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Air monitoring of volatile organic compounds at relevant receptors during hydraulic fracturing operations in Washington County, Pennsylvania

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Abstract A 3-month air monitoring study was conducted in Washington County, Pennsylvania, at the request of local community members regarding the potential risks resulting from air emissions of pollutants related to hydraulic fracturing operations. Continuous air monitoring for total volatile organic compounds was performed at two sampling sites, including a school and a residence, located within 900 m of a hydraulic fracturing well pad that had been drilled prior to the study. Intermittent 24-hour air samples for 62 individual volatile organic compounds were also collected. The ambient air at both sites was monitored during four distinct periods of unconventional natural gas extraction activity: an inactive period prior to fracturing operations, during fracturing operations, during flaring operations, and during another inactive period after operations. The results of the continuous monitoring during fracturing and flaring sampling periods for total volatile organic compounds were similar to the results obtained during inactive periods. Total volatile organic compound 24-hour average concentrations ranged between 0.16 and 80 ppb during all sampling periods. Several individual volatile compounds were detected in the 24-hour samples, but they were consistent with background atmospheric levels measured previously at nearby sampling sites and in other areas in Washington County. Furthermore, a basic yet conservative screening level evaluation demonstrated that the detected volatile organic compounds were well below health-protective levels. The primary finding of this study was that the operation of a hydraulic fracturing well pad in Washington County did not substantially affect local air concentrations of total and individual volatile organic compounds.

KEYWORDS Air quality · Continuous air monitoring · Community monitoring · Hydraulic fracturing · Volatile organic compounds

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Introduction

Unconventional natural gas development (UNGD) is prevalent throughout much of western Pennsylvania (PA), USA, which overlies the Marcellus Shale natural gas formation. Between January 2005 and July 2015, over 9300 unconventional wells were spudded in the area (PADEP 2015). The rate of natural gas development coupled with the lack of exposure data for air concentrations of substances related to UNGD has led to various studies that have intended to characterize UNGD-related air emissions (Eapi et al. 2014; Litovitz et al. 2013; Macey et al. 2014; PADEP 2010, 2011a, 2011b; Roy et al. 2014; Swarthout et al. 2015; Zielinska et al. 2014; Bunch et al. 2014; McKenzie et al. 2012). At various stages of well pad development (construction,

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drilling, hydraulic fracturing, flaring, flowback), methane, silica, National Ambient Air Quality Standards (NAAQS) criteria pollutants (nitrogen oxides, sulfur oxides, carbon monoxide, and particulate matter), hydrogen sulfide, and volatile organic compounds (VOCs) have been detected in the air (Moore et al. 2014). Ideally, flaring of hydrocarbons produces only water and carbon dioxide; however, incomplete combustion and the presence of sulfur and nitrogen compounds in the flare feed can result in emissions of methane, VOCs, sulfur oxides, nitrogen oxides, and carbon monoxide (Evans et al. 2000). At sufficient airborne concentrations, several of these compounds have the potential to induce health effects ranging from sensory irritation (acute exposure) to cancer (chronic exposure).

VOCs are a class of hundreds of compounds that may produce a wide variety of health effects, the most common of which is upper respiratory irritation from acute exposure (Salonen et al. 2009). Total VOCs (TVOCs) from shale gas extraction contribute 0.35 to 1.5 % of the TVOC emissions from all industrial sectors in Pennsylvania (Litovitz et al. 2013). Main sources of TVOC emissions during natural gas production include emissions from pneumatics, wellhead compressors, blowdown vents, heaters, condensate tanks, and production fugitives (Roy et al. 2014).

Washington County in southwestern Pennsylvania has experienced a sharp increase in natural gas production from hydraulic fracturing operations in the past 6 years. Both the rapid development of shale gas infrastructure in this region and reports of health effects attributed to UNGD processes have caused concern, particularly due to the proximity of some schools to well pads. The study described herein was initiated through a request from a local school board on behalf of parents who expressed concern regarding a newly-constructed well pad located in close proximity to their children's school. At the time that the study was performed, no relevant exposure data existed for the area.

The primary objective of this study was to address the specific concerns of the community: primarily potential exposure to VOCs, but also to hydrogen sulfide, carbon monoxide, and explosive gases. Total explosive gas level (including methane), carbon monoxide, and hydrogen sulfide were monitored because of community interest, but are not discussed in the present study. No acutely hazardous conditions were identified. Carbon monoxide and explosive gas results are not discussed due to a lack of documented chronic health effects. Hydrogen sulfide results are not discussed due to an instrument resolution that was insufficient for comparison of results to low-concentration health- or odor-based ambient air benchmark values such as the Pennsylvania Department of Environmental Protection daily ambient standard of 5 ppb (PADEP 2012). Rather, results for these species were communicated to the community members in an unpublished report. Furthermore, for this study, it was determined that particulate matter and silica were not of interest because the well pad had already been constructed. Nitrogen oxides and sulfur oxides were not monitored because of the limited scope of the sampling campaign.

In order to address the community concerns related to VOCs, ambient air concentrations of VOCs that (1) are commonly postulated to be emitted during the hydraulic fracturing process and (2) are associated with adverse health effects at elevated concentrations were assessed. The assessment was achieved through a continuous, 3-month air monitoring campaign at the local high school and at a private residence near a well pad. This sampling period captured two distinct operational periods of well pad activity, as well as a baseline period with no well pad activity, and a post-activity period. Continuous air monitoring allowed for characterization of ambient concentration fluctuations, including peaks, of TVOCs. Communication with the concerned community was conducted prior to and throughout the air monitoring campaign. As recommended by the Agency for Toxic Substances and Disease Registry (ATSDR)'s Guidance on Public Health Assessment, continual updates on the sampling study were provided through meetings and interim reports (ATSDR 2005). Although limited in scope, the current study provides a dataset representing exposures to VOCs potentially related to hydraulic fracturing at locations where the local rural population lives and attends school. Further, this study highlights the challenges and opportunities associated with characterizing community exposures associated with UNGD.

Methods

Study design

Air sampling was performed near a multiple-unit hydraulic fracturing well pad in Washington County, PA. The locations of the sampling sites were selected based on relevant community receptors. Site A was a local high school building located 863 m due south of the

well pad and was generally upwind from the well pad. Site B was a residential home located 774 m east-southeast of the well pad and was generally downwind from the well pad. Figure 1 depicts the relative locations of the hydraulic fracturing pad and sampling sites A and B, and the predominant wind characteristics at both locations during the sampling period. In Fig. 1, wind rose overlays are used to indicate the predominant wind direction and wind speed magnitude.

Continuous air sampling for TVOCs was performed during four separate periods of well pad operations in 2011 and 2012. Baseline sampling was performed between November 14 and 29, 2011, when the well pad was relatively inactive and preparations were being made for hydraulic fracturing. Measurements were not collected from November 23 through November 28, 2011. The fracturing period commenced on November 30, 2011, and continued until flaring began on December 28, 2011. Flaring continued from December 28, 2011, through January 6, 2012. Lastly, sampling continued during the inactive period after flaring. The post-flaring sampling period lasted from January 7, 2012, through January 27, 2012. Discrete air samples for specific, individual VOCs were collected intermittently throughout the sampling periods.

Continuous air sampling methods

Continuous air monitoring was conducted using a combination of real-time, direct-reading equipment manufactured by RAE Systems: a MultiRae Plus gas monitor (MultiRAE), ppbRAE 3000 TVOC monitor (ppbRAE), and a RAELink3 system (RAELink) (TRS Environmental, Chicago, IL; RAE Systems, San Jose, CA). RAELink is a portable networking modem that provided wireless communication between the MultiRAE or ppbRAE and a host computer and datalogged the continuous monitoring results. Real-time data from both the MultiRAE and ppbRAE were relayed to the host computer and recorded every 60 s.

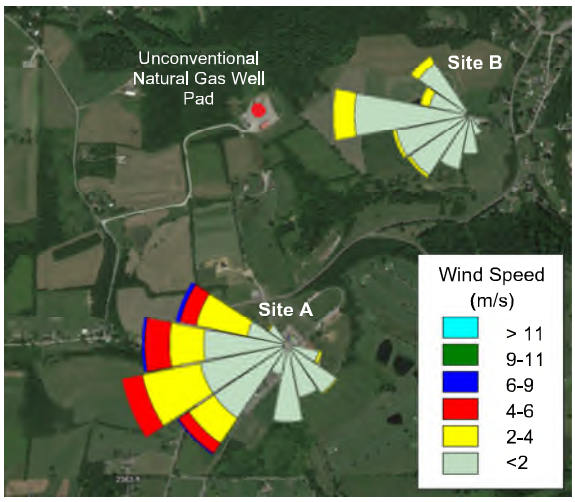

Fig. 1 Map of sampling sites with wind rose. Site A is the school building, Site B is the personal residence

The ppbRAE monitor was used as the primary measurement device for TVOC concentration. The TVOC concentration was detected using a photoionization detector (PID). The resolution of the instrument was 1 ppb in the concentration range of 0 to 10,000 ppb, and 10 ppb in the concentration range of 10,000 to 100,000 ppb. The MultiRAE detector was primarily used to measure total explosive gas levels, oxygen levels, carbon monoxide levels, and hydrogen sulfide levels that were of interest to the community, but not part of the present study. The MultiRAE was also used as a backup detector for TVOC levels. The MultiRAE monitor used a PID to measure TVOCs, with a resolution of 100 ppb in the 0 to 200,000 ppb concentration range and a resolution of 1000 ppb for concentrations greater than 200,000 ppb. However, due to the low resolution, any measurement below 500 ppb was potentially affected by the electrical noise of the instrument.

Both the MultiRAE and ppbRAE monitors were calibrated periodically in accordance with the manufacturer's specifications. On occasion, the monitors went offline and thus did not record measurements for varying periods of time. Reasons for going offline included power supply interruption and full datalog memories (which were reset to prevent this condition). Therefore, in some cases, the monitors were not collecting data for the entire duration of the sampling periods, as envisioned in the study design. Table 1 summarizes the total number of sampling days for which the monitors were operational in each period.

Analysis of TVOC results

Data were compiled and summary statistics were calculated using Microsoft Excel 2013 (Microsoft Corporation, Redmond, WA). For purposes of statistical comparison of TVOC measurements between sampling sites, it was assumed that the data collected each day represented an independent sample. The 24-h concentration was defined as the average of all 60-s data points

Table 1 Description of sampling period durations at each sampling location

Well pad activity	ppbRAE operating duration (days)		MultiRAE operating duration (days)	
	Site A	Site B	Site A	Site B
Baseline (no activity)—16-day sampling period	7	15	5	9
Fracturing—28-day sampling period	26	28	26	28
Flaring—10-day sampling period	9	10	7	10
Post-flaring (no activity)—21-day sampling period	10[a]	21	20	17

[a] ppbRAE PID sensor failure resulted in the loss of 11 days of sampling during this operating period

collected by the ppbRAE instrument from 12:00 AM to 11:59 PM on 1 day. Exploratory analysis confirmed that the TVOC distributions were neither normal nor lognormal in shape; therefore, a Kruskal-Wallis non-parametric statistical analysis was used for comparison of 24-h concentrations. Kruskal-Wallis tests were performed to determine if there were significant differences between the baseline, fracturing, flaring, and post-flaring periods at each site, as well as to determine if there were significant differences between site A and site B during each monitoring period. The null hypothesis in each case was that the mean 24-h concentration between each period and location was equal, and an alpha level of $p < 0.05$ was used to determine statistical significance. All Kruskal-Wallis analyses were completed using SYSTAT 11 (SYSTAT Software Inc., San Jose, CA).

Individual VOC air sampling methods

In order to evaluate specific compounds that may have been present as part of the TVOC concentration measured using the continuous monitors, 6-L Summa canisters were deployed to collect 24-h air samples. During the baseline phase, 24-h Summa canister samples were collected on November 17 and November 18, 2011; during the fracturing phase, 24-h Summa canister samples were collected on November 30, December 9, and December 27, 2011. During the flaring phase, 24-h Summa canister samples were collected on December 28, 2011, and during the post-flaring phase, 24-h Summa canister samples were collected on January 11, 2012. The samples were analyzed in accordance with a modified United States Environmental Protection Agency (USEPA) Method TO-15 and were analyzed for 62 individual VOCs (Air Toxics, LTD, Folsom, CA).

The electronic air monitoring devices were housed in a plastic crate to shelter them from inclement weather (e.g., rain, snow) and mounted on a secured shelving unit. The configuration of the air monitoring station allowed for sampling at a height of 5.2 ft. (1.6 m), approximating the breathing zone of a person. The Summa canisters were secured to the shelving units such that the inlet was at the approximate height of the continuous monitoring equipment. Additionally, the Summa canisters were equipped with curved sampling tubes to prevent rainwater from collecting inside of the sample.

Analysis of individual VOC results

Data were compiled and summary statistics were calculated using Microsoft Excel 2013 (Microsoft Corporation, Redmond, WA).

Meteorological conditions monitoring

Meteorological conditions, including wind direction, wind speed, temperature, humidity, precipitation, and barometric pressure, were monitored at both sampling sites throughout all sampling periods using a Davis Vantage Pro2 wireless weather station (TRS Environmental, Chicago, IL; Davis Instruments, Hayward, CA). This information allowed for a comparison to historical metrological conditions in the area, and documentation of weather events that may have affected the quality of sampling data. Further, an understanding of wind direction is vital for confirming upwind and downwind locations when characterizing environmental impacts of point source related-emissions, as was the goal of this study. Real-time results were relayed to a host computer every 10 min and logged. The meteorological station was located on the roof of a two-story building at site A at a height of approximately 26 ft. (7.9 m), and the meteorological station was located on ground-level at site B at a height of approximately 5 ft. (1.5 m).

Results

Meteorological conditions

A summary of the wind direction, wind speed, temperature, humidity, barometric pressure, and rainfall measured during all sampling periods is presented in the supplemental material (Table S-1). A severe precipitation event was documented on December 27, 2011, that impacted speciated VOC sampling that day.

While somewhat variable, the predominant wind direction was from the west-southwest and from the west for site A and site B, respectively. The predominant wind direction data indicated that site A was typically upwind of the well pad, and site B was typically downwind of the well pad, based on their locations, as shown in Fig. 1.

Continuous direct-reading air monitoring for total VOCs

A summary of the results for the average 24-h TVOC concentrations measured by the ppbRAE are presented in Table 2.

The continuous monitoring results show that, at site A, the average concentration of TVOCs was higher during the inactive periods (i.e., baseline and post-flaring) than during the fracturing and flaring activities. These results may be explained by less vehicle traffic at the school because of the local winter recess, which began on December 22, 2011, and ended on January 4, 2012, covering part of the fracturing time period and all of the flaring time period. At site B, the average TVOC concentrations during fracturing were similar to, but higher than, those observed during the inactive periods and were significantly less than all other periods during flaring. Based on observations of the field team, the activities at site B did not appear to be significantly different over the course of the study and the site was 'downwind' during both the fracturing and flaring periods. A reason for the very low VOC measurements at the site during flaring has therefore not been identified. Table 3 presents the p value results determined using Kruskal-Wallis tests for inter-sampling period 24-h concentration differences at both site A and site B. No statistically significant differences were observed between any sampling periods at either site. Additionally, the p values determined using Kruskal-Wallis tests for the 24-h concentrations between site A and site B were 0.61, 0.28, 0.33, and 0.44, respectively, which indicated no significant differences between sites A and B during any specific sampling period.

To understand potential time variation patterns in the data, the ppbRAE TVOC data were grouped by the hour of measurement and averaged for each sampling period. Figure S-1 in the supplemental material presents the average hourly concentration of TVOCs at each site for each sampling period. This time trend analysis demonstrates that there were only slight differences in the pattern of time variation of TVOC concentration between sampling periods at either site. The TVOC concentrations exhibited diurnal fluctuations that were expected based on differences in atmospheric stability class

Table 2 Total VOC continuous air monitoring results (measured by ppbRAE)

Site	Sampling period	24-h concentration measurements (ppb)		
		Mean	Standard deviation	Range
A[a]	Baseline	41	53	0–120
	Fracturing	7.3	10	0–31
	Flaring	4.6	6.8	0–22
	Post-flaring	80	53	0–160
B[b]	Baseline	22	48	0–160
	Fracturing	27	37	0–130
	Flaring	0.16	0.32	0–1.0
	Post-flaring	10	14	0–44

[a] MultiRae continuous monitoring results ranged between 0 and 520 ppb at site A, with mean 24-h concentrations of 230 ppb during baseline, 100 ppb during fracking, 210 ppb during flaring, and 78 ppb during post-flaring. These results were deemed less reliable because of the poor sensitivity of the instrument (100 ppb)

[b] MultiRae continuous results ranged between 0 and 1200 ppb at site B, with mean 24-h concentrations of 0 ppb during baseline, 150 ppb during fracking, 150 ppb during flaring, and 790 ppb during post-flaring. These results were deemed less reliable because of the poor sensitivity of the instrument (100 ppb)

Table 3 Kruskal-Wallis p values for comparisons between 24-h concentrations during each sampling period

Site	Sampling period	Fracturing	Flaring	Post-flaring
A	Baseline	0.52	0.28	0.18
	Fracturing	–	0.59	0.41
	Flaring	–	–	0.39
B	Baseline	0.23	0.46	0.082
	Fracturing	–	0.43	0.23
	Flaring	–	–	0.60

(based primarily on incoming solar radiation and eddy diffusivity) between daytime and nighttime periods (Tiwari et al. 2010; Filella and Penuelas 2006). Surprisingly, no trend in TVOCs at site A was observed that could be associated with higher vehicle traffic periods expected in a school area. The time variation of TVOCs observed in this monitoring study are typical of background TVOC levels from a variety of sources, and it appears that well pad operations did not exert an appreciable effect on the local air concentration of TVOCs.

Summa canister sampling of individual VOCs

A summary of the detected VOC concentrations from the Summa canister analyses performed at site A and site B is presented in Table 4. Heavy rain on December 27, 2011, caused the sampling inlet on the Summa canister at site A to become clogged and rendered this sample invalid; therefore, no results are reported for that canister. Laboratory reporting limits using USEPA Method TO-15 are specific to each individual chemical and ranged from 0.13 to 0.84 ppb. A full list of the 62 individual chemicals for which each of the samples were analyzed is available in the supplemental material (Table S-2).

Sampling during the baseline period at site A resulted in detection of ten of the 62 specific VOCs for which sampling was performed. During the fracturing and flaring periods, 11 and 6 of the VOC species were detected, respectively, and during post-flaring, 8 of the VOC species were detected. The concentrations of chemical compounds detected during the flaring and fracturing sampling periods were similar to those detected during the baseline sampling period. Sampling during the baseline period at site B resulted in detection of 5 of the 62 specific VOCs for which sampling was performed. During the fracturing and flaring periods, 10 and 8 of the VOC species were detected, respectively. The concentrations of the chemical compounds detected during the flaring and fracturing sampling periods were generally similar to those detected during the baseline sampling period.

Discussion

The need for data that provides an accurate characterization of community exposures related to UNGD operations has been acknowledged throughout the scientific community (Brown et al. 2014; Macey et al. 2014; USEPA 2013). Important concepts related to these exposures include: (1) differences in exposures before, during, and after well pad development and operation; (2) variations based on distance and orientation to the well site; (3) duration of the well site activities and that of the nearby community; and (4) non-well pad related activities that may contribute similar constituents to the local ambient air. At the time that this study was designed, limited information existed in the published literature with respect to the chemicals of interest. The study was therefore designed first and foremost to address the specific concerns of the parents in the school district. In doing so, this study produced a dataset that allowed many of these important exposure concepts to be evaluated.

The TVOC data provide a high-level overview of the differences between before, during, and after well pad activity air quality. Given the distance (863 m) and upwind orientation of site A from the well pad, air emissions from the well pad activities were unlikely to impact the TVOC concentrations at the school, and, as such, substantial differences in the concentrations between the well pad activity periods were not expected. However, the data for site A showed that the average 24-h TVOC concentrations were markedly lower during the fracturing and flaring periods; thus, a source unrelated to the well pad activities is likely to be responsible. It was hypothesized that the lower vehicle traffic volume at the school because of winter recess may be the variable associated with the lower TVOC levels. Given the distance (774 m) and downwind orientation of site B from the well pad, it was theorized that air emissions associated with well pad activities could influence air concentrations at the private residence. The average 24-h TVOC concentrations at site B were indeed higher during fracturing activities than during the baseline and post-flaring inactive periods; however, the differences in average concentrations were not statistically significant as demonstrated in Table 3. The opposite is seen for the flaring period at site B, where the average TVOC concentrations were lower than both baseline and post-flaring. The inconsistency and wide variability in the data are indicative of either influences of a site-related source (i.e., automobile and farm equipment emissions) or, possibly, instrumentation issues. The variability demonstrated very little, if any, association with atmospheric conditions or an indication of substantial source difference.

The speciated VOC data were similar to the TVOC data with respect to variability. Generally, all individual VOC concentrations detected during fracturing, flaring,

Table 4 Sampling results for detected individual VOCs

Site A individual VOC Sampling results								
Compound[a]	Baseline conc. (ppb)		Fracturing conc. (ppb)		Flaring conc. (ppb)	Post-flaring[b] conc. (ppb)	PADEP background concentration ranges	
	11/17/2011	11/18/2011	11/30/2011	12/9/2011	12/28/2011	1/11/2012	Florence[c]	Charleroi[d]
1,4-Dioxane	<0.13	<0.16	0.17	<0.14	<0.16	<0.15	–	–
2-Butanone	<0.66	<0.80	<0.67	0.90	<0.82	<0.76	0.28–0.56	0.19–2.6
2-Propanol	5.4	<0.80	<0.67	<0.72	<0.82	<0.76	0.31–0.60	–
Acetone	7.4	2.8	2.0	1.0	0.84	2.1	7.0–99	7.2–29
Benzene	0.16	<0.16	0.19	<0.14	0.20	0.22	0.092–0.25	0.12–0.36
Chloromethane	0.36	0.35	0.50	0.34	0.45	0.42	0.59–0.68	0.010–0.64
Cyclohexane	<0.17	<0.16	<0.13	0.22	<0.16	<0.15	–	5.7–14
Dichlorodifluoromethane	0.40	0.44	0.46	0.38	0.47	0.48	0.55–0.65	–
Ethanol	7.6	1.6	1.2	0.79	<0.82	1.1	–	–
Hexane	0.13	<0.16	0.28	<0.14	0.25	<0.15	0.034–0.035	0.59–1.5
Methylene chloride	<0.26	<0.32	<0.27	<0.29	<0.33	0.38	–	–
Toluene	0.23	<0.16	<0.13	1.8	<0.16	0.17	0.068–0.16	0.27–0.67
Trichlorofluoromethane	0.32	0.22	0.22	0.18	0.21	0.22	0.25–0.30	–
m,p-Xylene	0.14	<0.16	<0.13	<0.14	<0.16	<0.15	–	0.091–0.24
Site B individual VOC sampling results								
Compound[a]	Baseline conc. (ppb)		Fracturing conc. (ppb)			Flaring conc. (ppb)	PADEP background concentration ranges	
	11/17/2011	11/18/2011	11/30/2011	12/9/2011	12/27/2011	12/28/2011	Florence[c]	Charleroi[d]
Acetone	9.0	4.2	1.7	<0.64	1.6	1.1	7.0–99	7.2–29
Benzene	<0.17	<0.13	0.21	0.27	0.19	0.34	0.092–0.25	0.12–0.36
Chloromethane	0.32	0.29	0.49	0.14	0.42	0.41	0.59–0.68	0.010–0.64
Cyclohexane	<0.17	<0.13	0.20	<0.13	<0.15	<0.15	–	5.7–14
Ethanol	10	1.1	0.92	<0.64	0.82	<0.74	–	–
Dichlorodifluoromethane	0.32	0.32	0.46	0.18	0.48	0.50	0.55–0.65	–
Heptane	<0.17	<0.13	<0.17	<0.13	0.23	0.28	0.06	2.7–8.8
Hexane	<0.17	<0.13	0.28	<0.13	0.40	0.60	0.034–0.035	0.59–1.5
Toluene	<0.17	<0.13	<0.17	<0.13	0.16	0.22	0.068–0.16	0.27–0.67
Trichlorofluoromethane	0.21	0.14	0.22	<0.13	0.20	0.21	0.25–0.30	–

– not included in analytical methodology

[a] A total of 62 individual VOC analytes were analyzed for in each of the samples using EPA Method TO-15; only those analytes that were detected are presented in this table. The supplemental material (Table S-2) contains a full list of analytes and reporting limit ranges. Compounds not detected above the reporting limit in this table are reported as "< (reporting limit)"

[b] Post-flaring samples for individual VOCs were only collected at site A

[c] These data represent a range of 3 samples collected by the PADEP in Florence, Washington County, PA, in 2010 as part of the Southwestern Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Program. This site was considered to be unimpacted by UNGD activities

[d] These data represent a range of 6 samples collected by the PADEP in Charleroi, Washington County, PA, in 2009 as part of its routine toxic substances air monitoring program. This site was considered to be unimpacted by UNGD activities

or post-flaring varied by a factor of 0.2 to 2 from the baseline results, with a few exceptions. At site A, toluene was detected at an average concentration of 1.8 ppb during the fracturing period, and at an average concentration of 0.23 ppb during the baseline period, a difference of 8-fold. At site B, dichlorodifluoromethane (Freon 12) concentrations were slightly higher during flaring, with a detected concentration of 0.50 ppb versus a concentration of 0.32 ppb during baseline. Freon 12 is generally not associated with fracturing or flaring operations and thus serves as an example that the slight variations observed in the concentrations are likely caused by background sources unrelated to well pad activities. Overall, average concentration results for the fracturing and flaring periods generally varied by a factor of less than 2.

Unlike the TVOC data, the speciated VOC data can be used to understand the potential for health risks that may be associated with well pad activities through comparison to background concentrations measured in areas in which there is no local UNGD, as well as to health-based benchmarks for many of the measured compounds. The chemicals detected during the various sampling periods are ubiquitous in the ambient air, and reported nationally through various USEPA databases such as AirData and the National Air Toxics Assessment database. Additionally, locally measured data were available from Washington County, PA. The VOC concentrations from the Summa canisters were compared to results reported by the PADEP for background UNGD locations (Florence and Charleroi monitors, Washington County) that were sampled as part of their Southwestern Pennsylvania Marcellus Shale Short-Term Ambient Air Sampling Program (PADEP 2010). As demonstrated in Table 4, the results at sites A and B were similar to or less than the range of background concentrations reported by the PADEP for compounds that it detected, with four exceptions at site A, including 2-propanol, trichlorofluoromethane (Freon 11), toluene, and methylene chloride. Although the data indicated that the VOCs present in ambient air were similar to background levels, a screening-level human health risk assessment was still performed.

The exact duration of well pad construction, drilling, hydraulic fracturing, flaring, and flowback varies by well. Various sources agree, however, that these typical UNGD processes for a well pad in the Marcellus Shale region occur on a scale of weeks, rather than hours or years (Moore et al. 2014). Health-based exposure limits established for intermediate exposure durations, such as the USEPA's Regional Screening Levels (RSLs), are therefore the most appropriate values to use for estimating human health risk to airborne emissions associated with well pad construction, development, and completion (USEPA 2015a). RSLs are single values derived using equations that consider chemical-specific toxicity values, as well as some assumptions about exposure. RSLs are calculated using a commonly referenced, screening-level approach recommended by the USEPA. The value of an RSL reflects a level at which further investigation or site cleanup is warranted for USEPA Superfund sites (USEPA 2015a). For this study, resident subchronic RSLs for exposure to chemicals in air were selected for comparison to the measured VOC concentrations. Subchronic RSLs are suggested by the USEPA when the duration of exposure is less than 7 years, and suggested by ATSDR when the duration of exposure is less than 1 year (USEPA 2015a). The duration of this study and the general duration (weeks) of UNGD operations at one site are generally less than 1 year; therefore, the use of subchronic RSL values is appropriate. The USEPA online calculator for RSLs was used to determine the RSLs for each detected VOC. A 90-day exposure period was selected in order to reflect the 3-month duration of the present study. Additionally, a target hazard quotient of 1.0 and a target cancer risk of 1.0×10^{-6} were selected for the RSL calculations. Other parameters and outputs of the USEPA RSL calculations are provided in the supplemental material (USEPA 2015b).

Although each Summa canister sample was collected over a 24-h time period and daily Summa canister samples were well beyond the scope of the study, the low variability in concentrations for individual compounds across the six discrete study samples throughout the 3-month study period indicates that the measurements are reasonably representative of daily average concentrations. A conservative screening-level human health risk evaluation was conducted by comparing the maximum individual VOC concentrations measured in this study to their respective subchronic RSL values, when available. If no subchronic RSL was available, the chronic RSL was used. Table 5 provides a comparison between each detected VOC's subchronic RSL and its maximum detected concentration, presented as a risk ratio (ratio RSL:Max). The RSL:Max ratio is the number of times larger than the calculated RSL is compared to the maximum measured concentration in this study. Any ratio greater than 1.0 is considered protective of health effects. Table 5 lists the toxicity basis for the RSL for each listed chemical, as well as the target organ or

Table 5 Comparison between RSL and 24-h sampled value for individual volatile organics

Volatile organic compound	Maximum detected concentration (ppb)	Site at which maximum occurred	RSL (ppb)	Risk ratio RSL:Max
1,4-Dioxane	0.17	A	15.8	93
2-Butanone	0.90	A	1380	1500
2-Propanol	5.4	A	11,600	2100
Acetone	9.0	B	52,600	5800
Benzene	0.34	B	11.4	34
Chloromethane	0.50	A	5910	12,000
Cyclohexane	0.22	A	21,200	96,000
Dichlorodifluoromethane	0.50	B	821	1600
Ethanol	10	B	–	–
Heptane	0.28	B	–	–
Hexane	0.60	B	2300	3800
Methylene chloride	0.38	A	113	300
Toluene	1.8	A	5390	3000
Trichlorofluoromethane	0.32	A	723	2300
m,p-Xylene[a]	0.14	A	93.5	670

[a] The RSLs for m-xylene and p-xylene are both 93.5 ppb for the selected exposure parameters

organ system. Ethanol and heptane did not have subchronic or chronic RSL values. Also, separate calculations are performed for carcinogens. Three of the detected VOCs (benzene, 1,4-dioxane, and methylene chloride) are recognized carcinogens. For carcinogens, the RSL selected is the smaller of the carcinogenic RSL and the non-carcinogenic RSL.

All maximum 24-h VOC measurements were well below the corresponding subchronic or chronic RSL values. The background sources of each chemical were investigated and are presented in the supplemental material. The absence of VOC concentrations above RSL values, and the general lack of measurements above background, indicated that well pad activities had no meaningful effect on VOC levels in the area, and did not create a measurable impact on human health.

In addition to the PADEP Marcellus Shale short-term ambient air sampling project, several studies published in the peer-reviewed literature have reported the results of sampling for individual VOC species associated with UNGD in shale plays throughout the USA (Bunch et al. 2014; Macey et al. 2014; Steinzor et al. 2013; Swarthout et al. 2015; Zielinska et al. 2014). While these sampling campaigns often differed in geographical location or in sampling methodology, they allow for a qualitative comparison between those results and the results observed in the current study.

Steinzor et al. (2013) sampled for individual VOCs outside of homes near natural gas development areas in Pennsylvania using Summa canisters and USEPA TO-14 and TO-15 methods. Overall, Steinzor et al. detected 19 VOCs, including 2-butanone, acetone, chloromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, carbon tetrachloride, trichlorofluoromethane, toluene, dichlorodifluoromethane, hexane, benzene, methylene chloride, tetrachloroethylene, 1,2,4-trimethylbenzene, ethylbenzene, trichloroethylene, all three xylene isomers, and 1,2-dichloroethane (Steinzor et al. 2013). Of these, 1,1,2-trichloro-1,2,2-trifluoroethane, carbon tetrachloride, tetrachloroethylene, 1,2,4-trimethylbenzene, ethylbenzene, trichloroethylene, o-xylene, and 1,2-dichloroethane were not detected in the present study. Additionally, 1,4-dioxane, 2-propanol, cyclohexane, and heptane were not detected by Steinzor et al., but were detected in the present study. Otherwise, the concentrations reported by Steinzor et al. were generally consistent with the concentrations reported in the present study. The exceptions are methylene chloride and m,p-xylenes, which were both reported by Steinzor et al. at concentrations well above those observed in the present study.

Zielinska et al. sampled for individual VOCs near Barnett Shale well pads in Texas during the spring of 2010 using 6-L Summa canisters analyzed according USEPA TO-15, the same method used in the present

study. Individual VOC concentrations were not reported for the compounds; instead, percent compositions of the VOC samples were reported (Zielinska et al. 2014). Thus, comparison of Zielinska et al.'s results to the results from the current study was not possible.

Macey et al. (2014) summarized the air quality in areas near or at oil and gas production sites in Pennsylvania, Wyoming, Arkansas, Colorado, and Ohio using a 2- to 3-minute grab sampling methodology to characterize individual VOCs and a passive sampling methodology specific to formaldehyde. Grab samples were analyzed using USEPA Method TO-15 or TO-3. The authors only reported samples that were above ATSDR minimum risk level values or USEPA cancer risk levels (16 of 35 grab samples), rather than the results of all samples. Of compounds analyzed by the grab sampling methodology, the authors stated that benzene, toluene, xylenes, ethylbenzene, 1,3-butadiene, hexane, and hydrogen sulfide concentrations were above these health-based limits on at least one occasion, at distances 5 to 55 m from operations in Wyoming and Arkansas. Additionally, the authors reported that one sample of benzene collected 270 m from a PIG launch in PA was measured at 5.7 ppb (Macey et al. 2014). Indeed, all concentrations of the compounds of interest that were reported in the Macey et al. study were greater than those observed in the current study. This study design, however, is dissimilar to the present study because of the differences in distance from the source, operational timeframe, sample duration, and geographic region. Further, samples were collected by a number of individuals, which could create variability in results due to interpersonal differences in sampling methodology.

Bunch et al. (2014) analyzed individual VOC samples collected in the Barnett Shale region of Texas in late 2010 to 2011. These samples were previously collected as part of the existing Texas Commission on Environmental Quality air monitoring network and contained VOC samples at 7 locations, 5 of which were collected using automated gas chromatography samplers, and 2 of which were collected using Summa canisters analyzed by gas chromatography-mass spectrometry. Results for 1164 VOC samples were summarized for benzene, ethylbenzene, m,p-xylenes, o-xylene, hexane, and toluene. The ranges of 24-h concentrations varied widely, but all encompassed the values measured in the current study (Bunch et al. 2014).

Swarthout et al. (2015) sampled for a select group of VOCs in southwestern Pennsylvania in the summer of 2012, using 2-L Summa canisters with a multi-detector gas chromatography method (Swarthout et al. 2015). Of interest, they sampled for a number of alkanes, ethane, ethyne, and benzene. On average, benzene samples near wells showed a lower concentration of benzene (0.096 ppb) than did samples remote from wells (0.102 ppb). Benzene concentrations observed in the current study were higher than the mean, but within the range of benzene concentrations reported by Swarthout et al.

In addition to these peer-reviewed studies, beginning in 2014, the Allegheny County Health Department in Western Pennsylvania initiated a continuous, long-term ambient air monitoring program near UNGD at two locations in the county. Air monitoring began prior to the commencement of well pad preparation and is therefore a representative background phase, and continued through drilling and hydraulic fracturing operations. At the time of publication, this air monitoring program was ongoing, with intentions to continue through well completions. One air monitoring station was in the west-central portion of the county and is generally downwind from UNGD activity (Imperial Pointe), while the second was located in the northeastern portion of the county and is generally upwind of UNGD activity (Deer Lakes Park) (ACHD 2016). At Imperial Pointe, VOCs were monitored for using 24-h Summa canisters that were deployed every 6 days and analyzed by EPA TO-15, while at Deer Lakes Park, VOCs were monitored for using 14-day Radiello passive monitors. All air monitoring results were made available to the public as they were received by the department. At Imperial Pointe, acetone, benzene, 2-butanone, chloromethane, dichlorodifluoromethane, ethanol, hexane, isopropyl alcohol, methylene chloride, tetrachloroethene, toluene, m,p-xylene, acetaldehyde, propane, butane, 2-methylbutane, 2-methyl-2-propanol, 1,1-difluoroethane, difluorochloromethane, d-limonene, decanal, nonanal, 1-bromopentane, trimethylsilanol, trifluorodimethylsilane, pentane, undecane, 2-ethyl-1-hexanol, and "unknown" compounds were detected at sub-ppm levels. Generally, average detected concentrations were lowest during drilling, and at similar concentrations during background and fracking. With the exception of acetone and ethanol, all detected concentrations of compounds were less than 10 ppb. At Deer Lakes Park, benzene, toluene, m,p-xylenes, and n-hexane were detected. Generally, average concentrations were similar through the background, drilling, and fracking phases. All detected concentrations were less than 1 ppb (ACHD 2016). Because of the differences in sampling methodology, a comparison between the two Allegheny County

sites is not valid, nor is a comparison between the results reported in this manuscript and those from Deer Lakes Park. However, of the individual VOC species that were detected at both the Imperial Pointe site and in the current study, concentrations detected in the current study were similar to or less than those detected at Imperial Pointe.

Challenges and recommendations

To the authors' knowledge, this study was the first of its kind to conduct continuous monitoring of air concentrations with the intent to characterize exposures to sensitive receptors at multiple stages of well development in addition to monitoring VOCs during operation for multiple consecutive months. Site A was a school, and site B was a private residence; together, these two sites represent the locations where children spend the vast majority of their time. However, the data presented here are site specific, and not necessarily representative of other locations or scenarios.

Not unlike the questions regarding the risks of groundwater/drinking water contamination, the broader understanding of potential health risks associated with UNGD-related air emissions requires significantly more data than is currently publically available. Although emission factors for certain criteria pollutants (particulate matter and nitrogen oxides) and TVOCs are available for various activities and equipment used in UNGD, the authors are not aware of any air dispersion modeling efforts that have compared modeled estimates of exposure to measured concentrations (Roy et al. 2014). Datasets that contain exposure measurements from construction through gas production and their associated chemicals of interest would be ideal in order to maximize the utility of the air modeling options. Collecting this type of data would require significant financial and operational resources. Thus, public-private partnerships involving various stakeholders should be considered as a mechanism to advance the science on this topic.

Some operational challenges encountered during this study and recommendations for researchers conducting similar studies with limited funding in the future include:

- Lack of resolution for low-level concentrations of TVOCs—the VOC instrumentation logistically necessary for this type of assessment needs to be portable, quantifiable at ppb levels, and reliable in a variety of ambient air conditions (i.e., temperature extremes, humidity, etc.). An example of this type of instrumentation includes the automated gas chromatography samples employed by Bunch et al., or continuous use of Summa canister sampling (Bunch et al. 2014). Both of these options require significant financial resources and may not be feasible for long-term, widespread air sampling. Mobile PID sensors, such as those in the MultiRAE and ppbRAE, are much less expensive but have limitations. In this study, the MultiRAE VOC sensor was not sufficiently sensitive to ambient concentrations of VOCs, and therefore the ppbRAE had to be employed. Because the ppbRAE has detection limits in the ppb range, calibration of this instrument must be done carefully and cannot be zeroed in the ambient air. Improper calibration of this instrument can significantly affect results. Additionally, the ppbRAE PID sensor is highly sensitive to moisture in air and may report faulty data at high humidity.
- Lack of local background concentrations for constituents of interest—the airborne constituents of interest are numerous, and often ubiquitous in the ambient air as a result of other sources. As such, proper characterization of potential exposures attributable to UNGD operations requires aggregation of proper background concentration data. This type of data is often available for urban or industrialized areas as a result of air monitoring networks established by federal and state agencies. The network, however, generally does not include rural/suburban areas where UNGD often occurs. As with the issue regarding groundwater risk, it is important to obtain pre-drilling activity data; although in this case, the baseline should take place prior to any well pad development activities.

Conclusion

The primary finding of this study was that the presence and operation of a hydraulic fracturing well pad in Washington County, PA, did not substantially affect local air concentrations of total and individual VOCs. Individual organic compound concentrations measured as part of the study were consistent with previously measured background levels in the area. Total and individual VOC concentrations measured during fracturing

and flaring operations did not demonstrate a notable difference from concentrations measured prior to fracturing or after flaring ended. Lastly, all individual VOC concentrations in the monitored area were well below health-protective levels.

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