a nearby school campus associated with operations of a Marcellus Shale unconventional gas well pad, showed that measured $PM_{2.5}$ and VOC concentrations were consistently below acute and chronic health-based air comparison values. While the nearly 2 years of data collected at the three monitoring sites between 1000 and 2800 feet from the study well pad include some episodic short-term concentration increases that may be associated with the transient well pad development phases, the $PM_{2.5}$ and VOC measurements do not provide evidence of elevated long-term average concentrations at the three monitoring sites relative to a Washington County background site more distant from Marcellus Shale development. The study measurement data, which reflect not only any air emissions from the study well pad but also air emissions from other local and regional Marcellus Shale development, do not provide evidence indicating that the study well pad was a source of either acute or chronic $PM_{2.5}$ or VOC concentrations of potential health concern at the school campus; however, the study design did not include monitoring sites in the predominant wind direction or closer than 1000 feet from the well pad, and thus did not allow for the characterization of the full range of potential air exposure levels associated with the well pad development.

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Compliance with ethical standards

Conflict of interest During involvement in the study, authors were employed by Gradient or AECOM. The work reported in this paper was conducted during the normal course of employment. Range Resources, which provided financial support for this study and paper, developed and currently operates the study well pad, as well as other well pads in the local area. The authors had complete freedom in the design, implementation, and reporting of the research presented in this paper; the paper was reviewed by employees of Range Resources while in preparation. The authors retain sole responsibility for the writing and content of this paper, which represent the professional opinions of the authors and not necessarily those of Range Resources. One of the authors of this manuscript (C. Long) has testified in Pennsylvania on behalf of natural gas development companies at local zoning hearing board meetings and at a judicial hearing on the science of the air quality impacts of Marcellus Shale development activities.

References

1. Goetz JD, Floerchinger C, Fortner EC, Wormhoudt J, Massoli P, Knighton WB, et al. Atmospheric emission characterization of Marcellus shale natural gas development sites. Environ Sci Technol. 2015;49:7012–20. https://doi.org/10.1021/acs.est.5b00452.
2. Goetz JD, Avery A, Werden B, Floerchinger C, Fortner EC, Wormhoudt J, et al. Analysis of local-scale background concentrations of methane and other gas-phase species in the Marcellus Shale. Elementa. 2017;5:1. https://doi.org/10.1525/elementa.182.
3. McCawley M. Air contaminants associated with potential respiratory effects from unconventional resource development activities. Semin Respir Crit Care Med. 2015;36:379–87. https://doi.org/10.1055/s-0035-1549453.
4. Swarthout RF, Russo RS, Sive BC, Zhou Y, Miller BM, Mitchell BL, et al. Impact of Marcellus Shale natural gas development in southwest Pennsylvania on volatile organic compound emissions and regional air quality. Environ Sci Technol. 2015;49:3175–84. https://doi.org/10.1021/es504315f.
5. Allegheny County, Pennsylvania, Health Dept (ACHD). Imperial pointe ambient air sampling results/method EPA TO15+ tentatively identified compounds. 2016 Sep 21. 13 p. [217-3287]
6. Allegheny County, Pennsylvania, Health Dept (ACHD). Deer lakes ambient air sampling results/radiello passive monitors. 2016 Nov 29. 12 p. [217-3288]
7. Agency for toxic substances and disease registry (ATSDR). health consultation, exposure investigation, natural gas ambient air quality monitoring initiative, Brigich Compressor Station, Chartiers Township, Washington County, Pennsylvania. 2016 Jan 29. 94 p. [216-5252]
8. Pennsylvania Dept. of Environmental Protection (PADEP). Long-term ambient air monitoring project: marcellus shale gas facilities. 2018 Jul. 139 p. [218-8169]
9. US EPA Region III, Office of Air Monitoring and Analysis, Air Protection Division. EPA Region III Natural gas ambient air monitoring initiative (NGAAMI) in Southwestern Pennsylvania. 2015 Aug. 515 p. [216-5251]
10. Ghosh B. Impact of changes in oil and gas production activities on air quality in northeastern Oklahoma: ambient air studies in 2015-2017. Environ Sci Technol. 2018;52:3285–94. https://doi.org/10.1021/acs.est.7b05726.
11. Bunch AG, Perry CS, Abraham L, Wikoff DS, Tachovsky JA, Hixon JG, et al. Evaluation of impact of shale gas operations in the Barnett Shale region on volatile organic compounds in air and potential human health risks. Sci Total Environ. 2014;468-469:832–42. https://doi.org/10.1016/j.scitotenv.2013.08.080.
12. Zielinska B, Campbell D, Samburova V. Impact of emissions from natural gas production facilities on ambient air quality in the Barnett Shale area: a pilot study. J Air Waste Manag Assoc. 2014;64:1369–83. https://doi.org/10.1080/10962247.2014.954735.
13. Colborn T, Schultz K, Herrick L, Kwiatkowski C. An exploratory study of air quality near natural gas operations. Hum Ecol Risk Assess. 2014;20:86–105.
14. Southwest Pennsylvania Environmental Health Project. Community assessment of penn trafford outdoor air monitoring results. 2016 Jun 6. 11 p.
15. Health Effects Institute- Energy Research Committee. Human exposure to unconventional oil and gas development: a literature survey for research planning. Communication. 2020;132:217–4734.
16. Long CM, Briggs NL, Bamgbose IA. Synthesis and health-based evaluation of ambient air monitoring data for the Marcellus Shale region. J Air Waste Manag Assoc. 2019;69:527–47. https://doi.org/10.1080/10962247.2019.1572551.
17. Pennsylvania Dept. of Environmental Protection (PADEP), Office of Oil and Gas Management. Wells Drilled by County [Wells drilled between June 1, 2009 and June 1, 2019]. 2019. 2 p. https://www.dep.pa.gov/DataandTools/Reports/OilandGasReports/Pages/default.aspx.
18. Pennsylvania Dept. of Environmental Protection (PADEP). "PA Oil and Gas Mapping." 2019. Available from http://www.depgis.state.pa.us/PaOilAndGasMapping/OilGasWellsStrayGasMap.html.
19. Pennsylvania Dept. of Environmental Protection (PADEP), Bureau of Air Quality. Southwestern Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Report. 2010 Nov 1. 52 p. [214-8020]
20. US EPA. EPA Schools Monitoring Initiative Fact Sheet: December 2012 Update: Acrolein Monitoring Results. 2012. 3 p. [217-8448]
21. Agency for Toxic Substances and Disease Registry (ATSDR). Minimal risk levels (MRLs) [Narrative]. 2017 Jun 27. https://www.atsdr.cdc.gov/mrls/index.asp.
22. US EPA. Schools Air Toxics Monitoring Activity (2009): Uses of health effects information in evaluating sample results. 2009 Sep 10. 24 p. [216-5262]
23. US EPA, Office of Air Quality, Planning and Standards. Residual Risk: Report to Congress. 1999 Mar. Report No.: EPA-453/R-99-001.
24. Pennsylvania Dept. of Environmental Protection (PADEP), Bureau of Air Quality. Northeastern Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Report. 2011 Jan 12. 57 p. [214-8019]
25. Pennsylvania Dept. of Environmental Protection (PADEP), Bureau of Air Quality. Northcentral Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Report. 2011 May 6. 52 p.
26. McMullin TS, Bamber AM, Bon D, Vigil DI, Van Dyke M. Exposures and health risks from volatile organic compounds in communities located near oil and gas exploration and production activities in Colorado (U.S.A.). Int J Environ Res Public Health. 2018;15:1500. https://doi.org/10.3390/ijerph15071500.
27. Boyd, D. *Marcellus/Utica Activity: Operators Deploy Best Practices & Innovation as Marcellus/Utica Astound* (The American Oil & Gas Reporter, 2019). https://www.aogr.com/magazine/cover-story/operators-deploybest-practices-innovation-as-marcellus-utica-astound.
28. Seguljic TS, Martin JP. Air regulation requirements in the Marcellus and Utica shale region: Management approaches and case study. Environ Qual Manag. 2016;26:73–87. https://doi.org/10.1002/tqem.21479.
29. Agency for Toxic Substances and Disease Registry (ATSDR); Pennsylvania Department of Health (PDOH). Health consultation: public health evaluation of long-term air sampling data collected in the vicinity of natural gas operations, Washington County, Pennsylvania. 2018 Jul 18. 91 p. [218-8595]

30. Maskrey JR, Insley AL, Hynds ES, Panko JM. Air monitoring of volatile organic compounds at relevant receptors during hydraulic fracturing operations in Washington County, Pennsylvania. Environ Monit Assess. 2016;188:410. https://doi.org/10.1007/s10661-016-5410-4.
31. McCawley M (West Virginia University). Air, noise, and light monitoring results for assessing environmental impacts of horizontal gas well drilling operations (ETD-10 Project). 2013 May 3. 206 p. Report to West Virginia Dept. of Environmental Protection. Available from http://wvwri.org/wp-content/uploads/2013/10/A-N-L-Final-Report-FOR-WEB.pdf.
32. Macey GP, Breech R, Chernaik M, Cox C, Larson D, Thomas D, et al. Air concentrations of volatile compounds near oil and gas production: A community-based exploratory study. Environ Health. 2014;13:82. https://doi.org/10.1186/1476-069X-13-82.
33. Pekney N, Reeder M, Veloski G, Diehl JR. Data Report for Monitoring at Six West Virginia Marcellus Shale Development Sites using NETL's Mobile Air Monitoring Laboratory (July–November 2012). US Dept. of Energy (US DOE), National Energy Technology Laboratory (NETL); 2016 Jun 16. 104 p. Report No.: NETL-TRS-4-2016.
34. Strum M, Scheffe R. National review of ambient air toxics observations. J Air Waste Manag Assoc. 2016;66:120–33. https://doi.org/10.1080/10962247.2015.1076538.
35. Orak NH, Pekney NJ, Reeder M. Ambient air quality near a Marcellus shale well pad in southwestern Pennsylvania. Proceedings of the Air and Waste Management Association's 110th Annual Conference and Exhibition; 2017 Jun 7; Pittsburgh, PA. Available from https://www.eventscribe.com/2017/awma/ajaxcalls/PresentationInfo.asp?efp=SFRXUFlFQkIzMjEz&PresentationID=262009&rnd=0.2957729.
36. Range Resources. 2020 Corporate Sustainability Report. 2020. 76 p. Available from https://csr.rangeresources.com/wp-content/uploads/2020/09/Range_resources_CSR_report.pdf.
37. CNX. 2019 Corporate Responsibility Report. 2019. 45 p. Available from https://www.cnx.com/cnx/media/Pdf/CNX_2019CSR.pdf.
38. Addison, V. Producers are making use of natural gas to power rigs. Available from https://www.hartenergy.com/opinions/producers-are-making-use-natural-gas-power-rigs-121745.

ATTACHMENT C

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ARTICLE

Health-based evaluation of ambient air measurements of $PM_{2.5}$ and volatile organic compounds near a Marcellus Shale unconventional natural gas well pad site and a school campus

Christopher M. Long[1] · Nicole L. Briggs[2] · Brian A. Cochran[3] · Destiny M. Mims[2]

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Abstract

Background Limited air monitoring studies with long-term measurements during all phases of development and production of natural gas and natural gas liquids have been conducted in close proximity to unconventional natural gas well pads.

Objective Conducted in an area of Washington County, Pennsylvania, with extensive Marcellus Shale development, this study investigated whether operations at an unconventional natural gas well pad may contribute to ambient air concentrations of potential health concern at a nearby school campus.

Methods Almost 2 years of air monitoring for fine particulate matter ($PM_{2.5}$) and volatile organic compounds (VOCs) was performed at three locations between 1000 and 2800 feet from the study well pad from December 2016 to October 2018. $PM_{2.5}$ was measured continuously at one of the three sites using a beta attenuation monitor, while 24-h stainless steel canister samples were collected every 6 days at all sites for analysis of 58 VOCs.

Results Mean $PM_{2.5}$ concentrations measured during the different well activity periods ranged from 5.4 to 9.5 $\mu g/m^3$, with similar levels and temporal changes as $PM_{2.5}$ concentrations measured at a regional background location. The majority of VOCs were either detected infrequently or not at all, with measurements for a limited number of VOCs indicating the well pad to be a source of small and transient contributions.

Significance All measurement data of $PM_{2.5}$ and 58 VOCs, which reflect the cumulative contributions of emissions from the study well pad and other local/regional air pollutant sources (e.g., other well pads), were below health-based air comparison values, and thus do not provide evidence of either 24-hour or long-term air quality impacts of potential health concern at the school.

Keywords $PM_{2.5}$ · VOCs · Natural gas · Marcellus Shale · Air monitoring · Public health

Introduction

There has been a proliferation of air monitoring data collected at major U.S. shale gas plays to understand the potential air quality impacts of the recent expansion of unconventional natural gas development (UNGD) activities, including horizontal drilling and hydraulic fracturing. Air measurement studies have been conducted by academic researchers [1–4], governmental agencies [5–9], industry scientists and industry-funded consultants [10–12], and environmental advocates and non-profit groups [13, 14]. Air pollutants that have been commonly measured in these studies include both US Environmental Protection Agency (US EPA) criteria air pollutants (e.g., fine particulate matter [$PM_{2.5}$], nitrogen dioxide [NO_2]), and volatile organic compounds (VOCs) classified by US EPA as air toxics (e.g., benzene, ethylbenzene, formaldehyde, n-hexane, toluene, and xylenes).

The Health Effects Institute (HEI)- Energy Research Committee [15] recently published a review of published air quality studies relevant to potential UNGD-related

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✉ Christopher M. Long
clong@gradientcorp.com

[1] Gradient, Boston, MA, USA

[2] Gradient, Seattle, WA, USA

[3] Spectrum Environmental Solutions, Austin, TX, USA

human exposures, identifying the need for additional studies to address important gaps in knowledge. In particular, the HEI-Energy report [15] highlighted the need for more research to characterize the spatial and temporal variability in airborne exposure levels and the conditions contributing to this variability, including more air monitoring data representing a range of geographic locales, meteorological conditions, UNGD operational conditions, and exposure durations (e.g., from acute durations of hours to weeks to chronic durations of a year and longer). In our review of air quality data available for the Marcellus Shale region [16], we observed that the majority of datasets consist of short-term measurements collected over time periods of days to weeks, thus providing insufficient data to evaluate long-term exposure conditions for the full life cycle of well pad development. In addition, most of the available measurement data are for monitoring locations between 0.2 and 1 miles from the nearest UNGD site, with fewer data for closer monitoring locations.

Pennsylvania's Washington County is one area in the Marcellus Shale region that has experienced rapid unconventional natural gas development in the last 10–15 years. In Washington County alone, nearly 1700 unconventional wells have been drilled in the last decade, the most of any Pennsylvania county [17]. Public concerns have been raised regarding potential health risks posed by the proliferation of well pads and other associated natural gas infrastructure (e.g., compressor stations and processing facilities) in Washington County, with air emissions and exposures being particular concerns [7–9].

This air monitoring study was conducted in a part of Washington County with extensive Marcellus Shale development [18] (Figure S.1). The primary objective of the study was to investigate whether development activities and production operations at an unconventional natural gas well pad site may be contributing to ambient air concentrations of potential health concern at a nearby school campus. Almost 2 years of measurements for both $PM_{2.5}$ and individual VOC species were made at three monitoring locations, including two locations between the well pad and the school campus and all between 1000 and 2800 feet from the well pad site (Fig. 1), during all phases of development and production of natural gas and natural gas liquids. Wind data (direction and speed) were also continuously collected at two of the monitoring sites. Thus, this dataset is notable for the lengthy duration of air quality measurements in close proximity to a well pad during all phases of development and production, and the collection of local wind data for assessing the contribution of the well pad to measured air concentrations.

We conducted a public health evaluation of this air monitoring dataset by comparing short-term (24-h) and long-term (>1 year) average $PM_{2.5}$ and VOC concentrations to acute and chronic health-based air comparison values developed by public health agencies to serve as conservative and health-protective benchmarks. In addition, we compared $PM_{2.5}$ and VOC measurements to air

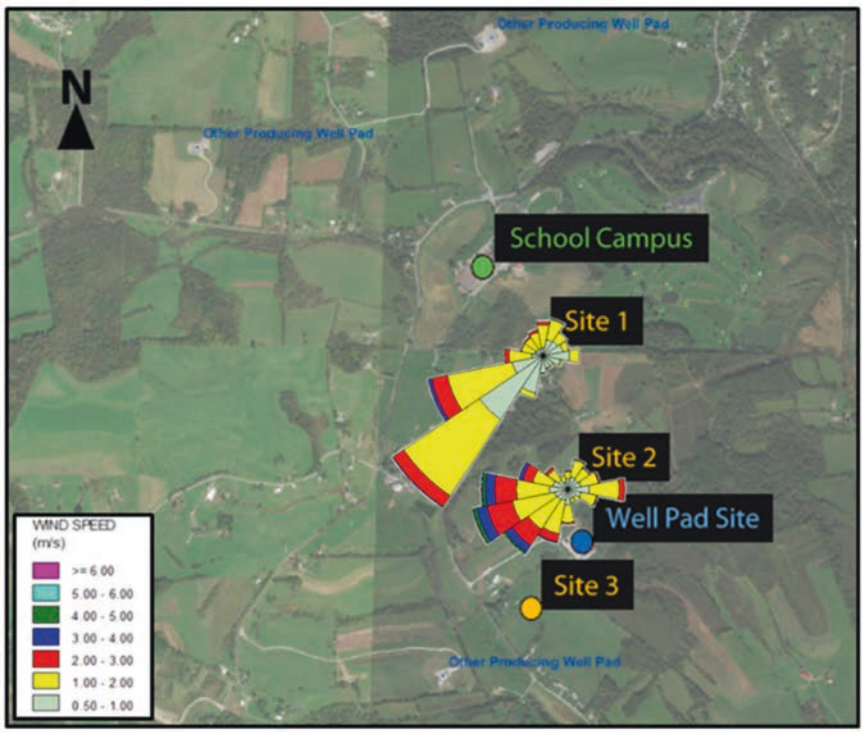

Fig. 1 Map of the three air monitoring sites relative to the study well pad site, the school campus, and other local producing well pads. Wind roses are also shown for Sites 1 and 2 where meteorological stations were operated.

concentrations measured at a background Washington County site more distant from oil and gas development activities and considered to be representative of regional background air quality. Although the study was designed to identify potential air quality impacts at the nearby school campus associated with operations at the study well pad site, the collected dataset reflects the cumulative contributions of air emissions from both the study well pad site and other local and regional sources.

Methods

Ambient air measurements

Three air monitoring sites were selected to address the primary study objective of evaluating air quality impacts at a nearby school campus associated with the development and operation of a UNGD well pad. Air monitoring sites 1 and 2 were located at distances of ≈2800 and 1000 feet, respectively, from the study well pad in the direction of the school campus (Fig. 1). Site 1 was the closest to the school campus (≈1500 feet to the southeast). The third monitoring site (site 3) was located about 1000 feet to the southwest of the well pad —i.e., upwind of the well pad for winds blowing in the direction of the school— to help evaluate whether other local sources, including the large number of other UNGD wells in the area (Figure S.1), may be important contributors to the site 1 and 2 measurements. Although an initial evaluation of the wind direction in the area indicated that winds were predominantly from the southwest, a monitoring site was not established to the northeast of the well pad because the area is wooded and inaccessible.

The monitoring program began in December 2016 during the site construction and set-up period of the study well pad and continued through October 2018 and after a full year of measurements were collected with all wells (six in total) in production. Table 1 shows the study air monitoring period relative to the different well pad activity periods, which included each of the typical well pad development phases, periods of lesser activity between the development phases that we have termed interlude periods, and the period when all wells were in production.

Ambient air measurements were made for $PM_{2.5}$ and 58 VOC species (see Table 1 for numbers of $PM_{2.5}$ measurement hours and VOC canister samples collected during each well pad activity period). Monitoring site 1 was chosen for the $PM_{2.5}$ measurements given that it was between the study well pad site and the school campus and in closer proximity to the school campus than site 2. Hourly average $PM_{2.5}$ measurements were collected continuously from February 2017 to October 2018 using a Met One Instruments Model

Table 1 Sampling dates and numbers of $PM_{2.5}$ measurement hours and VOC canister samples collected per study well pad activity period.

Study well pad activity period	Sampling dates	Number of monitoring site 1 $PM_{2.5}$ measurement hours in the period	Percentage of total sampling hours	# of VOC canister samples for study monitoring sites		
				# 1	# 2	# 3
Site construction and set-up	December 16, 2016–January 5, 2017	N/A	N/A	0	4	4
Vertical air drilling	January 5–February 18, 2017	177	1.2%	0	7	7
Interlude I	February 19–March 2, 2017	240	1.7%	2	2	2
Horizontal drilling	March 3–May 7, 2017	1546	10.9%	11	11	11
Interlude II	May 8–June 17, 2017	964	6.8%	6	6	6
Hydraulic fracturing	June 18–August 13, 2017	1302	9.2%	10	10	10
Interlude III	August 14–September 7, 2017	439	3.1%	4	4	4
Flowback	September 8–October 23, 2017	883	6.2%	8	8	8
Production	October 23, 2017–October 31, 2018	8618	60.8%	61	61	61

N/A Not Applicable, *$PM_{2.5}$* fine particulate matter less than 2.5 micrometers in diameter, *VOC* volatile organic compound.

BAM-1020 per the US EPA Federal Equivalent Method (FEM). Beginning on December 16, 2016, at sites 2 and 3, and February 15, 2018, at site 1, 24-h stainless steel canisters were collected for VOC analysis every 6 days through October 2018. Samples were analyzed using US EPA Method TO-15, focusing on 58 VOC species selected to match the set of TO-15 VOC species typically monitored by Pennsylvania Department of Environmental Protection (PADEP) at its air toxics sampling sites across the state. This expanded set of VOC analytes was selected based on prior experience of the well pad operator regarding typical air emission sources at its well pads. VOCs not known to be associated with UNGD activities (e.g., chlorinated solvents like carbon tetrachloride and methylene chloride) were retained as analytes. Acrolein was one of the 58 target VOCs, but we have not reported or evaluated the acrolein measurements based on determinations by both PADEP and US EPA that acrolein measurements obtained using this method are unreliable [8, 19, 20]. Wind speed and direction were also measured at both sites 1 and 2 using solar-powered portable met stations from February 8, 2017 to October 31, 2018, and December 16, 2016 to October 31, 2018, respectively; additional meteorological parameters (e.g., relative humidity, barometric pressure, and temperature) were also collected at site 1.

Data analysis

Microsoft Excel 2013 (Microsoft Corporation, Redmond, WA, USA), SigmaPlot (Systat Software, Inc., San Jose, CA, USA), R (R Core Team, Vienna, Austria), and ProUCL version 5.1 (US EPA, Washington, DC, USA) were used for statistical and graphical data analysis. For $PM_{2.5}$, we analyzed the hourly data, and also calculated 24-h daily average concentrations for days with 18 or more monitoring hours. For VOCs detected at least once, we substituted one-half the limit of detection (LOD) for non-detects (LODs were typically 0.06 parts per billion). The 95% upper confidence limits (UCLs) of mean concentrations were calculated for VOCs detected at least twice using US EPA's ProUCL software, with reporting of UCLs for the methods recommended by the software.

Correlations between measured concentrations at each site were examined using Spearman rank correlations. We conducted statistical testing to compare concentrations between sites, well activity periods, and wind directions using non-parametric tests that included the Kruskal–Wallis *H* Test and the Mann–Whitney rank sum test. Statistical significance was defined as a p value less than 0.05. For VOCs, we focused statistical testing on a subset of 14 of the 58 target VOCs that were consistently detected (i.e., detection frequencies >75%) at each of the monitoring sites.

The wind direction data collected at sites 1 and 2 were evaluated in several ways. Wind roses were prepared using WRPLOT View (Lakes Environmental, Waterloo, Ontario). To allow for the evaluation of wind directions on a daily basis corresponding to the VOC sampling periods, average daily wind directions were calculated, categorized according to an 8-point compass, and the percent of days in which the winds arrived from each of these directions was calculated. Given the hourly averaging time of the $PM_{2.5}$ measurements, the percent of hourly wind measurements in each of the eight directions was also calculated.

The $PM_{2.5}$ and VOC measurements were also compared to air concentrations measured at a monitoring site ≈10 miles away in Florence, PA, which has been used by PADEP as a background Washington County comparison site [8]. PADEP has described this rural monitoring site as being impacted primarily by regional transport [8]. $PM_{2.5}$ data for the study monitoring period were obtained for the Florence site from US EPA's Air Quality System (AQS). No VOC data are available from the Florence site for the study monitoring period, but maximum 24-h and mean VOC concentrations for 24-h canister samples collected every sixth day between October 2012 and December 2013 at the Florence monitoring site were obtained from PADEP [8] data summaries.

Health-based evaluation of ambient air measurements

We identified acute and chronic health-based air comparisons values (HBACVs) for this evaluation that are health-protective benchmarks developed by public health agencies. The US EPA $PM_{2.5}$ primary National Ambient Air Quality Standards (NAAQS), which are developed to be protective of the health of the general public as well as sensitive populations such as asthmatics, children, and the elderly, were used as $PM_{2.5}$ acute and chronic benchmarks. We compared the maximum 24-h daily average concentration to the level of the NAAQS (35 $\mu g/m^3$), a conservative comparison given that the standard is intended to be compared to a 3-year average of the 98th percentile of 24-h measurements at a site. The annual $PM_{2.5}$ NAAQS requires that the mean annual $PM_{2.5}$ concentration at a site, averaged over 3 years, remains below 12.0 $\mu g/m^3$. Given that $PM_{2.5}$ measurements were not available for a 3-year period, the mean concentration from the entire $PM_{2.5}$ sampling period was calculated and compared to the annual NAAQS.

The maximum 24-h measurement of each VOC detected at the three air monitoring sites was compared to acute HBACVs. We employed a tiered approach to identify acute HBACVs because there was not a single HBACV source inclusive of all measured VOCs. Agency for Toxic Substances and Disease Registry (ATSDR) acute inhalation

Minimal Risk Levels (MRLs) were considered to be the preferred source of HBACVs because they are developed to be protective of 24-h exposure durations according to a well-documented and conservative process based on the most sensitive substance-induced end point of relevance to humans [21]. ATSDR acute inhalation MRLs are derived for 1–14 day exposure durations, and therefore comparison to the 24-h air monitoring site measurements is conservative. If an ATSDR acute inhalation MRL was not available for a VOC, acute inhalation reference concentrations (RfCs) from the Department of Energy Oak Ridge National Laboratory (ORNL) Risk Assessment Information System (RAIS) were used. When neither a ATSDR MRL nor a RAIS RfC was available, we derived an acute HBACV by multiplying a US EPA chronic reference concentration (RfC) by 10 [22]. For ethanol, the US National Institute for Occupational Safety and Health (NIOSH) time-weighted average recommended exposure limit (REL) was selected as the acute HBACV. We were not able to identify acute HBACVs for 11 VOCs, however, the majority of these were not detected in any samples.

We evaluated chronic health risks by comparing 95% UCLs of mean VOC concentrations (or for VOCs detected just once, mean concentrations that were calculated using half of the LOD for non-detects) at each site to chronic HBACVs. We consider 95% UCLs to represent conservative estimates of chronic air exposure levels at the monitoring sites given not only the likelihood that they are overestimates of true long-term average concentrations, but also due to the transient nature of the well pad development phases. For non-carcinogenic VOCs, US EPA non-cancer RfCs were used as chronic HBACVs, and for known or suspected human carcinogens, the lower value of either the non-cancer US EPA RfC or the cancer-based estimated continuous lifetime concentration was used. Using US EPA inhalation unit risk (IUR) estimates, we calculated the cancer-based estimated continuous lifetime concentrations for a 1-in-10,000 excess lifetime cancer risk, consistent with the US EPA residual risk program and with long-term comparison levels developed as part of US EPA's School Air Toxics Initiative [22, 23].

Results

Wind measurement data

Wind roses constructed from wind data collected at monitoring sites 1 and 2 indicate that the prevailing local winds were from the west and southwest (Fig. 1), and thus did not generally blow emissions from the well pad towards the monitoring sites and the school campus. However, it is expected that winds blowing from the southerly and southeasterly directions would have transported study well pad air emissions to monitoring sites 1 and 2, and a detailed evaluation of wind directions at these sites confirmed that winds blowing from southeasterly and southerly directions were relatively common during each of the well pad activity periods (Table S.1).

Summary of $PM_{2.5}$ measurement data

Table 2 provides a summary of the hourly $PM_{2.5}$ measurement data collected from February 2017 to October 2018 at monitoring site 1, showing an overall mean $PM_{2.5}$ concentration of 7.1 μg/m^3 and mean concentrations for the different well activity periods that ranged from a low of 5.4 μg/m^3 for the vertical air drilling phase to a high of 9.5 μg/m^3 for the interlude III phase. Kruskal–Wallis H Tests identified statistically significant differences in hourly $PM_{2.5}$ concentrations between some of the well activity periods, including statistically higher concentrations for the interlude III and hydraulic fracturing periods and statistically lower concentrations for the vertical air drilling and production periods. When data were stratified by hours with winds from the south and southeast (i.e., from the direction of the study well pad site) versus winds from other directions, we observed statistically significant increased hourly $PM_{2.5}$ concentrations for the hours with southerly and southeasterly wind directions for all well activity periods except the interlude II and interlude III periods (Figure S.2); however, as illustrated by Fig. 2 which compares 24-h average $PM_{2.5}$ concentrations measured at monitoring site 1 with the corresponding 24-h average $PM_{2.5}$ concentrations measured at the PADEP Florence background site, highly similar $PM_{2.5}$ levels and temporal changes were observed as for a regional background site. Statistical testing showed no statistical difference between the two datasets (Mann–Whitney rank sum test, p value = 0.82).

Summary of VOC measurement data

Table S.2 provides a comprehensive set of summary statistics for the VOC measurement data by monitoring site, showing that the majority of the target VOC species were either detected infrequently or not at all. Only 14 VOCs were consistently detected (i.e., detection frequencies >75%) at each of the three monitoring sites—acetone, benzene, 2-butanone, carbon tetrachloride, chloromethane, dichlorodifluoromethane, ethanol, Freon 113, methanol, methylene chloride, n-hexane, propylene, toluene, and trichlorofluoromethane. While median concentrations for these VOCs were frequently less than 1 ppb and all were less than 10 ppb, maximum detected 24-h concentrations exceeded 100 ppb for a few of the VOCs (acetone, ethanol, and methanol). As shown in Table S.2, there were no

Table 2 Summary of hourly $PM_{2.5}$ measurements for monitoring site 1.

Study well pad activity period	Median hourly $PM_{2.5}$ conc. ($\mu g/m^3$)	Mean hourly $PM_{2.5}$ conc. ($\mu g/m^3$)	Standard deviation hourly $PM_{2.5}$ conc. ($\mu g/m^3$)	Maximum 1-h $PM_{2.5}$ conc. ($\mu g/m^3$)	Maximum 24-h $PM_{2.5}$ conc. ($\mu g/m^3$)
Site construction and set-up	N/A	N/A	N/A	N/A	N/A
Vertical air drilling	4.0	5.4	4.3	24.0	7.1
Interlude I	6.0	6.6	4.8	37.0	13.6
Horizontal drilling	6.0	6.8	4.4	54.0	14.4
Interlude II	6.0	6.8	4.0	29.0	14.2
Hydraulic fracturing	7.0	7.8	4.3	24.0	17.6
Interlude III	9.0	9.5	4.3	24.0	13.1
Flowback	6.0	7.0	4.9	41.0	14.4
Production	6.0	7.1	4.8	141.0	24.6
Total	6.0	7.1	4.7	141.0	24.6

The maximum 24-h $PM_{2.5}$ concentration was calculated for only days in which there were at least 18 hours of $PM_{2.5}$ data available.

N/A signifies that no data were collected for the period.

Conc concentration, *$PM_{2.5}$* fine particulate matter less than 2.5 micrometers in diameter

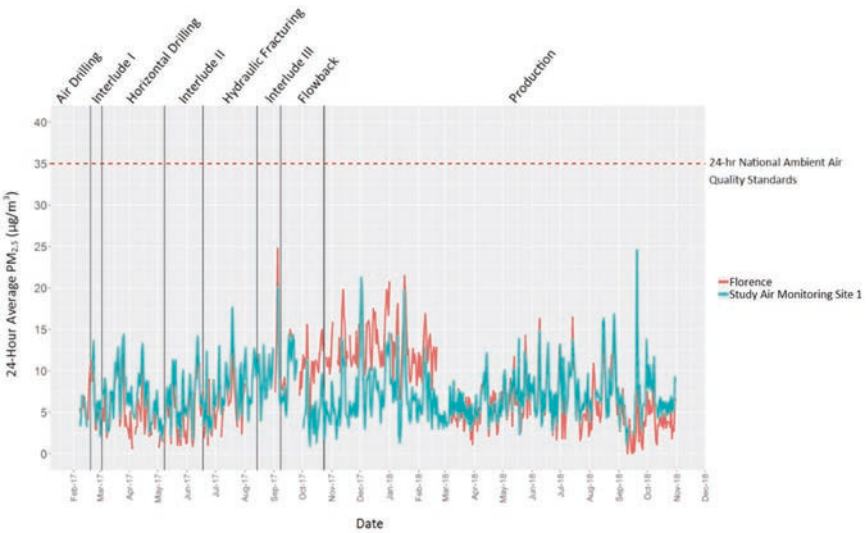

Fig. 2 Time series of 24-h $PM_{2.5}$ measurements at study monitoring site 1 and the PADEP background Florence site. PADEP Pennsylvania Department of Environmental Protection, $PM_{2.5}$ fine particulate matter less than 2.5 micrometers in diameter.

consistent patterns with respect to when maximum VOC concentrations were detected across VOCs and monitoring sites. For example, maximum detected concentrations for both acetone and methanol occurred in the interlude II, production, and interlude III periods for monitoring sites 1, 2, and 3, respectively; for toluene, maximum detected concentrations occurred in the horizontal drilling, production, and interlude II periods for monitoring sites 1, 2, and 3, respectively. For a limited number of VOCs, maximum concentrations occurred within the same well activity period for either all three sites or two out of three sites (e.g., benzene: site construction and set-up period for two sites; n-hexane: flowback period for all three sites; ethanol: production period for two sites; propylene: flowback period for two sites).

Correlational analysis revealed consistent moderate to strong correlations (Spearman's rank correlation coefficients r_s between 0.36 and 0.90) across the three monitoring sites between several groups of VOCs, suggesting that they may have common sources (Tables S. 3a, b, and c). These groupings included 2-butanone, acetone, ethanol, methanol, and toluene (for 2 of the 3 sites, also methylene chloride); chloromethane, dichlorodifluoromethane, and Freon 113; n-hexane and propylene (for 2 of the 3 sites, also toluene); and carbon tetrachloride and trichlorofluoromethane. Benzene exhibited statistically significant weak to moderate

correlations (r_s between 0.31 and 0.44) with propylene and toluene for all sites and with n-hexane for 2 of the 3 sites. For site 1, we also examined correlations between 24-h daily-average $PM_{2.5}$ concentrations and VOC concentrations, finding statistically significant weak correlations (r_s between 0.23 and 0.37) with benzene, carbon tetrachloride, methanol, n-hexane, and toluene. Although suggestive of possible common sources, the correlational analysis do not allow for the identification and apportionment of sources, such as any contributions from the study well pad site relative to other local well pads and area air emission sources (e.g., industrial sources and traffic).

Statistical testing using the Kruskal–Wallis *H* Test demonstrated no statistically significant differences in measured concentrations across the three monitoring sites for 9 of the 14 consistently detected VOCs. For the five VOCs where statistically significant differences by site were found (acetone, ethanol, methanol, methylene chloride, and toluene), multiple comparisons conducted using Dunn's Method consistently showed statistically significantly higher concentrations at monitoring sites 2 and 3 versus monitoring site 1, but no statistically significant differences between the site 2 and site 3 concentrations.

Focusing on sites 1 and 2 where there were concurrent wind direction measurements, Tables S.4 and S.5 compare summary statistics for the 14 consistently detected VOCs for sampling days with frequent winds from the southerly or southeasterly direction (i.e., from the study well pad site in the direction of the monitoring sites and the school campus) versus for other wind directions. These tables show relatively small difference in concentrations for the two sets of wind conditions (i.e., typical <1 ppb differences in median concentrations). For a limited number of the 14 VOCs, statistically significant increased concentrations were observed for sampling days with frequent winds from south and southeasterly directions versus other wind directions, including for acetone (site 1), benzene (site 2), 2-butanone (site 2), ethanol (site 1), n-hexane (sites 1 and 2), propylene (site 2), and toluene (sites 1 and 2). However, for site 3 (which is to the southwest of the study well pad), most of the same VOCs (all but ethanol and 2-butanone) were found to have statistically significantly higher concentrations for days with frequent southerly and southeasterly winds versus other wind directions, suggesting that other local/regional sources rather than the study well pad site may be responsible for the higher concentrations at monitoring sites 1 and 2 with southerly and southeasterly winds (the wind data for monitoring site 2 were used in this analysis due to the lack of site-specific wind data for monitoring site 3).

Additional statistical testing was conducted on the VOC data to investigate whether measured VOC concentrations were related to study well pad activity period. Given the small number of samples for some of the shorter duration well activity periods, well development and interlude periods were grouped together to form three broader activity periods—active well development periods (encompassing the site construction and set-up, vertical air drilling, horizontal drilling, hydraulic fracturing, and flowback periods), interlude periods (encompassing the three interlude periods), and the production period. This statistical analysis identified some statistically significant differences in VOC concentrations for these activity periods, although the results were not consistent across VOCs and monitoring sites and are thus difficult to interpret. For example, no statistically significant differences across the three activity periods were observed in the Kruskal–Wallis *H* Test for benzene (*p* values of 0.562, 0.379, 0.086), ethanol (*p* values of 0.061, 0.551, 0.347), or n-hexane (*p* values of 0.396, 0.170, 0.464). However, for both methanol and propylene, statistically significant differences were observed for the activity period factor for each of the three sites, with pairwise multiple comparisons on ranks (Dunn's Method) showing statistically significant lower methanol concentrations for the production period relative to the interlude periods for each site and to the active well pad development periods for one of the three sites, and statistically significant lower propylene concentrations for the production period relative to the active well pad development periods for all three sites.

Table S.6 compares summary statistics for VOCs measured at the three study monitoring sites with the corresponding values for 2012–2013 sampling conducted at the PADEP Florence background site [8]. As shown in this table, the same set of 12 VOCs was consistently detected at the Florence background site as at the study monitoring sites (note that neither ethanol nor methanol was monitored at the Florence site). Summary statistics were very similar between the two datasets for seven of the 12 VOCs, including benzene, 2-butanone, carbon tetrachloride, chloromethane, dichlorodifluoromethane, Freon 113, and trichlorofluoromethane. Six of these 7 VOCs are not well established to be associated with UNGD activities; although benzene is known to be present in UNGD site emissions, both mean and maximum benzene measurements for the study monitoring sites were generally lower than the Florence background site measurements. The 24-h maximum measurements for at least one of the three study monitoring sites were noticeably higher than the maximum measured Florence site concentrations for acetone, methylene chloride, n-hexane, propylene, and toluene. Although the study well pad site may have contributed to some of these maximum 24-h concentrations, an examination of the wind measurement data indicated that some of the maximum measurement days had few, if any, winds from the direction of the study

well pad site, suggesting the role of other sources unrelated to the study well pad site.

Comparison with health-based air comparison values (HBACVs)

The maximum 24-h $PM_{2.5}$ concentration for the entire $PM_{2.5}$ dataset was 24.6 μg/m^3 (based on data from 587 days with at least 18 hours of $PM_{2.5}$ data), which is well below the acute $PM_{2.5}$ HBACV of 35 μg/m^3. The overall mean $PM_{2.5}$ concentration plus or minus one standard deviation was 7.1 ± 4.7 μg/m^3, which is below the chronic $PM_{2.5}$ HBACV of 12 μg/m^3, even when including one standard deviation. Therefore, measured $PM_{2.5}$ concentrations near the study well pad are below established regulatory levels of both acute and chronic health concern.

For VOCs, Tables S.7 and S.8 provide the full set of comparisons to acute and chronic HBACVs. As shown in these tables, maximum measured 24-h VOC concentrations for each site were consistently below the acute HBACVs, while 95% UCLs of mean VOC concentrations calculated from all measurements and from only the production phase at each site were all below chronic HBACVs. Figures 3 and 4 illustrate the large differences that are typical between the measured VOC concentrations and the acute and chronic HBACVs for the BTEX compounds (benzene, toluene, ethylbenzene, and xylenes). There were four compounds detected at one or more of the air monitoring sites, but for which no appropriate acute or chronic benchmarks were identified: hexachloro-1,3-butadiene, m-dichlorobenzene, p-ethyltoluene, and trichlorofluoromethane. These VOCs are not expected to present either acute or chronic health risks due to the infrequent detections (for all but trichlorofluoromethane) and the low, sub-ppb detected concentrations (all).

Discussion

Given the long duration of air monitoring, our study provided a dataset that reflects a range of well pad development phases and operating conditions, meteorological conditions, and exposure durations in the Marcellus Shale region. For $PM_{2.5}$, the similar levels and diurnal trends between the study monitoring site and Florence background site indicate local/regional air quality as the dominant contributor to measured concentrations. Our analysis of $PM_{2.5}$ measurements across the different well activity periods suggest possible small $PM_{2.5}$ contributions at the measurement site from emissions at the study well pad site, such as for the hydraulic fracturing period; however, it bears mentioning that seasonal $PM_{2.5}$ trends are a likely confounder for data comparisons between well activity periods, and our analysis of $PM_{2.5}$ concentrations stratified by wind direction cannot differentiate between contributions from the study well pad and other local PM sources to the south and southeast. Both period-average and maximum 24-h concentrations for the well pad activity periods remained well below the US EPA NAAQS, indicating that if there were any $PM_{2.5}$ air quality impacts from development activities at the study well pad site, they did not contribute to NAAQS exceedances at the monitoring site. Given the location of the monitoring site between the study well pad site and the school campus, it is thus unlikely that the study well pad site caused any $PM_{2.5}$ NAAQS exceedances at the school campus.

Of the 14 consistently detected VOCs, seven (acetone, benzene, ethanol, methanol, n-hexane, propylene, toluene) have been associated with UNGD activities [9, 19, 24–26]. Of these seven VOCs, there were known sources of all but ethanol and methanol at the study well pad. Some of our study findings, including statistically significantly higher VOC concentrations (e.g., acetone, ethanol, methanol, methylene chloride, toluene) at the two monitoring sites closest to the study well pad site (sites 2 and 3) relative to the third site (1) and higher maximum 24-h VOC comparisons (e.g., acetone, methylene chloride, n-hexane, propylene, and toluene) at the study monitoring sites relative to data for the PADEP Florence background site, may indicate small and transient VOC contributions from the study well pad site at the monitoring sites. However, overall, there was significant variability in measured concentrations across different VOCs, sites, and sampling periods, and other findings suggest contributions from other local and regional sources. These findings include the measurement of maximum 24-h concentrations for a number of VOCs (e.g., acetone and methanol) during the nonactivity interlude periods at the study well pad site, and the similar statistically significant differences in VOC concentrations at monitoring site 3 with southerly and southeasterly winds as for monitoring sites 1 and 2. Half of the consistently detected VOCs (2-butanone, carbon tetrachloride, chloromethane, dichlorodifluoromethane, Freon 113, methylene chloride, trichlorofluoromethane) were frequently detected by PADEP during its short-term air monitoring studies conducted at UNGD sites in southwestern, northeastern, and north-central PA, and attributed to either regional or global air quality rather than Marcellus Shale development activities [19, 24, 25]. Other target VOCs reported to be associated with well development activities (e.g., 1,3-butadiene, ethylbenzene, xylenes, trimethylbenzenes) were infrequently detected despite the use of sensitive detection limits.

Regardless of VOC sources, the measured concentrations, which reflect the cumulative contributions of both air emissions from the study well pad site and from other local and regional air pollutant sources including other area well

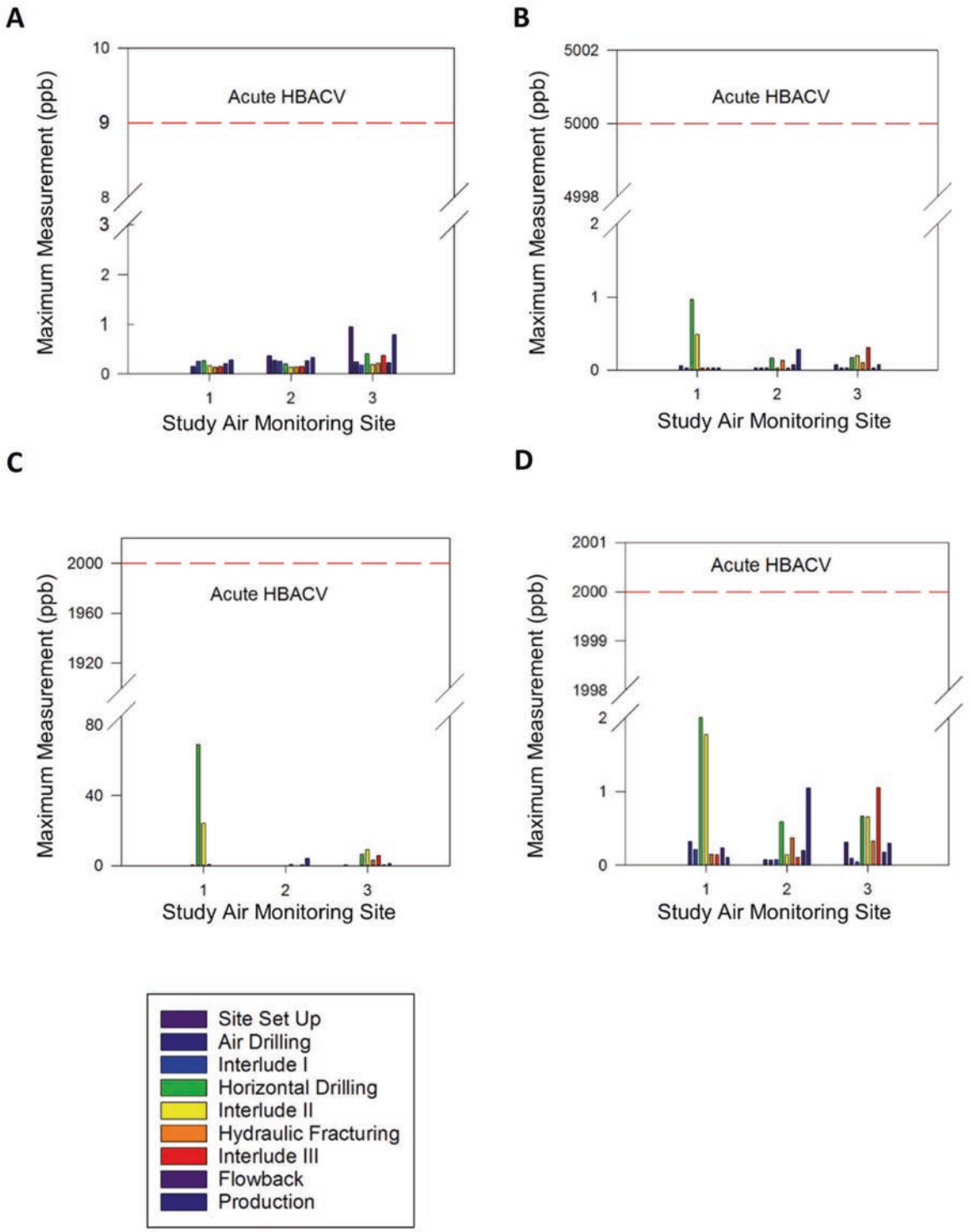

Fig. 3 Summary of maximum measured 24-h VOC concentrations by monitoring site and study well pad site development phase. **A** benzene, **B** ethylbenzene, **C** toluene, and **D** xylenes. Acute health-based air comparison values (HBACVs) are shown in red dashed lines. ppb parts per billion, VOC volatile organic compound. Measurements for m-, p-, and o-xylenes are summed in this figure because the applicable acute HBACV is for mixed xylenes.

pad sites, are consistently below levels of acute and chronic health concern. Given that two of the air monitoring sites are located between the study well pad site and the school campus, the VOC and $PM_{2.5}$ measurement data do not provide evidence of either 24-h or long-term average concentrations of potential health concern at the nearby school

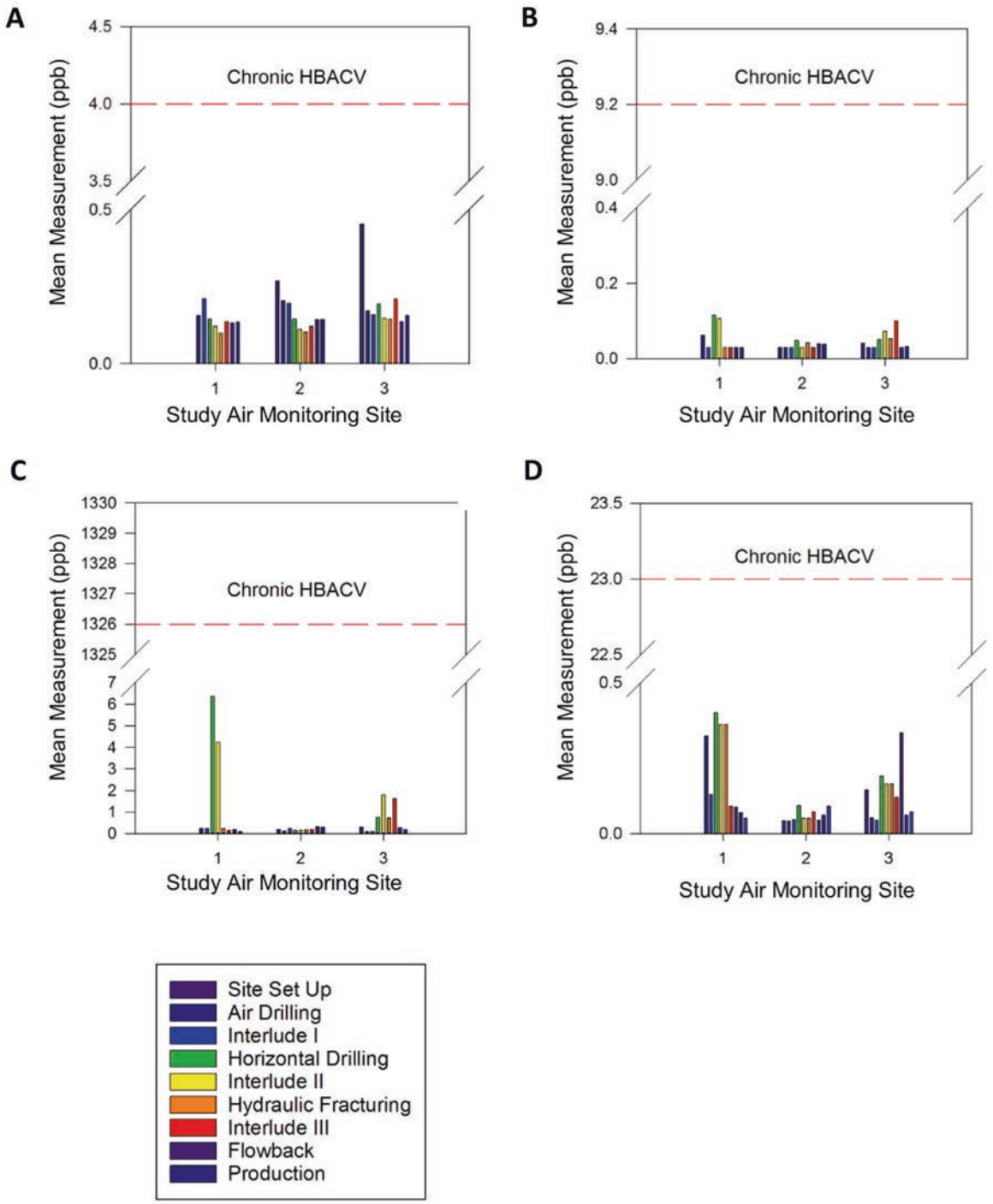

Fig. 4 Summary of mean VOC concentrations by monitoring site and study well pad site development phase. **A** benzene, **B** ethylbenzene, **C** toluene, and **D** xylenes. Chronic health-based air comparison values (HBACVs) are shown in red dashed lines. ppb parts per billion, VOC volatile organic compound. Measurements for m-, p-, and o-xylenes are summed in this figure because the applicable chronic HBACV is for mixed xylenes. Mean concentrations, and not 95% UCLs of the means, are shown due to the small number of samples and high fraction of non-detects for some development phases.

campus. More study is needed to confirm their broader generalizability, but these study findings supporting the lack of elevated chronic exposure levels when $PM_{2.5}$ and VOC concentrations were averaged across measurements made during all phases of well pad development may apply to other locales in the Marcellus Shale region with similar types of UNGD sites and operations.

These findings are consistent with operator efforts to control air emissions through continued refinement of best practices, as well as evolving governmental regulations

focused on air emissions. Operators have made continuous improvements to improve drilling performance, completion design, and production efficiency [27]. For example, during drilling, VOC emission rates are kept relatively low since hydrocarbon zones have not been stimulated, and emissions are combusted as required for safety. Range Resources has developed an enhanced flowback process using updated equipment and processes that is estimated to reduce air emissions during flowback by more than 80% [27]. Design changes, including a transition from flare stacks and enclosed burner units to vapor recovery compression and closed-loop systems, and upgrades to thief hatches on tank batteries [27], have been implemented to eliminate episodic high emission rates. In addition, operators such as Range Resources have deployed advanced technologies, including supervisory control and data acquisition software, remote telemetry monitoring systems, and infrared optical methane cameras, in order to oversee production and quickly respond to potential problems [27]. As discussed in Seguljic and Martin [28], both federal and Pennsylvania state regulations have evolved in recent years to target air emissions from well pad development and production operations.

Other recent studies in the Marcellus Shale region have similarly reported measured air pollutant concentrations to be generally below levels of human health concern for air sampling conducted in proximity to UNGD sites [4, 8, 9, 16, 19, 24, 25, 29, 30]. In particular, the Maskrey et al. [30] study was conducted in the same community as this study to investigate air quality impacts of development activities at another local UNGD well pad at the same school campus. Conducted on behalf of the local school board, this study made continuous measurements of total volatile organic compound (TVOC) concentrations and collected canister samples for individual VOC analysis at two monitoring sites (on the high school campus and at a private residence) over an ≈3-month period during four well pad activity periods: a baseline period before hydraulic fracturing commenced, the hydraulic fracturing period, the flaring period, and an inactive period following flaring. None of the VOC concentrations measured at either the high school or the private residence exceeded health-based benchmarks, and therefore the study investigators concluded that there was no measurable health impact from the well pad at either site.

The Allegheny County Health Department (ACHD) collected one of the few other long-term datasets for the Marcellus Shale region that included monitoring during all phases of development at nearby well pads. ACHD installed the Deer Lakes and Imperial Pointe temporary monitors in 2014 ≈0.85 and 0.3 miles, respectively, from the nearest well pads. The 4 years of VOC data available for each of these sites prior to their decommissioning in May 2017 have been categorized by ACHD according to activity time periods (baseline, site construction, drilling, fracking, and production) at the nearest well pads [5, 6]. All measured VOC concentrations are consistently low and below health-based benchmarks; for example, the highest 24-h benzene concentration measured during the ACHD monitoring was 0.8 ppb, while study-average benzene concentrations of 0.17 and 0.26 ppb were measured at the two sites [16].

Some studies have reported findings of elevated episodic air pollutant concentrations near UNGD sites during specific phases of development [31, 32]. As part of the West Virginia University (WVU) Air, Noise, and Light Monitoring Study, McCawley [31] reported elevated maximum 72-h benzene concentrations ranging from 8.2 to 85 ppb at four UNGD sites during drilling (horizontal or vertical) or hydraulic fracturing/flowback activities. In comparison, maximum 24-h benzene concentrations for this study ranged from 0.29 to 0.95 ppb and were either lower than or only slightly above measured benzene concentrations for the PADEP Florence background site (Table S.6). Differences in these findings may be due in part to the closer proximity (between 492 and 1312 feet [33]) of the monitoring sites to well pads in the WVU study, as well as differences in well pad design and operations and processes. In addition, as mentioned previously, our study did not have a monitoring site in the prevailing wind direction, and it is thus not possible to rule out the presence of higher benzene (or other VOC) concentrations associated with the study well pad site at other non-monitored locations.

While we did not identify any clear, consistent patterns in short-term $PM_{2.5}$ and VOC concentrations across the study well pad development phases, we acknowledge some important study limitations that have bearing on future studies investigating the temporal and spatial variability of air quality nearby to UNGD activity. Measurements in this study were focused on $PM_{2.5}$ and VOCs, which are important classes of air pollutants that have been associated with UNGD. However, there are a number of other air pollutants that have also been associated with UNGD via primary emissions or secondary atmospheric formation, including other criteria air pollutants (NO_2, carbon monoxide [CO], sulfur dioxide [SO_2], ozone [O_3]), and air toxics (e.g., acetaldehyde, formaldehyde, and hydrogen sulfide) [15, 16]. Hydrogen sulfide was not measured in this study based on prior analysis conducted by the site operator that indicated that this is not a sour gas region with significant hydrogen sulfide emissions. While it is thus not expected that hydrogen sulfide emissions at the well pad would have posed potential health risks at the school, this study did not address other air pollutants besides $PM_{2.5}$ and VOCs.

Similar to other air monitoring studies, this study was limited by the small number of air monitoring sites, and for VOCs, by the 24-h sample averaging time and every 6th

day sampling frequency. The $PM_{2.5}$ and VOC measurement data provide estimates of air exposure levels at the monitoring sites themselves and may not be representative of other locations or time periods. For example, the limited number of air monitoring sites did not allow for the characterization of the full range of potential air exposure levels associated with the well pad development. However, for the primary study objective of evaluating air quality impacts of the study well pad at the school campus, the study design, and specifically the location of two of the monitoring sites between the study well pad site and the school campus, provided reliable evidence that air quality impacts of potential health concern were unlikely at the school. It is possible that higher VOC concentrations may have occurred on non-sampling days, however, it bears mentioning that the collection of 24-h samples every 6th day is the standard US EPA sampling design for air toxics [34]. Moreover, with greater than 1 year of air sampling during the production phase, there were more than 60 air samples collected for VOC analysis at each of the three air monitoring sites, and thus a sizable dataset to represent both 24-h peak and long-term average VOC concentrations during the production phase of the study well pad.

It is recommended that future air monitoring studies conducted in proximity to UNGD well pads include higher resolution sampling (e.g., 1-h) for VOCs, as the standard 24-h sample duration does not allow for the characterization of episodic peak air pollutant events. These data are needed to assess whether brief, intermittent exposures (i.e., 1-h or less) may pose acute health risks. Only a small number of studies conducted in the Marcellus Shale region have measured VOC concentrations for sampling frequencies of 1-h or less [1, 2, 31, 34, 35]. Given the difficulty of disentangling the contributions of a specific local well pad site from other area oil & gas development sites, it is also recommended that studies be designed to facilitate source apportionment modeling.

Our study results indicated some higher $PM_{2.5}$ concentrations during the hydraulic fracturing phase when ≈100 temporary diesel-powered combustion sources (e.g., generators, light towers, pumps, pressure washers, heaters, and air compressors) are typically utilized at well pad sites. Although mean and maximum 24-h $PM_{2.5}$ concentrations remained below the corresponding NAAQS during this time period, our findings indicate a need for additional $PM_{2.5}$ monitoring during well completion activities to investigate possible off-site impacts of the combustion emissions. It bears mentioning that the industry has transitioned to greater direct use of natural gas in place of diesel fuel, or co-firing of natural gas with diesel fuel, for both drilling and well completion equipment [27, 36–38]. Flowback is generally recognized as a source of hydrocarbon emissions, and the high concentrations of some hydrocarbons (e.g., hexane and propylene) were detected during the flowback phase of the study well pad. Recognizing the recent transition to reduced emissions completions, our findings suggest that additional VOC monitoring during the flowback phase could be helpful to confirm the efficacy of reduced emissions completions for mitigating off-site VOC impacts.

In conclusion, this air quality and public health evaluation, which was designed to identify air quality impacts of potential health concern at a nearby school campus associated with operations of a Marcellus Shale unconventional gas well pad, showed that measured $PM_{2.5}$ and VOC concentrations were consistently below acute and chronic health-based air comparison values. While the nearly 2 years of data collected at the three monitoring sites between 1000 and 2800 feet from the study well pad include some episodic short-term concentration increases that may be associated with the transient well pad development phases, the $PM_{2.5}$ and VOC measurements do not provide evidence of elevated long-term average concentrations at the three monitoring sites relative to a Washington County background site more distant from Marcellus Shale development. The study measurement data, which reflect not only any air emissions from the study well pad but also air emissions from other local and regional Marcellus Shale development, do not provide evidence indicating that the study well pad was a source of either acute or chronic $PM_{2.5}$ or VOC concentrations of potential health concern at the school campus; however, the study design did not include monitoring sites in the predominant wind direction or closer than 1000 feet from the well pad, and thus did not allow for the characterization of the full range of potential air exposure levels associated with the well pad development.

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Compliance with ethical standards

Conflict of interest During involvement in the study, authors were employed by Gradient or AECOM. The work reported in this paper was conducted during the normal course of employment. Range Resources, which provided financial support for this study and paper, developed and currently operates the study well pad, as well as other well pads in the local area. The authors had complete freedom in the design, implementation, and reporting of the research presented in this paper; the paper was reviewed by employees of Range Resources while in preparation. The authors retain sole responsibility for the writing and content of this paper, which represent the professional opinions of the authors and not necessarily those of Range Resources. One of the authors of this manuscript (C. Long) has testified in Pennsylvania on behalf of natural gas development companies at local zoning hearing board meetings and at a judicial hearing on the science of the air quality impacts of Marcellus Shale development activities.

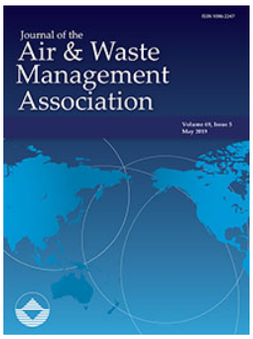
References

1. Goetz JD, Floerchinger C, Fortner EC, Wormhoudt J, Massoli P, Knighton WB, et al. Atmospheric emission characterization of Marcellus shale natural gas development sites. Environ Sci Technol. 2015;49:7012–20. https://doi.org/10.1021/acs.est.5b00452.
2. Goetz JD, Avery A, Werden B, Floerchinger C, Fortner EC, Wormhoudt J, et al. Analysis of local-scale background concentrations of methane and other gas-phase species in the Marcellus Shale. Elementa. 2017;5:1. https://doi.org/10.1525/elementa.182.
3. McCawley M. Air contaminants associated with potential respiratory effects from unconventional resource development activities. Semin Respir Crit Care Med. 2015;36:379–87. https://doi.org/10.1055/s-0035-1549453.
4. Swarthout RF, Russo RS, Sive BC, Zhou Y, Miller BM, Mitchell BL, et al. Impact of Marcellus Shale natural gas development in southwest Pennsylvania on volatile organic compound emissions and regional air quality. Environ Sci Technol. 2015;49:3175–84. https://doi.org/10.1021/es504315f.
5. Allegheny County, Pennsylvania, Health Dept (ACHD). Imperial pointe ambient air sampling results/method EPA TO15+ tentatively identified compounds. 2016 Sep 21. 13 p. [217-3287]
6. Allegheny County, Pennsylvania, Health Dept (ACHD). Deer lakes ambient air sampling results/radiello passive monitors. 2016 Nov 29. 12 p. [217-3288]
7. Agency for toxic substances and disease registry (ATSDR). health consultation, exposure investigation, natural gas ambient air quality monitoring initiative, Brigich Compressor Station, Chartiers Township, Washington County, Pennsylvania. 2016 Jan 29. 94 p. [216-5252]
8. Pennsylvania Dept. of Environmental Protection (PADEP). Long-term ambient air monitoring project: marcellus shale gas facilities. 2018 Jul. 139 p. [218-8169]
9. US EPA Region III, Office of Air Monitoring and Analysis, Air Protection Division. EPA Region III Natural gas ambient air monitoring initiative (NGAAMI) in Southwestern Pennsylvania. 2015 Aug. 515 p. [216-5251]
10. Ghosh B. Impact of changes in oil and gas production activities on air quality in northeastern Oklahoma: ambient air studies in 2015-2017. Environ Sci Technol. 2018;52:3285–94. https://doi.org/10.1021/acs.est.7b05726.
11. Bunch AG, Perry CS, Abraham L, Wikoff DS, Tachovsky JA, Hixon JG, et al. Evaluation of impact of shale gas operations in the Barnett Shale region on volatile organic compounds in air and potential human health risks. Sci Total Environ. 2014;468-469:832–42. https://doi.org/10.1016/j.scitotenv.2013.08.080.
12. Zielinska B, Campbell D, Samburova V. Impact of emissions from natural gas production facilities on ambient air quality in the Barnett Shale area: a pilot study. J Air Waste Manag Assoc. 2014;64:1369–83. https://doi.org/10.1080/10962247.2014.954735.
13. Colborn T, Schultz K, Herrick L, Kwiatkowski C. An exploratory study of air quality near natural gas operations. Hum Ecol Risk Assess. 2014;20:86–105.
14. Southwest Pennsylvania Environmental Health Project. Community assessment of penn trafford outdoor air monitoring results. 2016 Jun 6. 11 p.
15. Health Effects Institute- Energy Research Committee. Human exposure to unconventional oil and gas development: a literature survey for research planning. Communication. 2020;132:217–4734.
16. Long CM, Briggs NL, Bamgbose IA. Synthesis and health-based evaluation of ambient air monitoring data for the Marcellus Shale region. J Air Waste Manag Assoc. 2019;69:527–47. https://doi.org/10.1080/10962247.2019.1572551.
17. Pennsylvania Dept. of Environmental Protection (PADEP), Office of Oil and Gas Management. Wells Drilled by County [Wells drilled between June 1, 2009 and June 1, 2019]. 2019. 2 p. https://www.dep.pa.gov/DataandTools/Reports/OilandGasReports/Pages/default.aspx.
18. Pennsylvania Dept. of Environmental Protection (PADEP). "PA Oil and Gas Mapping." 2019. Available from http://www.depgis.state.pa.us/PaOilAndGasMapping/OilGasWellsStrayGasMap.html.
19. Pennsylvania Dept. of Environmental Protection (PADEP), Bureau of Air Quality. Southwestern Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Report. 2010 Nov 1. 52 p. [214-8020]
20. US EPA. EPA Schools Monitoring Initiative Fact Sheet: December 2012 Update: Acrolein Monitoring Results. 2012. 3 p. [217-8448]
21. Agency for Toxic Substances and Disease Registry (ATSDR). Minimal risk levels (MRLs) [Narrative]. 2017 Jun 27. https://www.atsdr.cdc.gov/mrls/index.asp.
22. US EPA. Schools Air Toxics Monitoring Activity (2009): Uses of health effects information in evaluating sample results. 2009 Sep 10. 24 p. [216-5262]
23. US EPA, Office of Air Quality, Planning and Standards. Residual Risk: Report to Congress. 1999 Mar. Report No.: EPA-453/R-99-001.
24. Pennsylvania Dept. of Environmental Protection (PADEP), Bureau of Air Quality. Northeastern Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Report. 2011 Jan 12. 57 p. [214-8019]
25. Pennsylvania Dept. of Environmental Protection (PADEP), Bureau of Air Quality. Northcentral Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Report. 2011 May 6. 52 p.
26. McMullin TS, Bamber AM, Bon D, Vigil DI, Van Dyke M. Exposures and health risks from volatile organic compounds in communities located near oil and gas exploration and production activities in Colorado (U.S.A.). Int J Environ Res Public Health. 2018;15:1500. https://doi.org/10.3390/ijerph15071500.
27. Boyd, D. *Marcellus/Utica Activity: Operators Deploy Best Practices & Innovation as Marcellus/Utica Astound* (The American Oil & Gas Reporter, 2019). https://www.aogr.com/magazine/cover-story/operators-deploybest-practices-innovation-as-marcellus-utica-astound.
28. Seguljic TS, Martin JP. Air regulation requirements in the Marcellus and Utica shale region: Management approaches and case study. Environ Qual Manag. 2016;26:73–87. https://doi.org/10.1002/tqem.21479.
29. Agency for Toxic Substances and Disease Registry (ATSDR); Pennsylvania Department of Health (PDOH). Health consultation: public health evaluation of long-term air sampling data collected in the vicinity of natural gas operations, Washington County, Pennsylvania. 2018 Jul 18. 91 p. [218-8595]

30. Maskrey JR, Insley AL, Hynds ES, Panko JM. Air monitoring of volatile organic compounds at relevant receptors during hydraulic fracturing operations in Washington County, Pennsylvania. Environ Monit Assess. 2016;188:410. https://doi.org/10.1007/s10661-016-5410-4.
31. McCawley M (West Virginia University). Air, noise, and light monitoring results for assessing environmental impacts of horizontal gas well drilling operations (ETD-10 Project). 2013 May 3. 206 p. Report to West Virginia Dept. of Environmental Protection. Available from http://wvwri.org/wp-content/uploads/2013/10/A-N-L-Final-Report-FOR-WEB.pdf.
32. Macey GP, Breech R, Chernaik M, Cox C, Larson D, Thomas D, et al. Air concentrations of volatile compounds near oil and gas production: A community-based exploratory study. Environ Health. 2014;13:82. https://doi.org/10.1186/1476-069X-13-82.
33. Pekney N, Reeder M, Veloski G, Diehl JR. Data Report for Monitoring at Six West Virginia Marcellus Shale Development Sites using NETL's Mobile Air Monitoring Laboratory (July–November 2012). US Dept. of Energy (US DOE), National Energy Technology Laboratory (NETL); 2016 Jun 16. 104 p. Report No.: NETL-TRS-4-2016.
34. Strum M, Scheffe R. National review of ambient air toxics observations. J Air Waste Manag Assoc. 2016;66:120–33. https://doi.org/10.1080/10962247.2015.1076538.
35. Orak NH, Pekney NJ, Reeder M. Ambient air quality near a Marcellus shale well pad in southwestern Pennsylvania. Proceedings of the Air and Waste Management Association's 110th Annual Conference and Exhibition; 2017 Jun 7; Pittsburgh, PA. Available from https://www.eventscribe.com/2017/awma/ajaxcalls/PresentationInfo.asp?efp=SFRXUFlFQkIzMjEz&PresentationID=262009&rnd=0.2957729.
36. Range Resources. 2020 Corporate Sustainability Report. 2020. 76 p. Available from https://csr.rangeresources.com/wp-content/uploads/2020/09/Range_resources_CSR_report.pdf.
37. CNX. 2019 Corporate Responsibility Report. 2019. 45 p. Available from https://www.cnx.com/cnx/media/Pdf/CNX_2019CSR.pdf.
38. Addison, V. Producers are making use of natural gas to power rigs. Available from https://www.hartenergy.com/opinions/producers-are-making-use-natural-gas-power-rigs-121745.

ATTACHMENT C

STUDY 30



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Christopher M. Long, Nicole L. Briggs & Ifeoluwa A. Bamgbose

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Synthesis and health-based evaluation of ambient air monitoring data for the Marcellus Shale region

Christopher M. Long[a], Nicole L. Briggs[b], and Ifeoluwa A. Bamgbose[a]

[a]Gradient, Cambridge, MA, USA; [b]Gradient, Seattle, WA, USA

ABSTRACT

In recent years, there has been a marked increase in the amount of ambient air quality data collected near Marcellus Shale oil and gas development (OGD) sites. We integrated air measurement data from over 30 datasets totaling approximately 200 sampling locations nearby to Marcellus Shale development sites, focusing on 11 air pollutants that can be associated with OGD operations: fine particulate matter ($PM_{2.5}$), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), acetaldehyde, benzene, ethylbenzene, formaldehyde, n-hexane, toluene, xylenes, and hydrogen sulfide (H_2S). We evaluated these data to determine whether there is evidence of community-level air quality impacts of potential health concern, making screening-level comparisons of air monitoring data with acute and chronic health-based air comparison values (HBACVs). Based on the available air monitoring data, we found that only a small fraction of measurements exceeded HBACVs, which is similar to findings from integrative air quality assessments for other shale gas plays. Therefore, the data indicate that air pollutant levels within the Marcellus Shale development region typically are below HBACV exceedance levels; however, the sporadic HBACV exceedances warrant further investigation to determine whether they may be related to specific site characteristics, or certain operations or sources. Like any air monitoring dataset, there is uncertainty as to how well the available Marcellus Shale air monitoring data characterize the range of potential exposures for people living nearby to OGD sites. Given the lesser amounts of air monitoring data available for locations within 1,000 feet of OGD sites as compared to locations between 0.2 and 1 miles, the presence of potential concentration hotspots cannot be ruled out. Additional air monitoring data, in particular more real-time data to further characterize short-term peak concentrations associated with episodic events, are needed to provide for more refined assessments of potential health risks from Marcellus Shale development.

Implications: While there is now a sizable amount of ambient air monitoring data collected nearby to OGD activities in the Marcellus Shale region, these data are currently scattered among different databases and studies. As part of an integrative assessment of Marcellus Shale air quality impacts, ambient air data are compiled for a subset of criteria air pollutants and hazardous air pollutants that have been associated with OGD activities, and compared to acute and chronic health-based air comparison values to help assess the air-related public health impacts of Marcellus Shale development.

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Introduction

Occurring primarily in Pennsylvania, West Virginia, New York, and eastern Ohio, but also occupying smaller portions of Virginia, Maryland, and Tennessee, the Marcellus Shale has become the top shale gas–producing resource in the United States (EIA 2017). To date, the majority of the development of the Marcellus Shale has occurred in Pennsylvania and West Virginia, where there are now over 10,000 and 3,000 active unconventional natural gas wells, respectively (PADEP 2017; WVGES 2017). The rapid development of the Marcellus Shale play, which was made possible by major technological advances that include horizontal drilling and high-volume hydraulic fracturing, has occurred since 2007 when the first commercial horizontal Marcellus Shale gas well was established in southeastern Pennsylvania (Soeder 2017). While the Marcellus Shale play is best known for its vast supply of recoverable natural gas (estimated to be as high as 3.2 trillion cubic meters or 114 trillion cubic feet, which is approximately equivalent to a 5-year supply for the United States at current consumption rates; Soeder 2017), Marcellus Shale wells can also be sources of both oil and condensate liquids.

CONTACT Christopher M. Long clong@gradientcorp.com Gradient, 20 University Road, Cambridge, MA 02138.

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In parallel with the rapid development of the Marcellus Shale play and other tight oil and shale gas plays in the United States, there have arisen concerns regarding the potential public health and environmental impacts of unconventional oil and gas development (OGD) activities. Concerns have been raised regarding a variety of different types of potential impacts of OGD activities, including those to air quality, water quality, psychosocial stress, noise, seismic activity, public health, worker health, and ecosystem health. Much of the early research has focused on water quality impacts, although a growing number of studies have addressed other types of impacts, particularly air quality impacts. Groups such as the Health Effects Institute (HEI) have recommended a multifaceted research program to address the broad range of potential OGD-related impacts (HEI 2015).

It is well established that each of the phases of development for a natural gas or oil well pad is associated with potential sources of air emissions, including criteria air pollutants, air toxics, and greenhouse gases (McCawley 2015; Moore et al. 2014). For example, diesel-powered construction equipment, including trucks, backhoes, and graders, can be sources of air emissions during the well pad construction phase. During the well drilling phase, sources of air emissions can include diesel-powered trucks, generators, compressors, and backhoes; diesel- and/or natural gas-powered drill rigs; as well as drilling muds. During the well completion phase, sources of air emissions can include diesel-powered trucks, diesel- and/or natural gas-powered hydraulic fracturing pumps, hydraulic fracturing fluids, flowback water, and sand handling operations. Finally, air emission sources during the production phase can include well-head compressors or pumps, well pad equipment bleeding and leaks (e.g., from valves or flanges), and diesel-powered trucks. With the exception of the production phase, the various phases of well pad development are transient in nature with typical durations on the order of days to weeks (Soeder 2017), meaning that potential well pad air emission sources will predominantly occur over short-term time periods. Natural gas infrastructure, including gas processing plants, compressor stations, and pipelines, can also be associated with air emissions.

Recent integrative assessments have been conducted for other shale plays (e.g., for the Barnett Shale region in Texas [Bunch et al. 2014] and the Niobrara Shale region in Colorado [CDPHE 2017; McMullin et al. 2018; McKenzie et al. 2018]), but we are not aware of such a broad assessment of air quality data for the Marcellus Shale region, despite a substantial increase in the amount of ambient air monitoring data collected nearby to Marcellus Shale development activities. Given that the available air quality data are currently scattered among different databases and studies, the objective of this assessment was thus to assemble the body of data and provide an integrative screening-level assessment of its implications for air-related public health impacts of OGD activities in the Marcellus Shale region. By identifying available air quality data representative of both long-term average exposure levels as well as short-term transient exposures (e.g., 1 minute, 1 hour), we sought to address the following question: Do ambient air monitoring data collected in the Marcellus Shale region provide evidence of community-level air quality impacts of potential health concern? This is slightly different from the question of whether Marcellus Shale development activities are causing community-level air quality impacts of potential health concern. Due to the use of ambient air data that reflect the combined impacts of a variety of local and regional air pollutant sources, our assessment cannot provide a reliable answer to the latter question. In other words, the occurrence of elevated air concentrations above health-based air comparison values (HBACVs) does not necessarily provide evidence of harmful air emissions from OGD activities due to the difficulty in apportioning the air quality impacts of OGD emissions versus other common emissions, even for air monitoring sites nearby to OGD activities. However, our assessment can identify whether air pollutants are frequently being found at concentrations of potential health concern nearby to OGD sites.

Though we compare data to acute and chronic health-based air comparison values in our assessment, it is important to distinguish this type of screening assessment from a quantitative risk assessment. We do not perform risk calculations typical of a quantitative human health risk assessment due to the large heterogeneity of the data across studies in terms of sampling locations, sample averaging times, measurement methods, study durations, etc. Rather, we perform a screening assessment of ambient air data that are expected to capture any local, community-level impacts of OGD-related activities. We focus on data for a subset of air pollutants that have been most consistently measured in Marcellus Shale air quality studies and that have received greater scrutiny as potential contributors to OGD-related health risks. These include both criteria air pollutants (fine particulate matter [$PM_{2.5}$], nitrogen dioxide [NO_2], sulfur dioxide [SO_2]), U.S. EPA hazardous air pollutants (HAPs; acetaldehyde, benzene, ethylbenzene, formaldehyde, n-hexane, toluene, and xylenes), and hydrogen sulfide (H_2S). Some of the few

available quantitative risk assessments conducted for shale play regions have reported findings suggesting that these air pollutants may be associated with the greatest potential for human health risks (CDPHE 2017; McKenzie et al. 2018, 2012; McMullin et al. 2018). We did not include the major natural gas constituents (methane, ethane, propane, butane) in our assessment because they are of low direct toxicity to humans (Goldstein et al. 2014; McKee et al. 2014). We also did not include ozone in the assessment because it is a secondary pollutant produced from emissions from many regional sources, and therefore local source attribution is complex.

Methods

Literature searches were performed using the U.S. National Library of Medicine's PubMed biomedical literature database (http://www.ncbi.nlm.nih.gov/pubmed/) and Elsevier's Scopus database (http://www.scopus.com/) to identify ambient air measurement data for monitoring locations nearby to Marcellus Shale OGD sites. We used the following general inclusion criteria so as to compile the largest amount of available data as possible representing the potential air quality impacts of OGD operations: (1) Availability of post-2007 data for air sampling for ambient air monitoring locations potentially impacted by Marcellus Shale development activities; (2) Original data reported in a governmental dataset or air monitoring study published in a peer-reviewed journal, governmental report, or other report; (3) Availability of information on monitoring locations relative to OGD-related activity and on key sampling parameters (e.g., sampling and analytical methods, sample duration, detection limits); (4) Reliance on standard, accepted sampling and analytical methods (e.g., U.S. EPA methods); and (5) Few, if any, other large local air pollutant sources, such as nearby highways and other local industry. We used 2008 as the first year for data inclusion, given that this year is recognized as the start of the surge of drilling activity in the Marcellus Shale region (Soeder 2017).

We broadly defined air monitoring locations potentially impacted by OGD activities in order to include all available air monitoring data potentially illustrative of OGD-related air quality impacts. Specifically, we included air monitoring locations if they were between 500 feet to 10 miles from OGD sites, based on the 500-foot minimum setback distance in Pennsylvania between an unconventional well and an occupied structure, and the 10-mile distance cut-off that has been used by some epidemiological studies (e.g., McKenzie et al. 2014; Stacy et al. 2015) to determine "exposed" populations in OGD regions. We excluded on-well pad measurements, point-source air testing data, and occupational exposure measurements since they are not generally representative of the off-site ambient air to which the general public may be exposed. We focused our efforts on identifying data for monitoring sites within 1 to 2 miles of OGD sites; this is consistent with research indicating that the air quality impacts of well pad sites diminish rapidly with distance away from air emission sources (Zielinska, Campbell, and Samburova 2014).

PubMed and Scopus literature searches were conducted to locate search terms in article titles, abstracts, and keywords. The set of search terms was developed iteratively, beginning with less restrictive search terms and adding to them to obtain a comprehensive, but focused, body of relevant studies. The final set of search terms included: (Marcellus OR Pennsylvania OR West Virginia OR Virginia OR Maryland OR Ohio OR New York) AND air AND (quality OR concentration OR concentrations OR observation OR observations OR measurement OR measurements OR sample OR samples OR mixing ratio OR mixing ratios) AND (natural gas OR shale).

The PubMed and Scopus literature searches were supplemented using Google searches, by checking article and report reference lists, and by consulting two living bibliographies of studies bearing on OGD impacts, namely the HEI Energy Research Program "Unconventional Oil and Gas Development Bibliography (HEI, 2018)" and the Physicians, Scientists, and Engineers (PSE) for Healthy Energy Repository for Oil and Gas Energy Research (ROGER). Using these additional resources, we were able to identify pertinent governmental air monitoring datasets and reports, as well as reports and data from non-governmental research institutions, all of which would not have been indexed in either PubMed or Scopus.

In general, we erred on the side of including most air quality datasets and studies that we identified as reporting ambient air measurement data for the Marcellus Shale region. We excluded only a small number of datasets and studies, including the following: (1) Preliminary results reported by scientists at the U.S. Department of Energy (U.S. DOE) National Energy Technology Laboratory (NETL) for air monitoring conducted in 2012 at a Greene County (Pennsylvania) well pad and from 2011 to 2014 at a Washington County (Pennsylvania) well pad. Currently, data from these studies have only been reported in conference presentations and abstracts, and are not yet available in either study reports or peer-reviewed publications (Orak, Pekney, and Reeder 2017; Pekney et al. 2013). While

there are limited data that could be drawn from these proceedings, it is not readily possible to determine if they are raw or preliminary data, rather than final, quality-controlled data that could be used in our assessment; (2) $PM_{2.5}$ data reported by Lewis, Hamel, and Brown (2016) for monitoring at several residences between 500 and 2,500 feet from a nearby well pad conducted in Penn Township, Pennsylvania, using a low-cost, handheld PM monitor known as the Speck. While we included data on volatile organic compounds (VOC) from this study in our assessment, we excluded the $PM_{2.5}$ data given that studies have reported findings that raise questions regarding the accuracy and reliability of $PM_{2.5}$ data from the Speck (EPA 2014a; SCAQMD, n.d; Manikonda et al. 2016); (3) VOC data reported by the Pennsylvania Department of Environmental Protection (PADEP) for Open-Path Fourier Transform Infrared (OP-FTIR) measurements during their three short-term ambient air sampling studies (PADEP, 2010; 2011a, 2011b). These data were excluded due to the poor sensitivity of the OP-FTIR as compared to the VOC canister and field gas chromatograph/mass spectrometer (GC/MS) samples also collected as part of this study; (4) Data from indoor air sampling conducted inside the Sky View Elementary School in Morgantown, West Virginia, as part of the U.S. EPA-commissioned TechLaw (2012) study. Only the outdoor air sampling data from this study were used, given that indoor sources may have contributed to measured concentrations for indoor samples, in particular for acetaldehyde and formaldehyde; (5) Air monitoring data for state and local air quality monitors in states besides Pennsylvania that have extensive Marcellus Shale development activities, including West Virginia in particular. Unlike PADEP, the West Virginia DEP (WVDEP) has not installed air quality monitors to specifically measure the impacts of Marcellus Shale development activities, and its existing network of air quality monitors is heavily impacted by other major industrial sources, including coal mines and chemical facilities. Similar to WVDEP, there has been a lack of air quality monitors in Ohio specifically sited near OGD sites, although plans called for the Ohio EPA to commence air monitoring in 2017 near a midstream natural gas processing facility in Harrison County, Ohio (Ohio EPA 2017).

For the datasets and studies included in the assessment, we extracted air monitoring data in varying forms, including full datasets, data summary tables, and study summary statistics. We were generally able to obtain full datasets for governmental monitoring, from both state and county air monitoring websites, as well as from the U.S. EPA AQS database. Criteria air pollutant data for all state and local air quality monitors and air toxics data for the Pinnacle State Park monitor in New York were obtained from the U.S. EPA AQS, with 2016 being the last full year of available data. Air toxics data for PADEP air monitors were obtained from the PADEP website and were generally only available for sampling conducted through 2015. For one published study (Goetz et al. 2017), the authors freely provided the full dataset of high-resolution measurements at the Dryad data repository (https://doi.org/10.5061/dryad.g8h54). For most non-governmental datasets, however, the raw data were not available and we therefore used existing summary statistics.

We summarized study measurement data by air pollutant, calculating summary statistics whenever we had access to full datasets or compiling summary statistics provided in the paper or report. Summary statistics that were calculated or compiled included the number of samples and detects (or percentage of detects), and mean, median, and maximum concentrations, with the latter three statistics often reported as ranges across either multiple sampling sites or years of data. The lack of raw data from many studies and variability in the summary statistics available from study to study contributed to the qualitative nature of our data assessment, which is based on tabular and graphical summaries rather than a rigorous statistical analysis.

We compared the compiled air quality data to acute and chronic HBACVs (Table 1). In these comparisons, we considered the monitoring data from state and local air monitors and from published and other studies separately in order to understand the similarities and differences between these different types of dataset. Importantly, the HBACVs we relied upon are not bright lines above which health effects are expected; instead, due to the use of conservative (i.e., health-protective) assumptions and safety and/or uncertainty factors, they typically specify exposure levels that are typically at least several hundredfold lower than the exposure level at which the actual adverse effect was observed in people or laboratory animals (EPA 2004). The exceedance of HBACVs should thus be viewed as indicating that further assessment of the potential exposure scenario is warranted, such as determining how well the data represent actual human exposure conditions and how close measured concentrations are to actual health effect levels.

For chronic HBACVs, we relied upon the U.S. EPA primary National Ambient Air Quality Standards (NAAQS) for criteria air pollutants. For HAPs and H_2S, we relied upon non-cancer U.S. EPA Reference

Table 1. Summary of acute and chronic health-based air comparison values.

Air Pollutant	Acute HBACV[a]	Units	Source	Chronic HBACV[b]	Units	Source
SO_2	75	ppb	U.S. EPA 1-hour NAAQS	30	ppb	Former U.S. EPA annual NAAQS
NO_2	100	ppb	U.S. EPA 1-hour NAAQS	53	ppb	U.S. EPA annual NAAQS
$PM_{2.5}$	35	µg/m^3	U.S. EPA 24-hour NAAQS	12	µg/m^3	U.S. EPA annual NAAQS
Acetaldehyde	260	ppb	CalOEHHA 1-hour REL	5.0	ppb	U.S. EPA RfC
Benzene	8.5	ppb	CalOEHHA 1-hour REL	4.1	ppb	Cancer-based estimated continuous lifetime exposure concentration
Ethylbenzene	5,000	ppb	ATSDR Acute MRL	9.2	ppb	Cancer-based estimated continuous lifetime exposure concentration
Formaldehyde	40	ppb	ATSDR Acute MRL	6.3	ppb	Cancer-based estimated continuous lifetime exposure concentration
n-Hexane	2,900,000[c]	ppb	1-hour AEGL-2	200	ppb	U.S. EPA RfC
Toluene	2,000	ppb	ATSDR Acute MRL	1,300	ppb	U.S. EPA RfC
o-Xylene[d]	2,000	ppb	ATSDR Acute MRL	23	ppb	U.S. EPA RfC
m,p-Xylenes[d]	2,000	ppb	ATSDR Acute MRL	23	ppb	U.S. EPA RfC
Hydrogen Sulfide	30	ppb	CalOEHHA 1-hour REL	1.4	ppb	U.S. EPA RfC

Notes: HBACV = Health-based comparison values; NA = Not available; NO_2 = Nitrogen dioxide; $PM_{2.5}$ = Fine particulate matter; ppb = Parts per billion; SD = Standard deviation; SO_2 = Sulfur dioxide; U.S. EPA = United States Environmental Protection Agency.

[a] As explained in the text, U.S. EPA NAAQS for $PM_{2.5}$, NO_2, and SO_2; for all other air pollutants of interest, the lowest value of U.S. Agency for Toxic Substances and Disease Registry (ATSDR) acute inhalation Minimal Risk Levels (MRLs), California Office of Environmental Health Hazard Assessment (OEHHA) 1-hour Acute Reference Exposure Levels (RELs), 1-hour Acute Exposure Guideline Levels (AEGLs) developed by the National Advisory Committee for Acute Exposure Guideline Levels for Hazardous Substances (NAC), and 1-hour American Industrial Hygiene Association (AIHA) Emergency Response Planning Guidelines (ERPGs).

[b] As explained in the text, U.S. EPA NAAQS for $PM_{2.5}$ and NO_2; a former U.S. EPA NAAQS for SO_2; for all other air pollutants of interest, the lowest value of either non-cancer U.S. EPA Reference Concentrations (RfCs) or estimated continuous lifetime exposure concentrations associated with an assumed 100-in-a-million excess lifetime cancer risk.

[c] No AEGL-1 value available, so AEGL-2 value used.

[d] The ATSDR acute MRL is for mixed xylenes, i.e., the combination of m,p, and o-xylenes, while the U.S. EPA RfC of 0.10 mg/m^3 (23 ppb) applies to each xylene isomer individually.

Concentrations (RfCs) and estimated continuous lifetime exposure concentrations associated with a 100-in-a-million excess lifetime cancer risk. For calculating estimated continuous lifetime exposure concentrations for known or suspected human carcinogens (acetaldehyde, benzene, ethylbenzene, and formaldehyde), we relied upon inhalation unit cancer risks available from both U.S. EPA (acetaldehyde, benzene, and formaldehyde) and the California Office of Environmental Health Hazard Assessment (OEHHA) (ethylbenzene only). We based them on a 100-in-a-million lifetime cancer risk consistent with the U.S. EPA residual risk program and with long-term comparison levels developed as part of U.S. EPA's School Air Toxics Initiative (EPA 2009). For air pollutants of interest with both RfCs and cancer-based estimated continuous lifetime concentrations, we used the lower of the two values as the chronic HBACVs.

Although the chronic HBACVs are most appropriate for comparison with long-term exposure concentrations representative of a lifetime of exposure (i.e., 70 years), it is common practice to assume that annual average air concentrations are representative of chronic long-term exposures and we thus compared the chronic HBACVs to annual average air concentrations whenever they were available. Given that many short-term studies conducted sampling over just a few days, weeks, or months, we also compared the chronic HBACVs to air monitoring data with shorter averaging times (e.g., the average of several 24-hour measurements). This comparison of short-term data to chronic HBACVs was done to more fully utilize the body of available data, since most studies did not measure air concentrations for a year or longer. However, this comparison is assumed to be conservative (i.e., erring on the side of overestimating potential risks) because many of the sampling studies targeted transient time periods (e.g., drilling and well completion phases) when OGD emissions were expected to be higher than for typical long-term conditions.

For acute HBACVs, we again relied upon the U.S. EPA primary NAAQS for criteria air pollutants and the lowest of four sets of acute inhalation values specifically developed to be protective of the general public and identified by U.S. EPA as appropriate for hazard identification and dose–response assessment for acute exposure to HAPs (EPA 2014b), namely U.S. Agency for Toxic Substances and Disease Registry (ATSDR) acute inhalation Minimal Risk Levels (MRLs), California OEHHA 1-hour Acute Reference Exposure Levels (RELs), 1-hour Acute Exposure Guideline Levels (AEGLs) developed by the National Advisory Committee for Acute Exposure Guideline Levels for Hazardous Substances (NAC), and 1-hour American Industrial Hygiene Association (AIHA) Emergency

Response Planning Guidelines (ERPGs). Both the AEGLs and ERPGs are available for varying degrees of severity of effects, and we primarily relied upon 1-hour AEGL-1 and ERPG-1 values that represent the lowest acute exposure thresholds that are protective of mild health effects such as discomfort, irritation, and other mild reversible effects. For n-hexane, no AEGL-1 value is available due to insufficient data; so we relied upon the AEGL-2 value. With the exception of $PM_{2.5}$ (for which we compared 24-hour average concentrations to the daily $PM_{2.5}$ NAAQS), sampling data collected over periods of several minutes up to 8 hours was compared with these acute HBACVs. This is a conservative comparison for the ATSDR acute MRLs that are derived to protect against exposure durations of 1–14 days.

Results and discussion

We identified approximately 20 datasets from regulatory agency reports, published studies, and other studies and whitepapers, as well as 15 state and county air monitoring sites meeting our inclusion criteria, totaling approximately 200 sampling locations in areas with Marcellus Shale development (Table 2). As discussed more below (and summarized in Table S.2), individual air monitoring datasets and studies have various strengths and limitations, but when pooled they provide an informative dataset for examining air quality nearby to Marcellus Shale development. As shown in Table 2, we identified a larger body of data for the VOCs (BTEX, n-hexane) and two of the criteria pollutants of interest ($PM_{2.5}$ and NO_2) than for the carbonyls (acetaldehyde and formaldehyde), SO_2, and H_2S. While most regulatory, published, and other studies were conducted over study durations of days to months, the state and local air monitoring site datasets provide annual average data, frequently for multi-year periods. The majority of air monitoring site datasets and studies provide data with 24-hour or longer averaging times, but there is a growing body of studies reporting data with averaging times of 1 hour or less that can be used to evaluate episodic short-term air quality impacts. More specifically, Goetz et al. (2015, 2017), Swarthout et al. (2015), PADEP (2010, 2011a, 2011b), Macey et al. (2014), Pekney et al. (2014), and the WVU Air, Noise, and Light Monitoring Study (McCawley 2013; Pekney et al. 2016) measured 1-hour or sub-hourly concentrations for four or more pollutants of interest. The U.S. DOE NETL studies conducted at well pads in Washington County and Greene County also made extensive 1-hour measurements, but full datasets are not currently available for these studies (Orak, Pekney, and Reeder 2017; Pekney et al. 2013). A few other studies measured 1-hour or sub-hourly concentrations for a couple of air pollutants of interest (see Table S.1).

Relatively few data were identified for monitoring sites within 500 to 1,000 feet of OGD sites, with the majority of monitoring sites ranging between 0.2 and 1 miles from the nearest OGD site (Tables S.1 and S.3). Several studies (e.g., PADEP 2010, 2011a, 2011b; Swarthout et al. 2015; Steinzor, 2013; Lewis, Hamel, and Brown 2016; McCawley 2013; Pekney et al. 2016) provide limited monitoring data that provide snapshots of air concentrations within approximately 500 to 1,000 feet of OGD sites. At least one longer-term dataset has been collected within 600 feet of a well pad that provides information on both long-term trends in air concentrations across multiple phases of well pad development as well as episodic short-term air quality impacts, namely the U.S. DOE NETL Washington County Well Pad Monitoring Study (Orak, Pekney, and Reeder 2017); however, the full dataset from this study is not currently available, and these data could not be evaluated in this assessment. Most of the data compiled for our evaluation are thus more relevant to what we've termed community-level air exposure levels than exposure levels of the people living closest to the OGD sites (i.e., for locations not directly abutting OGD sites, but instead nearby locations within the potential area of air quality impacts where greater amounts of people may reside).

Recent studies with extensive datasets

Several of the studies that we evaluated are notable for the strong datasets that they provide, which enhance our understanding of air pollutant concentrations in the Marcellus Shale region. Goetz et al. (2015) and Goetz et al. (2017) collected a large quantity of 1-second data at sampling locations 480 to 1,100 meters downwind of a variety of OGD sites (production well pads, a well pad with a drill rig, a well pad undergoing a well completion, and compressor stations) in wet and dry Marcellus Shale gas regions in both southwest and northwest Pennsylvania as part of an emissions estimation study. The authors provided online access to the raw data for acetaldehyde, benzene, toluene, and NO_2. Goetz et al. also measured submicron particle mass (PM_1) and C_2-benzene (e.g., ethylbenzene, xylenes) concentrations, although these data are not reported in either paper or the raw data files. We used the raw 1-second data for acetaldehyde, benzene, toluene, and NO_2 to calculate 5-minute and 24-hour averages for this evaluation. Goetz et al. (2015) provided detection

Table 2. Summary of 2008–2016 air monitoring data identified for the Marcellus Shale.

	Measured Air Pollutants of Interest										
	U.S. EPA Criteria Air Pollutants			U.S. EPA Hazardous Air Pollutants							Other
Study/Dataset	NO_2	SO_2	$PM_{2.5}$	Acetaldehyde	Benzene	Ethylbenzene	Formaldehyde	n-Hexane	Toluene	Xylenes	H_2S
Regulatory Agency Studies											
ATSDR (2016b)				✓			✓				✓
ATSDR (2016a)			✓								
PADEP (2010)[1]	✓	✓			✓	✓	✓	✓	✓	✓	✓
PADEP (2011a)[1]	✓	✓			✓	✓	✓	✓	✓	✓	✓
PADEP (2011b)[1]	✓	✓			✓	✓	✓	✓	✓	✓	✓
Pennsylvania Dept. of Environmental Protection (PADEP) (2018)[2]	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓
U.S. EPA Region III (2015)			✓		✓	✓			✓	✓	
Published Studies											
Goetz et al. (2015), 2017)[3]	✓			✓	✓	✓			✓	✓	
Macey et al. (2014)[4]					✓	✓	✓	✓	✓	✓	✓
Maskrey et al. (2016); ChemRisk (2012)[5]					✓	✓		✓	✓	✓	✓
Pekney et al. (2014)[6]	✓		✓		✓	✓		✓	✓	✓	
Steinzor (2013)					✓	✓		✓	✓	✓	
Swarthout et al. (2015)[7]				✓	✓	✓		✓	✓	✓	
Other Studies and Whitepapers											
TechLaw, Inc (2012)				✓	✓	✓	✓	✓	✓	✓	✓
U.S. DOE NETL Greene County Well Pad Monitoring Study (Pekney et al. 2013; Hammack 2015)[8]	✓	✓	✓		✓	✓		✓	✓	✓	
U.S. DOE NETL Washington County Well Pad Monitoring Study (Orak, Pekney, and Reeder 2017)[8]	✓		✓		✓	✓		✓	✓	✓	
WVU Air, Noise, and Light Monitoring Study (McCawley 2013; Pekney et al. 2016)	✓	✓	✓		✓	✓		✓	✓	✓	
Lewis, Hamel, and Brown (2016)[9]			✓		✓	✓		✓	✓	✓	
ACHD Air Quality Monitors											
Deer Lakes	✓				✓	✓		✓	✓	✓	
Imperial Pointe					✓			✓	✓	✓	
PADEP Air Quality Monitors											
Towanda	✓		✓								
Slippery Rock					✓	✓		✓	✓	✓	
Holbrook		✓	✓								
Montoursville		✓									
Springville					✓	✓		✓	✓	✓	
Tioga County	✓		✓								
Charleroi	✓	✓	✓		✓	✓		✓	✓	✓	
Florence[10]	✓	✓	✓		✓	✓		✓	✓	✓	
Houston[11]	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓
Washington	✓	✓	✓								
Greensburg	✓	✓	✓		✓	✓		✓	✓	✓	
Mehoopany					✓	✓		✓	✓	✓	
NY DEC Air Quality Monitors											
Pinnacle State Park	✓	✓	✓		✓	✓			✓	✓	

Notes: ACHD = Allegheny County Health Department; AQS = Air quality system; H_2S = Hydrogen sulfide; NO = Nitric oxide; NO_2 = Nitrogen dioxide; NO_x = Nitrogen oxide; NY DEC = New York Department of Environmental Conservation; OP-FTIR = Open-Path Fourier Transform Infrared; PADEP = Pennsylvania Department of Environmental Protection; $PM_{2.5}$ = Fine particulate matter; SO_2 = Sulfur dioxide; U.S. DOE NETL = United States Department of Energy National Energy Technology Laboratory; U.S. EPA = United States Environmental Protection Agency; VOC = Volatile organic compound; WVU = West Virginia University.

(1) OP-FTIR data available for several of the air pollutants of interest (NO_2, SO_2, formaldehyde, H_2S) were not compiled due to high detection limits.

(2) The Houston site that was part of this study has been retained by PADEP as a state air monitoring site; given their availability on U.S. EPA's AQS, data for $PM_{2.5}$, NO_2, and H_2S collected during the 2012–2013 time period of the PADEP (2018) study are provided in Supplementary Tables (S.4, S.6, S.14) under the PADEP Air Quality Monitors/Houston heading rather than under the Regulatory Study/PADEP (2018) heading.

(3) PM_1 and C_2-benzenes (ethylbenzene, xylenes) measured, but quantitative data not provided in publications or raw data files.

(4) Only limited data available for sampling conducted in PA for 2 months in 2013, including data for benzene, formaldehyde, n-hexane, and toluene (presumably other air pollutants- ethylbenzene, xylenes, and H_2S- were measured, but not detected).

(5) H_2S data were not used in this assessment due to insufficient instrument resolution.

(6) NO_2 or SO_2 data were not used in this assessment due to the lack of any data or summary statistics in the paper.

(7) Although ethylbenzene was measured as part of this study, no data were provided in the paper.

(8) No data used in this assessment given that only preliminary data available in conference proceedings and abstracts.

(9) $PM_{2.5}$ data were not compiled for this assessment given the use of an unvalidated $PM_{2.5}$ instrument.

(10) October 2012–December 2013 data for VOCs available from July 2018 PADEP "Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facilities" report (PADEP 2018). These data are provided in Supplementary Tables (S.8, S.9, S.11, S.12, S.13) under the Regulatory Agency Studies/PADEP (2018) heading rather than under the PADEP Air Quality Monitors/Florence heading.

(11) September 2012-December 2013 data for VOCs and carbonyls (acetaldehyde, formaldehyde) available from July 2018 PADEP "Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facilities" report (PADEP 2018). These data are provided in Supplementary Tables (S.7 through S.13) under the Regulatory Agency Studies/PADEP (2018) heading rather than under the PADEP Air Quality Monitors/Houston heading.

limits for the acetaldehyde, benzene, and toluene measurements, and we converted the concentrations of those species that were below the detection limit to half of these detection limits prior to the averaging. No detection limit was identified for the NO_2 data, so the calculated averages are likely biased low due to the fact that some of the data points are zero or slightly lower than zero and thus are presumably below the detection limit of the instrument. Histograms of the 5-minute averages calculated from this dataset show that most are in the lowest concentration categories, with a small subset of measurements showing higher short-term concentrations (Figure 1). All the 5-minute benzene and toluene concentrations were below 8 and 12 ppb, respectively, and all the acetaldehyde measurements were below 10 ppb. In addition, most of the NO_2 measurements were less than or equal to 1 ppb, and the maximum 5-minute concentration was 46 ppb, which is well below the 1-hour NO_2 NAAQS of 100 ppb. This sampling methodology is clearly of use for characterizing short-term episodic air quality impacts nearby to OGD sites, but the absence of detection of any peak events in this limited dataset cannot be extrapolated to other sites or even other time periods at these sites due to the limited duration of sampling (total of 28 sampling hours across all monitoring sites).

PADEP maintains an extensive statewide network of criteria air pollutant and air toxics monitors across the state, including in both dry and wet gas areas of Marcellus Shale development (e.g., Bradford, Butler, Greene, Susquehanna, Tioga, Washington, Westmoreland, and Wyoming Counties). Several of these monitors were purposely sited to be downwind of nearby OGD sources including well pads, compressor stations, and natural gas processing facilities (e.g., the Houston monitor in Washington County, the Mehoopany monitoring in Wyoming County, the Springville monitor in Susquehanna County, the Tioga monitor in Tioga County, and the Towanda monitor in Bradford County, which were all installed between 2012 and 2014) (PADEP 2016). For the 12 PADEP monitors in Marcellus Shale development areas for which we compiled air monitoring data, distances to the nearest well pad range from approximately 0.2 up to 3 miles (Table S.3). Figure 2 illustrates the large number of active well pad sites in close proximity to the PADEP monitoring sites used in this evaluation. Some of these monitors are also in close proximity to other OGD air emissions sources – such as the Houston monitor, which is approximately half a mile from a large gas processing facility and about 1.5 miles from a large compressor station. Air monitoring data available for these monitors include hourly $PM_{2.5}$, NO_2, SO_2, and H_2S data, and 24-hour VOC and carbonyls (acetaldehyde, formaldehyde) data (Table S.3). Data for acetaldehyde and formaldehyde are only available for sampling conducted between August 2012 and December 2013 at the Houston site and the temporary Henderson site as part of the PADEP "Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facilities" (PADEP 2018). Additional carbonyl samples have also been collected at the Houston air monitoring site since December 2013, although these data are not available from PADEP due to technical issues that resulted in most of the data being voided by the contract lab (personal communication, Renee

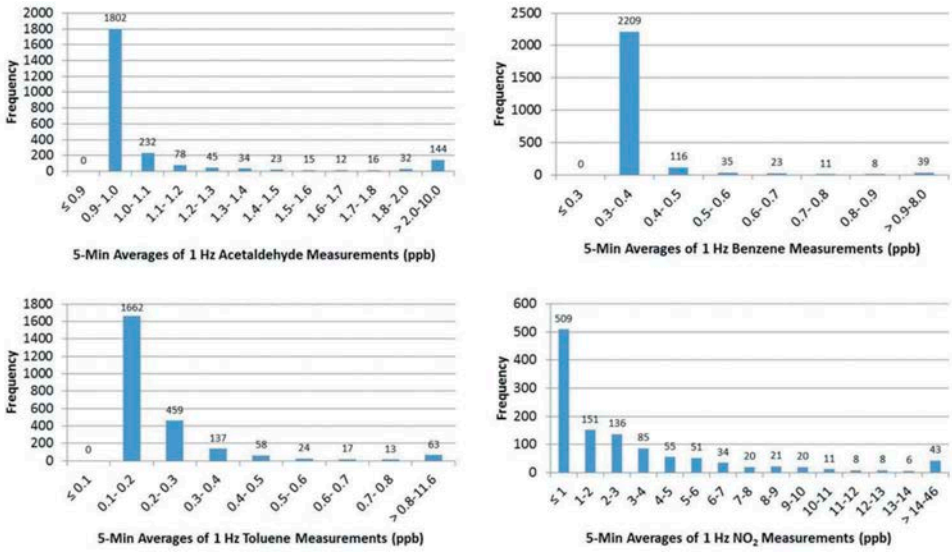

Figure 1. Histograms of 5-minute air monitoring concentrations calculated from 1 hertz (Hz) data collected by Goetz et al. (2015), Goetz et al. (2017)).

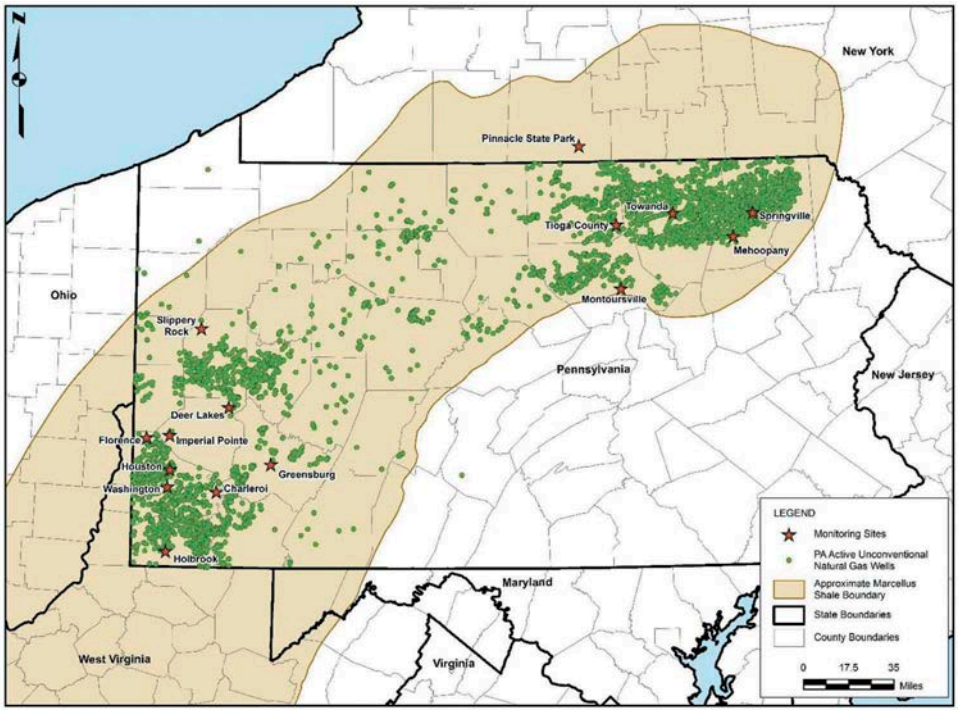

Figure 2. Location of state and local air monitoring sites in the Marcellus Shale Region relative to active unconventional natural gas wells (PADEP 2017; U.S. Energy Information Administration (EIA) 2017; U.S. Census Bureau 2016a, 2016b).

Bartholomew, Section Chief, Air Toxics Monitoring, Pennsylvania Department of Environmental Protection, April 2017).

Given their close proximity to OGD air emission sources and the frequent availability of multi-year records of air monitoring data, the PADEP monitors provide useful datasets for assessing air quality in the Marcellus Shale region. In particular, these monitors provide the longest time series of VOC data available for the shale region (Tables 3 and 4), including a couple of sites with records dating from 2009 or 2010, a time period of rapid OGD increases in the Marcellus Shale. Figure 3 shows the cumulative number of active wells from 1980 to 2016 for Westmoreland County, where the PADEP Greensburg monitor is located. As shown in Figure 4, mean concentrations of benzene, xylenes, ethylbenzene, toluene, and n-hexane at the Greensburg monitor have been fairly stable between 2010 and 2015, which is also true of the other six monitors listed in Tables 3 and 4.

PADEP's "Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facilities" (PADEP 2018) is an additional source of nearly 1.5 years of data for each of the air pollutants of interest except SO_2 at four air monitoring sites in Washington County, PA. These sites are surrounded by producing well pads and in close proximity (within 0.5 miles) to other major OGD facilities, including a large natural gas processing facility and compressor stations. As a follow-up study to the three PADEP short-term air sampling studies conducted between April and December 2010 in three regions of PA with Marcellus Shale development activities (PADEP 2010, 2011a, 2011b), this study was specifically conducted between July 2012 and December 2013 to "determine any chronic or long-term risks to the public from individual or multiple shale gas sources" (PADEP 2018). ATSDR prepared a public health evaluation based on the PADEP long-term air sampling data (ATSDR 2018).

This study is notable for the collection of long-term VOC, aldehyde, and H_2S data, which provide useful information for assessing chronic exposures at the community-based monitoring locations. PADEP (2018) concluded that calculated chronic cancer risks and non-cancer hazards for the project HAP sites were comparable to those for a historical PA background ambient monitoring site. Given the 24-hour sample duration and the 1-in-6–day sampling schedule, the VOC and aldehyde data do not provide information on episodic short-term exposures. H_2S measurements were made at two of the four sites, although two different methods were used and PADEP (2018) concluded that only the hourly H_2S data for the Houston site are reliable due to methodological problems at the other site as well as potential confounding from an adjacent sewage treatment facility. Figure 5 provides a histogram of the hourly H_2S data available for the

Table 3. Range of annual averages of mean 24-hour HAP measurements for PADEP and NYDEC monitors in or near Marcellus Shale development areas.

Monitor	State	Measurement Period for Available Data	Benzene (ppb)	Ethylbenzene (ppb)	n-Hexane (ppb)	Toluene (ppb)	m,p-Xylenes (ppb)	o-Xylene (ppb)
PADEP Permanent Air Monitoring Network Sites[1]								
Charleroi	PA	2009, 2011–2015	0.17–0.37	0.02–0.04	0.10–0.41	0.31–0.43	0.07–0.14	0.02–0.04
Florence	PA	2012–2013	0.18	ND	0.08	0.13	ND	ND
Greensburg	PA	2010–2015	0.17–0.30	0.02–0.04	0.09–0.14	0.30–0.51	0.07–0.12	0.03–0.04
Houston	PA	2012–2015	0.13–0.18	ND	0.21–0.78	0.19–0.25	0.04–0.06	0.01
Mehoopany	PA	2014–2015	0.09–0.10	0.03	0.02–0.06	0.11–0.28	0.03–0.12	0.04
Slippery Rock	PA	2009–2015	0.14–0.24	0.01–0.05	0.05–0.07	0.10–0.23	0.01–0.09	0.01–0.04
Springville	PA	2013–2015	0.18–0.21	ND	0.02–0.03	4.01–5.33	0.02	ND
PADEP Temporary Sites Used During the 2012–2013 Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facilities[2]								
Henderson Road	PA	2012–2013	0.38	ND	0.28	0.16	0.02	ND
Jaspen Way	PA	2012–2013	0.17	0.02	0.19	0.18	0.12	0.03
Welsh Road	PA	2012–2013	0.23	ND	0.17	1.68	0.03	ND
NYDEC Air Monitoring Network Sites[3]								
Pinnacle State Park	NY	2012–2016	0.09–0.15	0.007–0.02	N/A	0.08–0.24	0.02–0.04	0.007–0.02

Notes: (1) With the exception of 2012–2013 data for the Florence and Houston sites, annual average concentrations obtained from the PADEP website (http://www.dep.pa.gov/Business/Air/BAQ/MonitoringTopics/ToxicPollutants/Pages/Toxic-Monitoring-Sites-in-Pennsylvania.aspx) where PADEP calculated annual average concentrations for years in which <85% of the samples were non-detects; ND indicates when annual average concentrations not available from PADEP due to high percentage (>85%) of non-detects. For the Florence and Houston sites, 2012–2013 average concentrations obtained from the Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facility final report (PADEP 2018); these are overall averages for the duration of the summer 2012 to December 2013 PADEP measurement campaign and thus no ranges are provided for the Florence site when VOC data are only available from this study.
(2) As for the 2012–2013 data for the Florence and Houston sites, 2012–2013 average concentrations for these sites were obtained from the Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facility final report (PADEP 2018); these are overall averages for the duration of the summer 2012 to December 2013 PADEP measurement campaign and thus no ranges are provided. For consistency with PADEP reporting for the permanent air monitoring network sites, average concentrations only provided when <85% of samples were non-detects, and ND indicates when annual average concentrations not provided due to high percentage (>85%) of non-detects..
(3) Pinnacle State Park data were obtained from the U.S. EPA website (https://www.epa.gov/outdoor-air-quality-data). No n-hexane measurements made at the Pinnacle State Park site (indicated as N/A).

Table 4. Range of annual maximum 24-hour HAP measurements for PADEP and NYDEC monitors in or near Marcellus Shale development areas.

Monitor	State	Measurement Period for Available Data	Benzene (ppb)	Ethylbenzene (ppb)	n-Hexane (ppb)	Toluene (ppb)	m,p-Xylenes (ppb)	o-Xylene (ppb)
PADEP Permanent Air Monitoring Network Sites[1]								
Charleroi	PA	2009, 2011–2015	0.39–3.12	0.06–0.20	0.21–1.50	0.67–2.76	0.24–0.83	0.07–0.21
Florence	PA	2012–2013	0.59	ND	0.21	0.25	0.08	ND
Greensburg	PA	2010–2015	0.37–0.60	0.06–0.35	0.20–0.44	0.72–2.50	0.20–0.78	0.07–0.19
Houston	PA	2012–2015	0.23–0.44	0.05–0.08	0.78–17.90	0.52–1.33	0.17–0.28	0.05–0.10
Mehoopany	PA	2014–2015	0.14–0.32	0.07–0.17	0.07–1.01	0.27–5.10	0.26–0.82	0.09–0.20
Slippery Rock	PA	2009–2015	0.30–0.70	0.03–0.20	0.12–0.33	0.22–2.00	0.07–0.43	0.03–0.13
Springville	PA	2013–2015	0.33–0.40	0.06–0.08	0.10–0.21	10.50–17.93	0.21–0.31	0.05–0.12
PADEP Temporary Sites Used During the 2012–2013 Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facilities[2]								
Henderson Road	PA	2012–2013	0.15	0.06	1.1	0.40	0.23	0.08
Jaspen Way	PA	2012–2013	0.69	0.19	0.53	0.72	0.87	0.20
Welsh Road	PA	2012–2013	0.63	0.05	0.49	9.82	0.15	0.05
NYDEC Air Monitoring Network Sites[3]								
Pinnacle State Park	NY	2012–2016	0.18–0.25	0.03–0.14	N/A	0.31–1.4	0.05–0.60	0.03–0.20

Notes: (1) With the exception of 2012–2013 data for the Florence and Houston sites, annual maximum concentrations obtained from the PADEP website (http://www.dep.pa.gov/Business/Air/BAQ/MonitoringTopics/ToxicPollutants/Pages/Toxic-Monitoring-Sites-in-Pennsylvania.aspx). For the Florence and Houston sites, 2012–2013 maximum concentrations obtained from the Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facility final report (PADEP 2018); these are overall maximums for the duration of the summer 2012 to December 2013 PADEP measurement campaign and thus no ranges are provided for the Florence site when VOC data are only available from this study.
(2) As for the 2012–2013 data for the Florence and Houston sites, 2012–2013 maximum concentrations for these sites were obtained from the Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facility final report (PADEP 2018); these are overall maximums for the duration of the summer 2012 to December 2013 PADEP measurement campaign and thus no ranges are provided. ND indicates no detections of a VOC.
(3) Pinnacle State Park data were obtained from the U.S. EPA website (https://www.epa.gov/outdoor-air-quality-data). No n-hexane measurements made at the Pinnacle State Park site (indicated as N/A).

Houston site for the years 2013 and 2014, showing a significant number of non-detects (>70%) and a maximum 1-hour concentration of 6 ppb that is well below the acute HBACV of 30 ppb (note that almost all data points for 2012 were zero or negative and are not shown due to a possible instrumental problem).

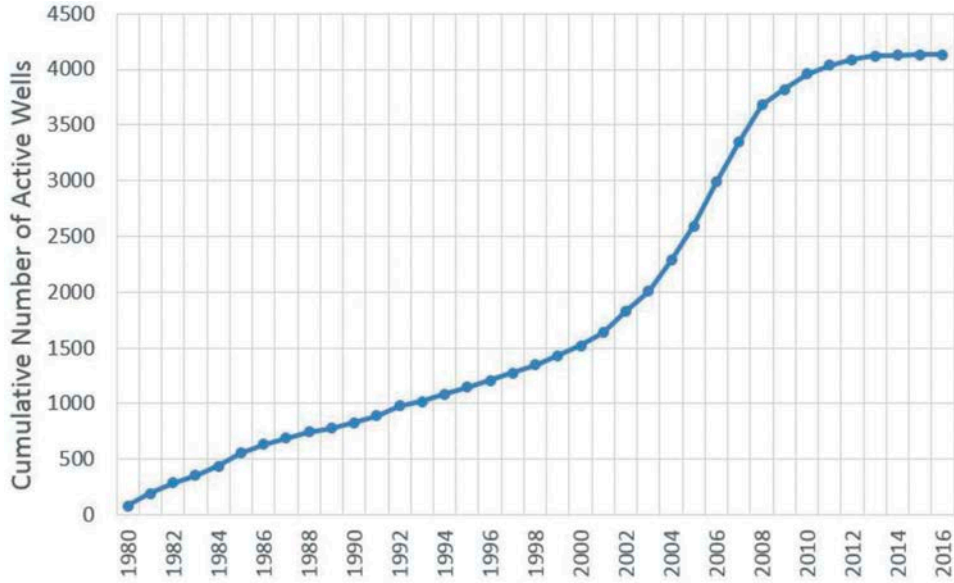

Figure 3. Time series of Westmoreland County oil and gas wells from 1980 to 2016. Data are based on the spud dates of currently active wells (PADEP 2017).

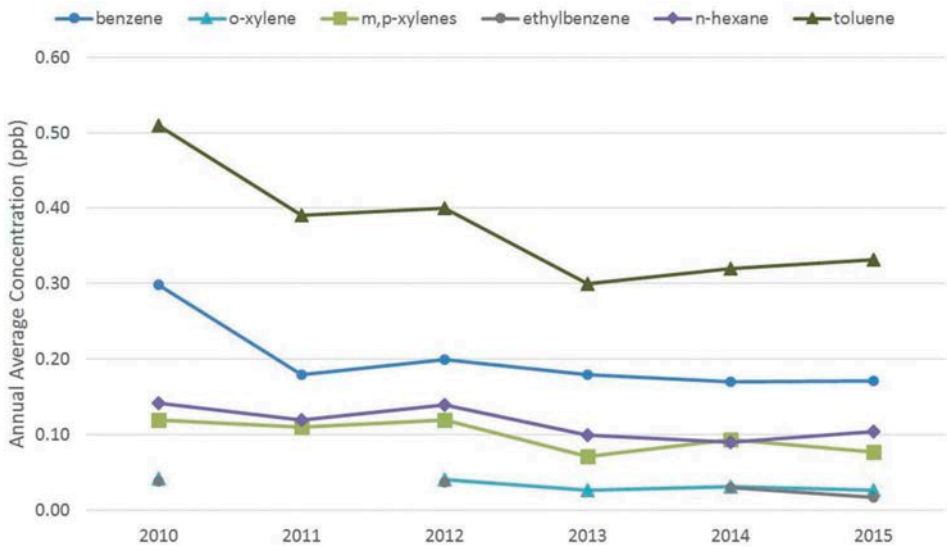

Figure 4. Measured VOC concentrations at the PADEP Greensburg monitoring site in Westmoreland County from 2010 to 2015. The absence of some data points for ethylbenzene (2011 and 2013) and o-xylene (2011) indicates that the VOC was detected in less than 15% of samples and PADEP did not report an annual average concentration.

Air quality during baseline versus OGD activity time periods

Only a limited number of air monitoring studies conducted in proximity of well pads and other OGD air emission sources have made baseline air measurements before the start of OGD activities, which can provide data on local background air concentrations for comparison with measurements during OGD activity periods. For example, the Allegheny County Health Department (ACHD) installed the Deer Lakes and Imperial Pointe temporary monitors in 2014 to monitor the air quality impacts of developing OGD activity in Allegheny County, PA, with the Deer Lakes monitor located approximately 0.85 miles from the closest well pad and the Imperial Pointe monitor located approximately 0.3 miles from the closest well pad. The 4 years of data available for each of these sites (2014–2017 data; ACHD 2018a, 2018b) have been categorized by ACHD according to

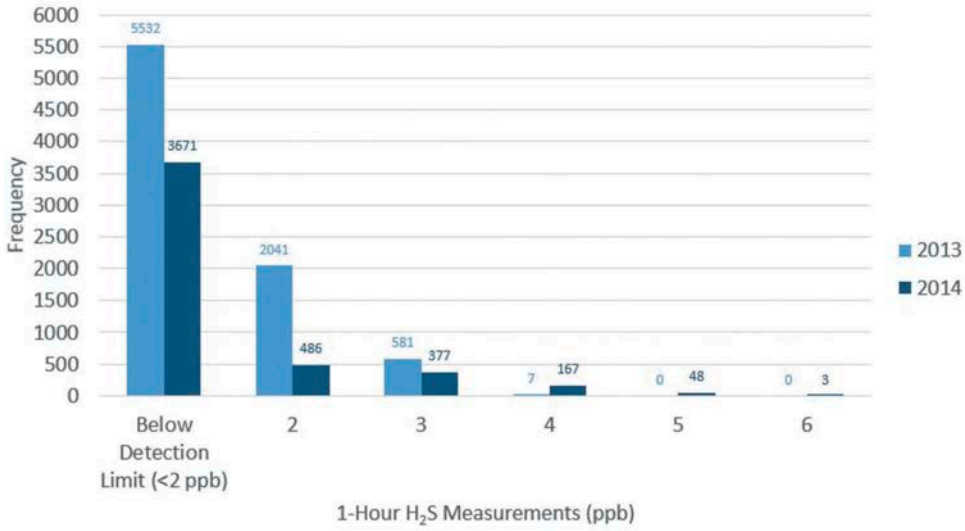

Figure 5. Histogram of PADEP Houston monitor hydrogen sulfide measurements for 2013–2014. Note that Pennsylvania Dept. of Environmental Protection (PADEP) (2018) refers to the Houston site as the Meddings Road site.

activity time periods (baseline, site construction, drilling, fracking, and production) at the nearest well pads. Both monitors were decommissioned in May 2017.

Plots of the mean and maximum HAP concentrations for each site show that there is some variability in concentrations across the different time periods (Figures 6 and 7). For the Deer Lakes site where 14-day air samples were collected, the mean concentrations of benzene and toluene were similar during OGD activity and baseline periods, as are the maximum benzene concentrations. The maximum toluene concentration during the baseline period was about half of the maximum toluene measured during an OGD activity period (drilling), suggesting that some OGD activities may be associated with short-term toluene emissions. Regardless, all measured toluene concentrations were less than 1 ppb and thus very low; similarly low concentrations of m,p-xylenes and n-hexane (<1 ppb) were measured during the drilling period, with non-detects for other phases of development at the nearest well pad. For the Imperial Pointe monitor where 24-hour air samples were collected, toluene was the only pollutant of interest detected during the baseline period, and measurements of toluene during OGD activity periods had peak concentrations approximately 2–8 times the baseline measurements, although mean concentrations for all activity periods but the site construction period were similar to the baseline mean. There were only infrequent detects of low concentrations of benzene, n-hexane, and xylenes (<2 ppb) at the Imperial Pointe monitor during OGD activity periods. As discussed below, overall mean concentrations of all species at both sites are well below chronic HBACVs.

For their study in Washington County, PA, Maskrey et al. (2016) sampled during four different activity periods at the closest multiple-unit well pad, including a baseline sampling period when "the wellpad was relatively inactive and preparations were being made for hydraulic fracturing." Benzene, n-hexane, and toluene were detected during both the baseline and OGD activity periods; m,p-xylenes were detected only during the baseline period; and ethylbenzene and o-xylene were not detected during any sampling period. The average benzene, n-hexane, and toluene concentrations during OGD activity periods were higher than during baseline periods; however, the concentrations of these species did not exceed 2 ppb during any period and therefore, as discussed further below, provide no evidence of VOC concentrations of public health concern.

Comparison of air quality data to acute and chronic HBACVs

Comparisons with HBACVs are useful for understanding whether measured air concentrations are at levels of potential human health concern. In Tables 5 and 6, air pollutant concentrations across all Marcellus Shale monitoring sites and studies are compared with acute and chronic HBACVs. For the acute HBACVs, any study or monitoring site with data averaging times of 8 hours or less was considered (except for $PM_{2.5}$, for which 24-hour concentrations were used to match the averaging time of the HBACV), and for the chronic HBACVs, two comparison datasets were considered: annual average concentrations calculated from state

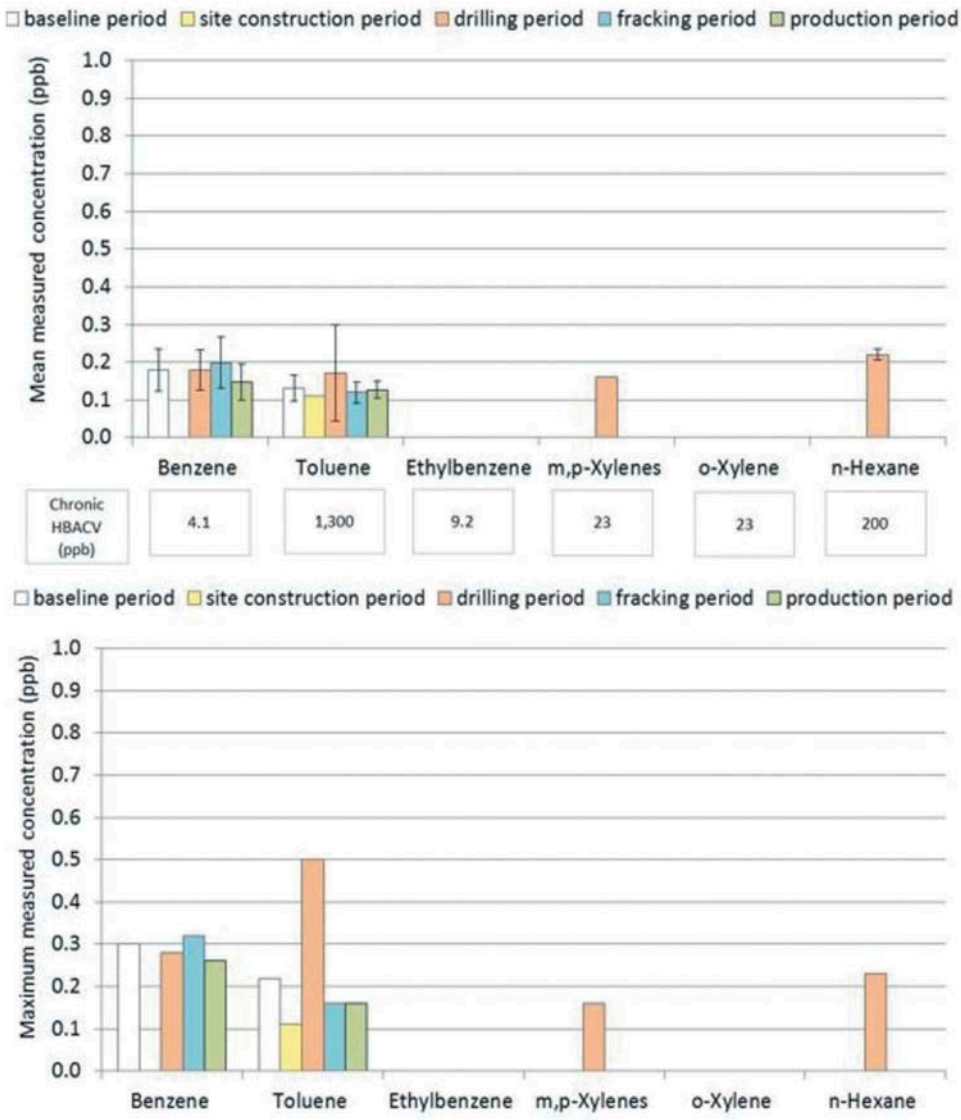

Figure 6. Mean and maximum measured HAP concentrations for 14-day samples collected between June 2014 and May 2017 at the ACHD Deer Lakes air monitoring site. NO_2 measurements made at this site are excluded from this figure because these measurements were only collected during the baseline period. The absence of bars for some VOCs (ethylbenzene, o-xylene) and for some phases of development (e.g., the site construction phase for benzene; all phases but the drilling phase for m,p-xylenes and n-hexane) indicates a lack of any detections. Mean concentrations are for detects only given the lack of detection limits in ACHD (2018a); mean concentrations include confidence intervals of ±1 *SD*, except when the bar represents a single data point. The sources of the chronic health-based air comparison values (HBACVs) are detailed in Table 1.

and local air monitoring network data, and average concentrations of data collected during other Marcellus Shale study measurement campaigns. A dataset consisting of average concentrations from the various Marcellus Shale air quality studies is not a preferred dataset for comparison to chronic HBACVs, because with a few notable exceptions (e.g., PADEP 2018), most of the study data were collected over periods of days to weeks and therefore may not be representative of long-term exposures. Although there is large uncertainty as to whether these concentrations are representative of long-term exposures for which chronic HBACVs are developed, we used these data in the chronic HBACV comparisons so as to fully utilize the available data.

We found that most of the available Marcellus Shale air measurements are below or only slightly above health-based standards and guidelines. As shown in Tables 5 and 6, all available data for NO_2, acetaldehyde, ethylbenzene, n-hexane, toluene, and xylenes are below the acute and chronic HBACVs. For benzene, formaldehyde, SO_2, $PM_{2.5}$, and H_2S, there were measurements above one or both of the HBACVs; however, for most of these pollutants, the benchmark exceedances are

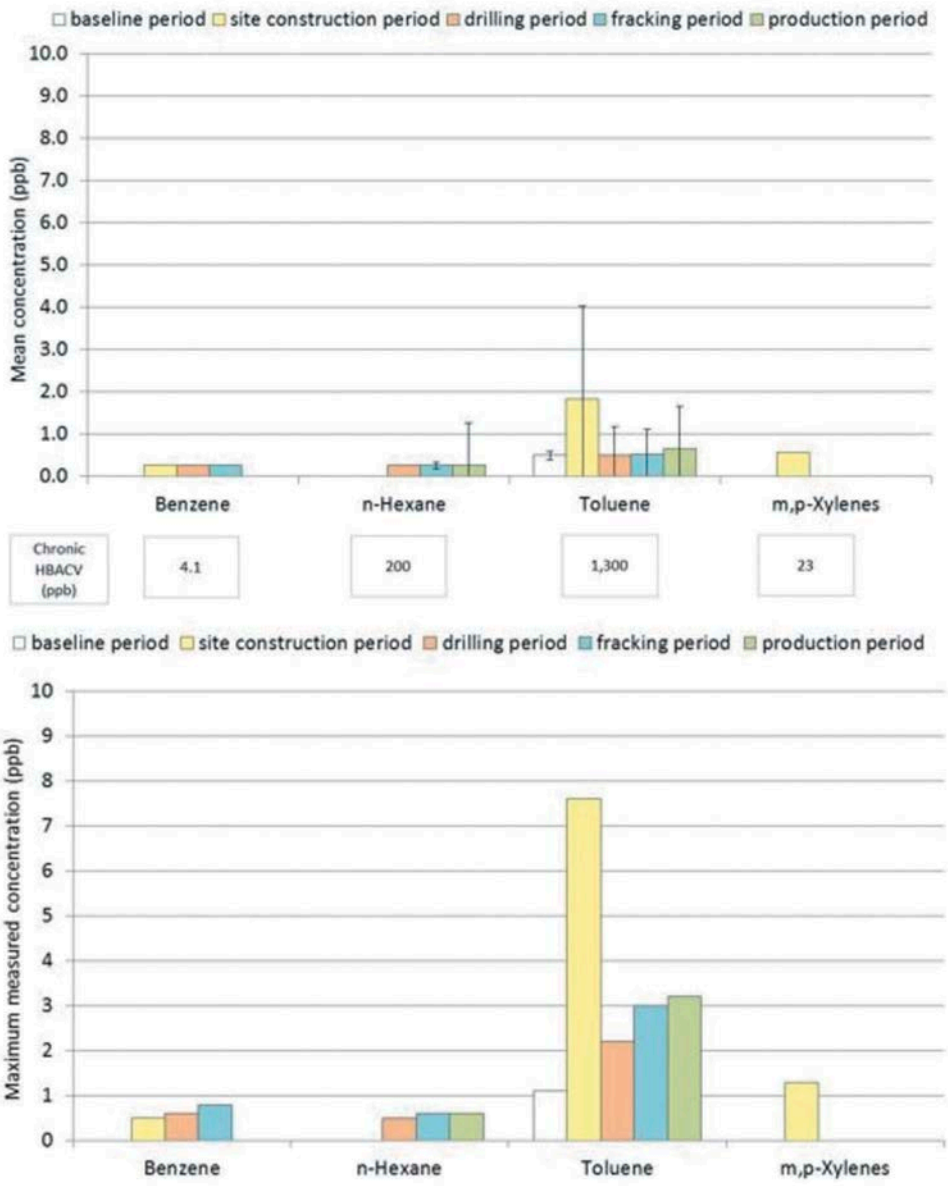

Figure 7. Mean and maximum measured HAP concentrations for 24-hour sampling between March 2014 and May 2017 at the ACHD Imperial Pointe air monitoring site. Mean concentrations assume half of the detection limit for non-detects and include confidence intervals of ±1 *SD*, except when the bar represents a single data point. Similar to Figure 6, the absence of bars for some VOCs and development phases indicates an absence of any detections. The sources of the chronic health-based air comparison values (HBACVs) are detailed in Table 1.

limited to a small fraction of available measurements and sites, rather than being representative of the breadth of available measurements.

There were some exceedances of acute HBACVs for a subset of the air pollutants of interest: SO_2, $PM_{2.5}$, formaldehyde, and H_2S. These exceedances were for a limited number of the available datasets with high-resolution sampling data (e.g., hourly and sub-hourly data) and thus provide evidence of sporadic short-term air pollutant events of potential health concern, rather than evidence of frequent occurrences of short-term peak events that coincide with the significant increases in OGD activities in these counties. For example, most of the exceedances of the SO_2 and $PM_{2.5}$ acute HBACVs are for 2008 and 2009 measurements. Some of the lowest maximum 1-hour SO_2 and 24-hour $PM_{2.5}$ concentrations have been observed at the monitors specifically sited by PADEP to be downwind of oil and gas sites. For example, PADEP discontinued SO_2 monitoring at the Holbrook monitoring site in Greene County, which is located in an area with extensive unconventional shale gas activities, due to the

Table 5. Comparison of short-term measurements with acute health-based air comparison values (HBACVs).

	Measured Concentrations from State and Local Monitoring Sites	Measured Concentrations from Published Studies and Other Reports	Acute HBACVs	
Pollutant	**Range of Maximums[1]**	**Range of Maximums[2]**	**HBACV**	**Source**
Criteria Air Pollutants				
NO_2 (ppb)	15–80	6.4–63.1	100	U.S. EPA 1-hour NAAQS
SO_2 (ppb)	5.5–164	3.8–16.4	75	U.S. EPA 1-hour NAAQS
$PM_{2.5}$ (μg/m^3)	13.7–41.1	13–36.7	35	U.S. EPA 24-hour NAAQS
Hazardous Air Pollutants				
Acetaldehyde (ppb)	N/A	1.77–9.96	260	CalOEHHA 1-hour REL
Benzene (ppb)	N/A	0.24–7.97	8.5	CalOEHHA 1-hour REL
Ethylbenzene (ppb)	N/A	<0.5–19.4	5,000	ATSDR Acute MRL
Formaldehyde (ppb)	N/A	3.8–49.7	40	ATSDR Acute MRL
n-Hexane (ppb)	N/A	0.176–375.8	2,900,000	1-hour AEGL-2
Toluene (ppb)	N/A	0.359–28.2	2,000	ATSDR Acute MRL
m,p-Xylenes (ppb)[3]	N/A	0.124–16.9	2,000	ATSDR Acute MRL
o-Xylene (ppb)[3]	N/A	0.038–9.0	2,000	ATSDR Acute MRL
Other Air Pollutants				
Hydrogen sulfide (ppb)	6	2–55.8	30	CalOEHHA 1-hour REL

Notes: (1) All concentrations are measurements with averaging times of 1 hour, except for $PM_{2.5}$, which are 24-hour concentrations.
(2) All concentrations are measurements with averaging times ranging from minutes to up to 8 hours, except for $PM_{2.5}$, which are 24-hour concentrations.
(3) The ATSDR acute MRL is for mixed xylenes, i.e., the combination of m,p, and o-xylenes.
N/A signifies that no study reported data with an appropriate averaging time.
AEGL = Acute Exposure Guideline Levels; ATSDR = Agency for Toxic Substances and Disease Registry; CalOEHHA = California Office of Environmental Health Hazard Assessment; MRL = Minimal risk level; NAAQS = National Ambient Air Quality Standards; NO_2 = Nitrogen dioxide; $PM_{2.5}$ = Fine particulate matter; ppb = Parts per billion; SO_2 = Sulfur dioxide; REL = Reference exposure levels; RfC = Reference concentration; U.S. EPA = United States Environmental Protection Agency.

consistent record of low hourly SO_2 concentrations measured between 2010 and 2016 when annual maximum 1-hour SO_2 concentrations ranged from 12 to 35 ppb (PADEP 2016). In 2016, maximum 24-hour $PM_{2.5}$ concentrations of 14.5 and 20.9 μg/m^3 were measured at newly installed $PM_{2.5}$ monitors at the Holbrook and Towanda (Bradford County) sites; between 2014 and 2016, maximum $PM_{2.5}$ concentrations ranging from 17.6 to 21.5 μg/m^3 were recorded at the Tioga County site (Table S.6). Between 2012 and 2014, when $PM_{2.5}$ monitoring was conducted at the Houston site in Washington County, which is located close to a large gas processing facility and a large compressor station, maximum 24-hour $PM_{2.5}$ concentrations ranged from 20.1 to 29.7 μg/m^3. While we identified only four H_2S datasets, the exceedances of the acute HBACV of 30 ppb are for only maximum 5-minute measurements from a single study (ATSDR 2016b).

Although overall there were few exceedances of acute HBACVs, it is important to note the relative scarcity of high-resolution air monitoring data for each of the air pollutants of interest that are necessary for better characterizing the timing, frequency, and maximum-impact locations of short-term episodic air quality impacts from OGD operations. As discussed by McMullin et al. (2018), a number of dynamic factors are expected to contribute to variability in short-term air quality impacts from OGD operations (e.g., episodic emissions, local-scale meteorological conditions, operator-specific processes, different durations of processes) and complicate the extrapolation of the available body of high-resolution measurements to other time periods and sites. It is encouraging that Marcellus Shale air quality studies are increasingly collecting high-resolution data, and that most of these data are below levels of health concern; but more data are needed to confirm that measurements are capturing the variability in short-term air quality impacts that may arise from the various OGD-related air emissions sources, and to identify whether specific activities or phases of operation may contribute to short-term episodic air quality impacts of potential health concern. These data are particularly needed for residential locations closest to OGD operations.

Table 6. Comparison of measurements with chronic health-based air comparison values (HBACVs).

	Measured Concentrations from State and Local Monitoring Sites	Measured Concentrations from Published Studies and Other Reports	Chronic HBACVs	
Pollutant	**Range of Means[1]**	**Range of Means[2]**	**HBACV**	**Source**
Criteria Air Pollutants				
NO_2 (ppb)	1.33–11.59	0.9–23	53	U.S. EPA annual NAAQS
SO_2 (ppb)	0.21–7.76	2.3–3.3	30	Former U.S. EPA annual NAAQS[3]
$PM_{2.5}$ (µg/m^3)	4.66–14.64	7–19	12	U.S. EPA annual NAAQS
Hazardous Air Pollutants				
Acetaldehyde (ppb)	0.82	0.48–2.3	5.0	U.S. EPA RfC
Benzene (ppb)	0.09–0.37	0.089–48.7	4.1	Cancer-based estimated continuous lifetime exposure concentration
Ethylbenzene (ppb)	0.004–0.05	0.002–1.4	9.2	Cancer-based estimated continuous lifetime exposure concentration
Formaldehyde (ppb)	2.90	0.67–27.4	6.3	Cancer-based estimated continuous lifetime exposure concentration
n-Hexane (ppb)	0.02–0.78	0.03–6.2	200	U.S. EPA RfC
Toluene (ppb)	0.08–5.33	0.07–32.1	1,300	U.S. EPA RfC
m,p-Xylenes (ppb)[4]	0.001–0.14	0.024–3.2	23	U.S. EPA RfC
o-Xylene (ppb)[4]	0.005–0.04	0.003–2.9	23	U.S. EPA RfC
Other Air Pollutants				
Hydrogen sulfide (ppb)[5]	2.4	0.53–2	1.4	U.S. EPA RfC

Notes: (1) Mean concentrations are generally annual average measurements. In addition, for VOCs and carbonyls, overall means for sampling conducted from September/October 2012 to December 2013 as part of the PADEP "Long-term Ambient Air Monitoring Project: Marcellus Shale Gas Facilities" (PADEP 2018) at two sites (the Houston and Florence sites) are also included. These data are included for state and local monitoring sites given that these sites are permanent sites within the state air monitoring network. Despite additional carbonyls sampling since 2013, no post-2013 carbonyls data are currently available for the Houston site due to technical issues that resulted in carbonyls data being voided by the contract lab (personal communication, Renee Bartholomew, Section Chief, Air Toxics Monitoring, Pennsylvania Department of Environmental Protection, April 2017).

(2) Mean concentrations for several temporary sites included as part of the PADEP (2018) study are overall study means for sampling conducted between summer 2012 (June or August) and December 2013. For all other studies, averages are for measurements taken over days, weeks, or months, depending on the study.

(3) The annual SO_2 NAAQS was revoked in 2010, and there has not been an annual NAAQS for this pollutant since that year.

(4) The ATSDR acute MRL is for mixed xylenes (i.e., the combination of m,p, and o-xylenes), whereas the U.S. EPA RfC of 0.10 mg/m^3 (23 ppb) applies to each xylene isomer individually.

(5) The mean monitoring site measurement is the average of all hourly H_2S measurements during 2013–2014 at the Houston monitor.

NAAQS = National Ambient Air Quality Standards; NO_2 = Nitrogen Dioxide; $PM_{2.5}$ = Fine particulate matter; ppb = Parts per Billion; SO_2 = Sulfur Dioxide; RfC = Reference Concentration; US EPA = United States Environmental Protection Agency.

Chronic HBACV exceedances were also observed for a subset of the air pollutants of concern ($PM_{2.5}$, benzene, formaldehyde, and H_2S). These exceedances were generally limited to a small number of the available datasets, particularly the more limited datasets with measurements representative of time periods of days to weeks rather than chronic exposure periods of 1 year or longer. These chronic HBACV exceedances are thus suggestive of possible long-term air concentrations of potential chronic health concern at a limited number of monitored sites, but it remains unclear how representative the limited monitoring data are of chronic exposure periods.

For example, of the more than 20 datasets with benzene measurements made over at least multi-day time periods, only mean benzene concentrations from the WVU Air, Noise, and Light Monitoring Study (McCawley 2013; Pekney et al. 2016) exceeded the chronic HBACV of 4.1 ppb (Table 6). Ranging from 4.2 to 48.7 ppb, mean benzene concentrations from four of the seven sites included in the study exceeded the chronic HBACV, due to elevated concentrations for some of the small number of 72-hour canister samples taken at each site (4–8 samples per site). At each of these well pad sites, either drilling (horizontal or vertical) or hydraulic fracturing/flowback was occurring during the air sampling. Given that these short-term activities typically occur over time periods of days to weeks for a well on a well pad, there is uncertainty as to how representative these 72-hour samples are of chronic exposure periods. The study investigators also noted the diesel-fueled generator used at some of these sites as a possible air emissions source. Recognizing these uncertainties, these data provide evidence of elevated short-term benzene concentrations close to well pads that have the potential to contribute to long-term benzene exposures above the

chronic HBACV, depending on the frequency and duration of benzene emission sources. Other studies with longer records of measurements, however, do not provide evidence of long-term benzene concentrations of potential health concern, including the ACHD (2018a, 2018b) and the PADEP (2018) datasets.

The levels of the maximum 72-hour benzene concentrations at these four sites (8.2 to 85 ppb) indicate that 1-hour benzene concentrations within these sampling periods were also presumably in excess of the acute HBACV of 8.5 ppb (note that these data are not included in the Table 5 comparisons with the acute HBACVs given that they do not have 1-hour averaging times that correspond to the acute HBACVs). These data from the WVU Air, Noise, and Light Monitoring Study thus provide evidence of possible short-term benzene concentrations of potential acute health concern at some of the study sites. However, it is also important to note that hourly average benzene concentrations were also measured continuously at six of the seven sites in this study, including all four sites with the elevated benzene measurements, using a Perkin Elmer Ozone Precursor Analyzer System in the U.S. DOE NETL Mobile Air Monitoring Laboratory (Pekney et al. 2016). The NETL mobile laboratory was stationed at a single downwind location during the 1–4 week monitoring periods at each site, and was generally in close proximity to one or two, but not all, of the canister sampling locations (Pekney et al. 2016). Despite a sub-ppb quantitation limit, benzene was detected in less than 10% of the hourly samples for each of the six sites, which was the threshold above which hourly VOC data were reported (Pekney et al. 2016). The hourly benzene results thus do not support the frequent occurrence of elevated episodic short-term benzene concentrations, albeit for sampling at one location in close proximity to the study well pads.

For formaldehyde, the only exceedance of the chronic HBACV of 6.3 ppb was for a 2-day average concentration of 27.4 ppb from the Macey et al. (2014) study, while average concentrations representative of longer time periods from PADEP (2018) and ATSDR (2016b) ranged from 0.67 to 3.4 ppb and were thus well below the HBACV. The Macey et al. (2014) study was focused on characterizing potential short-term air emission events, as sampling was conducted by volunteers when they observed odors, could see emissions, or experienced acute health symptoms; as a result, there is uncertainty as to the relevance of these samples to long-term exposure conditions. Likewise, the highest study-average $PM_{2.5}$ concentrations of 17–19 μg/m^3 were measured during the 2-month ATSDR Brooklyn Township study (ATSDR 2016a), while substantially lower annual average $PM_{2.5}$ concentrations in the range of 4.7–9.3 μg/m^3 have been observed between 2012 and 2016 for four $PM_{2.5}$ monitors specifically sited by PADEP to be downwind of OGD activities (Table S.6). These shorter-duration data should not be dismissed as being irrelevant to potential chronic health concerns, but additional long-term data are needed to further investigate whether transient processes and episodic emissions events at well pads can contribute to long-term air pollutant concentrations of potential chronic health concern.

Limitations and uncertainties

Given that they are actual measured concentrations, ambient air monitoring data have long been used for evaluating airborne chemical exposures (EPA 2004). It is widely recognized, however, that air monitoring data have inherent limitations for characterizing population air pollutant exposures. In particular, ambient air monitoring data provide estimates of air exposure levels at the monitoring sites themselves at the times of monitoring, and may not be representative of actual exposure conditions, broader geographic areas, or other time periods. This fundamental limitation of air monitoring data is not unique to Marcellus Shale air quality data. Like any air monitoring dataset, there is uncertainty as to how well the available Marcellus Shale air monitoring data characterize the range of potential exposures for people living nearby to OGD sites. This uncertainty may be amplified in the Marcellus Shale region as compared to air monitoring in an area with a single point source such as a power plant, given that the variability in OGD air emissions – as well as the high density of different OGD sites in some areas – may contribute to rapid changes in air pollutant concentrations across time and space.

The relative sparseness of air monitoring sites in the Marcellus Shale region is especially a challenge for the characterization of air pollutant hotspots, in particular for episodic peak air pollutant events. Relatively few studies have measured VOC concentrations for sampling frequencies of 1-hour or less, and the available studies with such high-resolution measurements (e.g., Goetz et al. 2017, 2015; McCawley 2013; Orak, Pekney, and Reeder 2017; Pekney et al. 2016) have generally conducted sampling at a single location nearby to a well pad or other OGD site. There is thus uncertainty as to whether the available data are capturing maximum, intermittent acute exposure levels associated with episodic peak events. Moreover, it is unclear whether the available Marcellus Shale monitoring data include super-emitting sites – defined as high-emission facilities that represent a small fraction of the total body of facilities, but which contribute the majority of air emissions (Allen 2016; Lyon et al. 2016). While super-emitting sources such as venting wells, pneumatic controllers, leaking tanks, and compressors are possible in the Marcellus Shale region, Lyon et al. (2016) reported a smaller number of high-emitting hydrocarbon

sources for the Marcellus Shale region (1%) as compared to other shale gas plays (e.g., 14% for the Bakken, 5.4% for the Eagle Ford, 3.5% for the Barnett), based on infrared camera surveys that they conducted by helicopter for over 8,000 oil and gas well pads in seven U.S. basins.

Another important limitation of using air monitoring data to characterize OGD impacts in the Marcellus Shale region is that ambient monitors measure levels of total (all-source) ambient pollutants. In other words, they are not specific to a single source type, such as well pad emissions. In particular, $PM_{2.5}$ and SO_2 are regional pollutants that have many emission sources, and the state and local air monitoring networks are clearly impacted by other significant local and regional sources of these pollutants (e.g., power plants, steel and coke plants, industrial boilers, mobile sources). Air toxics such as the BTEX species also have a number of common emission sources, including vehicular emissions in particular. While studies of Marcellus Shale development air quality impacts have attempted to site monitors in areas not highly influenced by other local air pollution sources, it is expected that local and regional air pollution sources remain significant contributors to both short-term episodic air pollution events and long-term average pollutant concentrations in most of the available datasets.

Conclusion

As described in this assessment, there is now available a sizable body of Marcellus Shale air monitoring data that provides insights on the nature and potential public health significance of community-level air quality impacts of OGD-related activities. Overall, this assessment of short-term and longer-term data for air monitoring conducted in proximity to OGD air emission sources in the Marcellus Shale region showed that the available air pollutant measurements were generally less than acute and chronic HBACVs. We identified a small number of sporadic exceedances of acute and chronic HBACVs for the air pollutants of interest that were not focused on specific pollutants, time periods, or measurement sites. Therefore, the available data indicate that air pollutant levels within the Marcellus Shale development region typically are below HBACV exceedance levels; however, the sporadic HBACV exceedances warrant further investigation to better understand the representativeness of the exceedances and whether there may be public health concerns associated with specific site characteristics or certain operations or sources (e.g., leaks, super-emitters).

We have highlighted limitations to the available air monitoring data, including the relative sparseness of samplers around OGD sites (particularly for locations within 1,000 feet of OGD sites), the limited availability of high-resolution data needed to characterize episodic peak air quality impacts, and the short duration of sampling (i.e., days to months rather than a year or years) of many studies. As a result of these limitations and spatial and temporal variability in OGD-related air quality impacts, it is unlikely that the available data are representative of the full range of potential air quality impacts and human exposures, either on a short-term (e.g., hourly) or chronic (e.g., annual average) basis. In order to help compensate for limitations in the available data, we assumed that short-term measurements made over days to weeks are representative of long-term air concentrations so as to fully utilize the available data and to minimize the underestimation of exposure.

Several of the studies from which we obtained air monitoring data compared their measurements with health-protective levels and reached similar conclusions regarding a lack of or limited evidence of potential health risks, including EPA (2015), PADEP (2018, 2010, 2011a, 2011b), ATSDR (2018), Maskrey et al. (2016), and Swarthout et al. (2015). Our findings are also consistent with those reported for two other integrative air quality data assessments for different shale gas plays. For example, scientists at the Colorado Department of Public Health & Environment (CDPHE) recently conducted a screening-level public health assessment of air quality data from 47 datasets collected in areas of Colorado with substantial oil and gas operations (CDPHE 2017; McMullin et al. 2018). Finding that all measured air concentrations of 62 VOCs included in the assessment were below short-term and long-term health-based reference values, CDPHE concluded, "Overall, available air monitoring data suggest low risk of harmful health effects from combined exposure to all substances." Working with several different datasets for air sampling conducted along Colorado's Northern Front Range in summer 2014, which included some of the same data evaluated by the CDPHE scientists, McKenzie et al. (2018) reached similar findings regarding a lack of evidence of elevated health risks for data representing locations at least 500 feet from OGD facilities. For a limited amount of air monitoring data collected within 500 feet from OGD facilities, McKenzie et al. reported evidence of higher acute non-cancer hazards and cancer risks that exceeded regulatory thresholds. Though suggestive of higher chronic health risks for populations living the closest to OGD sites, it should be noted that these risk estimates are highly uncertain given that the study authors extrapolated from daily 1-minute grab air samples collected over about a month to estimate both 1-hour and chronic (>1 year) exposures.

Utilizing a dataset consisting of 4.6 million data points from six different monitoring locations selected to represent community-wide ambient air exposures in the Dallas–Fort Worth area within Texas's Barnett Shale region, Bunch compared 1-hour and 24-hour data with federal and state acute or short-term HBACVs and annual average concentrations with chronic HBACVs. Based on their assessment, Bunch et al. (2014) concluded, "The analyses demonstrate that, for the extensive number of VOCs measured, shale gas production activities have not resulted in community-wide exposures to those VOCs at levels that would pose a health concern."

There is a continuing need for additional air monitoring studies that are carefully designed to collect data representative of potential human exposures, including not only typical long-term exposures for nearby communities but also peak episodic exposures. Sampling sites should be carefully selected based on a number of factors, including to be downwind of nearby OGD operations; to reflect heterogeneity in residential proximity; to be representative of the range of local meteorology and terrain; and to capture different OGD site types and operations (e.g., each of the phases of well pad development). Depending on detailed profiles of air pollutants emitted from OGD operations, consideration should be given to monitoring of additional OGD constituents and reaction products, such as polycyclic aromatic hydrocarbons (PAHs) and alcohols. For example, there is a general absence of data from the Marcellus Shale region for PAHs, although a recent study conducted in the nearby Utica Shale region in Ohio reported low PAH concentrations comparable to or lower than both urban and rural background PAH levels (Paulik et al. 2016). Interpretation of PAH measurements may be challenging, however, due to the large number of contributing sources, including vehicle emissions and wood-burning. Besides providing either full datasets or complete summary statistics, it is recommended that future datasets and studies categorize data according to well pad development phases, as done by some studies including ACHD (2018a, 2018b) and Maskrey et al. (2016).

Efforts are also needed to publicly disseminate some of the more comprehensive datasets that have already been collected. For example, it is our understanding that the U.S. DOE NETL air monitoring studies conducted at a Greene County (PA) well pad in 2012 and at a Washington County (PA) well pad from 2011 to 2014 used near-continuous instruments to measure both short-term episodic air quality impacts and long-term average concentrations of a suite of criteria air pollutants and VOCs for different phases of well pad development, including baseline measurements prior to the start of well pad development (Orak, Pekney, and Reeder 2017; Pekney et al. 2013).

Once additional data are available to address some of the limitations in the currently available body of Marcellus Shale air measurement data, it may be possible to conduct a quantitative human health risk assessment to characterize any potential human health risks associated with community-level air quality impacts of Marcellus Shale development. As emphasized in this assessment, such a quantitative risk assessment should address potential health risks associated with both episodic peak exposures as well as chronic exposures.

Disclosure statement

The authors are employed by Gradient, a private environmental consulting firm. The work reported in this paper was conducted during the normal course of employment. This paper was prepared with financial support from the American Petroleum Institute (API) and was reviewed by members of API while in preparation. The authors retain sole responsibility for the writing and content of this paper, which represent the professional opinions of the authors and not necessarily those of API or its member companies. Gradient has worked with natural gas development companies active in the Marcellus Shale region over the past 36 months; none of these clients were involved with the conception or drafting of this manuscript. One of the authors of this manuscript (C. Long) has testified in Pennsylvania at a judicial hearing and local zoning hearing board meetings on the science of the air quality impacts of Marcellus Shale development activities.

About the authors

Christopher M. Long is a Senior Risk Assessor and Toxicologist with Gradient in Cambridge, MA.

Nicole L. Briggs is a Senior Air Quality Scientist with Gradient in Seattle, WA.

Ifeoluwa A. Bamgbose is an Environmental Toxicologist with Gradient in Cambridge, MA.

References

Agency for Toxic Substances and Disease Registry (ATSDR). 2016a. Health consultation: Brooklyn township PM2.5, Brooklyn township, Susquehanna County, Pennsylvania. 35, Accessed April 22. https://www.atsdr.cdc.gov/HAC/pha/BrooklynTownship/BrooklynTwnsp_pm2-5_HC_Final_04-22-2016_508.pdf.

Agency for Toxic Substances and Disease Registry (ATSDR). 2016b. Health Consultation, Exposure Investigation, Natural Gas Ambient Air Quality Monitoring Initiative, Brigich Compressor Station. Chartiers Township, Washington County, Pennsylvania. 94p., January 29.

Agency for Toxic Substances and Disease Registry (ATSDR); Pennsylvania Department of Health. 2018. Health Consultation: Public Health Evaluation of Long-Term Air Sampling Data Collected in the Vicinity of Natural Gas Operations, Washington County, Pennsylvania. 91, July 18.

Allegheny County, Pennsylvania, Health Dept. (ACHD). 2018a. *Deer lakes ambient air sampling results/radiello passive monitors (2014-2017)*. 14 Pittsburgh, PA: ACHD.

Allegheny County, Pennsylvania, Health Dept. (ACHD). 2018b. *Imperial pointe ambient air sampling results/method EPA TO15 + tentatively identified compounds (2014-2017)*. 15. Pittsburgh, PA: ACHD.

Allen, D. T. 2016. Emissions from oil and gas operations in the United States and their air quality implications. *J. Air Waste Manag. Assoc.* 66 (6):549–75. doi:10.1080/10962247.2016.1171263.

Bunch, A. G., C. S. Perry, L. Abraham, D. S. Wikoff, J. A. Tachovsky, J. G. Hixon, J. D. Urban, M. A. Harris, and L. C. Haws. 2014. Evaluation of impact of shale gas operations in the Barnett Shale region on volatile organic compounds in air and potential human health risks. *Sci. Total Environ.* 468-469:832–42. doi:10.1016/j.scitotenv.2013.08.080.

ChemRisk. 2012. Letter Report to R. Dinnen (Fort Cherry School District) re: Air Monitoring Results for the Fracking and Flaring Phases of Gas Extraction Operations at the Chiarelli Well Pad. 89. February 3.

Colorado Dept. of Public Health and Environment (CDPHE). 2017. Assessment of potential public health effects from oil and gas operations in Colorado. Denver, CO: Oil and Gas Health Information and Response Program. 66. February 21.

Goetz, J. D., A. Avery, B. Werden, C. Floerchinger, E. C. Fortner, J. Wormhoudt, P. Massoli, S. C. Herndon, C. E. Kolb, W. B. Knighton, et al. 2017. Analysis of local-scale background concentrations of methane and other gas-phase species in the Marcellus Shale. *Elementa* 5:1. doi:10.1525/elementa.182.

Goetz, J. D., C. Floerchinger, E. C. Fortner, J. Wormhoudt, P. Massoli, W. B. Knighton, S. C. Herndon, C. E. Kolb, E. Knipping, S. Shaw, et al. 2015. Atmospheric emission characterization of Marcellus shale natural gas development sites. *Environ. Sci. Technol.* 49 (11):7012–20. doi:10.1021/acs.est.5b00452.

Goldstein, B. D., B. W. Brooks, S. D. Cohen, A. E. Gates, M. E. Honeycutt, J. B. Morris, J. Orme-Zavaleta, T. M. Penning, and J. Snawder. 2014. The role of toxicological science in meeting the challenges and opportunities of hydraulic fracturing. *Toxicol. Sci.* 139 (2):271–83. doi:10.1093/toxsci/kfu061.

Hammack, R. W. 2015. Environmental monitoring at a marcellus shale site in Greene County, Pennsylvania. Presented at California Well Stimulation (CWS) Forum, Los Angeles, CA. 31. July 24.

Health Effects Institute (HEI). 2015. Strategic research agenda on the potential impacts of 21st century oil and natural gas development in the Appalachian region and beyond. Scientific Committee on Unconventional Oil and Gas Development in the Appalachian Basin. 240. October.

Health Effects Institute (HEI). 2018. Unconventional oil and gas development bibliography: April 2018 monthly update. Energy Research Program. 126. April.

Lewis, C., K. Hamel, and D. Brown. 2016. *Community assessment of Penn Trafford outdoor air monitoring results*. 11. June 6. McMurray, PA: Southwest Environmental Health Project.

Lyon, D. R., R. A. Alvarez, D. Zavala-Araiza, A. R. Brandt, R. B. Jackson, and S. P. Hamburg. 2016. Aerial surveys of elevated hydrocarbon emissions from oil and gas production sites. *Environ. Sci. Technol.* 50:4877–86. doi:10.1021/acs.est.6b00705.

Macey, G. P., R. Breech, M. Chernaik, C. Cox, D. Larson, D. Thomas, and D. O. Carpenter. 2014. Air concentrations of volatile compounds near oil and gas production: A community-based exploratory study. *Environ. Health* 13:82. doi:10.1186/1476-069X-13-82.

Manikonda, A., N. Zikova, P. K. Hopke, and A. R. Ferro. 2016. Laboratory assessment of low-cost PM monitors. *J. Aerosol Sci.* 102:29–40. doi:10.1016/j.jaerosci.2016.08.010.

Maskrey, J. R., A. L. Insley, E. S. Hynds, and J. M. Panko. 2016. Air monitoring of volatile organic compounds at relevant receptors during hydraulic fracturing operations in Washington County, Pennsylvania. *Environ. Monit. Assess.* 188 (7):410. doi:10.1007/s10661-016-5410-4.

McCawley, M. 2013. Air, noise, and light monitoring results for assessing environmental impacts of horizontal gas well drilling operations (ETD-10 project). Report to West Virginia Dept. of Environmental Protection. 206. May 3. Accessed on December 21, 2016 at http://wvwri.org/wp-content/uploads/2013/10/A-N-L-Final-Report-FOR-WEB.pdf.

McCawley, M. 2015. Air contaminants associated with potential respiratory effects from unconventional resource development activities. *Semin. Respir. Crit. Care Med.* 36 (3):379–87. doi:10.1055/s-0035-1549453.

McKee, R. H., D. Herron, M. Saperstein, P. Podhasky, G. M. Hoffman, and L. Roberts. 2014. The toxicological properties of petroleum gases. *Int. J. Toxicol* 33 (Suppl.1):28S–51S. doi:10.1177/1091581813504225.

McKenzie, L. M., B. D. Blair, J. Hughes, W. B. Allshouse, N. Blake, D. Helmig, P. Milmoe, H. Halliday, D. R. Blake, and J. L. Adgate. 2018. Ambient non-methane hydrocarbon levels along colorado's northern front range: Acute and chronic health risks. *Environ. Sci. Technol.* 52 (8):4514–25. doi:10.1021/acs.est.7b05983.

McKenzie, L. M., R. Guo, R. Z. Witter, D. A. Savitz, L. S. Newman, and J. L. Adgate. 2014. Birth outcomes and maternal residential proximity to natural gas development in rural Colorado. *Environ. Health Perspect.* 122 (4):412–17. doi:10.1289/ehp.1306722.

McKenzie, L. M., R. Z. Witter, L. S. Newman, and J. L. Adgate. 2012. Human health risk assessment of air emissions from development of unconventional natural gas resources. *Sci. Total Environ.* 424:79–87. doi:10.1016/j.scitotenv.2012.02.018.

McMullin, T. S., A. M. Bamber, D. Bon, D. I. Vigil, and M. Van Dyke. 2018. Exposures and health risks from volatile organic compounds in communities located near oil and gas exploration and production activities in Colorado (U.S.A.). *Int. J. Environ. Res. Public Health* 15 (7):1500. doi:10.3390/ijerph15071500.

Moore, C. W., B. Zielinska, G. Petron, and R. B. Jackson. 2014. Air impacts of increased natural gas acquisition, processing, and use: A critical review. *Environ. Sci. Technol.* 48 (15):8349–59. doi:10.1021/es4053472.

Ohio Environmental Protection Agency (OhioEPA). 2017. *2017-2018 Ohio EPA air monitoring network plan (Draft)*. 32. June. Columbus, OH: Ohio DEP.

Orak, N. H., N. J. Pekney, and M. Reeder. 2017. Ambient air quality near a Marcellus shale well pad in southwestern Pennsylvania. Presented at the Air and Waste Management

Association's 110th Annual Conference and Exhibition, Pittsburgh, PA. June 7. Accessed at https://www.eventscribe.com/2017/awma/ajaxcalls/PresentationInfo.asp?efp=SFRXUFlFQkIzMjEz&PresentationID=262009&rnd=0.2957729.

Paulik, L. B., C. E. Donald, B. W. Smith, L. G. Tidwell, K. A. Hobbie, L. Kincl, E. N. Haynes, and K. A. Anderson. 2016. Emissions of polycyclic aromatic hydrocarbons from natural gas extraction into air. *Environ. Sci. Technol.* 50:7921–29. doi:10.1021/acs.est.6b02762.

Pekney, N., G. Veloski, M. Reeder, J. Tamilia, J. R. Diehl, and R. W. Hammack. 2013. Measurement of air quality impacts during hydraulic fracturing on a Marcellus Shale well pad in Greene County, Pennsylvania. Presented at American Association of Petroleum Geologists (AAPG) Annual Convention and Exhibition, Pittsburgh, PA, May 19-22. 20.

Pekney, N., M. Reeder, G. Veloski, and J. R. Diehl. 2016. Data report for monitoring at six west virginia Marcellus Shale development sites using NETL's mobile air monitoring laboratory (July–November 2012). Pittsburgh, PA: US Dept. of Energy (US DOE), National Energy Technology Laboratory (NETL) NETL-TRS-4-2016. 104. June 16.

Pekney, N. J., G. Veloski, M. Reeder, J. Tamilia, E. Rupp, and A. Wetzel. 2014. Measurement of atmospheric pollutants associated with oil and natural gas exploration and production activity in Pennsylvania's Allegheny national forest. *J. Air Waste Manag. Assoc.* 64 (9):1062–72. doi:10.1080/10962247.2014.897270.

Pennsylvania Dept. of Environmental Protection (PADEP). 2010. Southwestern Pennsylvania Marcellus Shale short-term ambient air sampling report. Harrisburg, PA: Bureau of Air Quality. 52. November 1.

Pennsylvania Dept. of Environmental Protection (PADEP). 2011a. Northeastern Pennsylvania Marcellus Shale short-term ambient air sampling report. Harrisburg, PA: Bureau of Air Quality. 57. January 12.

Pennsylvania Dept. of Environmental Protection (PADEP). 2011b. Northcentral Pennsylvania Marcellus Shale short-term ambient air sampling report. Harrisburg, PA: Bureau of Air Quality. 52. May 6.

Pennsylvania Dept. of Environmental Protection (PADEP). 2016. Proposed Commonwealth of Pennsylvania Department of Environmental Protection 2016 Annual Ambient Air Monitoring Network Plan. 181. June.

Pennsylvania Dept. of Environmental Protection (PADEP). 2017. Marcellus Shale well count data. Accessed at http://www.depreportingservices.state.pa.us/ReportServer/Pages/ReportViewer.aspx?/Oil_Gas/OG_Well_Inventory.

Pennsylvania Dept. of Environmental Protection (PADEP). 2018. *Long-term ambient air monitoring project: Marcellus Shale gas facilities*. 139.July. Harrisburg, PA: PADEP.

Soeder, D. J. 2017. *Unconventional: Natural gas development from Marcellus Shale*, Vol. 527, 143. Boulder, CO: Geological Society of America, Inc.

South Coast Air Quality Management District (AQMD). n.d. *Field evaluation: Speck sensor (Draft)*. Air Quality Sensor Performance Evaluation Center (AQ-SPEC). 10. Diamond Bar, CA: SCAQMD.

Stacy, S. L., L. L. Brink, J. C. Larkin, Y. Sadovsky, B. D. Goldstein, B. R. Pitt, and E. O. Talbott. 2015. Perinatal outcomes and unconventional natural gas operations in southwest Pennsylvania. *PLoS ONE* 10 (6): e0126425. doi:10.1371/journal.pone.0126425.

Steinzor, N., W. Subra, and L. Sumi. 2013. Investigating links between shale gas development and health impacts through a community survey project in Pennsylvania. *New Solutions* 23 (1):55–83. doi:10.2190/NS.23.1.e.

Swarthout, R. F., R. S. Russo, B. C. Sive, Y. Zhou, B. M. Miller, B. L. Mitchell, E. Horsman, E. M. Lipsky, D. C. McCabe, and E. Baum. 2015. Impact of Marcellus Shale natural gas development in southwest Pennsylvania on volatile organic compound emissions and regional air quality. *Environ. Sci. Technol.* 49 (5):3175–84. doi:10.1021/es504315f.

TechLaw, Inc. 2012. Trip report, air sampling event, skyview elementary school site, Morgantown, Monongalia County, West Virginia. Wheeling, WV: Report to U.S. EPA Region III. 98. January 30.

U.S. Energy Information Administration (EIA). 2017. Drilling productivity report (For key tight oil and shale gas regions). 11. June. Accessed on June 28, 2017 at https://www.eia.gov/petroleum/drilling/archive/2017/06/pdf/dpr-full.pdf.

U.S. EPA. 2004. Air toxics risk assessment reference library, volume 1: Technical resources manual. Office of Air Quality Planning and Standards. EPA-453-K-04-001A, 899. April.

U.S. EPA. 2009. *Schools air toxics monitoring activity (2009): Uses of health effects information in evaluating sample results*. 24. September 10. Washington, DC.

U.S. EPA. 2014a. Evaluation of field-deployed low cost PM sensors. Office of Research and Development, National Exposure Research Laboratory. EPA/600/R-14/464. 76. December.

U.S. EPA. 2014b. *Acute dose-response values for screening risk assessments*. Table 2. 8. September 18. Washington, DC.

U.S. EPA Region III. 2015. EPA region III natural gas ambient air monitoring initiative (NGAAMI) in Southwestern Pennsylvania. Office of Air Monitoring and Analysis, Air Protection Division. 515. August.

US Census Bureau. 2016a. "Cartographic boundary shapefiles - States." Accessed at https://www.census.gov/geo/maps-data/data/cbf/cbf_state.html

US Census Bureau. 2016b. "Cartographic boundary shapefiles - counties." Accessed at https://www.census.gov/geo/maps-data/data/cbf/cbf_counties.html

West Virginia Geological and Economic Survey (WVGES) 2017. "Marcellus Shale well count data." Accessed June 29, 2017. at http://www.wvgs.wvnet.edu/www/datastat/devshales.htm

Zielinska, B., D. Campbell, and V. Samburova. 2014. Impact of emissions from natural gas production facilities on ambient air quality in the Barnett Shale area: A pilot study. *J. Air Waste Manag. Assoc.* 64 (12):1369–83. doi:10.1080/10962247.2014.954735.

ATTACHMENT C

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Drinking water, fracking, and infant health☆

Elaine L. Hill[a,*], Lala Ma[b]

[a] Department of Public Health Sciences & Department of Economics, University of Rochester Medical Center, 265 Crittenden Blvd., Box 420644, Rochester, NY 14642, United States

[b] Department of Economics, Gatton College of Business and Economics, University of Kentucky, Business & Economics Building, Lexington, KY 40506, United States

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ABSTRACT

This study assesses the health risks associated with drinking water contamination using variation in the timing and location of shale gas development (SGD). Our novel dataset, linking health and drinking water outcomes to shale gas activity through water sources, enables us to provide new estimates of the causal effects of water pollution on health and to isolate drinking water as a specific mechanism of exposure for SGD. We find consistent and robust evidence that drilling shale gas wells negatively impacts both drinking water quality and infant health. These results indicate large social costs of water pollution and provide impetus for re-visiting the regulation of public drinking water.

There is a well-established literature in economics that exposure to pollution has negative health consequences (Black et al., 2007; Chay and Greenstone, 2003; Currie and Walker, 2011; Deryugina et al., 2019; Hill, 2018; Isen et al., 2017; Knittel et al., 2016; Sanders and Stoecker, 2015; Schlenker and Walker, 2016). While work in this area has predominantly focused on the health impacts of air pollution, water pollution is a salient issue. Federal regulations such as the Safe Drinking Water Act and the Clean Water Act are motivated to control the health impacts of water pollution, and the recent water crisis in Flint, MI (Grossman and Slusky, 2019) has brought concerns about public drinking water quality to the forefront. Despite its relevance to policy and current environmental issues, the health effects of water pollution, especially at levels below regulatory thresholds, are not well-understood and the associated literature on causal impacts is thin.

This paper begins to fill this gap by assessing the infant health risks associated with drinking water contamination. Our identification strategy exploits the rapid expansion of shale gas development (SGD), commonly known as "fracking," which has raised water-related health concerns for exposed populations (Muehlenbachs et al., 2015). We build a novel data set that links gas well activity to (1) infant health outcomes recorded from the universe of birth records in Pennsylvania, and (2) all ground water-based Community Water System (CWS) drinking water contaminant measurements. This is accomplished by using the exact geographic

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* Corresponding author.
E-mail address: elaine_hill@urmc.rochester.edu (E.L. Hill).

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locations of maternal residences, gas wells, and public drinking water sources, as well as the dates of births, well bore activities, and water measurements. Combined, these data allow us to infer exposure to drinking water pollution from shale gas operations at both a high spatial and temporal resolution. We then use a difference-in-differences approach to estimate the impact of drilling near public water sources on public drinking water quality and the health of infants born to mothers who live in those systems.

Our paper makes two main contributions. First, we provide novel estimates on the *causal* impacts of water quality on health at mild levels as detected in developed countries. Isolating the health effects of water pollution has been difficult because data on water quality below thresholds of concern have been lacking. We innovate upon existing work by using the universe of public drinking water measurements to identify health effects below regulatory thresholds. The implications of our findings are especially important when viewed together with theory that predicts longer-term and inter-generational impacts on human capital accumulation and well-being from early-life exposures (Almond and Currie, 2011; Almond et al., 2018; Cunha and Heckman, 2007; Grossman, 1972; 1999) and recent empirical evidence on the importance of place for inter-generational mobility (Chetty and Hendren, 2018).

We are also the first paper to document that the pollution of public water supplies from fracking is affecting infant health. Our unique data on water source locations allow us to distinguish *in utero* exposure to SGD via water source proximity to gas wells drilled during gestation as opposed to exposure based solely on residential proximity. A finding that SGD operations have impacted water quality and health calls for regulation to internalize these consequences from an efficiency standpoint. The appropriate policy prescription to mitigate these impacts relies on identifying the mechanism of exposure.

We find consistent evidence that SGD affects both drinking water quality and birth outcomes. Drilling an additional gas well within a kilometer of ground water sources increases sampled SGD water chemicals by 1 percent and detection of regulated SGD chemicals by between 10 and 20 percent. The magnitude of this increase is large enough to surpass public health goals for these chemicals, but are too small to trigger a health based drinking water violation (reducing the likelihood that consumers are aware of the increase). This is striking considering that our data are based on water measurements taken after municipal treatment. Moreover, this is likely an underestimate of water contamination from SGD given the lack of comprehensive regulation (and measurement) of all SGD related contaminants. *In utero* exposure to an additional SGD well drilled within 1 km of water sources negatively affects birth outcomes, *conditional on drilling near the maternal residence*: gestation length is reduced by 0.15 weeks and birth weight falls by 25 g (using either water system or mother fixed effects). In terms of dichotomous birth outcome measures, drilling has increased the incidence of preterm birth (PTB) and low birth weight (LBW) by approximately 11–13 percent relative to the mean. These health impacts persist with a number of robustness checks, and cannot be explained by competing environmental exposures or compositional changes by virtue of mobility or fertility decision responses to SGD.

The paper is organized as follows. Section 1 provides a background on water pollution, health, and SGD. Section 2 describes our data sources and provides summary statistics. Section 3 outlines our empirical model and the conceptual framework on which it is based. We present main results in Section 4 and follow with robustness checks and heterogeneity of treatment effects in Section 5. In Section 6, we discuss the policy implications of our findings and limitations. Finally, Section 7 concludes.

1. Background: Water, health, and SGD

Water Quality and Health It is well-known that high levels of water contamination can damage health (Brainerd and Menon, 2014; Ebenstein, 2010; Lai, 2017; McKinnish et al., 2014). However, evidence from extreme levels of pollution or changes in water quality may not be applicable to wealthy countries, where both the levels of and changes in water pollution are much lower. In the US, there is very little evidence on the health impacts of drinking water beyond a handful of historical studies (Anderson et al., 2020; Beach et al., 2016; Cutler and Miller, 2005; Ferrie et al., 2012).

A critical hurdle in quantifying the health impacts of drinking water contamination is the ability to accurately measure exposure from currently available data. One approach is to use ambient water quality, e.g. as measured from US Geological Survey (USGS) water monitors. Water monitors, however, are not randomly placed and may not be located near where contamination has occurred. Moreover, the subsequent step to link contamination to health requires identifying whether the point of contamination is near the source of drinking water, since most of the US population relies on municipal tap water (EPA, 2015). However, the locations of public water sources are not available for most states. Next, even with source locations, the type of water source (ground water or surface water) has implications for capturing pollution risk. The exposure area for systems relying on ground water is fairly consistent with the intake point (e.g., wellhead) of a water system. On the other hand, surface water systems, which service the majority of the population, can have far-ranging exposure areas that are difficult to model, and can depend on the body of water, elevation, and water flow.

Another approach is to examine drinking water quality directly, which can be private or public. For private water sources (e.g., private wells), there are no regulatory requirements for sampling and therefore difficult to capture water quality. Data on public water, for which there are sampling requirements, predominantly focus on recording violations if they occur and miss the sampling effort behind each violation. Sampling requirements are also set for *regulated* chemicals only; increases in non-regulated chemicals (highly likely given the range of chemicals used in the SGD process) will be overlooked. This complicates the application of research findings to improve water pollution control policies: If contamination of public water supplies yields negative health effects, should one increase the regulatory stringency for currently-regulated contaminants or expand the set of regulated contaminants?

The small body of quasi-experimental work that has examined drinking water impacts at current levels in the US have focused on infant health outcomes (Currie et al., 2013; Grossman and Slusky, 2019; Guilfoos et al., 2017; Marcus, 2021). In particular, violations of public drinking water thresholds have been shown to increase the chances of negative birth outcomes for exposed infants (Currie et al., 2013). Contaminant levels below regulatory or actionable thresholds, however, may have consequences for

health, as have been demonstrated in the context of environmental pathways other than water (Aizer et al., 2018; Deryugina et al., 2019; Schlenker and Walker, 2016). Evaluation of health impacts at levels below current regulation require data on drinking water samples that *do not* violate regulatory standards. Recent papers have used this type of water sampling data to study water system compliance with the Safe Drinking Water Act (Bennear et al., 2009; Grooms, 2016), but few, other than (DiSalvo and Hill, 2019), have extended the analysis to examine health. In addition, all of the above studies, including the current study, have the problem of being unable to speak to *how* one should expand water control regulation. Increased data collection on a more comprehensive set of water chemicals going forward would aid in translating water-health research findings into actionable policy.

SGD and Water Quality Over the last decade, technological innovations in high-volume horizontal hydraulic fracturing have allowed for the cost-effective recovery of energy resources from tight rock formations, such as shale. Shale gas development (SGD) has a life cycle that involves multiple phases, including well pad preparation, drilling the well, hydraulic fracturing, and production.[1] In Pennsylvania, wells are classified as unconventional if they are drilled horizontally and stimulated with high volume hydraulic fracturing ("fracking"). Well pad preparation typically takes approximately 30 days (Tustin et al., 2017) and includes clearing land and building access roads. Each well pad contains multiple wells and wells are typically drilled for 30–60 days, requiring longer drilling periods depending on depth and directional distance ("laterals") (Tustin et al., 2017). During the drilling phase, the well is cased with metal and cement to protect groundwater supplies. In Pennsylvania, the average depth is 6000 ft (National Energy Technology Laboratory, 2013) and lateral distances can be 2000 to 10000 ft (U.S. EPA, 2016). Once drilling is complete, the stimulation phase occurs with hydraulic fracturing and typically lasts an average of 7 days. The fracturing process injects millions of gallons of water mixed with fracturing chemicals ("fracking fluid") at high pressure to fracture the shale and release the natural gas trapped in the shale. At the end of this phase, the injected fluid returns to the surface; this is called flowback. This flowback fluid can be stored on site in tanks or surface water impoundments (open lined pits) and eventually is trucked off to be reused or treated. Finally, the production phase can last months to years as the well produces natural gas. During the production phase, water will continue to return to the surface, which is called produced water.

Shale gas operations have yielded a range of benefits, from reductions in energy costs and crime to improvements in greenhouse gas emissions (Allcott and Keniston, 2017; Bartik et al., 2019; Feyrer et al., 2017; Hausman and Kellogg, 2015; Mason et al., 2015; Street, 2018). However, various costs associated with SGD exist and are borne by populations that are exposed to these operations (Black et al., 2021). SGD has been associated with air pollution, water pollution, light, noise, and earthquakes. Work in both epidemiology and economics have used measures of exposure based on where individuals live relative to where drilling takes place to measure these effects.[2] While informative, the health effects arising from these studies do not distinguish the effects of water pollution from other factors that are correlated with proximity to drilling activity. Evidence in support of a water contamination pathway is thus incomplete (Currie et al., 2017; Hill, 2018).[3]

There are numerous channels through which shale gas operations can impact water resources. SGD operations have the potential to cause groundwater contamination in all stages of the SGD life cycle (Shrestha et al., 2017; Sun et al., 2019; Torres et al., 2016). The primary pathways that SGD can impact groundwater are through spills during chemical mixing and during on-site treatment and waste management, well casing failures (during fracking and through well aging), induced fractures, tank leaks, and pipeline leaks; thus, the likelihood and extent of contamination depend on how SGD operations and waste are managed, and on geological features such as depth and permeability (Mason et al., 2015; Shrestha et al., 2017; Torres et al., 2016).[4] Shanafield et al. (2019) found that groundwater contamination most likely comes from spills at the well pad, which can be as high as 1 in 100 for each well, and would occur during the pre-production phase that includes well pad development, drilling, chemical mixing, hydraulic fracturing, flowback waste treatment and disposal, and connecting the well to the pipeline to begin production. The Pennsylvania DEP issued 120 violations in 2012 (8% failure rate) for faulty casing and cementing, and (Darrah et al., 2014) forecast that 40% of wells in Northeastern, PA will fail. Bonetti et al. (2021) study *surface water* contamination from SGD and found small increases in salts associated with SGD 90 to 180 days after drilling. This literature suggests that systematic groundwater contamination is more likely during pre-production (i.e., drilling), but the high casing failure rate also suggests that SGD could have longer-term implications for ground water quality, leaving the SGD phases that most likely affect ground water quality unclear ex ante.

Concerns over water quality impacts have led the US Environmental Protection Agency (EPA) on a six-year scientific assessment of the hydraulic fracturing impacts on drinking water resources. While the review concluded that hydraulic fracturing activities *can* impact water resources (U.S. EPA, 2016), it still highlights the lack of studies and need for more research. Moreover, the existing evidence on the impacts of SGD on ground water sources makes it difficult for regulators to put currently-known information into practice. Part of the challenge the scientific community faces is that there is a lack of reliable information about the set of chemicals used in hydraulic fracturing, creating uncertainty around which chemicals to measure for regulatory purposes. Perhaps due to this uncertainty, there is currently no specific regulation to protect public drinking water resources from SGD. The health effects of drinking water contamination are even less understood, since many of the documented SGD chemicals have no toxicity information

[1] See Hill (2018) for a detailed discussion of leasing and permitting. Hill (2018) also provides a detailed discussion of the mechanisms of exposure. U.S. EPA (2016) provides additional institutional details.

[2] Overall, these studies find an increased risk of low birth weight (Currie et al., 2017; Hill, 2013; 2018) and premature birth (Hill, 2013). See Black et al. (2021) for a recent review of economic, environmental, and health impacts of SGD.

[3] Currently, the evaluated health impacts of SGD include asthma, birth outcomes, psychosocial well-being, pneumonia, cardiovascular disease, various cancers, sexually transmitted infections, and hospitalizations. For recent overviews of this literature, see Deziel et al. (2020) and Johnston et al. (2018).

[4] For comprehensive reviews, see Kuwayama et al. (2013) and U.S. EPA (2016).

and few are even measured in drinking water (U.S. EPA, 2016). For example, only 29 of the 1173 SGD contaminants documented from the EPA report are regulated by the Safe Drinking Water Act.[5]

These critical gaps in the existing literature impede an evaluation of whether and how much to revise regulatory standards for drinking water, and how best to regulate the emerging industry of SGD while retaining its economic and environmental benefits. Our study design and context has advantages over previous work in this respect. First, the use of the universe of water sampling data allows us to evaluate whether health effects *below regulatory thresholds* exist. Next, the variation in water pollution comes from changes at the water source, which would imply a clear policy prescription if water quality (and health) were affected, e.g., to contain pollution at water source areas. Finally, there has been very little regulation of SGD. Drilling decisions during our study period are primarily driven by shale resource productivity and availability, and are largely exogenous (Bartik et al., 2019; Kearney and Wilson, 2018). The shale gas context, combined with our novel data on water sources, provides a unique opportunity to exploit quasi-random variation in water quality so as to improve our understanding of the potential impacts of water contamination on health. An important aforementioned limitation is that our estimate of the SGD impacts on drinking water may still be understated if unobserved, unregulated co-pollutants are also increasing. That many UOGD chemicals are unknown to the public due to state exemptions for chemical disclosure renders it even more difficult to know *how* water policy should be expanded to improve public health. Thus, our paper provides rationale for increasing disclosure requirements for the SGD industry.

2. Data

We draw upon three main sources to produce a unique data set linking shale gas operations to infant birth outcomes through its impact on drinking water: (1) birth records from the Pennsylvania Department of Health (PADOH), (2) public water system service boundary maps and source locations from the Pennsylvania Department of Environmental Protection (PADEP), and (3) gas well data from the Carnegie Museum of Natural History Pennsylvania Unconventional Natural Gas Wells Geodatabase (UNCGDB). Additionally, we use public water sampling measurements for each water system from the PADEP to assess the "first-stage" water quality impact. We categorize shale gas chemicals based on a list of chemicals published by various federal agencies.[6] We also draw upon several other sources to augment our main data set and check for robustness. We provide brief overviews of each main source of data in this section, before describing the data construction process and summary statistics. Detailed data descriptions, including web sources, are given in Appendix 8.1.

Confidential birth certificate records for the universe of births in PA beginning from 2003 through 2015 include the maternal address associated with each birth, which we geocode to longitude and latitude. The data provide birth outcomes, such as birth weight and gestation period (calculated from conception and birth dates), demographic information of mothers, and maternal health behaviors and pregnancy risks. Digitized public drinking water system maps then provide service area boundaries for Community Water Systems (CWS), which determine the public drinking water system on which a mother relies based on her address. The gas well database, which contains all unconventional natural gas wells drilled or permitted through 2015, includes the exact locations of these gas wells, the permit date, the date when drilling began, and total production as of 2015. We then use a snapshot of ground water-based public water systems as of 2015 to identify the water systems that are exposed to shale gas activity. Crucially, the water source location data allow us to link shale gas operations to both the quality of water provided by water systems as well as the infants that are born to mothers that rely on public water provided by those systems.

Fig. 1 overlays Pennsylvania natural gas wells and community water systems.

The Marcellus shale play stretches from the southwest corner of the state to the northeast. As such, regions exposed to SGD will be predominantly rural, and comparisons of either births or water quality in these areas with that in cities (i.e. Philadelphia) would be inappropriate. We thus retain all births that are exposed to shale gas development within 10 km based on maternal address.[7] This includes those living in ground water-based community water systems with any source within 10 km of drilling as well as those living in residences within 10 km of any drilling.[8,9] This sample limitation leaves a total of $N = 325{,}439$ births, where maternal characteristics of subgroups exposed to drilling within 1 and between 1 and 5 km are fairly similar to those exposed to drilling between 5 and 10 km (Appendix Table 8.3.6).

With each birth spatially linked to every shale gas well within 10 km of its water source (or residence), we then calculate the total number of wells within 10 km of the infant's CWS source (or residence) that were drilled *within the gestation period* of that infant. We use number of drilled wells as our measure of the intensive margin because the drilling process itself is most likely to impact ground

[5] See Appendix Table 8.3.2 for the list including number of drinking water quality samples available in Pennsylvania.

[6] We list these contaminants and whether they are SGD related because they are fracturing fluid or produced water chemicals in Appendix Table 8.3.2.

[7] This sample limitation is similarly important for water quality, shown in Appendix Table 8.3.1.

[8] A system can have multiple sources. In this case, we consider the system within the vicinity as long as any one of its source locations are within the 10-kilometer buffer.

[9] We limit our investigation to ground water systems because we do not have surface water protection areas, which would delineate the exposure area to surface water systems. We abstract from these systems for the purposes of a cleaner exposure definition since surface water exposure areas can vary in exposure range depending on the waterbody (e.g. a pond versus a river), and leave investigation of surface drinking water impacts for future work.

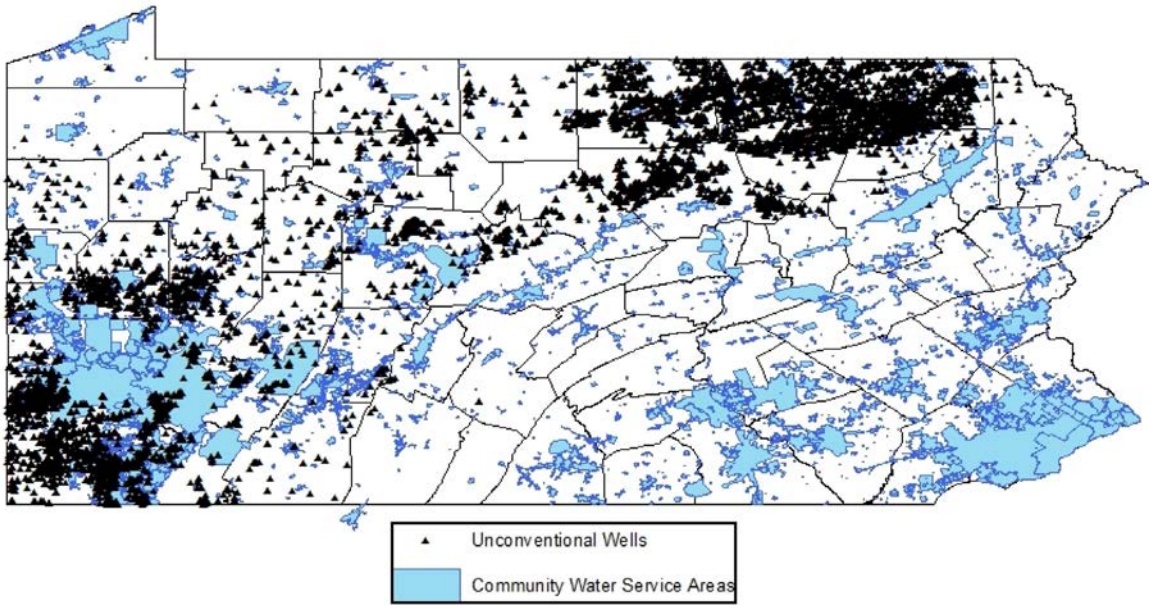


Fig. 1. Gas Wells and Community Water Systems.

water (as opposed to quantity of gas produced) and is also used in most other studies (Black et al., 2021; Bonetti et al., 2021).[10] We additionally aggregate these "threats" at various buffers within 10 km (i.e. between 1 and 5 km) to distinguish the impact of threats at different proximities. We do this as there are typically multiple well bores (drilled at different times) located near any given groundwater source, and, as such, no clear "before" or "after" exposure period. While this complicates our definition of a treatment period, it provides good variation in exposure to shale gas operations that one can exploit. Fig. 2, which delineates the new well bores drilled and the affected counties by year, is indicative of this as drilling varies both on the extensive and intensive margins. In these data, a quarter of gas wells are in production but are missing a drilling date. For the count of gas well threats in close proximity to water sources and residences, we impute the drilling date with the first production date minus 150 days, which is the average number of days between drilling and first production based on data from DrillingInfo, Inc. In Appendix Table 8.3.11, we verify that our results are robust to not imputing missing drilling dates and other forms of imputation.[11]

Our analysis sample is further restricted to residences that are within a community water system. The final estimation sample is thus composed of infants on ground water-sourced community water systems exposed to SGD within 10 km of their water source or residence. Table 1, Panel A presents the average exposure to drilled wells by water source and by residence. The average infant in our full sample is exposed during gestation to 0.002 shale gas wells within a kilometer of its source and 0.005 wells within a kilometer of its residence. Conditional on being exposed, the number of wells drilled respectively increases to 1.5 and 2.3. When we simply count the total (or cumulative) wells drilled before birth as opposed to focusing on within gestation, exposure through the source and the home respectively increases to 1.9 and 2.7, conditional on being exposed. Next, in anticipation of our fixed effects models, Table 1 Panel B counts the number of water systems and mothers that experience any change in exposure at the source. Of 49 systems with any water source within a kilometer of wells, infants in 42 systems experience some change in cumulative exposure to well bores versus those in 38 systems who experience changes in within-gestation exposure. Out of 1541 mothers (within-mother sample Table 1 Panel B) who are exposed to gas wells within a kilometer of their source, 952 and 275 respectively experience a change in cumulative and gestational exposure (i.e., conceive children exposed to different amounts of gas wells).

We use a similar procedure to construct our water quality data for water measurements beginning from 2011 through the third quarter of 2015, where a unit of observation is a contaminant sampling measurement (in parts per million or ppm) on a particular date.[12] For each water measurement, we aggregate the total number of well bores within 10 km of the CWS source (and various proximities within) that have been drilled by the time that water measurement was taken. We remove samples that are greater than the 99th percentile of the sampling result distribution to prevent outliers from driving our results. Focusing on the set of contaminants that have been associated with SGD: of the 171,615 water measurement observations from systems within 10 km of CWS sources,

[10] Additional options could be quantity of water and chemicals used in the drilling process or the number of wells with casing failures or spills. Our choice is a function of data availability and quality. It also facilities comparison to other studies.

[11] We find larger effect sizes when we do not impute.

[12] Because information was electronically submitted by drinking water systems only beginning in 2011, we use the water measurements beginning in 2011 as our main estimation sample. See Appendix 8.1 for additional details.

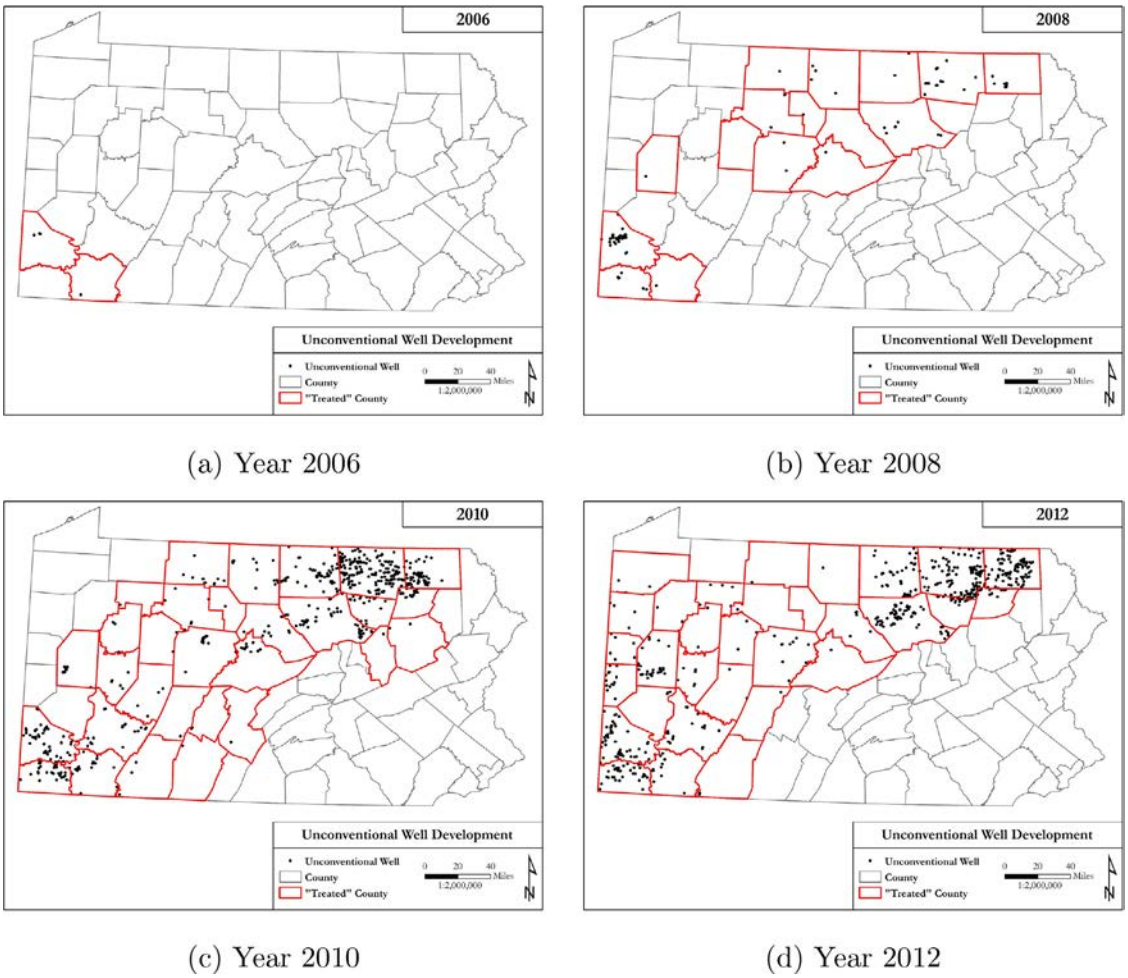


Fig. 2. New Well Bores Drilled by Year.

approximately 40% (or 69,239) are contaminants that have been tied to SGD. For this SGD-related sample, there are, respectively, 0.18, 0.45, and 27 well bores drilled, on average, within 1, 1.5 and 10 km of source locations (Appendix Table 8.3.3).

3. Empirical strategy

Birth Outcomes Our baseline specification follows a difference-in-differences (DD) approach. We compare changes in birth outcomes (in response to drilling during gestation) for infants born in systems with drinking water sources near drilled wells to similar changes for infants in systems with sources that are farther away but still within 10 km. Previous literature has found impacts on ground water quality using private wells from as close as 1 km to as far as 5 (Johnston et al., 2018). To allow the data to inform us of the exposure buffer, we estimate the drilling impacts at 1-kilometer bins for distances to the source of between 0 and 5 km. Specifically, we regress the birth outcome (Y_{ijt}) for a birth i in CWS j at time t on the number of well bores drilled *during the infant's gestation period* at different distances from the CWS source:[13]

$$Y_{ijt} = \sum_{\ell=0}^{4} \beta_\ell wells_{ijt}^{(\ell,\ell+1]} + \beta_5 wells_{ijt}^{\leq 10} + \beta_6 Rwells_{ijt}^{\leq 1} + X_{it} + m_t + cws_j + \epsilon_{ijt} \quad (1)$$

The main birth outcomes we examine include birth weight (grams) and gestation length (weeks), as well as indicators of low birth weight (weight < 2500 g) or prematurity (gestation length < 37 weeks). The explanatory variables, $wells_{ijt}^{(\ell,\ell+1]}$, gives the total number of well bores within $(\ell, \ell+1]$ kilometers of infant i's water source that are drilled during gestation, for $\ell = 0, \ldots, 4$. The variable, $wells_{ijt}^{\leq 10}$, returns the exposure to wells drilled during gestation within 10 km of water sources, capturing air exposure from, for

[13] The continued operations of the well could also impact ground water (see Section 1). We also estimate models with cumulative number of wells but find smaller and often not statistically precise effects.

Table 1
Summary Statistics.

	A. Average Exposure to Gas Wells by Infant (N = 325,439)				
		Within Gestation		Cumulative	
Proximity to Source	N	Mean	Mean | Exposed	Mean	Mean | Exposed
<1km	8142	0.002	1.525	0.011	1.944
<3km	37,127	0.035	2.640	0.185	5.247
<5km	83,011	0.103	3.886	0.566	7.899
<10km	129,567	0.458	7.575	2.481	21.523
Proximity to Residence	N	Mean	Mean | Exposed	Mean	Mean | Exposed
<1km	11,735	0.005	2.268	0.027	2.700
<3km	81,203	0.088	3.412	0.474	6.326
<5km	154,288	0.330	4.609	1.736	10.864
<10km	303,463	1.685	7.723	1.685	4.588
Imputed	N	Mean	Mean | Exposed	Mean	Mean | Exposed
Source<1km	8142	0.004	2.116	0.030	2.794
Residence<1km	11,735	0.006	2.226	0.038	2.914

	B. Count of Exposed Water Systems or Mothers					
	Within CWS (*N = 574*)			Within Mom (*N = 67,987*)		
Count:	Systems	Δ Cum. Exposure	Δ Gest. Exposure	Moms	Δ Cum. Exposure	Δ Gest. Exposure
Source<1km	49	42	38	1541	952	275
Source<3km	205	173	155	7500	3783	1825
Source<5km	270	244	230	16,937	9917	4210
Source<10km	420	357	340	26,714	10,332	6616

Note: Table provides summary statistics of exposure to gas wells by births, water systems, or mothers. The final sample is composed of infants on ground water-sourced community water systems exposed to SGD either within 10 km of their water source or residence.

example, trucking activity. We also control for *in utero* exposure to the number of well bores drilled within 1 km of the maternal residence during gestation, $Rwells_{ijt}^{\leq 1}$, in all models, following previous work that has found proximity impacts on infant outcomes within this buffer (Currie et al., 2017; Hill, 2013). Our main coefficients of interest $\beta_0 - \beta_4$ returns the change in birth outcome given an increase in number of well bores within a specific buffer of the mother's water sources, relative to the impact of drilling between 5 and 10 km.

Causal inference based on the estimated relationship rests on the assumption that birth impacts captured by drilling activities that are "far" from water sources represent changes in infant health that would have occurred in the absence of drilling near the source. With the appropriate exposure buffer (discussed later in Section 4 on results), we separate our infants into a treatment and control group to check for pre-existing trends in birth outcomes before SGD and find no evidence of differential trends in outcomes prior to 2009, when large-scale drilling began in PA.[14] The main specification includes a number of additional control variables. Controls for maternal characteristics, X_{it}, include the mother's age, race, education, enrollment in Medicaid and in the Special Supplemental Nutrition Program for Women, Infants, and Children (WIC) at birth, and a host of pregnancy risks (e.g. pre-gestational diabetes and smoking).[15] We also include the following controls: average gestational temperature and precipitation near the maternal residence,

[14] With the majority of the estimated impacts lying within 1 km of water sources, we use this exposure buffer to check for pre-existing trends. We retain the residuals from a regression of our outcomes of interest on all but the key explanatory variables (corresponding to β_0 through β_1 in Eq. (1)), and then plot the difference in these residuals between infants whose water sources are near (<1 km) versus far (2–10 km) from drilling for each quarter from 2003 to 2008. Figures 2 and 3 present this analysis respectively for birth weight and gestation length. While we find no evidence of trends, we note that our estimates of the difference in residuals lack the precision to rule out pre-treatment effects of the same magnitude as our main estimates.

[15] Specifically, controls for maternal characteristics include dummy variables for mother's age group (19 to 24, 25 to 35, and 35 or older), race/ethnicity (Hispanic or black), educational attainment (high school only, some college, associates degree, and college or more), marital status, WIC enrollment at birth, and Medicaid payment. Controls for pregnancy risks include indicators for whether the mother smoked cigarettes during or in the 3 months prior to the pregnancy, had previous live births, had previous dead births, had any pre-gestational risks (including diabetes, poor outcome for a previous birth, a previous birth that was preterm, and infertility risk), and had any risks during the current pregnancy (including gestational diabetes and vaginal bleeding). In addition to maternal characteristics, we control for the gender of the infant and birth order fixed effects.

which can directly impact birth outcomes (Deschênes et al., 2009) as well as vary exposure to water contaminants;[16] a direct measure of changes in water quality of the mother's water system that is *not* related to SGD, which is in the form of the number of coliform and disinfectant by-product exceedances of federally established legal limits during gestation;[17] and the number of permitted well bores during an infant's gestation – this can control for differences in expected well productivity, which can impact fertility and birth outcomes through local economic development (Hill, 2018; Kearney and Wilson, 2018).[18] In addition, we include month-by-year fixed effects (m_t) and a fixed effect for each CWS, cws_j. These help to control for seasonal differences in birth outcomes and unobserved differences across water systems that might impact health. In certain specifications, we limit time-invariant, unobserved differences in family backgrounds with comparisons within siblings, i.e. through the use of mother fixed effects.[19]

We augment our baseline specification to ensure that the impacts we recover are through the mechanism of water contamination. Of utmost concern is that our estimated infant health impacts could be driven by changes in air quality (Alexander and Schwandt, 2019; Almond et al., 2009; Chay and Greenstone, 2003; Currie and Neidell, 2005; Currie and Walker, 2011; Isen et al., 2017; Schlenker and Walker, 2016). The negative impacts on health from other media of contamination that would most affect mothers living in close physical proximity to gas well activity would cause us to overstate the impacts of water quality changes. There are potential benefits, however, from living in close proximity of drilling activity if a household receives royalties or lease payments for allowing drilling on its property. Beyond the inclusion of gas well exposure via the maternal residence, we address air quality concerns more directly by including several controls to capture potential air quality impacts on birth outcomes. First, we control for a measure of ambient air quality at the Census block-group-by-year level that is calculated from TRI data using EPA's Risk-Screening Environmental Indicators (RSEI) Model. Second, SGD-related transport is hypothesized to increase air pollutants; we control for the distance between maternal address and the closest PA state-owned and maintained public road to reduce the possibility that our results are caused by traffic-induced air quality changes.

Our empirical health model is grounded in the conceptual framework laid out in several important papers, notably Heckman (2007), Almond and Currie (2011), and Almond et al. (2018). Our problem of measuring the impact of SGD on health can be cast in a similar two-period health production model, modified to focus on the production of neonatal health based on parental investments in response to SGD. Under certain substitutability assumptions in health production, parental investments are compensatory. Thus, parents would increase investment in infant health to counter a negative shock such as SGD (Almond and Currie, 2011). The monetized health impact of SGD that ignores these behaviors would underestimate the true costs. On the other hand, the local impacts of SGD could be positive (e.g., from royalties) or negative (e.g., due to pollution) (Bartik et al., 2019; Muehlenbachs et al., 2015), meaning that even if responses are compensatory, whether investment actually increases depends on whether the *net* impacts of SGD are positive.

Our quasi-experimental framework is set up to both limit the parental response and identify a negative water pollution impact. The exposure definition based on water *sources* allows us to control for the wells drilled near residences, which helps to remove the local impacts from shale development due to mineral rights (positive) and local disamenities such as air pollution (negative). By doing so, we are more likely to isolate the negative, water-related portion of the SGD shock. Next, the exposure definition reduces the salience of SGD activities to households since people are unlikely to be aware of and respond to the threat at their water source,[20] which allows us to better control the mitigation response. With parental investments fixed (in response to shocks), then the impact that we measure is closer to an estimate of the pure biological impact of shocks on health (Royer, 2009).

Water Quality Finally, whether SGD has impacted birth outcomes through drinking water quality requires understanding whether drinking water is actually impacted. Currently, there is no consensus regarding this "first stage" question from the scientific community. As such, establishing this relationship is an important, necessary step to asking the question of whether SGD impacts health through water; if no direct water quality impacts exist, then the scope for SGD impacts to be mediated through water would be indeed limited.

The model to estimate water quality impacts builds upon previous work in Hill and Ma (2017) and follows that for infant health closely. Our specification is again a difference-in-differences approach that compares water quality changes (in response to drilling) at water systems with sources near well bores to that for systems with sources between 5 and 10 km. Specifically, we model the logarithm of water quality measurement i (ppm), r_{ijt}, for a community water system j to depend on the number of well bores drilled at different buffers within 10 km.

The regression controls for sample-specific attributes (X_{it}) such as hour-of-day of when a sample was collected, the laboratory at which sampled results were measured, the contaminant group to which a pollutant belongs, sample type (distribution, entry point,

[16] Schlenker and Roberts (2009) provide daily minimum and maximum temperatures and total precipitation for 2.5 mile^2 cells. Appendix 8.1 gives more details about these controls.

[17] Water chemicals not considered to be related to SGD will be used as an outcome variable in our assessment of water quality impacts as a placebo check (described in the next section).

[18] As we show in the water quality results later in the paper, permitting does not impact water quality, and thus any response of infant outcomes to permitting activity should be unrelated to water quality changes.

[19] We note that inclusion of mother fixed effects does not avoid other forms of time-varying endogeneity (e.g., delaying fertility or moving out of state so that we do not observe a second birth or miscarriage that could be due to exposure). Infants with siblings are also more likely to be low birth weight or premature. We control for the latter by including a birth order fixed effect.

[20] The data used in this paper are not publicly available and would be difficult for individuals to determine. Furthermore, we show evidence that families move in response to drilling near their residences but **not** near their water source, and *measured* water quality does not fall enough to trigger MCL violations (the level at which residents would be informed of water contamination).

etc.), number of MCL violations in the previous 30, 90 and 180 days, and temperature and precipitation. We also include county-by-year fixed effects (ν_{jt}), month-of-year fixed effects (m_t), and a fixed effect for each CWS, cws_j. The following gives our baseline specification:

$$r_{ijt} = \sum_{\ell=0}^{4} \beta_\ell wells_{ijt}^{(\ell,\ell+1]} + \beta_5 wells_{ijt}^{\leq 10} + X_{it} + \nu_{jt} + m_t + cws_j + \epsilon_{it} \quad (2)$$

where $wells_{ijt}^{(\ell,\ell+1]}$ denotes the number of well bores between ℓ and $\ell+1$ kilometers of the water source drilled by time t. The parameters of interest, β_ℓ for $\ell = 0 \ldots 4$, return the impact of drilling an additional well bore between ℓ and $\ell+1$ kilometers from the water source on SGD-related contaminants, relative to changes in water quality trends over the same period as captured by water quality changes at water systems with more distant gas well threats. As with the infant health model, we check the validity of the parallel trends assumption and find no evidence that of pre-existing trends between water quality provided by systems near and far from drilling.[21]

We can explore the heterogeneity of effects by distinguishing the impacts from well bores that are drilled uphill versus downhill from sources, and those that ever produce any oil or gas as opposed to never-produce. In each case, the total number of threats within a certain proximity can be decomposed into those from each type of threat for a given way of distinguishing threats,

$$wells_{ijt}^{(\ell,\ell+1]} = TypeA_{ijt}^{(\ell,\ell+1]} + TypeB_{ijt}^{(\ell,\ell+1]} \quad (3)$$

where 'TypeA' and 'TypeB' would refer to, for example, the number of up- and down- gradient threats within the $(\ell, \ell+1]$-kilometer interval when separately estimating impacts by elevation. Gas well threats are defined to be 'uphill' from a ground water source if the surface elevation of the well bore is higher than the surface elevation at the source intake. If elevation affects ground water flow, one would expect uphill threats to have stronger impacts on drinking water quality than those down hill of intake wells. Unproductive wells are typically left inactive because the cost is often prohibitive to permanently plug wells (Muehlenbachs, 2015). A priori, we do not know whether producing wells are more likely to contaminate nearby drinking water sources than wells that are just drilled and never produce. Separately testing these dimensions not only serves as robustness checks, but provides insight into potential mechanisms of contamination.

Our main analysis focuses on SGD-related chemicals; we estimate the impact of gas well threats on non-SGD related chemicals as a placebo check. We also test whether gas well threats that occur *after* water measurements are taken impact SGD-related chemicals. In addition, we assess the robustness of our water quality results with an additional data set on water sampling data from U.S. Geological Survey (USGS) ground water monitors. Construction of the data follows the same procedure as that used for public water system water quality, except the water sampling data is matched to gas wells via the location (i.e. longitude and latitude) of the USGS water monitor. The same specification is used as before, where controls for weather and contaminant group indicators are included, as well as fixed effects for month-of-year and county-year. These checks would further bolster the case that our estimated impacts are, in fact, causal.

4. Results

Water Quality We first provide evidence that public drinking water quality has been compromised by shale gas development. Fig. 3 plots the impacts on various water quality measures for both SGD and non-SGD chemicals.[22] In Panel A of Table 2, we provide point estimates for a subset of these water quality measures, and additionally distinguish between gas wells drilled within 0.5 km and 0.5 to 1 km. In all regressions, we control for water system fixed effects, county-by-year fixed effects, and month-of-year fixed effects in addition to sample-specific characteristics.

These results make clear that drilling an additional gas well within 1 km of water sources increases chemicals related to SGD in public drinking water. For example, well bores drilled between 0.5 and 1 km of water sources increases average sampling of contaminants by 0.94 percent ($p < 0.05$) and detection of SGD chemicals by 2.6 percentage points (pp) ($p < 0.01$) or close to 11 percent given a 0.24 baseline rate of detection. If these estimated impacts result from correlated environmental changes, then one would likely see increases in non-SGD related chemicals as well. We see no such effects for non-SGD chemicals in Fig. 3.[23] The impacts of gas wells drilled within 0.5 km are generally larger in magnitude, but are estimated with less precision. This pattern is intuitive as we would expect that systems with sources further away from gas wells are less likely to be affected by surface spills or activity that might impact ground water. Gas well threats at distances farther than 1 km are an order of magnitude smaller and are not statistically significant, indicative of no effect. This is consistent with most of the scientific work to date investigating ground water impacts (Johnston et al., 2018). Estimates are robust to two-way clustering on both the spatial (CWS) and temporal (month-of-year) dimensions. We additionally explore the heterogeneity of effects in panel B of Table 2. Because elevation affects groundwater flow, we differentiate the water quality impacts of uphill well bores from those downhill. Unsurprisingly, we find that it is the uphill threats that are disproportionately affecting drinking water quality. We also find that the effect of an additional gas well drilled is driven primarily by producing wells as opposed to wells that never produce.

[21] See Fig. 1.

[22] Point estimates for the 1 km impact on SGD chemicals in Fig. 3 are provided in Panel A of Appendix Table 8.3.4.

[23] Point estimates for the non-SGD sample using log result as the dependent variable are provided in the last column of Table 2, panel A.

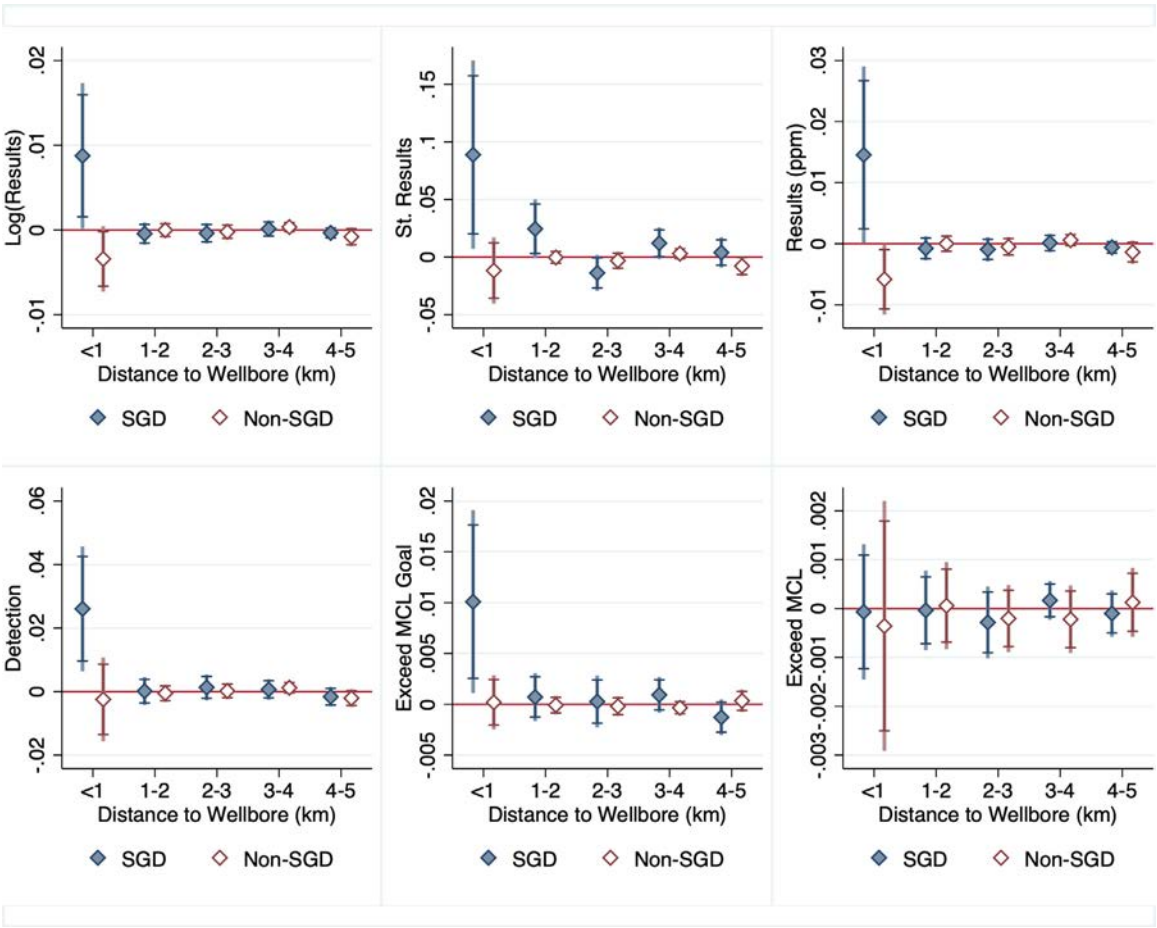


Fig. 3. Water Quality Impacts. *Note:* Figure plots water quality impacts of drilling for SGD and non-SGD chemicals. The continuous measures are the sampling results in logs and levels (ppm), and 'St. Result,' which refers to sampling results that are standardized with respect to the mean and standard deviation of contaminants in its chemical group. The dichotomous measures include detection (results greater than 0), 'MCL' (the federally enforceable threshold for water quality), and 'MCL goal,' a more stringent public health goal for water quality.

We perform a number of placebo checks. Panel B of Table 2 presents the impact of well bores drilled 180 days after water measurements are taken (column 3), and finds that there is no effect of threats incurred in the future on drinking water quality. This would be the case if our estimates are causal. Permitting of well bores similarly has no impact on water quality (column 4).

In additional robustness checks, we re-estimate our main water quality model using alternative water outcomes (Appendix Table 8.3.4, panel A) and subgroups of chemicals (Appendix Table 8.3.4, panel B). We find evidence of increased detection of chemical groups that are consistent with the scientific literature on SGD and water quality: detection of inorganic compounds generally increases by 18% relative to the mean ($p < 0.05$) and detection of lead increases by 190% ($p < 0.05$). There is also some evidence that synthetic organic compounds have increased (50%, $p < 0.1$). On the other hand, detection of nitrates and nitrites seems to have decreased. We present these results as we think they are interesting, but caution strong takeaways given the rare occurrences of many of these chemicals (e.g. synthetics and nitrates/nitrites are both detected only 0.58 percent of the time in our sample).

The estimated effects on SGD chemicals in ambient water as captured by USGS water monitors are qualitatively similar (Appendix Table 8.3.5). In particular, the marginal impact of wells drilled within a kilometer of USGS ground water monitors is, on average, 3.0 percent ($p < 0.01$). The estimated effect increases to 6.2 percent ($p < 0.01$) for wells drilled upgradient to monitors, and 3.3 percent ($p < 0.01$) for those that are ever in production. As before, the magnitude of impacts is smaller and not statistically significant for non-SGD related chemicals.

We highlight two additional findings that have policy implications. First, we find no evidence that the number of exceedances of the legally binding threshold for contaminants (i.e., the Maximum Contaminant Level (MCL)) has increased (Fig. 3). However, we do find a 13% increase in samples that exceed public health goals (i.e., MCL goals). In other words, while the contaminant increases are not large enough to trigger MCL violations from the state water authority, they may still have measurable health impacts. This echoes work that finds the benefit-cost ratio of current US water regulations to be uncertain once a more comprehensive set of regulation

Table 2
Water Quality Impacts of SGD Chemicals.

	A. Water Quality Impacts of Drilled Well Bores			
Sample	SGD Chemicals			Non-SGD
Dep. Var.	Log Result	Detection	Std. Result	Log Result
Bores, <0.5km	0.0133**	0.0587***	0.0840	0.00245
	(0.00675)	(0.0166)	(0.0716)	(0.00417)
Bores, 0.5-1km	0.00907**	0.0263***	0.0912**	−0.00280
	(0.00413)	(0.00965)	(0.0365)	(0.00230)
Bores, 1-2km	−0.000347	2.26e-05	0.0273**	0.000364
	(0.000772)	(0.00209)	(0.0118)	(0.000468)
Bores, 2-3km	−0.000300	0.00146	−0.0135*	−0.000255
	(0.000618)	(0.00197)	(0.00740)	(0.000449)
Bores, 3-4km	0.000148	0.000737	0.0103*	0.000324
	(0.000528)	(0.00164)	(0.00618)	(0.000337)
Bores, 4-5km	−0.000247	−0.00250*	0.00408	−0.000857
	(0.000427)	(0.00149)	(0.00585)	(0.000537)
Obs.	69,237	69,237	65,573	102,370
	B. Heterogeneity & Placebo Tests (SGD Chemicals)			
Dep. Var.: Log Result	Uphill (A) vs.	Produced (A) vs.	Future	Permitted
Threat Type:	Downhill	Never Produced	Drilling	Wells
Type A Bores, <1km	0.0101**	0.0131*		
	(0.00448)	(0.00730)		
Type B Bores, <1km	0.00497	0.00555		
	(0.00321)	(0.00402)		
Bores, Next 180 days, <1km			0.00587	
			(0.00393)	
Permitted Bores, <1km				0.00642
				(0.00499)
Obs.	69,237	69,237	69,237	69,237

Note: Table presents water quality impacts of SGD. Each column is a separate regression. The estimation sample consists of either SGD or non-SGD related water measurements from ground water-based community water systems with any water source within 10 km of any gas well. In panel A, the main regressors of interest are *drilled* well bores (at various distances to the water source). Across columns, we vary the sample (SGD or non-SGD related) and the dependent variable. Panel B re-estimates the specification in column 1 of panel A, except (1) it does not separate out well bores drilled within 0.5 and 1 km, and (2) either distinguishes well bores within 1 km as being Type A (uphill or producing) or Type B (downhill or never producing), or (3) adds additional variables for which we would expect no impact (future drilling or permitted well bores). Impacts at 1 km for "Future Drilling" and "Permitted Wells" in panel B are not shown. Robust standard errors in parentheses are clustered at the CWS level. *** $p < 0.01$, ** $p < 0.05$, * $p < 0.1$.

benefits are included (Keiser et al., 2019). Second, the estimated impacts from water quality monitors are somewhat larger, suggesting that public water systems are at least partially successful at mitigating the impacts of water contaminants.

Our results clearly support the hypothesis that water quality has been compromised by shale gas operations. The magnitude of the contamination, however, is less clear. Several chemicals measured in the USGS water monitoring data are not present in the public drinking water data (e.g. bromides and chlorides) because they are not regulated under the Safe Drinking Water Act. In fact, 97.5 percent of SGD chemicals listed in the aforementioned EPA report are not sampled by public drinking water systems due to the same reason. Moreover, our estimated impacts examine the cumulative impact of drilling on water quality since we cannot assign "gestation periods" to water samples as we do for infants. These considerations indicate that the cumulative drinking water quality impacts based on measurements of regulated contaminants are likely understated. This has implications for the interpretation of our results and policy, a point we return to in later discussion.

Infant Health Impacts We found robust evidence that public drinking water quality was compromised by shale gas development near water sources, which leads us to investigate the potential for health impacts. We present the average impacts of increasing the number of drilled wells on health outcomes in Table 3 with fixed effects for the public water system (panel A) and mother fixed effects (panel B).[24] In all regressions, we control for maternal characteristics, pregnancy risks, temperature and precipitation, number of disinfectant byproduct and coliform MCL violations, number of well bores drilled <1 km of the residence, and month-by-year fixed effects described in Section 3. Standard errors are clustered at the level of the fixed effect. The main estimates are plotted in Fig. 4.

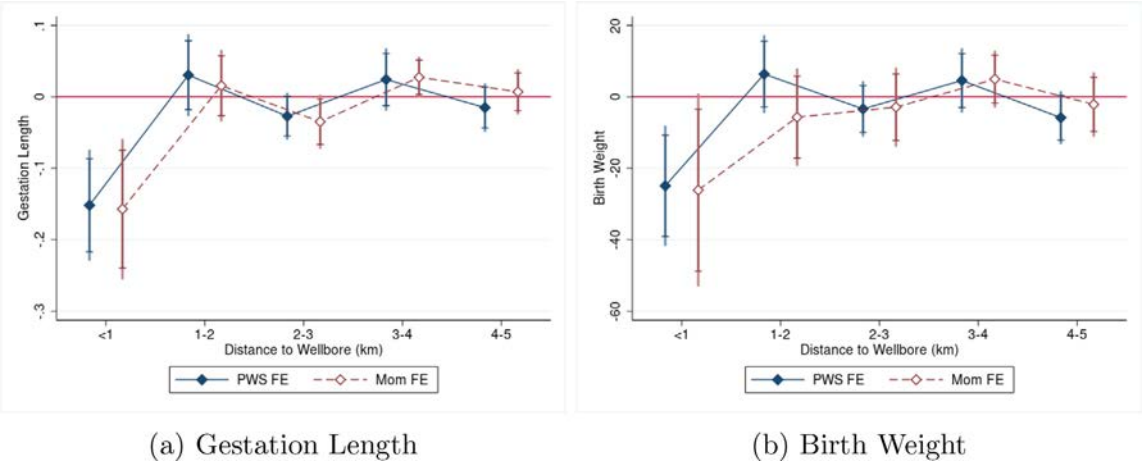
Estimation of the CWS and mother fixed effects (FE) models find fairly precise impacts of drilling within 1 km on gestation length — each gas well drilled within 1 km of an infant's water source during pregnancy reduces gestation length by between 0.13 weeks

[24] Only within-1 km impacts are shown in Table 3. The estimated impacts at all distances are presented in Appendix Table 8.3.7.

Table 3
Within-Gestation Drilling Birth Impacts.

	A. Water System (CWS) Fixed Effects			
Dep. Var.:	Gestation Length	Birth Weight	Premature	Low Birth Weight
Bores, <1km	−0.152***	−24.92***	0.0104**	0.00850*
	(0.0395)	(8.593)	(0.00485)	(0.00449)
Obs.	325,419	325,419	325,419	325,419
Mean	38.56	3292	0.0952	0.0772
	B. Mother Fixed Effects			
Dep. Var.:	Gestation Length	Birth Weight	Premature	Low Birth Weight
Bores, <1km	−0.157***	−26.10*	0.0152**	0.0123*
	(0.0502)	(13.78)	(0.00750)	(0.00720)
Obs.	152,944	152,944	152,944	152,944
Mean	38.40	3267	0.114	0.0924

Note: Table presents estimated impacts of bores drilled within 1 km of CWS sources on birth outcomes relative to well bores drilled between 5 and 10 km. Each column represents a separate regression, where the mean of the dependent variable is provided in the last row. The impacts of drilling in areas between 1 and 5 km from the source are included in the regressions, but not shown. All regressions control for maternal characteristics, pregnancy risks, temperature and precipitation, # of coliform and disinfectant by-product MCL violations, # of bores drilled <1km of the residence, and fixed effects for the month-of-year and for the water system. Panel B includes fixed effects for the mother. The estimation sample is composed of infants on ground water-sourced community water systems exposed to SGD either within 10 km of their water source or residence. Standard errors are clustered at the level of the fixed effect.



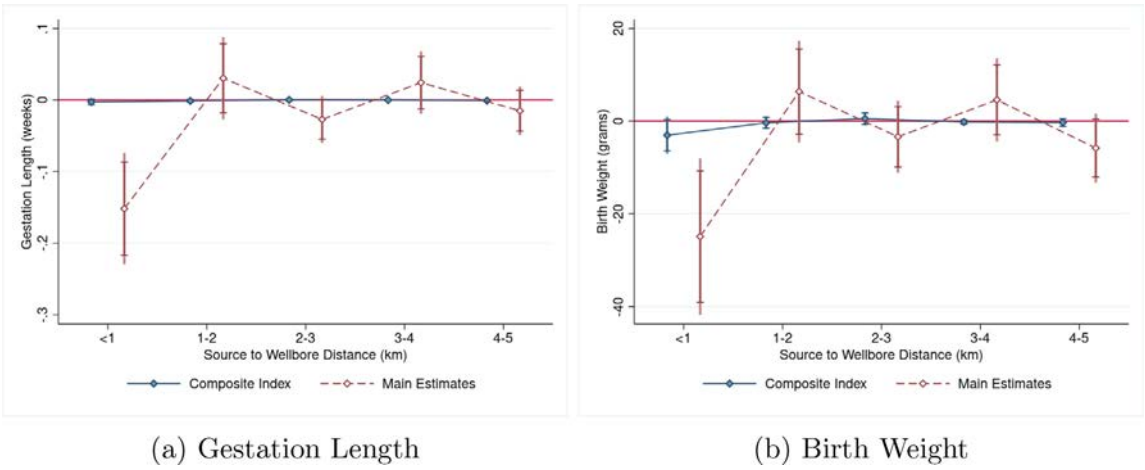
(a) Gestation Length (b) Birth Weight

Fig. 4. Birth Impacts of Drilling within Gestation.

(Mom FE, $p < 0.05$) to 0.15 weeks (CWS FE, $p < 0.01$). In terms of birth weight, each well bore decreases birth weight by 24.9 g ($p < 0.01$) when controlling for CWS fixed effects and by 26.1 g with the inclusion of mother fixed effects ($p < 0.1$).[25]

Researchers commonly use binary metrics of whether births are preterm, meaning that the fetus had a gestation length of less than 37 weeks, and whether birth weight is at least 2500 g, below which is considered a low birth weight infant. These thresholds denote levels at which medical interventions are often necessary, and provide outcomes that are easier to assign economic costs to in a cost-benefit assessment. We examine these threshold outcomes in the last two columns of Table 3. Impacts on the incidence of prematurity range from 1.0 pp and 1.5 pp ($p < 0.05$). Given an average incidence of prematurity of 9.5 percent for the CWS FE sample and 11 percent for the Mom FE sample, these effects translate to about an 11–13 percent increase in chance of preterm birth. The increased incidence of low birth weight is respectively 0.85 and 1.2 pp for the CWS and mother fixed effects models ($p < 0.10$), which

[25] Estimates with CWS fixed effects using the mother FE sample are comparable. Results are available from the authors upon request.



(a) Gestation Length (b) Birth Weight

Fig. 5. Impact of Drilling on Composite Index of Mother Characteristics *Note:* Figure plots the impact of drilling on a projection of birth outcomes on maternal characteristics and compares it to our main estimates of the birth impact. Specifically, we regress birth outcomes onto maternal characteristics, predict the outcomes based on thes characteristics, and then use the predicted outcomes as the dependent variable in our main specifications of interest.

also translate to an effect of around 11 to 13 percent.[26] Our main estimates with CWS fixed effects are robust to two-way clustering on CWS and birth month-of-year.

To contextualize the magnitude of our findings, Grossman and Slusky (2019) find an 8-gram reduction in average birth weight (BW) for the crisis in Flint, Michigan and Flynn and Marcus (2021) find Clean Water Act grants increased BW by 8-grams. For low birth weight (LBW) and preterm birth (PTB), Marcus (2021) find exposure to a leaking underground storage tank during gestation increases the probability of LBW and PTB by 7–8 percent, Dave and Yang (2020) find increased lead in Newark, NJ drinking water increased LBW and PTB by 14–22 percent, and DiSalvo and Hill (2019) find increases in LBW and PTB of 6 and 10.2 percent, respectively, in response to large increases in water contamination below regulatory limits. Related literature on residential proximity to SGD and infant health also finds an ~25 percent increase in chance of LBW (Currie et al., 2017; Hill, 2018). Considering the quantified impacts of neonatal health on future outcomes discussed earlier, the magnitudes of our estimated effects are meaningful.

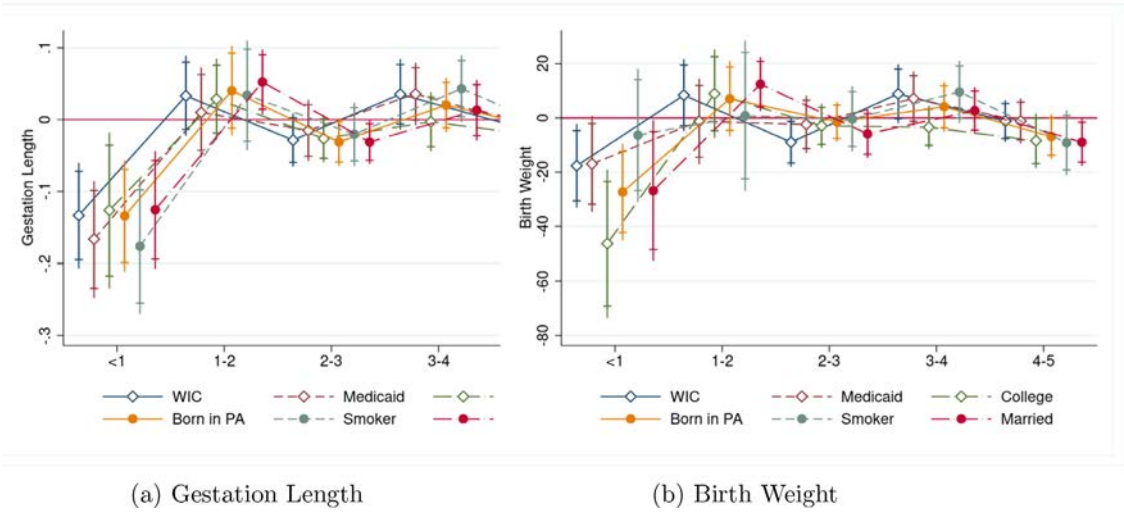
5. Robustness and heterogeneity of effects

This section evaluates the robustness of our estimated impacts with placebo tests and heterogeneity analysis. We assess whether impacts are driven by compositional changes reflecting the types of mothers who choose to have children or migration/sorting. We also evaluate the extent to which our estimates are driven by correlated changes in environmental nuisances in areas with drilling. We explore heterogeneity of impacts based maternal characteristics and the timing of drilling impacts. Additional robustness checks are presented in the appendix, including the effect of limiting to singleton births, alternative imputations for missing drilling dates, and reverse causality.

Various behavioral responses are important to consider when interpreting our results. In response to environmental risks, exposed groups may switch to bottled water (Graff Zivin et al., 2011; Wrenn et al., 2016), alter fertility decisions (Kearney and Wilson, 2018), or move (Banzhaf and Walsh, 2008). If mothers engage in such avoidance measures, then our estimates might be driven by changes in sample composition in response to gas well development. We first test whether our results reflect compositional changes in the types of mothers who select into fertility near gas well development. We create a composite index of selection factors by projecting birth outcomes on to maternal characteristics, and then use the predicted outcomes as the dependent variable in our main specifications of interest. If our estimates are not driven by selection, then we should not see evidence that drilling yields an effect in these projected outcomes. We plot the resulting coefficients on drilling at different distances to water sources in Fig. 5 along with our main effects for comparison. We do not find evidence that our effects are driven by maternal composition.

We also estimate our birth impacts using subgroups based on the mother's socioeconomic status (SES), such as educational attainment and Medicaid use. If individuals are indeed taking measures to mitigate exposure, then the largest negative health impacts should be concentrated among the low SES groups, those with arguably less ability to invest in costly avoidance measures (Currie et al., 2013; Neidell, 2009). Fig. 6 plots the impacts (using CWS FE) against exposure distance by SES sub-group. There is no evidence that infants born to more economically disadvantaged mothers are disproportionately affected. If anything, we actually find that college-educated women see somewhat larger impacts. If educational attainment is also an indicator of income, then this would suggest avoidance behavior is less likely to be an issue.

[26] preterm infants are mechanically exposed to fewer gas wells than those who are full term. Instrumenting for full gestational exposure (Currie et al., 2013) does not change our results.



(a) Gestation Length (b) Birth Weight

Fig. 6. Impacts by Mother's Socioeconomic Status.

Table 4
Probability of Moving.

Drilling Location:	Near Water Source		Near Residence	
Dep. Var.:	Switch CWS	Switch ZIP	Switch CWS	Switch ZIP
Bores, <1km	−0.00373	−0.00166	0.0202***	0.0149***
	(0.0121)	(0.00957)	(0.00763)	(0.00529)
Bores, 1-2km	−0.00686	−0.00741	−3.39e-05	0.000189
	(0.00569)	(0.00547)	(0.00298)	(0.00259)
Bores, 2-3km	0.00206	0.00148	−0.000984	0.00396*
	(0.00414)	(0.00450)	(0.00277)	(0.00238)
Bores, 3-4km	−0.00147	−0.000625	0.000247	0.000950
	(0.00236)	(0.00286)	(0.00204)	(0.00143)
Bores, 4-5km	0.000384	−0.00164	−0.00173	−0.00197
	(0.00247)	(0.00312)	(0.00174)	(0.00179)
Obs.	152,944	152,944	142,773	142,773
Mean	0.308	0.409	0.314	0.403

Note: Table regresses an indicator for whether a mother switched water systems or ZIP codes on the number of gas wells drilled within the vicinity of a CWS source ("Near Water Source") and the maternal address ("Near Residence") using the sample of mothers who we observe to have multiple births. The same set of controls as the specifications of Table 3 are used (see Table 3 for a description). Dependent variable means are provided in the last row. For all specifications, CWS fixed effects are included.

Next, we test for a sorting response using the sample of mothers for whom we observe multiple births. Table 4 estimates whether mothers are more likely to switch water systems or ZIP codes in response to an additional gas well drilled within the vicinity of their water source (columns 1 and 2) or near their residence (columns 3 and 4). The same set of controls used in the specifications of Table 3 are used, and CWS fixed effects are included for all specifications. We find no statistically significant impacts of gas well activity near water sources on the likelihood to move. Interestingly, we do find some evidence that well bores drilled in close proximity of the maternal residence increases the chance of moving. That mothers are not so responsive to drilling in our setting is potentially reasonable if SGD near water sources are less observable than that near the residence: the two types of exposure are highly, but not perfectly, correlated, and mothers may assume that piped public water protects them from contamination from the industry, as indicated by perceived risks being primarily associated with private ground water wells (Muehlenbachs et al., 2015). We test that our results are similar when we remove mothers whose residence is within 1 km of any gas well to ensure that selective migration in response to drilling near the residence is not driving our results.[27] These findings bolster our identification strategy using water source locations to define exposure. We infer from these tests that our estimated impacts of SGD on birth outcomes are not driven by differential sorting or fertility decisions by maternal SES in response to gas well development.

As Pennsylvania has had a history of coal mining dating back to the1920ı́s, one may be concerned that our estimates are picking up the impact of these activities, which often coincide with areas that are currently engaged in SGD.[28] To this end, we identify the

[27] Estimates are available from the authors upon request.
[28] See Appendix Fig. 7 for a map.

Table 5
Comparison of Well Bore Threats near Home versus Source.

Dep. Var.: Low Birth Weight Model:	Previous Literature	Full Sample: Near Home or Source	Sample Limit: Public Water	Add Controls	Add Water Source Threats
Any Well <1 km of Home	0.00745*	0.00876***	0.0124***	0.00661	0.00678*
	(0.00385)	(0.00303)	(0.00425)	(0.00401)	(0.00401)
Wells <1 km of Source					0.00707*
					(0.00402)
Observations	290,732	398,724	321,691	325,419	325,419

Note: Table compares our estimated impacts for low birth weight along various dimensions of SGD exposure. As in Table 3, missing spud dates are imputed for all specifications. Column 1 follows previous literature and uses a binary indicator for having any gas well within 1 km of the maternal residence prior to birth (2004–2013 years; residences within 10 km of shale gas wells). Column 2 expands to our full sample of 2003–2015 birth data and includes residences that are served by water systems within 10 km of a shale gas well. Column 3 limits to only those residences served by public water. Column 4 includes our main specification controls (adding maternal, weather, and permit controls) and expands the sample to include residences either served by public water or located within 10 km of any gas well. Column 5 additionally controls for our main threat variable of interest, the number of gas wells drilled during gestation.

public water systems that have any drinking water sources within 1, 5 and 10 km of historical coal seams or any coal seams (active or historical), and estimate our model on a sub-sample that removes infants who belong to any of those groups. Doing so reduces the potential for coal mining to explain our estimates. Results are stable regardless of how we limit the distance between coal seams and water sources (Appendix Table 8.3.9).[29]

In our analysis of the timing of drilling and water quality, we find that SGD-related contamination increases 90 days after the drilling of the well (spud date). The contamination continues for up to 270 days after drilling and then returns to baseline. With this in mind, we estimate the health impacts of the *cumulative* number of gas wells drilled before birth. As expected from our analysis on timing, the magnitudes of the impacts decrease, suggesting that it is *in utero* threats that matter the most.[30] Our current data on SGD stages, however, is limited (e.g. we do not observe the timing of fracking). We are therefore unable to identify the exact SGD processes (e.g., drilling, spills, hydraulic fracturing, production, casing failures, tank leaks) that are causing the health effects that we find. Our analysis, however, suggests that most of the impacts are concentrated in the period immediately after drilling. Future work should explore the specific weaknesses of the process causing groundwater contamination.

We perform additional robustness checks available in the Appendix. Well bores drilled *after* an infant is born do not impact birth outcomes (Appendix Table 8.3.10), and the impacts on singleton births are similar. In Appendix Table 8.3.11, we show how various forms of drilling date imputation changes our results. The absence of imputation increases the magnitude of our results and other forms of imputation do not change the qualitative conclusions. Together, these results lead us to believe that unconventional drilling has had an independent impact on birth outcomes through contamination of public drinking water.

6. Discussion

We set out to examine the infant health impacts of water pollution using exogenous variation in water quality caused by shale gas development near drinking water sources. Our findings indicate that drilling near an infant's public water source yields poorer birth outcomes and more SGD-related contaminants in public drinking water. We discuss the implications of our results for shale gas regulation and drinking water policy as well as their limitations.

Shale gas development creates multiple "first stage" effects on environmental quality: light, noise, air, and water pollution (Black et al., 2021; Bonetti et al., 2021; Boslett et al., 2021; Casey et al., 2018; Hill and Ma, 2017; Hill, 2018; McCawley, 2017; Zhang et al., 2019). It is important for policy to reconcile the shale gas and infant health literature and compare residential proximity health effects (Currie et al., 2017; Hill, 2018) to those measured in this paper from public water system source proximity. Table 5 begins by replicating the previous literature on the proximity impacts of SGD in column 1 using a binary indicator for having any well within 1 km of the maternal residence prior to birth. Each subsequent column progressively alters the sample (column 2 and 3) or control variables (column 4) to be consistent with our main specification. The final column, which includes both source and residential proximity exposures to SGD, finds that each additional well drilled during gestation within 1 km of a public water source increases the risk of low birth weight by about 0.71 pp and any well drilled within 1 km of the residence increases low birth weight by 0.68 pp.[31]

These results, combined with the current epidemiological and economic literature, are supporting the following conclusions. Shale gas development influences the environment by reducing ambient air quality and increasing ground water contamination. The effects for air quality (residential proximity) persist for multiple years after drilling and potentially at larger distances from the

[29] We perform this check for our water quality model as well and find similar results. Estimates are available from the authors upont request.
[30] These results are presented in Appendix Table 8.3.8.
[31] The results here are slightly attenuated to those reported in Table 3 due to a change from controlling for # of wells within 1 km of the residence to any well within 1 km of the residence. They are qualitatively similar, with 0.68 pp translating to a 9% increase in LBW compared to our preferred estimate of 11% in Table 3.

residence (Currie et al., 2017; Hill, 2018).[32] The separate effects of water pollution from drilling at source locations are sustained primarily during gestation (i.e., these effects are more short term and less persistent). A policy to directly limit the health impacts from water pollution is to require a minimum "setback" distance at which drilling operations can take place near water sources. As minor reductions in surface area for extraction does little to obstruct access to subsurface resources with the innovations in horizontal drilling, modest setback requirements are likely to yield significant increases in benefits without the accompanying increase in economic costs.

With respect to the benefits of water quality control, we believe our results provide compelling evidence that water pollution causes negative infant health effects even at mild levels (i.e. at levels that do not trigger regulatory violations). The magnitudes of our infant health effects support water pollution as a potentially important contributor to various health and socioeconomic disparities in adulthood. The implied elasticity of health impacts with respect to *regulated* water contaminants in this paper, however, is likely to be an upper bound since we only observed SGD contaminants that are currently monitored under the Safe Drinking Water Act. The same issue also limits our ability to directly apply these results to re-assess drinking water policy.

Co-pollutants that are unobserved (either because the scientific community does not know of their existence or because sampling is not required) imply that our estimate of the SGD impacts on drinking water are understated. It also implies that the associated health impacts may be either due to an increase in observed, regulated contaminants or a correlated increase in unregulated contaminants that we do not observe. Since monetizing health impacts for benefit-cost analysis requires information on the effects of specific contaminants, our results are thus unable to speak to whether regulation should increase the stringency of existing contaminants or expand the set of regulated contaminants. Future work to collect and assess the health impacts of a more comprehensive set of water chemicals would be fruitful. It would be very expensive, however, for drinking water systems to regulate each of the 2500 suspected SGD contaminants. Our study supports a simple policy solution to confront the potentially massive number of SGD chemicals in water: mitigate water contamination at the source to prevent adverse infant health effects mediated through water pollution.

7. Conclusion

This study seeks to understand and quantify the impacts of drinking water quality on infant health while exploiting exogenous changes in water quality induced by shale gas development (SGD). Our novel data links together the locations of new mothers' residences, community water system's water source locations, and the locations of shale gas wells in Pennsylvania. We find robust and consistent evidence of an effect of shale gas development within 1 km of ground water sources on water quality. Importantly, we also find consistent evidence that water quality changes due to SGD produces measurable impacts on birth outcomes: the incidences of preterm birth and low birth weight increase by between 9 and 13 percent, respectively. We determine that our results are unlikely to be driven by correlated air quality changes associated with congestion/traffic or coal, nor are they driven by maternal mobility and fertility decisions in response to SGD. Our infant health impacts are similar in magnitude to air pollution studies, such as EZ-Pass reducing LBW and PTB by ~10% (Currie and Walker, 2011) or living downwind of coal plant increasing LBW by 6.5% (Yang et al., 2017).

Over three decades have passed since the enactment of federal regulations to protect our water resources. Despite successfully reducing water contamination in public drinking water systems, 9 to 45 million people, representing 4 to 28% of the US population, were affected by health-based violations between 1982 and 2015 (Allaire et al., 2018). Concurrently, SGD has been taking place near a non-trivial portion of the US population and has real potential to threaten water resources and health: 17.6 million people live within a mile of an oil or gas well (Czolowski et al., 2017) and 8.6 million people are served by water systems with sources within a mile of a well (U.S. EPA, 2016).

The paper's findings indicate large social costs of water pollution through health and highlight drinking water as a specific exposure pathway for an emerging industry with little environmental regulation. In particular, our estimates reveal that SGD increases regulated contaminants found in drinking water, but not enough to trigger regulatory violations, and that these operations yield measurable health impacts that could either be due to increases in regulated water contaminants below the threshold or unregulated water contaminants that we, unfortunately, cannot observe. Future work to identify the sources of water contamination is needed to determine whether net benefits would arise from increasing the stringency of currently-regulated contaminants or expanding the set of regulated contaminants. Nonetheless, these findings suggest that the external costs of our water and resulting birth impacts are non-trivial. Researchers have shown that neonatal health has a significant effect on both mortality within one year and mortality up to age 17 (Oreopoulos et al., 2008). Further, these outcomes are strong predictors of a host of longer term outcomes, such as human capital accumulation, welfare take-up, earnings, and labor force participation (Black et al., 2007; Figlio et al., 2014; Johnson and Schoeni, 2011; Oreopoulos et al., 2008). Motivated by water pollution's effects on infant health and the potential impacts on long-run measures of well-being, our work provides an impetus for the re-evaluation of existing drinking water policies and possibly the regulation of the shale gas industry.

Declaration of No Conflict of Interest

We have no relevant or material financial interests that relate to the research described in "Drinking Water, Fracking, and Infant Health."

[32] Hill (2018) showed reported air pollution persisting for up to 5 years after the drilling date. The residential exposure may also capture other proximity impacts such as light, noise, stress, traffic, or stress associated with nearby drilling. However, air quality does appear to be a large externality and a plausible one that would have impacts on infant health.

Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jhealeco.2022.102595.

CRediT authorship contribution statement

Elaine L. Hill: Conceptualization, Formal analysis, Data curation, Methodology, Writing – original draft, Funding acquisition. **Lala Ma:** Conceptualization, Formal analysis, Data curation, Methodology, Writing – original draft.

References

Aizer, A., Currie, J., Simon, P., Vivier, P., 2018. Do low levels of blood lead reduce children's future test scores? Am. Econ. J. 10 (1), 307–341.
Alexander, D., Schwandt, H., 2019. The Impact of Car Pollution on Infant and Child Health: Evidence from Emissions Cheating. IZA Discussion Paper No. 12427.
Allaire, M., Wu, H., Lall, U., 2018. National trends in drinking water quality violations. Proc. Natl. Acad. Sci. 115 (9), 2078–2083.
Allcott, H., Keniston, D., 2017. Dutch disease or agglomeration? The local economic effects of natural resource booms in modern America. Rev. Econ. Stud. 85 (2), 695–731.
Almond, D., Currie, J., 2011. Human capital development before age five. Handb. Lab. Econ. 4 (Part B), 1315–1486.
Almond, D., Currie, J., Duque, V., 2018. Childhood circumstances and adult outcomes: act II. J. Econ. Lit. 56 (4), 1360–1446.
Almond, D., Edlund, L., Palme, M., 2009. Chernobyl's subclinical legacy: prenatal exposure to radioactive fallout and school outcomes in Sweden. Q. J. Econ. 124 (4), 1729–1772.
Anderson, D.M., Charles, K.K., Rees, D.I., 2020. Re-examining the contribution of public health efforts to the decline in urban mortality. Am. Econ. J. 143–175.
Banzhaf, S.H., Walsh, R.P., 2008. Do people vote with their feet? An empirical test of Tiebout's mechanism. Am. Econ. Rev. 98 (3), 843–863.
Bartik, A.W., Currie, J., Greenstone, M., Knittel, C.R., 2019. The local economic and welfare consequences of hydraulic fracturing. Am. Econ. J. 11 (4), 105–155.
Beach, B., Ferrie, J., Saavedra, M., Troesken, W., 2016. Typhoid fever, water quality, and human capital formation. J. Econ. Hist. 76 (1), 41–75.
Bennear, L.S., Jessoe, K.K., Olmstead, S.M., 2009. Sampling out: regulatory avoidance and the total coliform rule. Environ. Sci. Technol. 43 (14), 5176–5182.
Black, K.J., Boslett, A.J., Hill, E.L., Ma, L., McCoy, S.J., 2021. Economic, environmental, and health impacts of the fracking boom. Annu. Rev. Resour. Econ. 13.
Black, S.E., Devereux, P.J., Salvanes, K.G., 2007. From the cradle to the labor market? The effect of birth weight on adult outcomes. Q. J. Econ. 122 (1), 409–439.
Bonetti, P., Leuz, C., Michelon, G., 2021. Large-sample evidence on the impact of unconventional oil and gas development on surface waters. Science 373 (6557), 896–902.
Boslett, A., Hill, E., Ma, L., Zhang, L., 2021. Rural light pollution from shale gas development and associated sleep and subjective well-being. Resour. Energy Econ. 64, 101220.
Brainerd, E., Menon, N., 2014. Seasonal effects of water quality: the hidden costs of the Green Revolution to infant and child health in India. J. Dev. Econ. 107, 49–64.
Casey, J.A., Wilcox, H.C., Hirsch, A.G., Pollak, J., Schwartz, B.S., 2018. Associations of unconventional natural gas development with depression symptoms and disordered sleep in Pennsylvania. Sci. Rep. 8 (1), 11375.
Chay, K., Greenstone, M., 2003. The impact of air pollution on infant mortality: evidence from geographic variation in pollution shocks induced by a recession. Q. J. Econ. 118 (3), 1121–1167.
Chetty, R., Hendren, N., 2018. The impacts of neighborhoods on intergenerational mobility I: childhood exposure effects. Q. J. Econ. 133 (3), 1107–1162.
Cunha, F., Heckman, J., 2007. The technology of skill formation. Am. Econ. Rev. 97 (2), 31–47.
Currie, J., Graff Zivin, J., Meckel, K., Neidell, M., Schlenker, W., 2013. Something in the water: contaminated drinking water and infant health. Can. J. Econ. 46 (3), 791–810.
Currie, J., Greenstone, M., Meckel, K., 2017. Hydraulic fracturing and infant health: new evidence from Pennsylvania. Sci. Adv. 3 (12), e1603021.
Currie, J., Neidell, M., 2005. Air pollution and infant health: what can we learn from California's recent experience? Q. J. Econ. 120 (3), 1003–1030.
Currie, J., Walker, R., 2011. Traffic congestion and infant health: evidence from E-ZPass. Am. Econ. J. 3 (1), 65–90.
Cutler, D., Miller, G., 2005. The role of public health improvements in health advances: the twentieth-century United States. Demography 42 (1), 1–22.
Czolowski, E.D., Santoro, R.L., Srebotnjak, T., Shonkoff, S.B., 2017. Toward consistent methodology to quantify populations in proximity to oil and gas development: a national spatial analysis and review. Environ. Health Perspect. 125 (8), 086004.
Darrah, T.H., Vengosh, A., Jackson, R.B., Warner, N.R., Poreda, R.J., 2014. Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales. Proc. Natl. Acad. Sci. 111 (39), 14076–14081.
Dave, D.M., Yang, M., 2020. Lead in Drinking Water and Birth Outcomes: A Tale of Two Water Treatment Plants. Technical Report. National Bureau of Economic Research.
Deryugina, T., Heutel, G., Miller, N.H., Molitor, D., Reif, J., 2019. The mortality and medical costs of air pollution: evidence from changes in wind direction. Am. Econ. Rev. 109 (12), 4178–4219.
Deschênes, O., Greenstone, M., Guryan, J., 2009. Climate change and birth weight. Am. Econ. Rev. 99 (2), 211–217.
Deziel, N.C., Brokovich, E., Grotto, I., Clark, C.J., Barnett-Itzhaki, Z., Broday, D., Agay-Shay, K., 2020. Unconventional oil and gas development and health outcomes: a scoping review of the epidemiological research. Environ. Res. 109124.
DiSalvo, R., Hill, E., 2019. The Effects of Drinking Water Contamination on Birth Outcomes: new estimates from drinking water samples. Working Paper.
Ebenstein, A., 2010. The consequences of industrialization: evidence from water pollution and digestive cancers in China. Rev. Econ. Stat. 94 (1), 186–201.
EPA, U., 2015. Information about public water systems. https://www.epa.gov/dwreginfo/information-about-public-water-systems. Accessed: 2021-11-16.
Ferrie, J.P., Rolf, K., Troesken, W., 2012. Cognitive disparities, lead plumbing, and water chemistry: prior exposure to water-borne lead and intelligence test scores among world war two us army enlistees. Econ. Hum. Biol. 10 (1), 98–111.
Feyrer, J., Mansur, E.T., Sacerdote, B., 2017. Geographic dispersion of economic shocks: evidence from the fracking revolution. Am. Econ. Rev. 107 (4), 1313–1334.
Figlio, D., Guryan, J., Karbownik, K., Roth, J., 2014. The effects of poor neonatal health on children's cognitive development. Am. Econ. Rev. 104 (12), 3921–3955.
Flynn, P., Marcus, M.M., 2021. A Watershed Moment: The Clean Water Act and Infant Health. Technical Report. National Bureau of Economic Research.
Graff Zivin, J., Neidell, M., Schlenker, W., 2011. Water quality violations and avoidance behavior: evidence from bottled water consumption. Am. Econ. Rev. 101 (3), 448–453.
Grooms, K.K., 2016. Does water quality improve when a safe drinking water act violation is issued? A study of the effectiveness of the SDWA in California. BE J. Econ. Anal. Policy 16 (1), 1–23.
Grossman, D.S., Slusky, D.J., 2019. The impact of the flint water crisis on fertility. Demography 56 (6), 2005–2031.
Grossman, M., 1972. On the concept of health capital and the demand for health. J. Polit. Economy 80 (2), 223–255.
Grossman, M., 1999. The Human Capital Model of the Demand for Health. Working Paper 7078. National Bureau of Economic Research.
Guilfoos, T., Kell, D., Boslett, A., Hill, E.L., 2017. The economic and health effects of the 2014 chemical spill in the Elk River, West Virginia. Am. J. Agric. Econ. 100 (2), 609–624.
Hausman, C., Kellogg, R., 2015. Welfare and distributional implications of shale gas. Brookings Pap. Econ. Act..
Heckman, J.J., 2007. The economics, technology, and neuroscience of human capability formation. Proc. Natl. Acad. Sci. 104 (33), 13250–13255.
Hill, E., Ma, L., 2017. Shale gas development and drinking water quality. Am. Econ. Rev. 107 (5), 522–525.
Hill, E.L., 2013. The Impact of Oil and Gas Extraction on Infant Health in Colorado. Working Paper. Charles H. Dyson School of Applied Economics and Management, Cornell University.

Hill, E.L., 2018. Shale gas development and infant health: evidence from Pennsylvania. J. Health Econ. 61 (2018), 134–150.
Isen, A., Rossin-Slater, M., Walker, W.R., 2017. Every breath you take-every dollar you'll make: the long-term consequences of the clean air act of 1970. J. Polit. Economy 125 (3), 848–902.
Johnson, R.C., Schoeni, R.F., 2011. The influence of early-life events on human capital, health status, and labor market outcomes over the life course. BE J. Econ. Anal. Policy 11 (3).
Johnston, J.E., Lim, E., Roh, H., 2018. Impact of upstream oil extraction and environmental public health: a review of the evidence. Sci. Total Environ..
Kearney, M.S., Wilson, R., 2018. Male earnings, marriageable men, and nonmarital fertility: evidence from the fracking boom. Rev. Econ. Stat. 100 (4), 678–690.
Keiser, D.A., Kling, C.L., Shapiro, J.S., 2019. The low but uncertain measured benefits of us water quality policy. Proc. Natl. Acad. Sci. 116 (12), 5262–5269.
Knittel, C.R., Miller, D.L., Sanders, N.J., 2016. Caution, drivers! children present: traffic, pollution, and infant health. Rev. Econ. Stat. 98 (2), 350–366.
Kuwayama, Y., Olmstead, S.M., Krupnick, A., 2013. Water Resources and Unconventional Fossil Fuel Development: Linking Physical Impacts to Social Costs. Resources for the Future Discussion Paper 13-34.
Lai, W., 2017. Pesticide use and health outcomes: evidence from agricultural water pollution in China. J. Environ. Econ. Manage. 86, 93–120.
Marcus, M., 2021. Going beneath the surface: petroleum pollution, regulation, and health. Am. Econ. J. 13 (1), 1–37.
Mason, C.F., Muehlenbachs, L.A., Olmstead, S.M., 2015. The economics of shale gas development. Annu. Rev. Resour. Econ. 7 (1), 269–289.
McCawley, M.A., 2017. Does increased traffic flow around unconventional resource development activities represent the major respiratory hazard to neighboring communities?: knowns and unknowns. Curr. Opin. Pulm. Med. 23 (2), 161–166.
McKinnish, T., Rees, D.I., Langlois, P.H., 2014. Seasonality in birth defects, agricultural production and urban location. Econ. Hum. Biol. 15, 120–128.
Muehlenbachs, L., 2015. A dynamic model of cleanup: estimating sunk costs in oil and gas production. Int. Econ. Rev. 56 (1), 155–185.
Muehlenbachs, L., Spiller, E., Timmins, C., 2015. The housing market impacts of shale gas development. Am. Econ. Rev. 105 (12), 3633–3659.
National Energy Technology Laboratory, N., 2013. Modern shale gas development in the United States: an update.
Neidell, M., 2009. Information, avoidance behavior, and the health effect of ozone on asthma hospitalizations. J. Hum. Resour. 44 (2), 450–478.
Oreopoulos, P., Stabile, M., Walld, R., Roos, L., 2008. Short-, medium-, and long-term consequences of poor infant health, an analysis using siblings and twins. J. Hum. Resour. 43 (1), 88–138.
Royer, H., 2009. Separated at girth: US twin estimates of the effects of birth weight. Am. Econ. J. 1 (1), 49–85.
Sanders, N.J., Stoecker, C., 2015. Where have all the young men gone? Using sex ratios to measure fetal death rates. J. Health Econ. 41 (May 2015), 30–45.
Schlenker, W., Roberts, M.J., 2009. Nonlinear temperature effects indicate severe damages to us crop yields under climate change. Proc. Natl. Acad. Sci. 106 (37), 15594–15598.
Schlenker, W., Walker, W.R., 2016. Airports, air pollution, and contemporaneous health. Rev. Econ. Stud. 83 (2), 768–809.
Shanafield, M., Cook, P.G., Simmons, C.T., 2019. Towards quantifying the likelihood of water resource impacts from unconventional gas development. Groundwater 57 (4), 547–561.
Shrestha, N., Chilkoor, G., Wilder, J., Gadhamshetty, V., Stone, J.J., 2017. Potential water resource impacts of hydraulic fracturing from unconventional oil production in the Bakken shale. Water Res. 108, 1–24.
Street, B., 2018. The Impact of Economic Opportunity on Criminal Behavior: Evidence from the Fracking Boom.
Sun, Y., Wang, D., Tsang, D.C., Wang, L., Ok, Y.S., Feng, Y., 2019. A critical review of risks, characteristics, and treatment strategies for potentially toxic elements in wastewater from shale gas extraction. Environ. Int. 125, 452–469.
Torres, L., Yadav, O.P., Khan, E., 2016. A review on risk assessment techniques for hydraulic fracturing water and produced water management implemented in onshore unconventional oil and gas production. Sci. Total Environ. 539, 478–493.
Tustin, A.W., Hirsch, A.G., Rasmussen, S.G., Casey, J.A., Bandeen-Roche, K., Schwartz, B.S., 2017. Associations between unconventional natural gas development and nasal and sinus, migraine headache, and fatigue symptoms in Pennsylvania. Environ. Health Perspect. 125 (2), 189–197.
U.S. EPA, E.P.A., 2016. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States. Technical Report. https://www.epa.gov/hfstudy.
Wrenn, D.H., Klaiber, H.A., Jaenicke, E.C., 2016. Unconventional shale gas development, risk perceptions, and averting behavior: evidence from bottled water purchases. J. Assoc. Environ. Resour. Econ. 3 (4), 779–817.
Yang, M., Bhatta, R.A., Chou, S.-Y., Hsieh, C.-I., 2017. The impact of prenatal exposure to power plant emissions on birth weight: evidence from a Pennsylvania power plant located upwind of New Jersey. J. Policy Anal. Manage. 36 (3), 557–583.
Zhang, R., Li, H., Khanna, N., Sullivan, D., Krupnick, A., Hill, E., 2019. Air pollution impacts of shale gas development in Pennsylvania.

ATTACHMENT C

STUDY 32

Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction

Robert B. Jackson[a,b,1], Avner Vengosh[a], Thomas H. Darrah[a], Nathaniel R. Warner[a], Adrian Down[a,b], Robert J. Poreda[c], Stephen G. Osborn[d], Kaiguang Zhao[a,b], and Jonathan D. Karr[a,b]

[a]Division of Earth and Ocean Sciences, Nicholas School of the Environment and [b]Center on Global Change, Duke University, Durham, NC 27708; [c]Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627; and [d]Geological Sciences Department, California State Polytechnic University, Pomona, CA 91768

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Horizontal drilling and hydraulic fracturing are transforming energy production, but their potential environmental effects remain controversial. We analyzed 141 drinking water wells across the Appalachian Plateaus physiographic province of northeastern Pennsylvania, examining natural gas concentrations and isotopic signatures with proximity to shale gas wells. Methane was detected in 82% of drinking water samples, with average concentrations six times higher for homes <1 km from natural gas wells ($P = 0.0006$). Ethane was 23 times higher in homes <1 km from gas wells ($P = 0.0013$); propane was detected in 10 water wells, all within approximately 1 km distance ($P = 0.01$). Of three factors previously proposed to influence gas concentrations in shallow groundwater (distances to gas wells, valley bottoms, and the Appalachian Structural Front, a proxy for tectonic deformation), distance to gas wells was highly significant for methane concentrations ($P = 0.007$; multiple regression), whereas distances to valley bottoms and the Appalachian Structural Front were not significant ($P = 0.27$ and $P = 0.11$, respectively). Distance to gas wells was also the most significant factor for Pearson and Spearman correlation analyses ($P < 0.01$). For ethane concentrations, distance to gas wells was the only statistically significant factor ($P < 0.005$). Isotopic signatures ($\delta^{13}C$-CH_4, $\delta^{13}C$-C_2H_6, and δ^2H-CH_4), hydrocarbon ratios (methane to ethane and propane), and the ratio of the noble gas ^4He to CH_4 in groundwater were characteristic of a thermally postmature Marcellus-like source in some cases. Overall, our data suggest that some homeowners living <1 km from gas wells have drinking water contaminated with stray gases.

carbon, hydrogen, and helium isotopes | groundwater contamination | geochemical fingerprinting | fracking | hydrology and ecology

Unconventional sources of gas and oil are transforming energy supplies in the United States (1, 2). Horizontal drilling and hydraulic fracturing are driving this transformation, with shale gas and other unconventional sources now yielding more than one-half of all US natural gas supply. In January of 2013, for instance, the daily production of methane (CH_4) in the United States rose to $\sim 2 \times 10^9$ m^3, up 30% from the beginning of 2005 (3).

Along with the benefits of rising shale gas extraction, public concerns about the environmental consequences of hydraulic fracturing and horizontal drilling are also growing (4, 5). These concerns include changes in air quality (6), human health effects for workers and people living near well pads (5), induced seismicity (7), and controversy over the greenhouse gas balance (8, 9). Perhaps the biggest health concern remains the potential for drinking water contamination from fracturing fluids, natural formation waters, and stray gases (4, 10–12).

Despite public concerns over possible water contamination, only a few studies have examined drinking water quality related to shale gas extraction (4, 11, 13). Working in the Marcellus region of Pennsylvania, we published peer-reviewed studies of the issue, finding no evidence for increased concentrations of salts, metals, or radioactivity in drinking water wells accompanying shale gas extraction (4, 11). We did find higher methane concentrations and less negative $\delta^{13}C$-CH_4 signatures, consistent with a natural gas source, in water for homeowners living <1 km from shale gas wells (4). Here, we present a more extensive dataset for natural gas in shallow water wells in northeastern Pennsylvania, comparing the data with sources of thermogenic methane, biogenically derived methane, and methane found in natural seeps. We present comprehensive analyses for distance to gas wells and ethane and propane concentrations, two hydrocarbons that are not derived from biogenic activity and are associated only with thermogenic sources. Finally, we use extensive isotopic data [e.g., $\delta^{13}C$-CH_4, δ^2H-CH_4, $\delta^{13}C$-C_2H_6, $\delta^{13}C$-dissolved inorganic carbon ($\delta^{13}C$-DIC), and δ^2H-H_2O] and helium analysis ($^4He/CH_4$) to distinguish among different sources for the gases observed (14–16).

Our study area (Figs. S1 and S2) is within the Appalachian Plateaus physiographic province (17, 18) and includes six counties in Pennsylvania (Bradford, Lackawanna, Sullivan, Susquehanna, Wayne, and Wyoming). We sampled 81 new drinking water wells from the three principle aquifers (Alluvium, Catskill, and Lock Haven) (Fig. S1) (11). We combined the data with results from 60 previously sampled wells in Pennsylvania (4) and included a few wells from the Genesee Formation in Otsego County of New York (4). The typical depth of drinking water wells in our study was 60–90 m (11). We also sampled a natural methane seep at Salt Springs State Park in Franklin Forks, Pennsylvania (N 41.91397, W 75.8663; Susquehanna County) to compare with drinking water from homes in our study, some located within a few kilometers of the spring.

Descriptions of the underlying geology, including the Marcellus Formation found 1,500–2,500 m underground, are presented in refs. 4 and 11 and Fig. S2. Previous researchers have characterized the region's geology and aquifers (19–23). Briefly, the two major bedrock aquifers are the Upper Devonian Catskill Formation, comprised primarily of a deltaic clastic wedge gray-green to gray-red sandstone, siltstone, and shale, and the underlying Lock Haven Formation, consisting of interbedded fine-grained sandstone, siltstone, and silty shale (19, 22, 24). The two formations can be as deep as ~1,000 m in the study area and have been exploited elsewhere for oil and gas historically. The sedimentary sequences are gently folded and dip shallowly (1–3°) to the east and south (Fig. S2), creating alternating exposures of synclines and anticlines at the surface (17, 23, 25). These formations are overlain by the Alluvium aquifer, comprised of unconsolidated glacial till, alluvium sediments, and postglacial deposits found primarily in valley bottoms (20, 22).

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[1]To whom correspondence should be addressed. E-mail: jackson@duke.edu.

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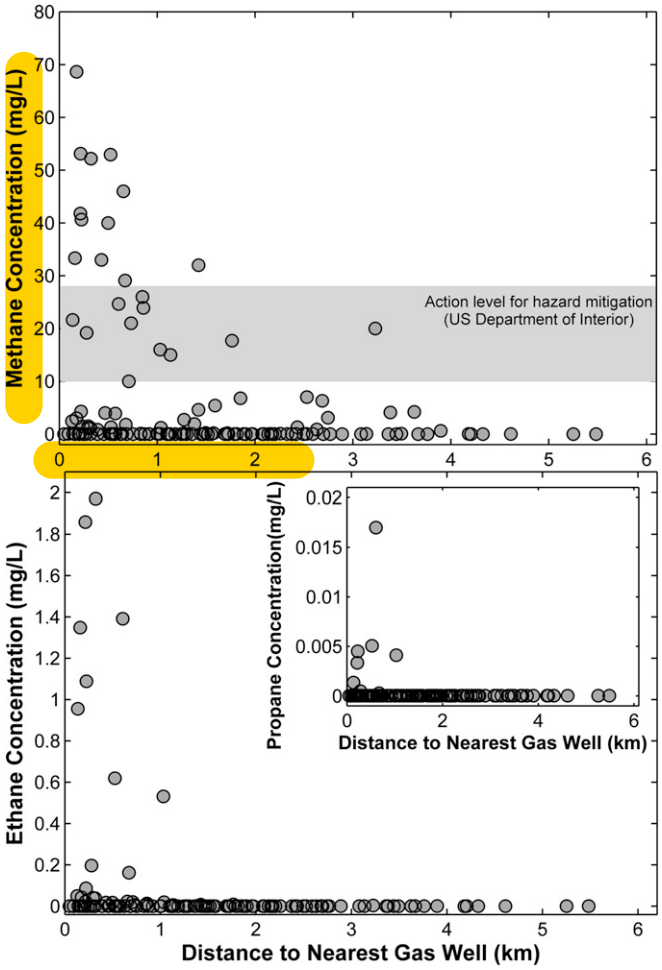

Fig. 1. Concentrations of (*Upper*) methane, (*Lower*) ethane, and (*Lower Inset*) propane (milligrams liter^{-1}) in drinking water wells vs. distance to natural gas wells (kilometers). The locations of natural gas wells were obtained from the Pennsylvania DEP and Pennsylvania Spatial Data Access databases (54). The gray band in *Upper* is the range for considering hazard mitigation recommended by the US Department of the Interior (10–28 mg CH_4/L); the department recommends immediate remediation for any value >28 mg CH_4/L.

Results and Discussion

Dissolved methane was detected in the drinking water of 82% of the houses sampled (115 of 141). Methane concentrations in drinking water wells of homes <1 km from natural gas wells (59 of 141) were six times higher on average than concentrations for homes farther away ($P = 0.0006$, Kruskal–Wallis test) (Fig. 1 and Fig. S3). Of 12 houses where CH_4 concentrations were greater than 28 mg/L (the threshold for immediate remediation set by the US Department of the Interior), 11 houses were within 1-km distance of an active shale gas well (Fig. 1). The only exception was a home with a value of 32 mg CH_4/L at 1.4-km distance.

Similar to the results for methane, concentrations of ethane (C_2H_6) and propane (C_3H_8) were also higher in drinking water of homes near natural gas wells (Fig. 1). Ethane was detected in 40 of 133 homes (30%; 8 fewer homes were sampled for ethane and propane than for methane). Propane was detected in water wells in 10 of 133 homes, all approximately <1 km from a shale gas well ($P = 0.01$) (Fig. 1, *Lower Inset*). Ethane concentrations were 23 times higher on average for homes <1 km from a gas well: 0.18 compared with 0.008 mg C_2H_6/L ($P = 0.001$, Kruskal–Wallis). Seven of eight C_2H_6 concentrations >0.5 mg/L were found <1 km from a gas well (Fig. 1), with the eighth point only 1.1 km away (Fig. 1). Moreover, the higher ethane concentrations all occurred in groundwater with methane concentrations >15 mg/L ($P = 0.003$ for the regression of C_2 and C_1) (Fig. S4), although not all higher methane concentration waters had elevated ethane.

Ratios of ethane to methane (C_2/C_1) and propane to methane (C_3/C_1) were much higher for homes within ~1 km of natural gas wells (Fig. 2). Our high C_3/C_1 samples were also an order of magnitude greater than in salt-rich waters from a natural methane seep at the nearby Salt Springs State Park (mean $[C_3]/[C_1]$ = 0.000029 and [C3] = 0.0022 mg/L for the salt spring samples). Because microbes effectively do not produce ethane or propane in the subsurface (26, 27), our observed values within ~1 km of drilling seem to rule out a biogenic methane source, and they are consistent with both wetter (higher $C_2 + C_3$ content) gases found in the Marcellus Formation and our earlier observation of methane in drinking water wells in the region (4).

Along with distance to gas wells (4), proximity to both valley bottom streams (i.e., discharge areas) (28) and the Appalachian Structural Front (ASF; an index for the trend in increasing thermal maturity and degree of tectonic deformation) has been suggested to influence dissolved gas concentrations. Of these factors, distance to gas wells was the dominant statistical factor in our analyses for both methane ($P = 0.0007$) (Table 1, multiple regression analysis) and ethane ($P < 0.005$) (Table 1). In contrast, neither distance to the ASF ($P = 0.11$) nor distance to valley bottom streams ($P = 0.27$) was significant for methane concentrations analysis using linear regression. For single correlation factors, distance to gas wells was again the dominant statistical term ($P = 0.0003$ and $P = 0.001$ for Pearson and Spearman coefficients, respectively). Distance to the ASF was slightly significant by Pearson and Spearman correlation analyses ($P = 0.04$ and $P = 0.02$, respectively), whereas distance to valley bottom streams was slightly significant only for the nonparametric Spearman analysis ($P = 0.22$ for Pearson and $P = 0.01$ for Spearman) (Table 1). For observed ethane concentrations, distance to gas wells was the only factor in our dataset that was statistically significant ($P < 0.005$, regardless of whether analyzed by multiple regression, Pearson correlation, or Spearman analyses) (Table 1).

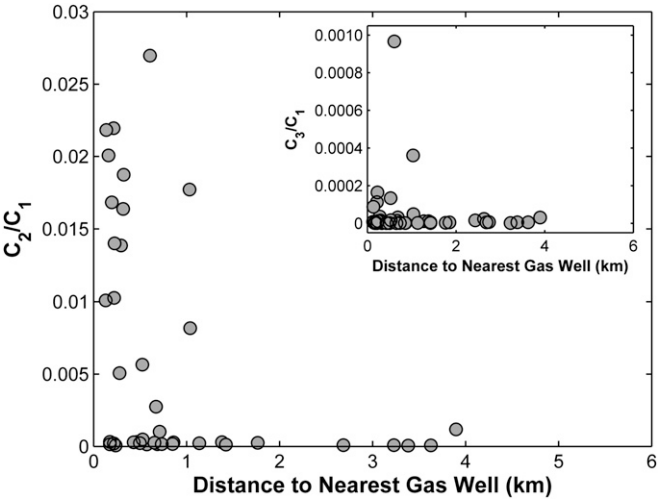

Fig. 2. The ratio of ethane to methane (C_2/C_1) and (*Inset*) propane to methane (C_3/C_1) concentrations in drinking water wells as a function of distance to natural gas wells (kilometers). The data are plotted for all cases where [CH_4], [C_2H_6], and [C_3H_8] were above detection limits or [CH_4] was >0.5 mg/L but [C_2H_6] or [C_3H_8] was below detection limits using the detection limits of 0.0005 and 0.0001 mg/L for [C_2H_6] and [C_3H_8], respectively.

Table 1. Statistical analyses for [CH_4] and [C_2H_6]

	Distance to gas wells	Distance to streams	Distance to ASF
[CH_4]			
Multiple regression	$P = 0.0007$	$P = 0.27$	$P = 0.11$
Pearson r	$P = 0.0003$	$P = 0.22$	$P = 0.04$
Spearman ρ	$P = 0.007$	$P = 0.01$	$P = 0.02$
[C_2H_6]			
Multiple regression	$P = 0.0034$	$P = 0.053$	$P = 0.45$
Pearson r	$P = 0.003$	$P = 0.36$	$P = 0.11$
Spearman ρ	$P = 0.004$	$P = 0.95$	$P = 0.21$

Isotopic signatures and gas ratios provide additional insight into the sources of gases in groundwater. Signatures of δ^{13}C-CH_4 > −40‰ (reference to Vienna Pee Dee Belemnite standard) generally suggest a thermogenic origin for methane, whereas δ^{13}C-CH_4 values < −60‰ suggest a biogenically derived methane source (27, 29, 30). Across our dataset, the most thermogenic δ^{13}C-CH_4 signatures (i.e., most enriched in ^{13}C) in drinking water were generally found in houses with elevated [CH_4] <1 km from natural gas wells (Fig. 3*A*). In fact, all drinking water wells with methane concentrations >10 mg/L, the US Department of Interior's threshold for considering remediation, have δ^{13}C-CH_4 signatures consistent with thermogenic natural gas. Our data also show a population of homes near natural gas wells with water that has δ^{13}C-CH_4 signatures that seem to be microbial in origin, specifically those homes shown in Fig. 3*A*, lower left corner. The combination of our δ^{13}C-CH_4 (Fig. 3*A*) and δ^{2}H-CH_4 data (Fig. 3*B*) overall, however, suggests that a subset of homes near natural gas wells has methane with a higher thermal maturity than homes farther away.

Analyses of δ^{13}C-CH_4 and δ^{13}C-C_2H_6 can help constrain potential sources of thermally mature natural gases (14, 15, 30). Because organic matter cracks to form oil and then natural gas, the gases initially are enriched in higher aliphatic hydrocarbons C_2 and C_3 (e.g., $C_3 > C_2 > C_1$; i.e., a relatively wet gas). With increasing thermal maturity, the heavier hydrocarbons are progressively broken down, increasing the C_1:C_2^+ ratio and leading to isotopic compositions that become increasingly heavier or enriched (31). In most natural gases, the isotopic composition (δ^{13}C) of $C_3 > C_2 > C_1$ (i.e., δ^{13}C of ethane is heavier than methane). In thermally mature black shales, however, this maturity trend reverses, creating diagnostic isotopic reversals in which the δ^{13}C-CH_4 becomes heavier than δ^{13}C-C_2H_6 ($\Delta^{13}C = \delta^{13}$C-$CH_4 - \delta^{13}$C-$C_2H_6 > 1$) (14, 15, 28, 30, 32).

For 11 drinking water samples in our dataset with sufficient ethane to analyze isotopic signatures, 11 samples were located <1.1 km from drilling, and 6 samples exhibited clear isotopic reversals similar to Marcellus production gases (Fig. 4). Conversely, five drinking water samples and spring water from Salt Springs State Park showed the more common trend consistent with Upper Devonian production gases (Fig. 4). In the study area, these isotopic values suggest multiple sources for hydrocarbon gases. The Upper Devonian gases are likely introduced into the shallow crust either by natural processes over geologic time or through leakage around the casing in the annular space of the production well. In contrast, natural gas with heavy δ^{13}C-CH_4 and $\Delta^{13}C > 0$ likely stems from Marcellus production gases or a mixture of Marcellus gases and other annulus gases that migrated to the surface during drilling, well completion, or production.

Similar to our data, independent CH_4 measurements taken by the US Environmental Protection Agency (EPA) in Dimock, Pennsylvania (Residential Data Reports found at http://www.epaosc.org/site/doc_list.aspx?site_id=7555) in January of 2012 also show three δ^{13}C-CH_4 values in drinking water wells between −24.98‰ and -29.36‰ δ^{13}C-CH_4 and five samples with δ^{13}C-CH_4 values in the range of Marcellus gas defined in ref. 28. The heaviest methane isotopic signatures in the EPA samples

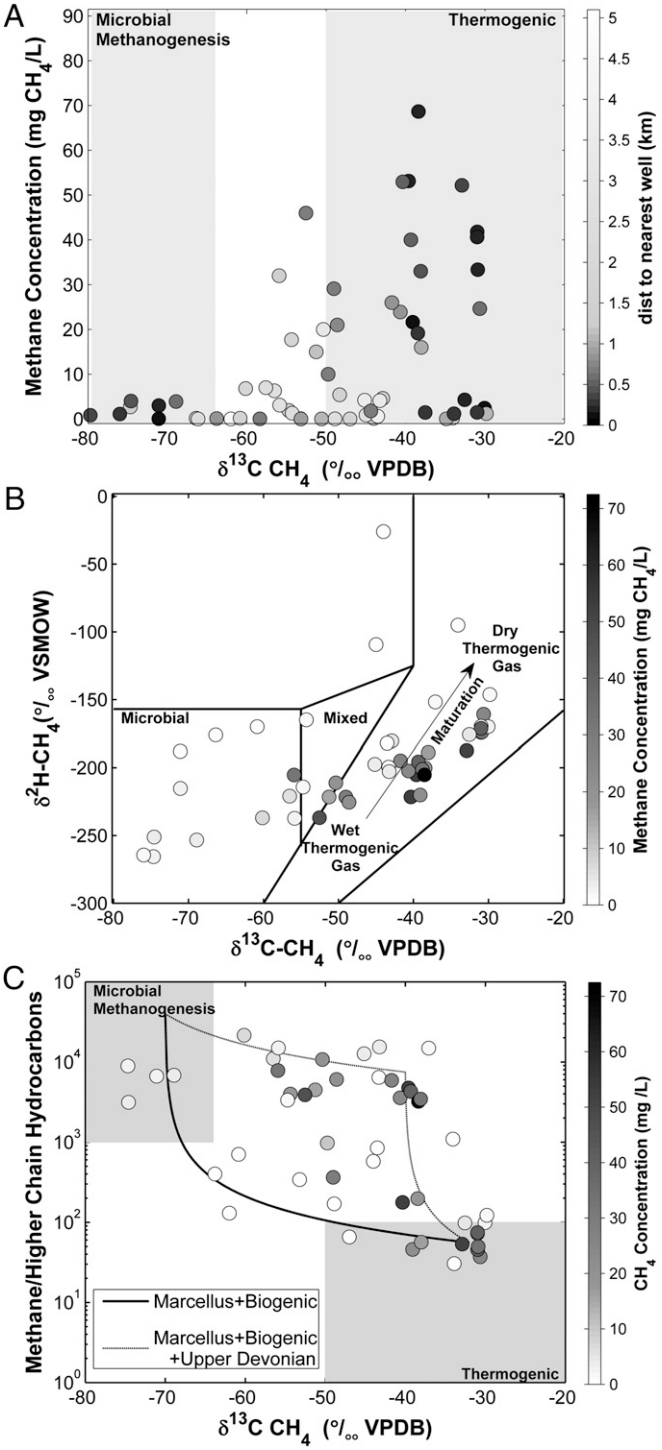

Fig. 3. (*A*) Methane concentration, (*B*) δ^{2}H-CH_4, and (*C*) methane to ethane + propane ratio plotted against δ^{13}C-CH_4. The grayscale shading refers to (*A*) distance to nearest gas wells and (*B* and *C*) methane concentration. The solid lines in *B* distinguishing natural gas sources are from ref. 27; the mixed line in *B* comes from the standard mixing equations in ref. 14. *C* shows two hypothetical trajectories: simple mixing between thermogenically and biogenically derived gas (lower curve) and either diffusive migration or a three-component mixture between Middle and Upper Devonian gases and shallow biogenic gases (upper curve).

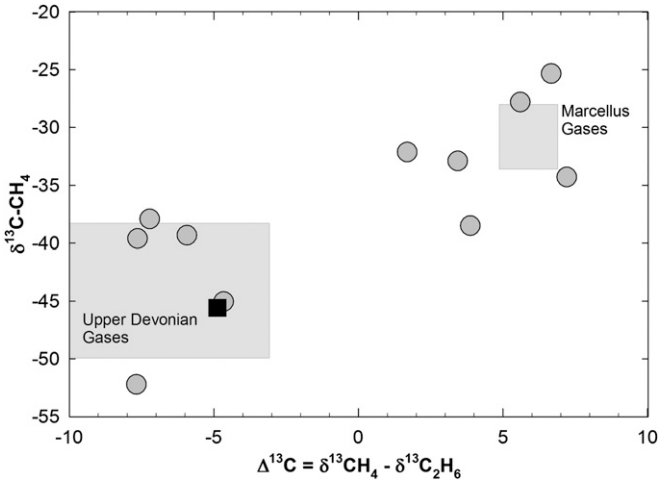

Fig. 4. Stable isotope signatures (‰ VPDB) of methane (δ^{13}C-CH_4) vs. δ^{13}C for methane minus ethane ($\Delta^{13}C = \delta^{13}CH_4 - \delta^{13}C_2H_6$); 6 of 11 drinking water samples exhibited isotopic reversals and δ^{13}C-CH_4 values consistent with Marcellus production gas (14, 28, 55). In contrast, five drinking water samples and the salt spring at Salt Springs State Park (filled square) had δ^{13}C-CH_4 and $\Delta^{13}C < 0$ consistent with Upper Devonian production gases (14, 55). Eleven drinking water samples had sufficient ethane concentrations for isotopic determinations. Ten of the samples were <1 km distance from shale gas wells, and one sample is at 1.1 km distance (the point in the lower left corner of the plot).

(−24.98‰ δ^{13}C-CH_4) exceeded the values observed for ethane (−31.2‰ δ^{13}C-C_2H_6), an isotopic reversal ($\Delta^{13}C$ = 6.22‰) characteristic of Marcellus or other deeper gas compared with gases from Upper Devonian sequences (14, 28).

Helium is an inert noble gas with a radiogenic isotope, ^{4}He, that is a major component of thermogenic natural gas. Similar to hydrocarbon components, the abundance and isotopic composition of helium can help distinguish between potential sources and/or residence times of fluids in the crust, including natural gases (15, 16, 33). Across our dataset, the ratio of ^{4}He:CH_4 in most drinking water wells showed a typical range between $\sim 2 \times 10^{-3}$ and 1×10^{-2}, independent of distance to natural gas wells (Fig. 5). In contrast, a subset of points with elevated [CH_4] has a ^{4}He:CH_4 ratio significantly below the range established for shallow drinking water in the region and consistent with a mixture between shallow groundwater and Marcellus production gases there ($\sim 2–5 \times 10^{-4}$) (Fig. 5) (15).

The relative proportions of methane to higher-chain hydrocarbons, such as ethane and propane, can also be used to help differentiate biogenically and thermogenically derived methane as well as different thermogenic sources of natural gas (34). As described above, low ratios of methane to higher-chain hydrocarbons (~<100) in water typically suggest a hydrocarbon gas derived from a thermogenic source, whereas ratios of methane to higher-chain hydrocarbons >>1,000 suggest a microbial origin for the gas (27). Across our hydrocarbon dataset, ~15 samples seem to fall within the range corresponding to thermogenic gas, whereas the composition of 5 or 6 samples seems to be microbial in origin (Fig. 3*C*). The other points fell on two intermediate trajectories. One trajectory is simple mixing between thermogenically and biogenically derived gas (lower curve in Fig. 3*C*). The other trajectory reflects either diffusive migration or a more complex, three-component mixture between Middle and Upper Devonian gases and shallow biogenic sources (30, 35) (upper trajectory in Fig. 3*C*).

The relative distribution of ethane and propane provides additional insight into the source and mixture of gases. The ratio of propane to methane concentrations plotted against [C_3H_8] (Fig. S5) shows that at least 6 of 10 water samples with detectable [C_3H_8] had an order of magnitude greater [C_3]/[C_1] ratio and [C_3] content than spring water from the natural methane seep at the Salt Springs State Park. The salt spring is the only location for which we found detectable [C_3] outside of our 11 samples (mean [C_3]/[C_1] = 0.000029 and [C3] = 0.0022 mg/L for the Salt Springs samples) (Fig. S5).

The abundance and relative proportions of aliphatic hydrocarbons (i.e., propane and ethane) and methane in groundwater are also useful for comparing with production gases (14, 36) and samples from the Salt Springs State Park. Ratios of propane to ethane (C_3/C_2) in our dataset were generally higher than ratios for the Salt Springs State Park, and ratios of methane to ethane (C_1/C_2) were generally lower (Fig. S6), approaching ratios for Marcellus gases in some cases (Fig. S6). We also observed that the highest methane concentrations coincided with increased abundances of ethane and propane and a higher proportion of propane relative to ethane (Fig. S7). The observed gas composition in groundwater samples also had a substantially higher proportion of propane relative to ethane than water from the Salt Springs State Park, which is known to have historic methane-rich discharges (11, 37) (Fig. S7). Based on limited available production data, the Marcellus production gases have a wetness ($C_2 + C_3$) of at least 1–2% and C_3/C_2 of ~>0.03%, whereas Upper Devonian gases, specifically those gases observed in Upper Devonian aquifers before shale gas development (30), tend to be relatively depleted in wetter gases; samples from the Salt Springs State Park had intermediate wetness, which is discussed above (14, 30). As a result, increasing proportions of C_3/C_2 tend to be more representative of gases from Marcellus-producing wells (Fig. S6) than Upper Devonian Formations or Salt Springs State Park.

An enrichment of ^{13}C in DIC (e.g., δ^{13}C-DIC > +10‰) and positive correlations between δ^{13}C-DIC and δ^{13}C-CH_4 and between δ^2H-H_2O and δ^2H-CH_4 have all been used as indicators of microbial methane sourced from relatively shallow depths (~<550 m) (38, 39). Most of our δ^{13}C-DIC values were 20–25‰ lighter (more negative) than typical for DIC influenced by microbially derived methane in shallow groundwater, and the δ^{13}C-CH_4 values of the samples showed no evidence of a positive relationship with δ^{13}C-DIC (and even a slight negative relationship; $P = 0.003$) (Fig. S8, *Upper*). We also found no statistical relationship between the δ^2H values of methane and δ^2H of water (Fig. S8, *Lower*). Based on these data and similar to the observations in the work by Osborn et al. (4), most of the methane in our samples does not

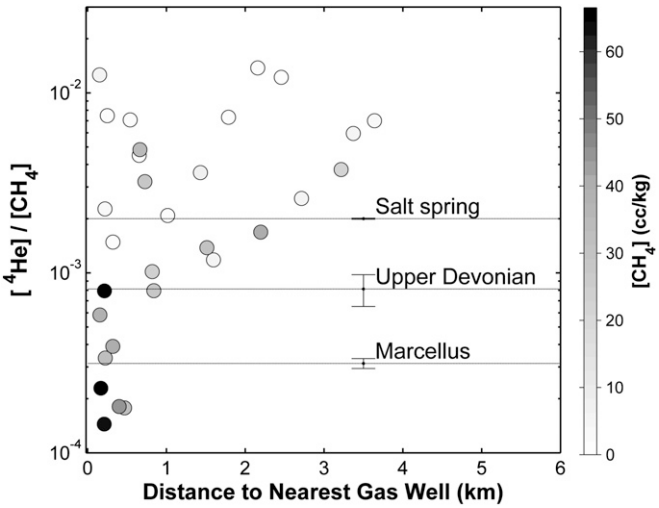

Fig. 5. The ratio of ^{4}He:CH_4 concentrations in drinking water wells vs. distance to gas wells (kilometers). The values are compared with water samples (mean ± SE) from the salt spring at Salt Springs State Park (n = 3) and Marcellus (n = 4) and Upper Devonian (n = 5) production gases (15).

seem to be derived locally in the shallow aquifers, and the gas composition is not consistent with extensive microbial production from methanogenesis or sulfate reduction. Methanotrophy also does not seem to be occurring broadly across our dataset; it would decrease [CH_4] and C_1:C_2 ratios and increase $\delta^{13}CH_4$ values, reducing the differences that we observed for distance to gas wells. Overall, the combined results suggest that natural gas, derived at least in part from thermogenic sources consistent with Middle Devonian origin, is present in some of the shallow water wells <1 km away from natural gas wells.

The two simplest explanations for the higher dissolved gas concentrations that we observed in drinking water are (*i*) faulty or inadequate steel casings, which are designed to keep the gas and any water inside the well from leaking into the environment, and (*ii*) imperfections in the cement sealing of the annulus or gaps between casings and rock that keep fluids from moving up the outside of the well (4, 40–42). In 2010, the Pennsylvania Department of Environmental Protection (DEP) issued 90 violations for faulty casing and cementing on 64 Marcellus shale gas wells; 119 similar violations were issued in 2011.

Distinguishing between the two mechanisms is important because of the different contamination to be expected through time. Casing leaks can arise from poor thread connections, corrosion, thermal stress cracking, and other causes (43). If the protective casing breaks or leaks, then stray gases could be the first sign of contamination, with less mobile salts and metals from formation waters or chemicals from fracturing fluids potentially coming later. In contrast, faulty cement can allow methane and other gases from intermediate layers to flow into, up, and out of the annulus into shallow drinking water layers. In such a scenario, the geochemical and isotopic compositions of stray gas contamination would not necessarily match the target shale gas, and no fracturing chemicals or deep formation waters would be expected, because a direct connection to the deepest layers does not exist; also, such waters are unlikely to migrate upward. Comprehensive analyses of well integrity have shown that sustained casing pressure from annular gas flow is common. A comprehensive analysis of ~15,500 oil and gas wells (43) showed that 12% of all wells drilled in the outer continental shelf area of the Gulf of Mexico had sustained casing pressure within 1 y of drilling, and 50–60% of the wells had it from 15 y onward. For our dataset, there is a weak trend to higher methane concentrations with increasing age of the gas wells ($P = 0.067$ for [CH_4] vs. time since initial drilling). This result could mean that the number of drinking water problems may grow with time or that drilling practices are improving with time; more research is needed before firm conclusions can be drawn.

In addition to well integrity associated with casings or cementing, two other potential mechanisms for contamination by hydraulic fracturing/horizontal drilling include enhancing deep-to-shallow hydraulic connections and intersecting abandoned oil and gas wells. Horizontal drilling and hydraulic fracturing can stimulate fractures or mineralized veins, increasing secondary hydraulic connectivity. The upward transport of gases is theoretically possible, including pressure-driven flow through open, dry fractures and pressure-driven buoyancy of gas bubbles in aquifers and water-filled fractures (44, 45). Reduced pressures after the fracturing activities could also lead to methane exsolving rapidly from solution (46). If methane were to reach an open fracture pathway, however, the gas should redissolve into capillary-bound water and/or formation water, especially at the lithostatic and hydrostatic pressures present at Marcellus depths. Legacy or abandoned oil and gas wells (and even abandoned water wells) are another potential path for rapid fluid transport. In 2000, the Pennsylvania DEP estimated that it had records for only 141,000 of 325,000 oil and gas wells drilled historically in the state, leaving the status and location of ~184,000 abandoned wells unknown (47). However, historical drilling activity is minimal in our study area of northeastern Pennsylvania, making this mechanism unlikely there.

This study examined natural gas composition of drinking water using concentration and isotope data for methane, ethane, propane, and ^{4}He. Based on the spatial distribution of the hydrocarbons (Figs. 1 and 2), isotopic signatures for the gases (Figs. 3 and 4), wetness of the gases (Fig. 2 and Figs. S5, S6, and S7), and observed differences in ^{4}He:CH_4 ratios (Fig. 5), we propose that a subset of homeowners has drinking water contaminated by drilling operations, likely through poor well construction. Future research and greater data disclosure could improve understanding of these issues in several ways. More research is needed across the Marcellus and other shale gas plays where the geological characteristics differ. For instance, a new study by Duke University and the US Geological Survey showed no evidence of drinking water contamination in a part of the Fayetteville Shale with a less fractured or tectonically deformed geology than the Marcellus and good confining layers above and below the drinking water layers (48). More extensive predrilling data would also be helpful. Additional isotopic tools and geochemical tracers are needed to determine the source and mechanisms of stray gas migration that we observed. For instance, a public database disclosing yearly gas compositions (molecular and isotopic $\delta^{13}C$ and δ^2H for methane and ethane) from each producing gas well would help identify and eliminate sources of stray gas (49). In cases where carbon and hydrogen isotopes may not distinguish deep Marcellus-derived methane from shallower, younger Devonian methane, the geochemistry of ^{4}He and other noble gases provides a promising approach (15, 50). Another research need is a set of detailed case studies of water-quality measurements taken before, during, and after drilling and hydraulic fracturing. Such studies are underway, including partnerships of EPA- and Department of Energy-based scientists and industry in Pennsylvania, Texas, and North Dakota. In addition to predrilling data, disclosure of data from mud-log gases and wells to regulatory agencies and ideally, publicly would build knowledge and public confidence. Ultimately, we need to understand why, in some cases, shale gas extraction contaminates groundwater and how to keep it from happening elsewhere.

Methods

A total of 81 samples from drinking water wells were collected in six counties in Pennsylvania (Bradford, Lackawanna, Sullivan, Susquehanna, Wayne, and Wyoming), and results were combined with 60 previous samples described in the work by Osborn et al. (4). The samples were obtained from homeowner associations and contacts with the goal of sampling Alluvium, Catskill, and Lock Haven groundwater wells across the region. For analyses of ^{4}He (Fig. 5), samples from 30 drinking water wells were used to estimate concentration ratios of ^{4}He:CH_4. Wells were purged to remove stagnant water and then monitored for pH, electrical conductance, and temperature until stable values were recorded. Samples were collected upstream of any treatment systems and as close to the water well as possible, preserved in accordance with procedures detailed in *SI Text*, and returned immediately to Duke University for analyses. The chemical and isotope (δ^{13}C-DIC, δ^2H-H_2O, and $\delta^{18}O$-H_2O) compositions of the collected waters were measured at Duke University's Environmental Stable Isotope Laboratory. Values of $\delta^{18}O$-H_2O and δ^2H-H_2O were measured using temperature conversion elemental analysis/continuous flow isotope ratio MS using a ThermoFinnigan temperature conversion elemental analyzer and Delta+XL mass spectrometer and normalized to Vienna Standard Mean Ocean Water (analytical precision of ± 0.1‰ and ±1.5‰ for $\delta^{18}O$-H_2O and δ^2H-H_2O, respectively). Samples of ^{4}He were collected in refrigeration-grade copper tubes flushed with water before sealing with stainless steel clamps and analyzed using a VG 5400 MS at the University of Rochester (15, 51).

Dissolved gas samples were collected in the field using procedures detailed by Isotech Laboratories (52), stored on ice until delivery to their facilities, and analyzed for concentrations and isotopic compositions of methane, ethane, and propane. Procedures for gas analyses are summarized in ref. 4. Isotech Laboratories uses chromatographic separation followed by combustion and dual-inlet isotope ratio MS to measure dissolved gas concentrations, $\delta^{13}C$-CH_4, and $\delta^{13}C$-C_2H_6 (detection limits for C_1, C_2, and C_3 were 0.001, 0.0005, and 0.0001 mol %, respectively). Dissolved [CH_4] and $\delta^{13}C$-CH_4 were also determined by cavity ring-down spectroscopy in the Duke Environmental Stable Isotope Laboratory on eight samples using a Picarro G2112i.

Dissolved [CH_4] was equilibrated using a head-space equilibration method (53) and diluted when necessary using zero air. A set of 33 groundwater samples with a range of [CH_4] and δ^{13}C-CH_4 was collected in duplicate and analyzed at both Duke University and Isotech Laboratories (Fig. S9). Hydrocarbon concentrations in groundwater were converted to milligrams of CH_4 L^{-1} from a correlation with mol % ($R^2 = 0.95$). As in refs. 4 and 11, the derived distances to gas wells represent planimetric lengths from sampling locations to nearest gas wells and do not account for the direction or extent of horizontal drilling underground. Distances to streams were determined as the shortest lengths from sampled locations to valley centerlines using the national stream network as the base map; distance to the Appalachian Structural Front was measured using GIS software. Statistical analyses were performed using MATLAB and R software.

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1. Kargbo DM, Wilhelm RG, Campbell DJ (2010) Natural gas plays in the Marcellus Shale: Challenges and potential opportunities. *Environ Sci Technol* 44(15):5679–5684.
2. Kerr RA (2010) Energy. Natural gas from shale bursts onto the scene. *Science* 328(5986): 1624–1626.
3. US Energy Information Administration (2013) *Natural Gas Monthly March 2013* (US Energy Information Administration, Washington, D.C.), DOE/EIA 0130(2013/03).
4. Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108(20):8172–8176.
5. Schmidt CW (2011) Blind rush? Shale gas boom proceeds amid human health questions. *Environ Health Perspect* 119(8):A348–A353.
6. Pétron G, et al. (2012) Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study. *J Geophys Res* 117(D4):D04304.
7. Ellsworth WL, et al. (2012) *Are Seismicity Rate Changes in the Midcontinent Natural or Manmade?* (US Geological Survey, Menlo Park, CA).
8. Howarth RW, Ingraffea A, Engelder T (2011) Natural gas: Should fracking stop? *Nature* 477(7364):271–275.
9. Jiang M, et al. (2011) Life cycle greenhouse gas emissions of Marcellus shale gas. *Environ Res Lett* 6(3):034014.
10. DiGiulio DC, Wilkin RT, Miller C, Oberley G (2011) *Investigation of Ground Water Contamination Near Pavillion, Wyoming* (US Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Ada, OK), p 74820.
11. Warner NR, et al. (2012) Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proc Natl Acad Sci USA* 109(30):11961–11966.
12. Chapman EC, et al. (2012) Geochemical and strontium isotope characterization of produced waters from Marcellus Shale natural gas extraction. *Environ Sci Technol* 46(6):3545–3553.
13. Boyer EW, et al. (2012) *The Impact of Marcellus Gas Drilling on Rural Drinking Water Supplies* (The Center for Rural Pennsylvania, Harrisburg, PA).
14. Jenden PD, Drazan DJ, Kaplan IR (1993) Mixing of thermogenic natural gases in northern Appalachian basin. *Am Assoc Pet Geol Bull* 77(6):980–998.
15. Hunt AG, Darrah TH, Poreda RJ (2012) Determining the source and genetic fingerprint of natural gases using noble gas geochemistry: A northern Appalachian Basin case study. *Am Assoc Pet Geol Bull* 96(10):1785–1811.
16. Poreda RJ, Craig H, Arnorsson S, Welhan JA (1992) Helium isotopes in Icelandic geothermal systems. 1. He-3, gas chemistry, and C-13 relations. *Geochim Cosmochim Acta* 56(12):4221–4228.
17. Frey MG (1973) Influence of Salina salt on structure in New York-Pennsylvania part of Appalachian Plateau. *Am Assoc Pet Geol Bull* 57(6):1027–1037.
18. Faill R (1985) The Acadian Orogeny and the Catskill Delta. *Geol Soc Am Spec Pap* 201: 15–38.
19. Lohman SW (1957) *Ground Water in Northeastern Pennsylvania* (Pennsylvania Department of Conservation and Natural Resources, Harrisburg, PA), p 31.
20. Geyer A, Wilshusen JP (1982) *Engineering Characteristics of the Rocks of Pennsylvania; Environmental Geology Supplement to the State Geologic Map* (Pennsylvania Geological Survey, Harrisburg, PA), p 300.
21. Taylor L (1984) *Groundwater Resources of the Upper Susquehanna River Basin, Pennsylvania: Water Resources Report 58* (Pennsylvania Department of Environmental Resources, Office of Parks and Forestry, Bureau of Topographic and Geologic Survey, Harrisburg, PA), p 136.
22. Williams J, Taylor L, Low D (1998) *Hydrogeology and Groundwater Quality of the Glaciated Valleys of Bradford, Tioga, and Potter Counties, Pennsylvania: Water Resources Report 68* (Commonwealth of Pennsylvania Department of Conservation and Natural Resources, Harrisburg, PA), p 89.
23. Lash GG, Engelder T (2011) Thickness trends and sequence stratigraphy of the Middle Devonian Marcellus Formation, Appalachian Basin: Implications for Acadian foreland basin evolution. *Am Assoc Pet Geol Bull* 95(1):61–103.
24. Brett CE, Baird GC, Bartholomew AJ, DeSantis MK, Straeten CAV (2011) Sequence stratigraphy and a revised sea-level curve for the Middle Devonian of eastern North America. *Palaeogeogr Palaeoclimatol Palaeoecol* 304(1-2):21–53.
25. Trapp H, Jr., Horn MA (1997) *Ground Water Atlas of the United States: Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia HA 730-L* (USGS, Office of Ground Water, Reston, VA).
26. Bernard BB (1978) Light hydrocarbons in marine sediments. PhD dissertation (Texas A&M Univ, College Station, TX).
27. Schoell M (1980) The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim Cosmochim Acta* 44(5):649–661.
28. Molofsky LJ, Connor JA, Wylie AS, Wagner T, Farhat SK (2013) Evaluation of methane sources in groundwater in northeastern Pennsylvania. *Groundwater* 51(3):333–349.
29. Whiticar MJ (1999) Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem Geol* 161(1-3):291–314.
30. Revesz KM, Breen KJ, Baldassare AJ, Burruss RC (2010) Carbon and hydrogen isotopic evidence for the origin of combustible gases in water supply wells in north-central Pennsylvania. *Appl Geochem* 25(12):1845–1859.
31. Tilley B, et al. (2011) Gas isotope reversals in fractured gas reservoirs of the western Canadian Foothills: Mature shale gases in disguise. *Am Assoc Pet Geol Bull* 95(8):1399–1422.
32. Burruss RC, Laughrey CD (2010) Carbon and hydrogen isotopic reversals in deep basin gas: Evidence for limits to the stability of hydrocarbons. *Org Geochem* 41(12):1285–1296.
33. Ballentine CJ, Burgess R, Marty B (2002) Tracing fluid origin, transport and interaction in the crust. *Noble Gases in Geochemistry and Cosmochemistry*, eds Porcelli D, Ballentine CJ, Wieler R (Mineralogical Society of America, Washington, D.C.), pp 539–614.
34. Prinzhofer AA, Huc AY (1995) Genetic and post-genetic molecular and isotopic fractionations in natural gases. *Chem Geol* 126(3-4):281–290.
35. Baldassare FJ, Laughrey CD (1997) Identifying the sources of stray methane by using geochemical and isotopic fingerprinting. *Environ Geosci* 4(2):85–94.
36. Laughrey CD, Baldassare FJ (1998) Geochemistry and origin of some natural gases in the Plateau province of the central Appalachian basin, Pennsylvania and Ohio. *Am Assoc Pet Geol Bull* 82:317–335.
37. Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108:8172–8176.
38. Osborn SG, McIntosh JC (2010) Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl Geochem* 25(3):456–471.
39. Martini AM, et al. (1998) Genetic and temporal relations between formation waters and biogenic methane: Upper Devonian Antrim Shale, Michigan Basin, USA. *Geochim Cosmochim Acta* 62(10):1699–1720.
40. Bachu S, Watson TL (2009) Review of failures for wells used for CO_2 and acid gas injection in Alberta, Canada. *Energy Procedia* 1(1):3531–3537.
41. Johns JE, Aloisio F, Mayfield DR (2011) Well integrity analysis in Gulf of Mexico wells using passive ultrasonic leak detection method. Society of Petroleum Engineers 142076-MS.
42. Jackson RB, Rainey Pearson B, Osborn SG, Warner NR, Vengosh A (2011) *Research and Policy Recommendations for Hydraulic Fracturing and Shale-Gas Extraction. Center on Global Change* (Duke Univ, Durham, NC).
43. Brufatto C, et al. (2003) From mud to cement—building gas wells. *Oilfield Review* 15(3):62–76.
44. Myers T (2012) Potential contaminant pathways from hydraulically fractured shale to aquifers. *Ground Water* 50(6):872–882.
45. Schedl A, McCabe C, Montanez I, Fullagar P, Valley J (1992) Alleghenian regional diagenesis: A response to the migration of modified metamorphic fluids derived from beneath the Blue Ridge-Piedmont thrust sheet. *J Geol* 100(3):339–352.
46. Cramer B, Schlomer S, Poelchau HS (2002) Uplift-related hydrocarbon accumulations: The release of natural gas from groundwater. *Geolog Soc Special Pubs* 196(1):447–455.
47. DEP (2000) Pennsylvania's Plan for Addressing Problem Abandoned Wells and Orphaned Wells (Department of Environmental Protection, Bureau of Oil and Gas Management, Harrisburg, PA), Document # 550-0800-001.
48. Kresse TM, et al. (2012) Shallow Groundwater Quality and Geochemistry in the Fayetteville Shale Gas-Production Area, North-Central Arkansas, 2011 (USGS), US Geological Survey Scientific Report 2012–5273 (Lafayette Publishing Service Center, Lafayette, LA).
49. Jackson RB, Osborn SG, Vengosh A, Warner NR (2011) Reply to Davies: Hydraulic fracturing remains a possible mechanism for observed methane contamination of drinking water. *Proc Natl Acad Sci USA* 108(43):E872.
50. Sherwood Lollar B, Ballentine CJ (2009) Noble gas-derived insights into deep carbon. *Nat Geosci* 2(8):543–547e.
51. Poreda RJ, Farley KA (1992) Rare gases in Samoan xenoliths. *Earth Planet Sci Lett* 113(1-2):129–144.
52. Isotech Laboratories (2011) *Collection of Groundwater Samples From Domestic and Municipal Water Wells for Dissolved Gas Analysis* (Isotech Laboratories, Champaign, IL).
53. Kampbell DH, Vandegrift SA (1998) Analysis of dissolved methane, ethane, and ethylene in ground water by a standard gas chromatographic technique. *J Chromatogr Sci* 36(5):253–256.
54. Pennsylvania Spatial Data Access (PASDA) (2012) *Online Mapping, Data Access Wizard, Oil and Gas Locations* (Pennsylvania Department of Environmental Protection, Harrisburg, PA).
55. Baldassare F (2011) *The Origin of Some Natural Gases in Permian Through Devonian Age Systems in the Appalachian Basin and the Relationship to Incidents of Stray Gas Migration* (EPA Technical Workshops for Hydraulic Fracturing Study, Chemical & Analytical Methods, Murrysville, PA).

ATTACHMENT C

STUDY 33

Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing

Stephen G. Osborn[a], Avner Vengosh[b], Nathaniel R. Warner[b], and Robert B. Jackson[a,b,c,1]

[a]Center on Global Change, Nicholas School of the Environment, [b]Division of Earth and Ocean Sciences, Nicholas School of the Environment, and [c]Biology Department, Duke University, Durham, NC 27708

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Directional drilling and hydraulic-fracturing technologies are dramatically increasing natural-gas extraction. In aquifers overlying the Marcellus and Utica shale formations of northeastern Pennsylvania and upstate New York, we document systematic evidence for methane contamination of drinking water associated with shale-gas extraction. In active gas-extraction areas (one or more gas wells within 1 km), average and maximum methane concentrations in drinking-water wells increased with proximity to the nearest gas well and were 19.2 and 64 mg CH_4 L^{-1} ($n = 26$), a potential explosion hazard; in contrast, dissolved methane samples in neighboring nonextraction sites (no gas wells within 1 km) within similar geologic formations and hydrogeologic regimes averaged only 1.1 mg L^{-1} ($P < 0.05$; $n = 34$). Average δ^{13}C-CH_4 values of dissolved methane in shallow groundwater were significantly less negative for active than for nonactive sites (-37 ± 7‰ and -54 ± 11‰, respectively; $P < 0.0001$). These δ^{13}C-CH_4 data, coupled with the ratios of methane-to-higher-chain hydrocarbons, and δ^{2}H-CH_4 values, are consistent with deeper thermogenic methane sources such as the Marcellus and Utica shales at the active sites and matched gas geochemistry from gas wells nearby. In contrast, lower-concentration samples from shallow groundwater at nonactive sites had isotopic signatures reflecting a more biogenic or mixed biogenic/thermogenic methane source. We found no evidence for contamination of drinking-water samples with deep saline brines or fracturing fluids. We conclude that greater stewardship, data, and—possibly—regulation are needed to ensure the sustainable future of shale-gas extraction and to improve public confidence in its use.

groundwater | organic-rich shale | isotopes | formation waters | water chemistry

Increases in natural-gas extraction are being driven by rising energy demands, mandates for cleaner burning fuels, and the economics of energy use (1–5). Directional drilling and hydraulic-fracturing technologies are allowing expanded natural-gas extraction from organic-rich shales in the United States and elsewhere (2, 3). Accompanying the benefits of such extraction (6, 7) are public concerns about drinking-water contamination from drilling and hydraulic fracturing that are ubiquitous but lack a strong scientific foundation. In this paper, we evaluate the potential impacts associated with gas-well drilling and fracturing on shallow groundwater systems of the Catskill and Lockhaven formations that overlie the Marcellus Shale in Pennsylvania and the Genesee Group that overlies the Utica Shale in New York (Figs. 1 and 2 and Fig. S1). Our results show evidence for methane contamination of shallow drinking-water systems in at least three areas of the region and suggest important environmental risks accompanying shale-gas exploration worldwide.

The drilling of organic-rich shales, typically of Upper Devonian to Ordovician age, in Pennsylvania, New York, and elsewhere in the Appalachian Basin is spreading rapidly, raising concerns for impacts on water resources (8, 9). In Susquehanna County, Pennsylvania alone, approved gas-well permits in the Marcellus formation increased 27-fold from 2007 to 2009 (10).

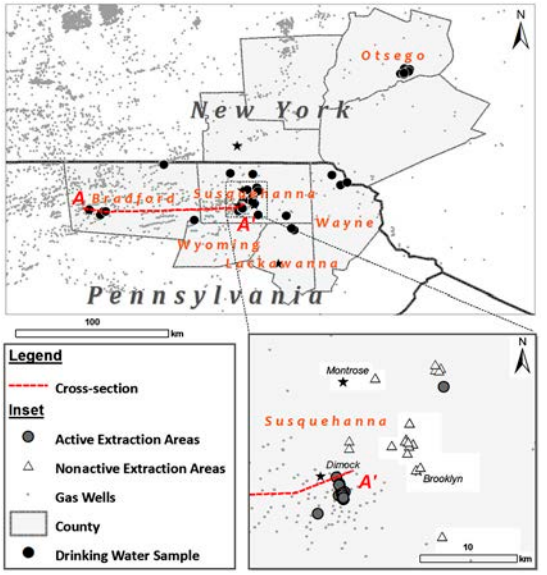

Fig. 1. Map of drilling operations and well-water sampling locations in Pennsylvania and New York. The star represents the location of Binghamton, New York. (*Inset*) A close-up in Susquehanna County, Pennsylvania, showing areas of active (closed circles) or nonactive (open triangles) extraction. A drinking-water well is classified as being in an active extraction area if a gas well is within 1 km (see *Methods*). Note that drilling has already spread to the area around Brooklyn, Pennsylvania, primarily a nonactive location at the time of our sampling (see inset). The stars in the inset represent the towns of Dimock, Brooklyn, and Montrose, Pennsylvania.

Concerns for impacts to groundwater resources are based on (*i*) fluid (water and gas) flow and discharge to shallow aquifers due to the high pressure of the injected fracturing fluids in the gas wells (10); (*ii*) the toxicity and radioactivity of produced water from a mixture of fracturing fluids and deep saline formation waters that may discharge to the environment (11); (*iii*) the potential explosion and asphyxiation hazard of natural gas; and (*iv*) the large number of private wells in rural areas that rely on shallow groundwater for household and agricultural use—up to one million wells in Pennsylvania alone—that are typically unregulated and untested (8, 9, 12). In this study, we analyzed groundwater from 68 private water wells from 36- to 190-m deep in

Author contributions: S.G.O., A.V., and R.B.J. designed research; S.G.O. and N.R.W. performed research; A.V. contributed new reagents/analytic tools; S.G.O., A.V., N.R.W., and R.B.J. analyzed data; and S.G.O., A.V., N.R.W., and R.B.J. wrote the paper.

The authors declare no conflict of interest.

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[1]To whom correspondence should be addressed. E-mail: jackson@duke.edu.

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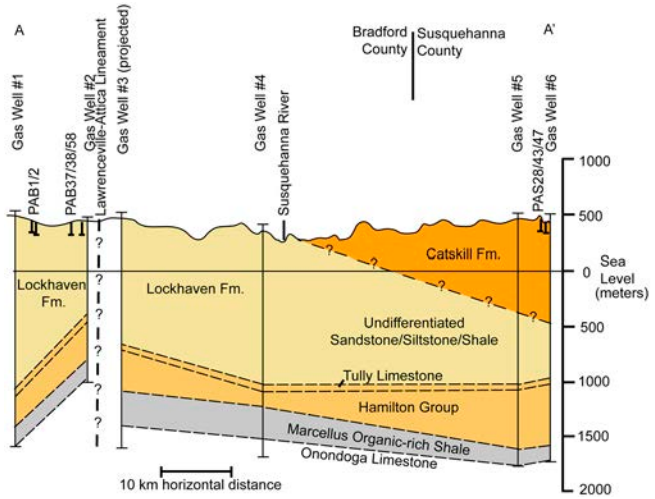

Fig. 2. Geologic cross-section of Bradford and western Susquehanna Counties created from gas-well log data provided by the Pennsylvania Department of Conservation and Natural Resources. The approximate location of the Lawrenceville-Attica Lineament is taken from Alexander et al. (34). The Ordovician Utica organic-rich shale (not depicted in the figure) underlies the Middle Devonian Marcellus at approximately 3,500 m below the ground surface.

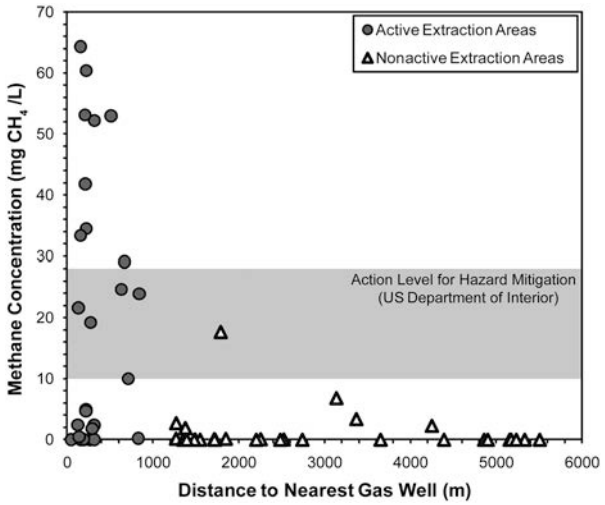

Fig. 3. Methane concentrations (milligrams of CH_4 L^{-1}) as a function of distance to the nearest gas well from active (closed circles) and nonactive (open triangles) drilling areas. Note that the distance estimate is an upper limit and does not take into account the direction or extent of horizontal drilling underground, which would decrease the estimated distances to some extraction activities. The precise locations of natural-gas wells were obtained from the Pennsylvania Department of Environmental Protection and Pennsylvania Spatial Data Access databases (ref. 35; accessed Sept. 24, 2010).

northeast Pennsylvania (Catskill and Lockhaven formations) and upstate New York (Genesee formation) (see Figs. 1 and 2 and *SI Text*), including measurements of dissolved salts, water isotopes (^{18}O and ^{2}H), and isotopes of dissolved constituents (carbon, boron, and radium). Of the 68 wells, 60 were also analyzed for dissolved-gas concentrations of methane and higher-chain hydrocarbons and for carbon and hydrogen isotope ratios of methane. Although dissolved methane in drinking water is not currently classified as a health hazard for ingestion, it is an asphyxiant in enclosed spaces and an explosion and fire hazard (8). This study seeks to evaluate the potential impact of gas drilling and hydraulic fracturing on shallow groundwater quality by comparing areas that are currently exploited for gas (defined as active—one or more gas wells within 1 km) to those that are not currently associated with gas drilling (nonactive; no gas wells within 1 km), many of which are slated for drilling in the near future.

Results and Discussion

Methane concentrations were detected generally in 51 of 60 drinking-water wells (85%) across the region, regardless of gas industry operations, but concentrations were substantially higher closer to natural-gas wells (Fig. 3). Methane concentrations were 17-times higher on average (19.2 mg CH_4 L^{-1}) in shallow wells from active drilling and extraction areas than in wells from nonactive areas (1.1 mg L^{-1} on average; $P < 0.05$; Fig. 3 and Table 1). The *average* methane concentration in shallow groundwater in active drilling areas fell within the defined action level (10–28 mg L^{-1}) for hazard mitigation recommended by the US Office of the Interior (13), and our maximum observed value of 64 mg L^{-1} is well above this hazard level (Fig. 3). Understanding the origin of this methane, whether it is shallower biogenic or deeper thermogenic gas, is therefore important for identifying the source of contamination in shallow groundwater systems.

The $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 values and the ratio of methane to higher-chain hydrocarbons (ethane, propane, and butane) can typically be used to differentiate shallower, biologically derived methane from deeper physically derived thermogenic methane (14). Values of $\delta^{13}C$-CH_4 less negative than approximately −50‰ are indicative of deeper thermogenic methane, whereas values more negative than −64‰ are strongly indicative of microbial methane (14). Likewise, $\delta^{2}H$-CH_4 values more negative than about −175‰, particularly when combined with low $\delta^{13}C$-CH_4 values, often represent a purer biogenic methane origin (14).

The average $\delta^{13}C$-CH_4 value in shallow groundwater in active drilling areas was -37 ± 7‰, consistent with a deeper thermogenic methane source. In contrast, groundwater from nonactive areas in the same aquifers had much lower methane concentrations and significantly lower $\delta^{13}C$-CH_4 values (average of -54 ± 11‰; $P < 0.0001$; Fig. 4 and Table 1). Both our $\delta^{13}C$-CH_4 data and $\delta^{2}H$-CH_4 data (see Fig. S2) are consistent with a deeper thermogenic methane source at the active sites and a more biogenic or mixed methane source for the lower-concentration samples from nonactive sites (based on the definition of Schoell, ref. 14).

Because ethane and propane are generally not coproduced during microbial methanogenesis, the presence of higher-chain hydrocarbons at relatively low methane-to-ethane ratios (less than approximately 100) is often used as another indicator of deeper thermogenic gas (14, 15). Ethane and other higher-chain hydrocarbons were detected in only 3 of 34 drinking-water wells from nonactive drilling sites. In contrast, ethane was detected in 21 of 26 drinking-water wells in active drilling sites. Additionally, propane and butane were detected (>0.001 mol %) in eight and two well samples, respectively, from active drilling areas but in no wells from nonactive areas.

Further evidence for the difference between methane from water wells near active drilling sites and neighboring nonactive sites is the relationship of methane concentration to $\delta^{13}C$-CH_4 values (Fig. 4*A*) and the ratios of methane to higher-chain hydro-

Table 1. Mean values ± standard deviation **of methane concentrations (as milligrams of CH_4 L^{-1}) and carbon isotope composition in methane in shallow groundwater $\delta^{13}C$-CH_4 sorted by aquifers and proximity to gas wells (active vs. nonactive)**

Water source, *n*	milligrams CH_4 L^{-1}	$\delta^{13}C$-CH_4, ‰
Nonactive Catskill, 5	1.9 ± 6.3	−52.5 ± 7.5
Active Catskill, 13	26.8 ± 30.3	−33.5 ± 3.5
Nonactive Genesee, 8	1.5 ± 3.0	−57.5 ± 9.5
Active Genesee, 1	0.3	−34.1
Active Lockhaven, 7	50.4 ± 36.1	−40.7 ± 6.7
Total active wells, 21	19.2	−37 ± 7
Total nonactive wells, 13	1.1	−54 ± 11

The variable *n* refers to the number of samples.

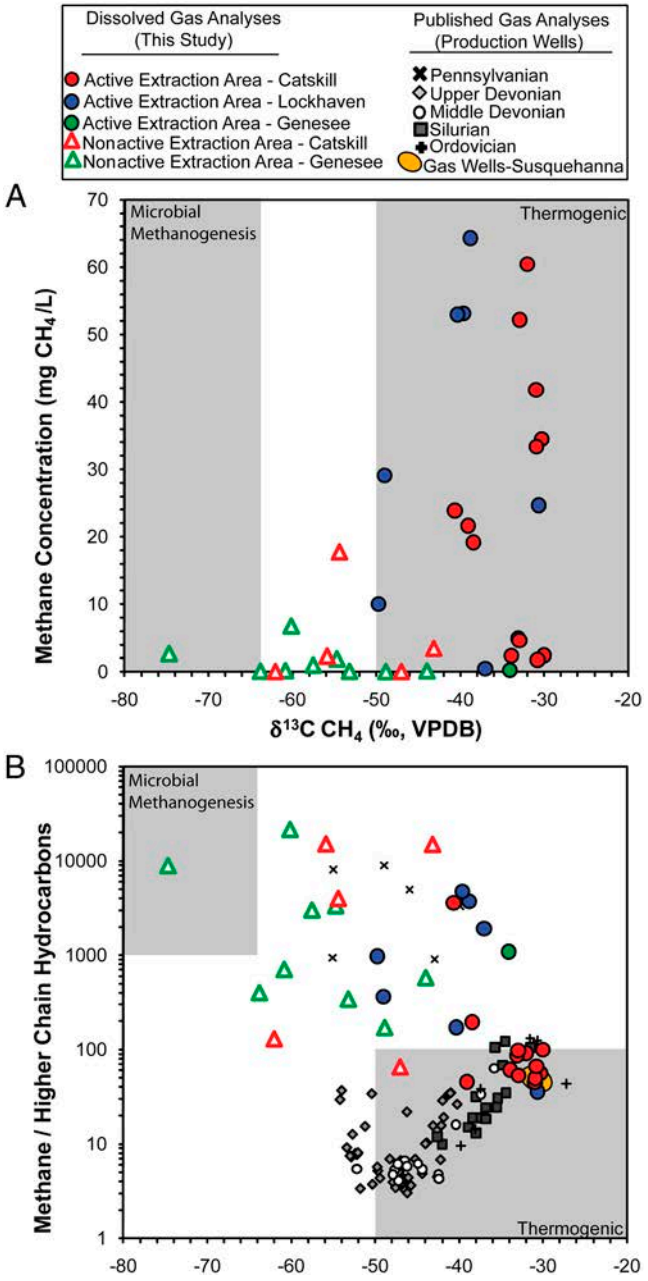

Fig. 4. (*A*) Methane concentrations in groundwater versus the carbon isotope values of methane. The nonactive and active data depicted in Fig. 3 are subdivided based on the host aquifer to illustrate that the methane concentrations and δ^{13}C values increase with proximity to natural-gas well drilling regardless of aquifer formation. Gray areas represent the typical range of thermogenic and biogenic methane taken from Osborn and Mcintosh (18). VPDB, Vienna Pee Dee belemnite. (*B*) Bernard plot (15) of the ratio of methane to higher-chain hydrocarbons versus the δ^{13}C of methane. The smaller symbols in grayscale are from published gas-well samples from gas production across the region (16–18). These data generally plot along a trajectory related to reservoir age and thermal maturity (Upper Devonian through Ordovician; see text for additional details). The gas-well data in the orange ovals are from gas wells in our study area in Susquehanna County, Pennsylvania (data from Pennsylvania Department of Environmental Protection). Gray areas represent typical ranges of thermogenic and biogenic methane (data from Osborn and McIntosh, ref. 18).

carbons versus δ^{13}C-CH_4 (Fig. 4*B*). Methane concentrations not only increased in proximity to gas wells (Fig. 3), the accompanying δ^{13}C-CH_4 values also reflected an increasingly thermogenic methane source (Fig. 4*A*).

Using a Bernard plot (15) for analysis (Fig. 4*B*), the enriched δ^{13}C-CH_4 (approximately $> -50‰$) values accompanied by low ratios of methane to higher-chain hydrocarbons (less than approximately 100) in drinking-water wells also suggest that dissolved gas is more thermogenic at active than at nonactive sites (Fig. 4*B*). For instance, 12 dissolved-gas samples at active drilling sites fell along a regional gas trajectory that increases with reservoir age and thermal maturity of organic matter, with samples from Susquehanna County, Pennsylvania specifically matching natural-gas geochemistry from local gas wells (Fig. 4*B*, orange oval). These 12 samples and local natural-gas samples are consistent with gas sourced from thermally mature organic matter of Middle Devonian and older depositional ages often found in Marcellus Shale from approximately 2,000 m below the surface in the northern Appalachian Basin (14–19) (Fig. 4*B*). In contrast, none of the methane samples from nonactive drilling areas fell upon this trajectory (Fig. 4*B*); eight dissolved-gas samples in Fig. 4*B* from active drilling areas and all of the values from nonactive areas may instead be interpreted as mixed biogenic/thermogenic gas (18) or, as Laughrey and Baldassare (17) proposed for their Pennsylvanian gas data (Fig. 4*B*), the early migration of wet thermogenic gases with low-δ^{13}C-CH_4 values and high methane-to-higher-chain hydrocarbon ratios. One data point from a nonactive area in New York fell squarely in the parameters of a strictly biogenic source as defined by Schoell (14) (Fig. 4*B*, upper-left corner).

Carbon isotopes of dissolved inorganic carbon (δ^{13}C-DIC $> +10‰$) and the positive correlation of δ^2H of water and δ^2H of methane have been used as strong indicators of microbial methane, further constraining the source of methane in shallow groundwater (depth less than 550 m) (18, 20). Our δ^{13}C-DIC values were fairly negative and show no association with the δ^{13}C-CH_4 values (Fig. S3), which is not what would be expected if methanogenesis were occurring locally in the shallow aquifers. Instead, the δ^{13}C-DIC values from the shallow aquifers plot within a narrow range typical for shallow recharge waters, with the dissolution of CO_2 produced by respiration as water passes downward through the soil critical zone. Importantly, these values do not indicate extensive microbial methanogenesis or sulfate reduction. The data do suggest gas-phase transport of methane upward to the shallow groundwater zones sampled for this study (<190 m) and dissolution into shallow recharge waters locally. Additionally, there was no positive correlation between the δ^2H values of methane and δ^2H of water (Fig. S4), indicating that microbial methane derived in this shallow zone is negligible. Overall, the combined gas and formation-water results indicate that thermogenic gas from thermally mature organic matter of Middle Devonian and older depositional ages is the most likely source of the high methane concentrations observed in the shallow water wells from active extraction sites.

A different potential source of shallow groundwater contamination associated with gas drilling and hydraulic fracturing is the introduction of hypersaline formation brines and/or fracturing fluids. The average depth range of drinking-water wells in northeastern Pennsylvania is from 60 to 90 m (12), making the average vertical separation between drinking-water wells and the Marcellus Shale in our study area between approximately 900 and 1,800 m (Fig. 2). The research area, however, is located in tectonically active areas with mapped faults, earthquakes, and lineament features (Fig. 2 and Fig. S1). The Marcellus formation also contains two major sets of joints (21) that could be conduits for directed pressurized fluid flow. Typical fracturing activities in the Marcellus involve the injection of approximately 13–19 million liters of water per well (22) at pressures of up to 69,000 kPa. The majority of this fracturing water typically stays underground and could in principle displace deep formation water upward into shallow aquifers. Such deep formation waters often have high concentrations of total dissolved solids >250,000 mg L^{-1}, trace

toxic elements, (18), and naturally occurring radioactive materials, with activities as high as 16,000 picocuries per liter (1 pCi L^{-1} = 0.037 becquerels per liter) for ^{226}Ra compared to a drinking-water standard of 5 pCi L^{-1} for combined ^{226}Ra and ^{226}Ra (23).

We evaluated the hydrochemistry of our 68 drinking-water wells and compared these data to historical data of 124 wells in the Catskill and Lockhaven aquifers (24, 25). We used three types of indicators for potential mixing with brines and/or saline fracturing fluids: (*i*) major inorganic chemicals; (*ii*) stable isotope signatures of water ($\delta^{18}O$, $\delta^{2}H$); and (*iii*) isotopes of dissolved constituents ($\delta^{13}C$-DIC, $\delta^{11}B$, and ^{226}Ra). Based on our data (Table 2), we found no evidence for contamination of the shallow wells near active drilling sites from deep brines and/or fracturing fluids. All of the Na^{+}, Cl^{-}, Ca^{2+}, and DIC concentrations in wells from active drilling areas were consistent with the baseline historical data, and none of the shallow wells from active drilling areas had either chloride concentrations >60 mg L^{-1} or Na-Ca-Cl compositions that mirrored deeper formation waters (Table 2). Furthermore, the mean isotopic values of $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$-DIC, $\delta^{11}B$, and ^{226}Ra in active and nonactive areas were indistinguishable. The ^{226}Ra values were consistent with available historical data (25), and the composition of $\delta^{18}O$ and $\delta^{2}H$ in the well-water appeared to be of modern meteoric origin for Pennsylvania (26) (Table 2 and Fig. S5). In sum, the geochemical and isotopic features for water we measured in the shallow wells from both active and nonactive areas are consistent with historical data and inconsistent with contamination from mixing Marcellus Shale formation water or saline fracturing fluids (Table 2).

There are at least three possible mechanisms for fluid migration into the shallow drinking-water aquifers that could help explain the increased methane concentrations we observed near gas wells (Fig. 3). The first is physical displacement of gas-rich deep solutions from the target formation. Given the lithostatic and hydrostatic pressures for 1–2 km of overlying geological strata, and our results that appear to rule out the rapid movement of deep brines to near the surface, we believe that this mechanism is unlikely. A second mechanism is leaky gas-well casings (e.g., refs. 27 and 28). Such leaks could occur at hundreds of meters underground, with methane passing laterally and vertically through fracture systems. The third mechanism is that the process of hydraulic fracturing generates new fractures or enlarges existing ones above the target shale formation, increasing the connectivity of the fracture system. The reduced pressure following the fracturing activities could release methane in solution, leading to methane exsolving rapidly from solution (29), allowing methane gas to potentially migrate upward through the fracture system.

Methane migration through the 1- to 2-km-thick geological formations that overlie the Marcellus and Utica shales is less likely as a mechanism for methane contamination than leaky well casings, but might be possible due to both the extensive fracture systems reported for these formations and the many older, uncased wells drilled and abandoned over the last century and a half in Pennsylvania and New York. The hydraulic conductivity in the overlying Catskill and Lockhaven aquifers is controlled by a secondary fracture system (30), with several major faults and lineaments in the research area (Fig. 2 and Fig. S1). Consequently, the high methane concentrations with distinct positive $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 values in the shallow groundwater from active areas could in principle reflect the transport of a deep methane source associated with gas drilling and hydraulic-fracturing activities. In contrast, the low-level methane migration to the surface groundwater aquifers, as observed in the nonactive areas, is likely a natural phenomenon (e.g., ref. 31). Previous studies have shown that naturally occurring methane in shallow aquifers is typically associated with a relatively strong biogenic signature indicated by depleted $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 compositions (32) coupled with high ratios of methane to higher-chain hydrocarbons (33), as we observed in Fig. 4*B*. Several models have been developed to explain the relatively common phenomenon of rapid vertical transport of gases (Rn, CH_4, and CO_2) from depth to the surface (e.g., ref. 31), including pressure-driven continuous gas-phase flow through dry or water-saturated fractures and density-driven buoyancy of gas microbubbles in aquifers and water-filled fractures (31). More research is needed across this and other regions to determine the mechanism(s) controlling the higher methane concentrations we observed.

Based on our groundwater results and the litigious nature of shale-gas extraction, we believe that long-term, coordinated sampling and monitoring of industry and private homeowners is needed. Compared to other forms of fossil-fuel extraction, hydraulic fracturing is relatively poorly regulated at the federal level. Fracturing wastes are not regulated as a hazardous waste under the Resource Conservation and Recovery Act, fracturing wells are not covered under the Safe Drinking Water Act, and only recently has the Environmental Protection Agency asked fracturing

Table 2. Comparisons of selected major ions and isotopic results in drinking-water wells from this study to data available on the same formations (Catskill and Lockhaven) in previous studies (24, 25) and to underlying brines throughout the Appalachian Basin (18)

	Active		Nonactive		Previous studies (background)		
	Lockhaven formation *N* = 8	Catskill formation *N* = 25	Catskill formation *N* = 22	Genesee group *N* = 12	Lockhaven formation (25) *N* = 45	Catskill formation (24) *N* = 79	Appalachian brines (18, 23) *N* = 21
Alkalinity as HCO_3^-, mg L^{-1}	285 ± 36	157 ± 56	127 ± 53	158 ± 56	209 ± 77	133 ± 61	150 ± 171
mM	[4.7 ± 0.6]	[2.6 ± 0.9]	[2.1 ± 0.9]	[2.6 ± 0.9]	[3.4 ± 1.3]	[2.2 ± 1.0]	[2.5 ± 2.8]
Sodium, mg L^{-1}	87 ± 22	23 ± 30	17 ± 25	29 ± 23	100 ± 312	21 ± 37	33,000 ± 11,000
Chloride, mg L^{-1}	25 ± 17	11 ± 12	17 ± 40	9 ± 19	132 ± 550	13 ± 42	92,000 ± 32,000
Calcium, mg L^{-1}	22 ± 12	31 ± 13	27 ± 9	26 ± 5	49 ± 39	29 ± 11	16,000 ± 7,000
Boron, μg L^{-1}	412 ± 156	93 ± 167	42 ± 93	200 ± 130	NA	NA	3,700 ± 3,500
$\delta^{11}B$ ‰	27 ± 4	22 ± 6	23 ± 6	26 ± 6	NA	NA	39 ± 6
^{226}Ra, *p*Ci L^{-1}	0.24 ± 0.2	0.16 ± 0.15	0.17 ± 0.14	0.2 ± 0.15	0.56 ± 0.74	NA	6,600 ± 5,600
$\delta^{2}H$, ‰, VSMOW	−66 ± 5	−64 ± 3	−68 ± 6	−76 ± 5	NA	NA	−41 ± 6
$\delta^{18}O$, ‰, VSMOW	−10 ± 1	−10 ± 0.5	−11 ± 1	−12 ± 1	NA	NA	−5 ± 1

Some data for the active Genesee Group and nonactive Lockhaven Formation are not included because of insufficient sample sizes (NA). Values represent means ±1 standard deviation. NA, not available.

N values for $\delta^{11}B$ ‰ analysis are 8, 10, 3, 6, and 5 for active Lockhaven, active Catskill, nonactive Genesee, nonactive Catskill, and brine, respectively. *N* values for ^{226}Ra are 6, 7, 3, 10, 5, and 13 for active Lockhaven, active Catskill, nonactive Genesee, nonactive Catskill, background Lockhaven, and brine, respectively. $\delta^{11}B$ ‰ normalized to National Institute of Standards and Technology Standard Reference Material 951. $\delta^{2}H$ and $\delta^{18}O$ normalized to Vienna Standard Mean Ocean Water (VSMOW).

firms to voluntarily report a list of the constituents in the fracturing fluids based on the Emergency Planning and Community Right-to-Know Act. More research is also needed on the mechanism of methane contamination, the potential health consequences of methane, and establishment of baseline methane data in other locations. We believe that systematic and independent data on groundwater quality, including dissolved-gas concentrations and isotopic compositions, should be collected before drilling operations begin in a region, as is already done in some states. Ideally, these data should be made available for public analysis, recognizing the privacy concerns that accompany this issue. Such baseline data would improve environmental safety, scientific knowledge, and public confidence. Similarly, long-term monitoring of groundwater and surface methane emissions during and after extraction would clarify the extent of problems and help identify the mechanisms behind them. Greater stewardship, knowledge, and—possibly—regulation are needed to ensure the sustainable future of shale-gas extraction.

Methods

A total of 68 drinking-water samples were collected in Pennsylvania and New York from bedrock aquifers (Lockhaven, 8; Catskill, 47; and Genesee, 13) that overlie the Marcellus or Utica shale formations (Fig. S1). Wells were purged to remove stagnant water, then monitored for pH, electrical conductance, and temperature until stable values were recorded. Samples were collected "upstream" of any treatment systems, as close to the water well as possible, and preserved in accordance with procedures detailed in *SI Methods*. Dissolved-gas samples were analyzed at Isotech Laboratories and water chemical and isotope (O, H, B, C, Ra) compositions were measured at Duke University (see *SI Methods* for analytical details).

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1. Pacala S, Socolow R (2004) Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. *Science* 305:968–972.
2. Tour JM, Kittrell C, Colvin VL (2010) Green carbon as a bridge to renewable energy. *Nature Mater* 9:871–874.
3. Kerr RA (2010) Natural gas from shale bursts onto the scene. *Science* 328:1624–1626.
4. Raupach MR, et al. (2007) Global and regional drivers of accelerating CO_2 emissions. *Proc Natl Acad Sci USA* 104:10288–10293.
5. US Energy Information Administration (2010) *Annual Energy Outlook 2010 with Projections to 2035* (US Energy Information Administration, Washington, DC), DOE/EIA-0383; http://www.eia.doe.gov/oiaf/aeo/pdf/0383(2010).pdf.
6. US Environmental Protection Agency (2011) Hydraulic Fracturing. (US Environmental Protection Agency, Washington, DC), http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/.
7. Kargbo DM, Wilhelm RG, Campbell DJ (2010) Natural gas plays in the Marcellus shale: Challenges and potential opportunities. *Environ Sci Technol* 44:5679–5684.
8. Revesz KM, Breen KJ, Baldassare AJ, Burruss RC (2010) Carbon and hydrogen isotopic evidence for the origin of combustible gases in water supply wells in north-central Pennsylvania. *Appl Geochem* 25:1845–1859.
9. Zoback M, Kitasei S, Copithorne B Addressing the environmental risks from shale gas development. *Worldwatch Institute Briefing Paper 1* (Worldwatch Inst, Washington, DC), http://blogs.worldwatch.org/revolt/wp-content/uploads/2010/07/Environmental-Risks-Paper-July-2010-FOR-PRINT.pdf.
10. Pennsylvania Department of Environmental Protection, Bureau of Oil and Gas Management (2010) 2009 Year End Workload Report. (Pennsylvania Dept of Environmental Protection, Bureau of Oil and Gas Management, Harrisburg, PA), http://www.dep.state.pa.us/dep/deputate/minres/oilgas/2009%20Year%20End%20Report-WEBSITE.pdf.
11. Colborn T, Kwiatkowski C, Schultz K, Bachran M (2010) Natural gas operations from a public health perspective. *Hum Ecol Risk Assess*, in press.
12. Pennsylvania Department of Environmental Protection (2011) Private Water Wells in Pennsylvania. (Pennsylvania Dept of Environmental Protection, Harrisburg, PA), http://www.dep.state.pa.us/dep/deputate/watermgt/wc/Subjects/SrceProt/well/.
13. Eltschlager KK, Hawkins JW, Ehler WC, Baldassare F (2001) *Technical Measures for the Investigation and Mitigation of Fugitive Methane Hazards in Areas of Coal Mining* (US Dept of the Interior, Office of Surface Mining Reclamation and Enforcement, Pittsburgh).
14. Schoell M (1980) The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim Cosmochim Acta* 44:649–661.
15. Bernard BB (1978) Light hydrocarbons in marine sediments. PhD Dissertation (Texas A&M Univ, College Station, TX).
16. Jenden PD, Drazan DJ, Kaplan IR (1993) Mixing of thermogenic natural gases in northern Appalachian Basin. *Am Assoc Pet Geol Bull* 77:980–998.
17. Laughrey CD, Baldassare FJ (1998) Geochemistry and origin of some natural gases in the Plateau Province Central Appalachian Basin, Pennsylvania and Ohio. *Am Assoc Pet Geol Bull* 82:317–335.
18. Osborn SG, McIntosh JC (2010) Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl Geochem* 25:456–471.
19. Repetski JE, Ryder RT, Harper JA, Trippi MH (2006) Thermal maturity patterns in the Ordovician and Devonian of Pennsylvania using conodont color alteration index (CAI) and vitrinite reflectance (%Ro). *Northeastern Geology Environmental Sciences* 28:266–294.
20. Martini AM, et al. (1998) Genetic and temporal relations between formation waters and biogenic methane: Upper Devonian Antrim Shale, Michigan Basin, USA. *Geochim Cosmochim Acta* 62:1699–1720.
21. Engelder T, Lash GG, Uzcategui RS (2009) Joint sets that enhance production from Middle and Upper Devonian gas shales of the Appalachian Basin. *Am Assoc Pet Geol Bull* 93:857–889.
22. Pennsylvania Department of Environmental Protection (2011) (Pennsylvania Dept of Environmental Protection, Harrisburg, PA), Marcellus Shale, http://www.dep.state.pa.us/dep/deputate/minres/oilgas/new_forms/marcellus/marcellus.htm.
23. New York State Department of Health, Bureau of Environmental Radiation Protection (2009) (New York State Dept of Health, Troy, NY), Comments, July 21, 2009, Supplemental Generic Environmental Statement on the Oil and Gas Regulatory Program Well Permit Issuance for Horizontal Drilling and Hydraulic-Fracturing to Develop the Marcellus Shale and other Low Permeability Gas Reservoirs; http://www.riverkeeper.org/wp-content/uploads/2010/01/Riverkeeper-DSGEIS-Comments-Appendix-3-NYSDOH-Environmental-Radiation-Memo.pdf.
24. Taylor LE (1984) Groundwater Resources of the Upper Susquehanna River Basin, Pennsylvania: Water Resources Report 58. (Pennsylvania Dept of Environmental Resources-Office of Parks and Forestry—Bureau of Topographic and Geologic Survey, Harrisburg, PA) 139.
25. Williams JH, Taylor L, Low D (1998) Hydrogeology and Groundwater Quality of the Glaciated Valleys of Bradford, Tioga, and Potter Counties, Pennsylvania: Water Resources Report 68. (Commonwealth of Pennsylvania Dept of Conservation and Natural Resources, Harrisburg, PA) p 89.
26. Kendall C, Coplan TB (2001) Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrol Processes* 15:1363–1393.
27. Van Stempvoort D, Maathuis H, Jaworski E, Mayer B, Rich K (2005) Oxidation of fugitive methane in groundwater linked to bacterial sulfate reduction. *Ground Water* 43:187–199.
28. Taylor SW, Sherwood Lollar B, Wassenaar LI (2000) Bacteriogenic ethane in near-surface aquifers: Implications for leaking hydrocarbon well bores. *Environ Sci Technol* 34:4727–4732.
29. Cramer B, Schlomer S, Poelchau HS (2002) Uplift-related hydrocarbon accumulations: the release of natural gas from groundwater. 196 (Geological Society Special Publications, London), 447–455.
30. Geyer AR, Wilshusen JP (1982) Engineering characteristics of the rocks of Pennsylvania; environmental geology supplement to the state geologic map, 1982 Pennsylvania Geological Survey. (Dept of Environmental Resources, Office of Resources Management, Harrisburg, PA).
31. Etiope G, Martinelli G (2002) Migration of carrier and trace gases in the geosphere: An overview. *Phys Earth Planet Inter* 129:185–204.
32. Aravena R, Wassenaar LI (1993) Dissolved organic carbon and methane in a regional confined aquifer, southern Ontario, Canada: Carbon isotope evidence for associated subsurface sources. *Appl Geochem* 8:483–493.
33. Coleman DD, Liu C, Riley KM (1988) Microbial methane in the shallow Paleozoic sediments and glacial deposits of the Illinois, USA. *Chem Geol* 71:23–40.
34. Alexander SS, Cakir R, Doden AG, Gold DP, Root SI (2005) Basement depth and related geospatial database for Pennsylvania: Pennsylvania Geological Survey, 4th ser., Open-File General Geology Report 05-01.0. (Pennsylvania Dept of Conservation and Natural Resources, Middletown, PA), http://www.dcnr.state.pa.us/topogeo/openfile.
35. Pennsylvania Spatial Data Access (PASDA) Online mapping, data access wizard, oil and gas locations. (Pennsylvania Dept of Environmental Protection, Harrisburg, PA), http://www.pasda.psu.edu/uci/SearchResults.aspx?searchType=mapservice&condition=OR&entry=PASDA.

ATTACHMENT C

STUDY 34

A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States

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A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States

Avner Vengosh,*[,†] Robert B. Jackson,[†,‡] Nathaniel Warner,[§] Thomas H. Darrah,[∥] and Andrew Kondash[†]

[†]Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States

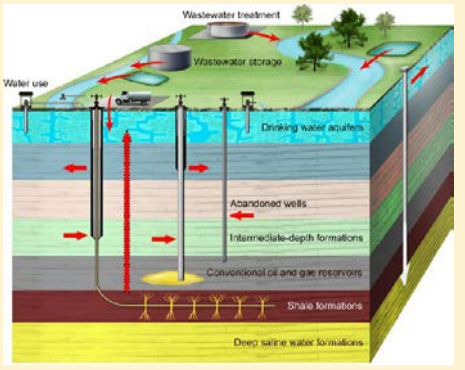
[‡]School of Earth Sciences, Woods Institute for the Environment, and Precourt Institute for Energy, Stanford University, Stanford, California 94305, United States

[§]Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire 03755, United States

[∥]School of Earth Sciences, The Ohio State University, Columbus, Ohio 43210, United States

Supporting Information

ABSTRACT: The rapid rise of shale gas development through horizontal drilling and high volume hydraulic fracturing has expanded the extraction of hydrocarbon resources in the U.S. The rise of shale gas development has triggered an intense public debate regarding the potential environmental and human health effects from hydraulic fracturing. This paper provides a critical review of the potential risks that shale gas operations pose to water resources, with an emphasis on case studies mostly from the U.S. Four potential risks for water resources are identified: (1) the contamination of shallow aquifers with fugitive hydrocarbon gases (i.e., stray gas contamination), which can also potentially lead to the salinization of shallow groundwater through leaking natural gas wells and subsurface flow; (2) the contamination of surface water and shallow groundwater from spills, leaks, and/or the disposal of inadequately treated shale gas wastewater; (3) the accumulation of toxic and radioactive elements in soil or stream sediments near disposal or spill sites; and (4) the overextraction of water resources for high-volume hydraulic fracturing that could induce water shortages or conflicts with other water users, particularly in water-scarce areas. Analysis of published data (through January 2014) reveals evidence for stray gas contamination, surface water impacts in areas of intensive shale gas development, and the accumulation of radium isotopes in some disposal and spill sites. The direct contamination of shallow groundwater from hydraulic fracturing fluids and deep formation waters by hydraulic fracturing itself, however, remains controversial.



1. INTRODUCTION

Production from unconventiognal natural gas reservoirs has substantially expanded through the advent of horizontal drilling and high-volume hydraulic fracturing (Figure 1). These technological advances have opened vast new energy sources, such as low-permeability organic-rich shale formations and "tight-sand" reservoirs, altering the domestic energy landscape in the United States.[1−3] The total production of natural gas has increased by more than 30% during the past decade. In 2012, unconventional shale gas and tight sand productions were respectively accounting for 34% and 24% of the total natural gas production in the U.S. (0.68 trillion m^3).[4]

The increase in energy production has been broadly distributed across the United States (Figure 2) and densely distributed within specific shale plays (Figure 3). Unconventional hydrocarbon extraction from organic-rich shale formations is now active in more than 15 plays in the U.S. In PA alone, 7234 shale gas wells were drilled into the Marcellus Formation[5] in addition to the 34 376 actively producing conventional oil and gas wells in that state (2012 data; Figure 3).[6] At the end of 2012, the Marcellus Shale (29%), Haynesville Shale (23%), and Barnett Shale (17%) dominated production of natural gas (primarily methane, ethane, and propane) from shales in the U.S., with the remaining 31% of total shale gas production contributed by more than a dozen basins (Figure 1). Oil and hydrocarbon condensates are also targeted in numerous basins, including the Barnett, Eagle Ford, Utica-Point Pleasant, and Bakken. [4]

Future energy forecasts suggest that U.S. unconventional natural gas production from shale formations will double by

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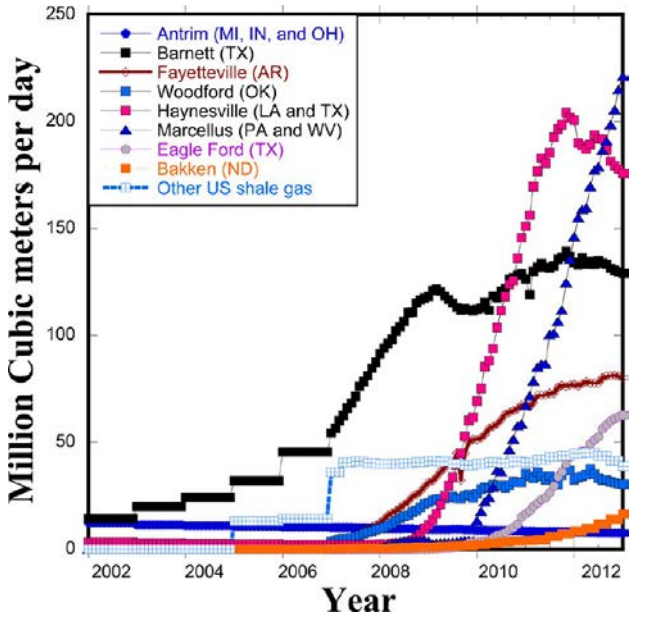

Figure 1. Evolution of the volume of natural gas production from different unconventional shale plays in the U.S. Data from the U.S. Energy Information Administration.[4]

2035 and generate ~50% of the total domestic natural gas production.[4] Similarly, U.S. domestic oil production from unconventional shale formations is projected to increase by as much as 15% over the next several decades.[7] Unconventional extraction (horizontal drilling and high volume hydraulic fracturing) for shale gas has already expanded to Canada[8] and will soon be launched on a global scale, with significant reservoirs in South America, northern and southern Africa, Europe, China,[9,10] and Australia.[11,12] The current global estimate of natural gas reserves in unconventional shale is approximately 716 trillion m^3 (2.53×10^{13} Mcf).[11,12]

Despite the large resource potentials and economic benefits, the rapid expansion of shale gas development in the U.S. has triggered an intense public debate over the possible environmental and human health implications of the unconventional energy development. Some primary concerns include air pollution, greenhouse gas emissions, radiation, and groundwater and surface water contamination.[1,3,13−36] These concerns have been heightened because the 2005 Energy Policy Act exempts hydraulic fracturing operations from the Safe Drinking Water Act (SDWA). The only exception to the exemption is the injection of diesel fuel. Additionally, because environmental oversight for most oil and gas operations is conducted by state rather federal agencies, the regulation, monitoring, and enforcement of various environmental contamination issues

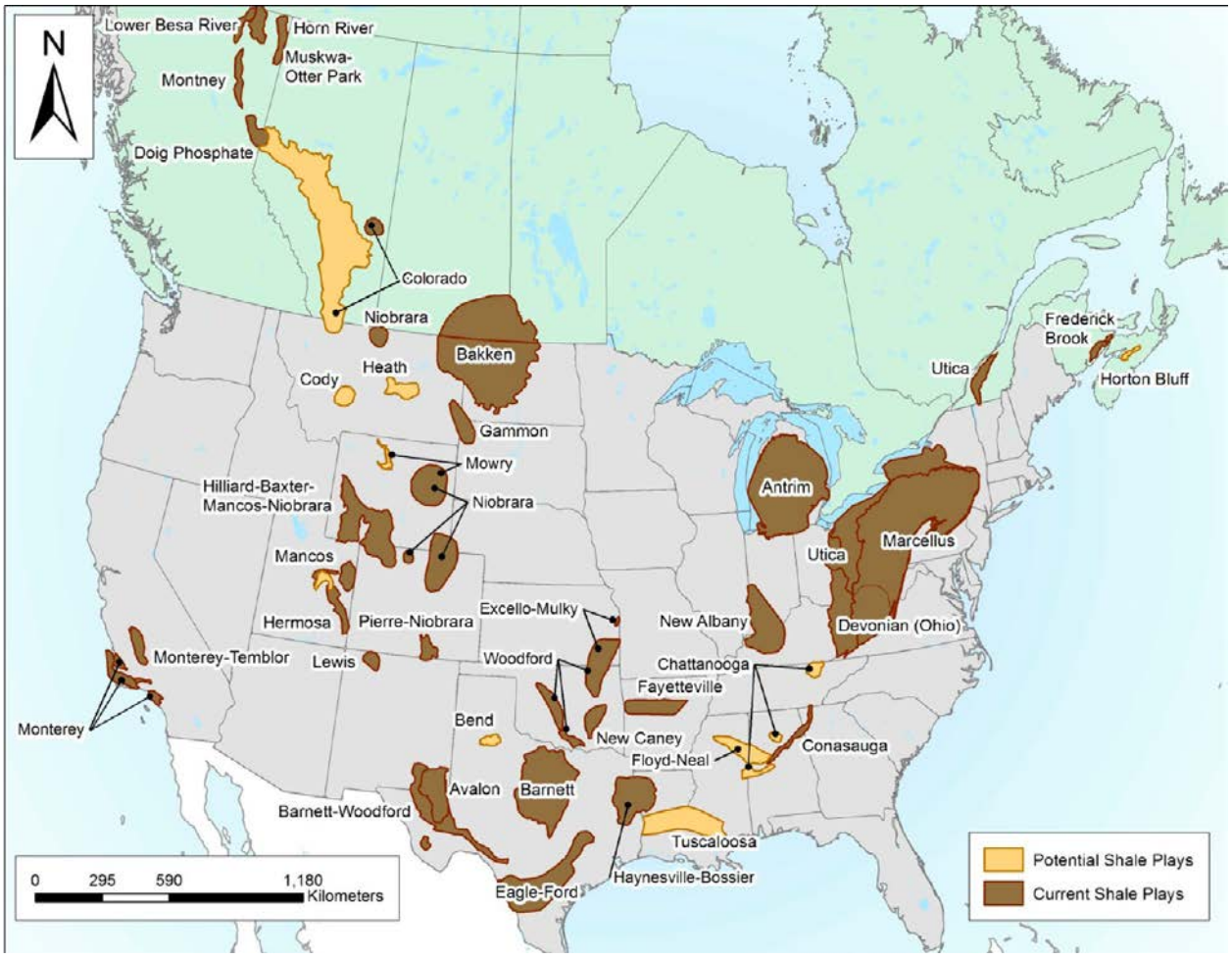

Figure 2. Map of unconventional shale plays in the U.S. and Canada, based on data from the U.S. Energy Information Administration.[4]

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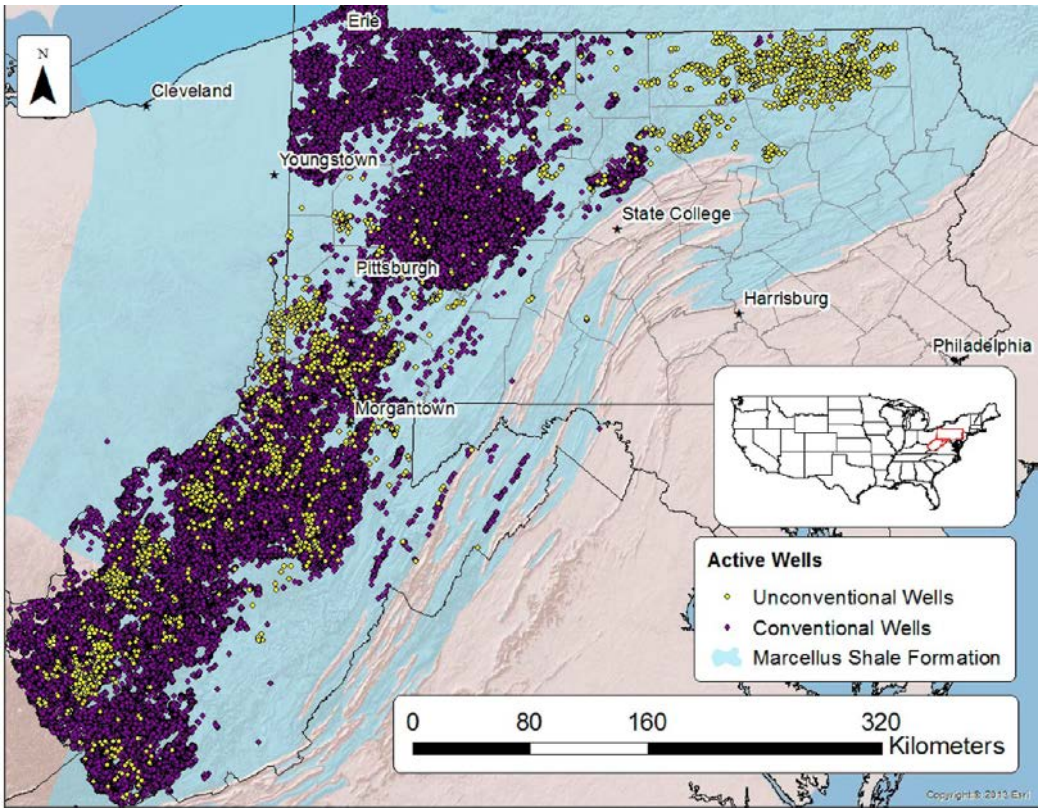

Figure 3. Map of active unconventional (yellow) and conventional (purple) oil and gas wells in Pennsylvania and West Virginia. Note areas of coexisting conventional and unconventional development (e.g., southwestern PA and WV) relative to areas of exclusively unconventional development (e.g., northeastern PA). Well locations were obtained from the West Virginia Geological Survey (http://www.wvgs.wvnet.edu/) and the Pennsylvania Department of Environmental Protection's oil and gas reporting Web site (https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Welcome/Welcome.aspx). The background topographic map, Marcellus Formation outline, and state boundaries were downloaded from http://www.pasda.psu.edu/ and the Carnegie Museum of Natural History.[148]

related to unconventional shale gas development are highly variable throughout the U.S.[37−39]

This paper provides an overview and synopsis of recent investigations (updated to January 2014) into one set of possible environmental impacts from unconventional shale gas development: the potential risks to water resources. We identify four potential modes of water resource degradation that are illustrated schematically in Figure 4 and include (1) shallow aquifers contaminated by fugitive natural gas (i.e., stray gas contamination) from leaking shale gas and conventional oil and gas wells, potentially followed by water contamination from hydraulic fracturing fluids and/or formation waters from the deep formations; (2) surface water contamination from spills, leaks, and the disposal of inadequately treated wastewater or hydraulic fracturing fluids; (3) accumulation of toxic and radioactive elements in soil and the sediments of rivers and lakes exposed to wastewater or fluids used in hydraulic fracturing; and (4) the overuse of water resources, which can compete with other water uses such as agriculture in water-limited environments.

2. GROUNDWATER CONTAMINATION

2.1. Stray Gas Contamination. Elevated levels of methane and other aliphatic hydrocarbons such as ethane and propane in shallow drinking water wells pose a potential flammability or explosion hazard to homes with private domestic wells. The saturation level of methane in near-surface groundwater is about ∼28 mg/L (∼40 cc/L) and thus the U.S. Department of the Interior recommends monitoring if water contains more than 10 mg/L (∼14 cc/L) of methane and immediate action if concentrations rise above 28 mg/L. Several states have defined a lower threshold (e.g., 7 mg/L in PA), from which household utilization of methane-rich groundwater is not recommended.

Stray gas migration in shallow aquifers can potentially occur by the release of gas-phase hydrocarbons through leaking casings or along the well annulus, from abandoned oil and gas wells, or potentially along existing or incipient faults or fractures[40] with target or adjacent stratigraphic formations following hydraulic fracturing and drilling (Figure 4).[27] The latter mechanism poses a long-term risk to shallow groundwater aquifers. Microseismic data suggest that the deformation and fractures developed following hydraulic fracturing typically extend less than 600 m above well perforations, suggesting that fracture propagation is insufficient to reach drinking-water aquifers in most situations.[41] This assertion is supported by noble gas data from northeastern PA,[42] yet stray gas migration through fractures and faults is considered a potential mechanism for groundwater contamination.[40]

Across the northeastern Appalachian Basin in PA, the majority of shallow groundwater had detectable, naturally occurring methane with thermogenic stable-isotope fingerprints (e.g., $\delta^{13}C-CH_4$ and $\delta^{2}H-CH_4$).[27−29,42,43] These findings imply that the high methane in shallow aquifers from this region is predominantly thermogenic in origin.[28,29,42,43] In northeastern PA, however, a subset of shallow drinking water wells consistently showed elevated methane, ethane, and

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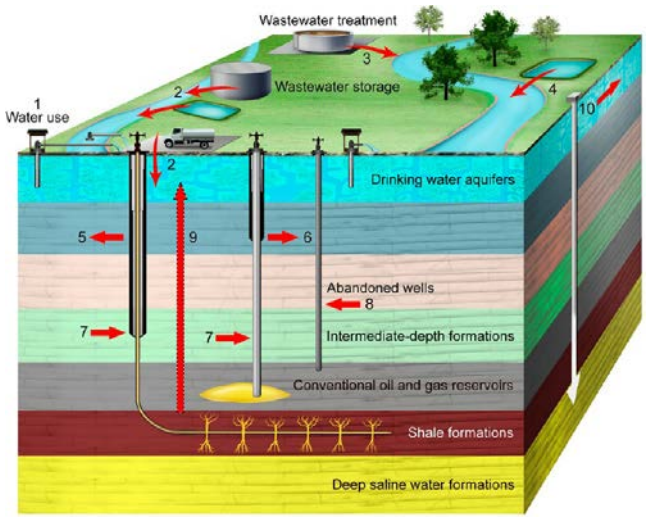

Figure 4. Schematic illustration (not to scale) of possible modes of water impacts associated with shale gas development reviewed in this paper: (1) overuse of water that could lead to depletion and water-quality degradation particularly in water-scarce areas; (2) surface water and shallow groundwater contamination from spills and leaks of wastewater storage and open pits near drilling; (3) disposal of inadequately treated wastewater to local streams and accumulation of contaminant residues in disposal sites; (4) leaks of storage ponds that are used for deep-well injection; (5) shallow aquifer contamination by stray gas that originated from the target shale gas formation through leaking well casing. The stray gas contamination can potentially be followed by salt and chemical contamination from hydraulic fracturing fluids and/or formational waters; (6) shallow aquifer contamination by stray gas through leaking of conventional oil and gas wells casing; (7) shallow aquifer contamination by stray gas that originated from intermediate geological formations through annulus leaking of either shale gas or conventional oil and gas wells; (8) shallow aquifer contamination through abandoned oil and gas wells; (9) flow of gas and saline water directly from deep formation waters to shallow aquifers; and (10) shallow aquifer contamination through leaking of injection wells.

propane concentrations (i.e., relatively low hydrocarbon ratios (C_1/C_2)) and relatively enriched thermogenic carbon isotope fingerprints in groundwater exclusively <1 km from shale gas drilling sites. A subset of samples with evidence for stray gas contamination display isotopic reversals ($\Delta^{13}C = \delta^{13}CH_4 - \delta^{13}C_2H_6 > 0$) and proportions of methane, ethane and propane that were consistent with Marcellus production gases from the region, while some other wells had natural gas compositions consistent with production gases in conventional wells from the overlying Upper Devonian formations.[27,29] New evaluations of the helium content[29] and noble gas geochemistry[42] in these samples further supports a distinction between naturally occurring "background" hydrocarbon gases and groundwater with stray gas contamination in wells located near (<1 km) shale gas drilling sites. "Background" gases typically had lower proportions of ethane and propane and elevated helium concentrations that reflect the history of natural gas migration from the Marcellus source rock to the Upper Devonian reservoir rocks throughout geological time.[29,42] Thus, the combination of gas geochemical fingerprinting suggests that stray gas groundwater contamination, where it occurs, is sourced from the target shale formations (i.e., the Marcellus Formation) in some cases, and from intermediate layers (e.g., Upper Devonian Formations) in others.

In cases where the composition of stray gas is consistent with the target shale formation, it is likely that the occurrence of fugitive gas in shallow aquifers is caused by leaky, failing, or improperly installed casings in the natural gas wells. In other cases, hydrocarbon and noble gas data also indicated that fugitive gas from intermediate formations apparently flowed up through the outside of the well annulus and then leaked into the overlying shallow aquifers.[27,29,42] In these cases, the isotopic signatures and hydrocarbon ratios matched the gases in intermediate formations rather than Marcellus shale production gases. In sum, the combined evidence of hydrocarbon stable isotopes, molecular hydrocarbon ratios, and helium geochemistry indicate that stray gas contamination occurs in a subset of wells <1km from drilling in northeastern PA.

In contrast to these reports, other investigators[22,43,44] have suggested that higher methane concentrations in shallow groundwater were natural and could be explained by topographic factors associated with groundwater discharge zones. Geochemical data do suggest that some natural gas migrated to shallow aquifers in northeastern PA through geologic time. However, these characteristics occur in areas with higher hydraulic connectivity between the deep and shallow formations.[34,42] A recent analysis showed that topography was indeed a statistically significant factor in some cases but did not explain the variations in methane and ethane concentrations with respect to distance to gas wells.[29]

Additional evidence for stray gas contamination because of poor well construction is provided by the isotopic composition of surface casing vent flow (SCV). Integrating the $\delta^{13}C$ data of methane (C1), ethane (C2), and propane (C3)[45−47] showed that stray gas contamination associated with conventional oil wells in Alberta, Canada reflected methane sourced from intermediate formations leaking into shallow aquifers and not from the production formations such as the Lower Cretaceous Mannville Group.[48] Jackson et al. (2013)[49] listed several other case studies that demonstrate evidence for stray gas contamination. While such studies have shown evidence for methane, ethane, and propane contamination associated with conventional oil production[48,50] and coal bed methane,[45] Muehlenbachs (2013)[51] also showed direct evidence for SCV leakage from intermediate zones in newly completed and hydraulically stimulated horizontal shale gas wells in the Montney and Horn River areas of northeastern British Columbia, Canada.[51] Methane leaking from the annulus of conventional oil and gas wells was also demonstrated in PA.[52,53] Combined, these studies suggest that stray gas contamination can result from either natural gas leaking up through the well annulus, typically from shallower (intermediate) formations, or through poorly constructed or failing well casings from the shale target formations.

The migration of natural gas to the surface through the production casing and/or well annulus is "a common occurrence in the petroleum industry"[51] and can affect a large fraction of conventional wells. Among the 15 000 production oil wells tested from the Gulf of Mexico, 43% have reported cement damage after setting that leads to sustained casing pressure (SCP). These effects increased with time; whereas 30% reported damage during the first 5 years after drilling, the percentage increased to 50% after 20 years.[54] Likewise, the BP Deepwater Horizon oil spill was partly attributed to the fact that "cement at the well bottom had failed to seal off

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hydrocarbons".[55] In PA the overall reports of cementing, casing, and well construction violations total 3% of all shale gas wells.[22] However a closer look at the distribution of violations shows large variations in percentage with time (before and after 2009), space, and type of wells.[5,56] In particular, the percentage of well violations was much higher in northeastern and central counties in PA (10−50%).[5] Consequently, reports of stray gas contamination in areas of unconventional shale gas development in the northeastern Appalachian Basin (U.S.) and Montney and Horn River Basins (Canada) may be associated with leaking of oil and gas wells.

In contrast to the results from the Marcellus, Montney, and Horn River Basins, the Fayetteville Shale in north-central Arkansas showed no evidence of methane contamination in groundwater. Studies in this area showed low methane concentrations with a mostly biogenic isotopic fingerprint.[36,57] The authors hypothesized the potential for stray gas contamination likely depends on both well integrity and local geology, including the extent of local fracture systems that provide flow paths for potential gas migration.[36]

In addition to groundwater, surface waters could serve as an indicator of regional migration from unconventional shale gas development. To date, streams in areas of shale gas drilling have not shown systematic evidence of methane contamination. A new methodology for stream-gas sampling as a reconnaissance tool for evaluating natural and anthropogenic methane leakage from natural gas reservoirs into surface waters was recently demonstrated using inorganic and gas geochemical tracers and could be applied more widely in areas of oil and gas development.[59]

2.2. Groundwater Contamination with Salts or Other Dissolved Constituents. The presence of fugitive gas in shallow drinking water wells could potentially lead to salinization and other changes of water quality in three possible ways. First, the leaking of natural gas can be associated with the flow of hydraulic fracturing fluids and saline formation waters to overlying shallow aquifers. Given the buoyancy of gas, the flow rate of denser saline water would be substantially slower than the flow of natural gas, and would depend on both the pressure gradients and hydraulic connectivity between the overpressurized annulus or leaking sites on the wells and the overlying aquifers.[53]

An EPA study[60] near the town of Pavillion, Wyoming found water contamination in two shallow monitoring wells. Although this initial study was questioned for adequate sampling protocols,[22] a follow up study by the U.S. Geological Survey confirmed elevated levels of specific conductance (1500 mS/cm), pH (10−11), methane (25−27 mg/L), ethane, and propane.[61] However, the mechanisms that caused the apparent contamination of the shallow groundwater in this area are still under investigation (i.e., contamination from surface ponds or subsurface leaking cement from shale gas wells).

The ability to trace and identify contamination from shale gas exploration is limited because of the relatively short time frame since the beginning of large-scale shale gas exploration in early-2000s compared to typical groundwater flow rates (i.e., decades). However, an evaluation of water contamination associated with conventional oil and gas exploration provides a much longer time frame for evaluating possible groundwater contamination. Possible evidence of long-term (2000−2007) increases in the salinity of groundwater associated with conventional oil and gas drilling was reported from Garfield County, CO. There, a rise of chloride concentrations in drinking water wells was associated with an increase of methane with a thermogenic isotopic fingerprint, both of which were associated with an increase in the number of conventional oil and gas wells.[62] The fraction of drinking water wells that had chloride concentrations >250 mg/L (EPA threshold for drinking water) in groundwater from Garfield County doubled between 2002 (4%) and 2005 (8%), with chloride up to 3000 mg/L in drinking water wells.[62] The parallel rise in salinity and methane with a thermogenic isotope signature in Garfield County could reflect either migration from leaking oil and gas wells or contamination from unlined surface impoundments.[62] Overall, the geochemical composition of the salinized groundwater in such scenarios would mimic the composition of either the formation water in the production formations[34] or the fluids in the shallower or intermediate units (that typically have a different water chemistry). While there might be evidence for water contamination in some areas of conventional oil and gas exploration, groundwater sites in areas affected by stray gas contamination near shale gas sites in northeastern PA have not to our knowledge shown signs of salinization induced directly by leaking natural gas wells.[27,29,34] Unlike other areas in PA, northeastern PA was developed recently and almost exclusively for shale gas (Figure 3), with few legacy wells reported in the area. Thus, any water contamination in this area attributable to natural gas extraction would be related to current shale gas operations rather than to older legacy wells. Therefore conclusions regarding contamination from saline water and hydraulic fracturing fluids flow are restricted in both space and time and further studies are needed to address this question.

A second mode of groundwater contamination that could evolve from stray gas contamination is oxidation of fugitive methane via bacterial sulfate reduction.[50] Evidence for dissimilatory bacterial sulfate reduction of fugitive methane near conventional oil wells in Alberta, Canada, includes sulfide generation and ^{13}C-depleted bicarbonate, with lower residual sulfate concentrations relative to the regional groundwater.[50] Bacterial sulfate reduction reactions due to the presence of fugitive methane could trigger other processes such as reductive dissolution of oxides in the aquifer that would mobilize redox-sensitive elements such as manganese, iron, and arsenic from the aquifer matrix and further reduce groundwater quality. Low levels of arsenic and other contaminants, recorded in some drinking water aquifers in TX, were suggested to be linked to contamination from the underlying Barnett Shale,[63] although evidence for a direct link to the Barnett remains uncertain.

A third hypothetical mode of shallow groundwater contamination associated with the presence of stray gas contamination is the formation of toxic trihalomethanes (THMs), typically co-occurring with high concentrations of halogens in the saline waters. THMs are compounds with halogen atoms (e.g., Cl, Br, or I) substituted for hydrogens in the methane molecule. The formation of THMs were previously recorded in untreated groundwater in the U.S., unrelated to shale gas activities, but associated with agricultural contamination of shallow aquifers.[64,65] Numerous studies have demonstrated that the presence of halogens together with organic matter in source waters can trigger the formation of THMs, specifically in chlorinated drinking water (see references in Section 2.1). However, no data has to our knowledge been reported for the presence of THMs in groundwater associated with stray gas contamination from shale gas wells.

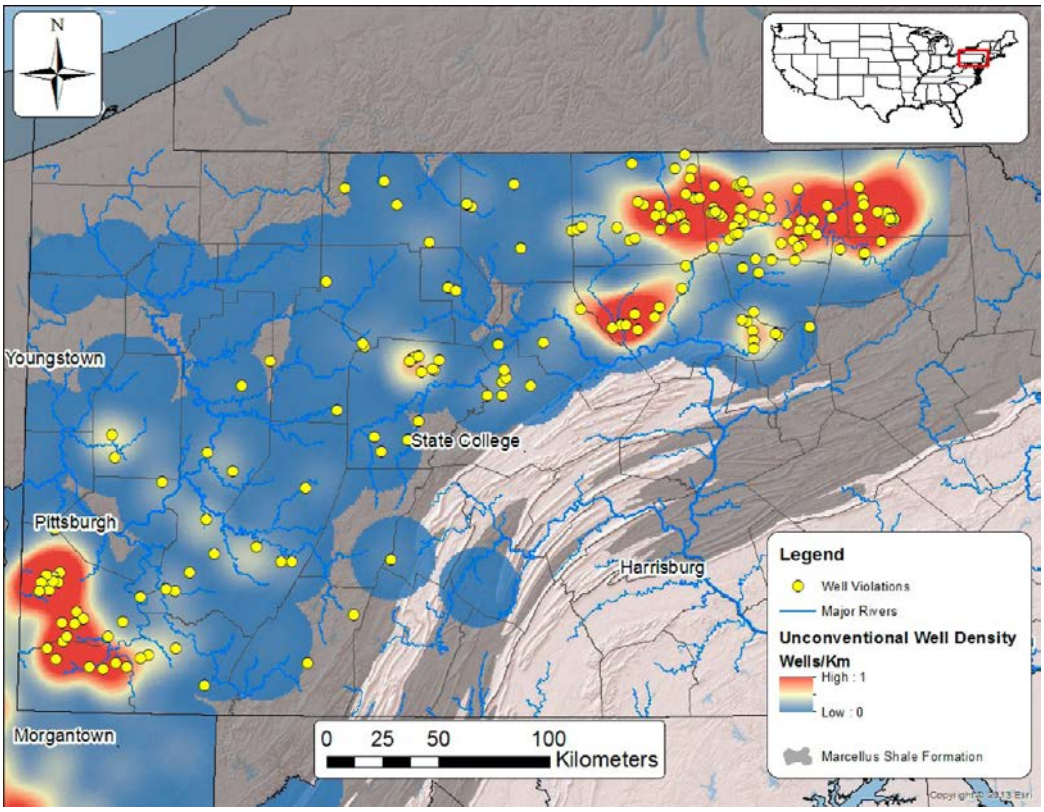

Figure 5. Map of Pennsylvania with density of unconventional well drilling and occurrence of reported environmental violations. Warm colors (red) represent areas of higher density of unconventional well drilling while cooler colors (blue) are areas of lower drilling density. Unconventional wells with reported violations of a release to the environment are shown by yellow dots. Violations include discharge of industrial waste to streams, drill cuttings, oil, brine and/or silt, discharged without a permit, and polluting substances discharged to waterways. Data on violations was obtained from http://www.fractracker.org/downloads/. Unconventional well density was derived from unconventional well data points obtained from the Pennsylvania Department of Environmental Protection's oil and gas reporting Web site (https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Welcome/Welcome.aspx). Background maps, the Marcellus Formation, and state boundaries were downloaded from http://www.pasda.psu.edu/ and the Carnegie Museum of Natural History[148]

In addition to the effects of poor oil and gas-well integrity, shallow aquifers could potentially be contaminated by the migration of deep hypersaline water or hydraulic fracturing fluids through conductive faults or fractures.[15,34] The potential upward flow of fluids from the impermeable shale formations is highly debated; one model has suggested that the advective preferential flow through fractures could allow the transport of contaminants from the fractured shale to overlying aquifers in a relatively short time of six years or less.[15] Other studies have disputed this model,[66−68] suggesting that the upward flow rate of brines would typically be fairly low because of the low permeability of rocks overlying the shale formations, low upward hydraulic gradients, and the high density of fluids.[41,69,70] The hydraulic conductivity along a fault zone seems to have an important effect on the potential for upward migration of hydraulic fracturing fluid or underlying brines.[40]

Evidence for cross-formational fluid flow of deep saline groundwater into overlying shallow aquifers, independent of oil and gas operations, was demonstrated in the Devonian oil-bearing formations in southwestern Ontario, Canada,[71] east-central Michigan Basin,[72] Ogallala Aquifer, Southern High Plains, Texas,[73,74] and shallow aquifers overlying the Marcellus Shale in northeastern PA.[34] The latter case appears to be an example of a naturally occurring process in which deep-seated Middle Devonian Marcellus-like saline waters (deterimined by Br/Cl and $^{87}Sr/^{86}Sr$ ratios) migrated upward to shallow Upper Devonian aquifers in northeastern PA. In this area of PA, which had little oil and gas drilling prior to recent shale gas development (Figure 3), the presence of elevated salts was recorded in a subset of domestic wells during the 1980s.[34] These findings indicate that the salinization phenomenon is not related to recent unconventional drilling in shales.[34] The presence of naturally occurring saline groundwater in areas of shale gas development in the Appalachian Basin poses challenges for quantifying contamination from active shale gas development, including the ability to distinguish naturally occurring groundwater salinization from anthropogenic sources of groundwater pollution.

3. SURFACE WATER CONTAMINATION

Few studies have analyzed the major chemical constituents in injected hydraulic fracturing fluids (although considerable information is available on the Web site www.fracfocus.org). Based on the available information, hydraulic fracturing fluids include water (either fresh water or reused hydraulic fracturing water), proppants (sand, metabasalt, or synthetic chemicals added to "prop" incipient fractures open), acids (e.g., hydrochloric acid), additives to adjust fracturing fluid viscosity (guar gum, borate compounds), viscosity reducers (ammonium persulfate), corrosion inhibitors (isopropanol, acetaldehyde), iron precipitation control (citric acid), biocides (glutaraldehyde), oxygen scavengers (ammonium bisulfite), scale inhib-

itors (e.g., acrylic and carboxylic polymers), and friction reducers (surfactants, ethylene glycol, polyacrylamide).[22,49,75−77] Based on different hazardous components of hydraulic fracturing fluid additives used in wells from the Marcellus Shale, it was suggested that sodium hydroxide, 4,4-dimethyl, oxazolidine, and hydrochloric acid would be good indicators to monitor water contamination upon a leak or a spill of hydraulic fracturing fluids.[78]

More information is available on the inorganic chemistry of the "flowback" fluids (fluids that return to the surface after the hydraulic fracturing process is complete) and produced waters (fluids that are extracted together with the natural gas during production). Flowback water is a mixture of the injected hydraulic fracturing fluids and the natural fluids within the formation (e.g., brine). In some cases the injected fluid contains recycled flowback water from one or more different drill sites. About 10−40% of the volume of the injected fracturing fluids returns to the surface after hydraulic fracturing, and the flow rates of flowback water slow with time to levels of 2−8 m^3/day during the production stage of a shale gas well.[75] The typical salinity of flowback water increases with time after hydraulic fracturing due to an increasing proportion of the formation water mixing with injection fluids.[79] Produced waters are typically composed of naturally occurring hypersaline formation water, and can also contain oil, bitumen, and hydrocarbon condensates with high concentrations of total dissolved organic carbon (up to 5500 mg/L), in addition to the added organic chemicals that were reported in flowback waters (e.g., solvents, biocides, scale inhibitors).[34,35,49,75,79,80−86] In most flowback and produced waters, the concentrations of toxic elements such as barium, strontium, and radioactive radium are positively correlated with the salinity.[34,49,79,81,82] Some flowback and produced waters, such as those found in the Marcellus shale, are also enriched in arsenic and selenium[87] that are associated with the high metal contents in shale rock.[88] The correlation of toxic and radioactive elements with salinity suggests that many of the potential water quality issues associated with wastewaters from unconventional shale gas development may be attributable to the geochemistry of the brines within the shale formations. The total dissolved salts (TDS) content of produced water ranges from below seawater (25 000 mg/L) to 7 times more saline than seawater, depending on the shale formation. For example, the Fayetteville (25 000 mg/L), Barnett (60 000 mg/L), Woodford (110 000−120 000 mg/L), Haynesville (110 000−120 000 mg/L), and Marcellus (up to 180 000 mg/L) shale formations vary by nearly an order of magnitude in TDS values.[83] The salinity, strontium, and barium contents vary geographically within formations as shown for the Marcellus shale.[79,82] The volume and the salinity of flowback waters also vary spatially among shale gas wells. [75]

In some cases the flowback and produced waters are stored in ponds near the drilling sites. The salinity variations of the wastewater generate chemical stratification within the ponds that is also associated with anoxic conditions of the bottom waters in the ponds.[89,90] The high salinity and temperature of the flowback water and the anoxic conditions control the microbial community in these storage ponds by increasing the proportion of halotolerant and anaerobic bacteria species.[76,77,89−91]

Given that produced waters have much higher salinities than surface waters (typically TDS ≪ 1000 mg/L), even small inputs can impact freshwater quality. We consider three potential modes of impacts on surface water: (1) surface leaks and spills of flowback and produced water associated with shale gas operations (e.g., overflow or breaching of surface pits, insufficient pit lining, onsite spills); (2) direct, unauthorized, or illegal disposal of untreated wastewater from shale gas operations; and (3) inadequate treatment and discharge of shale gas wastewater (e.g., treatment at plants not sufficiently designed to remove halogens, radionuclides, or heavy metals).

The first mode of impact from spills and leakage typically occurs near drilling locations. Figure 5 presents the locations of sites where violations related to spills and leaks associated with shale gas operations have been reported in PA (data on violations was obtained from http://www.fractracker.org/downloads/). The occurrence and frequency of the spills and leaks appear to coincide with the density of shale gas drilling,[92] as demonstrated by the co-occurrence of Marcellus unconventional well density in northeastern and western PA (Figure 5). An analysis shows that the number of reported violations increases in areas closer to higher (>0.5 well per km^2) shale gas drilling density, and the frequency of violations per shale gas well doubles in areas of higher drilling density (Supporting Information Figure S1). One of the unique features of the unconventional energy production of low permeable shale and tight sand formations is the rapid decrease of the natural gas production, up to 85% during the first three years of operation.[93,94] In order to overcome this decline in production, unconventional wells are drilled at high rates, and over 20 000 wells have been constructed since the mid 2000s through the U.S. The rapid growth and intensity of unconventional drilling could lead to a higher probability of surface spills or leaks and potential stray gas contamination of adjacent drinking water wells.

Spills or leaks of hydraulic fracturing and flowback fluids can pollute soil, surface water, and shallow groundwater with organics, salts, metals, and other constituents. A survey of surface spills from storage and production facilities at active well sites in Weld County, Colorado that produces both methane gas and crude oil, showed elevated levels of benzene, toluene, ethylbenzene, and xylene (BTEX) components in affected groundwater. Following remediation of the spills, a significant reduction (84%) was observed in BTEX levels in the affected wells.[95] As mentioned earlier, an EPA study[60] in Pavillion, Wyoming found increased concentrations of benzene, xylenes, gasoline range organics, diesel range organics, hydrocarbons, and high pH in two shallow monitoring wells.[60] The U.S. Geological Survey conducted a follow up study and found similar elevated levels of specific conductance (1500 mS/cm), pH (10−11), methane (25−27 mg/L), ethane and propane, yet low levels of organic compounds.[61] The shallow groundwater contamination was linked in part to surface pits used for the storage/disposal of drilling wastes and produced and flowback waters.[60] Similarly, leaks, spills, and releases of hypersaline flowback and produced waters are expected to impact the inorganic quality of surface water because these brines contain highly elevated concentrations of salts (Cl, Br), alkaline earth elements (e.g., Ba, Sr), metalloids (e.g., Se, As), and radionuclides (e.g., Ra).

A second mode of contamination would be disposal of untreated wastewater from shale gas operations. A joint U.S. Geological Survey and U.S. Fish and Wildlife Service study showed that the unauthorized disposal of hydraulic fracturing fluids to Acorn Fork Creek in southeastern Kentucky in May and June 2007 likely caused the widespread death or distress of aquatic species.[96] Likewise, an experimental release of hydraulic

fracturing fluids in a forest in WV has shown severe damage and mortality to ground vegetation over a very short time (10 days). Over a longer time (two years), about half of the trees were dead and sodium and chloride increased by 50 fold in the soil.[97]

A third mode of surface water contamination can occur through improper handling and disposal of hydraulic fracturing fluids and associated wastewater. These types of environmental releases may occur through the disposal of inadequately treated wastewater. In the U.S., wastewater from unconventional energy production is managed in various ways; wastewater is sometimes recycled for subsequent hydraulic fracturing operations, injected into deep injection wells, or treated. The treatment options include publicly owned treatment works (POTWs), municipal wastewater treatment plants (WWTP), or commercially operated industrial wastewater treatment plants. In addition to these wastewater management techniques, some states allow operators to spread the fluids onto roads for dust suppression or deicing.[23,35,39,98−102]

The disposal of inadequately treated wastewater from shale gas operations may contaminate surface waters at the disposal sites.[23,35,99] Effluent discharge from treatment sites in PA were characterized by high levels of salinity (TDS up to 120 000 mg/L), toxic metals (e.g., strontium, barium), radioactive elements (radium isotopes), and organic constituents such as benzene and toluene.[23] For example, chlorine concentrations were elevated 6000-fold above stream background levels at the point of wastewater effluent discharge into surface water at a treatment facility, while bromide was enriched by up to 12 000-fold.[35] In spite of significant dilution, bromide levels in downstream streamwater (~2 km) were still elevated (16-fold) above background stream levels.[35]

Such bromide enrichment in waterways has important implications for downstream municipal water treatment plants, given the potential formation of carcinogenic THMs in chlorinated drinking water.[103−111] As the volume of wastewater treatment from unconventional energy development has expanded, bromide concentrations downstream from wastewater disposal sites along the Monongahela River in PA,[112] and THM concentrations, especially of brominated species, increased in municipal drinking water in Pittsburgh, PA.[113] Both sources of contamination were linked directly to the disposal and ineffective removal of bromide from wastewater from shale gas development.[112−114] In spite of a 2011 ban on the disposal of shale gas wastewater to streams in PA, evidence for the Marcellus wastewater disposal based on isotopic ratios[35] and elevated Br levels collected from the Clarion River after May 2011 was suggested[113] to reflect either illegal dumping or incomplete implementation of the ban where a portion of unconventional wastewater is still being transferred to brine treatment facilities. [113]

In several disposal sites examined in PA, the wastewater effluent had Marcellus-like geochemical fingerprints such as high TDS, low SO_4/Cl ratio[99] and distinctive Br/Cl, $^{228}Ra/^{226}Ra$, and $^{87}Sr/^{86}Sr$ ratios.[35] These geochemical parameters suggest that at least some of the stream contamination in western Pennsylvania was related to wastewater disposal from shale gas operations, in addition to the legacy disposal of wastewater from conventional oil and gas activities on longer (decades) time scales. The potential formation of THMs in bromide-rich water is not restricted to shale gas operations, and could also result from disposal of wastewaters from conventional oil and gas or coalbed methane operations. Overall, more data is needed to evaluate the impact of wastewater management in the Marcellus and other unconventional shale gas basins, especially in areas where surface water discharge for dust and ice control is still common.

The increasing volume and the potential environmental impacts associated with wastewater treatment have increased the demand for deep well injection sites, catalyzed the development of new suitable treatment processes, and led to the reuse and recycling of a larger fraction of the wastewater. In many states (e.g., Texas), deep injection is the most commonly applied wastewater management practice, although reuse and recycling is becoming increasingly common during the last several years.[102] However, each of these wastewater management methods has environmental risks. For example, the injection of high volumes of wastewater into deep disposal wells may induce seismicity and earthquakes,[115−122,123] and groundwater near injection wells may become contaminated by cement failure or issues of injection well integrity.[124] In addition, many of the injection wells are associated with storage ponds that could also pose environmental risks upon leakage from improper lining and management.

4. THE ENVIRONMENTAL LEGACY OF CHEMICAL RESIDUES IN AREAS OF DISPOSAL AND LEAKS

Over time, metals, salts, and organics may build up in sediments, scales, and soil near wastewater disposal and/or spill sites. Each respective compound has a fixed solubility and reactivity (e.g., adsorption), the latter commonly described by the distribution coefficient (K_d) that varies as a function of pH, Eh, temperature, and the occurrence of other components in the water. As a result, the physicochemical conditions of surface waters and the distribution coefficients of each compound will determine how it interacts with particulate matter (e.g., colloidal particles) or river sediments. Ultimately, these properties will determine the long-term environmental fate of such reactive contaminants; reactive constituents would be adsorbed onto soil, stream, or pond sediments and potentially pose long-term environmental and health risks.

Marcellus wastewaters contain elevated levels of naturally occurring radionuclides (NORM) in the form of radium isotopes.[34,35,81,85] The elevated radium levels in Marcellus brines is due to the mobilization of radium from uranium-rich source rocks into the liquid phase under high salinity and reducing conditions.[85] Disposal of the NORM-rich Marcellus waste fluids to freshwater streams or ponds would cause radium adsorption onto the stream sediments in disposal and/or spill sites because radium adsorption is inversely correlated with salinity.[125−128] Disposal of treated wastewater originating from both conventional and unconventional oil and gas production in western Pennsylvania has caused radium accumulation on stream sediments downstream of a disposal site from a brine treatment facility.[35] The radium accumulated in the stream sediments had $^{228}Ra/^{226}Ra$ ratios identical to those of the Marcellus brines, thus linking this accumulation directly to the disposal of unconventional shale gas wastewater. The level of radioactivity found in sediments at one brine-treatment discharge site exceeded the management regulations in the U.S. for a licensed radioactive waste disposal facility.[35] Elevated NORM levels were also found in soils near roads associated with road spreading of conventional oil and gas brines for deicing[129] and on pond bottom sediments associated with a spill from hydraulic fracturing activities.[58] High NORM levels were recorded also in soil and sludge from reserve pits used in unconventional natural gas mining.[130] In addition to the high γ

Table 1. Water Use and Wastewater Production Per Shale Gas Well in Different Shale Gas Basins in the U.S. Based on Previous Reports and on Data Compiled in This Study[a]

basin	water use per well (m^3)	wastewater per well (m^3)	source
Horn River Basin (British Columbia, Canada)	50 000		Johnson and Johnson (2012)[136]
Marcellus Shale, PA (<2010)	7700−38 000		Kargbo et al. (2010)[1]
Marcellus Shale, PA (2008−2011)	11 500−19 000	5200	Lutz et al. (2013) [101]
Marcellus Shale, PA (2012)		3500	this study
Woodford Shale, OK	16 000		Murray (2013)[135]
Barnett Shale, TX	10 600		Nicot and Scanlon (2012)[134]
Haynesville Shale, TX	21 500		Nicot and Scanlon (2012)[134]
Eagle Ford, TX	16 100		Nicot and Scanlon (2012)[134]
Niobrara, CO (2012)	13 000	4000	this study

[a]Calculations for water use and wastewater volume per well for Marcellus Shale in PA were made for 2012 data retrieved from PA Department of Environmental Protection's oil and gas reporting website (https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Welcome/Welcome.aspx) and for the Niobrara Shale in CO were taken from the Colorado Oil and Gas Conservation Commission (http://cogcc.state.co.us/).

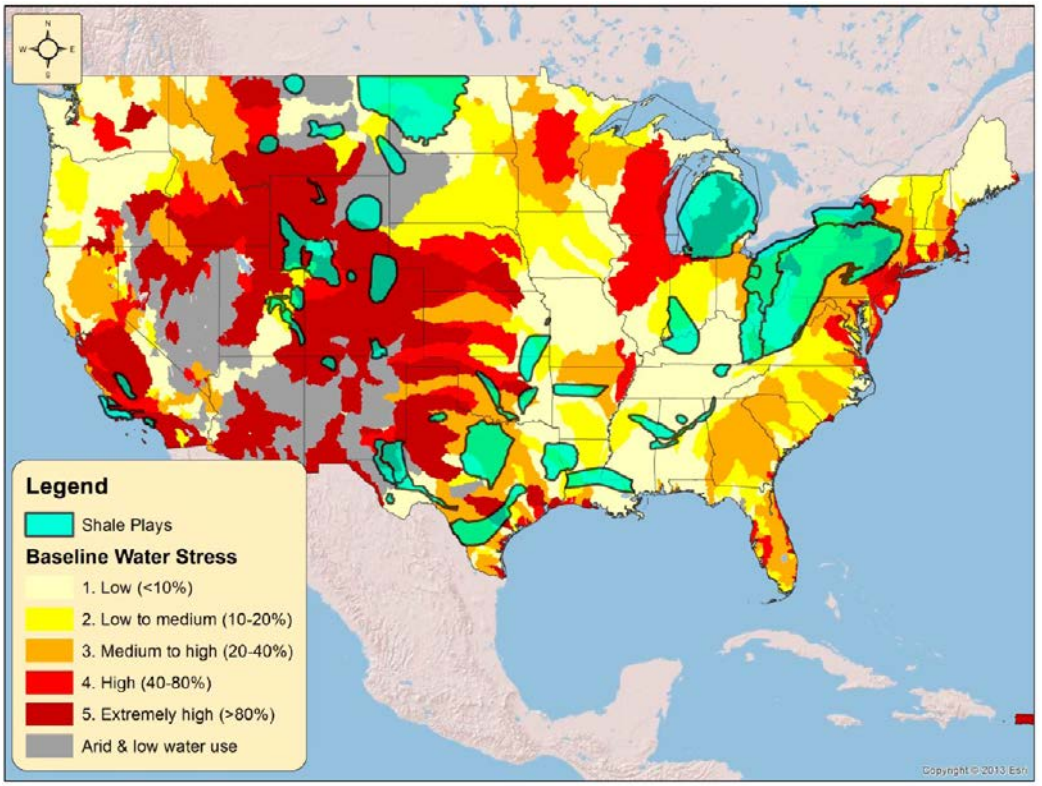

Figure 6. Map of the baseline water stress conditions[139] in relation to shale play locations across the U.S. Note that many of the western shale plays are associated with high to severe baseline water stress, which reflects the ratio between water withdrawals and availability.[139]

radiation associated with radionuclides from the ^{226}Ra decay series (^{214}Pb, ^{214}Bi, ^{210}Pb) and ^{232}Th- decay series (^{228}Ra, ^{228}Th, ^{208}Tl), elevated beta radiation was observed, up to 50 000 Bq/kg.[130]

These results highlight the risks associated with the disposal or spill of NORM-rich flowback and produced waters; even if the disposal is within regulations, the high volumes of wastewater can lead to a buildup of radium, and radiation can pose substantial environmental and health risks. Likewise, radium-bearing barite is a common constituent of scale and sludge deposits that are associated with conventional oil and gas exploration.[130−133] Elevated radium levels were recorded in soil and pipe-scale near oil production sites in the U.S., with ^{226}Ra activity up to ~490 000 Bq/kg.[131] We expect that solid wastes from drilling and soil near shale gas drilling sites as well as solids from brine treatment facilities[132] will sometimes have similar high levels of radioactivity. We conclude that reactive residuals in brines, such as metals and radioactive elements, can accumulate in river and lake sediments and could pose long-term environmental and health effects by slowly releasing toxic elements and radiation in the impacted areas.

5. WATER SCARCITY AND SHALE GAS DEVELOPMENT

Evaluations of the water footprint for shale gas development have been based on the amount of water used for drilling and hydraulic fracturing. Reports of the water consumption for shale gas development from the Marcellus,[101] Barnett, Haynesville, Eagle Ford,[134] Woodford Shale,[135] and Horn River in British Columbia[8,49,136] showed that water use varies

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from 8000 to 100 000 m^3 (2−13 million gallons) per unconventional well (Table 1).

Total water use for shale gas development overall is relatively low compared to other water withdrawal sources, such as cooling water for thermoelectric-power generation, which consists ∼40% of total freshwater withdrawals in the U.S.[137,134,135] Based on two independent reports,[6,138] the total number of shale gas wells in the U.S. was about 20 000 in 2012. That number of wells accounts for an overall (cumulative) water footprint (based on an average of 15 000 m^3 used per well) of $\sim 300 \times 10^6$ m^3. A different study has suggested a similar volume of water use of $\sim 250 \times 10^6$ m^3.[139] Assuming that 10% of the water used for thermoelectric-power generation is lost through evaporation[137] ($\sim 27.8 \times 10^9$ m^3 out of 278×10^9 m^3 per year), the total water volume that has been consumed during the past decade for hydraulic fracturing ($\sim 300 \times 10^6$ m^3) was only ∼1% of that annual water loss from cooling thermoelectric-power generation.

However, in geographic areas with drier climates and/or higher aquifer consumption, such as Texas, Colorado, and California, groundwater exploitation for hydraulic fracturing can lead to local water shortages[134] and subsequent degradation of water quality. Even in wet areas, variations in the stream flows can induce water shortage upon water extraction for hydraulic fracturing.[140] In small to moderate streams in the Susquehanna River Basin of northern Appalachian Basin, water withdrawals for hydraulic fracturing can exceed the natural flows, particularly during low-flow periods.[37] Likewise, water use for hydraulic fracturing in southern Alberta, Canada has become limited because the river waters is already allocated for other users, and in other locations in British Columbia, the variability in stream discharge is a limiting factor for withdrawals for shale gas exploration.[8] In addition to detailed water balance evaluations in several basins,[134,135] nearly half of the shale gas wells in the U.S. were developed in basins with high water scarcity, particularly in Texas and Colorado.[139] The overlap of the shale plays with water basins where water withdrawal exceeds 40% of the annual replenishment[139] is illustrated in Figure 6 and consistent with the exceptional 2013 drought conditions in western U.S. (SI Figure S2). Alternative water sources, such as brackish to saline groundwater,[8] treated domestic wastewater, and/or acid mine drainage in the Appalachian Basin[141−143] should be considered as potential alternatives for drilling and hydraulic fracturing in these areas. Likewise, the increased reuse of shale gas wastewater for hydraulic fracturing could mitigate the water gap.[75]Overall the expected rise in unconventional wells will increase the water use and possibly the water footprint in the U.S.

6. POSSIBLE SOLUTIONS

Given the different risks to water resources that are associated with shale gas development in the U.S., we consider several plausible solutions that could mitigate some of the identified

Second, the debate whether the occurrence of natural gas in drinking water is naturally occurring or related directly to contamination through leaking from shale gas wells could be addressed by mandatory baseline monitoring that would include modern geochemical techniques such as major and trace elements, $\delta^{18}O$ and $\delta^{2}H$ in water and $\delta^{13}C$ in DIC, methane concentration, and stable isotopes of methane ($\delta^{13}C-CH_4$, $\delta^{2}H-CH_4$) for adequate characterization of the chemical and isotopic composition of regional aquifers in areas of shale gas development. The baseline data, followed by data generation from continuous monitoring and production gas chemistry should become accessible to the scientific community and will be used to evaluate cases where water contamination may occur. Third, transparency and data sharing, including full disclosure of all hydraulic fracturing chemicals, are critical for establishing an open and scientific discussion that could alleviate potential legal and social conflicts.

With respect to wastewater management, enforcing zero discharge policy for untreated wastewater and establishing adequate treatment technologies could prevent surface water contamination. Currently two types of wastewater treatment are used; thermal evaporation/distillation and brine treatment through lime and Na_2SO_4 addition.[100,144]While thermal evaporation/distillation removes all dissolved salts in the wastewater, brine treatment with lime and Na_2SO_4 addition only removes metals such as barium and NORM but does not remove halogens (chloride and bromide)[23,35] In order to reduce the potential formation of THM compounds in downstream drinking water facilities, additional remediation technologies, such as complete desalination,[145] should be introduced for removal of the dissolved salts to levels acceptable for healthy stream ecology (e.g., TDS <500 mg/L). Likewise, reduction of the radioactivity from wastewater and safe disposal of NORM-rich solid wastes and/or solid residues from treatment of wastewater is critical in preventing contamination and accumulation of residual radioactive materials.[35] Since disposal of wastewater through deep-well injection is not always possible and large volume of injection could induce seismicity in some areas, developing remediation technologies for adequate treatment and safe disposal of wastewater is critical for protecting waterways.

Finally, the possible limitation of fresh water resources for shale gas development could be mitigated by either using alternative water resources that would substitute for fresh water or using other types of liquids (e.g., gel) for hydraulic fracturing. The beneficial use of marginal waters (i.e., water with low quality that cannot be used for the domestic or agricultural sectors) is that in many cases such water is discharged and can harm the environment; using these water sources for hydraulic fracturing could therefore have multiple advantages. For example, the use of acid mine drainage (AMD) for hydraulic fracturing could mitigate the current AMD discharge and contamination of numerous waterways in eastern U.Sly. Experimental blending of AMD and Marcellus flowback waters has shown that the blending causes the formation of Sr-Barite salts that in turn capture some of the contaminants in both fluids (e.g., sulfate and iron in AMD, barium, strontium, and radium in flowback waters).[143] In the Horn River Basin of British Columbia, Canada, saline groundwater with TDS of up to 30 000 mg/L is treated to remove H_2S and other gases and used for hydraulic fracturing.[8] The current upper limit for salinity (for adjusting to friction reducers) in hydraulic fracturing fluids is about 25 000 mg/L, although a salt-tolerant and water-based friction reducer has been developed to enable recycling of even higher saline wastewater for hydraulic fracturing.[146] Consequently, utilization of saline, mineralized, and other types of marginal waters should be considered for

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hydraulic fracturing and drilling, particularly in areas highly water scarcity. Recycling shale gas wastewater with marginal waters can generate both a new water source for hydraulic fracturing and mitigate the environmental effects associated with the wastewater disposal. Likewise, oil and gas produced waters can be beneficially used upon adequate treatment and management[147]

7. CONCLUSIONS

Our survey of the literature has identified four plausible risks to water resources associated with shale gas development and hydraulic fracturing, as illustrated in Figure 4. The first risk is contamination of shallow aquifers in areas adjacent to shale gas development through stray gas leaking from improperly constructed or failing gas wells. Over a longer-time scale, the quality of groundwater in aquifers where stray gas contamination has been identified could potentially be impacted by both leaking of saline water and hydraulic fracturing fluids from shale gas wells and by secondary processes induced by the high content of methane in the groundwater (i.e., sulfate reduction). Thus, evidence of stray gas contamination could be indicative of future water quality degradation, similar to that observed in some conventional oil and gas fields. The second risk is contamination of water resources in areas of shale gas development and/or waste management by spills, leaks, or disposal of hydraulic fracturing fluids and inadequately treated wastewaters. The third risk is accumulation of metals and radioactive elements on stream, river and lake sediments in wastewater disposal or spill sites, posing an additional long-term impact by slowly releasing toxic elements and radiation to the environment in the impacted areas. The fourth risk is the water footprint through withdrawals of valuable fresh water from dry areas and overexploitation of limited or diminished water resources for shale gas development.

Much of the debate on the possibility of water contamination is related to the availability of baseline water chemistry data in aquifers before shale gas development. Yet full baseline data is often unavailable, given the lack of systematic and component-specific monitoring of private wells and surface water systems across the U.S. Developing novel geochemical and isotopic tracers that would confirm or refute evidence for contamination can help fill this data gap. The study of water contamination is often based on the characterization of water quality in a regional aquifer and/or surface water away from contamination sites, rather than monitoring water quality changes through time. Retrospective studies of water contamination associated with shale gas development should therefore include a comprehensive investigation of the hydrology, hydrogeology, water chemistry, and isotopic tracers for delineating the sources and mechanisms of water contamination in questioned areas.

Finally, more studies are needed across a broader geographic area, particularly because many shale gas developments occur in areas that have been historically exploited for conventional oil and gas (e.g., PA, WV, CO, TX, and in the future also CA). Most of the scientific publications thus far have addressed water issues in the Appalachian Basin, whereas information for many other basins is limited or not available. Future research should include studies from other basins in order to overcome these gaps and determine the overall risks to water resources from shale-gas development. Importantly, many of the risks identified in the literature thus far appear possible to mitigate with increased engineering controls during well construction and alternative water-management or water-disposal options to alleviate the impact of shale-gas development on water resources.

■ ASSOCIATED CONTENT

Supporting Information

Supplement figures on the association of water spill violations to shale gas well density and water scarcity are presented in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 919-681-8050; fax: 919-684-5833; e-mail: vengosh@duke.edu.

Notes

Notes. The authors declare no competing financial interest.

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■ REFERENCES

(1) Kargbo, D. M.; Wilhelm, R. G.; Campbell, D. J. Natural gas plays in the Marcellus Shale: challenges and potential opportunities. *Environ. Sci. Technol.* **2010**, *44* (15), 5679−5684.

(2) Kerr, R. A. Natural gas from shale bursts onto the scene. *Science* **2010**, *328* (5986), 1624−1626.

(3) Schnoor, J. L. Shale gas and hydrofracturing. *Environ. Sci. Technol.* **2012**, *46* (9), 4686−4686.

(4) *Annual Energy Outlook 2013*; United States Energy Information Administration, 2013.

(5) Brantley, S. L.; Yoxtheimer, D.; Arjmand, S.; Grieve, P.; Vidic, R.; Pollak, J.; Llewellyn, G. T.; Abad, J.; Simon, C. Water resource impacts during unconventional shale gas development: The Pennsylvania Experience. *Int. J. Coal Geol.* **2014** (http://dx.doi.org/10.1016/j.coal.2013.12.017).

(6) Ridlington, E.; Rumpler, J. *Fracking by the Numbers: Key Impacts of Dirty Drilling at the State and National Level*; Environment America Research & Policy Center, 2013; p 46.

(7) *Annual Energy Outlook 2014 Early Release Overview*; United States Energy Information Agency, 2013.

(8) Rivard, C.; Lavoie, D.; Lefebvre, R.; Séjourné, S.; Lamontagne, C.; Duchesne, M. An overview of Canadian shale gas production and environmental concerns. *Int. J. Coal Geol.*, **2013**, in press (http://dx.doi.org/10.1016/j.coal.2013.12.004).

(9) Hu, D.; Xu, S. Opportunity, challenges and policy choices for China on the development of shale gas. *Energy Policy.* **2013**, *60*, 21−26.

(10) Xingang, Z.; Jiaoli, K.; Bei, L. Focus on the development of shale gas in China, Based on SWOT analysis. *Renewable Sustainable Energy Rev.* **2013**, *21*, 603−613.

(11) Boyer, C.; Clark, B.; Jochen, V.; Lewis, R.; Miller, C. K. Shale gas: A global resource. *Oilfield Rev* **2011**, *23*, 28−39.

(12) *World Energy Outlook 2012*; International Energy Agency (IEA): Paris, France, 2012.

(13) Howarth, R.; Santoro, R.; Ingraffea, A. Methane and the greenhouse-gas footprint of natural gas from shale formations. *Clim. Change* **2011**, *106* (4), 679−690.

(14) Howarth, R. W.; Ingraffea, A.; Engelder, T. Natural gas: Should fracking stop? *Nature* **2011**, *477* (7364), 271−275.

(15) Myers, T. Potential contaminant pathways from hydraulically fractured shale to aquifers. *Ground Water.* **2012**, *50* (6), 872−882.

(16) Walton, J.; Woocay, A. Environmental issues related to enhanced production of natural gas by hydraulic fracturing. *J. Green Build.* **2013**, *8* (1), 62−71.
(17) Eaton, T. T. Science-based decision-making on complex issues: Marcellus shale gas hydrofracking and New York City water supply. *Sci. Total Environ.* **2013**, *461−462*, 158−169.
(18) Rozell, D. J.; Reaven, S. J. Water pollution risk associated with natural gas extraction from the Marcellus Shale. *Risk Anal.* **2012**, *32* (8), 1382−1393.
(19) Vengosh, A.; Warner, N. R.; Jackson, R. B.; Darrah, T. The effects of shale gas exploration and hydraulic fractruing on the quality of water resources in the United States. *Procedia Earth Planet. Sci.* **2013**, *7*, 863−866.
(20) Hatzenbuhler, H.; Centner, T. J. Regulation of water pollution from hydraulic fracturing in horizontally-drilled wells in the Marcellus Shale Region, USA. *Water.* **2012**, *4* (4), 983−994.
(21) Schmidt, C. W. Blind rush? Shale gas boom proceeds amid human health questions. *Environ. Health Perspect.* **2011**, *119*, a348−a353.
(22) Vidic, R. D.; Brantley, S. L.; Vandenbossche, J. M.; Yoxtheimer, D.; Abad, J. D. Impact of shale gas development on regional water quality. *Science* **2013**, *340*, 6134.
(23) Ferrar, K. J.; Michanowicz, D. R.; Christen, C. L.; Mulcahy, N.; Malone, S. L.; Sharma, R. K. Assessment of effluent contaminants from three facilities discharging Marcellus Shale wastewater to surface waters in Pennsylvania. *Environ. Sci. Technol.* **2013**, *47* (7), 3472−3481.
(24) Dale, A. T.; Khanna, V.; Vidic, R. D.; Bilec, M. M. Process based life-cycle assessment of natural gas from the Marcellus Shale. *Environ. Sci. Technol.* **2013**, *47* (10), 5459−5466.
(25) Pacsi, A. P.; Alhajeri, N. S.; Zavala-Araiza, D.; Webster, M. D.; Allen, D. T. Regional air quality impacts of increased natural gas production and use in Texas. *Environ. Sci. Technol.* **2013**, *47* (7), 3521−3527.
(26) Olmstead, S. M.; Muehlenbachs, L. A.; Shih, J. S.; Chu, Z. Y.; Krupnick, A. J. Shale gas development impacts on surface water quality in Pennsylvania. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110* (13), 4962−4967.
(27) Osborn, S. G.; Vengosh, A.; Warner, N. R.; Jackson, R. B. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 8172−8176.
(28) Osborn, S. G.; Vengosh, A.; Warner, N. R.; Jackson, R. B. Reply to Saba and Orzechowski and Schon: Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108* (37), E665−E666.
(29) Jackson, R. B.; Vengosh, A.; Darrah, T. H.; Warner, N. R.; Down, A.; Poreda, R. J.; Osborn, S. G.; Zhao, K.; Karr, J. D. Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110* (28), 11250−11255.
(30) Jackson, R. B.; Osborn, S. G.; Vengosh, A.; Warner, N. R. Reply to Davies: Hydraulic fracturing remains a possible mechanism for observed methane contamination of drinking water. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108* (43), E872.
(31) Allen, D. T.; Torres, V. M.; Thomas, J.; Sullivan, D. W.; Harrison, M.; Hendler, A.; Herndon, S. C.; Kolb, C. E.; Fraser, M. P.; Hill, A. D.; Lamb, B. K.; Miskimins, J.; Sawyer, R. E.; Seinfeld, J. H. Measurements of methane emissions at natural gas production sites in the United States. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, DOI: 10.1073/pnas.1304880110.
(32) Petron, G.; Frost, G.; Miller, B. R.; Hirsch, A. I.; Montzka, S. A.; Karion, A.; Trainer, M.; Sweeney, C.; Andrews, A. E.; Miller, L.; Kofler, J.; Bar-Ilan, A.; Dlugokencky, E. J.; Patrick, L.; Moore, C. T.; Ryerson, T. B.; Siso, C.; Kolodzey, W.; Lang, P. M.; Conway, T.; Novelli, P.; Masarie, K.; Hall, B.; Guenther, D.; Kitzis, D.; Miller, J.; Welsh, D.; Wolfe, D.; Neff, W.; Tans, P. Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study. *J. Geophys. Res., Atmos.* **2012**, 117.
(33) Tutuncu, A. Environmental challenges of gas and oil shale stimulation. In *SEG Technical Program Expanded Abstracts* 2011; pp 3707−3709.
(34) Warner, N. R.; Jackson, R. B.; Darrah, T. H.; Osborn, S. G.; Down, A.; Zhao, K.; White, A.; Vengosh, A. Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (30), 11961−11966.
(35) Warner, N. R.; Christie, C. A.; Jackson, R. B.; Vengosh, A. Impacts of shale gas wastewater disposal on water quality in western Pennsylvania. *Environ. Sci. Technol.* **2013**, *47* (20), 11849−11857.
(36) Warner, N. R.; Kresse, T. M.; Hays, P. D.; Down, A.; Karr, J. D.; Jackson, R. B.; Vengosh, A. Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville Shale development, north-central Arkansas. *Appl. Geochem.* **2013**, *35*, 207−220.
(37) Rahm, B. G.; Riha, S. J. Toward strategic management of shale gas development: Regional, collective impacts on water resources. *Environ. Sci. Policy.* **2012**, *17*, 12−23.
(38) Rahm, D. Regulating hydraulic fracturing in shale gas plays: The case of Texas. *Energ. Policy* **2011**, *39* (5), 2974−2981.
(39) Rahm, B. G.; Bates, J. T.; Bertoia, L. R.; Galford, A. E.; Yoxtheimer, D. A.; Riha, S. J. Wastewater management and Marcellus Shale gas development: Trends, drivers, and planning implications. *J. Environ. Manage.* **2013**, *120*, 105−113.
(40) Kissinger, A.; Helmig, R.; Ebigbo, A.; Class, H.; Lange, T.; Sauter, M.; Heitfeld, M.; Klünker, J.; Jahnke, W. Hydraulic fracturing in unconventional gas reservoirs: risks in the geological system, part 2. *Environ. Earth Sci.* **2013**, *70*, 3855−3873.
(41) Flewelling, S. A.; Tymchak, M. P.; Warpinski, N. Hydraulic fracture height limits and fault interactions in tight oil and gas formations. *Geophys. Res. Lett.* **2013**, *40* (14), 3602−3606.
(42) Darrah, T. H.; Vengosh, A.; Jackson, R. B.; Warner, N. R.; Poreda, R., *Constraining the Source and Migration of Natural Gas in Shallow Aquifers within Active Shale Gas Production Zone: Insights from Integrating Noble Gas and Hydrocarbon Isotope Geochemistry*; Geological Society America Annual Meeting: Charlotte, NC, 6 November 2012.
(43) Molofsky, L. J.; Connor, J. A.; Wylie, A. S.; Wagner, T.; Farhat, S. K. Evaluation of methane sources in groundwater in northeastern Pennsylvania. *Groundwater* **2013**, *51* (3), 333−349.
(44) Molofsky, L. J.; Connor, J. A.; Farhat, S. K.; Wylie, A. S.; Wagner, T. Methane in Pennsylvania water wells unrelated to Marcellus shale fracturing. *Oil Gas J.* **2011**, September, 54−67.
(45) Tilley, B.; McLellan, S.; Hiebert, S.; Quartero, B.; Veilleux, B.; Muehlenbachs, K. Gas isotope reversals in fractured gas reservoirs of the western Canadian Foothills: Mature shale gases in disguise. *AAPG Bull.* **2011**, *95* (8), 1399−1422.
(46) Tilley, B.; Muehlenbachs, K. Gas maturity and alteration systematics across the Western Canada Sedimentary Basin from four mud gas isotope depth profiles. *Org. Geochem.* **2006**, *37* (12), 1857−1868.
(47) Tilley, B.; Muehlenbachs, K. Isotope reversals and universal stages and trends of gas maturation in sealed, self-contained petroleum systems. *Chem. Geol.* **2013**, *339*, 194−204.
(48) Rowe, D.; Muehlenbachs, K. Isotopic fingerprints of shallow gases in the Western Canadian sedimentary basin: tools for remediation of leaking heavy oil wells. *Org. Geochem.* **1999**, *30* (8A), 861−871.
(49) Jackson, R. E.; Gorody, A. W.; Mayer, B.; Roy, J. W.; Ryan, M. C.; Van Stempvoort, D. R. Groundwater protection and unconventional gas extraction: the critical need for field-based hydrogeological research. *Ground Water.* **2013**, *51* (4), 488−510.
(50) Van Stempvoort, D.; Maathuis, H.; Jaworski, E.; Mayer, B.; Rich, K. Oxidation of fugitive methane in ground water linked to bacterial sulfate reduction. *Ground Water.* **2005**, *43* (2), 187−199.
(51) Muehlenbachs, K. *Identifying the Sources of Fugitive Methane Associated with Shale Gas Development*; Resources For the Future: Washington, DC, 2011.

(52) Harrison, S. S. Evaluating system for ground-water contamination hazards due to gas-well drilling on the glaciated Appalachian Plateau. *Ground Water.* **1983**, *21* (6), 689−700.
(53) Harrison, S. S. Contamination of aquifers by overpressuring the annulus of oil and gas wells. *Ground Water.* **1985**, *23* (3), 317−324.
(54) Brufatto, C.; Cochran, J.; Conn, L.; Ower, D. From mud to cement—Building gas wells. *Oil Field Review***2003**, Autum, 62−76.
(55) Graham, B.; Reilly, W. K.; Boesch, D. F.; Garcia, T. D.; Murray, C. A.; F., U. *Deep Water: The Gulf Oil Disaster and the Future of Offshore Drilling*; National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, 2011.
(56) Ingraffea, A. R.; Burchell, A.; Howarth, R.; Colborn, T.; Wilson, W.; Doe, P.; Wood, M. C. Hydrocarbon Development from Shale: A set of important, unsolved problems. In *American Geophysical Union Fall Meeting*; San Fransisco, CA, December 9−13,2013.
(57) Kresse, T. M.; Warner, N. R.; Hays, P. D.; Down, A.; Vengosh, A.; Jackson, R. B. *Shallow Groundwater Quality and Geochemistry in the Fayetteville Shale Gas-Production Area, North-Central Arkansas, 2011:* ; USGS: 2012. 31.
(58) Warner, N. R.; Jackson, R. B.; Vengosh, A. *Tracing the Legacy of Accidental Spills and Releases of Marcellus Wastewater in Pennsylvania*; Geological Society of America: Denver, CO, 27−30 October 2013.
(59) Heilweil, V. M.; Stolp, B. J.; Kimball, B. A.; Susong, D. D.; Marston, T. M.; Gardner, P. M. A stream-based methane monitoring approach for evaluating groundwater impacts associated with unconventional gas development. *Ground Water.* **2013**, *51* (4), 511−524.
(60) DiGiulio, D. C.; Wilkin, R. T.; Miller, C.; Oberley, G. *Investigation of Ground Water Contamination near Pavillion, Wyoming (Draft Report)*; U.S. Environmental Protection Agency, 2011.
(61) Wright, P. R.; McMahon, P. B.; Mueller, D. K.; Clark, M. L. *Groundwater-Quality and Quality-Control Data for Two Monitoring Wells near Pavillion, Wyoming,*; U.S. Geological Survey, 2012; p 26.
(62) Thyne, T. *Review of Phase II Hydrogeologic Study (Prepared for Garfield County)*, 2008.
(63) Fontenot, B. E.; Hunt, L. R.; Hildenbrand, Z. L.; Carlton, D. D., Jr; Oka, H.; Walton, J. L.; Hopkins, D.; Osorio, A.; Bjorndal, B.; Hu, Q. H.; Schug, K. A. An evaluation of water quality in private drinking water wells near natural gas extraction sites in the Barnett Shale formation. *Environ. Sci. Technol.* **2013**, *47* (17), 10032−10040.
(64) Carter, J. M.; Lapham, W. W.; Zogorski, J. S. Occurrence of volatile organic compounds in aquifers of the United States. *J. Am. Water Resour. As.* **2008**, *44* (2), 399−416.
(65) Carter, J. M.; Moran, M. J.; Zogorski, J. S.; Price, C. V. Factors associated with sources, transport, and fate of chloroform and three other trihalomethanes in untreated groundwater used for drinking water. *Environ. Sci. Technol.* **2012**, *46* (15), 8189−8197.
(66) Cohen, H. A.; Parratt, T.; Andrews, C. B. Potential contaminant pathways from hydraulically fractured shale to aquifers. *Ground Water.* **2013**, *51* (3), 317−319.
(67) Myers, T. Potential contaminant pathways from hydraulically fractured shale to aquifers author's reply. *Ground Water.* **2013**, *51* (3), 319−321.
(68) Saiers, J. E.; Barth, E. Potential contaminant pathways from hydraulically fractured shale aquifers. *Ground Water.* **2012**, *50* (6), 826−828.
(69) Engelder, T. Capillary tension and imbibition sequester frack fluid in Marcellus gas shale. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (52), E3625−E3625.
(70) Flewelling, S. A.; Sharma, M. Constraints on upward migration of hydraulic fracturing fluid and brine. *Ground Water* **2013**, *52* (1), 9−19.
(71) Weaver, T. R.; Frape, S. K.; Cherry, J. A. Recent cross-formational fluid flow and mixing in the shallow Michigan Basin. *Geol. Soc. Am. Bull.* **1995**, *107* (6), 697−707.
(72) Long, D. T.; Wilson, T. P.; Takacs, M. J.; Rezabek, D. H. Stable-isotope geochemistry of saline near-surface ground water: East-central Michigan basin. *Geol. Soc. Am. Bull.* **1988**, *100* (10), 1568−1577.
(73) Mehta, S.; Fryar, A. E.; Banner, J. L. Controls on the regional-scale salinization of the Ogallala aquifer, Southern High Plains, Texas, USA. *Appl. Geochem.* **2000**, *15* (6), 849−864.
(74) Mehta, S.; Fryar, A. E.; Brady, R. M.; Morin, R. H. Modeling regional salinization of the Ogallala aquifer, Southern High Plains, TX, USA. *J. Hydrol.* **2000**, *238* (1−2), 44−64.
(75) Gregory, K. B.; Vidic, R. D.; Dzombak, D. A. Water management challenges associated with the production of shale gas by hydraulic fracturing. *Elements* **2011**, *7* (3), 181−186.
(76) Struchtemeyer, C. G.; Elshahed, M. S. Bacterial communities associated with hydraulic fracturing fluids in thermogenic natural gas wells in North Central Texas, USA. *FEMS Microbiol. Ecol.* **2012**, *81* (1), 13−25.
(77) Struchtemeyer, C. G.; Morrison, M. D.; Elshahed, M. S. A critical assessment of the efficacy of biocides used during the hydraulic fracturing process in shale natural gas wells. *Int. Biodeterior. Biodegrad.* **2012**, *71*, 15−21.
(78) Aminto, A.; Olson, M. S. Four-compartment partition model of hazardous components in hydraulic fracturing fluid additives. *J. Nat. Gas Sci. Eng.* **2012**, *7*, 16−21.
(79) Barbot, E.; Vidic, N. S.; Gregory, K. B.; Vidic, R. D. Spatial and temporal correlation of water quality parameters of produced waters from devonian-age shale following hydraulic fracturing. *Environ. Sci. Technol.* **2013**, *47* (6), 2562−2569.
(80) Orem, W.; Tatu, C.; Varonka, M.; Lerch, H.; Bates, A.; Engle, M.; Crosby, L.; McIntosh, J. Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale. *Int. J. Coal Geol.* **2014** (http://dx.doi.org/10.1016/j.coal.2014.01.003).
(81) Haluszczak, L. O.; Rose, A. W.; Kump, L. R. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Appl. Geochem.* **2013**, *28*, 55−61.
(82) Chapman, E. C.; Capo, R. C.; Stewart, B. W.; Kirby, C. S.; Hammack, R. W.; Schroeder, K. T.; Edenborn, H. M. Geochemical and strontium isotope characterization of produced waters from marcellus shale natural gas extraction. *Environ. Sci. Technol.* **2012**, *46* (6), 3545−3553.
(83) Osborn, S. G.; McIntosh, J. C.; Hanor, J. S.; Biddulph, D. Iodine-129, $^{87}Sr/^{86}Sr$, and trace element geochemistry of Northern Appalachian Basin brines: Evidence for basinal-scale fluid migration and clay mineral diagenesis. *Am. J. Sci.* **2012**, *312*, 263−287.
(84) Engle, M. A.; Rowan, E. L. Interpretation of Na-Cl-Br systematics in sedimentary basin brines: Comparison of concentration, element ratio, and isometric log-ratio approaches. *Math. Geosci.* **2013**, *45* (1), 87−101.
(85) Rowan, E. L.; Engle, M. A.; Kirby, C. S.; Kraemer, T. F. *Radium Content of Oil- And Gas-Field Produced Waters in the Northern Appalachian Basin (USA)—Summary and Discussion of Data: U.S. Geological Survey Scientific Investigations Report 2011−5135*; U.S. Geological Survey, 2011.
(86) Engle, M. A.; Rowan, E. L. Geochemical evolution of produced waters from hydraulic fracturing of the Marcellus Shale, northern Appalachian Basin: A multivariate compositional data analysis approach. *Int. J. Coal Geol.* **2013** (http://dx.doi.org/10.1016/j.coal.2013.11.010).
(87) Balaba, R. S.; Smart, R. B. Total arsenic and selenium analysis in Marcellus shale, high-salinity water, and hydrofracture flowback wastewater. *Chemosphere* **2012**, *89* (11), 1437−1442.
(88) Chermak, J. A.; Schreiber, M. E. Mineralogy and trace element geochemistry of gas shales in the United States: Environmental implications. *Int. J. Coal Geol.* **2013** DOI: 10.1016/j.coal.2013.12.005.
(89) Morali Mohan, A. M.; Hartsock, A.; Bibby, K. J.; Hammack, R. W.; Vidic, R. D.; Gregory, K. B. Microbial community changes in hydraulic fracturing fluids and produced water from shale gas extraction. *Environ. Sci. Technol.* **2013**, *47*, 13141−13150.
(90) Mohan, A. M.; Hartsock, A.; Hammack, R. W.; Vidic, R. D.; Gregory, K. B. Microbial communities in flowback water impoundments from hydraulic fracturing for recovery of shale gas. *FEMS Microbiol. Ecol.* **2013**, *86* (3), 567−580.

(91) Davis, J. P.; Struchtemeyer, C. G.; Elshahed, M. S. Bacterial Communities Associated with Production Facilities of Two Newly Drilled Thermogenic Natural Gas Wells in the Barnett Shale (Texas, USA). *Microb. Ecol.* **2012**, *64* (4), 942−954.
(92) Entrekin, S.; Evans-White, M.; Johnson, B.; Hagenbuch, E. Rapid expansion of natural gas development poses a threat to surface waters. *Front. Ecol. Environ.* **2011**, *9* (9), 503−511.
(93) Hughes, J. D. In *Tight oil: A solution to U.S. import dependence?*, Geological Society of America, Abstracts with Programs: Denver, CO, 2013; p 398.
(94) Hensen, J. In *It is more than a simple bell curve.*, Geological Society of America, Abstracts with Programs: Denver, CO, 2013; p 399.
(95) Gross, S. A.; Avens, H. J.; Banducci, A. M.; Sahmel, J.; Panko, J. M.; Tvermoes, B. E. Analysis of BTEX groundwater concentrations from surface spills associated with hydraulic fracturing operations. *J. Air Waste Manage. Assoc.* **2013**, *63* (4), 424−432.
(96) Papoulias, D. M.; Velasco, A. L. Histopathological analysis of fish from Acorn Fork Creek, Kentucky exposed to hydraulic fracturing fluid releases. *Southeastern Naturalist* **2013**, *12*, 90−111.
(97) Adams, M. B. Land application of hydrofracturing fluids damages a deciduous forest stand in West Virginia. *J. Environ. Qual.* **2011**, *40* (4), 1340−1344.
(98) Wilson, J. M.; VanBriesen, J. M. Oil and gas produced water management and surface drinking water sources in Pennsylvania. *Environ. Pract.* **2012**, *14* (4), 288−300.
(99) Wilson, J. M.; Wang, Y.; VanBriesen, J. M. Sources of high total dissolved solids to drinking water supply in southwestern Pennsylvania. *J. Environ. Eng.* **2013**, DOI: 10.1061/(ASCE)EE.1943-7870.0000733.
(100) Veil, J. A. *Water Management Technologies Used by Marcellus Shale Gas Producers*; prepared for US Department of Energy Office of Fossil Fuel Energy, National Energy Technology Laboratory, 2010.
(101) Lutz, B. D.; Lewis, A. N.; Doyle, M. W. Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. *Water Resour. Res.* **2013**, *49* (2), 647−656.
(102) Maloney, K. O.; Yoxtheimer, D. A. Production and disposal of waste materials from gas and oil extraction from the Marcellus Shale play in Pennsylvania. *Environ. Pract.* December **2012**, *14* (4), 278-287.
(103) Chen, B. Y.; Westerhoff, P. Predicting disinfection by-product formation potential in water. *Water Res.* **2010**, *44* (13), 3755−3762.
(104) Chowdhury, S.; Champagne, P.; McLellan, P. J. Factorial analysis of trihalomethanes formation in drinking water. *Water Environ. Res.* **2010**, *82* (6), 556−566.
(105) Chowdhury, S.; Champagne, P.; McLellan, P. J. Investigating effects of bromide ions on trihalomethanes and developing model for predicting bromodichloromethane in drinking water. *Water Res.* **2010**, *44* (7), 2349−2359.
(106) Xue, S.; Zhao, Q. L.; Wei, L. L.; Jia, T. Effect of bromide ion on isolated fractions of dissolved organic matter in secondary effluent during chlorination. *J. Hazard. Mater.* **2008**, *157*, 25−33.
(107) Pan, Y.; Zhang, X. R. Four groups of new aromatic halogenated disinfection byproducts: Effect of bromide concentration on their formation and speciation in chlorinated drinking water. *Environ. Sci. Technol.* **2013**, *47* (3), 1265−1273.
(108) Jones, D. B.; Saglam, A.; Song, H. C.; Karanfil, T. The impact of bromide/iodide concentration and ratio on iodinated trihalomethane formation and speciation. *Water Res.* **2012**, *46* (1), 11−20.
(109) Kitis, M.; Yigita, N. O.; Harmana, B. I.; Muhammetoglu, H.; Muhammetoglu, A.; Karadirek, I. E.; Demirel, I.; Ozdenc, T.; Palancic, I. Occurrence of trihalomethanes in chlorinated groundwaters with very low natural organic matter and bromide concentrations. *Environ. Forensics* **2010**, *11* (3), 264−274.
(110) Pressman, J. G.; Richardson, S. D.; Speth, T. F.; Miltner, R. J.; Narotsky, M. G.; Hunter, E. S.; Rice, G. E.; Teuschler, L. K.; McDonald, A.; Parvez, S.; Krasner, S. W.; Weinberg, H. S.; McKague, A. B.; Parrett, C. J.; Bodin, N.; Chinn, R.; Lee, C. F.; Simmons, J. E. Concentration, chlorination, and chemical analysis of drinking water for disinfection byproduct mixtures health effects research: US EPA's four lab study. *Environ. Sci. Technol.* **2010**, *44* (19), 7184−7192.
(111) Richardson, S. D.; Plewa, M. J.; Wagner, E. D.; Schoeny, R.; DeMarini, D. M. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutat. Res., Rev. Mutat. Res.* **2007**, *636* (1−3), 178−242.
(112) Wilson, J.; Vanbriesen, J. Source water changes and energy extraction activities in the Monongahela River, 2009−2012. *Environ. Sci. Technol.* **2013**, *47*, 12575−12582.
(113) States, S.; Cyprych, G.; Stoner, M.; Wydra, F.; Kuchta, J.; Monnell, J.; Casson, L. Marcellus Shale drilling and brominated THMs in Pittsburgh, Pa., drinking water. *J. Am. Water Works Ass.* **2013**, *105* (8), 53−54.
(114) Hladik, M. L.; Focazio, M. J.; Engle, M. Discharges of produced waters from oil and gas extraction via wastewater treatment plants are sources of disinfection by-products to receiving streams. *Sci. Total Environ.* **2014**, *466*, 1085−1093.
(115) Ellsworth, W. L. Injection-induced earthquakes. *Science* **2013**, *341* (6142), 142.
(116) Rutqvist, J.; Rinaldi, A. P.; Cappa, F.; Moridis, G. J. Modeling of fault reactivation and induced seismicity during hydraulic fracturing of shale-gas reservoirs. *J. Petrol. Sci. Eng.* **2013**, *107*, 31−44.
(117) Frohlich, C. Two-year survey comparing earthquake activity and injection-well locations in the Barnett Shale, Texas. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (35), 13934−13938.
(118) Frohlich, C.; Hayward, C.; Stump, B.; Potter, E. The Dallas-Fort Worth Earthquake Sequence: October 2008 through May 2009. *Bull. Seismol. Soc. Am.* **2011**, *101* (1), 327−340.
(119) Horton, S. Disposal of hydrofracking waste fluid by injection into subsurface aquifers triggers earthquake swarm in central Arkansas with potential for damaging earthquake. *Seismol. Res. Lett.* **2012**, *83* (2), 250−260.
(120) Gan, W.; Frohlich, C. Gas injection may have triggered earthquakes in the Cogdell oil field, Texas. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110* (47), 18786−18791.
(121) Keranen, K. M.; Savage, H. M.; Abers, G. A.; Cochran, E. S. Potentially induced earthquakes in Oklahoma, USA: Links between wastewater injection and the 2011 M-w 5.7 earthquake sequence. *Geology* **2013**, *41* (6), 699−702.
(122) van der Elst, N. J.; Savage, H. M.; Keranen, K. M.; Abers, G. A. Enhanced Remote Earthquake Triggering at Fluid-Injection Sites in the Midwestern United States. *Science* **2013**, *341* (6142), 164−167.
(123) Llenos, A. L.; Michael, A. J. Modeling earthquake rate changes in Oklahoma and Arkansas: Possible signatures of induced seismicity. *Bull. Seismol. Soc. Am.* **2013**, *103* (5), 2850−2861.
(124) Yuan, Z.; Gardoni, P.; Schubert, J.; Teodoriu, C. Cement failure probability analysis in water injection well. *J. Petrol. Sci. Eng.* **2013**, *107*, 45−49.
(125) Krishnaswami, S.; Bhushan, R.; Baskaran, M. Radium isotopes and 222Rn in shallow brines, Kharaghoda (India). *Chem. Geol.* **1991**, *87* (2), 125−136.
(126) Webster, I. T.; Hancock, G. J.; Murray, A. S. Modelling the effect of salinity on radium desorption from sediments. *Geochim. Cosmochim. Acta* **1995**, *59* (12), 2469−2476.
(127) Sturchio, N. C.; Banner, J. L.; Binz, C. M.; Heraty, L. B.; Musgrove, M. Radium geochemistry of ground waters in Paleozoic carbonate aquifers, midcontinent, USA. *Appl. Geochem.* **2001**, *16* (1), 109−122.
(128) Vinson, D. S.; Vengosh, A.; Hirschfeld, D.; Dwyer, G. S. Relationships between radium and radon occurrence and hydrochemistry in fresh groundwater from fractured crystalline rocks, North Carolina (USA). *Chem. Geol.* **2009**, *260* (3−4), 159−171.
(129) Skalak, K. J.; Engle, M. A.; Rowan, E. L.; Jolly, G. D.; Conko, K. M.; Benthem, A. J.; Kraemer, T. F. Surface disposal of produced waters in western and southwestern Pennsylvania: Potential for accumulation of alkali-earth elements in sediments. *Int. J. Coal Geol.*
(130) Rich, A. L.; Crosby, E. C. Analysis of reserve pit sludge from unconventional natural gas hydraulic fracturing and drilling operations

for the presence of technologically enhanced naturally occurring radioactive material (TENORM). *New Solutions* **2013**, *23* (1), 117−135.
(131) Zielinski, R. A.; Otton, J. K.; Budahn, J. R. Use of radium isotopes to determine the age and origin of radioactive Barite at oil-field production sites. *Environ. Pollut.* **2001**, *113* (3), 299−309.
(132) Crabtree, M.; Eslinger, D.; Fletcher, P.; Miller, M.; Johnson, A.; King, G. Fighting scale—Removal and prevention. *Oilfield Rev.* **1999**, *11*, 35−45.
(133) Swann, C.; Matthews, J.; Ericksen, R.; Kuszmaul, J. *Evaluations of Radionuclides of Uranium, Thorium, And Radium Associated with Produced Fluids, Precipitates, And Sludges from Oil, Gas, And Oilfield Brine Injection wells in Mississippi University*; MS:Mississippi Mineral Resources Institute/Department of Pharmacology/Department of Geology and Geological Engineering, University of Mississippi, 2004; p 83.
(134) Nicot, J. P.; Scanlon, B. R. Water use for shale-gas production in Texas, U.S. *Environ. Sci. Technol.* **2012**, *46* (6), 3580−3586.
(135) Murray, K. E. State-scale perspective on water use and production associated with oil and gas operations, Oklahoma, U.S. *Environ. Sci. Technol.* **2013**, *47* (9), 4918−4925.
(136) Johnson, E. G.; Johnson, L. A. *Hydraulic Fracture Water Usage in Northeast British Columbia: Locations, Volumes, And Trends*; Geoscience Reports: Victoria, BC, Canada, 2012.
(137) Kenny, J. F.; Barber, N. L.; Hutson, S. S.; Linsey, K. S.; Lovelace, J. K.; Maupin, M. A. *Estimated Use of Water in the United States in 2005*; U.S. Geological Survey Circular 1344. Reston, VA, 2009. 52.
(138) FracFocus FracFocus 2.0. http://fracfocus.org/ (accessed 10/17/2013).
(139) Freyman, M.; Salmon, R. *Hydraulic Fracturing and Water Stress: Growing Competitive Pressures for Water*; CERES: Boston, MA, 2013; p 12.
(140) Mitchell, A. L.; Small, M.; Casman, E. A. Surface water withdrawals for Marcellus Shale gas development: Performance of alternative regulatory approaches in the Upper Ohio River Basin. *Environ. Sci. Technol.* **2013**, *47* (22), 12669−12678.
(141) He, C.; Zhang, T.; Vidic, R. D. Use of abandoned mine drainage for the development of unconventional gas resources. *Disrupt. Sci. Technol.* **2013**, *1*, 169−176.
(142) Yoxtheimer, D.; Blumsack, S.; Murphy, T. The Decision to use acidic coal mine drainage for hydraulic fracturing of unconventional shale-gas wells. *Environ. Pract.* December **2012**, *14* (4), 301−-307.
(143) Kondash, A. J.; Warner, N. R.; Lahav, O.; Vengosh, A. Radium and barium removal through blending hydraulic fracturing fluids with acid mine drainage. *Environ. Sci. Technol.* **2014**, *48* (2), 1334−1342.
(144) Veil, J. A. *White Paper on SPE Summit on Hydraulic Fracturing*; Society of Petroleum Engineers: Houston TX, 2011.
(145) Hickenbottom, K. L.; Hancock, N. T.; Hutchings, N. R.; Appleton, E. W.; Beaudry, E. G.; Xu, P.; Cath, T. Y. Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations. *Desalination* **2013**, *312*, 60−66.
(146) Ferguson, M. L.; Eichelberger, P. B.; Qiu; Roell, R. L. *Innovative Friction Reducer Provides Improved Performance and Greater Flexibility in Recycling Highly Mineralized Produced Brines*; Society of Petroleum Engineers (SPE), 2013.
(147) Guerra, K.; Dahm, K.; Dundorf, S. *Oil and Gas Produced Water Management and Beneficial Use in the Western United States*; U.S. Department of the Interior, Bureau of Reclamation, Technical Service Center, Water and Environmental Resources Division, Water Treatment Engineering Research Group: Denver, CO, 2011; p 113.
(148) *Carnegie Museum of Natural History Pennsylvania Unconventional Natural Gas Wells Geodatabase*; Pittsburgh, PA: Carnegie Museum of Natural History, 2000−2013.

ATTACHMENT C

STUDY 35

RESEARCH SUMMARY

Large-Sample Evidence on the Impact of Unconventional Oil and Gas Development on Surface Waters

by Pietro Bonetti, Christian Leuz, Giovanna Michelon; Science

KEY TAKEAWAYS

1. The application of hydraulic fracturing to develop oil and natural gas has led to a sharp increase in U.S. energy production and generated enormous benefits. As drilling activity has increased, however, a robust debate has begun regarding the pros and cons at a local level. Advocates point to increased economic activity. Opponents point to possible air and water pollution.

2. Several studies have documented instances of groundwater contamination related to hydraulic fracturing wells, but there is limited evidence linking the practice to surface water impacts. This study provides the first evidence that hydraulic fracturing is related to increased salt concentrations in surface waters for several shales across the United States.

3. The study combines surface water measurements with 46,479 hydraulic fracturing wells to examine whether new drilling and development activities are associated with elevated salt concentrations (bromide, chloride, barium and strontium) in 408 U.S. watersheds over an eleven-year period.

4. The authors found a very small but consistent increase in barium, chloride and strontium, but not bromide, in watersheds with new hydraulic fracturing wells. The elevated levels were well below environmental and health advisory levels. The increases in salt levels were largest during the early phases of production when wells generate large amounts of flowback and produced water.

5. The salt concentrations were most pronounced for wells that produced larger amounts of water and for wells located in areas where the deep formations exhibited higher levels of salinity. This evidence ties the elevated salt concentrations more closely to hydraulic fracturing activities.

6. Salt concentrations were highest when observed within a year from drilling, at monitoring stations that were within 15 kilometers and (likely) downstream from a well.

Introduction

The discovery of hydraulic fracturing is considered by many to be the most important change in the energy sector since the introduction of nuclear generated electricity more than 50 years ago. As a result of its discovery, U.S. production of oil and natural gas has increased to unforeseen levels. This has led to abruptly lower energy prices, stronger energy security and even lower air pollution and carbon dioxide emissions by displacing coal in electricity generation.

As drilling activity has increased, however, a robust debate has begun within communities where development is occurring—and those where it could occur—regarding the pros and cons at a local level. Advocates point to increased economic activity, including tax revenue and jobs. Opponents, on the other hand, point to potential disadvantages such as possible air and water pollution and adverse health effects.

Potential harm to water quality is a key concern because of the unique hydraulic fracturing process, where water mixed with chemical additives and propping agents like sand are injected at a high pressure to create fractures in rocks to allow oil or gas to flow. In addition to concerns surrounding the hydraulic fracturing fluid itself, these wells produce large amounts of wastewater—flowback from the hydraulic fracturing fluid and produced water from the deep formations. The latter is naturally occurring water, into which organic and inorganic constituents from the formation have dissolved, resulting in high salt concentrations.

Some studies have documented groundwater contamination related to hydraulic fracturing, though the results differ across shales. There is even less evidence to date showing a link between hydraulic fracturing and surface water contamination. Prior studies documented localized instances of contamination in surface waters mostly related to known and isolated spills and leaks rather than widespread and systemic contamination. This study provides the first evidence that hydraulic fracturing is related to increased salt concentrations in surface waters across several U.S. shales and many watersheds.

Research Design

The study investigates the potential impact of hydraulic fracturing on surface water quality. The authors used a geo-coded database that combined surface water measurements with 46,479 hydraulic fracturing wells from 24 shales across 408 watersheds from 2006 to 2016.

They specifically analyzed concentrations of bromide, chloride, barium and strontium because these ions are usually found in high concentrations in flowback and produced water from wells, they do not biodegrade, and they have been found several years after spills. Using a statistical approach, the authors work to identify anomalous changes in ion concentration associated with new wells in the same watersheds. The statistical model explains more than 80 percent, and in many cases more than 90 percent, of the background variation in ion concentrations across watersheds and through time.

Findings

In areas where there were new hydraulic fracturing wells there were also elevated salt concentrations in surface waters. The authors found very small but consistent increases in barium, chloride and strontium concentrations, but not bromide. These elevated levels existed in Pennsylvania—which accounted for almost 41 percent of the sample—and for all U.S. watersheds at comparable magnitude and significance. However, the elevated levels were well below the U.S. Environmental Protection Agency's limits and advisory levels for what is considered safe.

Figure 1 · Hydraulic Fracturing Wells and Water Quality

Ions	Sample	Mean Concentration	Cum.#Wells	HUC10 Impact (µ g/L) HUC4 Model	HUC8 Model
Bromide	PA	134.31	112.00	11.14	2.96
	ALL	97.38	166.61	**5.68**	3.25
Chloride	PA	19,772.05	94.17	**1,098.86**	**1,322.44**
	ALL	47,522.55	83.87	**2,152.80**	**2,232.55**
Barium	PA	39.66	106.49	**2.15**	**1.61**
	ALL	59.37	74.91	0.98	1.02
Strontium	PA	121.52	104.07	**5.31**	**5.19**
	ALL	59.37	74.66	**10.11**	**8.88**

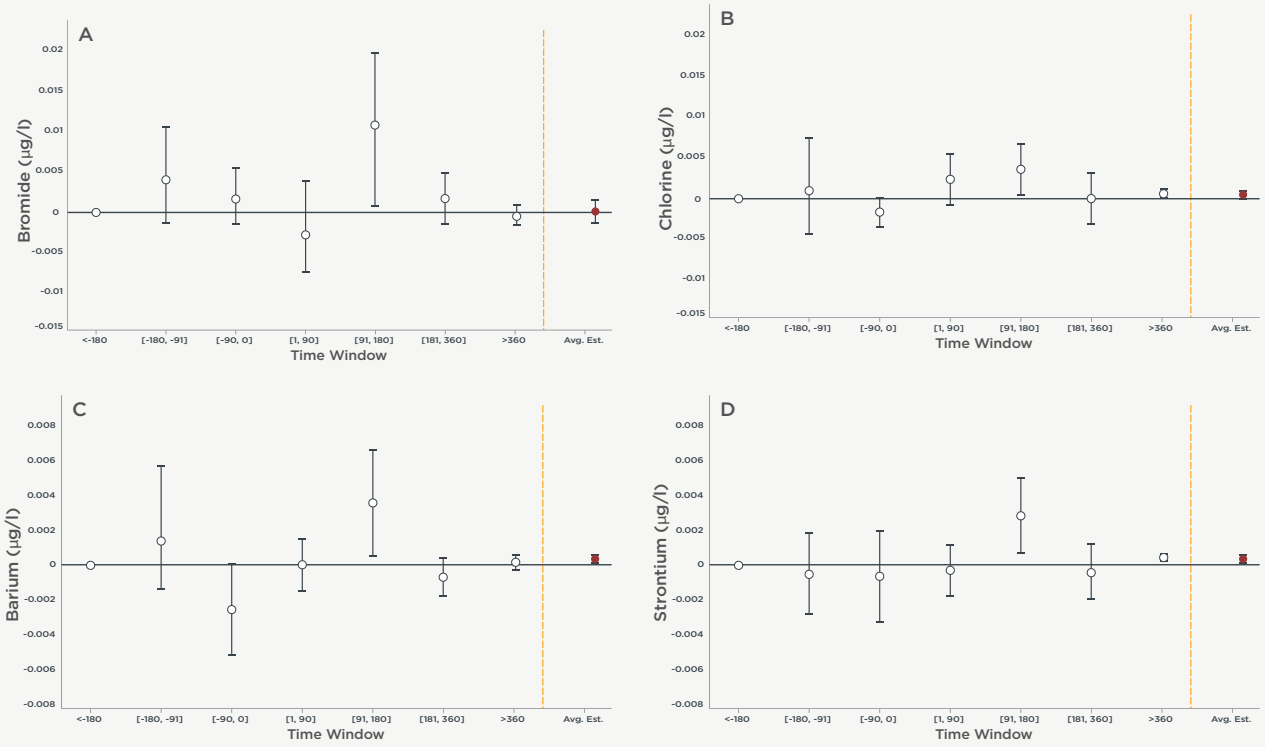
Coefficient estimates x 10^3

Note: This figure plots OLS coefficients and confidence intervals for the associations between ion concentrations and cumulative HF well counts (#wellsHUC10), estimated using eq. S1 and two different model specifications, HUC4 and HUC8 (Table S4). We report results for treated watersheds (HUC10s) in Pennsylvania (PA) and for all treated U.S. watersheds (ALL). The last two columns report the cumulative impact in the average watershed (HUC10 Impact µg/L) implied by the coefficient estimates, obtained by multiplying the respective coefficient with the sample mean ion concentration and the cumulative number of wells in the average HUC10 over the sample period. Bold impact numbers are based on significant coefficients. The EPA maximum contaminant level (MCL) is 250,000 µg/L for Cl^- and 2,000 µg/L for Ba. The EPA does not provide a MCL for Br^- and Sr. Health advisory levels for one-day and lifetime exposure to Sr are 25,000 µg/L and 4,000 µg/L, respectively.

"Our work provides the first large-sample evidence showing that hydraulic fracturing is related to the quality of nearby surface waters for several U.S. shales. Though we estimated very small water impact, one has to consider that most measurements were taken in rivers or streams and that the average fracturing well in our dataset was not particularly close to the monitors in the watershed."

CHRISTIAN LEUZ, JOSEPH SONDHEIMER PROFESSOR OF INTERNATIONAL ECONOMICS, FINANCE AND ACCOUNTING AT THE UNIVERSITY OF CHICAGO'S BOOTH SCHOOL OF BUSINESS

Figure 2 · Temporal Analysis of Salt Concentrations Around Initial Well Drilling Dates



Note: Temporal analysis of ion concentrations around well spud dates. (A) Br^-, (B) Cl^-, (C) Ba, (D) Sr. Panels A to D plot OLS coefficients for well counts calculated over fixed time intervals around the spud dates, together with the 95% confidence interval (see Table S8, Panel B, Columns (1)-(4), for the estimation of these coefficients). For comparison, the red dot marks the coefficient of #wellsHUC10 from Table S4, Panel A, Column (4), and its 95% confidence interval.

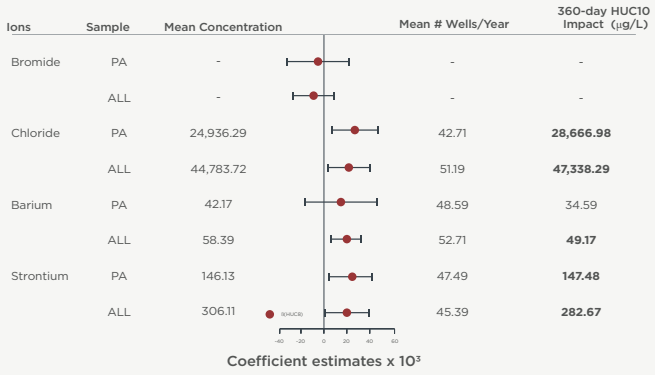
The elevated salt concentrations occur after well completion and during the early phases of production, when large amounts of flowback and produced water are collected. The study found the greatest increases in salt concentrations 91-180 days after drilling began, though they were still small in magnitude. The 91–180-day period marks a time after the drilling is complete and during the early phases of production when large amounts of flowback and produced water are collected. This timing suggests a link between elevated concentrations and the unconventional oil and gas development process. Additionally, any impact likely declines over time.

The salt concentrations were most pronounced for wells with larger amounts of produced water, further drawing the tie between elevated salt concentrations and hydraulic fracturing activities. The authors analyzed wells with both above-average and below-average amounts of produced water. They found that in the watersheds with wells that produced more water, salt concentrations were higher—though still below EPA's limits and health advisory levels. This evidence ties the elevated salt concentrations more closely to hydraulic fracturing activities.

Increases in salt concentrations were more pronounced for wells located in areas where the deep formations exhibited higher levels of salinity. The authors explored whether the associations between elevated salt concentrations and hydraulic fracturing were stronger in areas where wells were expected to produce water with higher salinity, given the variation in regional geochemistry and the salinity of deep formations. They found that the association is indeed more pronounced in sub-basins where deep formations exhibit higher levels of salinity. This suggests that produced water is likely part of the explanation for the elevated salt concentrations.

The high salt concentrations were most pronounced at monitoring stations located closer to wells and at stations likely located downstream from wells. The authors also explored whether the associations between wells and salt concentrations were more pronounced when wells and monitors were closer together and wells were likely upstream from water monitors. They found that the highest salt concentrations were observed within a year from drilling at monitoring stations assigned as downstream from a well and within 15 kilometers from a well. Although the concentrations were an order of magnitude larger than the long-run increases (mentioned above/Fig. 2), they were still well below the EPA maximum contaminant and health advisory levels.

Figure 3 · Hydraulic Fracturing Wells and Water Quality Using Time, Distance and Well Position



Note: This figure plots WLS coefficients and confidence intervals for the associations between ion concentrations and an indicator for a new HF well, estimated using eq. S2 (Table S12, Panel C). For this analysis, we pair wells and monitors in a watershed. For each pair, we determine that well and monitor are within 15km and that the well is assigned as likely upstream of the monitor, and we only use water measurements taken up to 360 days after the spud date. We report results for treated watersheds (HUC10s) in Pennsylvania (PA) and for all treated U.S. watersheds (ALL). The last column reports the 360-day impact on the average watershed (HUC10 Impact μg/L) implied by the coefficient estimates, obtained by multiplying the respective coefficient with the sample mean ion concentration and the average number of new wells per year in the average HUC10. We computed the 360-day impact only for positive coefficients. For this reason, we do not report the mean ion concentration and average number of wells per year for Br^-. Bold impact numbers are based on significant coefficients. See Fig. 1 for EPA maximum contaminant and other health advisory levels.

Policy Implications

While the study suggests that hydraulic fracturing had a small impact on surface water quality, it is important to recognize that not all wells are close to surface water and not all monitors are in locations where they could detect an effect (e.g., the closest monitor could be upstream). Thus, the estimated impact could be small due to distance from the well to the water.

In addition, the study was hampered by the availability and measurement frequency of water quality data. Hydraulic fracturing fluids contain chemical substances that are potentially more dangerous than salts. But the authors were not able to look for these chemicals because they are not widely covered by public databases. Further, more frequent measurement closer to wells and around the time of new drillings would allow for more granular analyses. Thus, an important policy implication of this study is that better and more frequent water measurement is needed to fully understand the surface water impact of unconventional oil and gas development. For instance, federal and state environmental agencies could consider placing monitoring stations in a more targeted fashion to better track potential water quality impacts. More extensive water measurement for a broader array of substances also requires adequate funding for these agencies.

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