

Elevated Atmospheric Levels of Benzene and Benzene-Related Compounds from Unconventional Shale Extraction and Processing: Human Health Concern for Residential Communities



Alisa L. Rich^{1,2} and Helen T. Orimoloye¹

¹Department of Environmental and Occupational Health Science, University of North Texas Health Science Center, Fort Worth, TX, USA.

²WHO Chemical Risk Assessment Network, Geneva, Switzerland.

ABSTRACT

BACKGROUND: The advancement of natural gas (NG) extraction across the United States (U.S.) raises concern for potential exposure to hazardous air pollutants (HAPs). Benzene, a HAP and a primary chemical of concern due to its classification as a known human carcinogen, is present in petroleum-rich geologic formations and is formed during the combustion of bypass NG. It is a component in solvents, paraffin breakers, and fuels used in NG extraction and processing (E&P).

OBJECTIVES: The objectives of this study are to confirm the presence of benzene and benzene-related compounds (benzene[s]) in residential areas, where unconventional shale E&P is occurring, and to determine if benzene[s] exists in elevated atmospheric concentrations when compared to national background levels.

METHODS: Ambient air sampling was conducted in six counties in the Dallas/Fort Worth Metroplex with passive samples collected in evacuated 6-L Summa canisters. Samples were analyzed by gas chromatography/mass spectrometry, with sampling performed at variable distances from the facility fence line.

RESULTS: Elevated concentrations of benzene[s] in the atmosphere were identified when compared to U.S. Environmental Protection Agency's Urban Air Toxics Monitoring Program. The 24-hour benzene concentrations ranged from 0.6 parts per billion by volume (ppbv) to 592 ppbv, with 1-hour concentrations from 2.94 ppbv to 2,900.20 ppbv.

CONCLUSION: Benzene is a known human carcinogen capable of multisystem health effects. Exposure to benzene is correlated with bone marrow and blood-forming organ damage and immune system depression. Sensitive populations (children, pregnant women, elderly, immunocompromised) and occupational workers are at increased risk for adverse health effects from elevated atmospheric levels of benzene[s] in residential areas with unconventional shale E&P.

KEYWORDS: benzene, benzene-related compounds, occupational exposure, natural gas extraction and processing, elevated atmospheric levels, Urban Air Toxics Monitoring Program, carcinogen, health effects

CITATION: Rich and Orimoloye. Elevated Atmospheric Levels of Benzene and Benzene-Related Compounds from Unconventional Shale Extraction and Processing: Human Health Concern for Residential Communities. *Environmental Health Insights* 2016;10 75–82 doi: 10.4137/EHI.S33314.

TYPE: Original Research

RECEIVED: August 20, 2015. **RESUBMITTED:** December 16, 2016. **ACCEPTED FOR PUBLICATION:** December 18, 2015.

ACADEMIC EDITOR: Timothy Kelley, Editor in Chief

PEER REVIEW: Four peer reviewers contributed to the peer review report. Reviewers' reports totaled 843 words, excluding any confidential comments to the academic editor.

FUNDING: Authors disclose no external funding sources.

COMPETING INTERESTS: Authors disclose no potential conflicts of interest.

CORRESPONDENCE: Alisa.Rich@unthsc.edu

COPYRIGHT: © the authors, publisher and licensee Libertas Academica Limited. This is an open-access article distributed under the terms of the Creative Commons CC-BY-NC 3.0 License.

Paper subject to independent expert blind peer review. All editorial decisions made by independent academic editor. Upon submission manuscript was subject to anti-plagiarism scanning. Prior to publication all authors have given signed confirmation of agreement to article publication and compliance with all applicable ethical and legal requirements, including the accuracy of author and contributor information, disclosure of competing interests and funding sources, compliance with ethical requirements relating to human and animal study participants, and compliance with any copyright requirements of third parties. This journal is a member of the Committee on Publication Ethics (COPE).

Published by Libertas Academica. Learn more about this journal.

Introduction

Due to advances in horizontal drilling and hydraulic fracturing (*fracking*) technology, the extraction of natural gas (NG) and natural gas liquids (NGLs) in unconventional shale geologic formations is occurring at an unprecedented rate across the United States (U.S.). Many of these energy-rich formations lie beneath developed urban areas. Extraction of energy within these urban areas has been termed “urban drilling.” The number of gas wells in the Barnett Shale formation (North Texas) increased from 276 (2000) to more than 24,967 (2014), representing an 8,946% increase.¹ Development of energy from these formations may be beneficial to the economy, but consideration of the effect on the atmosphere, climate, and people who live near these facilities should also be addressed. This

study is one of the first field studies to identify benzene and benzene-related compounds (benzene[s]) in the atmosphere at various concentrations from emissions associated with extraction and processing (E&P) of NG in residential areas where urban drilling is occurring.

Communities have raised concerns for a potential increased exposure to hazardous air pollutants (HAPs) associated with NG E&P operation emissions and the effects worsening air quality may have on human health.² HAPs (“toxic air pollutants”) or (“air toxics”) have been defined by the U.S. Environmental Protection Agency (U.S. EPA) as “pollutants that cause or may cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental and ecological effects.”³ The 1990 Clean



Air Act Amendments (CAAA) direct the U.S. EPA to set standards for all major sources of air toxics. The U.S. EPA is required to control chemicals identified and designated by the 1990 CAAA list of 187 HAPs, which include benzene.⁴ Emissions from NG and NGL E&P may contain HAPs or toxic air pollutants known or suspected to cause cancer and other serious health effects. Benzene is a primary chemical of concern due to its classification by the International Agency for Research on Cancer (IARC) as a Group 1 carcinogen and a Group A known human carcinogen according to the U.S. EPA.^{5,6} Exposure to benzene has been correlated to an increased risk of leukemia (acute myelogenous, acute lymphoblastic leukemia, and chronic myeloid leukemia), aplastic anemia, and myelodysplastic syndrome (MDS).^{7,8} Additionally, many HAPs are volatile organic compounds (VOCs) and contribute to the formation of ozone and act as a factor in climate change. Ozone and climate change are implicated in affecting human health adversely.⁹ Extraction in energy-rich reservoirs is occurring in regions already deemed as nonattainment areas according to the U.S. EPA National Ambient Air Quality Standards. Transportation has historically been considered the primary factor in North Texas air quality problems. A more comprehensive look at other major contributing factors, including emissions from NG and NGL E&P, must be considered in the overall plan of attainment for a more holistic approach.

Previous studies identified air pollutants including particulate matter, nitrogen and sulfur oxides, carbon monoxide, methane and associated C₁–C₆ hydrocarbons, sulfide compounds, and VOCs in emissions from NG and NGL E&P operations.^{10–26} Reporting guidelines for fugitive air emissions require quantifying total VOCs but do not require identification of specific VOCs that are HAPs, including benzene or benzene[s].

The extraction of NG from an unconventional shale geologic formation is a multistage process involving pad site construction, well drilling operations, hydraulic fracturing, flowback and stimulation of the well for production, and completion of the well before production occurs. Production and processing of NG may include separation, dehydration (removing water from the gas stream) and desulfurization (removal of sulfur compounds), storage of liquids (natural or light gas liquids, condensate and produced water) in tanks, compression, and transmission. After the well is completed, maintenance may require workover or intervention operations to restimulate or clear the well to increase production.²⁷ During each of these stages, VOCs, including benzene and benzene-related chemicals, may escape into the atmosphere from fugitive emissions and equipment leaks.²⁸

Unconventional gas reservoirs are shale or limestone in origin with low-permeability source rock (*tight* deposits), requiring hydraulic fracturing and horizontal drilling to extract methane from the compacted layers of rock. Conventional reservoirs are sedimentary (sands, sandstone, limestone, and dolomites) in origin with large permeable rock reservoirs

that allow the gas to migrate more freely compared to unconventional tight depositions. Benzene occurs naturally in these petroleum-rich (oil and NG) geologic formations. It is also formed during the combustion of bypass NG, the predominant fuel used for the compression of NG. Benzene and benzene[s] are a component of many solvents, paraffin breakers, and fuels used during E&P operations, as reported by the U.S. House of Representatives Committee on Energy and Commerce, Minority Staff report *Chemicals Used in Hydraulic Fracturing*,²⁹ and can occur naturally as a product of pyrolysis.³⁰

The intrinsic chemical and physical properties of VOCs determine whether they exist as a gas or in vapor state. Due to its low boiling point (80.1 °C, 176.2 °F), benzene can easily vaporize (at a temperature of 25 °C, 77 °F, 0.13 atm) and migrate into indoor air from outside sources.^{31–33} It is also highly flammable in the presence of open flames and sparks. As an aromatic hydrocarbon with high volatility, benzene is often present in higher concentration in the atmosphere than aliphatic compounds.^{34,35} Benzene may be emitted to the atmosphere as a primary chemical in emissions or leaks and can undergo reactions in the atmosphere forming secondary benzene[s]. Degradation in the atmosphere occurs primarily by indirect phototransformation. With high stability and minimal reactivity, the half-life of benzene in the atmosphere can range from 3 to 10 days (tropospheric half-life is 7–22 days), enabling it to be transported locally and regionally.³⁶

Although highly stable in the atmosphere, benzene reacts with other compounds, particularly OH radicals, primarily by substitution of hydrogen atoms and addition of methyl groups. As double bonds can be cleaved by oxidative reagents such as ozone, it can rapidly add bromine (Br) or chlorine (Cl) atoms forming chlorobenzene (C₆H₅Cl) or bromobenzene (C₆H₅Br).³⁷ Its low flash point (–11.1 °C, 12.02 °F) increases the risk of explosion when chlorine and light react with vapors of benzene. Benzene is capable of mixing with acetone [(CH₃)₂CO], alcohol (C_nH_{2n+1} + OH), carbon disulfide (CS₂), carbon tetrachloride (CCL₄), and chloroform (CHCl₃), common chemical compounds used in NG extraction, without separating into two phases. This miscibility increases the risk for human exposure.³⁸ Secondary compounds formed during this process may be toxic to humans as well.

Many VOCs present in NG emissions are aromatic double-bonded benzene hydrocarbons, existing in a gaseous vapor state not far removed from its liquid phase. This allows it to be easily absorbed onto surfaces or condensed into a liquid. Benzene and benzene-related compounds are soluble in water (1.8 g/L at 25 °C), enabling them to migrate easily into subsurface soil and groundwater. With low density (0.879 g/mL at 20 °C, 68 °F), benzene easily penetrates groundwater and becomes miscible. It can form soil gas at distances from the original contamination source.^{39,40}

Elevated benzene compounds in the atmosphere may present an increased potential for adverse health effects to the



general public, occupational workers, and particularly sensitive populations (children, pregnant women, the elderly, and immunocompromised) whose unique physiology may place them at a greater risk.⁴¹⁻⁴³

Objectives

The objectives of this study are to evaluate ambient air for the presence of benzene and benzene[s] in residential areas where unconventional shale E&P is occurring and to determine if atmospheric levels of benzene and benzene[s] are elevated due to E&P activity when compared to the U.S. EPA Urban Air Toxics Monitoring Program (UATMP). The UATMP is the most comprehensive air monitoring program in the U.S. and includes urban, suburban, rural, and industrial monitored sites across the U.S.

Materials and Methods

Ambient air sampling was performed in primarily residential areas of six counties in the Dallas/Fort Worth Metroplex influenced by urban drilling and emissions from unconventional shale gas E&P operations. Five of the six counties (Parker, Tarrant, Johnson, Denton, and Somerville) were classified as nonattainment areas at the time of sampling, and the sixth county (Wise) was deemed as nonattainment status in 2012. The residential areas were chosen due to the presence and expansion of urban drilling within residential neighborhoods and low potential for confounding emission sources. Fifty sets of monitoring data were obtained in 39 different locations over a two-year period (2008–2010). Ambient air sampling was captured using certified sterilized evacuated stainless steel 6-L Summa canisters, with a certified 24-hour mass-flow regulator attached. The 24-hour regulator allowed for continuous sampling of ambient air over a 24-hour period of time as compared to an instantaneous/grab sample. Grab samples have inherent error and may capture peak emissions during equipment start-up, which is not reflective of constant state emissions. A 24-hour sample period does not reflect maximum high emission readings or minimum emissions but rather allows for the ability to assess constant conditions or average chemical concentrations and is more representative of a chronic chemical exposure. Canisters were placed in a stable location at ground level. If the environment posed a risk of particulate matter interference with the flow regulator, a J-hook was attached to the flow meter, preventing clogging of the regulator intake valve. Field sampling procedures followed the American Society for Testing and Materials Method D-1357-95 (2011), *Standard Practice for Planning the Sampling of the Ambient Atmosphere*. Canisters were retrieved from the field and delivered to the laboratory within 12 hours of recovery. Samples were analyzed for benzene and benzene[s] using gas chromatography/mass spectrometry according to the EPA Compendium Method Toxic Organics (TO-14A) by a certified laboratory within 24 hours of receipt. Chemical concentration values below laboratory minimal detection

level (MDL) were deemed nondetect (ND). ND does not equate to zero; therefore, in statistical analysis, the MDL is taken into consideration. As benzene is known to be present in the combustion emissions of many fuels, analysis of the samples for the presence of lower chain C_1 – C_6 hydrocarbons by performance of Light Hydrocarbon test was requested along with the TO-14A. The Light Hydrocarbon test captures the compounds of methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and pentane (C_5), known products of NG extraction. Meteorological conditions on the dates of sampling were retrieved from the web site of Quality Controlled Local Climatological Data, the National Climatic Data Center (www.ncdc.noaa.gov), using the closest airport to each sampled location. Meteorological data were recorded for each sample and included temperature ranges (minimum and maximum), wind direction and velocity (minimum and maximum miles/hour), humidity, and any precipitation event. Equipment and processes at E&P sites can vary; therefore, emissions can vary depending on the distance from the site monitoring occurred and equipment present at the time of monitoring. A comprehensive evaluation of equipment variability and distance from receptor was previously published by authors.²⁶ Complaints related to emissions vary as to the magnitude of the specific chemical concentration, odor characteristics (acrid vs. sweet), and health impact. Additionally, specific chemicals may have more pungent unfavorable odors (ie, sulfur compounds) and therefore draw a higher complaint response.

Sampling was performed at variable distances from the fence line of facilities in order to capture a more true ambient air condition in residential areas affected by E&P emissions rather than capturing direct emissions from a facility with fence line monitoring. The majority of the sampling was performed in rural or residential areas with light transportation emissions other than E&P emissions. In this study, the distance from other potential emission sources, including gas stations and major road intersection, was also identified in relation to locations monitored.

Results

Ambient air sampling confirmed elevated concentrations of benzene and 18 benzene[s] in ambient air in residential areas where unconventional shale NG and NGL E&P operations were occurring. Benzene was present in 78% (39 of 50) of the locations sampled. Concentrations ranged from 0.6 parts per billion by volume (ppbv) to 592 ppbv, based on 24-hour passive sampling (Table 1). Acute one-hour concentrations for benzene ranged from 2.93 ppbv to 2,900.20 ppbv.⁴⁴ The summary statistics of 24-hour and 1-hour chemical concentrations are provided in Table 1. The number of NDs varied widely among benzene[s]. Toluene was present in 94% of samples and strongly correlated to benzene[s]. Xylene (m- & p-) was present in 86% of samples. While some benzene[s] are emitted directly into the atmosphere (primary compounds), other

**Table 1.** Summary statistics – 24-hour and 1-hour chemical concentrations.

CHEMICALS (UNIT)	24-Hr					1-Hr					ND
	MIN (ppbv)	MAX (ppbv)	MEDIAN (ppbv)	MEAN (ppbv)	SD (ppbv)	MIN (ppbv)	MAX (ppbv)	MEDIAN (ppbv)	MEAN (ppbv)	SD (ppbv)	
Benzene	0.6	592	0.89	18.53	83.75	2.94	2900.2	5	87.39	402.58	39
Toluene/methylbenzene	0.34	276	2.55	19.45	48.77	1.67	1352.12	11.57	78.17	217.4	3
Ethylbenzene	0.2	113	0.53	4.42	16.03	0.98	553.58	5.59	36.22	102.51	23
Xylene, m&p	0.25	221	1.68	15.69	43.1	1.22	1082.67	9.17	72.63	205.76	7
Xylene, o-	0.2	39.4	0.85	3.19	6.7	0.98	193.02	6.13	19.51	36.2	15
Trimethylbenzene, 1,3,5-	0.2	9.95	0.59	1.43	2.12	0.98	48.74	6.5	11.6	12.39	25
Trimethylbenzene, 1,2,4-	0.2	60.4	0.4	3.45	10.79	0.98	295.6	5.78	35.03	75.72	27
Styrene/Vinylbenzene	0.2	43.4	0.37	1.91	6.22	0.98	212.62	4.23	17.56	43.4	26
Dichlorobenzene, 1,4-	0.2	4.43	0.3	0.55	0.66	0.98	21.7	2.2	2.73	1.27	45
Trichlorobenzene, 1,2,4-	0.28	13.5	0.67	1.12	1.93	1.37	66.14	3.52	10.9	22.4	10
Trimethyl benzene	0.3	366	1.4	15.18	58.39	1.47	1793.03	5.78	35.03	75.72	46
Ethylmethyl benzene	0.3	42.8	1.4	3.15	6.74	1.47	209.68	120.1	131.86	72.78	47
1-Propynyl benzene	0.3	7.2	1.4	1.74	1.13	35.29	166.67	100.98	100.98	92.89	47
Propyl benzene	0.3	23.5	1.4	2.08	3.16	1.47	115.13	115.2	115.2	NA	48
Diethyl benzene	0.3	93.4	1.4	4.14	13.56	1.47	457.57	312.5	312.5	NA	48
Methyl-methylethyl benzene/methylcumene	0.3	84.7	1.4	3.31	11.65	1.47	414.94	414.94	414.94	205.55	48
Tetramethyl benzene	0.3	36.4	1.4	2.76	5.69	1.47	178.32	144.85	144.85	47.49	48
1-Methyl propenylbenzene	0.3	51	1.4	2.63	6.96	1.47	249.85	250	250	NA	49
2-Methyl propenylbenzene	0.3	95.9	1.4	3.53	13.2	1.47	469.81	469.81	469.81	NA	49

benzene[s] may be formed secondarily through exchanges or conversions with chemicals present in the atmosphere. The infrequent detection of certain benzene compounds indicates that they may be secondary atmospheric compounds rather than primary compounds from direct emissions.

Chemical concentrations in the atmosphere are dependent on distance from the facility to the receptor, meteorological conditions (wind, temperature, humidity, precipitation), and specific chemical characteristics. Vertical dispersion is influenced by a wide range of temporal and spatial scales. VOCs, by their very nature, are volatile and easily change phase from liquid to gas, depending on the temperature and vapor pressure of the specific chemical. Atmospheric concentrations of benzene[s] are dependent on whether the emission source is one of combustion, pyrolysis, or fugitive leaks from tanks, valves, or pipelines. In a previous publication by the authors,²⁶ a chemical fingerprint was statistically correlated with combustion, blown wells, and presence of methane. Benzene, toluene, ethylbenzene, and xylene (BTEX) and trimethylbenzene (1,2,4-TMB and 1,3,5-TMB) compounds were highly correlated to compressors and therefore to products of combustion. Due to the high volatility of benzene, the atmospheric half-life varies with evaporation, resulting in 2.7- to 5-hour half-life, while combustion can result in an 8-day half-life and photolysis can result in 16.9-day half-life. The scavenging effect of precipitation on VOCs is well known and is a significant sink for atmospheric

benzene. Benzene being highly reactive may also combine with other chemicals forming secondary benzene[s].

The variability of benzene in the atmosphere is further presented in Figure 1. Benzene showed the highest variability in the atmosphere with several high readings (592, 81.7, 77.7, and 55.4 ppbv), affecting the central tendency and median. While a single value (outlier) could be considered to skew statistical data, it is never considered irrelevant and deleted. All data are relevant when evaluating human health risk, and single high values can be valuable indicators for acute high chemical exposure and indicators for incomplete combustion of fuel or a mechanical defect. The primary chemicals with the greatest variability consistently appear to be BTEX compounds from combustion emissions.

To determine if other emission sources could be contributing factors to atmospheric benzene concentrations, the distance from the site monitored to the nearest gas station was calculated.⁴⁵ Research indicates that emissions from gas stations influence atmospheric conditions within 250 m of a station with concentrations of ethylbenzene and xylenes being higher due to gasoline evaporation.⁴⁶ In total, 87% of locations monitored were >0.5 miles (804.7 m) from the nearest gas station, with only five locations <0.5 miles as presented in Figure 2.

Further analysis of the potential influence of transportation emissions on atmospheric benzene concentrations was conducted by calculating the distance from the site monitored

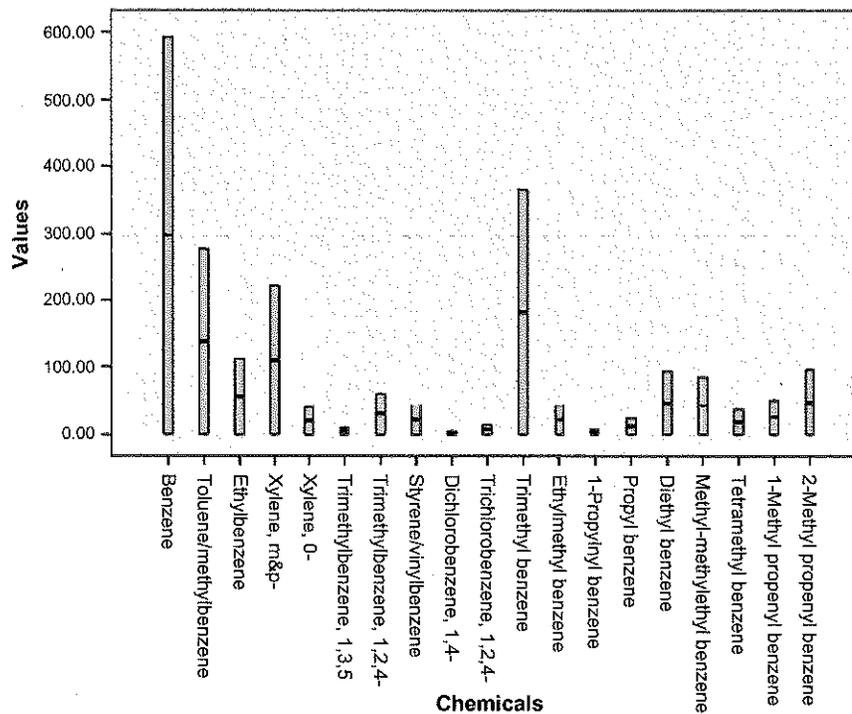


Figure 1. Variability in atmospheric Benzene[s] concentrations.

to the closest intersection. Studies on roadway vehicle emissions show that emissions can affect atmospheric conditions within 500 feet (152.4 m) of the roadway.⁴⁷ Five locations monitored in this study were within a half mile (2,640 feet, 804.7 m) of a roadway intersection. The closest monitored site was 897 feet (273.4 m) from a roadway intersection [Fig. 3]. Therefore, the contributing source of atmospheric benzene in this study was determined not to be from roadway emissions.

Atmospheric chemical concentrations in this study were then compared to the U.S. EPA UATMP study. The UATMP study is the most comprehensive monitoring program in the U.S. and includes urban, suburban, rural, and industrial locations across the country.⁴⁸ Years 2008–2011 were included for a more comprehensive analysis. Of the 19 benzene compounds found in this study, only 11 compounds were monitored consistently in the UATMP studies and could be directly compared. The maximum values are presented in Table 2.

When comparing the concentrations of benzene and benzene[s] present in the residential areas of the Barnett Shale to the UATMP study, concentrations in this study exceeded the national average with few exceptions (styrene 2010, propylbenzene 2011) for the years monitored. 1,4-Dichlorobenzene and 1,2,4-trichlorobenzene could not be compared for 2010 due to noncollection (Table 3).

Benzene was found to be 5,532%, 7,503%, and 27,281% higher in this study when compared to the UATMP studies for years 2008–2011. Toluene/methylbenzene was 453%, 437%, and 1,215% higher. Ethylbenzene was 376,666%, 339%, and

1,558% higher. Xylene (m- & p-) was 3,384%, 1,514%, and 8,185% higher. Xylene (o-) was 1,698%, 912%, and 4,436% higher. 1,3,5-TMB was 404%, 581%, and 5,320% higher. 1,2,4-TMB was 790%, 2,119%, and 10,747% higher. Styrene/vinylbenzene was 679% (2008–2009) and 1,418% (2011) higher but recorded 41% lower in 2010 due to a high reading in the UATMP study of 105 ppbv. 1,4-Dichlorobenzene

Table 2. Comparison of benzene and benzene-related chemical concentrations to UATMP national concentrations.

POLLUTANT	CURRENT STUDY MAX (ppbv)	UATMP 2008–09 MAX (ppbv)	UATMP 2010 MAX (ppbv)	UATMP 2011 MAX (ppbv)
Benzene	592	10.7	7.89	2.17
Toluene/Methylbenzene	276	60.9	63.1	22.7
Ethylbenzene	113	0.03	33.3	7.25
Xylene, m&p-	221	6.53	14.6	2.7
Xylene, o-	39.4	2.32	4.32	0.888
Trimethylbenzene, 1,3,5-	9.95	2.46	1.71	0.187
Trimethylbenzene, 1,2,4-	60.4	7.64	2.85	0.562
Styrene/Vinylbenzene	43.4	6.39	105	3.06
Dichlorobenzene, 1,4-	4.43	1.26	*NC	1.26
Trichlorobenzene, 1,2,4-	13.5	0.57	*NC	0.067
Propylbenzene	23.5	2.0	2.89	46.4

Note: *NC = Not collected.



Table 3. Benzene and benzene[s] exceedances over UATMP national maximum (ppbv).

POLLUTANT	CURRENT STUDY MAX (PPBV)	2008-09 % EXCEED UATMP MAX	2010 % EXCEED UATMP MAX	2011 % EXCEED UATMP MAX
Benzene	592	5,532+	7,503+	27,281+
Toluene/Methylbenzene	276	453+	437+	1,215+
Ethylbenzene	113	376,666+	339+	1,558+
Xylene, m&p-	221	3,384+	1,514+	8,185+
Xylene, o-	39.4	1,698+	912+	4,436+
Trimethylbenzene, 1,3,5-	9.95	404+	581+	5,320+
Trimethylbenzene, 1,2,4-	60.4	790+	2,119+	10,747+
Styrene/Vinylbenzene	43.4	679+	41-	1418+
Dichlorobenzene, 1,4-	4.43	351+	*NC	351+
Trichlorobenzene, 1,2,4-	13.5	2,368+	*NC	20,149+
Propylbenzene	23.5	1175+	813+	50-

Note: *NC = Not Collected.

was 351% higher for 2008–2009 and 2011, with 2010 as a nonreporting year. 1,2,4-Trichlorobenzene was 2,368% and 20,149% higher, with 2010 as a nonreporting year. Propylbenzene was 1,175% and 813% higher in years 2008–2009 and 2010, respectively, while UATMP concentrations were 50% higher in year 2011. There was no explanation given for the higher ambient concentrations of styrene/vinylbenzene or propylbenzene for the years reported.

Benzene concentrations were also found to be elevated when compared to the background benzene levels reported in rural and urban/suburban areas (0.47 ppbv in rural areas and 1.8 ppbv in urban/suburban areas).⁴⁹ However, these values were obtained from the research conducted by Shah and Singh in 1988 and may not be reflective of current atmospheric background levels.⁵⁰

Several of the benzene[s] found in ambient air monitoring are known to be used in drilling mud products and components of chemicals used in hydraulic fracturing operations. Xylenes were found to be present in 44 products used in hydraulic fracturing, toluene/methylbenzene was found in 29 products, ethylbenzene in 28 products, 1,2,4-TMB in 21 products, TMBs in 5 products, 1,3,5-TMB in 3 products, and diethylbenzene in 1 product. Benzene compounds may also be present in diesel, heavy aromatic distillate, hydrocarbons, hydrocarbon mixtures or hydrotreated light, or middle petroleum distillates often used in the drilling operation or fracking fluids. Proprietary labeled compounds (in drilling muds or fluids) used during hydraulic fracturing are exempt from specific compound identification and may contain additional benzene[s], although not directly identified.

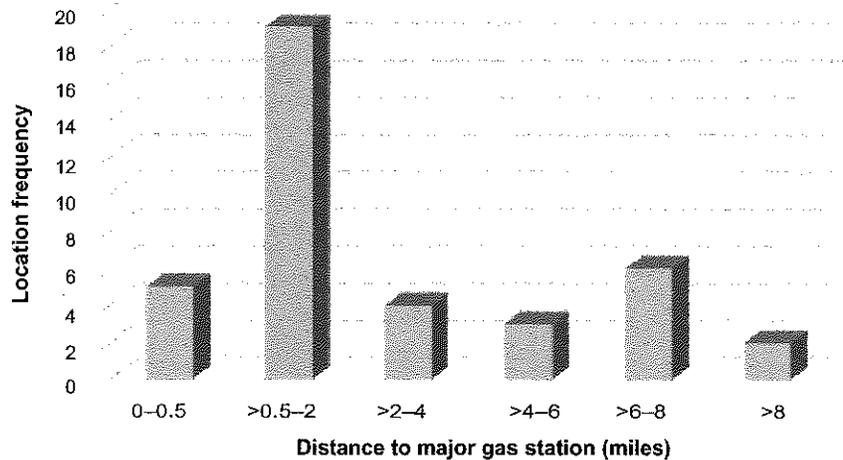


Figure 2. Distance from the site monitored to the nearest gas station.

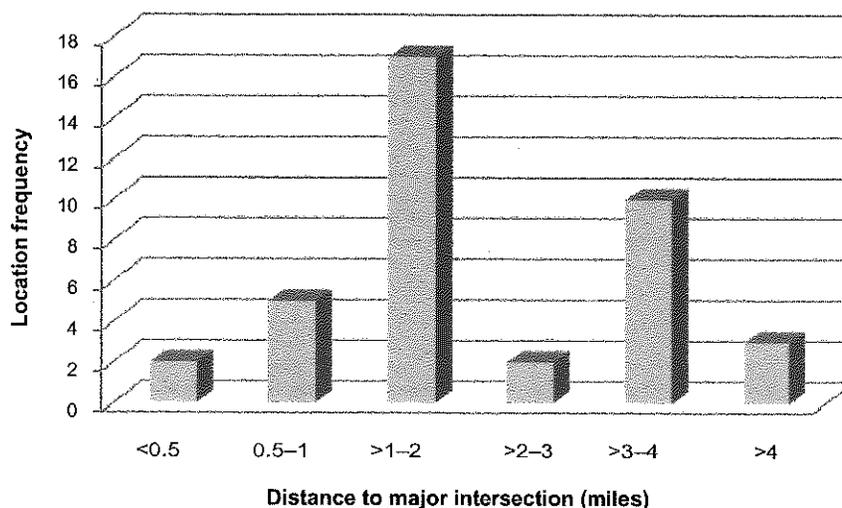


Figure 3. Distance from the site monitored to major intersection.

Once fracturing is completed, the drilling mud must be cleared from the well in order to stimulate production. A flow-back operation returns or clears the fluids from the wellbore and may result in the release of benzene[s] to the atmosphere. Returned fluids contain high levels of VOCs, including benzene, which can be toxic at high concentrations to workers.⁵¹ Fluids cleared from the well are under high pressure when released into the atmosphere and are capable of long-range atmospheric migration, contributing to regional air pollution and climate change.

Conclusion

Benzene and benzene-related chemicals were found to be present in elevated atmospheric concentrations near unconventional shale E&P operations in residential areas when compared to national background levels.

Benzene has been classified as a known human carcinogen (Group 1 and Group A), and as such, no level above zero (0) has been determined to be safe and may be capable of multisystem health effects. Exposure to benzene has been correlated with bone marrow and blood-forming organ damage and immune system depression. Residential areas and occupational workers exposed to high benzene[s] concentrations may have an increased risk of leukemia (acute myelogenous, acute lymphoblastic leukemia, and chronic myeloid leukemia), aplastic anemia, and MDS. Sensitive populations (children, pregnant women, the elderly, and immunocompromised) may be at an elevated risk for adverse health effects due to their unique physiological needs and demands.

While development of these energy-rich geologic formations may be beneficial to the economy, consideration of the effects these chemicals may have on the atmosphere, air quality, and the health of people living near these

facilities, particularly the sensitive populations, must also be addressed.

Author Contributions

Conceived and designed the experiments: ALR. Analyzed the data: ALR, HTO. Wrote the first draft of the manuscript: ALR. Contributed to the writing of the manuscript: ALR, HTO. Agree with manuscript results and conclusions: ALR, HTO. Jointly developed the structure and arguments for the paper: ALR, HTO. Made critical revisions and approved final version: ALR. Both authors reviewed and approved of the final manuscript.

REFERENCES

1. Texas RRC. Barnett Shale Information. Barnett Shale Drilling Permits Issued 2000 through May 2015. Available at: <http://www.rrc.state.tx.us/oil-gas/major-oil-gas-formations/barnett-shale-information>. Accessed July 13, 2015.
2. Fustinoni S, Campo L, Satta G, et al. Environmental and lifestyle factors affect benzene uptake biomonitoring of residents near a petrochemical plant. *Environ Int*. 2012;39(1):2-7.
3. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. *Pollutants and Sources*. Washington, DC: US EPA; 2013.
4. U.S. Environmental Protection Agency, Technology Transfer Network - Air Toxics Web Site. Original List of Hazardous Air Pollutants. Available at: <http://www3.epa.gov/airtoxics/188polls.html>. Accessed September 24, 2013.
5. International Agency for Research on Cancer (IARC). *Monographs on the Evaluation of the Carcinogenic Risk of Benzene*. Vol. 100F-Evaluation. Lyon: International Agency for Research on Cancer Research; 2012.
6. Energy and Commerce Leaders Question EPA's Record on Hydraulic Fracturing Studies. Energy and Commerce Committee. Available at: <http://energycommerce.house.gov/press-release/energy-and-commerce-leaders-question-epas-record-hydraulic-fracturing-studies>. Accessed July 1, 2015.
7. Duarte-Davidson R, Courage C, Rushton L, Levy L. Benzene in the environment: an assessment of the potential risks to the health of the population. *Occup Environ Med*. 2001;58(1):2-13.
8. Smith MT. Advances in understanding benzene health effects and susceptibility. *Annu Rev Public Health*. 2010;31:133-48.
9. Hamlat M, Djeflal S, Kadi H. Assessment of radiation exposures from naturally occurring radioactive materials in the oil and gas industry. *Appl Radiat Isot*. 2001;55(1):141-6.



10. Armendariz A. Emissions from Natural Gas Production in the Barnett Shale Area and Opportunities for Cost-Effective Improvements. Report for Environmental Defense Fund; 2009. Available at: http://www.edf.org/documents/9235_Barnett_Shale_Report.pdf. Accessed January, 2013.
11. Bar-Ilan A, Parikh J, Grant T, Shah A, Pollack K. Recommendations for Improvements to the CENRAP States' Oil and Gas Emissions Inventories. Report prepared by ENVIRON International Corporation for the Central States Regional Air Partnership. Available at: http://www.wrpair.org/forums/ogwg/documents/2008-11_CENRAP_O&G_Report_11-3.pdf. Accessed October 11, 2014.
12. Eastern Research Group and Sage Environmental Consulting. City of Fort Worth Natural Gas Air Quality Study. Final report prepared for City of Fort Worth; 2011. Available at: <http://fortworthtexas.gov/gaswells/default.aspx?id=87074>. Accessed April 3, 2013.
13. Boyer D. "2006/2012 DFW modeling update." Presentation prepared by Texas Commission on Environmental Quality for the DFW Photochemical Modeling Technical Committee Meeting; Arlington, TX. Available at: <https://www.tceq.com/DocumentCenter/View/19260>. Accessed November 5, 2010.
14. Hopf NB, Kirkeleit J, Br rveit M, Succop P, Talaska G, Moen BE. Evaluation of exposure biomarkers in offshore workers exposed to low benzene and toluene concentrations. *Int Arch Occup Environ Health*. 2012;85(3):261-71.
15. Olaguer EP. The potential near-source ozone impacts of upstream oil and gas industry emissions. *J Air Waste Manage Assoc*. 2012;62(8):966-77.
16. Pring M, Hudson J, Renzaglia J, Smith B, Treimel S. Characterization of Oil and Gas Production Equipment and Develop a Methodology to Estimate State-wide Emissions. Final Report prepared by Eastern Research Group for Martha Maldonado of the Texas Commission on Environmental Quality, Air Quality Division; November 24, 2010; Morrisville, NC.
17. Safiri A, Gao X, Mannan MS. Dispersion modeling approach for quantification of methane emission rates from natural gas fugitive leaks detected by infrared imaging technique. *J Loss Prev Proc Ind*. 2011;24:138-45.
18. XTO Energy, Inc. Permit by Rule for the Havener Tank Battery located in Tarrant County, Texas, Attachment #7. Submitted by XTO Energy, Inc. to the TCEQ on May 24, 2010.
19. Coward R, Barron JG. Improving Sulphur Recovery at the Ram River Gas Plant. Paper presented at: Gas Conditioning Conference, University of Oklahoma, Norman, Oklahoma; 1983.
20. Dawodu OF, Meisen A. Amino degradation by carbonyl sulphide and carbon disulfide. Paper presented at: Laurance Reid Gas Conditioning Conference; 1989; University of Oklahoma, Oklahoma. Available at: <https://open.library.ubc.ca/cIRcle/collections/ubtheses/831/items/1.0059005>. Accessed October 21, 2015.
21. Eapi G, Sabnis M, Sattler M. Mobile measurement of methane and hydrogen sulfide at natural gas production site fence lines in the Texas Barnett Shale. *J Air Waste Manage Assoc*. 2014;64(8):927-44.
22. Mazumdar MM, Kaushik UP, Kumar KN, Prasad K, Durta BK. Desulphurization of petroleum feedstocks using alkalinized iron oxide. *Spec Issue Technol Am Occup Ther Assoc*. 1974;11(1):33-8.
23. Kunkel LV. The fundamentals of gas sweetening. Paper presented at: 60th Laurance Reid Gas Conditioning Conference; February 21-4, 1977; Norman, OK. Available at: <http://toc.proceedings.com/07434webtoc.pdf>. Accessed October 12, 2014.
24. Tuan HP, Janssen HGM, Cramers CA. Evaluation of the performance of various universal and selective detectors for sulfur determination in natural gas. *J High Resolut Chromatogr*. 1995;18:333-42.
25. Yuhua KW, Xianhou L, Jun L, Qingjian Z, Anlu X. Industrial Applications of the Fine Desulfurizers in Natural Gas Processing in China. Available at: http://www.haisocat.com/news_en/images/105619_1.pdf. Accessed April 28, 2013.
26. Rich AL, Grover JP, Sattler ML. An exploratory study of air emissions associated with shale gas development and production in the Barnett shale. *J Air Waste Manage Assoc*. 2014;64(1):61-72.
27. Schlumberger Oilfield Glossary. Definition of Well Workover and Intervention. Available at: <http://www.glossary.oilfield.slb.com/en/Disciplines/Well-Workover-and-Intervention.aspx>. Accessed October 09, 2014.
28. Hendler A, Nunn J, Lundeen J. VOC Emissions from Oil and Condensate Storage Tanks. Final Report prepared for the Texas Environmental Research Consortium; 2009. Available at: <http://files.harc.edu/Projects/AirQuality/Projects/H051C/H051CFinalReport.pdf>. Accessed October 11, 2014.
29. U.S. House of Representatives Committee on Energy and Commerce. Chemicals Used in Hydraulic Fracturing; 2011. Available at: <https://www.energycommerce.house.gov>. Accessed April 12, 2012.
30. U.S. Agency for Toxic Substance and Disease Registry (U.S. ATSDR). Toxicological Profile: Benzene; 2007. Available at: <http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=40&tid=14>. Accessed October 10, 2014.
31. U.S. EPA. *Carcinogenic Effects of Benzene: An Update (Final)*. Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington Office; 1998. [EPA/600/P-97/001F].
32. Wheeler AJ, Wong SL, Khouri C, Zhu J. Predictors of indoor BTEX concentrations in Canadian residences. *Health Rep*. 2013;24(5):11-7.
33. Bouhamra WS. Estimation of volatile organic compounds in Kuwaiti houses after the Gulf war. *Environ Pollut*. 1995;90(1):121-5.
34. Slemr J, Slemr F, Partridge R, D'Souza H, Schmidbauer N. Accurate measurements of hydrocarbons in the atmosphere (AMOHA): Three European inter-comparisons. *J Geophys Res*. 107;(D19):4409. doi:10.1029/2001JD001357,2002.
35. Gary W vanLoon, Duffy SJ, eds. *Tropospheric chemistry of Smog: In Environmental Chemistry: A global perspective*. 3rd Ed. New York, NY: Oxford University Press, Inc. 2011:82-3.
36. German Federal Ministry for Economic Cooperation and Development Bundesministerium f r wirtschaftliche Zusammenarbeit und Entwicklung (BMZ). Volume III: Compendium of Environmental Standards - Documentation on Monitoring and Evaluating Environmental Impacts. Chemical Substances and Groups of Substances/Register of Substances: Benzene. Available at: <http://ces.iisc.ernet.in/energy/HC270799/HDL/ENV/enven/vol316.htm>. Accessed April 28, 2014.
37. U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS) on Benzene. Washington, DC: National Center for Environmental Assessment, Office of Research and Development; 2009.
38. Sahlmel J, Devlin K, Burns A, Ferracini T, Ground M, Paustenbach D. An analysis of workplace exposures to benzene over four decades at a petrochemical processing and manufacturing facility (1962-99). *J Toxicol Environ Health A*. 2013;76(12):723-46.
39. Williams P, Sahlmel J, Knutsen J, Spencer J, Bunge AL. Dermal absorption of benzene in occupational settings: estimating flux and applications for risk assessment. *Crit Rev Toxicol*. 2011;41(2):111-42.
40. Snyder R, Hedli CC. An overview of benzene metabolism. *Environ Health Perspect*. 1996;104(6):1165-71.
41. Cooper C, Alley F. Estimating benzene exposure. In: David Cooper C, Alley FC, eds. *Air Pollution Control: A Design Approach*. 4th ed. Long Grove, IL: Waveland Press; 2011:20-2.
42. Karakitsios SP, Delis VK, Kassomenos PA, Pilidis GA. Contribution to ambient benzene concentrations in the vicinity of petrol stations: estimation of the associated health risk. *Atmos Environ*. 2007;41(9):1889-902.
43. Correa SM, Arilla G, Marques MRC, Oliveira K MPG. The impact of BTEX emissions from gas stations into the atmosphere. *Atmos Pollut Res*. 2012;3:163-9.
44. Batterman S, Cook R, Justin T. Temporal variation of traffic on highways and the development of accurate temporal allocation factors for air pollution analyses. *Atmos Environ*. 2015;107:351-63.
45. U.S. Environmental Protection Agency (U.S. EPA). National Monitoring Program National Report (UATMP, NATTS and CSATAM); 2008-11. Available at <http://www.epa.gov/ttnamti1/uatm.html>. Accessed April 28, 2013.
46. World Health Organization (WHO); International Programme on Chemical Safety (IPCS) INCHEM. Environmental Health Criteria 150: Benzene; 1993. Available at: <http://www.inchem.org/documents/ehc/ehc/ehc150.htm>. Accessed on October 11, 2014.
47. Shah JJ, Singh HB. Distribution of volatile organic chemicals in outdoor and indoor air. A National VOCs data base. *Environ Sci Technol*. 1988;22(12):1381-8.
48. CDC - NIOSH Science Blog. Reports of Worker Fatalities during Flowback Operations. Available at: <http://blogs.cdc.gov/niosh-science-blog/2014/05/19/flowback/>. Accessed July 1, 2015.