

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS (VOCs) FROM
HYDRAULIC FRACTURING FACILITIES IN KARNES COUNTY, TEXAS
AND IDENTIFICATION OF VOCs IN SHELBY COUNTY, TENNESSEE

By

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ABSTRACT

Volatile organic compounds (VOCs) are emitted by several sources and have the ability to cause short and long-term adverse health effects. In Karnes County, Texas, a high activity of hydraulic fracturing on the Eagle Ford Shale is the major source of VOC emissions. In Shelby County, Tennessee, automobile exhaust, household products, and industrial facilities are the main sources of VOC emissions. Air samples were collected in Karnes County and Shelby County and analyzed using gas chromatography-mass spectrometry (GC-MS) with a cryogenic preconcentrator outfitted with a glass bead trap and a Tenax® trap. The EPA TO-15 method was applied to analyze TO-15 compounds in Karnes County and non-TO-15 compounds in Shelby County. Samples collected in Karnes County were also analyzed using Fourier transform infrared spectroscopy (FT-IR) with a 10-meter gas cell to detect low molecular weight compounds. Benzene, toluene, ethylbenzene, xylene, and methane were commonly detected compounds near oil and gas facilities in Karnes County, Texas. In Shelby County, Tennessee, acetonitrile, cyclohexene, and cyclohexanone were frequently detected at relatively high concentrations.

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CHAPTER I

INTRODUCTION

Since the beginning of the Industrial Revolution, pollution has increasingly become a major issue in the United States of America. Millions of residents are exposed to chemical pollutants every day. In the 2009 State of the Air report, the American Lung Association reported that 60 percent of Americans live in areas that have experienced unhealthy air pollution.¹ Air pollution is produced when volatile compounds are released into ambient air from human activities. Most of the pollutants are volatile organic compounds (VOCs) that are emitted from manufacturing facilities, petroleum refineries, and automobiles. When VOCs are emitted into the ambient air, ozone is produced in the troposphere by complex chemical reactions involving oxidation of VOCs and nitric oxide (NO) in sunlight.² Hydroxyl radicals react with VOCs to produce peroxy radicals, and as a result, the peroxy radicals oxidize NO to nitrogen dioxide (NO₂). Afterwards, NO₂ undergoes photolysis to produce atomic oxygen (O), which reacts with O₂ to produce ozone (O₃). VOCs and ozone are classified as primary and secondary pollutants, respectively. Primary pollutants are directly emitted into the atmosphere from a source; whereas, secondary pollutants result from reactions involving the primary pollutants and are not directly emitted into the troposphere. Primary and secondary pollutants are hazardous to the environment and ecosystem since they affect the change of climate, the growth and decay of plants, and the health of humans and animals.³ The Environmental Protection Agency (EPA) classifies 187, originally 189, chemical compounds as hazardous air pollutants. Several hazardous air pollutants such as 1,3-butadiene, benzene, and chloroform are known to cause serious health effects, including cancer. Although VOCs are present in ambient air at trace levels, they have the ability to cause long and short term adverse health effects.

1.1 Hydraulic Fracturing

Hydraulic fracturing has provided access to large quantities of oil and natural gas, which are contained within shale formations deep below the ground's surface. In order to obtain the oil and natural gas from the shale formations, a well is drilled vertically into the ground and then horizontally once the shale has been reached, which is usually about 1.6 kilometers or more below the surface. Afterwards, a steel casing pipe is inserted into the whole length of the well and perforated within the target zones of the shale.⁴ A fracturing fluid containing water, sand, and chemical additives is pumped through the well and exits through the perforations. Once the fluid exits the perforations, it fractures the shale formation. The sand particles are transported to the porous channels of the shale and holds the fractures or fissures open. Figure 1 displays a diagram of the hydraulic fracturing process.

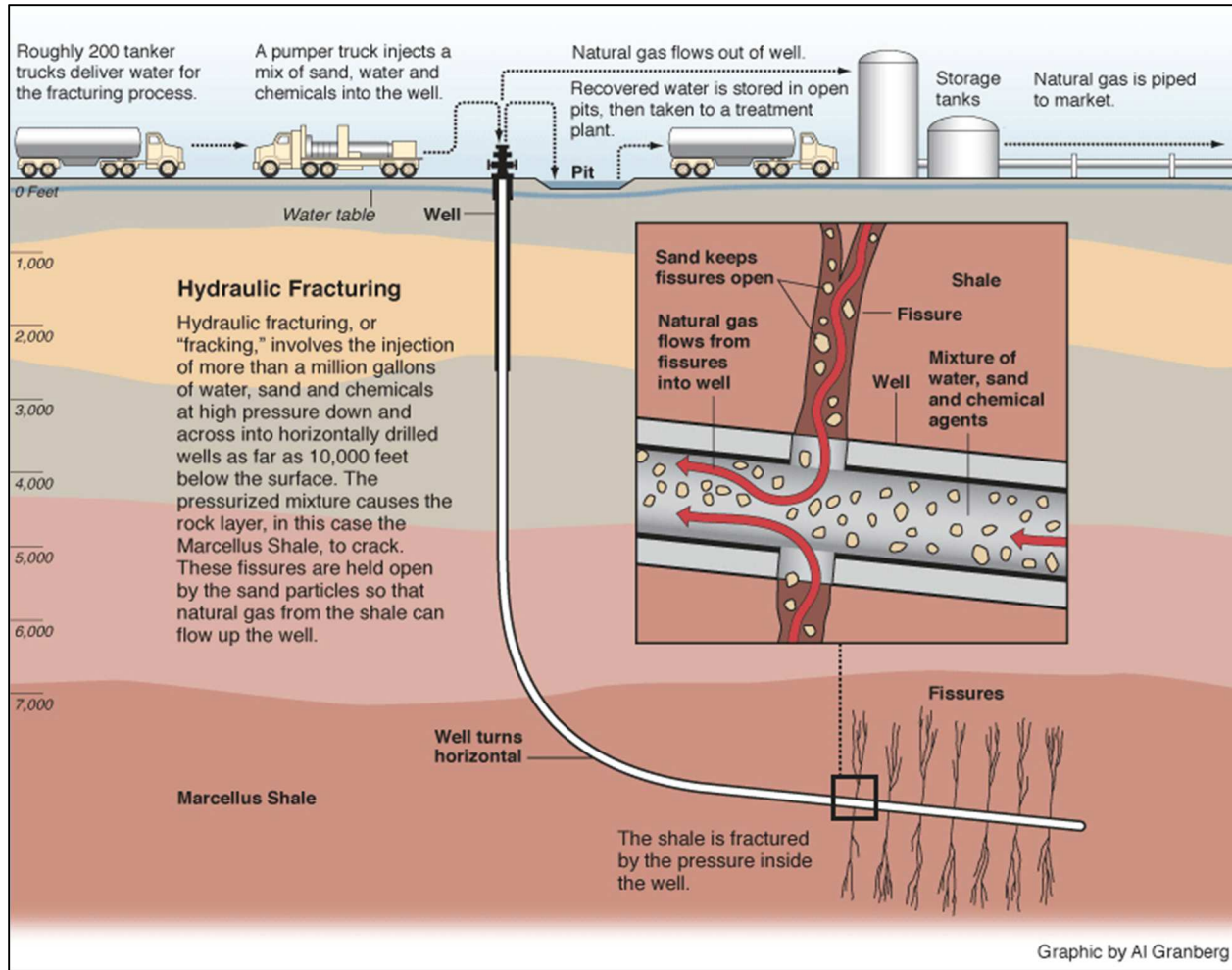


Figure 1. Diagram of hydraulic fracturing process⁴

1.2 Benefits of Hydraulic Fracturing

The development of hydraulic fracturing provides several advantages and disadvantages. The two main advantages are the access to massive amounts of oil and natural gas and the economic stimulation it provides. With several technologies combined to enable the process of hydraulic fracturing, the process has become more profitable for oil and gas companies in recent years.⁵ Hydraulic fracturing allows for oil and gas companies to reach reserves deep below the surface, which were difficult or nearly impossible to reach many years ago. As a result, the United States of America has experienced an increase in production of oil. For instance,

petroleum imports decreased from 29.248 quadrillion British thermal units (BTU) to 24.740 quadrillion BTU between 2005 and 2011.⁵

1.3 Disadvantages of Hydraulic Fracturing

Although hydraulic fracturing provides several important advantages, it also presents undesirable environmental consequences, which directly affect the residents living in regions with fracking activities. The various environmental issues caused by hydraulic fracturing have led to several areas attempting to ban hydraulic fracturing. For instance, five counties in California have voted to ban hydraulic fracturing in their areas.⁶ In contrast, the state of Texas, energy leader of the USA, has taken advantage of the financial success that hydraulic fracturing provides because there are several oil and natural gas shales scattered throughout the state. However, the environment at these oil and gas production facilities is negatively affected. The major environmental issues are water consumption, water contamination, and air pollution.

1.3.1 Water Consumption

In order to fracture oil and natural gas shales, large amounts of water are required. A hydraulically fractured well can require millions of gallons of water. Between January 2011 and February 2013, an estimated 1.5 million gallons of water was used per well for hydraulic fracturing.⁷ However, the amounts of water used within various areas across the country are not equal. Since hydraulic fracturing requires the use of surface water and groundwater, there are concerns about water shortage, which affect agricultural irrigation, drinking water wells, and surface water levels.⁸ In areas with extensive activities of hydraulic fracturing, high usage of

water can potentially decrease the amount of water availability for residential use, especially in the event of a drought.

1.3.2 Water Contamination

The quality of water can also be affected in areas with a high activity of hydraulic fracturing. Since effluent streams receive their water from groundwater, some surface water sources are also affected by groundwater withdrawals. As a result of excessive groundwater withdrawals, stream flows are reduced and the dilution rate of contaminants is lowered, which can potentially harm the ecosystem and aquatic life.⁸

Chemical additives in the hydraulic fracturing fluid can also affect the water quality. The two common components are biocides and polymeric lubricants; however, many other chemicals are also used. Glutaraldehyde and 2,2-dibromo-2-nitropropionamide (DBNPA) are the two most commonly used biocides. DBNPA's mode of action is significant since it releases bromide into the environment.⁹ Although the presence of bromide does not present a health risk, elevated concentration levels of bromide in drinking water sources lead to the production of brominated disinfection byproducts (DBP) due to the disinfectants applied by water treatment plants.¹⁰ Brominated DBPs are known to be cytotoxic and genotoxic.¹¹ Table 1 lists common biocides and their frequency of use in hydraulic fracturing. The majority of the chemical additives tend to remain in the water due to their low volatility and have the ability to affect water sources in local communities.

Table 1. Ten common biocides used in hydraulic fracturing⁹

NO.	COMPOUNDS	CAS Number	Frequency of Use
1	Glutaraldehyde	111-30-8	27%
2	Dibromonitripropionamide	10222-01-2	24%
3	Tetrakis (hydroxymethyl) phosphonium sulfate	55566-30-8	9%
4	Didecyl dimethyl ammonium chloride	7173-51-5	8%
5	Chlorine dioxide	10049-04-4	8%
6	Tributyl tetradecyl phosphonium chloride	81741-28-8	4%
7	Alkyl dimethyl benzyl ammonium chloride	68424-85-1	3%
8	Methylisothiazolinone	2682-20-4	3%
9	Chloromethylisothiazolinone	26172-55-4	3%
10	Sodium Hypochlorite	7681-52-9	3%

1.3.3 Air Pollution

In addition to water pollution, hydraulic fracturing also causes air pollution. Since hydraulic fracturing releases VOCs into the atmosphere, it is also linked to the production of ozone and smog as secondary pollutants. These contaminants can be present at unhealthy levels, which is a hazard to the surrounding communities. When exposed to these toxic pollutants, they can lead to respiratory illnesses, cancer, as well as eye, nose, and throat irritation.¹² Exposure to smog can also lead to irreversible damage to the lungs.¹³ Several sources around hydraulic fracturing facilities have been linked to air pollution. Drilling wells and pumping oil and natural gas from shale formations requires the use of heavy machinery and trucks. The heavy machinery and trucks lead to diesel emissions. As a result, hundreds of toxic chemicals are released into the atmosphere. The greatest concern for residents in the local community is fine diesel soot particles, which can lead to respiratory diseases when inhaled.¹² The hazardous levels of particulate matter from diesel emissions has caused the National Institute for Occupational Safety and Health (NIOSH) to express concern.¹² Hazardous air pollutants are also emitted

directly from the oil and natural gas wells. In addition to the wells, condensate tanks, dehydrators, wastewater impoundment pits, and pipelines also lead to air pollution.¹² Fugitive emissions of VOCs resulting from extraction, storage, and transportation of oil and natural gas cause the pollution of ambient air. Hydrogen sulfide is a common toxic compound found at oil and natural gas production facilities and can be hazardous at low concentrations. For instance, workers have complained of eye pain when exposed to hydrogen sulfide at a concentration of 6.4 ppm.¹⁴ Benzene, toluene, ethylbenzene, and xylene (BTEX) are also commonly detected near hydraulic fracturing sites and cause adverse health effects. Each of these compounds are known to have an effect on the central nervous system. The International Agency for Research on Cancer (IARC) determined that ethylbenzene is possibly carcinogenic to humans.¹⁵ Benzene, a known carcinogen, has been found at concentrations as high as 1000 ppb near unconventional oil and gas development gas flares, condensate tanks, and compressor units.¹⁶ The health effects caused by oil and natural gas represents a major disadvantage, which should not be overlooked despite the monetary profits and economic stimulation associated with hydraulic fracturing activities.

1.4 Karnes County and the Eagle Ford Shale

Karnes County is located in southern Texas, about 55 miles south of San Antonio. The county is made up of a collection of small towns and has a total population of about 15,000 people. The Eagle Ford Shale covers many counties in southern Texas including Karnes County, which has become an attractive location for oil and gas production. The Eagle Ford Shale is a Cretaceous sediment that stretches 400 miles, from southwestern Texas above Laredo to the region between San Antonio and Corpus Christi, and is about 50 miles wide.¹⁷ The Eagle Ford

Shale possesses some special characteristics, which makes the shale formation a location of significant investments by the oil and gas industry. The formation consists of organic-rich calcareous mudstones and chinks and has a low clay content, which makes the Eagle Ford Shale brittle.^{17,18} As a result, the Eagle Ford Shale is a main target for oil and gas production by hydraulic fracturing. Figure 2 illustrates the number of oil and gas wells that have been drilled along the Eagle Ford Shale.

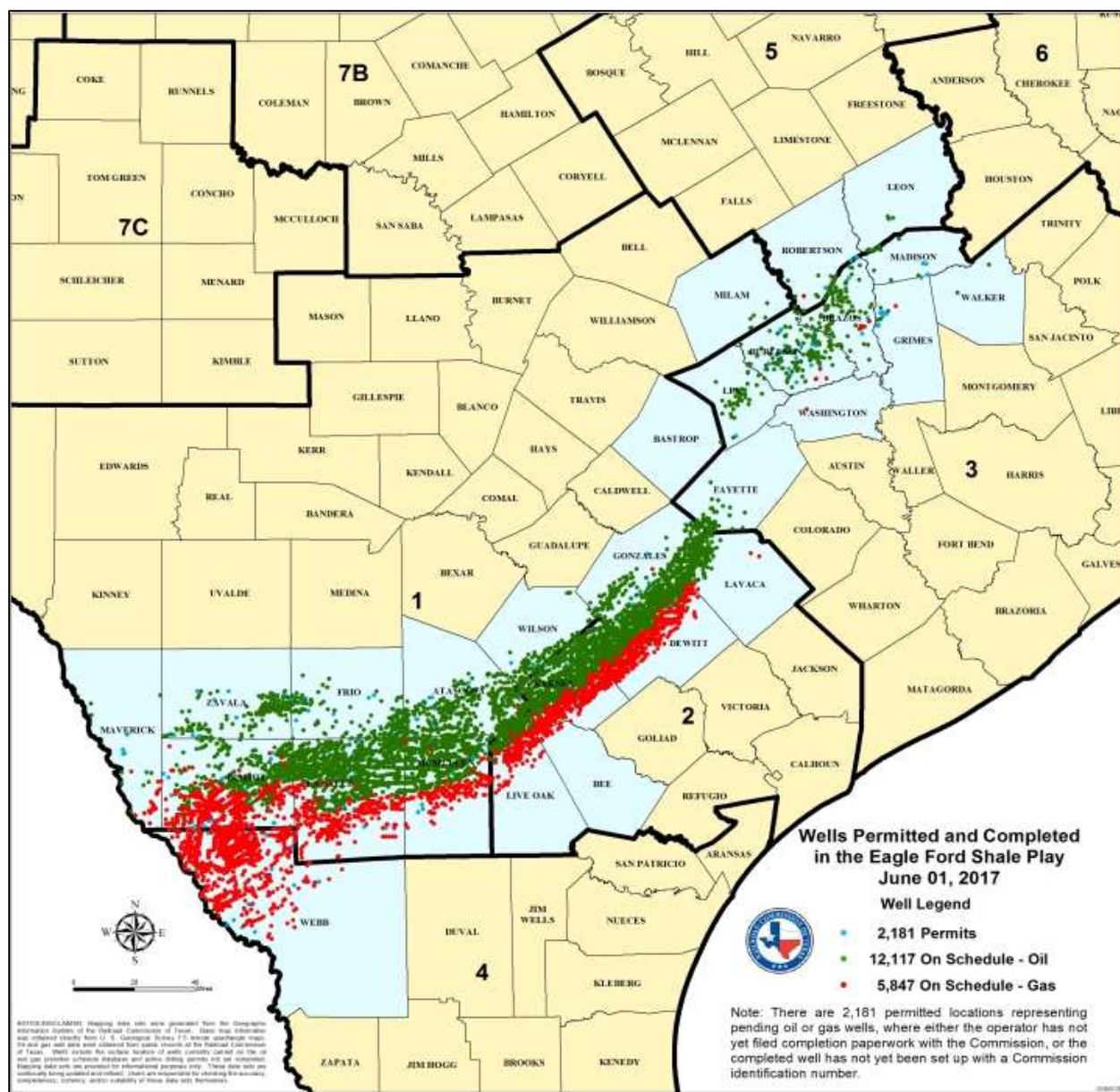


Figure 2. Numerous wells drilled along the Eagle Ford Shale¹⁹

As a result of the attractiveness of the Eagle Ford Shale, several hydraulic fracturing facilities are located around Karnes County, Texas. These facilities require the use of chemical additives, which have the ability to cause harm to the environment and create air pollution. Also, as the pockets of oil and natural gas are extracted from the ground, VOCs are continuously released into the air. Although the VOCs are at low concentrations, parts-per-billion levels,

exposure to the pollution for a long period of time can lead to short and long-term health effects. Several residents live too close to the wells and cannot enjoy extended periods of outdoor activities due to the toxic chemicals being released by oil and gas facilities. For instance, there are many oil and gas facilities in the area, and of the few that file their emissions data, the data show that they account for 25 compressor engines, 10 heater treaters, 6 flares, 4 glycol dehydrators and 65 storage tanks for oil, wastewater and condensate. These sites have the state approval from Texas to release a combined total of 189 tons of volatile organic compounds into the air each year.²⁰ Several of the VOCs released are classified as hazardous air pollutants.

For ambient air analysis near the oil and gas facilities in Karnes County, air samples were collected over a maximum period of 1 hour. The target VOCs consisted of BTEX, *n*-hexane, cyclohexane, and methane. Cyclohexane is the only target compound that is not classified as a hazardous air pollutant. Table 2 lists each compound's recommended exposure limit (REL) using a time-weighted average (TWA) that is based on a 10-hour workday during a 40-hour workweek.

Table 2. Target VOCs detected near oil and gas facilities and their recommended exposure limit

No.	COMPOUNDS	Health Effects	NIOSH REL (TWA)
1	Benzene	Carcinogenic	0.1 ppm
2	n-Hexane	Peripheral neuropathy	50 ppm
3	Ethylbenzene	Headache; Eye and skin irritant	100 ppm
4	Toluene	Headache; Dizziness; Eye irritant	100 ppm
5	o-Xylene	Nausea; Anorexia	100 ppm
6	m-Xylene	Nausea; Anorexia	100 ppm
7	p-Xylene	Nausea; Anorexia	100 ppm
8	Cyclohexane	Coma; Narcosis	300 ppm
9	Methane	Asphyxiation	1000 ppm

The exposure limits are reported by NIOSH to prevent illnesses and were compared to the concentrations of the target VOCs detected near the oil and gas facilities. However, residents living near the oil and gas facilities are exposed to the air pollutants over periods greater than 10 hours per day.

1.5 Air Pollution in Shelby County

Shelby County, Tennessee is one of the most populated counties in the United States of America. Since Shelby County has a large population and motorized vehicles are the main source of transportation, the area suffers from air pollution. For instance, Memphis, the county seat, was identified as one of the most challenging cities to live in with a high incidence of asthma in 2015, which poor air quality was a contributing factor.²¹ In addition to automobiles, industrial plants and household products emit volatile compounds into the ambient air. The concentration of compounds in the air usually depends on the weather. For instance, rainfalls can reduce the concentration of pollutants, which improves the air quality. In contrast, high temperatures increase the vapor pressure of pollutants leading to elevated levels of air pollution. Air samples were collected throughout the Shelby County area during winter, spring, summer, and fall. In the winter, temperatures ranged from 0 °C to 18 °C. The spring season had temperatures that ranged from 17 °C to 32 °C. The temperatures in the summer and fall seasons from 18 °C to 33 °C and 2 °C to 23 °C, respectively.

The compounds of interest consist of acetonitrile, cyclohexene, cyclohexanone, C₄-C₁₀ aldehydes, and isoprene. Acetonitrile is classified as a hazardous air pollutant and is commonly used in industry as a solvent. Cyclohexene is commonly used in industry for the production of Nylon 6 and Nylon 6,6 and reacts with ozone in the presence of OH radicals to produce glutaraldehyde, a disinfectant.²² Cyclohexanone is also commonly used for the production of

Nylon 6 and Nylon 6,6. In addition, aldehydes are abundantly present in ambient air due to industrial use and incomplete combustion of fuel. Target aldehyde compounds such as hexanal, heptanal, and octanal are also emitted from cooking oils at elevated temperatures.²³ Aldehyde compounds are a key source of ozone production in the atmosphere.²⁴ Isoprene is emitted globally at a range of about 500 to 750 Tg per year by vegetation.²⁵ Due to the high emission rate and reactivity, isoprene plays a significant role in the formation of ozone. The following table, Table 3, provides a comprehensive list of target compounds. Ultimately, acetonitrile, cyclohexene, and cyclohexanone were the significant compounds detected due to their high concentration levels. The NIOSH REL (TWA) for the three compounds are listed in Table 4 and were compared to the concentrations of the compounds detected during the sampling periods.

Table 3. Target compounds for ambient air analysis in Shelby County

No.	Compounds	CAS Number	M.W. (g/mol)	RT (min)
1	Acetonitrile	75-05-8	41.05	5.905
2	Isoprene	78-79-5	68.12	6.586
3	2-Methylpropanal	78-84-2	72.11	7.808
4	Methacrolein	78-85-3	70.09	8.13
5	Methyl vinyl ketone	78-94-4	70.09	8.569
6	Butanal	123-72-8	72.11	8.748
7	1-Butanol	71-36-3	74.12	11.66
8	Cyclohexene	110-83-8	82.14	12.572
9	Methoxyflurane	76-36-0	164.96	13.819
10	2-methyl-2-nitropropane	209-851-4	103.12	14.229
11	1-Pentanol	200-752-1	88.15	14.388
12	Dimethyl disulfide	624-92-0	94.20	14.674
13	(Z)-2-Penten-1-ol	1576-95-0	86.13	15.765
14	2-Bromopentane	107-81-3	151.04	16.428
15	Hexanal	66-25-1	100.15	16.715
16	2-Bromo-2-methylbutane	507-36-8	151.04	16.768
17	Cyclopentanone, 2-methyl-	1120-72-5	98.14	18.214
18	5-Methyl-2-hexanone	110-12-3	114.19	18.914
19	(E)-3-Hexen-1-ol	928-97-2	100.15	18.98
20	1-Chlorohexane	544-10-5	120.62	19.112
21	Cyclohexanone	108-94-1	98.15	19.9
22	Heptanal	111-71-7	114.18	20.2
23	2-Cyclohexen-1-one	930-68-7	96.13	20.922
24	Dimethyl trisulfide	3658-80-8	126.26	22.15
25	Octanal	124-13-0	102.17	22.695

Table 4. Target VOCs detected in Shelby County and their recommended exposure limit

No.	Compounds	Health Effects	NIOSH REL (TWA)
1	Acetonitrile	Asphyxia; Nausea	20 ppm
2	Cyclohexene	Drowsiness; Irritation to eyes and skin	300 ppm
3	Cyclohexanone	Headache; Narcosis; Coma	25 ppm

1.6 EPA Methods

The EPA has developed several methods for identifying and quantifying VOCs present in ambient air. Two common methods are TO-14a and TO-15, which have been developed for the measurement of similar lists of VOCs. However, the two methods differ in their analytical advantages and disadvantages.

1.6.1 EPA Method TO-14A vs EPA Method TO-15

EPA Methods TO-14a and TO-15 require the use of passivated stainless-steel canisters for air sampling. The canisters have a long lifetime and are protected from corrosive gases. The canisters are also rugged and sturdy, and they are not easily damaged. Although TO-14a and TO-15 share similarities, TO-15 proves to be more advantageous. As mentioned previously, the EPA has compiled a list of 187 hazardous air pollutants. The TO-15 method is applicable for 97 VOCs from the possible 187 that are present on the list.²⁶ TO-14a is not applicable for the same compounds as TO-15. The main disadvantage of Method TO-14A is due to the limitations that it is only applicable to non-polar compounds. However, Method TO-15 is suitable for the analysis of polar and nonpolar hazardous air pollutants. Polar compounds include alcohols, ketones, and esters.²⁶ Method TO-15 is more suitable for analyzing a wider range of VOCs, including polar VOCs, because water management or removal of water is handled differently for the TO-15

method during the analysis.²⁶ Water management is important since moisture can cause analytical problems such as retention time shifts and partition of polar VOCs into the aqueous phase.²⁶ TO-14a applies a permeable membrane dryer to remove water vapor from the sample; however, it is also responsible for the loss of polar compounds.²⁶ Method TO-15 reduces the water content with a dry purging technique, which greatly reduces the possibility of losing polar compounds from the air sample.

A high resolution gas chromatograph (GC) coupled to a mass spectrometer is used for analysis with Method TO-15. TO-15 offers two operational modes for the mass spectrometer in order to achieve different analytical goals. For a mass spectrometer with a linear quadrupole system, it is operated by using SCAN mode, which continuously scans a wide range of mass-to-charge ratios for both qualitative and quantitative analysis with a total ion chromatogram.²⁷ The linear quadrupole system also allows selected ion monitoring (SIM) to be used to achieve lower detection limits for compounds known to exist in the samples. However, for a mass spectrometer based on a standard ion trap, SCAN is the only applicable mode.²⁷ In contrast to Method TO-14A, Method TO-15 is not applicable for multiple detectors. However, gas chromatography-mass spectrometry (GC-MS) provides a definitive identification technique. Common compounds detected in ambient air using the TO-15 method are listed in Table 5.

Table 5. EPA Method TO-15 list of compounds

NO.	COMPOUNDS	CAS Number	MW (g/mol)	RT (min)
1	Propene	115-07-1	42.08	4.47
2	Freon 112	76-12-0	203.83	4.56
3	Chloromethane	74-87-3	50.49	4.74
4	Freon 114	76-14-2	170.92	4.86
5	Chloroethene	75-01-4	62.49	4.99
6	1,3-Butadiene	106-99-0	54.09	5.15
7	Bromomethane	74-83-9	94.94	5.44
8	Chloroethane	75-00-3	64.51	5.63
9	Ethanol	64-17-5	46.07	5.79
10	Bromoethene	593-60-2	106.95	6.00
11	Acetone	67-64-1	58.08	6.30
12	Freon 11	75-69-4	137.36	6.45
13	Isopropyl alcohol	67-63-0	60.10	6.57
14	1,1-Dichloroethene	75-35-4	96.94	7.12
15	Methylene chloride	75-09-2	84.93	7.25
16	Allyl chloride	107-05-1	76.52	7.38
17	Freon 113	76-13-1	187.37	7.55
18	Carbon disulfide	75-15-0	76.13	7.57
19	cis-1,2-Dichloroethene	156-59-2	96.94	8.28
20	1,1-Dichloroethane	75-34-3	98.96	8.51
21	Methyl tert-butyl ether	1634-04-4	88.15	8.64
22	Vinyl acetate	108-05-4	86.09	8.69
23	Methyl ethyl ketone	78-93-3	72.11	9.02
24	trans-1,2-Dichloroethene	156-60-5	96.94	9.47
25	n-Hexane	110-54-3	86.18	9.74
26	Ethyl acetate	141-78-6	88.11	9.82
27	Chloroform	67-66-3	119.37	9.83
28	Tetrahydrofuran	109-99-9	72.11	10.41
29	1,2-Dichloroethane	107-06-2	98.95	10.74
30	1,1,1-Trichloroethane	71-55-6	133.40	11.06
31	Benzene	71-43-2	78.11	11.63
32	Carbon tetrachloride	56-23-5	153.81	11.86
33	Cyclohexane	110-82-7	84.16	12.03
34	1,2-Dichloropropane	78-87-5	112.98	12.78
35	Bromodichloromethane	75-27-4	163.80	13.04
36	Trichloroethylene	79-01-6	131.4	13.10
37	2,2,4-Trimethylpentane	540-84-1	114.23	13.18
38	1,4-Dioxane	123-91-1	88.11	13.19

Table 5. EPA Method TO-15 list of compounds (cont.)

NO.	COMPOUNDS	CAS Number	MW (g/mol)	RT (min)
39	Methyl methacrylate	80-62-6	100.12	13.45
40	Heptane	142-82-5	100.21	13.56
41	cis-1,3-Dichloropropene	10061-01-5	110.97	14.37
42	Methyl isobutyl ketone	108-10-1	100.16	14.51
43	trans-1,3-dichloropropene	10061-02-6	110.97	15.18
44	1,1,2-Trichloroethane	79-00-5	133.40	15.45
45	Toluene	108-88-3	92.14	15.89
46	Methyl butyl ketone	591-78-6	100.16	16.41
47	Dibromochloromethane	124-48-1	208.28	16.56
48	1,1-Dibromoethane	557-91-5	187.86	16.96
49	Tetrachloroethene	127-18-4	165.82	17.74
50	Chlorobenzene	108-90-7	112.56	18.80
51	Ethylbenzene	100-41-4	106.17	19.39
52	m-Xylene	108-38-3	106.16	19.67
53	p-Xylene	106-42-3	106.16	19.67
54	Bromoform	75-25-2	252.73	19.73
55	Styrene	100-42-5	104.15	20.19
56	o-Xylene	95-47-6	106.16	20.34
57	1,1,2,2-Tetrachloroethane	79-34-5	167.84	20.35
58	Isopropylbenzene	98-82-8	120.20	21.21
59	2-Chlorotoluene	95-49-8	126.58	21.86
60	n-Propylbenzene	103-65-1	120.20	21.93
61	4-Ethyltoluene	622-96-8	120.20	22.15
62	1,3,5-Trimethylbenzene	108-67-8	120.19	22.26
63	tert-Butylbenzene	96-06-6	134.22	22.79
64	1,2,4-Trimethylbenzene	95-63-6	120.19	22.82
65	Benzylchloride	100-44-7	126.58	23.00
66	1,4-Dichlorobenzene	106-46-7	147.00	23.01
67	1,3-Dichlorobenzene	541-73-1	147.00	23.11
68	sec-Butylbenzene	135-98-8	134.22	23.20
69	1,2-Dichlorobenzene	95-50-1	147.01	23.57
70	n-Butylbenzene	104-51-8	134.22	24.00
71	1,2,4-Trichlorobenzene	120-82-1	181.45	25.91
72	Naphthalene	91-20-3	128.17	26.06
73	Hexachloro-1,3-butadiene	87-68-3	260.76	26.56

CHAPTER II

MATERIALS AND METHODS

A series of steps must be taken to determine the identity and concentration of VOCs present in air samples. The steps consist of cleaning canisters, collecting air samples using the canisters, analysis of the samples using GC-MS, as well as data analysis and quantitative calculation. These pertinent steps are necessary to measure the concentrations of target VOCs in Shelby County, Tennessee and around various hydraulic fracturing facilities in Karnes County, Texas.

2.1 Canister Cleaning

The SUMMA canisters must be cleaned before they can be used to collect air samples. To clean the canisters, the canister valve is opened to release the remaining volumes of the previous samples in excess of 0 psig. The emptied canister is subsequently connected to the Nutech cleaning system. The system allows four canisters to be connected and cleaned simultaneously. The Nutech system consists of a vacuum pump and an ultra-high purity (UHP) nitrogen cylinder. The Nutech 2100 canister cleaner has four stainless steel-flexible tubings to which the four canisters were connected. The canisters are also heated to 75 °C using heating jackets while undergoing the cleaning process. The technical standards for the Nutech cleaning system are maximum air filling pressure of 35 psi, temperature range from 4 °C to 40 °C, and humidity less than 80%. Once the canisters are connected to the canister cleaner, the nitrogen gas cylinder is opened, and the cleaning system is turned on. The cleaning process consists of three cycles of evacuation and pressurization. The UHP nitrogen is used to pressurize the canister, and the pressurization step is followed by evacuation. The overall cleaning process

takes approximately 90 minutes for completion. Afterwards, the valves on the canisters are closed before the UHP nitrogen gas cylinder and Nutech 2100 system are shut off. The canisters are removed, and a gauge was used to measure the pressure of each canister. The range of pressures after the cleaning process is between -29.00 and -30.00 in Hg.

2.2 Passive Samplers

Passive samplers are connected to the canisters to regulate the flow of air sample that fills the canister. Before the passive samplers can be used in the field, they must be calibrated. For calibration, a vacuum pump is attached to a canister and evacuates the canister to an internal pressure of approximately -29 in Hg. Afterwards, a passive sampler is placed onto the canister, and the canister valve is opened. For a 1-hour passive sampler, twelve readings of pressures were recorded every five minutes with the final reading close to -5.0 in Hg. During the calibration, the flowrate of air into a 6-liter canister for 1-hour passive samplers 1, 2, and 3 is approximately 80 mL/min, 81 mL/min, and 76 mL/min, respectively, within the sampling period of 60 minutes. For a 24-hour passive sampler, 24 readings were recorded every hour, and the flowrate of air into a 6-liter canister is 3.5 mL/min. Figure 3 illustrates a linear plot relating the pressure (in Hg) and time (minutes) for a 1-hour passive sampler connected to a 6-liter canister during a 60-minute period. The flowrate was calculated by using the slope, which the pressure (in Hg) was converted to milliliters.

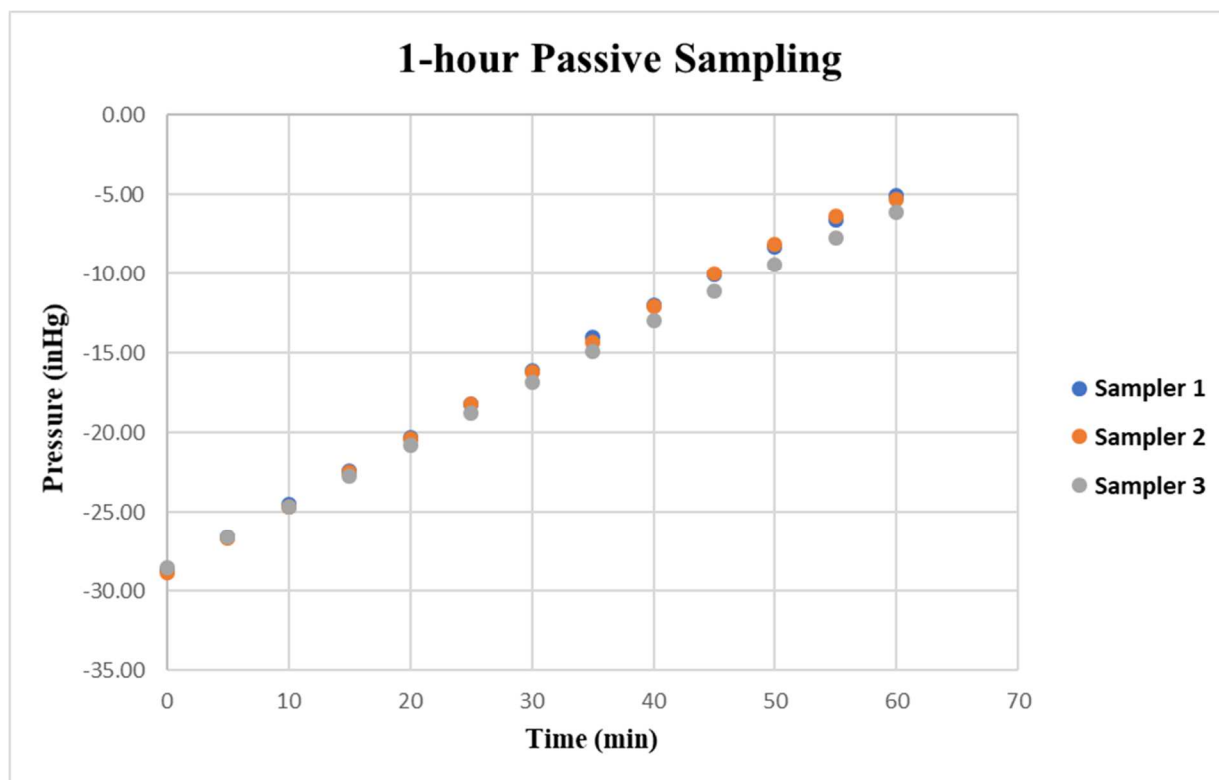


Figure 3. Flowrate calibration of 1-hour passive samplers

When used for field sampling, the passive samplers were simply connected to the canisters to regulate the flow of air into the canisters. Instantaneous grab sampling did not require the use of passive samplers. The canister valve was simply opened, which led to instantaneous collection of air samples.

2.3 Canister Handling and Sampling

Any time the canisters were cleaned and measured for pressure, a tag was placed on each canister. The tag included the pressure of the canister, the date that the canister was cleaned, and the name of the person who cleaned the canister. The collection of air samples from Karnes County, Texas involved collaboration with students and faculty from Northeastern University who carried out the field sampling with pre-cleaned and pre-evacuated canisters that were sent

from MTSU to a residence in Karnes City, Texas. The air samples were collected in the summer, July 8th of 2016, using the instantaneous grab sampling method. In the fall of 2016, October 10th to the 11th, air samples were collected in Karnes County, Texas by grab sampling using passive samplers. Since the sample collection was in a rural location, GPS coordinates of our location were recorded. Collecting air samples in Shelby County involved collaboration with students and faculty from University of Memphis. Pre-cleaned and pre-evacuated canisters were sent from MTSU to University of Memphis for 24-hour sampling at various field locations in Shelby County during all four seasons. After the air samples were collected, the canisters were either brought by an MTSU research team member or sent via FedEx to the MTSU Chemistry Laboratory for analysis.

2.4 Preparing the Internal Standard

The TO-14a internal standard was provided by Scotty Analyzed Gases (SAG) and contained bromochloromethane at 1.01 ppm, 1, 4-bromofluorobenzene at 1.00 ppm, d5-chlorobenzene at 1.04 ppm, and 1, 4-difluorobenzene at 1.03 ppm. To prepare the internal standard, a clean syringe was used to withdraw 18 mL from the SAG canister and injected into a clean and evacuated SUMMA or Silco canister. Afterwards, the canister was pressurized to approximately 30 psig using UHP nitrogen, resulting in a 1000-fold dilution, and connected to the Nutech 8900DS preconcentrator and Agilent GC-MS for analysis.

2.5 Instrumentation for Trace Gas Analysis

The analytical system for ambient air analysis consists of a 16-position autosampler, a preconcentrator, and the GC-MS instrument. The autosampler allows automated analysis of

multiple samples over an extended period of time for greater productivity. A Nutech 8900 DS preconcentrator instrument was used for analyte enrichment and removal of major background gases such as nitrogen, oxygen, carbon dioxide, and water vapor prior to GC-MS analysis. The ambient air analysis was performed on an Agilent 6890 gas chromatograph (GC) coupled to an Agilent 5973 mass selective detector (MS). The Restek Rxi-1ms chromatographic column is 60 meters in length, with a stationary phase of 1.00 micrometer thick, and has an internal diameter of 0.32 millimeters. Helium was used as a carrier gas with a flowrate of 1.5 mL/min. The preconcentrator required liquid nitrogen to achieve the necessary analytical enrichment while selectively removing major air constituents for the GC-MS to be able to detect VOCs present at ppb_v-levels in the air samples. For identification of compounds, the NIST 14 mass spectral library provided a database to be searched against so that match indices would allow the identification of compounds within the samples.

2.6 GC-MS Analysis

The Nutech 8900DS cryogenic preconcentrator is used to connect the 16-position autosampler to the Agilent 6890 GC coupled to the Agilent 5973 mass selective detector. Separate software for Nutech and Agilent instruments must be programmed properly to perform automated analysis. The software allows the operator to optimize the conditions for detecting and analyzing target compounds. The internal standard had an injection volume of 50 mL and a flow rate of 100 mL/min. The flow rate of the sample injected was 100 mL/min, and the volume that was injected was determined in the sequence. The preconcentrator consists of two traps, Trap 1 (glass bead trap) and Trap 2 (Tenax®), and the conditions of those two traps can be

optimized via settings of temperatures and holding times on the software. The following table, Table 6, illustrates the operating conditions for Nutech 8900 preconcentrator.

Table 6. Operating conditions for Nutech preconcentrator

<u>Nutech 8900 Autosampler Set Points</u>			
Trap 1 Settings		Trap 2 Settings	
Cooling Temperature	-150 °C	Cooling Temperature	-20 °C
Preheat Temperature	-10 °C	Desorb Temperature	200 °C
Preheat Time	25 sec	Desorb Flow	2 sec
Desorb Temperature	15 °C	Baked Temperature	210 °C
Desorb Flow	50 mL/min	Baked Time	240 sec
Desorb Time:	120 sec	Timeout	15 min
Bakeout Temperature	180 °C	Temperature Target Range	5 °C
Flush Flow	100 mL/min	Stable Time	2 sec
Flush Time	10 sec	Enabled Cooling w/He	No
Sweep Flow:	100 mL/min		
Sweep Time	30 sec	Sample	
		Purge Flow	20 mL/min
		Purge Time	30 sec
		Sample Flow	100 mL/min

Since the preconcentrator is coupled to a 16 position autosampler, a sequence with several samples can be analyzed in an automated mode. The preconcentrator process operates for approximately 18 minutes and consists of 14 steps before GC-MS analysis. The 14 steps and their associated parameters are listed in Table 7.

Table 7. Nutech preconcentrator steps and associated parameters

#	Steps of Nutech Preconcentrator	Conditions	Time Required
1	Setting Inlet Position		0:00-1:00
2	Venting		1:00-1:35
3	Cooling trap 1	-150°C	1:35-3:17
4	Purging the ISTD line	20 mL/min	3:17-3:35
5	Loading the ISTD	100 mL/min	3:35-4:06
6	Purging the sample to Trap 1, Inlet=1	20 mL/min	4:06-4:40
7	Loading Sample	100 mL/min	4:40-7:38
8	Flushing the line, cooling Trap 2	N/A	7:38-7:52
9	Sweeping the trap, cooling Trap 2	100 mL/min	7:52-8:20
10	Preheating Trap 1	-10°C	8:20-10:33
11	Transferring Trap 1 to Trap 2	50 mL/min	10:33-12:32
12	Cooling the cryofocuser	N/A	12:32-13:10
13	Transferring Trap 2 to the cryofocuser		13:10-17:54
14	Injecting GC		17:54-18:24
13	Trap 2 bakeout	210°C	18:24-25:32
14	GC delay	100 mL/min	25:32-49:30

The GC-MS setup was critical to detecting and analyzing VOCs. The chromatographic column consisted of a polydimethylsiloxane stationary phase, and helium was the mobile phase. The carrier gas, helium, was supplied to the instrument at a flowrate of 1.5 mL/min. The column oven was set to an initial temperature of 30 °C with a hold time of 3 minutes. The final oven temperature was reached with a total of three temperature ramps or gradients. For instance, Ramp No. 1 raised the oven temperature to 100 °C at 5 °C/min, and Ramp No. 2 raised the temperature to 150 °C at 12 °C/min. Finally, Ramp No. 3 raised the oven temperature to 220 °C at 15 °C/min. The following table, Table 8, illustrates the temperature programming for the oven. The overall GC-MS run time is 28 minutes for each sample.

Table 8. Temperature programming for oven

Initial Temperature	30 °C
Initial hold time	3 min
Ramp 1	30 °C to 100 °C @ 5°C/min
Ramp 2	100 °C to 150 °C @ 12 °C/min
Ramp 3	150 °C to 220 °C @ 15 °C/min
Final Temperature	220 °C
Final hold time	0.2 min
Total run time	28 min

Due to the mass of the target compounds, the mass spectrometer scan range was set to 35 to 350 amu with a scan rate of 200 amu/sec. The mass spectrometer was operated in full scan and SIM mode simultaneously. In addition, electron impact ionization mode was utilized with a source temperature of 260 °C to produce the desired ions.

2.7 Data Analysis Using ChemStation and TargetView™

Once the GC-MS run time ends, a chromatogram is produced for each sample. ChemStation and TargetView™ are two software products that are applied to the chromatograms to identify target compounds, provide retention times, and provide the peak areas of tentatively identified compounds. The ChemStation method can be programmed to automatically generate data for identification and quantification of unknown compounds at the conclusion of the GC-MS data acquisition period. When applying the TargetView™ software, the mass range is set to 35 to 350 amu, and the number of hits to print is set to 1. The minimum match factor is set to 700. TargetView™ subtracts the background noise from the original chromatogram and deconvolutes co-eluting compounds.

2.8 Fourier Transform Infrared Spectrometer (FT-IR) Analysis

The Varian 7000 FT-IR was used to analyze samples for methane, a low molecular weight pollutant. The air samples were transferred from the canisters into an evacuated 10-meter Tornado™ Specac gas cell. The resolution for the FT-IR was set 0.5 cm⁻¹, and the number of scans was set to 40. The total run time for each sample was approximately 3 minutes. Afterwards, the sample spectrum was compared to the REF5 standard spectra for the detected compounds, and the average subtraction factor was used to calculate the concentration of methane in the air samples.

2.9 Calculations

2.9.1 Calculating the Dilution Factor

A dilution was performed to reduce the likelihood of contamination in the preconcentrator and the column between samples due to the high analyte levels. When calculating the concentration of VOCs, the dilution factor (DF) as expressed below must be taken into consideration.

$$DF = \frac{14.7 + P_f}{14.7 + P_i}$$

DF is the dilution factor, P_i is the initial pressure in units of psig, and P_f is the final pressure after dilution in units of psig. The initial pressure is measured after sample collection and before dilution.

2.9.2 Calculating the Concentration of Samples Analyzed by GC-MS

The concentrations were calculated and reported in units of parts per billion per volume (ppb_v). The ppb_v units were used to express the relative concentrations of analytes in ambient air. Several methods can be applied to calculate the concentrations of compounds in air samples, and the method of calculation is dependent on the linear regression equation for the analytical calibration plot. The two following equations are applied when multiple canisters of different concentrations are used to produce a standard calibration. The x-axis represents the concentration of each compound, and the y-axis represents the peak areas of the tentatively identified compounds.

$$C_{SV}(\text{ppb}_v) = \frac{A_{TIC} - b}{m} \times \frac{100\text{mL}}{V_{inj}(\text{mL})} \times DF$$

A_{TIC} represents the area of the peak in the chromatogram for the tentatively identified compound. The y-intercept and slope for the corresponding linear regression plots are denoted by b and m , respectively. C_{sv} is the reported concentration after adjusting for the sample volume injected (V_{inj}).

A standard calibration is also produced by using one canister and simply injecting multiple volumes. The calibration curve was produced by relating the mass (ng) and peak areas of the tentatively identified compounds. The mass is represented by the x-axis and the peak area is represented by y-axis. In the following equations, A_{ng} is the mass of the target analyte or compound in nanograms, and MW represents the molecular weight of the target compound.

$$A_{ng} = \frac{A_{TIC} - b}{m} \times DF$$

Once the mass has been determined, the ideal gas equation and injection volume are applied to determine the absolute concentration of the target compound. In the following equation, P

represents pressure (atm), R is the ideal gas constant with the value of 0.0821 L-atm/mol-K, and T is the temperature in Kelvin. C_s is the concentration of the sample in ppb_v.

$$C_s(ppb_v) = \frac{A_{ng}}{\left(\frac{P}{RT}\right) \times MW \times V_{inj}(L)}$$

2.9.3 Calculating the Concentration of Samples Analyzed by FT-IR

The concentration of methane in the air samples was calculated using the Beer -Lambert Law and the average subtraction factor. In the following equation, SF is the subtraction factor, b_{std} is the path length of the cell for the standard in meters, c_{std} is the concentration of the standard in ppm, b_s is the path length of the cell for the sample in meters, and c_s is the concentration of the target sample reported in ppm.

$$c_s(ppm) = \frac{b_{std} \times c_{std}}{b_s \times SF} \times DF$$

CHAPTER III

RESULTS AND DISCUSSION

3.1 Ambient Air Analysis in Karnes County, Texas

There were several harmful VOCs detected in the ambient air around hydraulic fracturing facilities in Karnes County. The significant compounds were *n*-hexane, benzene, ethylbenzene, cyclohexane, toluene, and mixed xylenes. Each compound affects the central nervous system of humans. In addition, ethylbenzene is considered possibly carcinogenic to humans, and benzene is known to be a carcinogen. The samples were collected on July 8th, October 10th and October 11th of 2016, and the concentrations of VOCs detected on July 8th were significantly higher compared to samples collected October 10th and 11th. Table 9 lists the standard calibration of the target compounds. Figure 4 is an illustration of the sampling region in Karnes County, Texas. The area was of interest due to the numerous amounts of oil and gas facilities located in the area.

The temperature ranged from 26 °C to 34 °C on July 8th in Karnes City, Texas. Toluene and *n*-hexane were detected at concentrations above 100 ppb_v, and benzene and cyclohexane were detected at concentrations above 20 ppb_v. Figure 5 illustrates each compound's average concentration during the sampling period. The distribution of the target non-methane VOCs (NMVOCs) within the sampling region are displayed in Figure 7. Methane was detected during the sampling period at a range between 6 ppm_v and 37 ppm_v. Figure 8 illustrates the distribution of methane within the sampling region. The average concentration for methane was 13.5 ppm_v.

The temperatures ranged from 12 °C to 30 °C and 14 °C to 33 °C on October 10th and 11th, respectively. The concentrations ranged from 0.25 to 2.84 ppb_v. *n*-Hexane was detected at 2.84 ppb_v and benzene was detected at 1.02 ppb_v. Figure 6 illustrates each compound's average concentration detected during the sampling period, and Figure 9 displays the distribution of the

target NMVOCs within the sampling region. Due to instrument difficulties, samples collected during the period could not be analyzed for methane.

Table 9. Standard calibration of target compounds in Karnes County

Compound	MW (g/mol)	Calibration Equation	R ²
<i>n</i> -Hexane	86.18	$y=1.93 \times 10^6 x - 3.47 \times 10^5$	0.9962
Benzene	78.11	$y=4.10 \times 10^6 x - 5.45 \times 10^5$	0.9971
Cyclohexane	84.16	$y=2.00 \times 10^6 x - 4.35 \times 10^5$	0.9969
Toluene	92.14	$y=5.12 \times 10^6 x - 1.18 \times 10^6$	0.9967
Ethylbenzene	106.17	$y=7.46 \times 10^6 x - 2.22 \times 10^6$	0.9960
<i>m,p</i> -Xylene	106.16	$y=1.19 \times 10^7 x - 3.41 \times 10^6$	0.9952
<i>o</i> -Xylene	106.16	$y=6.57 \times 10^6 x - 2.00 \times 10^6$	0.9914

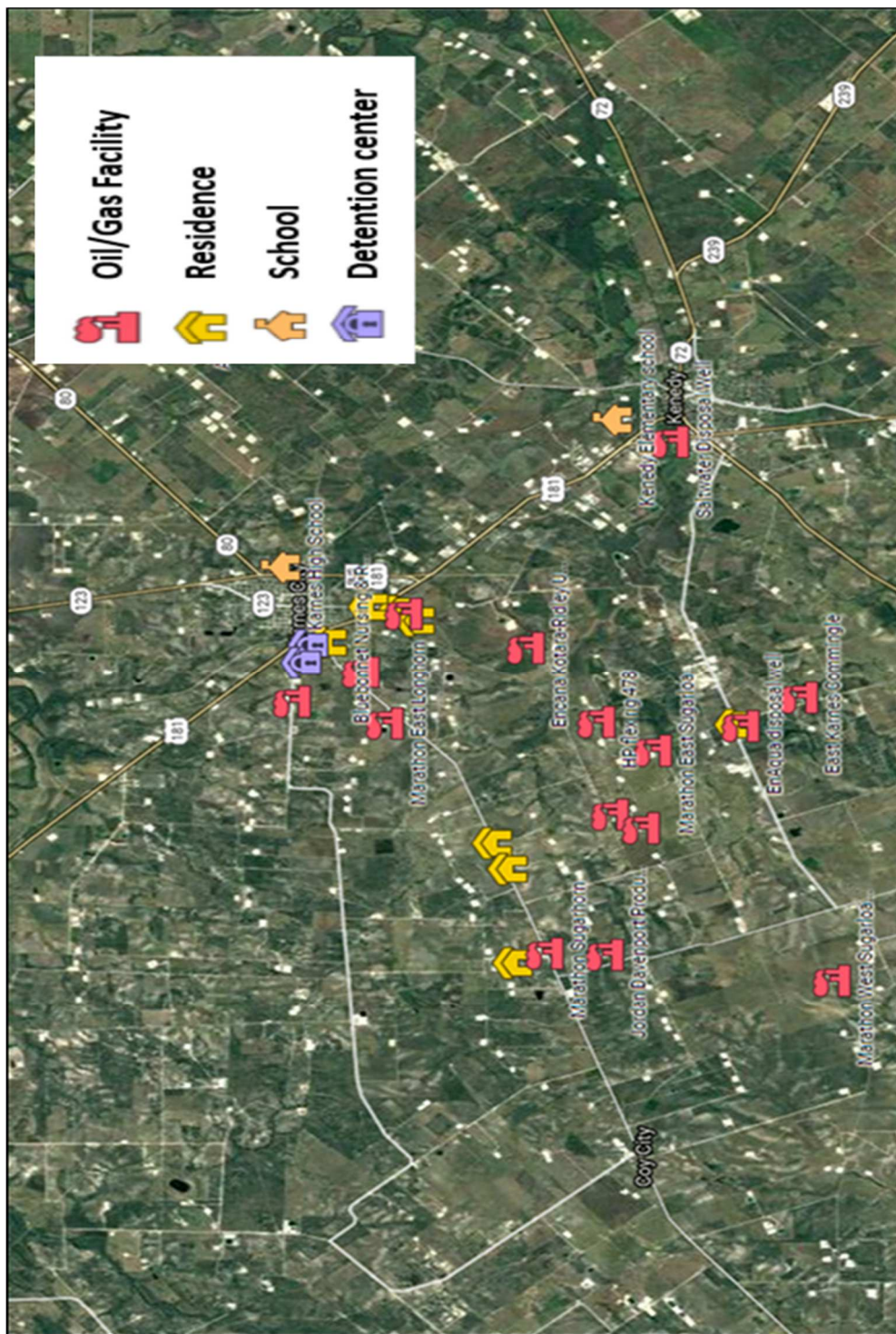


Figure 4. Air sampling region in Karnes County, Texas

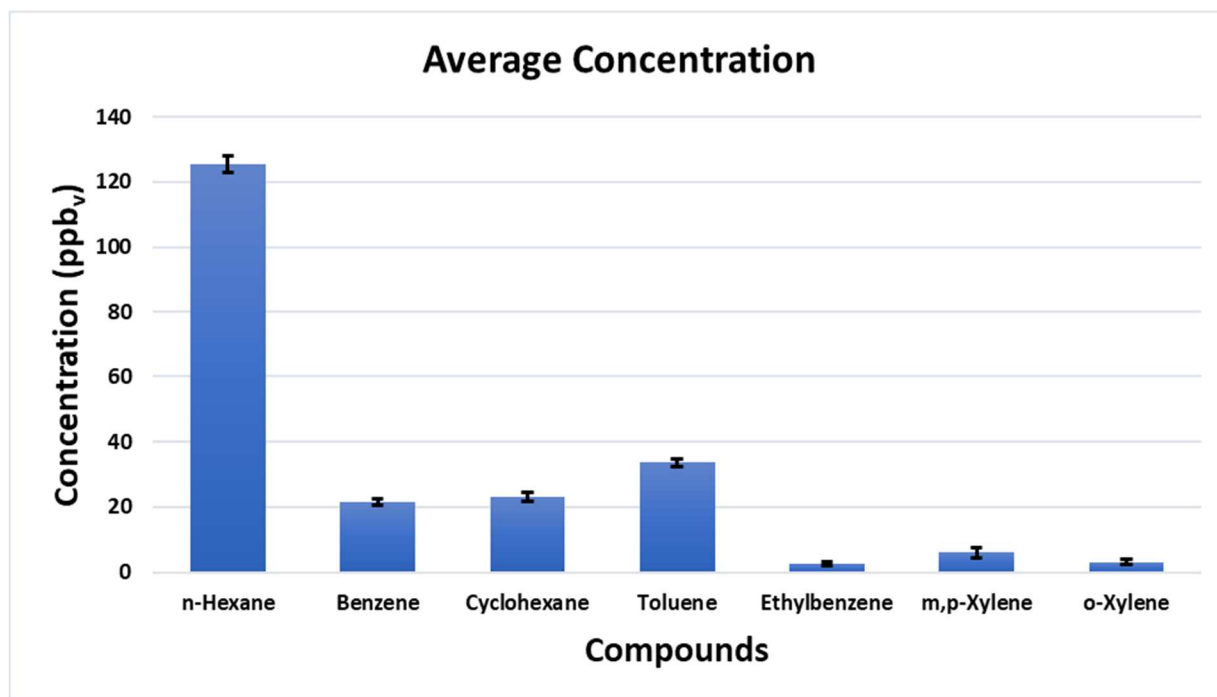


Figure 5. Average concentrations of target NMVOCs detected during July 8th, 2016 sampling period in Karnes County

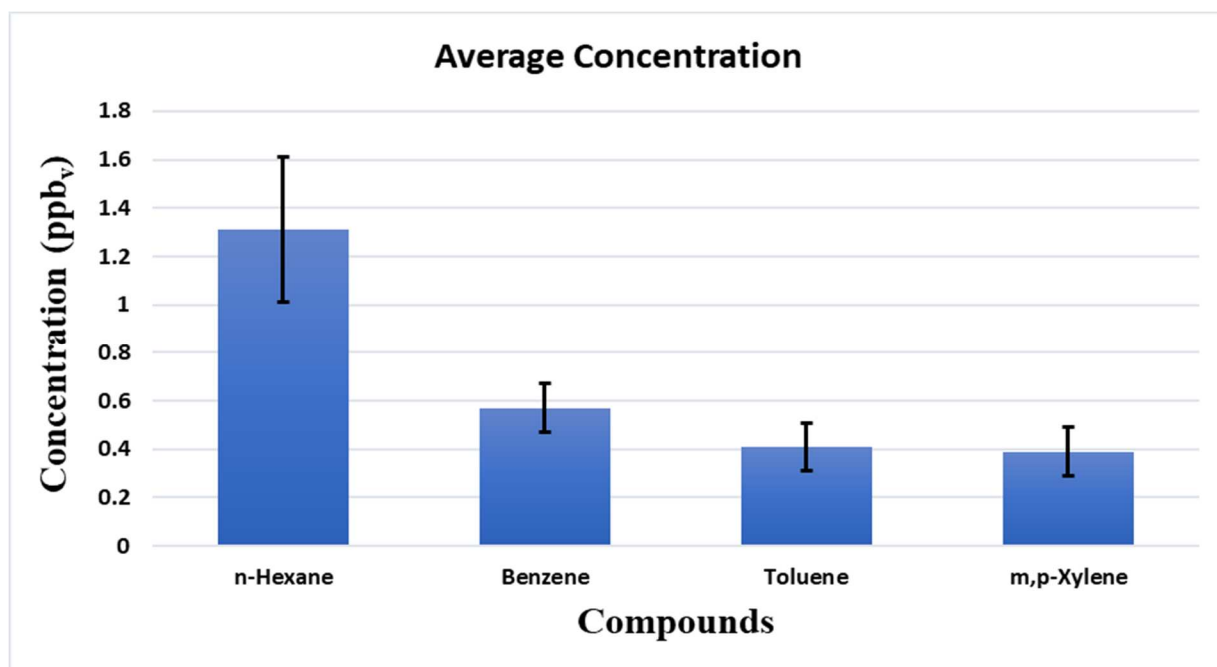


Figure 6. Average concentrations of target NMVOCs detected during October 10th to 11th, 2016 sampling period in Karnes County

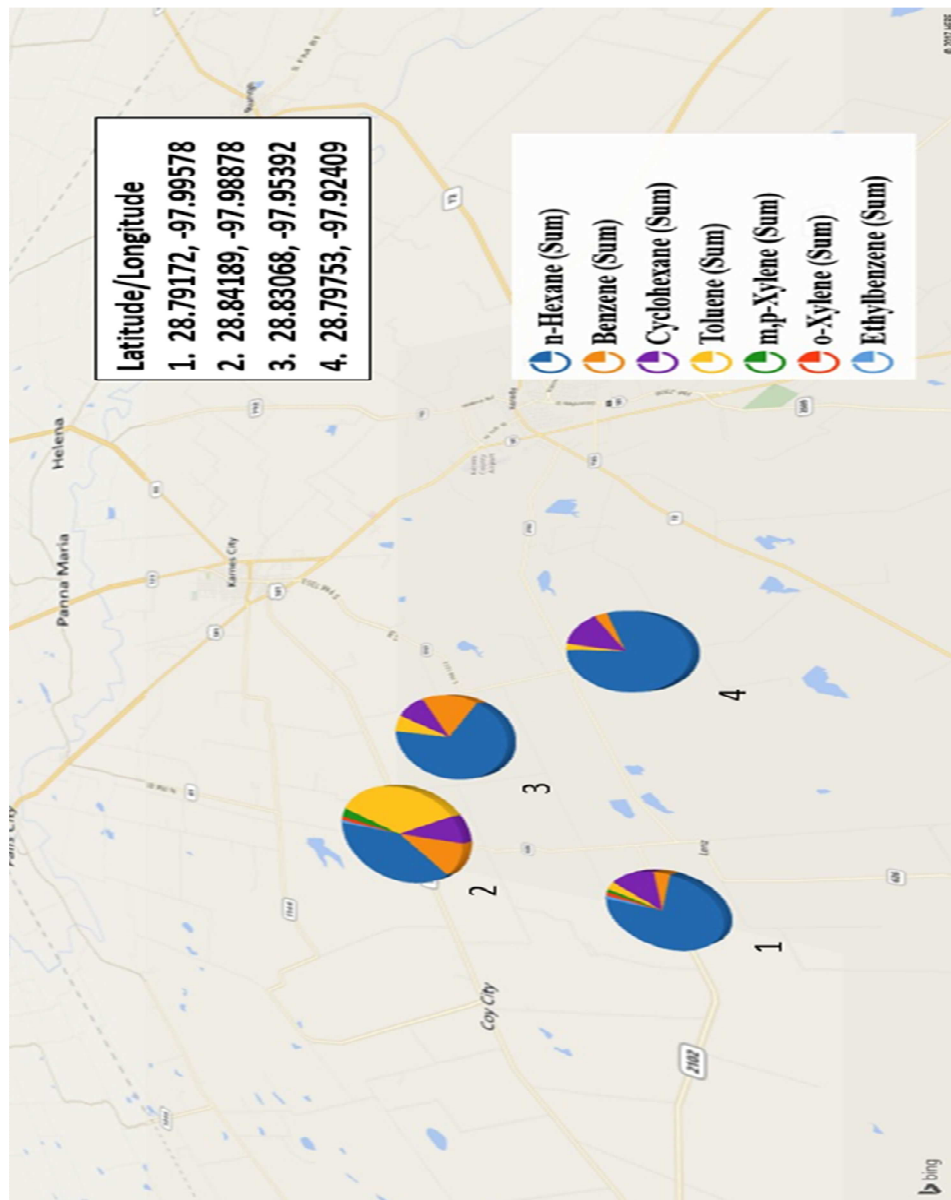


Figure 7. Distribution of target NMVOCs detected during July 8th, 2016 sampling period in Karnes County

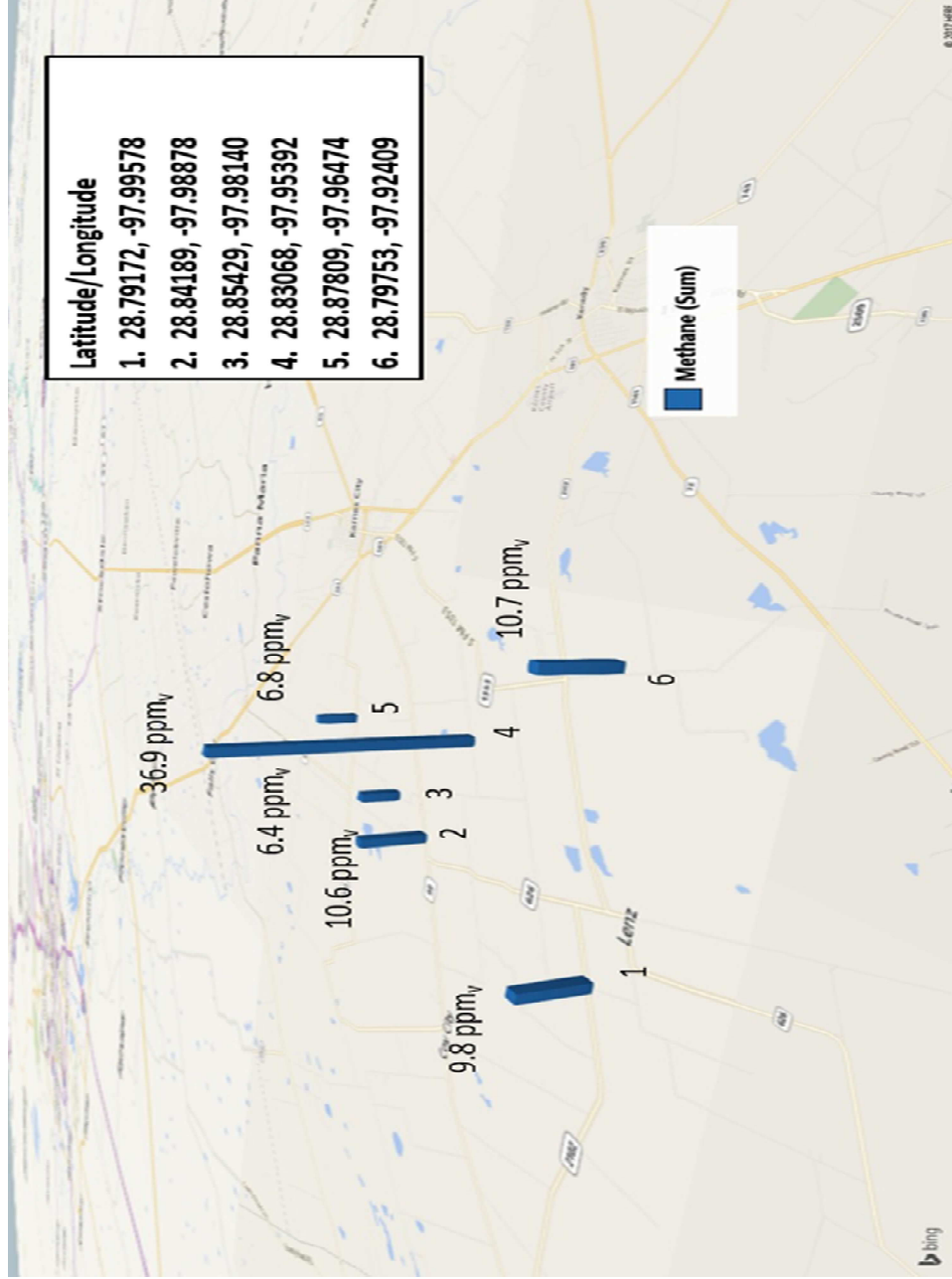


Figure 8. Distribution of methane detected during July 8th, 2016 sampling period in Kames County

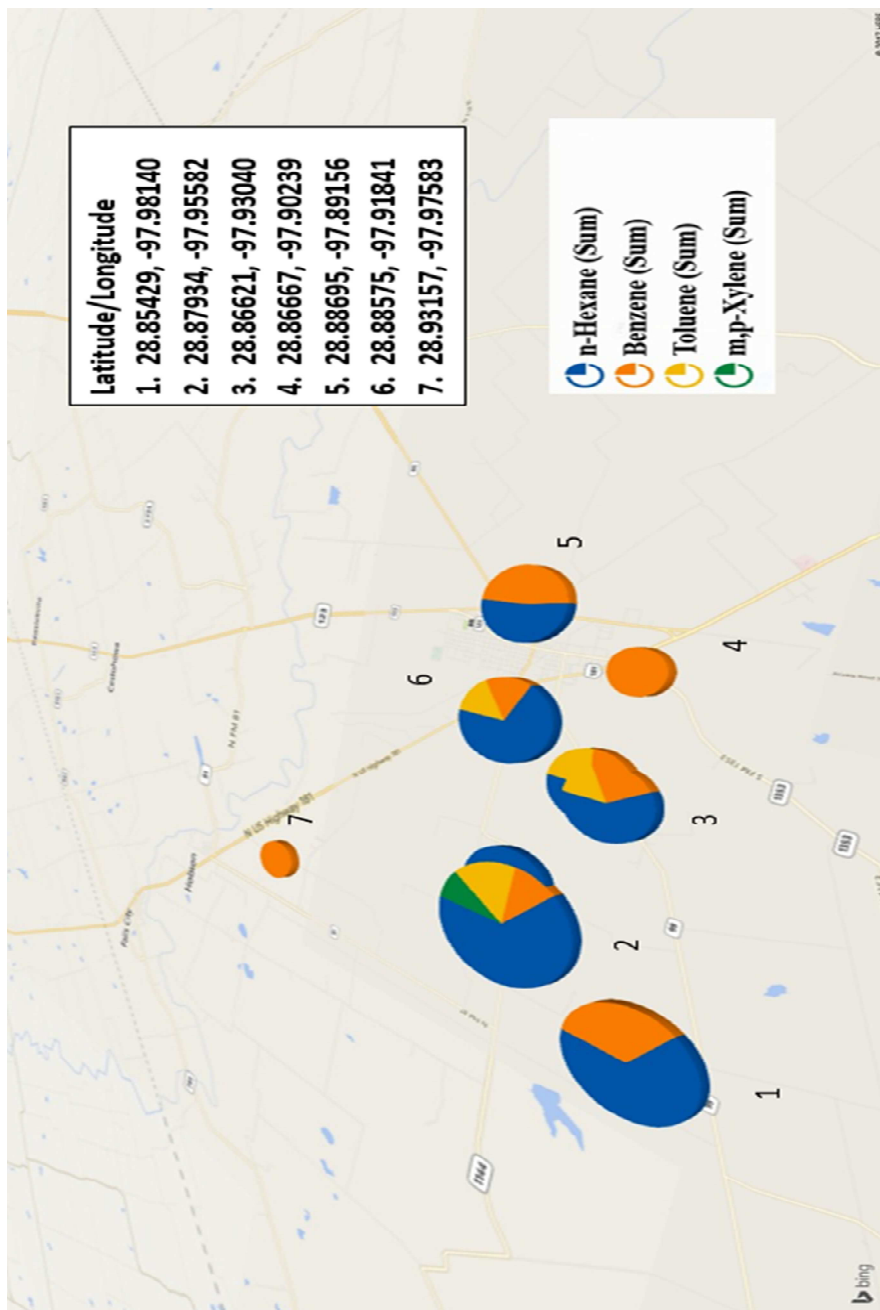


Figure 9. Distribution of target NMVOCs detected during October 10th to 11th, 2016 sampling period in Karnes County

The concentrations of the target NMVOCs detected in Karnes County were compared to concentrations detected at the Barnett Shale in northern Texas, southeast Texas near the Houston Ship Channel (HSC), Muskingum, Ohio, and the Negishi and Shiohama areas of Yokohama, Japan. A comparison of the average concentrations is displayed in Figure 10; however, the data collected during the July 8th sampling period have been omitted from the figure. The Barnett Shale is one of the most productive shale formations in the United States. In 2016, the average concentrations of *n*-hexane, benzene, toluene, ethylbenzene, *m,p*-xylenes, and *o*-xylene were detected at 15 ppb_v, 0.97 ppb_v, 3.3 ppb_v, 0.21 ppb_v, 4.3 ppb_v, and 0.52 ppb_v, respectively.²⁸ The HSC contains several refineries. The concentrations of the target NMVOCs were detected on September 2nd, 4th, 9th, 20th, and 26th of 2006 using an automated GC in an air monitoring station. The average concentrations of *n*-hexane, benzene, toluene, ethylbenzene, *m,p*-xylenes, and *o*-xylene were detected at 0.76 ppb_v, 0.38 ppb_v, 0.72 ppb_v, 0.09 ppb_v, 0.20 ppb_v, and 0.08 ppb_v, respectively.²⁹ Muskingum County, Ohio is located on the Marcellus Shale, and in 2013, the average concentration of *n*-hexane was detected at 0.92 ppb_v. Benzene was detected at 0.32 ppb_v. Cyclohexane, toluene, and *m,p*-xylenes were detected at 0.25 ppb_v, 0.54 ppb_v, and 0.52 ppb_v, respectively.³⁰ Between 2007 and 2008, average concentrations of *n*-hexane, benzene, toluene, ethylbenzene, *m,p*-xylenes, and *o*-xylene in the Negishi area were detected at 1.7 ppb_v, 0.70 ppb_v, 3.1 ppb_v, 0.80 ppb_v, 0.80 ppb_v, and 0.40 ppb_v, respectively.³¹ Also, in the Shiohama area, the average concentrations of *n*-hexane, benzene, toluene, ethylbenzene, *m,p*-xylenes, and *o*-xylene were detected at 2.4 ppb_v, 2.1 ppb_v, 5.2 ppb_v, 2.9 ppb_v, 2.1 ppb_v, and 0.70 ppb_v, respectively.³¹ The concentrations detected during the July 8th sampling period in Karnes County were significantly higher than the concentrations detected in northern Texas, HSC, Muskingum County, Negishi, and Shiohama. However, the concentrations detected during the October 10th

and 11th sampling period were relatively similar to concentrations detected at the HSC and Muskingum County. The concentrations detected during all samplings periods were significantly lower than the NIOSH REL (TWA). Although the concentrations were lower than the NIOSH REL (TWA), studies have shown that low exposure rates of carcinogen can potentially be harmful.²⁸ Also, residents in the Karnes County area have expressed concerns about their health since the increase in oil and gas production on the Eagle Ford Shale.

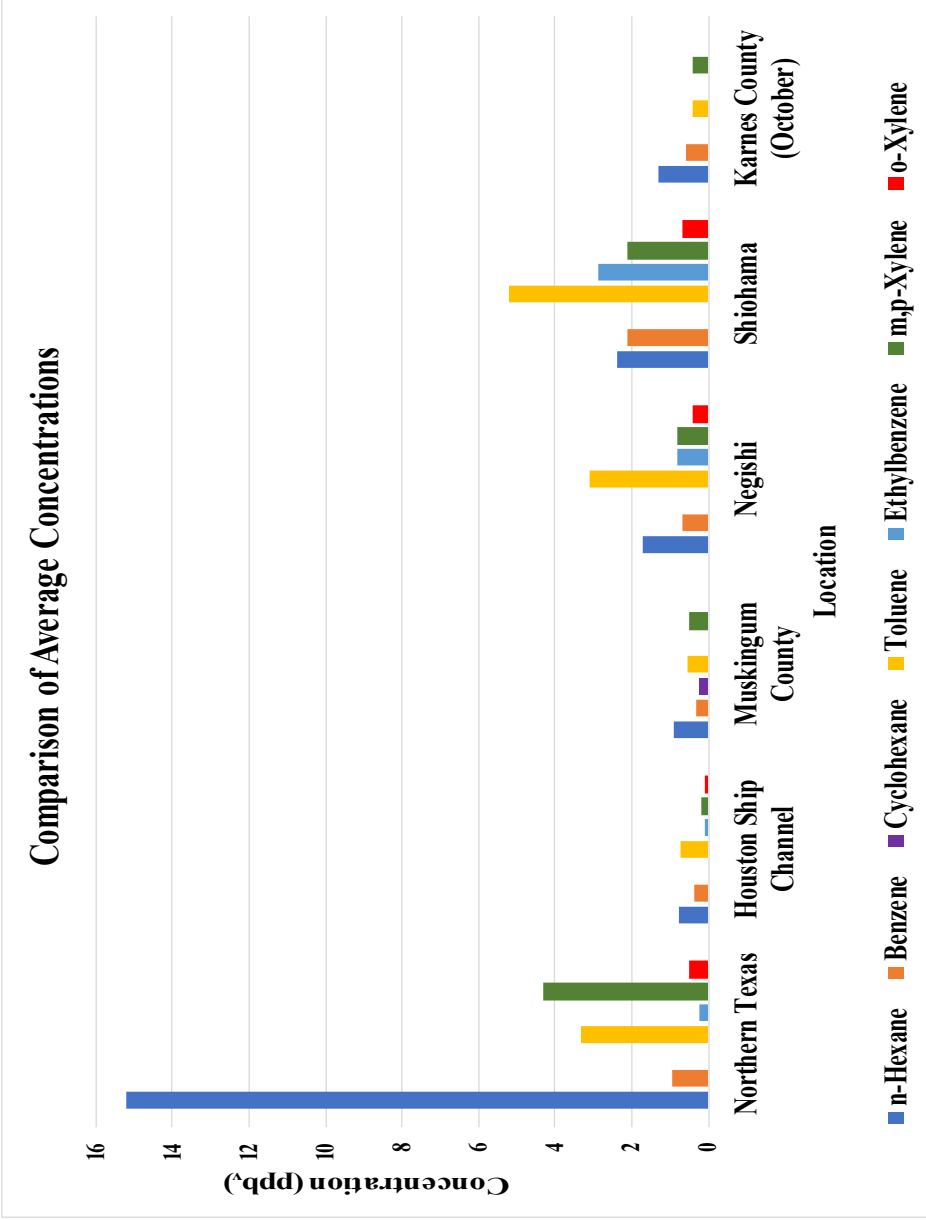


Figure 10. Comparison of average concentrations of NMVOCs detected at various areas near oil and gas facilities

3.2 Ambient Air Analysis in Shelby County, Tennessee

Air samples were collected in Shelby County during all four seasons from January 28, 2014 to December 4, 2014. Approximately 130 air samples were collected each season. The focus of this thesis project was to identify and quantify compounds that are not present on the target compound list of the TO-15 method. Among the non-TO-15 compounds detected, acetonitrile is the only compound classified as a hazardous air pollutant by the EPA. Other detected compounds not on the TO-15 list have relatively little toxicological information but they are found in higher concentrations than many TO-15 target compounds known to cause adverse human health effects. Although the majority of the compounds in ambient air are not considered hazardous, they may play a considerable role in the formation of ozone in the troposphere or contribute to global warming via the greenhouse effect. Table 10 lists the standard calibration of the target compounds. The significant compounds detected during the sampling periods were acetonitrile, cyclohexene, and cyclohexanone. The three compounds are used industrially and were detected at relatively high concentrations. A seasonal comparison of their average concentrations is displayed in Figure 11. The concentrations detected during the sampling periods were below the NIOSH REL (TWA).

Air sampling during the winter season occurred from January 28, 2014 to March 18, 2014. The temperature ranged from 0 °C to 18 °C during the sampling period. Acetonitrile, cyclohexene, and cyclohexanone were detected above 100 ppb_v. The concentrations of acetonitrile were significantly high around police and fire stations. The highest concentration of acetonitrile was detected at 520 ppb_v at a fire station in Memphis. Cyclohexene and cyclohexanone were both present at a residence in Collierville at 102 ppb_v and 129 ppb_v,

respectively. Figure 12 illustrates the distribution of the three compounds across the sampling region in Shelby County.

For the spring season, the sampling period started May 2, 2014 and ended June 16, 2014 with the temperature ranging from 17 °C to 32 °C. Cyclohexene and cyclohexanone were detected above 100 ppb_v. Their highest concentrations were detected at 229 ppb_v and 108 ppb_v, respectively. Acetonitrile was detected at concentrations above 50 ppb_v at several locations with the highest concentration being 93 ppb_v near an elementary school. The distribution of the three compounds within the sampling region in Shelby County are displayed in Figure 13.

Air sampling during the summer season occurred from July 30, 2014 to September 5, 2014. The temperature during the sampling period ranged from 18 °C to 33 °C. The maximum concentration of acetonitrile was detected at 16 ppb_v near a high school. The maximum concentrations of cyclohexene and cyclohexanone were detected at 79 ppb_v and 27 ppb_v, respectively, near an elementary school. Figure 14 displays the distribution of the three compounds across the sampling region in Shelby County.

In the fall season, air samples were collected from October 27, 2014 to December 4, 2014. The temperature ranged from 2 °C to 23 °C. Cyclohexene and cyclohexanone were detected at University of Memphis campus at concentrations of 32 ppb_v and 19 ppb_v, respectively. Acetonitrile was only detected once during the fall season, and its concentration was approximately 2 ppb_v. Figure 15 illustrates the distribution of the three compounds across the sampling region in Shelby County.

Table 11 lists the frequency of detection of each target compound and their source of emission for each season. The aldehyde compounds had a relatively high frequency of detection compared to other target compounds; however, the concentrations were also relatively low. Due

to the higher temperatures in the spring and summer seasons, compounds were more frequently detected during those two seasons. In addition, studies have shown that hazardous chemical releases occur more frequently during the Spring and Summer.³² As a result, VOCs are most likely detected more frequently and at higher concentrations during Spring and Summer. The compounds that were not detected at least once in any season have been omitted from the Table 11.

Table 10. Analytical calibration of non-TO-15 target compounds in Shelby County

Compound	MW (g/mol)	Calibration Equation	R ²
Acetonitrile	41.05	$6.84 \cdot 10^5 x - 1.47 \cdot 10^5$	0.9908
Isoprene	68.12	$1.51 \cdot 10^6 x + 8.42 \cdot 10^5$	0.9939
2-Methylpropanal	72.11	$1.44 \cdot 10^5 x + 1.81 \cdot 10^4$	0.9937
Methacrolein	70.09	$4.88 \cdot 10^5 x + 3.66 \cdot 10^5$	0.9969
Methyl vinyl ketone	70.09	$2.72 \cdot 10^5 x - 1.58 \cdot 10^5$	0.9902
Butanal	72.11	$2.01 \cdot 10^6 x - 5.65 \cdot 10^5$	0.9909
1-Butanol	74.12	$2.69 \cdot 10^5 x - 1.51 \cdot 10^5$	0.9927
Cyclohexene	82.14	$8.41 \cdot 10^5 x + 1.07 \cdot 10^6$	0.9988
Hexanal	100.15	$9.23 \cdot 10^5 x - 2.85 \cdot 10^5$	0.9895
Cyclohexanone	98.15	$7.91 \cdot 10^5 x - 9.78 \cdot 10^5$	0.9923
Heptanal	114.18	$1.24 \cdot 10^6 x - 6.97 \cdot 10^5$	0.9925
Dimethyl Trisulfide	126.26	$2.95 \cdot 10^6 x - 9.87 \cdot 10^5$	0.9902
Octanal	102.17	$2.15 \cdot 10^6 x - 1.92 \cdot 10^6$	0.9893

Table 11. Frequency of detection of target compounds in Shelby County and their emission source

No.	Compounds	Emission Source	Frequency of Detection (Winter)	Frequency of Detection (Spring)	Frequency of Detection (Summer)	Frequency of Detection (Fall)
1	Acetonitrile	Industrial, vehicles	62	106	12	1
2	Isoprene	biogenic	1	86	126	0
3	2-Methylpropanal	industrial	3	5	16	0
4	Methacrolein	industrial	0	1	8	0
5	Methyl vinyl ketone	industrial	0	1	6	0
6	Butanal	Vehicles, industrial	1	14	24	0
7	1-Butanol	biogenic, industrial	82	91	125	25
8	Cyclohexene	industrial	17	23	20	7
9	1-Pentanol	industrial	0	0	4	0
10	Dimethyl disulfide	biogenic	7	11	4	0
11	(Z)-2-Penten-1-ol	biogenic	0	0	1	1
12	Hexanal	biogenic, industrial, vehicles	4	21	26	0
13	2-Bromo-2-methylbutane	industrial	0	0	2	0
14	5-Methyl-2-hexanone	industrial, biogenic	0	0	2	1
15	(E)-3-Hexen-1-ol	biogenic	0	0	20	2
16	Cyclohexanone	industrial	20	25	8	5
17	Heptanal	vehicles, biogenic, industrial	5	19	21	0
18	2-Cyclohexen-1-one	industrial	23	94	68	3
19	Dimethyl trisulfide	biogenic	5	12	3	0
20	Octanal	biogenic, industrial, vehicles	57	57	65	0

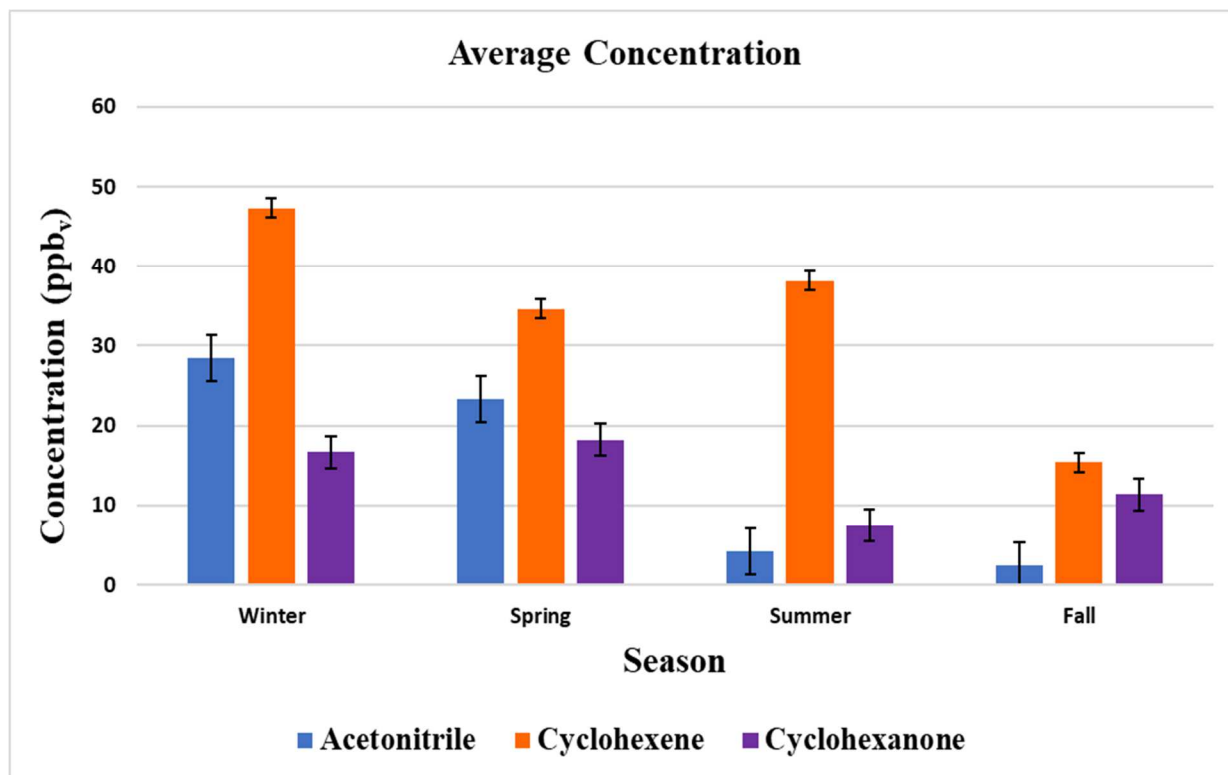


Figure 11. Seasonal comparison of the average concentrations of VOCs with high industrial use in Shelby County

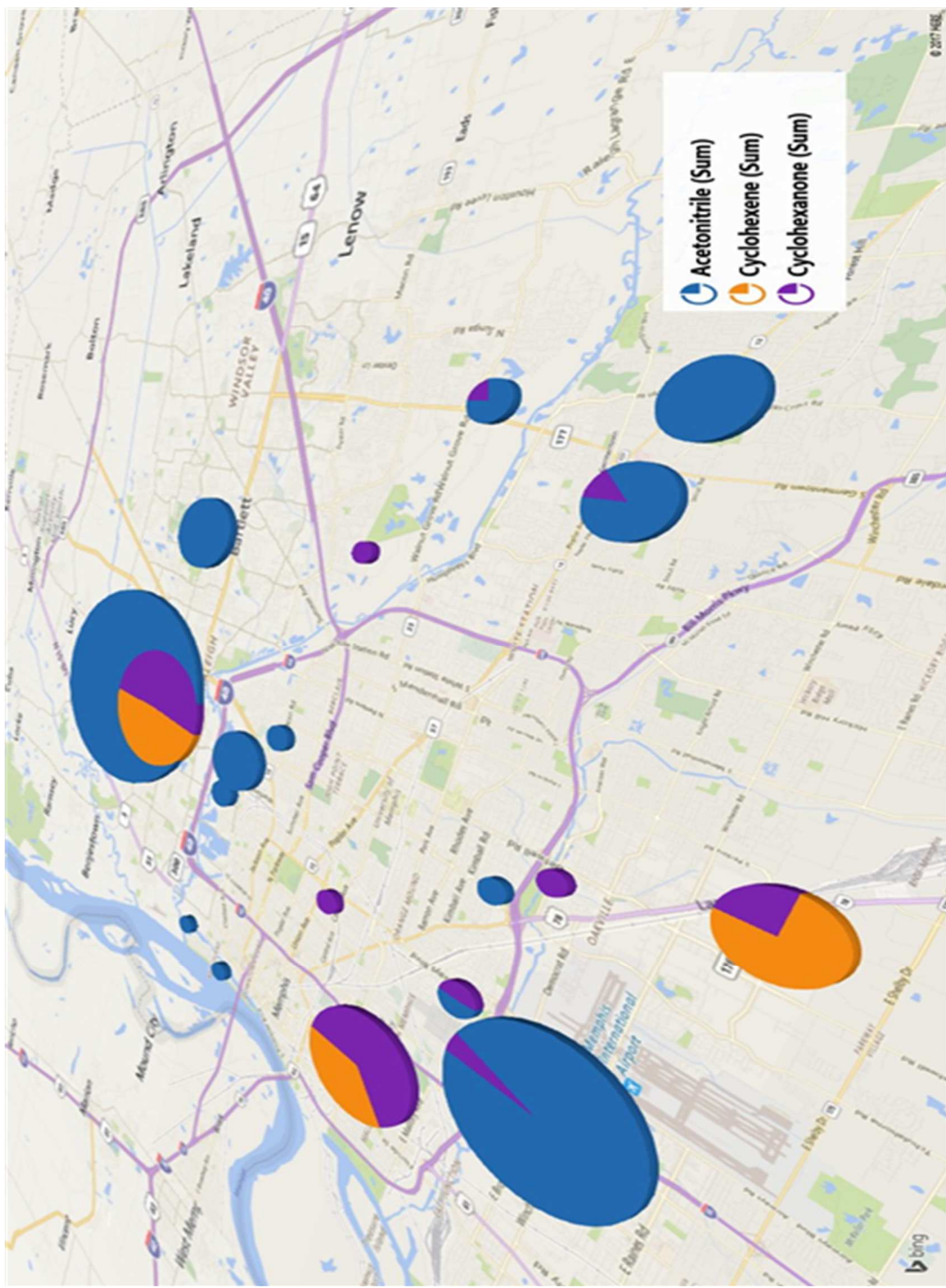


Figure 12. Distribution of VOCs with high industrial use detected during the winter sampling period in Shelby County

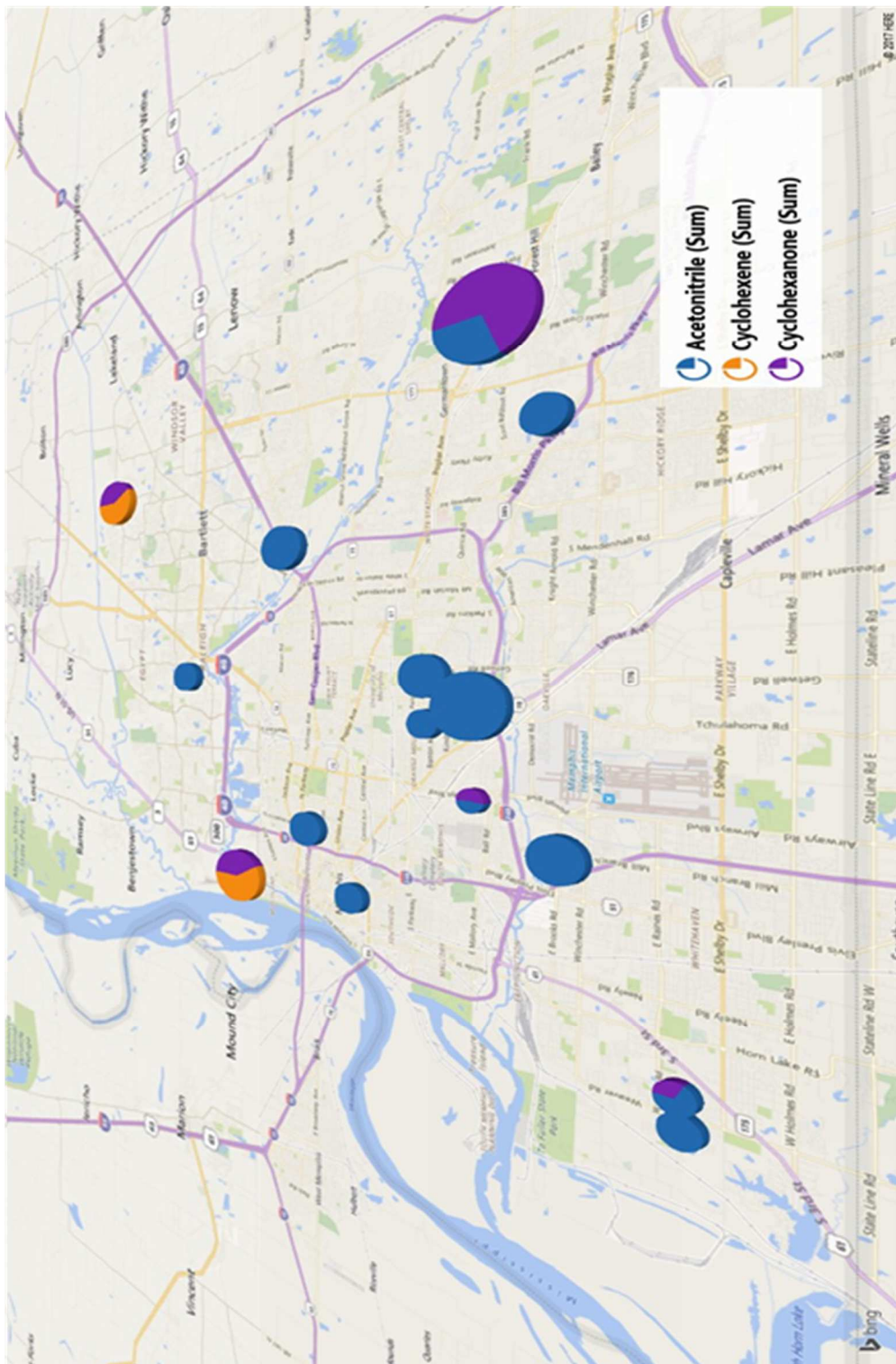


Figure 13. Distribution of VOCs with high industrial use detected during the spring sampling period in Shelby County

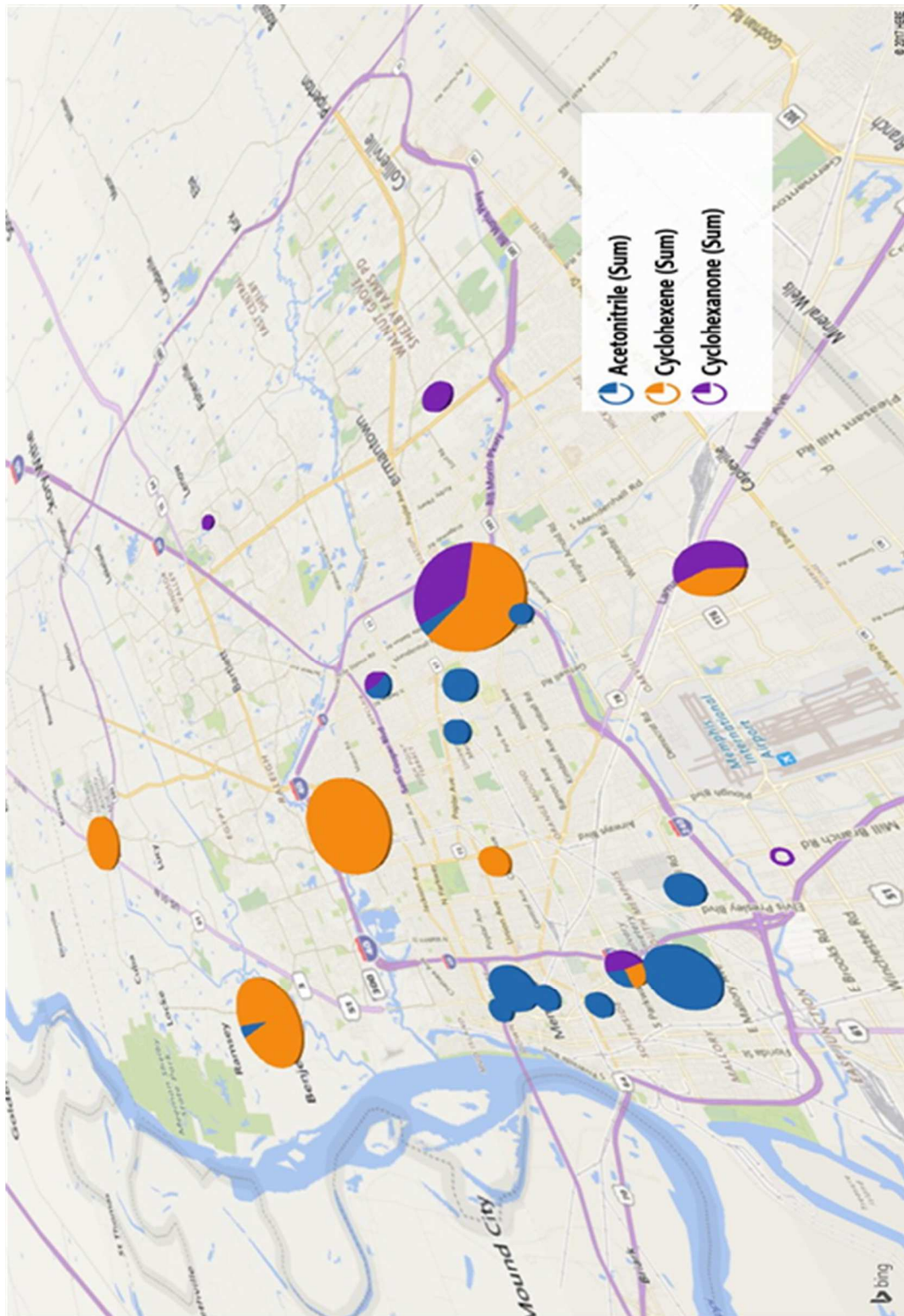


Figure 14. Distribution of VOCs with high industrial use detected during the summer sampling period in Shelby County

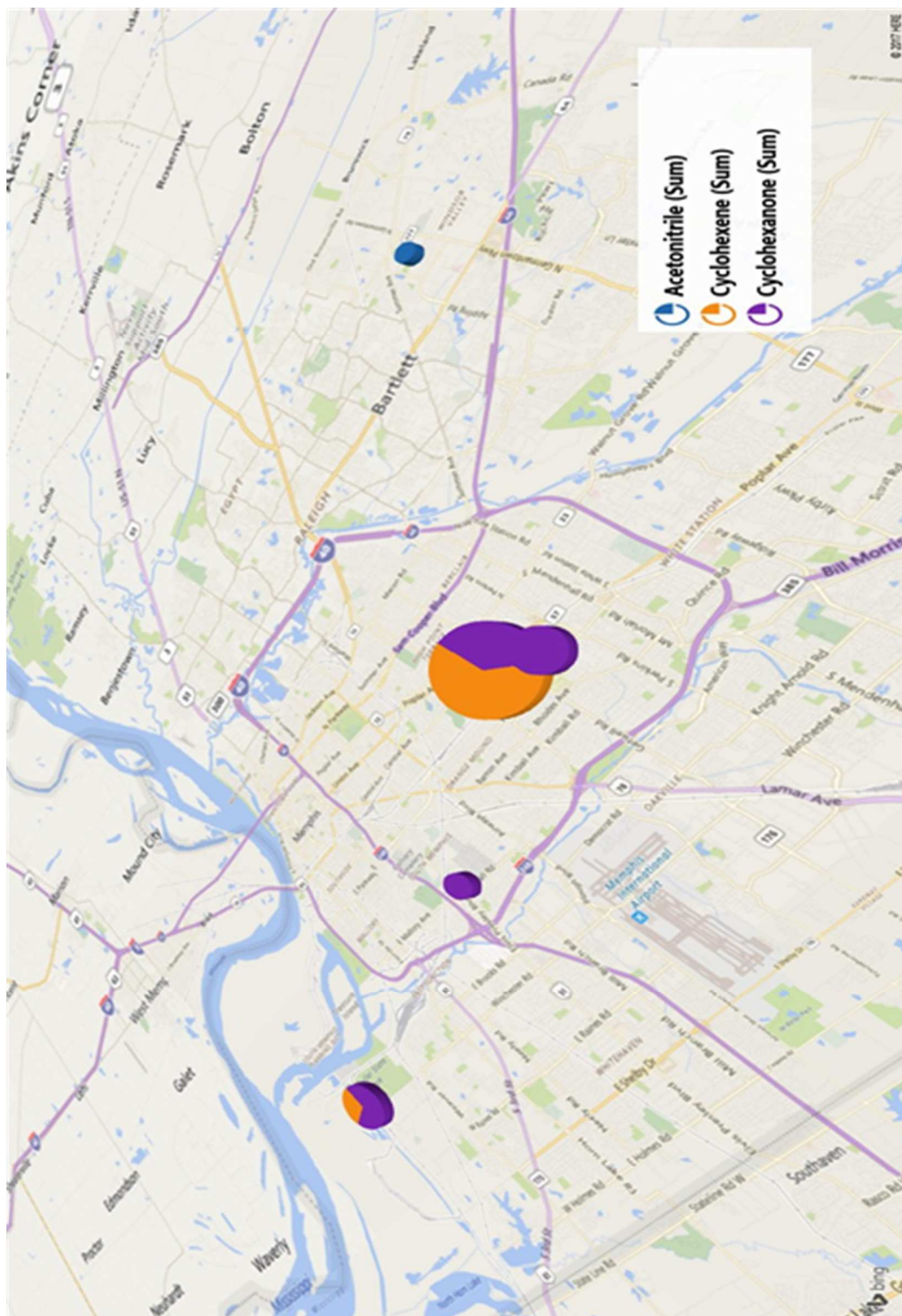


Figure 15. Distribution of VOCs with high industrial use detected during the fall sampling period in Shelby County

The following table, Table 12, represents an annual comparison of the minimum, mean, maximum concentrations of acetonitrile, cyclohexene, and cyclohexanone detected in Shelby County, Tennessee.

Table 12. Seasonal comparison of the range of concentrations detected in Shelby County

Compounds	Range of Concentrations (Winter)	Range of Concentrations (Spring)	Range of Concentrations (Summer)	Range of Concentrations (Fall)
Acetonitrile	0.43-520.64 ppb _v	1.44-535.86 ppb _v	1.40-16.54 ppb _v	2.41 ppb _v
Cyclohexene	0.33-102.82 ppb _v	0.38-229.44 ppb _v	1.65-79.57 ppb _v	3.35-32.27 ppb _v
Cyclohexanone	1.87-129.43	1.18-112.79 ppb _v	2.69-27.26 ppb _v	3.76-19.51 ppb _v

Since several industrial facilities report to the Toxics Release Inventory (TRI), the TRI database can be searched to determine the compounds that are being released by certain industrial facilities. In the Shelby County area, the TRI database reports that Chemours Memphis Plant and D & W Plating Company release acetonitrile. However, since the highest concentrations of acetonitrile were detected near schools, police stations, and fire stations, vehicle exhaust may be the major contributor to its emission. The TRI database does not list cyclohexene or cyclohexanone, so it was difficult to identify the companies emitting those compounds. It is assumed that companies in the plastics industry emitting ammonia are most likely responsible for the emissions of cyclohexene and cyclohexanone. As a result, Bryce Corporation may be emitting cyclohexene and cyclohexanone. In addition, cyclohexene is used as an intermediate for the production of cyclohexanol.³³ The TRI database lists cyclohexanol as an emitted compound from BASF Corporation, which is located in West Memphis. As a result, BASF Corporation may also emit cyclohexene. Since the concentrations of cyclohexene and cyclohexanone were usually present at high concentrations near schools, police stations, and fire

stations, it is difficult to hold Bryce Corporation and BASF Corporation responsible for the concentrations detected during the sampling periods.

3.3 Data Analysis Using TargetView™

TargetView™ is a useful software product for analyzing data, especially when confronted with over 500 samples, many of which have many detected ambient air pollutants. Uploading a library to identify target compounds in the samples is an effective method to reduce the amount of time spent analyzing every peak in the chromatograms. The following figure, Figure 15, is a chromatogram of a sample collected in Karnes County, Texas. Table 13 is the report produced by TargetView™. Since the target compounds were a part of the EPA TO-15 list, a target library was created for identifying the air pollutants via spectral comparison.

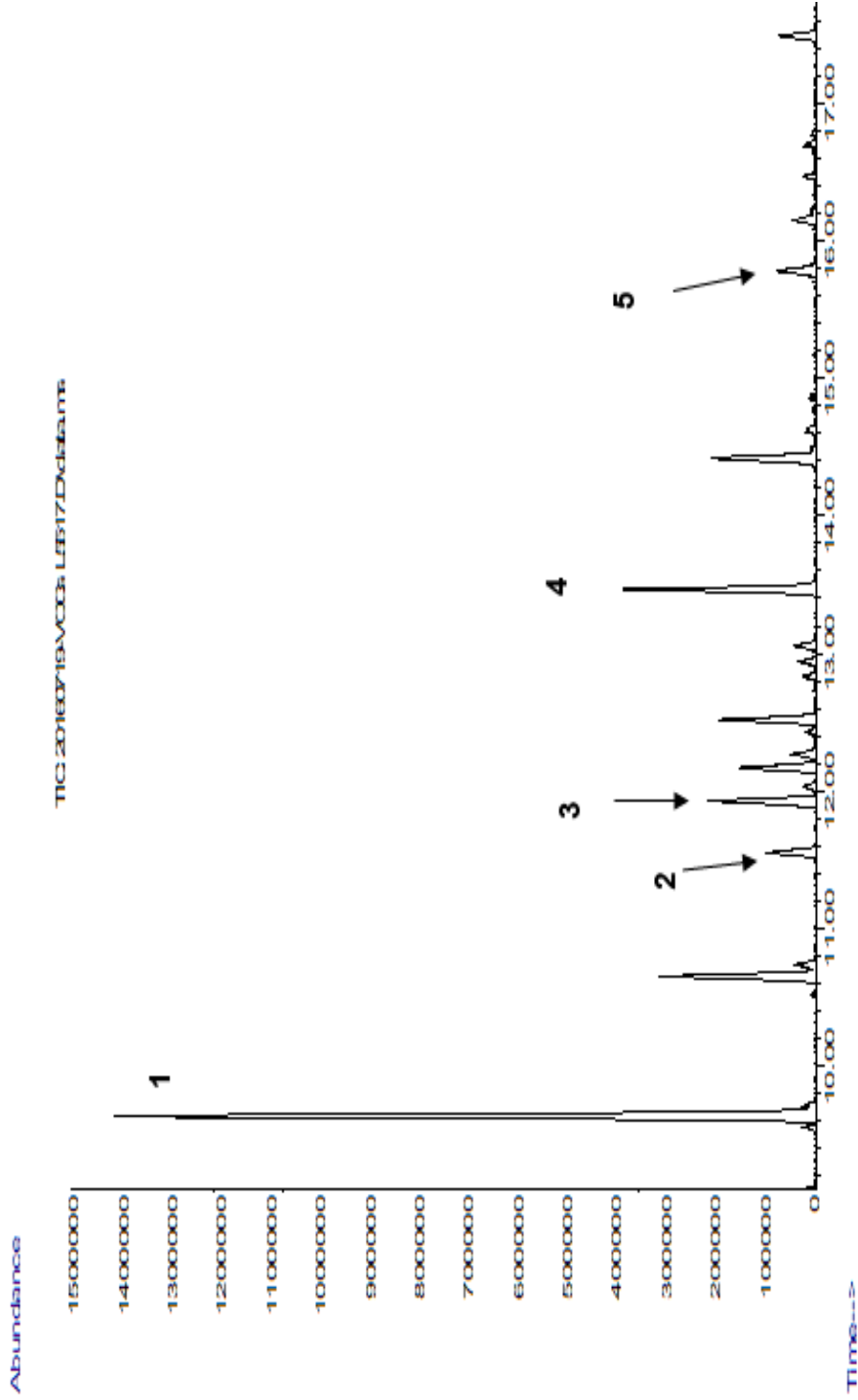


Figure 16. Chromatogram of sample collected in Karnes County

Table 13. Identification of target compounds reported by TargetView™

No.	Target Compound	CAS	RT (min)	Peak sum (TIC)	Match Factor
1	<i>n</i> -Hexane	110-54-3	9.6339	16871825	841
2	Benzene	71-43-2	11.548	955293	663
3	Cyclohexane	110-82-7	11.9234	1767353	744
4	Heptane	142-82-5	13.467	3162375	661
5	Toluene	108-88-3	15.776	505621	775

TargetView™ provided a reliable report; however, four of the five compounds fell below the 800-match factor threshold and required further verification. The software is also capable of detecting coeluting compounds that cannot be identified using conventional library search methods. The following chromatogram, Figure 17, is an example of coeluting compounds. The peak contains benzene and 1-butanol due to their similar retention times. The retention indices for benzene and 1-butanol are 647.5 index units and 660.1 index units, respectively. A conventional library search only identified benzene; whereas, the TargetView™ software was able to detect benzene and 1-butanol. Figure 18 displays the detection of benzene and 1-butanol.

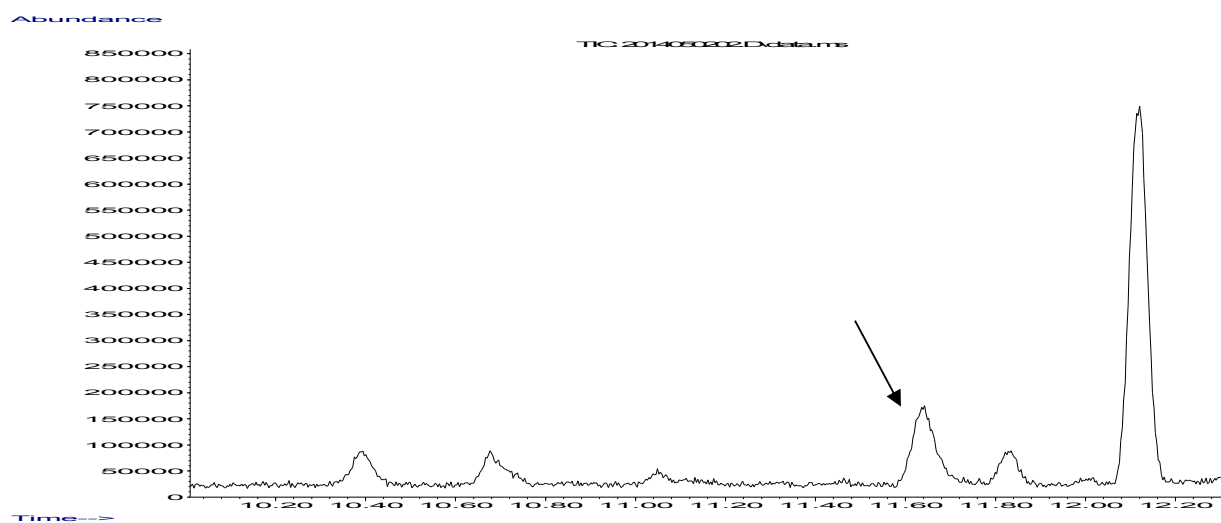


Figure 17. Chromatogram of sample with peak containing benzene and 1-butanol as coeluting compounds

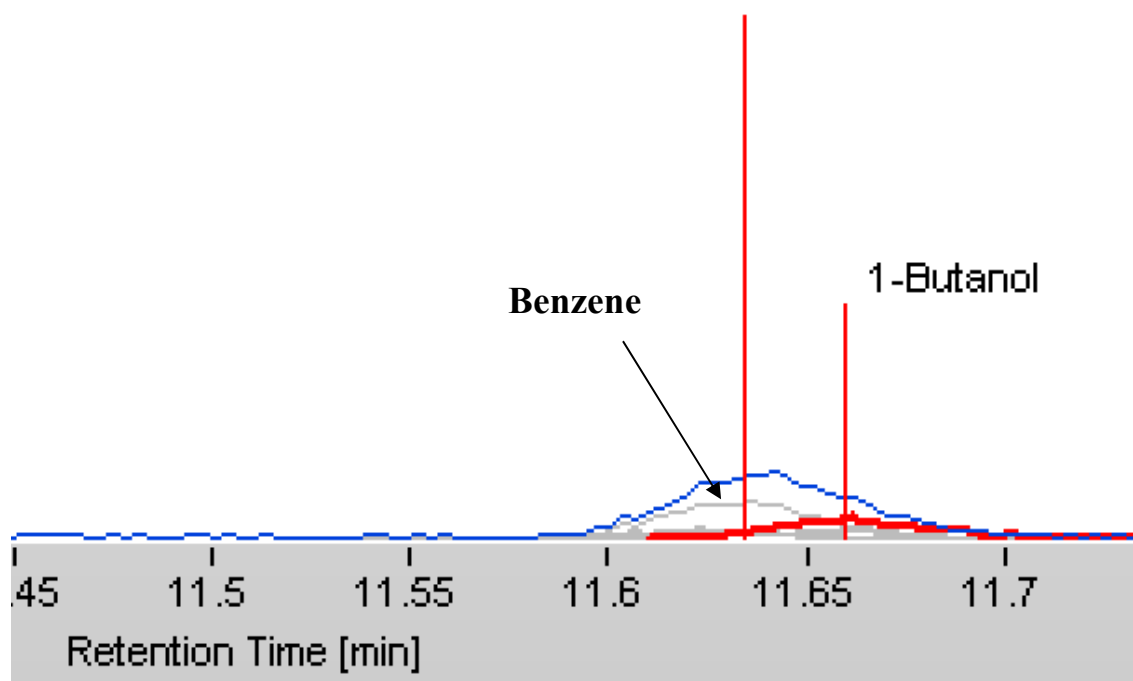


Figure 18. Detection of benzene and 1-butanol coelution using TargetView™

Although the TargetView™ software was able to detect benzene and 1-butanol as coeluting compounds, the match factor for each compound failed to meet the 800-match factor threshold.

Table 14 is the report produced by the TargetView™ software. However, this is an improvement relative to the conventional library search algorithm using ChemStation since only benzene was detected.

Table 14. TargetView™ report for benzene and 1-butanol coelution

No.	Target Compound	CAS	RT (min)	Peak sum (TIC)	Match Factor
1	Benzene	71-43-2	11.6344	1019292	730
2	1-Butanol	71-36-3	11.66	458577	683

The low match factor is due to the number of uncertain ions in the mass spectrum of the compounds. However, the prominent ion peaks of both compounds were detected. The following figures, Figure 19 and Figure 20, display the mass spectrum for the sample and the standard, or target, spectrum reported by TargetView™. Benzene has a prominent ion at 78 m/z, and 1-butanol has a prominent ion at 56 m/z.

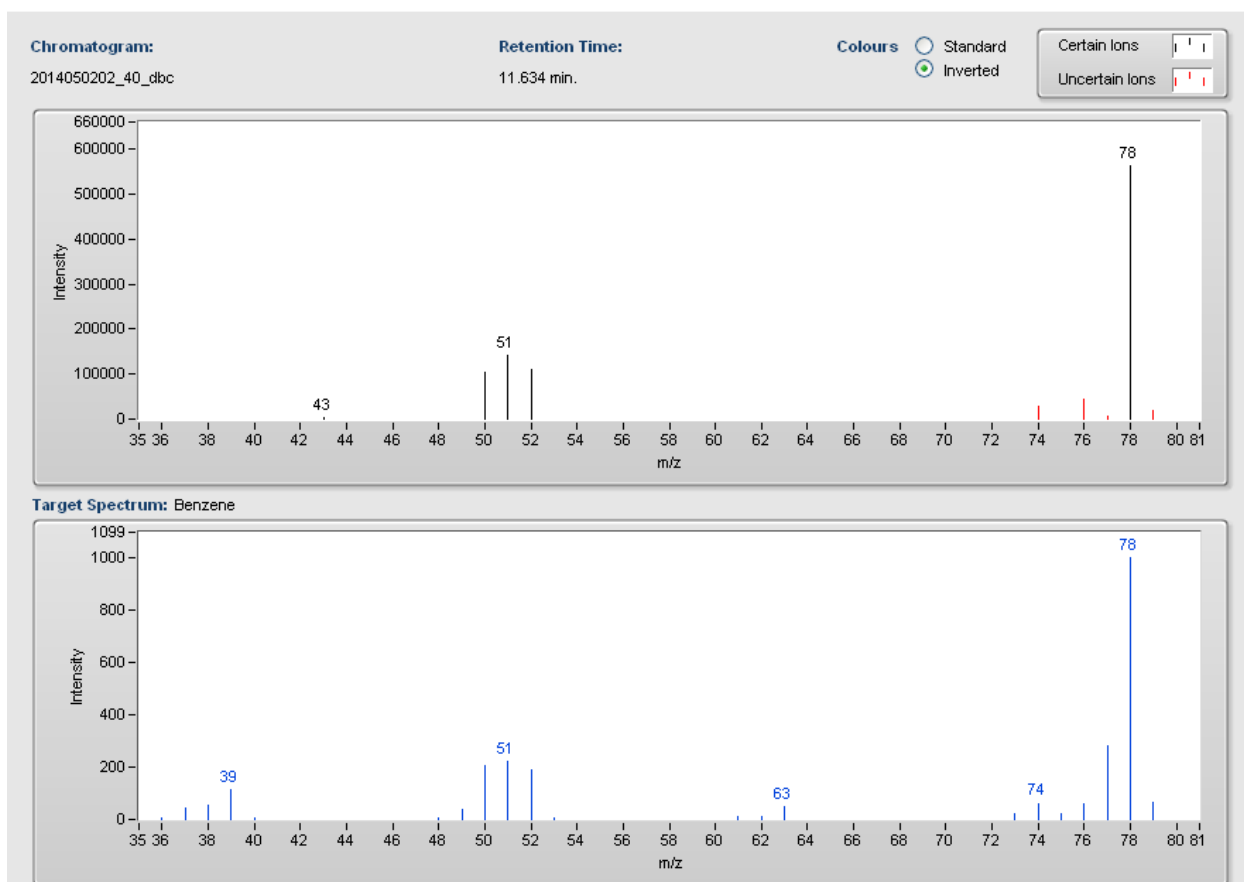


Figure 19. Sample and standard mass spectra of benzene with certain and uncertain ions reported by TargetView™

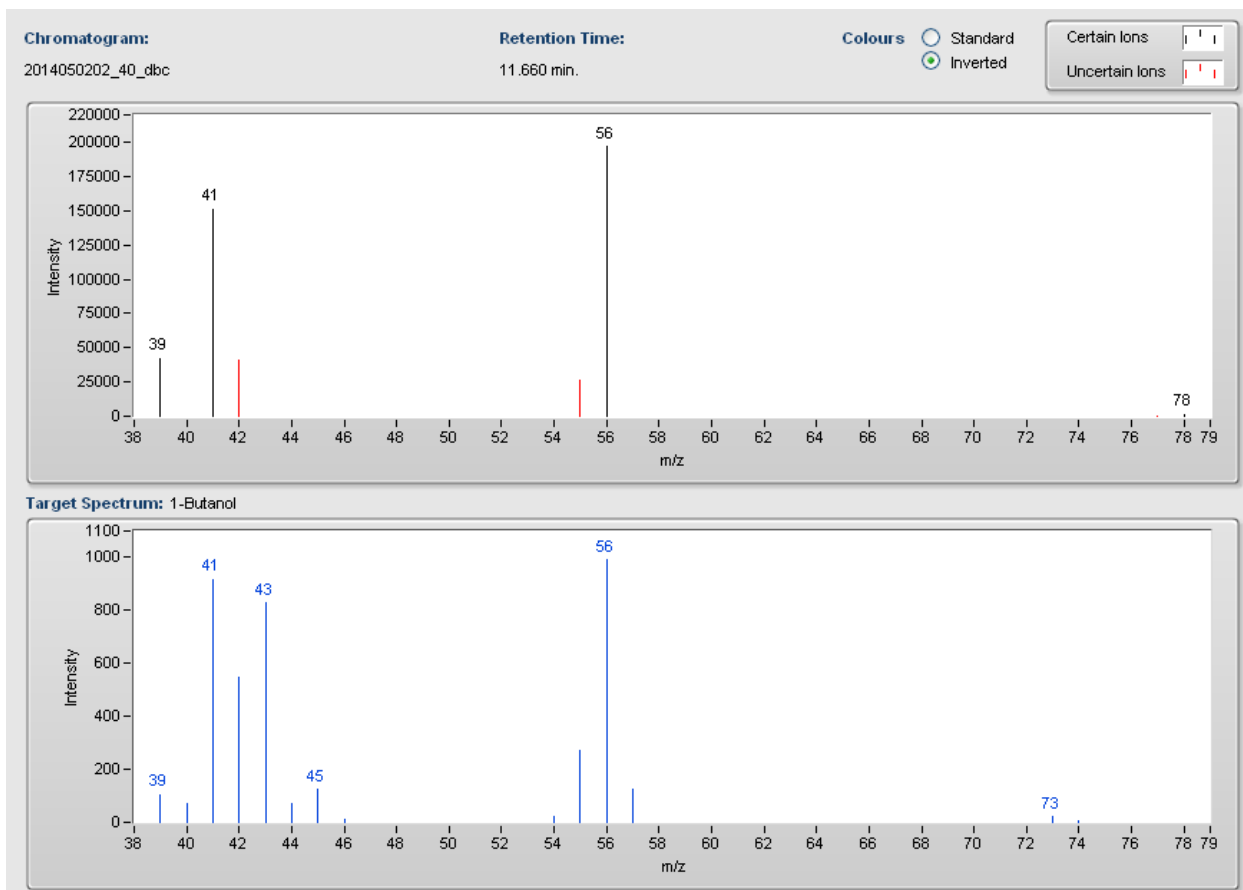


Figure 20. Sample and standard mass spectra of 1-butanol with certain and uncertain ions reported by TargetView™

CHAPTER IV

CONCLUSION

Karnes County, Texas is located on the Eagle Ford Shale and has been affected by the oil and gas industry. Although hydraulic fracturing provides an economic boost for the local economy, it also contributes to environmental pollution. The constant drilling and removal of oil and natural gas from the ground plus large trucks transporting the resources contributes to releasing harmful compounds into the air. Mobile sources, large trucks, and stationary sources, pumpjacks and flares, emit primary pollutants, and those primary pollutants undergo reactions to produce secondary pollutants. Due to heavy activity on the Eagle Ford Shale, residents of Karnes City frequently breathe harmful pollutants. The concentration of the target non-methane VOCs ranged from 0.25 to 151 ppb_v. Toluene and n-hexane were the only compound detected above 100 ppb_v. None of the target compounds exceeded their corresponding NIOSH REL (TWA). However, residents living within the sampling region are exposed to the air pollutants for periods exceeding 10 hours per day.

In Shelby County, the target compounds consisted of compounds that are not included on the EPA TO-15 list. However, many of the compounds are abundantly present and are highly reactive in the atmosphere. Acetonitrile, cyclohexene, and cyclohexanone were frequently detected and had relatively high concentrations. The concentrations of the three compounds ranged from 0.33 to 520 ppb_v. The three compounds were usually detected at high concentrations near schools, police stations, and fire stations but did not exceed the NIOSH REL (TWA).

TargetView™ provides a great tool for GC-MS analysis. When analyzing samples for target compounds, specific libraries uploaded to TargetView™ can help reduce the amount of

work hours. The ability to detect coelution is a significant feature of the software and proves to be advantageous over conventional library search methods.

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