



Evaluation of impact of shale gas operations in the Barnett Shale region on volatile organic compounds in air and potential human health risks



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HIGHLIGHTS

- VOCs associated with shale gas were all below health-based CVs.
- VOCs associated with shale gas showed acceptable chronic risk and hazard.
- Shale gas activities have not resulted in VOC levels that pose a health concern.
- Findings useful for understanding potential health risks in other shale plays

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ABSTRACT

Shale gas exploration and production (E&P) has experienced substantial growth across the U.S. over the last decade. The Barnett Shale, in north-central Texas, contains one of the largest, most active onshore gas fields in North America, stretching across 5000 square miles and having an estimated 15,870 producing wells as of 2011. Given that these operations may occur in relatively close proximity to populated/urban areas, concerns have been expressed about potential impacts on human health. In response to these concerns, the Texas Commission on Environmental Quality established an extensive air monitoring network in the region. This network provides a unique data set for evaluating the potential impact of shale gas E&P activities on human health. As such, the objective of this study was to evaluate community-wide exposures to volatile organic compounds (VOCs) in the Barnett Shale region. In this current study, more than 4.6 million data points (representing data from seven monitors at six locations, up to 105 VOCs/monitor, and periods of record dating back to 2000) were evaluated. Measured air concentrations were compared to federal and state health-based air comparison values (HBACVs) to assess potential acute and chronic health effects. None of the measured VOC concentrations exceeded applicable acute HBACVs. Only one chemical (1,2-dibromoethane) exceeded its applicable chronic HBACV, but it is not known to be associated with shale gas production activities. Annual average concentrations were also evaluated in deterministic and probabilistic risk assessments and all risks/hazards were below levels of concern. 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. With the high density of active wells in this region, these findings may be useful for understanding potential health risks in other shale play regions.

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1. Introduction

The United States (U.S.) has abundant shale gas resources and, as a result, shale gas provides a means for the U.S. to gain greater energy

independence. Shale gas (commonly referred to as natural gas) is the cleanest burning of all fossil fuels and is central to energy plans aimed at decreasing greenhouse gas emissions (DOE, 2009). Approximately 60% of the recoverable onshore natural gas in the U.S. is from unconventional reservoirs (i.e., reservoirs that require recovery operations other than conventional operating practices, such as shale gas, tight sands, and coalbed shale gas) (DOE, 2009). These hydrocarbon reservoirs are typically tight formations, meaning low permeability rock and the shale gas is often extracted from the source rock itself. Because of the low permeability, these reservoirs typically require horizontal drilling to maximize exposure of the formation to the wellbore. These reservoirs

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also require stimulation to increase the permeability, thereby making it economically feasible to extract the shale gas from the formation. Advances in both horizontal drilling and hydraulic fracturing technologies have contributed to the acceleration of shale gas production across the U.S. over the past decade.

This rapid increase in shale gas production has elicited public concern regarding the potential impact of such unconventional oil and gas operations on human health and the environment. The proximity of these shale gas operations to urban centers and densely populated areas has contributed to the development of public concern. Some of the primary concerns expressed to date have focused on contamination of surface water and groundwater as a result of failures associated with well drilling and hydraulic fracturing, and emissions of air contaminants associated with all phases of shale gas development. Though investigators have begun working to address some of these concerns, much of the attention and research has been focused on the potential impacts of hydraulic fracturing on potential groundwater contamination (USEPA, 2012). Fewer studies have focused on atmospheric emissions and, in particular, on the potential impacts of such emissions on human health (Bamberger and Oswald, 2012; Colborn et al., in press; Earthworks, 2012; McKenzie et al., 2012; Olaguer, 2012; PADEP, 2010).

The most extensive air monitoring network in place in any U.S. shale play is operated by the Texas Commission on Environmental Quality (TCEQ)^{1,2} in the Barnett Shale region in north-central Texas. Data from this air monitoring network provides a unique opportunity for evaluating potential community-wide exposures to air emissions and the potential for adverse health effects. There are several aspects of this air monitoring network that make it uniquely suited for assessing potential community-wide exposures to air emissions from shale gas production operations. First, the Barnett Shale is the largest and most productive onshore shale gas field in North America. It spans approximately 5000 square miles across 24 counties, and has approximately 15,870 producing shale gas wells (as of the end of 2011) (BSEEC, 2012). Second, the air monitoring network that is currently in operation in the Barnett Shale area is extensive — including seven monitors in six different locations that represent areas where the general public could potentially be exposed, different types of monitors including a number of automated gas chromatographs (autoGCs) that run continuously, and the measurement of more than 100 chemicals at each monitor. Third, the air monitors in the Barnett Shale have been in place since the early 2000s, making it possible to look at the relationship between changes in air concentrations across time relative to the exponential increase in shale gas wells in the region. And fourth, the air monitoring network has monitoring sites in areas of both richer (“wet”) and dry gas regions of the Barnett Shale. This is important as air emissions of VOCs are generally greater in rich/richer (wet) gas areas; therefore the diversity of monitor locations within the Barnett Shale provides data representing the spectrum of air emissions from different shale gas regions.

The goal of this current study was to evaluate potential community-wide exposures to VOCs in air in the Barnett Shale region as a means of assessing the potential impact of shale gas production activities on

human health. There are multiple sources that can potentially emit VOCs during shale gas activities such as engine combustion, condensate tank venting, and flaring. In an effort to be both conservative and comprehensive, this study included a series of assessments: (1) comparison of measured concentrations of VOCs to both odor-based air comparison values (OBACVs) and to acute and chronic health-based air comparison values (HBACVs), (2) evaluation of potential chronic non-cancer hazards and cancer risks associated with inhalation exposures in a deterministic risk assessment, and (3) evaluation of potential chronic non-cancer hazards and cancer risks associated with inhalation exposures in a probabilistic risk assessment. Relative to previous studies by other investigators, this study utilizes a much more robust data set — more VOCs measured, more monitoring locations, monitors operating for longer periods of time, automated gas chromatographs operating continuously, and monitors located in both dry and richer (“wet”) gas areas. Given the magnitude of shale gas operations in the Barnett Shale region and the comprehensive nature of this study, the findings may be useful for understanding potential health risks associated with inhalation exposures to VOCs in other shale plays.

2. Methods

2.1. Data collection

Data for all VOCs measured by the TCEQ at seven fixed-site monitors in the Dallas/Fort Worth region for the entire period of record (i.e. the start date of data collection through the end of 2011) were obtained from the TCEQ. Three of the monitors (Denton Airport South canister, Fort Worth Northwest canister, and Fort Worth Northwest autoGC) have been operating for about a decade, while the remaining monitors came online starting in 2010. Data were only analyzed through the end of 2011 because it was the most recent, complete year with validated data available at the time the analyses were conducted. The seven specific monitors were selected based on the following criteria: 1) they are located in the areas with the highest density of wells (note the highest density of wells occurs northwest of Fort Worth, as shown in Fig. 1), 2) they have minimal urban source impacts, and 3) they collectively represent emission data from all “types” of natural gas operations. Notably, these fixed-site monitors measure concentrations in ambient air as a whole and cannot necessarily be used to identify a specific point source. As a result, VOCs emitted from shale gas sources were not differentiated from VOCs emitted from other potential sources in the area (e.g. traffic). These seven monitors represent two different monitoring technologies: 1) automated gas chromatography (autoGC) samplers — which collect a continuous sample across a 40-minute period for each hour and samples are analyzed automatically on-site for 46 unique VOCs and 2) canister samplers — pressurized containers which collect a continuous sample over a period of 24 h every 6th day and are analyzed off-site by gas chromatography–mass spectrometry for 105 unique VOCs (Table 1). Two of the seven monitors were canisters, while the remaining five were autoGCs. These seven monitors were located at six different sites in the Barnett Shale region (the Fort Worth Northwest site has both an autoGC and a canister). The 24-hour canister data were publicly available for download from the Texas Air Monitoring Information System (TAMIS; TCEQ, 2013). The hourly autoGC data were requested and provided by TCEQ directly.

2.2. Data analysis

2.2.1. Summary statistics

Original data were downloaded as text files and subsequently imported into Microsoft Excel®. Non-detect values were reported as zero in the raw data. Any values reported below the detection limit (DL) in the original data file were retained and treated as detects (note — TCEQ reporting limits are below their published DLs and, as

¹ AMCV: air monitoring comparison value ATSDR: Agency for Toxic Substances and Disease Registry AutoGC: automated gas chromatograph Cal/EPA: California Environmental Protection Agency CV: comparison value DOE: Department of Energy EMEGs: environmental media evaluation guides ESLs: effects screening levels HBACV: health-based air comparison value IUR: inhalation unit risk KM: Kaplan Meier MRLs: minimal risk levels NAAQS: National Ambient Air Quality Standards OBACV: odor-based air comparison value PAC: protective action criteria RELs: reference exposure levels RFC: reference concentration RSC: risk specific concentration TAMIS: Texas Air Monitoring Information System TCEQ: Texas Commission on Environmental Quality USEPA: United States Environmental Protection Agency VOC: volatile organic compound.

² The TCEQ is the lead environmental agency for the state of Texas and, as such, is responsible for safeguarding the state's air resources from pollution, in a manner consistent with the protection of public health, general welfare, and physical property, including the esthetic enjoyment of air resources by the public and the maintenance of adequate visibility. The TCEQ's ambient air monitoring program has operated for more than 25 years and collects data from more than 120 fixed-site air monitors across Texas.

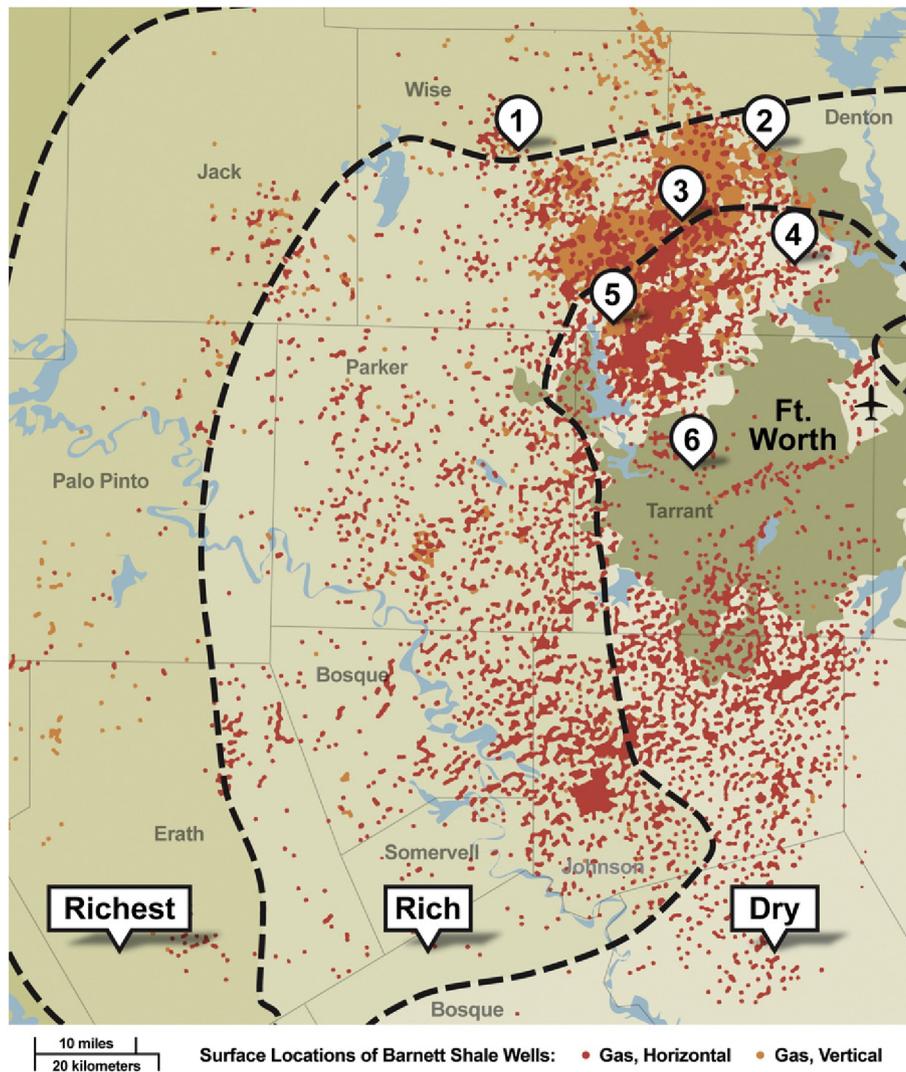


Fig. 1. Map of oil and gas wells in the Barnett Shale region (RRC, 2012). The sites used in study analyses were the following: 1 – Decatur Thompson (autoGC), 2 – Denton Airport South (canister), 3 – Dish Airfield (autoGC), 4 – Flower Mound Shiloh (autoGC), 5 – Eagle Mountain Lake, and 6 – Fort Worth Northwest (autoGC and canister). Dry gas areas typically have less air emissions, while the richest (“wet”) gas areas typically have greater air emissions.

such, there were numerous cases where VOCs were detected and reported at concentrations below their DLs). Data for each monitor were formatted and saved as comma-separated values (CSV) file for importing into open source statistical software R (R Development Core Team, 2012; version 2.15.2) for further calculations.

Maximum hourly autoGC measurements and maximum 24-hour canister measurements were determined for each site, year, and chemical. Because the raw data had a high percentage of non-detect measurements, annual average concentrations were calculated using the Kaplan Meier (KM) method, as it is the preferred method for handling

datasets with a large number of non-detects (USEPA, 2010). The KM method minimizes the potential biasing impact of censored data by incorporating censoring into the determination of the cumulative distribution function (CDF). The survival package in R (Therneau and Lumley, 2011) was used to generate the KM estimate of the cumulative distribution and to calculate statistical summaries for each monitor. The data were weighted on a monthly basis in inverse proportion to the number of observations for each month, omitting months with no data, which equalized the contribution of each month’s data to the annual summary statistics. Weighting the data compensated for the unequal sampling

Table 1

Description of seven datasets used in the study analyses.

Monitor ID	Type	Name	Sample duration; sampling schedule	Analysis period of record	Number of records	Numbers of chemicals	Number of data points
481210034	Canister	Denton Airport South	24 h; every 6th day	06/00–12/11	676	105	59,595
484391002	Canister	Fort Worth Northwest	24 h; every 6th day	11/03–12/11	488	105	44,001
484970088	AutoGC	Decatur Thompson	1 h; continuous	10/10–12/11	9,472	46	430,003
481211013	AutoGC	Dish Airfield	1 h; continuous	04/10–12/11	13,011	46	591,211
484390075	AutoGC	Eagle Mountain Lake	1 h; continuous	04/10–12/11	13,143	46	567,144
481211007	AutoGC	Flower Mound Shiloh	1 h; continuous	10/10–12/11	9,144	46	419,693
484391002	AutoGC	Fort Worth Northwest	1 h; continuous	01/04–12/11	57,758	46	2,526,176

frequency wherein more measurements were collected in some months than in others, and prevented unequal sampling from skewing the results. A minimum of three unique detected values was required for each chemical within each year in order for any statistical parameters to be calculated. From the KM-estimated CDF, annual averages and their associated confidence bounds were computed. Additional summary statistics were also generated (e.g., median and percentile values).

2.2.2. Detection frequencies

Given the magnitude of the dataset, the detection frequencies were calculated for each chemical for each year at each monitor to provide important information for understanding any exceedances of air comparison values. The detection frequencies were calculated by dividing the count of detected values by the sum of the count of the detected values and the count of the non-detect values. In doing so, missing data were excluded to avoid artificially increasing the number of non-detects.

2.2.3. Trend tests

The relevant VOCs were tested for standard linear and polynomial (e.g. quadratic, cubic, quartic tests assessing 1 – bendedness, 2 – bendedness, and 3 – bendedness) trends within each dataset for monitors that had at least two complete years of data. These trend tests were applied using the R software (R Development Core Team, 2012; version 2.15.2). The tests determined significant and insignificant differences among VOC concentrations between each individual year within a period of record, and across the entire period of record. The significance level was set at $\alpha = 0.05$.

2.2.4. Comparison to odor- and health-based air comparison values (OBACVs and HBACVs)

All VOCs measured by the TCEQ at both canister and autoGC samplers were compared to applicable acute and chronic HBACVs and OBACVs. A number of HBACVs and OBACVs were considered for use in evaluating the VOC data. These included:

- Agency for Toxic Substances and Disease Registry minimal risk levels/ environmental media evaluation guides (ATSDR acute MRLs/EMEGs) (ATSDR, 2011);
- California Environmental Protection Agency 1-hour reference exposure levels (Cal/EPA RELs) (Cal/EPA 2012);
- TCEQ short-term odor based effects screening levels (ESLs) – typically represent the lowest acceptable odor threshold (TCEQ, 2012);
- TCEQ health-based air monitoring comparison values (AMCVs) – short-term, 24-hour (for benzene only) and long-term AMCVs (noncarcinogenic and carcinogenic) (TCEQ, 2012);
- TCEQ health-based effects screening levels (ESLs) – short-term and long-term ESLs (noncarcinogenic and carcinogenic) (TCEQ, 2012);
- USEPA risk specific concentration (RSC) (chronic inhalation unit risks (IURs) (carcinogenic) converted to acceptable concentrations in air assuming a 1×10^{-5} risk level) (USEPA, 2012);
- US Environmental Protection Agency chronic reference concentrations (RfCs) (noncarcinogenic) (USEPA, 2012);
- US Environmental Protection Agency National Ambient Air Quality Standards (NAAQS) – 1-hour, 24-hour, annual and rolling 3-month (USEPA, 2012);
- US Department of Energy acute protective action criteria-1 (DOE PAC-1) (DOE, 2012).

Separate hierarchies of OBACVs and HBACVs were established for comparison to the 1-hour, 24-hour, and annual average VOC concentrations. In accordance with this approach, if an OBACV or HBACV was not available from the first tier, then a value from subsequent tiers was used. Once an OBACV or HBACV was identified, further comparisons to values from sources lower in the hierarchy were not made (i.e., only one OBACV and one HBACV were used per chemical/time). Since the TCEQ has established their own air comparison

values for purposes of evaluating the air monitoring data collected across their vast air monitoring network in the State of Texas, the TCEQ OBACVs and HBACVs were placed at the top of the hierarchy. When TCEQ HBACVs were not available, other values were selected, as appropriate to the given comparison exposure metric (e.g., 1-hour, 24-hour, or, annual) as indicated below.

The 1-hour maximum VOC concentrations were compared to applicable acute HBACVs based on the following hierarchy, only using the first available value:

- Tier 1: TCEQ short-term AMCVs
- Tier 2: TCEQ short-term ESLs
- Tier 3: USEPA 1-hour NAAQS
- Tier 4: ATSDR acute MRLs/EMEGs
- Tier 5: DOE PACs-1
- Tier 6: CalEPA 1-hour RELs.

The 24-hour maximum VOC concentrations were compared to short-term HBACVs based on the following hierarchy, only using the first available value:

- Tier 1: TCEQ 24-hour AMCV (benzene only)
- Tier 2: 24-hour NAAQS
- Tier 3: ATSDR acute MRLs/EMEGs.

The 1-hour maximum VOC concentrations and 24-hour maximum VOC concentrations for each year were also compared to applicable OBACVs (i.e., TCEQ odor-based ESLs). If any of the 1-hour maximum or 24-hour maximum values for a given chemical in a given year exceeded applicable acute or short-term HBACVs or OBACVs, then all 1-hour autoGC measurements or all individual 24-hour canister measurements within that year were compared to the acute or short-term HBACVs or OBACVs.

The annual average VOC concentrations for each year were compared to applicable chronic HBACVs (note – the lowest of the carcinogenic and non-carcinogenic HBACV was selected as the chronic HBACV) based on the following hierarchy, only using the first available value:

- Tier 1: TCEQ annual AMCVs
- Tier 2: TCEQ long-term ESLs
- Tier 3: USEPA annual or rolling 3-month average NAAQS
- Tier 4: USEPA chronic inhalation value (the lower of the RfCs or RSC).

2.2.5. Risk assessment

2.2.5.1. Identification of those measured VOCs reasonably believed to be associated with shale gas production operations. In addition to assessing the potential non-cancer hazards and cancer risks associated with all VOCs measured by the TCEQ at the seven canister and autoGC samplers in the Barnett Shale region (comparison to HBACVs and OBACVs – discussed above; Run 1 deterministic risk assessment [DRA] – discussed below), an effort was undertaken to identify those specific measured VOCs reasonably believed to be associated with shale gas operations (hereafter referred to as potentially relevant VOCs) for inclusion in more refined assessments (Run 2 deterministic risk assessment and probabilistic risk assessment – discussed below). This was necessary as the VOCs measured by the TCEQ are not specific to those VOCs believed to be associated with shale gas operations but rather reflect a standard list of VOCs measured at all TCEQ autoGCs and canisters across the state of Texas. The potentially relevant VOCs were identified by comparing the full list of VOCs measured by the TCEQ at all canisters and autoGC samplers across the state to those VOCs identified in the TCEQ Barnett Shale Special Inventory (BSSI) (TCEQ, 2011). The BSSI was conducted to determine the location, number, and type of emission sources located at upstream and midstream oil and gas operations with the Barnett Shale formation. Operations were reported in all 23 counties that comprise the Barnett

Shale area, and the TCEQ received special inventory data from companies that represent >99% of the 2009 production in the Barnett Shale formation. As such, the BSSI was selected as the best available resource to determine potentially relevant VOCs reasonably believed to be associated with oil and gas emissions. The 2011 BSSI identified eleven primary chemicals believed to be associated with shale gas production. Of these eleven, six chemicals are measured by the TCEQ at autoGC and/or canister samplers: benzene, ethylbenzene, m- and p-xylene (isomers were analyzed in aggregate), o-xylene, n-hexane, and toluene. The other five chemicals identified in the 2011 BSSI (i.e., acrolein, acetaldehyde, formaldehyde, methanol, and nitrogen oxides (NOx)) are not measured by the TCEQ's autoGC or canister samplers and, as such, could not be included in this study.

2.2.5.2. Deterministic risk assessment. A traditional deterministic risk assessment (DRA; Eqs. (1), (2) and (3); USEPA, 2009) was conducted to estimate potential cancer risks and non-cancer hazards associated with inhalation exposures to VOCs in the air for persons living in the vicinity of the seven Barnett Shale area air monitors. Two DRAs were conducted – 1) Run 1 – all of the monitored VOCs were evaluated and 2) Run 2 – only the potentially relevant VOCs were evaluated. All parameters used in the equations are defined in Table 2. Both Reasonable Maximum Exposure (RME) and Central Tendency Exposure (CTE) scenarios were evaluated. Standard assumptions were used for RME input parameters; for the CTE scenario, alternate lifetime and exposure duration assumptions (USEPA, 2011a) were employed (Table 2). It was conservatively assumed that a person was breathing air at the concentrations measured at a monitor for 24 h a day, 350 days/year. Measured air concentrations from 2011 (mean values were used for the CTE scenario and 95% UCLs were used for the RME scenario) were used in the DRA, as 2011 theoretically represents a worst-case scenario given that the total number of shale gas wells was greatest in this year.

For both the DRA and the PRA (discussed below), total noncancer hazard results (the sum of hazard quotients across chemicals) were compared to the standard acceptable hazard index (HI) of 1.0, with levels above this HI indicating a potential for concern. However, it is important to note that the noncancer hazards were conservatively summed across all chemicals regardless of target organ, rather than conducting an evaluation by target organ. Cancer risk estimates were evaluated relative to the standard USEPA acceptable risk range of 1×10^{-6} to 1×10^{-4} (USEPA, 1990).

$$\text{Noncancer hazard} = \frac{CA \times ET \times EF \times ED}{ATnc \times RfC \times 1000 \text{ } \mu\text{g}/\text{mg}} \quad (1)$$

$$\text{Cancer risk} = \frac{IUR \times CA \times ET \times EF \times ED}{ATc} \quad (2)$$

$$\text{Cancer risk (mutagens)} = \left(\frac{IUR \times CA \times ET \times EF \times ED_{.02} \times ADAF_{.02}}{ATc} \right) + \left(\frac{IUR \times CA \times ET \times EF \times ED_{.216} \times ADAF_{.216}}{ATc} \right) + \left(\frac{IUR \times CA \times ET \times EF \times ED_{.1630}}{ATc} \right) \quad (3)$$

The following hierarchies were employed to select the chronic non-carcinogenic and carcinogenic inhalation toxicity factors (RfCs and IURs, respectively, inherent inhalation rate of 20 m³/day) used in the DRA, in accordance with standard USEPA practice (USEPA, 2013a).

Non-carcinogenic toxicity factor

Tier 1: USEPA RfC identified in the USEPA Regional Screening (RSL) tables (USEPA, 2013a)

Tier 2: ATSDR chronic EMEG/MRL (ATSDR, 2011)

Tier 3: CalEPA chronic REL (CalEPA, 2012).

Carcinogenic toxicity factor

Tier 1: USEPA IUR from USEPA RSL table

Tier 2: IUR derived from ATSDR CREG (assuming 1×10^{-5} risk level)

Tier 3: Cal/EPA IUR.

2.2.5.3. Probabilistic risk assessment. A probabilistic approach was also employed to characterize the potential human health risk associated with the inhalation exposures to the potentially relevant VOCs. The process of first conducting a deterministic risk assessment and then conducting a probabilistic risk assessment on a refined list of chemicals is consistent with USEPA probabilistic risk assessment guidance (USEPA, 2011b). Total risk and hazard were calculated using the same equations described above for the DRA for inhalation exposures. The probabilistic risk assessment (PRA) incorporated distributions for two exposure factors (lifetime and exposure duration), as well as for the air concentration term. Other exposure factors were consistent with the DRA RME and CTE evaluations (i.e. exposure frequency of 350 days/year, and exposure time of 24 h/day). Toxicity values used in the PRA were identical to those used in the DRA.

The lifetime parameter was continuously distributed according to the data presented in Table 6 of the 2010 National Vital Statistics Report on death (Murphy and Kochanek, 2012). This table included the mortality for specified age ranges (i.e. five year increments) current as of 2010. The custom distribution generated for this data (and used in the PRA) indicated a median lifetime of 82 years, a mean lifetime of 79 years and a 95th percentile lifetime of 98 years.

Table 2
Exposure parameters for the deterministic risk assessment (DRA).

Parameter	Description	Units	Reasonable Maximum Exposure (RME) value	Reference	Central Tendency Exposure (CTE) value	Reference
ATc	Averaging time, carcinogens (LT × 365 days/year × 24 h/day)	h	613,200	USEPA (2013a)	683,280	USEPA (2011b)
ATnc	Averaging time, noncarcinogens (ED × 365 days/year × 24 h/day)	h	262,800	USEPA (2013a)	105,120	USEPA (2011b)
EF	Exposure frequency	days/year	350	USEPA (2013a)	350	USEPA (2013a)
ED	Exposure duration	year	30	USEPA (2013a)	12	USEPA (2011b)
ET	Exposure time	h/day	24	USEPA (2013a)	24	USEPA (2013a)
LT	Lifetime	year	70	USEPA (2013a)	78	USEPA (2011b)
<i>Values for mutagens</i>						
ADAF_02	Age-dependent adjustment factor, 0 < 2 years old	year	10	USEPA (2013a)	10	USEPA (2013a)
ADAF_216	Age-dependent adjustment factor, 2–16 years old	year	3	USEPA (2013a)	3	USEPA (2013a)
ED_02	Exposure duration, 0 < 2 years old	year	2	USEPA (2013a)	2	USEPA (2013a)
ED_216	Exposure duration, 2–16 years old	year	14	USEPA (2013a)	10	USEPA (2011c)
ED_1630	Exposure duration, >16–30 years old	year	14	USEPA (2013a)	0	USEPA (2011c)

The exposure duration parameter (i.e., the length of time that a resident was assumed to live near a monitor) was distributed using data from population mobility studies. The U.S. EPA Exposure Factors Handbook (USEPA, 2011c) recommended a study published by Johnson and Capel (1992) as a source of residential occupancy period (ROP). This study modeled ROP using U.S. Census Bureau data and determined a mean ROP of 12 years and a 95th percentile ROP of 33 years. Johnson and Capel published additional percentiles, which were used to inform the custom continuous distribution for exposure duration in the PRA. The resulting median, mean and 95th percentile exposure durations of the custom PRA distribution were 9, 12 and 33 years, respectively.

Distributions were also applied to the ambient air concentrations for each chemical of interest at the seven monitoring sites. Since the risk assessment was designed to evaluate chronic health effects associated with potential long-term exposures to VOCs in air, the PRA sampled from a distribution of annual mean air concentrations. Distributions of the annual mean were assumed to be normal, based on the central limit theorem, and were defined by the mean and 95th percentile specified by the 2011 KM mean air concentration and the 95th upper confidence level on that KM mean, respectively.

The PRA was conducted using Monte Carlo random sampling methods in Oracle® Crystal Ball (v. 11.1.2.0.00), iterating for 10,000 trials. CTE and RME estimates were derived from the risk distributions at the 50th and 95th percentiles, respectively.

3. Results

3.1. Summary statistics

After incorporating all available data from the seven monitors at the six sites of interest, approximately 4.6 million data points were available for this analysis (Table 1). Due to the large volume of data and unique analyses conducted as a part of this study, all summary statistics cannot be presented in this paper. As an example of the types of summary statistics calculated for each VOC at each monitor, summary statistics from 2011 for the six potentially relevant VOCs are presented in Tables 3 and 4 for the canister and the autoGC datasets, respectively. The detection frequencies for these six VOCs were generally high, with most exceeding 85% at all monitors. Of the seven monitors, the lowest detection frequencies were generally observed at the Eagle Mountain Lake monitor. Benzene, a common chemical detected in air and a compound potentially associated with shale gas operations, had more than 38,000 data points for 2011 alone. Benzene generally exhibited the highest detection frequency across all monitors relative to the other five VOCs reasonably believed to be associated with shale gas operations. Annual average concentrations for benzene ranged from 0.341 $\mu\text{g}/\text{m}^3$ to 0.815 $\mu\text{g}/\text{m}^3$ across all monitors. n-Hexane had the highest concentrations (263 $\mu\text{g}/\text{m}^3$ measured in a 1-hour sample) relative to the other VOCs as shown in Tables 3 and 4.

Table 3
Canister dataset statistics for the potentially relevant VOCs from 2011 only.

Parameter	Benzene	Ethylbenzene	m/p-Xylene	n-Hexane	o-Xylene	Toluene
<i>Denton Airport South (canister)</i>						
Number of data points	60	60	60	60	60	60
Detection frequency	100%	95%	100%	72%	52%	100%
Annual average (95LCL–95UCL) ($\mu\text{g}/\text{m}^3$)	0.664 (0.554–0.774)	0.176 (0.149–0.203)	0.541 (0.263–0.819)	2.675 (1.541–3.809)	0.190 (0.139–0.242)	1.030 (0.716–1.344)
25, 50, 75, 90th percentiles ($\mu\text{g}/\text{m}^3$)	0.35, 0.51, 0.86, 1.18	0.09, 0.17, 0.22, 0.26	0.13, 0.26, 0.61, 1.04	0.53, 0.92, 3.14, 6.87	0.09, 0.17, 0.22, 0.30	0.38, 0.64, 1.24, 1.88
Range of 24-hour samples ($\mu\text{g}/\text{m}^3$)	0.160–2.49	0.043–1.17	0.043–8.38	0.106–23.44	0.043–1.56	0.188–8.37
<i>Fort Worth Northwest (canister)</i>						
Number of data points	60	60	60	60	60	60
Detection frequency (%)	100%	95%	100%	72%	72%	100%
Annual average (95LCL–95UCL) (g/m^3)	0.815 (0.714–0.916)	0.301 (0.261–0.341)	0.676 (0.554–0.797)	0.967 (0.800–1.134)	0.263 (0.218–0.309)	1.308 (1.108–1.508)
25, 50, 75, 90th percentiles (g/m^3)	0.51, 0.77, 0.99, 1.37	0.17, 0.26, 0.39, 0.52	0.35, 0.52, 0.87, 1.17	0.56, 0.70, 1.23, 1.97	0.13, 0.22, 0.35, 0.43	0.72, 1.17, 1.58, 2.49
Range of 24-hour samples (g/m^3)	0.319–2.08	0.043–1.17	0.087–2.52	0.282–2.75	0.043–1.17	0.264–4.03

3.2. Detection frequencies

The detection frequencies for the potentially relevant VOCs ranged from 70 to 98% for the autoGC datasets (Table 5). n-Hexane and toluene had the highest detection frequency at 98% for each chemical. With respect to the canister datasets, the detection frequencies for the potentially relevant VOCs ranged from 63 to 100% (Table 6). Benzene and toluene had the highest detection frequency at 100% and 99%, respectively.

3.3. Trend tests

The standard linear and polynomial trend tests for the potentially relevant VOCs demonstrated that over 95% showed either no change in annual average concentrations across the entire period of record for each monitor, or showed a statistically significant linear decrease in the annual average concentrations across the entire period of record. Fig. 2 provides an example of such a downward trend for benzene. This decrease in the annual average benzene concentrations over time is noteworthy given the substantial increase in the number of wells in the Barnett Shale region over time. Fig. 2 also includes benzene data for a monitor in an urban area in the Dallas–Fort Worth Region that is not close to any shale gas operations (i.e., Dallas Hinton monitor) to provide information on historical trends in urban areas in northwest Texas. There was only one VOC that showed a very slight but statistically significant ($\alpha = 0.05$) linear increase in the annual average: n-hexane at the Fort Worth Northwest canister (though the annual average concentrations across all years were well below the OBACV and HBACV). Collectively, these results indicate that shale gas operations are not likely impacting community-wide ambient air concentrations of VOCs given the exponential increase in the number of wells over the last decade and lack of evidence of any notable increasing trends.

3.4. Comparison of maximum concentrations determined for each year to OBACVs

Maximum hourly and maximum 24-hour concentrations of all measured VOCs were compared to applicable OBACVs. The maximum hourly concentration of only one VOC exceeded the respective OBACV in only one year. Specifically, in 2007, the maximum 1-hour concentration of toluene measured at the Fort Worth Northwest autoGC was 653 $\mu\text{g}/\text{m}^3$, which was only slightly (i.e., 2%) above its respective OBACV of 640 $\mu\text{g}/\text{m}^3$. Because of the exceedance, all individual hourly concentrations for 2007 were evaluated. Other than the maximum hourly concentration, no other hourly concentrations exceeded the OBACV for toluene in 2007. This equates to an exceedance frequency of 0.00002% (one out of more than 4.6 million data points) across all monitors, chemicals, and years across the entire period of record for each monitor in the Barnett Shale region.

Table 4
AutoGC dataset statistics for the potentially relevant VOCs from 2011 only.

Parameter	Benzene	Ethylbenzene	m/p-xylene	n-Hexane	o-Xylene	Toluene
<i>Decatur Thompson (autoGC)</i>						
Number of data points	7799	7799	7799	7799	7799	7799
Detection frequency (%)	100%	70%	94%	100%	71%	100%
Annual average (95LCL–95UCL) ($\mu\text{g}/\text{m}^3$)	0.528 (0.520–0.535)	0.110 (0.107–0.112)	0.346 (0.335–0.357)	2.667 (2.587–2.748)	0.114 (0.111–0.117)	1.018 (0.996–1.039)
25, 50, 75, 90th percentiles ($\mu\text{g}/\text{m}^3$)	0.30, 0.45, 0.65, 0.93	0.07, 0.09, 0.13, 0.18	0.15, 0.23, 0.43, 0.69	0.84, 1.53, 3.00, 5.72	0.07, 0.09, 0.14, 0.20	0.52, 0.78, 1.23, 1.88
Range of 1-hour samples ($\mu\text{g}/\text{m}^3$)	0.085–4.90	0.016–7.28	0.027–28.4	0.182–54.3	0.005–10.1	0.065–41.1
<i>Dish Airfield (autoGC)</i>						
Number of data points	7700	7700	7700	7700	7700	7700
Detection frequency (%)	94%	48%	78%	100%	57%	100%
Annual average (95LCL–95UCL) ($\mu\text{g}/\text{m}^3$)	0.525 (0.516–0.535)	0.120 (0.118–0.121)	0.310 (0.300–0.320)	1.711 (1.634–1.788)	0.115 (0.113–0.117)	0.943 (0.904–0.982)
25, 50, 75, 90th percentiles ($\mu\text{g}/\text{m}^3$)	0.27, 0.41, 0.64, 1.01	0.08, 0.10, 0.15, 0.20	0.12, 0.18, 0.34, 0.66	0.44, 0.69, 1.29, 3.28	0.06, 0.09, 0.14, 0.20	0.33, 0.58, 1.10, 1.95
Range of 1-hour samples ($\mu\text{g}/\text{m}^3$)	0.011–8.05	0.005–2.25	0.016–13.4	0.094–52.5	0.005–3.08	0.049–98.7
<i>Eagle Mountain Lake (autoGC)</i>						
Number of data points	7592	7592	7592	7592	7592	7592
Detection frequency (%)	78%	29%	50%	91%	34%	86%
Annual average (95LCL–95UCL) ($\mu\text{g}/\text{m}^3$)	0.341 (0.334–0.347)	0.099 (0.098–0.101)	0.217 (0.211–0.223)	1.086 (1.007–1.166)	0.101 (0.099–0.103)	0.513 (0.496–0.529)
25, 50, 75, 90th percentiles ($\mu\text{g}/\text{m}^3$)	0.18, 0.27, 0.44, 0.64	0.05, 0.09, 0.13, 0.18	0.09, 0.15, 0.22, 0.44	0.23, 0.51, 1.07, 2.21	0.05, 0.09, 0.13, 0.18	0.14, 0.29, 0.64, 1.20
Range of 1-hour samples ($\mu\text{g}/\text{m}^3$)	.011–13.1	0.005–1.53	0.005–11.8	0.012–263	0.005–2.29	0.005–33.6
<i>Flower Mound Shiloh (autoGC)</i>						
Number of data points	7798	7798	7798	7749	7798	7798
Detection frequency (%)	99%	70%	87%	99%	71%	100%
Annual average (95LCL–95UCL) ($\mu\text{g}/\text{m}^3$)	0.409 (0.400–0.418)	0.125 (0.119–0.131)	0.315 (0.292–0.337)	0.806 (0.774–0.838)	0.136 (0.127–0.144)	0.784 (0.756–0.811)
25, 50, 75, 90th percentiles ($\mu\text{g}/\text{m}^3$)	0.23, 0.35, 0.51, 0.72	0.07, 0.10, 0.15, 0.21	0.12, 0.19, 0.34, 0.61	0.25, 0.46, 0.84, 1.52	0.07, 0.10, 0.15, 0.23	0.33, 0.54, 0.94, 1.55
Range of 1-hour samples ($\mu\text{g}/\text{m}^3$)	0.064–27.6	0.005–15.2	0.011–59.1	0.041–65.3	0.005–20.7	0.043–86.3
<i>Fort Worth Northwest (autoGC)</i>						
Number of data points	7537	7537	7537	7536	7537	7537
Detection frequency (%)	100%	96%	99%	100%	96%	100%
Annual average (95LCL–95UCL) ($\mu\text{g}/\text{m}^3$)	0.585 (0.574–0.597)	0.172 (0.167–0.177)	0.535 (0.518–0.552)	1.046 (1.019–1.074)	0.186 (0.180–0.191)	1.511 (1.462–1.560)
25, 50, 75, 90th percentiles ($\mu\text{g}/\text{m}^3$)	0.30, 0.44, 0.67, 1.10	0.07, 0.10, 0.18, 0.36	0.18, 0.30, 0.56, 1.15	0.38, 0.62, 1.20, 2.27	0.07, 0.10, 0.19, 0.39	0.57, 0.87, 1.57, 3.18
Range of 1-hour samples ($\mu\text{g}/\text{m}^3$)	0.043–6.81	0.005–5.35	0.016–18.2	0.070–24.9	0.005–5.11	0.081–57.6

3.5. Comparison of maximum concentrations determined for each year to acute/short-term HBACVs

Despite the tremendous amount of data evaluated in this assessment, none of the maximum hourly autoGC measurements, nor any of the maximum 24-hour canister measurements exceeded the respective acute HBACVs for any of the up to 105 VOCs at any of the sites, across the entire period of record for each site. This includes all of the potentially relevant VOCs as shown in Tables 5 and 6, as well as all other chemicals available in the dataset. This analysis demonstrates that VOCs measured in ambient air at monitors located in the Barnett Shale do not pose an acute health hazard as a result of inhalation exposures.

3.6. Comparison of annual average concentrations to chronic HBACVs

Out of 105 VOCs included in this analysis, only one chemical, 1,2-dibromoethane, had an annual average concentration that exceeded its respective chronic HBACV in a single year. Specifically, the annual average concentrations of 1,2-dibromoethane for 2011 were at $0.42 \mu\text{g}/\text{m}^3$ and $0.33 \mu\text{g}/\text{m}^3$ at the Denton Airport South canister and the Fort Worth Northwest canister, respectively, both of which exceeded the chronic HBACV of $0.0167 \mu\text{g}/\text{m}^3$ for this chemical. Because

there were no other exceedances in any other year across the entire period of record, this equates to an exceedance frequency of 0.08% (two out of 2501 annual averages across all monitors, chemicals, and years across the entire period of record for each monitor in the Barnett Shale region). Further investigation of these exceedances revealed that the average detection frequency across the entire period of record for 1,2-dibromoethane was 3.3% and 2.7% at the Denton Airport South canister and the Fort Worth Northwest canister, respectively (the detection frequencies in 2011 were 12% and 8%, respectively). This indicates that the annual average calculated for this chemical at both sites was based almost entirely on non-detect values. Notably, the detection limit (DL) of $1.54 \mu\text{g}/\text{m}^3$ for 1,2-dibromoethane is substantially higher than its respective chronic TCEQ HBACV. The limited number of detected results for 1,2-dibromoethane ranged from 0.08 to $0.92 \mu\text{g}/\text{m}^3$ at the Denton Airport South canister ($n = 7$), and from 0.23 to $0.54 \mu\text{g}/\text{m}^3$ at the Fort Worth Northwest canister ($n = 5$). None of these measured concentrations exceeded short-term HBACVs for this compound. Additionally, 1,2-dibromoethane is not a VOC that is reasonably expected to be associated with shale gas operations (TCEQ, 2011), but it is still used as a lead scavenger in aviation fuel and off-road applications in automobile racing (USEPA, 2013b).

Table 5
Description of autoGC datasets for the potentially relevant VOCs across the entire period of record.

Chemical	Total number of data points across all sites	Total number of detects across all sites	Detection frequency of data points across all sites	Range of hourly concentrations ($\mu\text{g}/\text{m}^3$)	1-Hour HBACV ($\mu\text{g}/\text{m}^3$)	Range of annual average concentrations ($\mu\text{g}/\text{m}^3$)	Chronic HBACV ($\mu\text{g}/\text{m}^3$)	OBACV ($\mu\text{g}/\text{m}^3$)
Benzene	101,318	97,287	96%	0.0053–28	575	0.25–0.77	4.5	8,600
Ethylbenzene	101,044	71,060	70%	0.0054–15	86,850	0.10–0.35	4.0	740
m/p-Xylene	101,141	86,095	85%	0.0054–59	7,382	0.21–0.41	610	350
o-Xylene	101,196	74,097	73%	0.0054–21	7,382	0.09–0.35	610	1,700
n-Hexane	100,044	98,441	98%	0.0117–263	6,345	0.79–2.67	670	5,300
Toluene	101,216	99,637	98%	0.0054–653	15,070	0.48–2.29	4,100	640

Table 6

Description of canister datasets for the potentially relevant VOCs across the entire period of record.

Chemical	Total number of data points across all sites	Total number of detects across all sites	Detection frequency of data points across all sites	Range of 24-hour concentrations ($\mu\text{g}/\text{m}^3$)	24-Hour HBACV ($\mu\text{g}/\text{m}^3$)	Range of annual average concentrations ($\mu\text{g}/\text{m}^3$)	Chronic BACV ($\mu\text{g}/\text{m}^3$)	OBACV ($\mu\text{g}/\text{m}^3$)
Benzene	1,164	1,163	100%	0.064–11	320	0.52–1.15	4.5	8,600
Ethylbenzene	1,164	826	71%	0.043–1.9	20,000	0.15–0.45	4.0	740
m/p-Xylene	1,164	967	83%	0.043–8.4	9,000	0.42–1.02	610	350
o-Xylene	1,164	735	63%	0.043–2.1	9,000	0.13–0.39	610	1,700
n-Hexane	1,164	977	84%	0.035–302	–	0.38–9.11	670	5,300
Toluene	1,164	1,158	99%	0.113–191	4,000	1.03–5.01	4,100	640

3.7. Deterministic risk assessment

In Run 1 of the DRA, which included all monitored VOCs, total hazard indices for both CTE and RME scenarios were less than 1.0 for all monitors (Table 7). The highest hazard indices occurred at the Fort Worth Northwest canister (0.35 and 0.40 for the CTE and RME scenarios, respectively). All total cancer risk estimates (Table 7) were within the acceptable cancer risk range with one exception: the total cancer risk calculated for the RME scenario at the Denton Airport South canister of 1.3×10^{-4} was slightly outside of the acceptable cancer risk range of 1.0×10^{-4} . However, 94% of this risk estimate was due to 1,2-dibromoethane (risk level of 1.2×10^{-4}). As discussed previously, the concentrations for 1,2-dibromoethane are driven largely by non-detected values, as this chemical was detected in less than 12% of the samples collected at the Denton Airport South canister during 2011. Thus, this single risk estimate does not reflect a realistic risk to human health. Similar to the RME scenario, the highest estimate of risk for the CTE scenario (4.0×10^{-5}) was also observed at the Denton Airport South canister, and was also driven by 1,2-dibromoethane. Similarly, in Run 2, which was focused on the six potentially relevant VOCs, the hazard indices for both CTE and RME scenarios were all below 1.0 for all monitors (Table 7). Again, the highest hazard indices (0.08 and 0.10 for the CTE and RME scenarios, respectively) occurred at the Fort Worth Northwest canister, even though this monitor is in an area that has fewer wells nearby than do the other monitors. Additionally, the

total cancer risk estimates were within the acceptable cancer risk range for both CTE and RME scenarios at all monitors.

3.8. Probabilistic risk assessment

All CTE and RME cancer risk estimates for the six potentially relevant VOCs were within the acceptable risk range at all monitors, and all hazard indices were below the level of concern at all monitors (Table 8). Similar to findings observed for the DRA, the highest hazard index and highest total cancer risk estimates occurred at the Fort Worth Northwest canister using the 95th percentile VOC concentrations (i.e., 0.09 and 3.2×10^{-6} for the RME scenario, respectively). Notably, all risk estimates were at the lower end of the acceptable risk range of 1×10^{-6} – 1×10^{-4} .

There was very little difference in the CTE hazard indices and cancer risks relative to the RME hazard indices and cancer risks. This lack of a remarkable difference between the scenarios is due in large part to the limited number of exposure parameters in the standard equations used to assess inhalation hazards and risk, and the limited number of those exposure parameters in the inhalation equations that could be distributed in the PRA. In the noncancer assessment, only the air concentration was distributed, and in the cancer assessment exposure duration, lifetime, and air concentration were distributed. The sensitivity analyses indicated that the parameter with the largest influence on

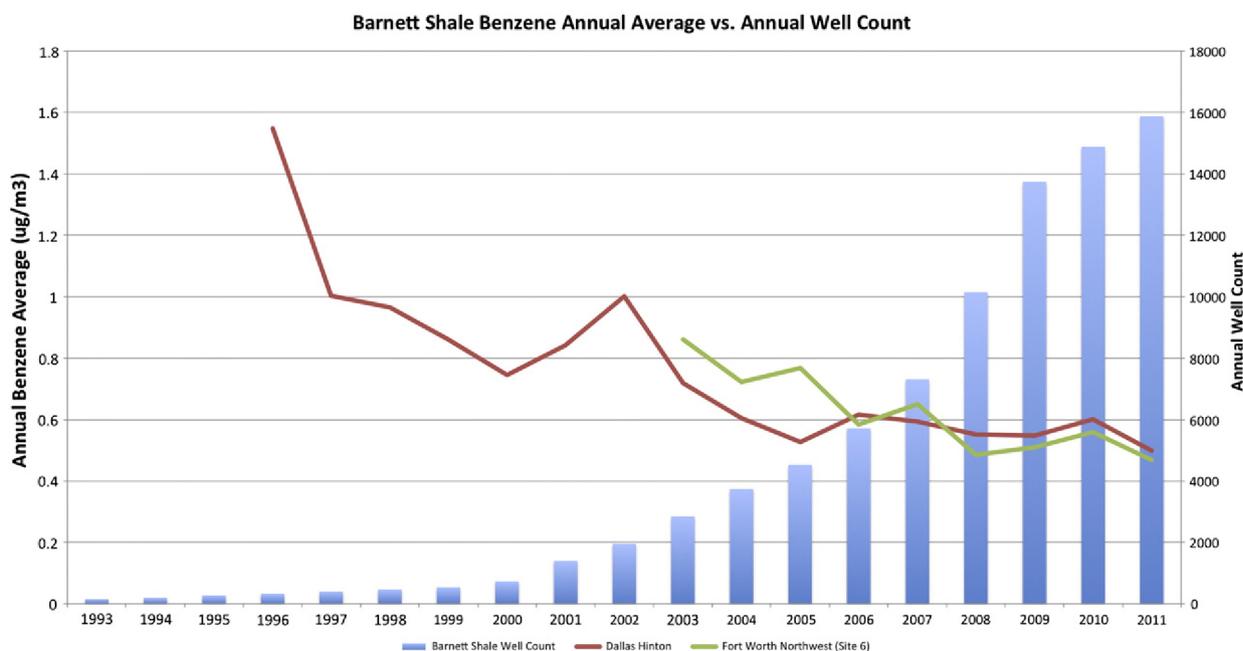


Fig. 2. Barnett Shale benzene annual average and annual well count over time.

Table 7

Deterministic risk assessment (DRA) results for all chemicals and for the potentially relevant VOCs. The acceptable risk range is 10^{-6} – 10^{-4} .

Monitor	Type	Reasonable Maximum Exposure (RME)		Central Tendency Exposure (CTE)	
		Total hazard	Total risk	Total hazard	Total risk
<i>Run 1 – Reasonable Maximum Exposure (RME) and Central Tendency Exposure (CTE) for all monitored VOCs</i>					
Ft Worth Northwest	Canister	0.40	9.8E–05	0.35	3.2E–05
Denton Airport South	Canister	0.36	1.3E–04	0.31	4.0E–05
Ft Worth Northwest	AutoGC	0.15	3.7E–06	0.14	1.3E–06
Flower Mound Shiloh	AutoGC	0.09	2.4E–06	0.09	8.2E–07
Eagle Mountain Lake	AutoGC	0.08	1.8E–06	0.08	6.4E–07
Dish Airfield	AutoGC	0.10	2.5E–06	0.10	8.6E–07
Decatur Thompson	AutoGC	0.09	2.5E–06	0.09	8.8E–07
<i>Run 2 – Reasonable Maximum Exposure (RME) and Central Tendency Exposure (CTE) for the potentially relevant VOCs</i>					
Ft Worth Northwest	Canister	0.10	3.3E–06	0.08	1.0E–06
Denton Airport South	Canister	0.08	2.7E–06	0.06	8.3E–07
Ft Worth Northwest	AutoGC	0.06	2.1E–06	0.06	7.4E–07
Flower Mound Shiloh	AutoGC	0.04	1.5E–06	0.04	5.2E–07
Eagle Mountain Lake	AutoGC	0.03	1.2E–06	0.03	4.3E–07
Dish Airfield	AutoGC	0.04	1.8E–06	0.04	6.5E–07
Decatur Thompson	AutoGC	0.04	1.8E–06	0.04	6.5E–07

uncertainty in total cancer risk was exposure duration. Lifetime also had an influence on total cancer risk variance, while the distributions for annual air concentrations only minimally influenced the total cancer risk variance.

4. Discussion

Comprehensive analysis of more than 4.6 million data points (representing data from six sites, seven monitors, up to 105 VOCs measured at each site, and periods of record that extend back to the year 2000), indicates 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. In addition to direct comparison of maximum hourly, 24-hour, and annual average concentrations to OBACVs and to acute and chronic HBACVs, both deterministic and probabilistic methods were employed to characterize potential hazard and risk. The deterministic method, though useful as an initial step in assessing hazard/risk due to its relative time effectiveness, is a highly conservative screening-level type approach for assessing hazard/risk since it is dependent upon upper bound point estimate input parameters and included all measured VOCs even though most are not known to be associated with shale gas operations. Despite these limitations, the results of the DRA indicated that hazard and risk estimates were within the range typically considered acceptable by regulatory agencies. Conduct of the PRA allowed for further refinement in the assessment not only by focusing on those VOCs reasonably believed to be associated with shale gas operations but also by allowing incorporation of distributions of values for several of the exposure parameters in lieu of the conservative single point

Table 8

Probabilistic risk assessment (PRA) results for the potentially relevant VOCs. The acceptable risk range is 10^{-6} – 10^{-4} .

Monitor	Type	95th percentile		50th percentile	
		Total hazard	Total risk	Total hazard	Total risk
Ft Worth Northwest	Canister	0.09	3.2E–06	0.08	7.1E–07
Denton Airport South	Canister	0.07	2.5E–06	0.06	5.6E–07
Ft Worth Northwest	AutoGC	0.06	2.2E–06	0.06	5.0E–07
Flower Mound Shiloh	AutoGC	0.04	1.6E–06	0.04	3.5E–07
Eagle Mountain Lake	AutoGC	0.03	1.3E–06	0.03	2.9E–07
Dish Airfield	AutoGC	0.04	2.0E–06	0.04	4.4E–07
Decatur Thompson	AutoGC	0.04	2.0E–06	0.04	4.4E–07

estimates used in Runs 1 and 2 of the DRA. The PRA yielded findings similar to the DRA, further demonstrating that shale gas operations have not resulted in community-wide exposures to the measured VOCs at levels that would pose a health concern.

These findings are consistent with those from a number of shorter-term, targeted air monitoring studies conducted in the Barnett Shale region. In 2010, the TCEQ conducted a short-term mobile monitoring study (12 sampling days) in the Barnett Shale region and found that air concentrations of VOCs near shale gas operations were not present at high enough concentrations to pose a health concern (TCEQ, 2010). In June of 2010, Titan Engineering conducted an ambient air quality study in the Barnett Shale region on behalf of the Barnett Shale Energy Education Council (BSEEC, 2010). In this study, Titan Engineering collected air samples in the vicinity of two compressor stations and eight completed well sites. Titan specifically targeted those sites projected to have the highest air emissions and analyzed samples for a host of VOCs and reduced sulfur compounds. The study authors concluded that these operations have negligible to minimal impact on ambient air concentrations of the compounds measured and in the limited number of instances where a few compounds were present above applicable AMCVs, the measured concentrations were concluded to not pose a significant increased risk to human health (BSEEC, 2010). In a study conducted by Eastern Research Group and Sage Environmental Consulting on behalf of the City of Fort Worth (CFW, 2011), air samples were collected at 8 locations representative of a range of activities (i.e., background, pre-production, and moderate and high levels of shale gas activities) in the Fort Worth area over a 2-month period and samples were analyzed for approximately 140 VOCs and carbonyls. None of the measured air concentrations exceeded the short-term health benchmarks used by the investigators to assess the potential for health risk. In a study conducted by the Desert Research Institute (DRI) on behalf of The Mickey Leland National Urban Air Toxics Research Center (NUATRC, 2011), DRI conducted saturation monitoring using passive samplers over a period of 28 days downwind of gas production areas – one location was near a well with emissions from condensate tanks and another location was near a compressor station near a small community. In the NUATRC (2011) study, average concentrations were generally below 1 ppb and substantially lower than short- and long-term TCEQ AMCVs. Additionally the DRI investigators found that air concentrations dropped off quickly with distance from a source as evident by the observation that concentrations of emissions from a condensate tank decreased to near background levels at a distance of approximately 100 m.

Although all of these shorter-term ambient air monitoring studies provide data that represents a relatively limited duration relative to the data from the TCEQ long-term, fixed-site autoGCs and canisters evaluated in this current study, these shorter-term studies provide important information in that they address some of the limitations of the TCEQ fixed-site ambient air monitoring network. Specifically, they address a broader range of specific air contaminants potentially associated with shale gas production operations (e.g., carbonyls, sulfur compounds, and short-chain alkanes) and include samples collected in close proximity to compressor stations and well pads. For example, while formaldehyde cannot be measured in air samples collected by the TCEQ fixed-site autoGCs and canisters in the Barnett Shale region, both the City of Fort Worth study (CFW, 2011) and the BSEEC study (2010) included an assessment of formaldehyde. Though formaldehyde was detected in the CFW (2011) study, it was determined that it was not present in high enough concentrations to pose a health concern. Additionally, the CFW (2011) study also included an air modeling component and demonstrated that the modeled formaldehyde concentrations were also below levels associated with adverse health effects. In the BSEEC (2010) study, it was determined that the formaldehyde concentrations measured in the study were the result of vehicular traffic and an unidentified, offsite source and were not related to shale gas production operations (BSEEC, 2010).

While ambient air monitoring data provides a tool for estimating potential human exposures, there is still uncertainty as such data only indicates what an individual may potentially be exposed to and not necessarily what is actually taken up into their body. The best tool for assessing an individual's actual exposure is biomonitoring, which involves the collection of blood and/or urine from individuals to actually measure the chemicals present in their bodies. While this provides important information regarding exposures to specific chemicals, it is not necessarily definitive with respect to identification of the specific source(s) of exposure. Nonetheless, biomonitoring is clearly the best indicator of an individual's exposure. Because of the concerns about the potential impact of shale gas operations in the Barnett Shale region on people's health, the Texas Department of State Health Services (TXDSHS) in conjunction with the Centers for Disease Control and Prevention (TXDSHS, 2010) conducted a biomonitoring study in Dish, TX, a community with a high density of shale gas production operations. In this study, blood and urine samples were collected from 28 residents in the community and analyzed for 33 VOCs. The TXDSHS concluded that the levels of VOCs measured in most Dish residents were not different from typical background levels in the general U.S. population. Further, the authors concluded that although some VOCs were detected above levels seen in the general US population in some of the blood samples, the pattern of VOC values was not consistent with a community-wide exposure to airborne contaminants, such as those that might be associated with shale gas drilling operations. Rather, the investigators concluded that other sources of exposure likely explained these findings (e.g., smoking and household cleaners). These data provide further evidence that individuals living in communities with extensive shale gas production activities are not being exposed to excessive levels of VOCs.

The data evaluated as a part of this current study are uniquely well-suited for evaluation of the impacts of shale gas production operations on air quality and in particular for evaluation of both potential acute and chronic health effects associated with inhalation exposures to VOCs. Further, the comprehensive analyses carried out as a part of the conduct of this current study represents the most robust assessment of potential human health effects conducted to date. Key aspects of this current study that differentiate it from other studies include: (1) use of data collected over a long period of time (a minimum of a year; some data collected for >10 years), (2) use of data from monitors that collect air samples continuously (i.e., autoGCs), (3) use of data from multiple sites – with monitors sited to capture community-wide exposures to VOCs in areas with extensive shale gas operations in both richer (wet) and dry gas areas, and (4) use of multiple quantitative approaches for assessing potential human health risks (i.e., comparison to HBACVs and quantitative risk-based approaches).

McKenzie et al. (2012) is the only other study to have employed a quantitative risk-based approach; however, the data evaluated were more limited in terms of the number of chemicals analyzed, volume of data used, and period of time over which samples were collected relative to the data used in the current study. In the McKenzie et al. (2012) study, air samples were collected in canisters over a 24-hour period at fixed-site monitoring stations along the perimeter of four well pads and analyzed for 78 hydrocarbons. The study also included an assessment of ambient air samples collected at a single fixed monitoring location every six days between January 2008 and November 2010 (163 samples). The goal was to quantitatively estimate potential cancer risks and non-cancer hazards for individuals that live <1/2 mile from wells and >1/2 mile from wells. The study found that subchronic exposures to trimethylbenzenes, xylenes, and aliphatic hydrocarbons presented the greatest potential for health effects, particularly for residents living <1/2 mile from wells. The study employed some exposure assumptions in the analysis that were overly conservative or not representative of the scenario under evaluation (e.g., assumptions related to the well development process, timeframes used to develop potential emission estimates, and emission impacts confounded by traffic from a major highway near a sample test site). As a result, the results reported

by McKenzie et al. (2012) may not be applicable for characterizing typical exposures and health hazards/risks.

It is important to note that there are a number of uncertainties inherent in analyses conducted in this current study. First, the analyses were based on a number of conservative default assumptions in both deterministic and probabilistic risk assessments. Several of these default parameters may have led to an overestimation of risk: exposure time of 24 h/day; exposure frequency of 350 days/year; inhalation rate of 20 m³/day; and using the 95% UCL for the RME scenario. Second, a large number of VOC measurements were not detected despite generally low analytical limits of detection. Nonetheless, those VOCs were not excluded from any of the assessments but rather were subject to a robust method (i.e., Kaplan Meier) to estimate annual average concentrations. Third, several chemicals identified in the BSSI (TCEQ, 2011) are not measured at any of the fixed-site autoGC or canister samplers operated by the TCEQ and, as such, could not be included in the analysis. Fourth, the fixed-site autoGC and canister samplers operated by the TCEQ in the Barnett Shale region were not explicitly sited to capture a specific source but rather are intended to provide an indication of community-wide exposures and, as such, there could be cases where specific individual property owners could potentially be exposed to higher or lower concentrations in air. Fifth, there are likely many sources of VOCs, such as traffic, but attempts to potentially identify specific sources of specific measured concentrations were beyond the scope of this current assessment and, as such, were not conducted at time. As indicated in Fig. 2, the similarity in benzene air concentrations at both Fort Worth Northwest (an urban monitor in the Barnett Shale region) and the Dallas Hinton (an urban monitor outside of the Barnett Shale region) monitors suggests that the measured benzene is likely primarily due to sources other than shale gas operations. Nonetheless, benzene was considered potentially relevant and was included in all assessments in this current study. Finally, while some of the analyses conducted by others include VOCs not identified as potentially relevant in this current study (e.g., 1,2,3-trimethylbenzene, 1,3-butadiene) based on the BSSI (TCEQ, 2011), these VOCs were in fact included in the assessment involving comparison of the measured concentrations to HBACVs and none were present at levels believed to pose a health concern. These VOCs were also included in Run 1 of the DRA and did not significantly contribute to total cancer risk or total noncancer hazard.

When the findings of the current study are considered along with the findings of other studies, including the comprehensive biomonitoring study conducted in the Barnett Shale region, the body of evidence demonstrates that shale gas production activities have not resulted in community-wide exposures to those VOCs in air at levels that would pose a health concern, despite the dramatic increase in shale gas operations in the region over the last decade. Although these analyses cannot specifically predict future exposures, it seems unlikely that future exposures of VOCs associated with shale gas operations would increase given the decreasing trends reported in this analysis in combination with increased technology that limits releases. Further, because the Barnett Shale region represents the most active onshore shale gas field in the U.S., with a high density of active wells in close proximity to the city of Fort Worth, TX and surrounding suburbs, the extensive air monitoring data available for this region provides a unique opportunity for evaluating the potential impacts of shale gas production activities on human health. Importantly, the findings of this current study may be useful for understanding potential health risks in other shale plays. While most of the air monitors in the Barnett Shale region are situated in dry gas areas (Fig. 1), a number of the monitors are situated in areas with richer gas which makes this dataset even more useful as VOC emissions are generally higher in rich/richer ("wet") gas areas. Nonetheless, the type of gas in a particular region, as well as other site-specific characteristics, should be considered when attempting to extrapolate the findings of this current study to other shale play regions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.08.080>.

References

- Agency for Toxic Substances and Disease Registry (ATSDR). Air Comparison Values in Units of Micrograms per Cubic Meter ($\mu\text{g}/\text{m}^3$) 2011. February.
- Bamberger M, Oswald R. Impacts of gas drilling on human and animal health. *New Solut* 2012;22(1):51–77.
- Barnett Shale Energy Education Council (BSEEC). Ambient air quality study – natural gas sites, cities of Fort Worth & Arlington, Texas. Prepared by TITAN Engineering, Inc.; 2010 [July].
- Barnett Shale Energy Education Council (BSEEC). Air quality and the Barnett Shale. Available at: <http://www.bseec.org/content/air-quality-and-barnett-shale>.
- California Environmental Protection Agency (Cal/EPA). Office of Environmental Health Hazard Assessment Reference Exposure Levels. (OEHHA RELs). 2012 Available at <http://www.oehha.org/air/allrels.html>.
- City of Fort Worth (CFW). City of Fort Worth natural gas air quality study, final report. Prepared by Eastern Research Group and Sage Environmental; 2011 [July 13].
- Colborn T, Schultz K, Herrick L, Kwiatkowski C. An exploratory study of air quality near natural gas operations. *Hum Ecol Risk Assess* 2013. <http://dx.doi.org/10.1080/10807039.2012.749447>. (in press).
- Commission and on Environmental Quality (TCEQ). Barnett Shale formation area monitoring project, phase I–III. Monitoring operations division. BS0912-FR; 2010 [January].
- Commission and on Environmental Quality (TCEQ). Barnett Shale special inventory. Spreadsheet of data provided from personal communication with Gail Hogberg on January 22, 2013; 2011.
- Commission and on Environmental Quality (TCEQ). Guidelines to develop toxicity factors. Revised RG-442, toxicology division.; 2012 [October].
- R Development Core Team. R: a language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing 3-900051-07-0; 2012 [URL <http://www.R-project.org/>].
- Earthworks. Gas patch roulette: how shale gas development risks public health in Pennsylvania. Prepared by Earthworks' Oil & Gas Accountability Project and Subra Company; 2012.
- Johnson T, Capel J. A Monte Carlo approach to simulating residential occupancy periods and its application to the general U.S. population. EPA-450/3-92-011. Research Triangle Park, N.C.: U.S. Environmental Protection Agency; 1992.
- McKenzie L, Witter R, Newman L, Adgate J. Human health risk assessment of air emissions from development of unconventional natural gas resources. *Sci Total Environ* 2012;424:79–87.
- Mickey Leland National Urban Air Toxics Research Center (NUATRC). Monitoring of emissions from Barnett Shale natural gas production facilities for population exposure assessment. Zielinska, E. Fujita, and D. Campbell, Desert Research Institute. No. 19; 2011.
- Murphy S, Kochanek K. Deaths: final data for 2010. National vital statistics reports. Vol 61 no 4. Hyattsville, MD: National Center for Health Statistics; 2012 [Retrieved from: http://www.cdc.gov/nchs/data/dvs/deaths_2010_release.pdf].
- Olaguer E. The potential near-source ozone impacts of upstream oil and gas industry emissions. *J Air Waste Manage Assoc* 2012;62(8):966–77.
- Pennsylvania Department of Environmental Protection (PADEP). Southwestern Pennsylvania Marcellus shale short-term ambient air sampling report. Commonwealth of Pennsylvania Department of Environmental Protection. Bureau of Air Quality; 2010 [November].
- Railroad Commission of Texas (RRC). Barnett Shale information; 2012 [February].
- Texas Commission on Environmental Quality (TCEQ). Texas Air Monitoring Information System (TAMIS). V4.0.5. Available at <http://www5.tceq.state.tx.us/tamis/index.cfm>.
- Texas Department of State Health Services (TXDSHS). Final report. Dish, Texas exposure investigation, Denton County; 2010 [May].
- Therneau T, Lumley T. Survival: survival analysis, including penalized likelihood. R package version 2.36-5. <http://CRAN.R-project.org/package=survival>.
- U.S. Environmental Protection Agency (USEPA). National oil and hazardous substances pollution contingency plan; final rule. 40 CFR part 300; 1990 [March].
- U.S. Environmental Protection Agency (USEPA). Risk assessment guidance for superfund, volume I: human health evaluation manual (part F, supplemental guidance for inhalation risk assessment), final. Office of Superfund Remediation and Technology Innovation, Environmental Protection Agency, Washington, D.C. EPA-540-R-070-002, OSWER 9285.7-82; 2009 [January].
- US Department of Energy (DOE). Modern shale gas development in the United States: a primer. Prepared by Ground Water Protection Council and ALL Consulting; 2009 [April].
- US Environmental Protection Agency (USEPA). ProUCL version 4.1.00 technical guide (draft). Statistical software for environmental applications for data sets with and without nondetect observations. EPA/600/R-07/041; 2010 [May].
- US Environmental Protection Agency (USEPA). Emissions factors & AP-42 compilation of air pollutant emission factors. Updated December 28, 2011. Available at <http://www.epa.gov/ttnchie1/ap42/>, 2011a.
- US Environmental Protection Agency (USEPA). Outdoor air – industry, business, and home: oil and natural gas production – additional information. Available at www.epa.gov/oaqps001/community/details/oil-gas_addl_info.html, [August].
- US Environmental Protection Agency (USEPA). Exposure factors handbook: 2011 edition, office of research and development. Washington, DC: National Center for Environmental Assessment; 2011c [EPA/600/R-090/052F, September].
- US Environmental Protection Agency (USEPA). Study of the potential impacts of hydraulic fracturing on drinking water resources. Progress report. EPA 601/R-12/011; 2012 [December].
- US Environmental Protection Agency (USEPA). Regional screening tables. Available at http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/index.htm.
- US Environmental Protection Agency (USEPA). Lead scavengers. Last updated April 16, 2013. Accessed July 31, 2013 at: <http://www.epa.gov/oust/cat/leadscav.htm>.