

THESIS

AIR TOXIC ASSESSMENT FOR SHORT-TERM AMBIENT AIR PILOT STUDY AT
PRIVATE HOUSE IN BATTLEMENT MESA NEAR OIL AND GAS DRILLING SITE

Submitted by

Hussain Alhaji

Department of Environmental and Radiological Health Sciences

In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Summer 2011

Master's Committee:

Advisor: Stephen Reynolds

William Brazile

Sonia Kreidnweis

ABSTRACT

AIR TOXIC ASSESSMENT FOR SHORT-TERM AMBIENT AIR PILOT STUDY AT PRIVATE HOUSE IN BATTLEMENT MESA NEAR OIL AND GAS DRILLING SITE

This pilot study evaluated the ambient air concentrations in Battlement Mesa, Colorado at private house near a well pad, for the four-day period of February 7 through February 10 of 2011. The natural gas site was operating in the production phase of oil and gas development process, and there were 12 wells commercial line. The overlying purpose of the study was to provide preliminary evaluation of air quality characteristics within Battlement Mesa with particular attention to Speciated Non-Methane Organic Compounds/Volatile Organic Compounds (SNMOC/VOCs), fine particulate matter ($PM_{2.5}$) and total volatile organic compounds (TVOC's). SNMOCs including benzene, toluene, ethylbenzene, and xylene (BTEX) compounds were collected and analyzed using a modified EPA Organic Compendium Method TO-12 over a 22-hour period using Summa-polished stainless steel canisters. $PM_{2.5}$ levels were measured using a direct reading photometer, a Personal Data RAM (pDR-1200) for 24-hour sampling period. Total VOCs, were measured in real-time using a Rae Systems PPB Rae 3000 photo ionization detector (PID). To measure the meteorological data, a portable weather station was deployed at the fire station site (FR) during the sampling period (about half mile from the sampling location).

Sampling was performed at two locations around the private house, and background samples were collected at the FR for each parameter. The large percentage of detection (high prevalence i.e. ~95%) in samples from all sites appears to indicate that local VOCs sources do have impacts on air pollution levels. Compounds that were detected in the highest concentrations were light alkanes (i.e. ethane, propane) and the BTEX group (benzene, toluene, ethylbenzene and xylenes). The BTEX group, benzene in particular, recorded a potential health risk compared to the Risk Based Concentration (RBC) developed by the Environmental Protection Agency (EPA). In general, the SNMOCs/VOCs levels detected were low for all samples. TVOCs levels were also low and are consistent with the BTEX group where the background site recorded higher levels than the sampling sites (Upstream “UP” and Downstream “DN” sites).

No exceedances of Federal National Ambient Air Quality Standards were recorded for PM_{2.5}. In addition, PM_{2.5} concentrations were generally highest in the UP site which is close to the well pad. Comparisons of PM_{2.5} data to data from other studies in Garfield County show that PM_{2.5} concentrations in Battlement Mesa (oil and gas development area) are similar to or higher than the Rifle area (urban area)

Meteorological monitoring was performed on a continuous basis with one-hour averages being generated. Wind speed and precipitation (snow) are the most pronounced meteorological parameters that are correlated with VOCs and PM_{2.5} levels.

Overall for the study, pollutant levels were found to be generally very low as compared to the standards and suggested guidelines. In some locations, it is likely that more elevated pollutant levels are the result of local or individual sources.

BTEX emissions sources should be evaluated more thoroughly and benzene in particular since elevated levels were observed. Given that benzene recorded a potential health hazard in the area (exceeded lower level for cancer risk), it is recommended that a comprehensive air study that measures VOCs at different seasons and at other well-development processes be conducted. The background site (FR) is affected by several emission sources. Therefore, it is recommended to relocate the background site to have a better representative background. A direct reading photometer method using the Personal Data RAM (pDR1200) is not the best method to collect the particulates during the winter season due to instrument related temperature bias. Therefore, an alternative method to measure the particulate matter is advised.

ACKNOWLEDGEMENTS

This research would not have been possible without the support of a great number of people. Firstly, I must thank my advisor Dr. Steven Reynolds for his advice and support, not only throughout this research, but during all my years at CSU. My committee members, Dr. William Brazile and Dr. Sonia Kreidnweis, also must be thanked for their time and effort in providing insightful comments and ideas for my thesis. Colorado School of Public Health and Garfield County Public Health Department provided valuable assistance and advice, particularly Roxana Witter, Lisa Mckenzie, Dr. John Adgate, Jim Rada, and Paul Reaser. Dr. Kirsten Khoeler also was a significant source of information for particulate sampling. I also want to thank Mr. Rubby Gibson, the landowner, for his participation in the study.

TABLE OF CONTENTS

Title Page	i
Abstract	ii
Acknowledgements.....	v
Table of Contents.....	vi
List of Acronyms	viii
CHAPTER 1: INTRODUCTION	1
CHAPTER 2: LITERATURE REVIEW	3
2.1 Overview of Natural Gas Development process:.....	3
2.2 Volatile Organic Compounds	5
2.2.1 Sources of VOCs:	5
2.3 VOCs from Oil and Gas industry:	7
2.4 Studies on VOCs from Oil and Gas Production:	9
2.5 Health Effects of VOCs	14
2.6 Regulations of VOCs	19
2.7 Fine Particulate Matters (PM _{2.5})	22
2.8 PM _{2.5} in Oil and Gas	22
2.9 Health Effects of PM _{2.5}	26
2.10 Regulations of PM _{2.5}	27
CHAPTER 3: PURPOSE AND SCOPE	29
3.1 Purpose:.....	29
3.2 Goals of the Study and Research Hypothesis	30
3.3 Scope:.....	31
CHAPTER 4: MATERIALS AND METHODS	32
4.1 Project Location	32
4.2 Sampling and Analytical Methods.....	36

4.2.1 Task Description	37
4.3 (SNMOCs) Sampling.....	37
4.4 Collection of Air Samples for Particulate Matter (PM _{2.5})	41
4.4.1 PM _{2.5} Sampling	41
4.4.2 PM _{2.5} Data Analysis.....	44
4.5 Total Volatile Organic Compounds (TVOCs).....	45
4.5.1 Data Analysis for TVOCs:.....	46
4.6 Meteorological Data.....	47
4.7 Reporting and Documentation Tasks.....	47
4.8 Quality Control and Criteria for Measurement Data	48
4.9 Statistical Analysis.....	49
CHAPTER 5: RESULTS AND DISCUSSION.....	51
5.1 Speciated Non-Methane Organic Compounds (SNMOCs)/VOCs Data	51
5.2 BTEX Concentrations Profile	57
5.3 Total SNMOC.....	65
5.4 Fine Particulate Matter (PM _{2.5}).....	73
5.5 Total Volatile Organic Compounds (TVOCs).....	80
5.6 Metrological Data	81
Discussion	83
5.7 SNMOC Data.....	83
5.8 SNMOC/VOCs Rule and Regulations.....	86
5.9 Particulate Matter (PM _{2.5}).....	93
5.10 Total Voltaile Organic Compounds (TVOCs).....	97
CHAPTER 6: CONCLUSIONS AND RECOMENDATIONS	100
Pilot Study Recommendations for Future Studies:.....	105
REFERENCES	108
APPENDICES	114

LIST OF ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
AIE	Australian Institute of Energy
ANOVA	Analysis of Variance
ASR	Air Specialists Resources
ATSDR	Agency of Toxic Substances & Disease Registry
BM	Battlement Mesa
BTEX	Benzene Toluene Ethylbenzene Xylene
CAA	Clean Air Act
CAAQS	California Ambient Air Quality Standards
CalEPA	California Environmental Protection Agency
COGCC	Colorado Oil and Gas Conservation Commission
CARB	California Air Resources Board
CAPP	Canadian Association of Petroleum Procedures
CDPHE	Colorado Department of Public Health and Environment
CSPH	Colorado School of Public Health
CSU	Colorado State University
DN	Downstream of the Private House
ERG	Eastern Research Group
EPA	Environmental Protection Agency
FR	Fire Station
GC	Garfield County
GCEAB	Garfield County Energy Advisory Board
GCPHD	Garfield County Public Health Department

HHS	Health and Human Services
$\mu\text{g}/\text{m}^3$	Microgram per Cubic Meter
NAAQS	National Ambient Air Quality Standards
NIOSH	National Institute of Occupational Safety and Health
OEHHA	Office of Environmental Health Hazard Assessment
OSHA	Occupational Safety and Health Agency
pDR	Personal Data RAM
PEL	Permissible Exposure Level
PID	Photo Ionization Detector
$\text{PM}_{2.5}$	Fine Particulate Matter
ppbC	Part Per Billion Concentration
ppbv	Part Per Billion by Volume
QA	quality Assurance
RBC	Risk Based Concentration
RELs	Reference Exposure Limits (CalEPA)
RELs	Recommended Exposure Limits (NIOSH)
RPD	Relative Percent Difference
RSLs	Regional Screening Levels
STEL	Short-Term Exposure Limit
SNMOCs	Speciated Non-Methane Organic Compounds
TLVs	Threshold Limit Values
TNMOC	Total Non-Methane Organic Compounds
TWA	Time Weighted Average
TERC	Texas Environmental Research Consortium
UP	Upstream of the Private House
VOCs	Volatile Organic Compounds

WD	Wind Direction
WRP	Watson Ranch Pad
WS	Wind Speed

CHAPTER 1: INTRODUCTION

Natural gas development and production is a major economic staple on the western slope of Colorado. Colorado is currently the heart of an oil and gas drilling rage. Garfield County, located in western Colorado, is one of the largest producers of natural gas in the state. The state has more than 25,700 active wells, and there are more than 5,000 of those wells in Garfield County (GC) (Colorado Oil and Gas Conservation Commission, 2009). Colorado is on a step to break records by approving many new drilling permits in Colorado counties (COGCC). While many operations take place far from the general public, there are operations situated in close proximity to residential areas. The increased drilling in these areas in recent years has raised the level of concern of citizens and local officials. In particular, residents of Battlement Mesa have been concerned with the prospect of the drilling of 200 natural gas wells development and production in their community. According to the United States census estimates, Battlement Mesa/Parachute is home to approximately 5000 individuals (U.S. Census Bureau, 2009). A local community activist group, the Grand Valley Citizens Alliance (GVCA) has been expressing concerns over the potential for adverse health effects for residents to the Colorado Oil and Gas Conservation Commission for several years. One of the residents near the Watson Ranch Pad (WRP) was willing to participate in a study to evaluate airborne concentrations on his own property.

The oil and natural gas well development processes consist of four main stages: drilling, plug-pull out, hydrologic fracturing (Frac'ing or Frcking), and flow back. In the next step, the well pad moves to the production mode after the well has been completed. The production stage is the process where the drilled well discharges natural gas into the commercial line (Understanding Natural Gas Development, GC, 2007). There are different sources of pollutants during these operations, such as: additive chemicals used in well development operations (e.g. hydraulic fracturing), the natural gas resource, wastes from well development activities (e.g. produced water), and diesel exhaust from trucks and generators (GC, 2007).

The ultimate goal of this study was to pilot air sampling for VOCs, $PM_{2.5}$, and TVOCs on one residential property near drilling production site. Additionally, it was used to gather baseline data on these parameters. Twenty two-hour ambient air samples with total of 18 samples were collected for analysis of speciated non-methane organic compounds/volatile organic compound (SNMOCs/VOC) close to the Watson Ranch Pad (WRP) in Battlement Mesa. Ambient fine-mode particulate matter ($PM_{2.5}$) was also collected via 24-hour integrated (filter-based) sampling at the residence. Moreover, total volatile organic compounds (TVOCs) and meteorological data were measured in this study. The air monitoring data were collected during the well production phase which lasts for 20-30 years.

CHAPTER 2: LITERATURE REVIEW

2.1 Overview of Natural Gas Development Process

According to the British Petroleum Company (2002), United States has about 5% of world's proven oil reserves (Australian Institute of Energy, 2004). The U.S. produces 9.9% of the world's oil and it imports 526 million tons of crude oil (AIE, 2004). Although the U.S.A. is the second largest producer of the natural gas (540,000 million m³), it also imports 113,000 million cubic meters, more than any other country (International Energy Agency (AIE)-2004).

The states of Colorado, Wyoming, Utah, Montana and New Mexico (Intermountain West) hold more natural gas than any other region in the U.S.A. It has 41 percent of the estimated proven and potential gas reserves in the nation and produces around 20 percent of the U.S. natural gas supply (Limerick et al, 2003).

According to the Garfield County Energy Advisory Board (EAB), Colorado is the fifth largest producer in the country because of the recent rapid development of gas resources in western Colorado. Furthermore, Garfield County is one of the fastest growing areas in the state for gas production, with over 4,000 active wells valued (2006) (Garfield County EAB, 2007). Despite the fact that natural gas is the cleanest burning fossil fuel, the drilling and production processes impact the land and the people who live near oil and gas development (Garfield County EAB, 2007). Natural gas extraction,

among other types of resource development, can negatively impact air and water quality (Garfield County EAB, 2007). Emissions from the internal combustion engines of drill rigs, vehicles, compressor stations and other mechanized equipment affect regional air quality (Garfield County EAB, 2007). Air quality has become an important issue for residents of the Grand Valley in the last few years. One of the main contributors of these potential problems is the natural gas development. As a result, Garfield County started an air quality study in 2005 to identify pollution sources (Garfield County EAB, 2007).

The oil and gas exploration process includes site selection, site preparation, drilling, well stimulation, well completion, well production and reclamation (Garfield County EAB, 2007). The following paragraph briefly discusses the natural gas drilling process.

The first step is site selection, where the geologists select a site to develop into a well pad, is based on collected information on the geology of potential sites to drill (Garfield County EAB, 2007). Site preparation is the second step of the natural gas drilling process and many activities are involved, such as transporting heavy machinery, building roads to access the well pad, and installing pipes to transport natural gas. After the selection and the preparation of the site, the drilling equipment, such as drill string and derrick structure, is constructed on site. Then a process called “spudding in” is used to drill an initial hole after ensuring that the load-bearing structure is secure. Next, a section of metal pipe (called conductor casing) is inserted into the hole to prevent blowouts and ensure the well’s integrity. Once the conductor casing is securely

cemented into place, the drill is bored to a depth of 900 feet below the ground surface. Two processes of casing called surface casing and production casing are performed. Eventually, the production casing runs thousands of feet deep to reach the hydrocarbon formations. After the drilling process is completed, the drill rig is disassembled and the well completion process begins. Well stimulation is another process in natural gas drilling. During this process, a method called hydraulic fracturing (also called fracking) is used to increase the flow rate of natural gas so it can easily flow to the surface. This method uses liquids (water and various chemicals) under high pressure to create fractures in the sediment surrounding the well bore (Garfield County EAB, 2007).

After the fracking process, the well bore needs to be cleared of water, fracking fluids, condensate, and oil and natural gas that are generated in the fracking process in order to allow natural gas to pass freely to the surface (flowback process). When the well completion process has been finished, the well pad moves into the production phase whereby the drilled well flows natural gas into the commercial line. When the well stops producing gas, the final process of natural gas drilling comes into place (i.e. well reclamation). During this process, the land surrounding the wellhead must be restored as closely as possible to its original condition (Garfield County EAB, 2007).

2.2 Volatile Organic Compounds (VOCs)

Volatile Organic Compounds (VOCs) are hydrocarbon compounds that are released into the atmosphere as gases from certain solids or liquids. VOCs consist of

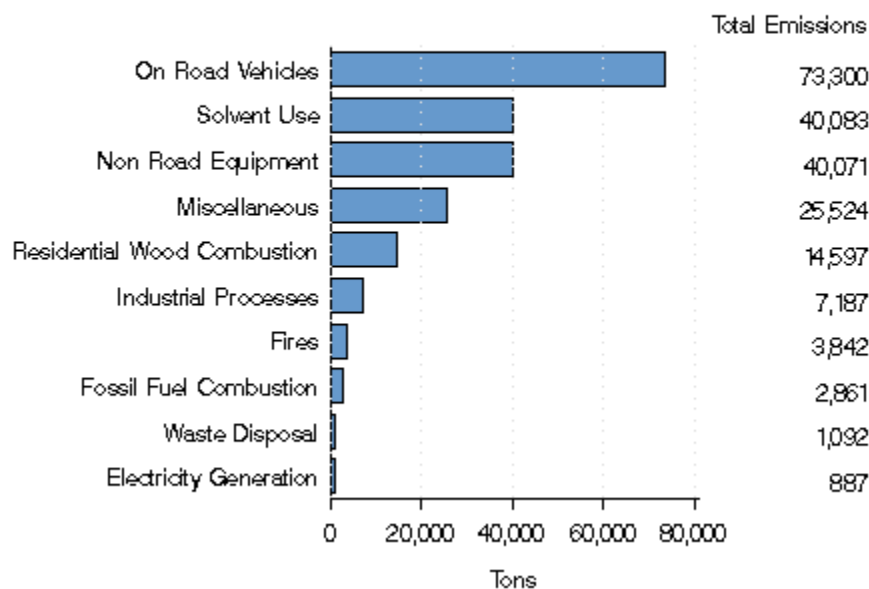
many different chemicals, some of which have short- and long-term adverse health effects (EPA, 2011).

2.2.1 Sources of VOCs

There are many general sources of VOCs, for example: motor vehicle exhaust, waste burning, gasoline marketing, industrial and consumer products, pesticides, degreasing operations, pharmaceutical manufacturing, and by-products from dry cleaning and other industrial operations (California Air Resources Board, 2011). The graph (figure 2.1) below shows the VOCs emissions by a source sector in Colorado in 2005 (EPA, 2005).

Figure 2. 1 VOCs Emissions by Source Sector in Colorado (2005)

Volatile Organic Compounds Emissions by Source Sector in Colorado in 2005



2.3 VOCs from Oil and Gas industry

During the drilling, processing, and delivery of oil and gas, a significant amount of volatile organic compounds are released (EPA, 2011). According to the EPA, oil and gas extraction is classified into five different subsectors regarding VOCs emissions data as shown in Table 2.1 below (EPA, 2011).

Table 2. 1 Oil and Gas Production Subsectors in the U.S.:

Subsector	VOC (tons/year)
Crude Petroleum & Natural Gas	60,040
Natural Gas Liquids	34,195
Drilling Oil And Gas Wells	59
Oil And Gas Exploration Service	12
Oil And Gas Field Services, NEC	243
Total	94,549

Note: Data obtained from the EPA website

A study was conducted by the Texas Environmental Research Consortium (TERC) to measure the speciated VOCs emissions from the oil and condensate wellhead and gathering site storage tanks in East Texas. The total estimated VOC emissions were 1,317 tons per day (TERC, 2009). During oil and gas extraction and distribution, there are abundant opportunities for VOCs to be emitted into the environment, such as venting, flaring, tank emissions, and waste pits.

Venting is considered to be the direct emission of natural gas into the atmosphere. VOCs released from the vents may occur at well sites, oil and gas processing facilities, during the separation and dehydration of natural gas, and at pipelines. Large volumes of VOCs emissions from well sites may be emitted every year. In 2002, gas wells in New Mexico vented more than 20 tons of VOCs to the atmosphere (Pollack, 2006).

On the other hand, flaring is defined as the combustion of natural gas prior discharge to the air. Since the complete combustion of VOCs never takes place even when flaring occurs, some VOCs will be released to the atmosphere (EPA, 2011). A field study conducted in Alberta, Canada found that sweet gas flared at oilfield battery sites burned with an efficiency of only 62 – 71%. Flaring of a sour gas solution, on the other hand, burned with 82-84% efficiency. Hydrocarbons found in the emissions above the flames included benzene, styrene, ethynyl benzene, ethyl-methyl benzenes, toluene, xylenes, and others (Stroscher, 1996). Moreover, VOCs can be emitted from oil and condensate storage tanks. Tank emissions can occur in three different ways: working losses, breathing losses, and flashing losses. As the pressure drops, some of the lighter (volatile) compounds dissolved in the liquids are released or flashed. These flashing losses/VOC emissions are often vented to the atmosphere through a tank's pressure relief valve or hatch (Oklahoma Department of Environmental Quality, 2004). VOCs emissions can be also released from the open waste pits. During drilling, stimulation or well workover, chemicals are injected into a well to perform certain functions (to kill bacteria, prevent pipe corrosion.). A portion of these chemicals return to the surface

with produced water or hydrocarbons. Many of these chemicals are volatile, and consequently, if the produced water is stored in open pits, the chemicals will escape into the atmosphere (TEDX, 2006).

2.4 Studies on VOCs from oil and gas production

Based on a recent study conducted in Colorado, there is a potential of VOCs associated with oil and natural gas production to be released at concentrations that are harmful to human health (CDPHE, 2002). In 2002, concerns raised by citizens in Battlement Mesa, Colorado, prompted the county, state, and the federal government to conduct a coordinated air study to evaluate the air quality around oil and gas sites within Garfield County. In this study, 20 air samples were collected from seven locations, including background. Those locations include two natural gas wells; wells with an active flare location; a residence location; and three other locations. The samples were collected in a two day period during the summer season (May 29-30, 2002). Six liter Summa canisters were used to analyze 42 VOCs by using the EPA method TO-14A for either 24-hour or 8-hour collection periods. The results show that out of 42 VOCs, only six compounds were detected: benzene; methyl ethyl ketone; acetone; toluene; m,p-xylene and o-xylene. None of these compounds were detected at concentrations that would pose a significant health risk to area residents. However, it was agreed that the equipment may not have been sensitive enough to detect a number of other VOCs, therefore other VOCs may have been present (Pierce, 2002).

Another two year study was conducted by Garfield County in 2005 to characterize county wide ambient air quality, as well as localized odor/emission problems from oil and gas facilities. The VOCs monitoring was conducted at fourteen fixed sites (including Parachute) for 24-hours on a once per month or once per quarter basis (from June 2005 to May 2007) using Summa-polished stainless steel canisters (using EPA methods TO-15 and O-14a). In addition, grab samples were also collected for volatile organic compounds at a number of locations based on odor complaints. A total of 89 samples were collected at all sites. (GCPHD & CDPHE, 2007). Forty three VOCs compounds were analyzed, and only 17 VOCs compounds were detected (GCPHD & CDPHE, 2007). BTEX group and acetone recorded the highest concentrations during the sampling period, but in general the VOC samples were extremely low for all samples (GCPHD & CDPHE, 2007). The benzene concentrations measured during the 2002 study (summer season) in Garfield County ranged from 0-6.5 $\mu\text{g}/\text{m}^3$. In the 2005, 89 samples had been taken in the second air quality study. The average benzene level was 5.7 $\mu\text{g}/\text{m}^3$, but the maximum reading was 180 $\mu\text{g}/\text{m}^3$ which can cause adverse health effects (i.e. increased risk for cancer) to the residents in that area. For the Parachute area, the average benzene level during the 2-year period study was 3 $\mu\text{g}/\text{m}^3$ (2005-2007) while in the summer of 2002 (May 29-30) the average benzene level was only 2.2 $\mu\text{g}/\text{m}^3$.

According to the Garfield County Emissions Inventory Report conducted in 2009 by the Colorado Department of Public Health and Environment (CDPHE), VOCs excluding benzene (benzene was reported separately) had the highest percentage of emissions (48%) as compared to the other sources (i.e. CO, NO₂, SO₂, PM₁₀ and benzene) in

Garfield County in 2007 (CDPHE, 2009). Oil and gas area and point sources were reported as the second highest contributor to VOCs emissions after biogenic sources as compared to other contributors such as highway vehicles, non-road, wood burning, railroads, and other point sources (CDPHE, 2009). Benzene was a very small annual emission, but dominated the oil and gas point source category with 67% compared to all other sources (CDPHE, 2009). Also, oil and gas stationary sources in Garfield County are 85% of the total stationary sources which include sand and gravel, gasoline services stations and other sources (CDPHE, 2009). Table 2.2 below shows the estimated Garfield County VOCs emissions (area sources) from oil and gas activities in 2002 and 2004. The estimated emissions were taken at different area sources such as drill rig engines, well completions, and pneumatic devices. The total estimated emissions in 2004 were higher than 2002 and that could be because of the development of new oil and gas well sites (CDPHE, 2009).

Table 2. 2: Comparison of VOCs Emissions between 2002 and 2004 in Garfield County

VOCs tons/year 2002				VOCs tons/year 2004			
Wellsite tanks	Wellsite pneumatic devices	Gas well completion	Total	Wellsite tanks	Wellsite pneumatic devices	Gas well completion	Total
56	252	2,852	3,160	74	334	3,790	4,198

Recently, Garfield County conducted an annual air quality monitoring study for the 2009 period (Jan 1st to Dec 31st). The last finalized report was in 2010, and there were five monitoring stations; Parachute, Rifle, Bell-Melton, Brock, and Rulison, which were all in close proximity to oil and gas development in the county. The EPA

Compendium method TO-12 was used to analyze Speciated non-Methane Organic Compounds (SNMOC/VOCs), with 24-hour samples collected at all sites on a 1 in 6 day schedule (total of 60 samples per site). In general, light alkanes were the largest measured compounds, which represented about 85% of total SNMOCs. The annual results showed higher concentrations in the winter and lower concentrations in the summer (Air Specialists Resources, 2010). The differences in temperature are the main reason for seasonal variations, as VOCs diminish faster during the summer due to higher reactivity at higher temperatures (ASR Inc., 2010). There is another factor that can affect the concentrations during the winter: other emission sources, including cold start engines and residential wood burning which are higher during the winter (ASR Inc., 2010). A comparison between 2008 and 2009 annual average SNMOCs found the total measured SNMOCs levels were lower at all sites in 2009 than 2008. One explanation for this substantial decline in Garfield and elsewhere is due to worldwide recession and depressed natural gas prices. Other reason is decreasing light alkane concentrations which are primary components of natural gas (ARS Inc., 2010). During this study, light alkanes made up between 83% and 89% of the total SNMOCs (ARS Inc., 2010). VOCs emissions can contribute to ozone (O₃) formation when there are photochemical interactions with nitrogen oxides in the presence of the sunlight (ARS Inc., 2010). Light alkanes; however, are some of the least reactive in terms of ozone formation, but the large quantities of these compounds increase the potential for ozone formation (ARS Inc., 2010).

On August 20, 2010, Antero Resources Inc. responded to a request from the Colorado Department of Public Health and Environment (CDPHE) to conduct an air sampling study to collect 24-hour ambient air samples for analysis of speciated non-methane organic compounds/volatile organic compound ("SNMOCs/VOCs") at the Watson Ranch Pad in the Battlement Mesa area near Parachute, Colorado. The SNMOCs samples were collected using EPA method TO-12. The air monitoring data was collected during the fracking/flowback phases of well development. Sampling events were conducted in a one day period (August 19-20, 2010). During the sampling event 12 wells had already been drilled, eight of the wells were on sales, two wells were undergoing fracture stimulation (being "frac'd") and three wells were on flowback. The working and breathing losses and flash vapors from condensate and produced water tanks generated by the eight wells on sales were being collected and routed to a combustor (ARS Inc., 2010).

In this study, airborne concentrations of air pollutants were measured at set back locations that reflect Colorado Oil and Gas Conservation Commission (COGCC) regulatory set back rules from occupied structures (350ft), and Antero's proposed set back distances (500ft). Those air samples were collected for the four cardinal directions around the Watson Ranch Pad (WRP) for total of 10 samples. Two samples were also collected close to a resident house in the southeast side of WRP, but the results of these two samples were similar to those collected at the east side. Table 2.3 provides some average selected SNMOCs (i.e. three top highest compounds & BTEX) results that were

obtained during the well completion and flow back operations of the well development process at the WRP.

Table 2. 3: Selected (Most abundant) SNMOCs levels ($\mu\text{g}/\text{m}^3$) at the west side of WRP

Chemical/ Direction	West		East		North		South	
	350 ft	500 ft	350 ft	500 ft	350 ft	500 ft	350 ft	500 ft
Ethane	271.0	220.0	108.8	107.0	89.77	76.24	123.0	102.06
Propane	118.4	97.4	52.11	51.09	42.86	37.51	56.87	47.96
Isobutane	38.0	31.3	17.47	17.00	14.55	12.83	18.72	15.92
Benzene	7.6	6.2	2.45	2.19	2.24	19.91	2.74	2.22
Toluene	31.4	24.7	7.53	6.51	7.60	112.5	8.56	6.65
Ethylbenzene	3.2	2.4	0.65	0.51	0.71	5.48	0.922	0.76
o-Xylene	6.8	5.1	1.20	0.68	1.22	7.81	1.24	0.93
m,p-Xylene	45.2	36.5	7.71	4.76	7.76	77.61	7.81	6.24

As table 2.3 shows, compounds that were collected at 350 feet from the well pad generally had higher concentrations than 500 feet setback at all directions. The west side of the WRP had the highest concentrations among all sites while the north side had the lowest SNMOCs levels.

2.5 Health Effects of VOCs

VOCs are organic chemical compounds that evaporate easily (volatile) at ambient temperatures (California Air Resources Board, 2006). Some VOCs could be

highly reactive and play a significant role in ozone formation. Other VOCs have adverse chronic and acute health effects. In some cases, VOCs can be both highly reactive and potentially toxic (CARB, 2006). Benzene, toluene, ethylbenzene, xylenes (BTEX), and 1-3 butadienes are examples of harmful VOCs.

The Childhood Cancers and Atmospheric Carcinogens study conducted by British researchers have found that “(1) that childhood cancers and leukemia in Great Britain exhibit geographical clustering of birth places; (2) they occur at increased densities around industrial sites with large scale combustion processes or using volatile organic compounds (VOCs)” (Knox, 2005). The author concluded that there is a significant association between childhood cancers/leukemia births and the atmospheric emissions (particularly, 1-3, butadiene, dioxins and benz(a)pyrene) from combustion processes, mainly from oil and organic evaporation (Knox, 2005).

In 2008, the University of Colorado School of Public Health (CSPH), Denver conducted a study to evaluate human health effects related to oil and gas development in neighborhood communities. They reviewed data and scientific articles related to oil and gas development. In general, they found that the chemicals being used and produced pose potential health risks to the residents (Witter et al., 2008). They have studied different oil and gas contaminants such as particulate matter, hydrogen sulfide, diesel fuel, and VOCs. Based on the materials reviewed for VOCs health effects, CSPH concluded with the following points:

- Benzene is a human carcinogen at lower levels of exposures than what have been reported in past times. As a result, residents near oil and gas production

sites are at risk for leukemia from those exposures. In addition, the halogenated hydrocarbons with low molecular weight are observed to cause liver, kidney and neurological disease, and likely increase renal and other cancers (Blocmen et al., 2004; Collins et al., 2003; Glass et al., 2003)

- Confirmations of cognitive and behavioral abnormalities and alterations in special sense function (such as impairment of color vision and perception) have been reported in occupationally exposed workers from these materials (Ray et al., 2007; Seniori et al, 2003).
- There was not adequate evidence to support that children are at an increased risk for fetal and neonatal impacts of these chemicals (Fevotte et al, 2006; Knox E. G., 2005).

The following section discusses the health effects of selected VOCs that are known to be associated with oil and gas development such as 1,3-Butadiene and BTEX compounds. The health effects are going to be based on the inhalation route of exposure but not on other routes of exposure.

1,3-Butadiene: 1,3-butadiene can be found at low levels in the ambient air around urban and suburban areas (EPA, 2000). However, higher levels of this chemical can be found in highly industrialized cities or near oil and gas facilities (ATSDR, 2007). At acute (short term) exposure by inhalation of elevated levels (i.e. >11mg/m³-STEL) to the 1,3-butadiene, irritation of the eyes, nasal passage, throat, and lungs may occur (ATSDR, 2007). For example, OSHA set a short-term exposure limit (STEL) for the 1,3-butadiene

that should not exceed 11 milligrams per cubic meter for 15 minutes time weighed average (TWA) (OSHA, 1998). There are some studies that demonstrated possible association between the long-term exposure to the 1,3-butadiene and cardiovascular disease (ATSDR, 2007). 1,3-butadiene has been classified by EPA as probable human carcinogen (Group B2) (EPA, 2000).

BTEX chemicals in general can cause central nervous system problems, skin irritation and effects on the respiratory system at short term exposure (ATSDR, 2007). In addition to these health problems, prolonged exposure to these compounds can also affect liver, kidney and blood systems (ATSDR, 2007).

Benzene: The Department of Health and Human Services (HHS) and the EPA have determined that benzene is a known human carcinogen (EPA, 2002). To minimize the potential for leukemogenesis posed by occupational exposure, a TLV-TWA of 1.6 mg/m³ and a TLV-STEL of 8 mg/m³ are recommended (Paxton M.B, 1994; Crump K., 1994). Exposures to high levels of benzene in occupational settings were found to have an increased occurrence of leukemia (EPA, 2002). The latency period for benzene induction of human leukemia has been reported from 2 to 50 years (Aksoy, 1985). Most known symptoms of acute exposure are dizziness, headaches, vomiting, loss of balance, and death (CAPP, 2006). Prolonged exposure to benzene primarily affects the skin (e.g., redness, drying) and blood system. A specific type of leukemia called acute myelogenous leukemia and other forms of leukemia may also occur by being exposed to benzene at a higher incidence rate (CAPP, 2006). The health effects of benzene may be increased if it is exposed with other chemicals (interference with other chemicals). For

example, if benzene is exposed to toluene at the same time, the toluene will decrease the ability of the body to remove benzene by competing with benzene for metabolic pathways (CAPP, 2006).

Toluene: The primary health effects of toluene are central nervous system problems for both short and long term exposures (EPA, 2000). Common symptoms of CNS problems from acute inhalation include fatigue, headache and nausea (EPA, 2000). Long term exposure causes irritation of upper respiratory tract and eyes, sore throat, dizziness, and headache. A TLV-TWA of 75 mg/m^3 is recommended to protect workers from Central Nervous System symptoms, and cardiac, renal and hepatic toxicities (Campagna, 2001). Studies have shown association between toluene exposure and health problems with newborn babies and pregnant women. Another association with increased incidence of spontaneous abortions was also found. However, these studies have not been concluded, as the EPA noted (EPA, 2000).

Ethylbenzene: Respiratory problems, such as throat irritation and chest constriction, as well as irritation of the eyes, and dizziness may result due to short-term exposure to ethylbenzene (EPA, 2000). Animal studies have shown effects on the blood, liver, and kidneys from chronic inhalation exposure to ethylbenzene (EPA, 2000). A TLV-TWA of 434 mg/m^3 and a TLV-STEL of 543 mg/m^3 are recommended to minimize the potential risks of disagreeable irritations (Bardodej Z, 1961).

Xylene: Acute exposure to xylene by inhalation causes irritation of eyes, nose, and gastrointestinal effects. Chronic inhalation exposure results in central nervous system (CNS) effects, such as headaches, dizziness, tremors and decrease in

coordination. Other health effects such as respiratory, cardiovascular and kidney have also been reported (EPA, 2000). A TLV-TWA of 434 mg/m³ and a TLV-STEL of 651 mg/m³ are recommended for occupational exposure to all isomers of xylene to minimize the potential for eye and upper respiratory tract irritation (ATSDR, 1990; Carpenter et al., 1975). These values also should provide substantial protection from necrosis, gastrointestinal disturbances, and chronic effects believed to result from exposure to higher concentrations (ATSDR, 1990).

2.6 Regulations of VOCs:

VOCs related to the oil and gas industry are regulated as air, soil, and water pollutants. A number of the VOCs emitted from oil and gas facilities are regulated as toxic air contaminants under the federal Clean Air Act. These compounds include BTEX, hexane, formaldehyde, and 1,3-butadiene. The U.S. EPA, Region 9, has developed Risk Based Concentration (RBC) guidelines for a number of air contaminants at Superfund Sites. These concentrations, known as Regional Screening Levels (RSLs) are believed to be protective of human health for the broader community population. The EPA uses the RSL concentrations as a screening tool. If the concentrations of the air contaminants are below the RSL concentrations, the EPA generally will not require any action to further reduce concentrations. The EPA has set ambient air RSLs for a number of VOCs. The Table 2.4 below includes some examples of RSL concentrations.

Table 2. 4: EPA Risk Based Concentrations for BTEX, and CalEPA RELs

Chemical	Risk Based Ambient Air Concentration $\mu\text{g}/\text{m}^3$		CalEPA RELs (December 2008)		
	Carcinogenic SL TR=1.0E-6	Non-Carcinogenic SL HI=1	Acute ($\mu\text{g}/\text{m}^3$)	8-hour	Chronic ($\mu\text{g}/\text{m}^3$)
Benzene	0.31	31	1,300	NA	60
Toluene	NA	5200	37,000	NA	300
Ethylbenzene	0.97	1000	NA	NA	2000
Xylene	NA	100	22,000	NA	700

Note: Acute: 1 hour averaging time

8-hour: 8 hours averaging time

Chronic: continuous exposures for up to lifetime

SL: Screening Level

TR: Target Risk

HI: Hazard Index

Chronic inhalation reference exposure levels for many air contaminants, including a number of VOCs, have been established by the California Environmental Protection Agency (CalEPA) (OEHHA, 2008). For example, they have established an inhalation reference exposure level of $60 \mu\text{g}/\text{m}^3$ for benzene based on hematological effects in humans (CalEPA, 2000). The CalEPA reference exposure level is a concentration at or below where adverse health effects are not likely to occur. Table 2.4 also shows the CalEPA's acute, 8-hour and chronic Reference Exposure Levels (RELs) for the BTEX group.

For some VOCs, occupational exposure limits have been set to protect worker health. In some cases, the limits are "advisory," e.g., those provided by the American

Conference of Governmental and Industrial Hygienist (ACGIH) (TLV booklet, 2009), and National Institute of Occupational Safety and Health (NIOSH). Other exposure limits, such as those set by the Occupational Safety and Health Administration (OSHA), are government regulations. Those occupational limits are different from the general public limits because they are designed to protect youthful healthy workers while the community limits are designed to protect the all of the public: elderly, children, and people with impairment (such as asthma). Examples of those occupational exposure limits are presented in table 2.5 below.

Table 2. 5: Examples of health and safety based exposure limits (Occupational Settings) for selected VOCs (i.e. BTEX)

Compound	TLVs TWA (mg/m³)	OSHA PEL (mg/m³)	NIOSH REL (mg/m³)
Benzene	1.6	3.2	0.32
Toluene	75	754	375
Ethylbenzene	434	435	435
O-Xylene	434	435	435

Note:

ACGIH TLV--American Conference of Governmental and Industrial Hygienists' threshold limit value expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effects.

NIOSH REL--National Institute of Occupational Safety and Health's recommended exposure limit; NIOSH-recommended exposure limit for an 8- or 10-h time-weighted-average exposure and/or ceiling

OSHA PEL--Occupational Safety and Health Administration's permissible exposure limit expressed as a time-weighted average; the concentration of a substance to which most workers can be exposed without adverse effect averaged over a normal 8-h workday or a 40-h workweek (EPA).

2.7 Fine Particulate Matter (PM_{2.5})

2.7.1 Sources of PM_{2.5}

The term Particulate Matter (PM) is used to describe a mixture of solid particles and liquid droplets in the air which include aerosols, smoke, fumes, dust, ash, and pollen (EPA, 2008). Fine particulate matter is particulate matter that is 2.5 micrometers in diameter and smaller (EPA, 2008). PM_{2.5} is one of the main air pollution concerns affecting the environment. The major components of PM_{2.5} include sulphates, carbonaceous materials, nitrates, trace elements, and water. PM_{2.5} can be classified by source as primary and secondary particles. Examples of primary particles are particles that come from wood burning and vehicle exhaust including cars and diesel trucks. Secondary particles can be formed in the atmosphere through chemical reactions of pollutant gases such as Volatile Organic Compounds (VOCs), Sulfur Oxides (Sox) and Nitrogen Oxides (NOx) (Chang and England, 2003).

2.8 PM_{2.5} in Oil and Gas Industry

According to the US EPA, the majority of PM_{2.5} ambient loading was on oil and gas industry attributed to fugitive dust emissions (34%) while the industrial processes and fuel combustion were responsible for 12% and 10% respectively (EPA, 2003). The major contributor to the PM_{2.5} levels in the oil and gas industry is the combustion processes. There are two sources of combustion: internal combustion sources (e.g. diesel fired engines) and external combustion sources (e.g. combustion flare). Oil and gas development operations such as well drilling and completion activities produce

emissions from diesel engines (trucks and drilling rigs) that are within the PM_{2.5} size fraction (EPA, 2008).

A regional case study was conducted by the EPA (2008) to assess the environmental implications of oil and gas production in Region 8 (CO, WY, UT, MT, SD, ND). According to this study, PM emissions from the oil and gas industry in Region 8 are insignificant, less than 0.1 percent of regional total, despite the fact that some of the areas in Region 8 exceeded the standards. However, those estimates are not very reliable due to limited data and variable definitions of the different kinds of PM. Between the years of 2002 and 2006, Colorado recorded a significant increase (28%) in criteria pollutant emissions from production including PM due to the rapid increase of oil and gas production in the region. PM has been one of the fastest growing criteria pollutants, and it is projected to increase by 27 percent in the next four-year period (CDPHE, 2007).

An ambient air quality monitoring study was conducted by the CDPHE in Garfield County from June 2005 through May 2007 in 7 different sites including Parachute. The main purpose of this study was to evaluate air quality with particular attention to PM of 10 microns or less and VOCs. PM₁₀ was sampled on an every third day basis for 24-hours. PM₁₀ sampling was performed using Andersen model 1200 high-volume samplers that are designated by the EPA as reference samplers for PM₁₀. Results show no violations of the 24-hour NAAQS of 150 µg/m³ were observed. In general, the 24-hour concentrations were 50 percent less than the NAAQS. For the same study, comparisons were made to other areas for PM₁₀, including Grand Junction, Delta, Aspen and Denver.

The comparisons were made between western Colorado areas and a large urban area. The results show that PM₁₀ levels in Garfield County are generally similar to or lower than concentrations in other areas of Colorado. Also, during the same period, filters from two sampling days (7/18/2005&1/11/2006) were analyzed to determine the potential sources of PM₁₀. They found that geologic material is the primary component of PM₁₀ particulate matter in the ambient air. They also concluded that the main source of carbon in the samples is the lighter weight fossil fuel combustion (CDPHE, 2007).

Another air toxic study was carried by the CDPHE in the summer of 2008. The ultimate goal was to set a basis for managing the impacts of air pollution caused by energy development in Garfield County. During the study, fine particulate matter (PM_{2.5}) was monitored for 24-hour periods during the highest levels of activity for a given energy development operation. A MiniVol Portable Air Sampler (Airmetrics) and gravimetric analysis were used to measure the PM_{2.5} levels. The sampling events took place at eight different sites, including one site located on the north side of the Parachute/Battlement Mesa area. The results show that all the values obtained at all 8 sites were well below the value of the 24-hour maximum exposure EPA standard for PM_{2.5} of 35 µg/m³. The well pad average concentrations ranged from 7.3 µg/m³ to 9.3 µg/m³, and the highest particulate concentration was recorded as 11.4 µg/m³. At the Parachute/ Battlement Mesa site, the concentrations fell in the 7 to 9 microgram per cubic meter range (CDPHE, 2009).

A recent air quality monitoring report was published by Garfield County Public Health Department (GCPHE) in 2010, and five monitoring stations were selected, which

include Parachute, Rifle, Bell-Melton, Brock, and Rulison. The PM samples were collected for 24-hour periods during 2009. Two methods were adopted in this study to collect the particulate matters: The Rupprecht and Patashnick Tapered Element Oscillating MicroBalance (TEOM), and the Federal Reference Method (FRM). The following table (Table 2.6) lists the summary results for particulates (PM₁₀ & PM_{2.5}) at Parachute and Rifle sites. Overall, the air quality measurements did not exceed the NAAQS for particulates (GCPHE, 2010).

Table 2. 6: 2009 Particulate levels at Rifle and Parachute

Site	Parameter	Frequency of detection	NAAQS		Measured	Date
			Averaging time	Standard		
Rifle	PM2.5	Hourly	Annual	15 µg/m ³	Arithmetic Mean: 9.0 µg/m ³	1/1-12/31
			24-hour	35 µg/m ³	Highest Max: 41 µg/m ³	1/2
	PM10	24-hour (1/3 day)+ hourly	24-hour	150 µg/m ³	Highest daily max.: 83 µg/m ³	3/29
Parachute	PM10	24-hour (1/3 day)	24-hour	150 ug/m3	Highest daily max.: 88 ug/m3	3/29

2.9 Health Effects of PM_{2.5}

Exposure to PM_{2.5} can have serious health effects. Fine particles are most closely associated with many health problems such as increased respiratory disease, decreased lung function, and even premature death (Pope et al, 2002; Gauderman et al, 2004; Kunizli et al, 2005). Fine particulate matter can be carried deeper into the lungs when inhaled due to their small size. These small particles are also able to carry toxic pollutants and penetrate to other parts in the body as they flow in the blood (Witter et al, 2008).

PM_{2.5} health effects are usually observed by conducting the epidemiological studies that attempt to find statistical associations between air pollution levels and health outcomes. Epidemiological studies play an important role in setting health and regulatory standards (Aunan, 1996). The following is a brief review of the epidemiological literature, both acute and chronic, on PM_{2.5} and its health effects.

A number of health effects are related to the acute impacts of PM_{2.5}. The increase in the mortality rate and the numbers of people admitted to hospital for cardiovascular or respiratory diseases have been linked to acute increases in ambient PM_{2.5} (Atkinson et al. 1999; Lipfert et al. 2000; Schwartz et al. 1996). The association between the daily mortality rate and the effects of five major air pollutants (PM, O₃, CO₂, SO₂, and NO₂) were assessed by Samet et al. in 2000 in twenty of the largest cities in the United States from 1987 to 1994. They concluded that for each increase in the PM (includes PM_{2.5}) level of 10ug/m³, there was an estimate increasing about 0.68 percent in the relative mortality rate from cardiovascular and respiratory causes. A strong

association has been confirmed between acute $PM_{2.5}$ levels with a number of harmful influences to individuals with asthma or other respiratory problems (McConnell et al. 1999; Peters et al. 1997; Wichmann and Peters 2000). High levels of acute $PM_{2.5}$ can affect the patient with cardiovascular problems and diabetes (Zeka et al. 2005).

Studies have also found an association between the long term $PM_{2.5}$ exposure (chronic) and health effects. To examine the chronic $PM_{2.5}$ impacts on health, the polluted cities were compared to clean cities and their associated life expectancy rates (Laden et al. 2000; Samet et al. 2000; Abbey et al. 1999; Hoek et al. 2002; Pope 2000). They found that polluted cities had higher deaths than expected and lower life expectancy by population than cleaner cities. They also found that increases in $PM_{2.5}$ were positively linked to increased mortality rates. Other health effects such as pulmonary function, cardiovascular morbidity, respiratory illness, and cancer have also been examined but there was not complete agreement on the findings (Pope, 2000).

2.10 Regulations of $PM_{2.5}$

Fine particulate matter ($PM_{2.5}$) is one pollutant of the six criteria pollutants that is regulated under National Ambient Air Quality Standards (NAAQS). The Clean Air Act requires the EPA to set two types of NAAQS for criteria pollutants (ground-level O_3 , particle pollution ($PM_{2.5}$ and PM_{10}), lead, NO_2 , carbon monoxide (CO), and sulfur dioxide (SO_2)). The types of standards are as follows:

- **Primary Standards:** These standards are designed to protect public health with an adequate margin of safety, including the health of sensitive populations such as asthmatics, children, and the elderly.
- **Secondary Standards:** These standards are designed to protect public welfare from adverse effects, including visibility impairment and effects on the environment (e.g., vegetation, soils, water, and wildlife).

The EPA adopted the first national air quality standards for the fine fraction of particulates, $PM_{2.5}$, in July 1997. The EPA set the annual $PM_{2.5}$ standard at 15 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) and the 24-hour $PM_{2.5}$ standard set at 65 $\mu\text{g}/\text{m}^3$ (EPA, 2011). In September 2006, the EPA revised the 24-hour $PM_{2.5}$ primary and secondary NAAQS from 65 $\mu\text{g}/\text{m}^3$ to 35 $\mu\text{g}/\text{m}^3$, and retained the existing annual arithmetic mean $PM_{2.5}$ standard of 15 $\mu\text{g}/\text{m}^3$ (EPA, 2011). A violation of the $PM_{2.5}$ standard occurs when the 3-year average of the weighted annual mean exceeds that annual standard, or the 3-year average of the 98th percentile 24-hour average value exceeds the 24-hour standard (EPA, 2011) . Table 2.7 below summarizes the NAAQS for $PM_{2.5}$.

Table 2.7: NAAQS for $PM_{2.5}$

Pollutant	Primary Standards		Secondary Standards	
	Level	Averaging time	level	Averaging time
$PM_{2.5}$	15 $\mu\text{g}/\text{m}^3$	Annual (arithmetic Mean)	Same as primary	
	35 $\mu\text{g}/\text{m}^3$	24-hour	Same as primary	

CHAPTER 3: PURPOSE AND SCOPE

3.1 Purpose:

Natural gas development and production is growing rapidly on the western slope of Colorado. Many of those operations take place in close proximity to residential areas. Human habitation and activity close to oil and gas production sites increases the chance that people will be exposed to the hazardous chemicals, emissions, and pollutants associated with these activities. This situation has raised public health concerns. In particular, residents of Battlement Mesa have been concerned with the prospect of the drilling of too many natural gas wells for development and production in their community. One of the most affected residents near the Watson Ranch Pad was willing to participate in a pilot study to evaluate airborne concentrations on his property.

This study was performed to pilot test methods and collect preliminary data that can be used to develop a more comprehensive study that could attempt to address concerns from the local citizen about air pollution and potential health effect, primarily due to dramatic increases in oil and gas development activity around the region.

3.2 Goals of the Study and Research Hypothesis:

Goals of the study:

1. Determine air concentrations of speciated non-methane organic compounds (SNMOCs, including benzene, toluene, ethylbenzene, and xylenes), total VOCs, and particulate matter (PM_{2.5}) at distance of about 800-1200 feet from a well pad that has 12 wells producing natural gas.
2. Determine if air concentrations of SNMOCs, PM_{2.5} and TVOCs levels are higher than background concentrations/levels during the production phase of well development process.
3. Determine if air concentrations of SNOMCs, PM_{2.5} and TVOCs decrease with setback distance (i.e. between UP and DN site)
4. The air quality data and lessons learned from conducting this first field pilot study can be used to plan future research for a comprehensive project.

Research Hypothesis:

H₀: *there are no measurable VOCs, Particulates on the resident property area (approximately 800- 1200 feet) affected by production activities of 12 producing wells on Watson Ranch Pad site compared to the background levels.*

H_A : *there are measurable VOCs, Particulates on the resident property area (800-1200 feet) affected by production activities of 12 producing wells on Watson Ranch Pad site compared to the background levels.*

Site Background: refers to a location that is not influenced by the releases of the production activities from Watson Ranch Pad site. This location is the Battlement Mesa fire house which is about a half mile from the site.

3.3 Scope:

The private house was chosen for this study for two reasons: one is the proximity of the house location to the well pad (nearest distance to the well pad), and the second is the resident's willingness to participate in this study to evaluate air pollutants around his property. Two different locations around the house were sampled: upstream of the house which is very close to the well pad (800feet) and downstream of the house which is the farthest from the well pad (1200feet); in addition to the background site (Battement Mesa Fire House-2400feet). Four parameters were evaluated during the study: Speciated Non-methane Organic Compounds (SNMOC/VOCs), Particulate Matter ($PM_{2.5}$), total VOCs, and meteorological data. Sampling events were carried out for four consecutive days starting on February 7, 2011. Evaluation days at the private house were chosen based upon the time constraints imposed by the sponsor and the thesis requirements.

Chapter 4: Materials and Methods

4.1 Project location:

Samples were collected upstream and downstream of the private residential property located at the west side of the perimeter of Antero Resource's (Antero) Watson Ranch pad (WRP), as illustrated on Figure 4.1 below, which is located at the Southwest border of Battlement Mesa. A photo of the landscape of the WRP and sampling set up is shown on figure 4.2. The sampling location is about 800-1000 feet from the well pad (≈ 800 ft from the fence, and ≈ 1000 ft from a nearby house). A single sample was also collected at the Battlement Mesa fire house each day as background. Those sampling locations including the background site were selected based on history of that sampling area. More specifically, the fire station has been used by Garfield County as a background site for many years in that area. GPS coordinates were taken at each sample location. The table 4.1 below shows the exact location for each sampling site:

Table 4. 1 Sampling Locations

Location	Distance (away from the well pad)	Coordinates -Latitude -Longitude
Upstream	800 feet	-N 39 25.975 -W 108 1.677
Downstream	1200 feet	-N 39 25.916 -W 108 1.768
Fire house	2400 feet	-N 39 27.388 -W 108 3.121

Figure 4. 1 Sampling Sites Map

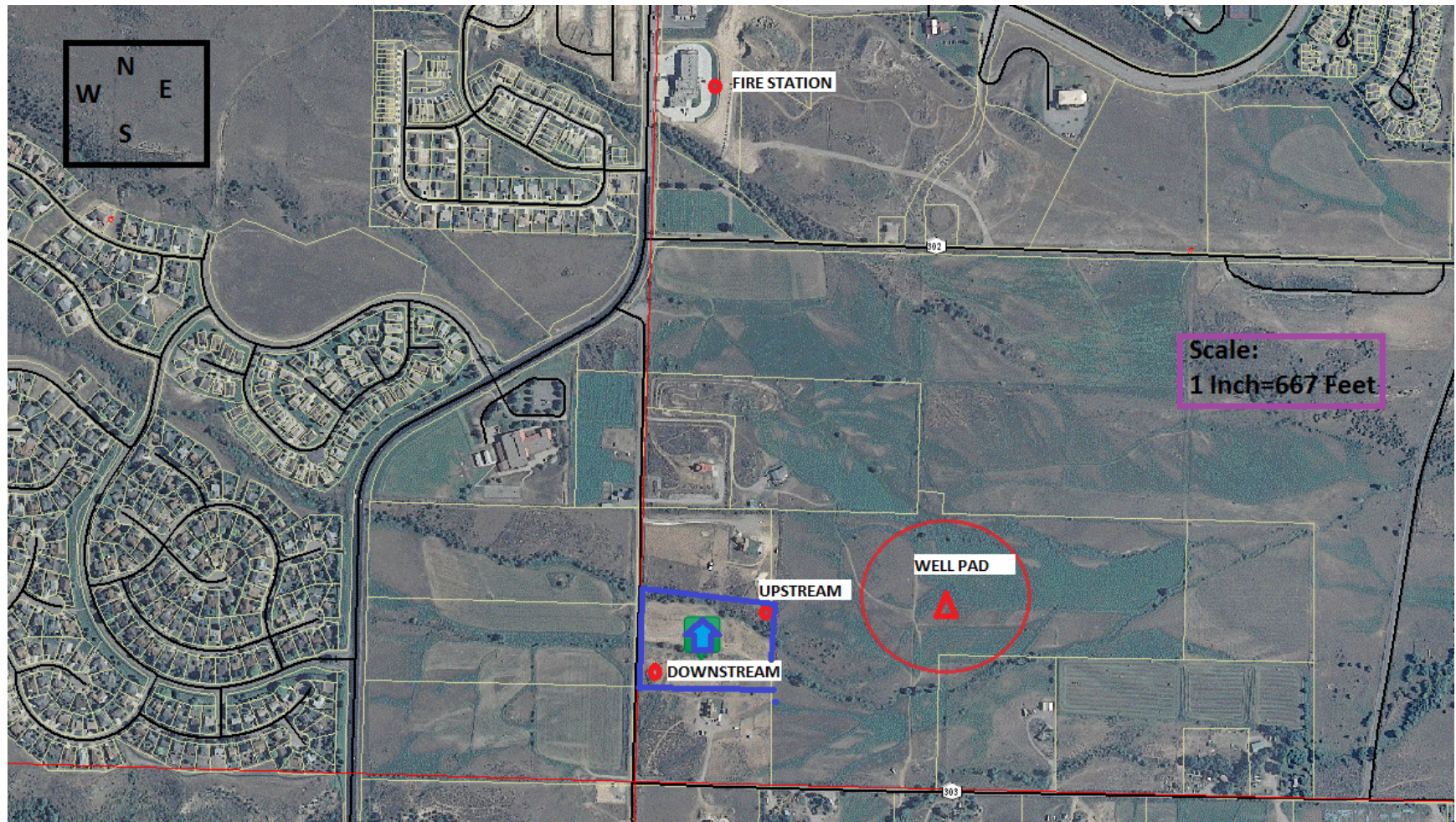
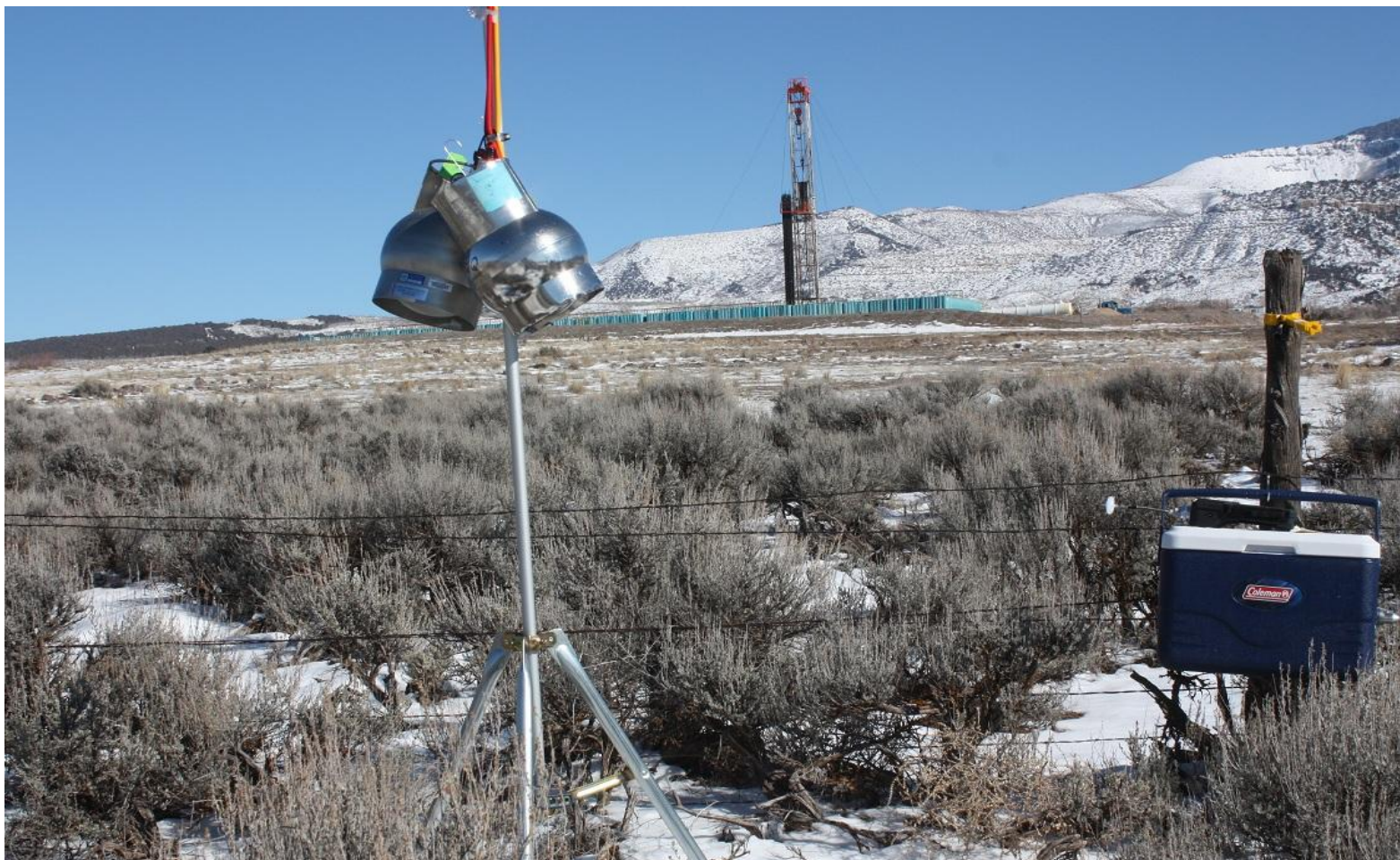


Figure 4. 2: WRP Landscape and sampling set up.



4.2 Sampling and Analytical Methods:

A summary of the sampling and analytical methods is presented in Table 4.2 and the following sections.

Table 4. 2: Summary of Sampling and Analytical Methods

Parameter	Sampling Method	Analytical Method
Speciated Non-methane Organic Compounds (SNMOCs)	Modified EPA Method TO-12 (Suma canister)	Modified EPA Method TO-12
Particulate Matter (PM _{2.5})	Personal Data Ram (pDR)	Photometer
Total Volatile Organic Compounds (VOCs)	Rae 3000 photo ionization detector (PID)	Photo ionization detector in the Rae logs real time level.
Meteorological Data	Weather Station at the fire station (RainWise MK- III)	Not applicable

4.2.1 Task Description:

Sampling activities were conducted on February 7-10, 2011 at the Watson Ranch Pad (WRP) location. The sampling took place at three different sites: upstream and downstream of the residential house and background samples were collected at the fire station. Table 4.3 below summarizes samples collected during the four days period.

Table 4. 3: Summary of Sample Collection

Day/location	Day 1	Day 2	Day 3	Day 4	TOTAL
SNMOC					
Upstream	1	1	1	1	4
Downstream	1	1	1	1	4
Fire station	1	1	1	1	4
Field duplicate	1	1	1	2	5
Field blank	1	-	-	-	1
TOTAL	5	4	4	5	18
PM_{2.5}					
Upstream	1	1	1	1	4
Downstream	1	1	1	1	4
Fire station	1	1	1	1	4
Field duplicate	-	-	-	-	-
blank	1	1	1	1	4
TOTAL	4	4	4	4	16

4.3 Speciated Non-Methane Organic Compounds (SNMOCs) Sampling:

Ambient air samples for SNMOC analysis were collected using six-liter stainless steel sample canisters with a preset stainless steel flow control orifice (Air Toxics LTD thru ERG, Folsom, CA). The EPA Method for the Determination of Non-Methane Organic Compounds in Ambient Air Using Cryogenic Preconcentration and Direct Flame

Ionization Detection (GC/FID) ("EPA Method TO-12") procedures were used during sampling and analytical activities and are described below.

Stainless steel sample canisters were cleaned and evacuated to approximately 29.5 inches of mercury ("Hg) by the Eastern Research Group (ERG) per EPA Method TO-12. Also, a pre-calibration was done for the canister's flow to maintain it to be about 3.2 cc/min in order to yield final sample pressure in a canister 6 to 7 "Hg which is the target final pressure for EPA SAT program. However, the final sample pressures between 1 and 10 "Hg are still considered valid samples. The sample canisters were batch tested prior to being shipped to Garfield County Public Health Department (GCPHD). Then the sample canisters were shipped to the Garfield County Public Health department in Rifle, Colorado and arrived intact and sealed (valves closed and inlet ports capped). Upon arriving, each canister and the other sampling equipment were inspected for condition and completeness of shipments. At the private residential land, each canister was unpacked and carried to a sampling location while still sealed.

At the sampling site, each sample canister was placed approximately three feet from the ground level by hanging the canister on a tripod as seen in the figure 4.2. A depiction of the sample canister locations can be found in Figure 4.1. At each sample location, the inlet port cap was removed from the sampling canister and a clean vacuum pressure gage was attached to the canister inlet port to measure the initial pressure. Then the gage was removed after the pressure reading was taken. A flow regulator was used for each canister during the sampling event. Once the sampling train connections were all properly assembled to avoid leaks, the canister valve was opened to begin

sample collection. The first sample collection period began at 12:00 p.m. on February 7, 2011 and ended at 10:00 a.m. on February 8, 2010. Sample collection start and end times are shown in the appendix 4.1.

Once the sampling was taking place, the initial vacuum reading, canister serial number, and time was recorded in a field book. The sample identifier and location was marked on a tag on each canister. After the sample period, the final vacuum reading and time were recorded in a field book at each location; the canister valve was closed; the regulator and pressure gage assembly were removed, and the canister inlet port re-capped. The sample canisters were repackaged and returned to the GCPHD in Rifle for expedited shipment. Finally, the sample canisters were shipped to the ERG lab the next business day by GCPHD.

4.3.1 SNMOC Data Analysis:

Each SNMOC air sample collected throughout the study was analyzed for 78 different compounds. These compounds are listed in Appendix 4.2 along with their Chemical Abstract Service (CAS) parameter code, and the method detection limits for each compound when being analyzed by this particular method, EPA Compendium Method TO-12.

In addition to the listed compounds, the sum of the speciated non-methane organic compounds (SNMOC), the sum of the unknown organic compounds and the total non-methane organic compounds (TNMOC) are also reported. The SNMOC concentrations are broken down into detectable concentrations for each of the 78 species of interest (Appendix 4.2), and their results are then summed to obtain the

value for the total SNMOC. To obtain the sum of the unknown species, the SNMOC value is subtracted from the TNMOC value (Colorado Department of Public Health and Environment (CDPHE), 2009).

The SNMOC, TNMOC, and unknown concentrations are presented in ppbC instead of $\mu\text{g}/\text{m}^3$ throughout this report, as a conversion to $\mu\text{g}/\text{m}^3$ is not possible since the exact number of carbons is not known for the TNMOC concentration. However, individual species concentration data will be presented as $\mu\text{g}/\text{m}^3$ throughout this report, instead of ppbC. This is done in an effort to maintain unit consistency, and to facilitate data comparison.

The Relative Percent Difference (RPD%)

In order to estimate how precisely the field sampling technique measured ambient air concentrations during the four days sampling period, the relative percent difference (RPD) approach was used in this study. The RPD can be calculated by using the following equation:

$$\text{RPD} = \frac{\text{abs}[X_1 - X_2]}{X} \times 100$$

X_1 : ambient air concentration of a given compound measured in one sample

X_2 : ambient air concentration of the same compound measured in a duplicate sample.

X: the arithmetic mean of X_1 and X_2

By this equation, compounds with relatively low measurement variability will have lower RPD and then better precision. Many sampling and analytical methods suggest that monitoring program should be able to achieve RPDs of 30 % or better (less than 30%), if methods are applied correctly.

4.4 Collection of air samples for Particulate Matter (PM_{2.5})

Filter weighing

In order to determine the concentration of an aerosol sample, filters must be weighed before and after the sampling to provide the best estimate of the true total mass of the sample. In the lab, the 37 mm glass fiber filter with air filter cartridge was used to calibrate the concentration estimates of for the direct reading device; personal Data RAM (pDR 1200, Thermo Scientific Corp., Waltham, Mass). Using the pre-weight and the post-weight of the filters and the known volume pulled through the filter by the personal sampling pump, the concentration (mg/m³) of the sample was determined. The detailed SOP for filter weighing is attached in the appendix 4.3.

4.4.1 PM_{2.5} Sampling

Particulate matter was measured using a Personal Data RAM (pDR-1200) as seen in the figure 4.3. It is designed to measure mass concentrations (mg/m³) of airborne particulate matter on a near real-time basis (here we used 1 minute resolution) with continuous read out and data logging of concentrations. The pDR-1200 requires an external sampling pump. The sampling pumps used in this study are SKC Leland Legacy pumps (SKC, Inc. #100-300, Eighty-Four, PA). The pumps operated at 4000 cc per minute (4 l/m) and the batteries of those pumps can run for over 24 hours. The flow rate of the pumps was pre-calibrated at the lab using a Rotameter device (secondary standard device). This rotameter was calibrated against a primary flow measuring device (DryCal-BIOS International Corporation-Butler, NJ) at the lab. The flow rate was also verified in

the field with the Rotameter, and then pump post calibration was performed at the field to ensure accurate measurements. The back-up 37 mm glass fiber filter was used to provide the true mass measured by the pDR and to determine a calibration factor for each unit. PM_{2.5} was sampled upstream and downstream of the landowner house during production operations. Also, PM_{2.5} was measured at the fire station as a background. A field blank was also collected each day to assure quality of the samples.

Figure 4.3: Personal Data RAM-1200



The PM_{2.5} was collected by pDR according to the SOP in Appendix 4.4 as follows:

The first step taken was the pDR identifier was verified on the sample collection form and the log interval was set to be every one minute. Then, the flow rate of the pump was calibrated and adjusted to 4 Liters per minute using the rotameter flow meter. After that, a clean air filter (green zeroing filter) was attached to the pDR cyclone inlet to prove the pDR with particle-free air. To zero the device, the pDR was turned on, and the pDR zero calibration was run by selecting “yes” to the calibration upon starting the unit. Next, the pump was started and the pDR flow rate was allowed to stabilize for at least one minute. When the “CALIBRATION: OK” message appeared on the pDR display, the pump was stopped and the green zeroing filter was disconnected and replaced by the cyclone to get it ready for sampling. After that, the SKC pump was started again for sampling and the starting flow rate was recorded on the sample collection form. Following this step, the data logging was started and the start time was recorded. Both the pump and the pDR were kept inside a cooler to protect the equipment from the weather conditions during the sampling period as shown on figure 4.4. Finally, after 24 hours sampling, the pDR was turned off and then the pump was turned off also. The post flow rate and the end time were recorded in the sample collection form.

Figure 4.4: PM_{2.5} Equipment inside the cooler



4.4.2 PM_{2.5} Data Analysis:

The PM_{2.5} concentration data was reported by the pDR in milligrams per meter cubed ($\mu\text{g}/\text{m}^3$). The concentration values were obtained by dividing the net weight of the particulates that accumulated on the filter over a 24 hour period by the total volume (flow rate*sampling time) of air drawn through the filter over that same 24 hour period. The calibration factor was also calculated by dividing calculated concentration (mg/m^3) by the overall average concentration (mg/m^3) obtained from the pDR. The adjusted (calibrated) concentration was obtained by multiplying the calibration factor by the direct reading measurement (mg/m^3).

4.5 Total Volatile Organic Compounds (TVOCs)

Total volatile organic compounds (TVOCs) was measured in real-time using a ppbRae 3000 Photo Ionization Detector as shown on figure 4.5 (RAE Systems Inc., DeMotte, IN) to supplement the method TO-12 results. The PID provides part-per-billion sensitivity for TVOCs with a detectable range from 0 - 999 ppb. The PID was calibrated in Rifle at an altitude similar to the study site. Ten minute short-term measurements were taken at each sampling location. In addition, the background site was sampled for 10-minutes. The following procedure was followed to measure total VOCs:

- The instrument was turned on by pressing and holding the MODE key
- When the display turned on, the MODE key was released.
- When the screen showed reading, the sampling was on
- When the spot was checking done, the MODE key was pressed and held for 3 seconds
- When the screen display showed “unit off” the finger was released from the MODE key.

Figure 4.5: ppb Rea 3000 PID



4.5.1 Data analysis for TVOCs:

The VOC real-time data obtained were reported as one-minute averages of three parameters: the minimum, average and maximum values obtained during the continuous air sampling. The values are reported in ppbv, so no conversions were necessary. In all future discussion of these data, the average values were used for comparison purposes, instead of the recorded minimums or maximums, except where otherwise noted. These averages were plotted with the wind speed and humidity data obtained from the meteorological equipment to determine any correlations between the data sets.

4.6 Meteorological Data

A RainWise MK-III sensor array and a RainWise CC-2000 computer interface (RainWise Inc., Bar Harbor, ME) were used in this study to collect meteorological data, including temperature, barometric pressure, relative humidity, wind speed, and wind direction. The sensor was located on top of a tripod tower, approximately 3 meters above the ground. The meteorological data was collected at the Battlement Mesa fire house where the background samples were collected which is about 2400 feet from the sampling sites. The sampling frequency of the meteorological data was hourly. This meteorological data is operated by Garfield County Public Health Department (GCPHD).

4.7 Reporting and Documentation Tasks

Reporting and Documentation of Field Activities

All field work data forms, including site maps, sample collection forms and field notebooks were collected and kept on a secure server. Appendix 4.4 contains an example sample collection form.

Reporting and Documentation of Laboratory Activities

ERG lab reported Method TO-12 results to CSU in Excel spreadsheets, as well as a CD summary report that contains the original chain-of-custody form and shipping and tracking manifests. All PM_{2.5} and TVOC data were downloaded into Excel spreadsheets. Meteorological data (date and time stamped wind speed and direction as well as temperature, barometric pressure, and relative humidity) was collected by Garfield

County Public Health (GCPHD) in a dot file and then exported into Excel spreadsheets for analysis.

4.8 Quality Control and Criteria for Measurement Data

Requirements for quality control of our data included training in and use of standard operating procedures to minimize potential contamination, accuracy of field sample and measurement data, completeness of data forms, error-free database records, and peer review of results and interpretations. Sample integrity was maintained throughout the sampling process from preparation of sampling containers at the ERG Lab to the field collection of samples, delivery of samples to the lab, and handling of samples within the lab. Data integrity was similarly maintained throughout the project progress, including collection of field data, transferring of sample inventory data to the ERG and CSU laboratories, data handling within the ERG and CSU laboratories, and management of data obtained from the ERG and laboratories. Both labs provided quality assurance (QA) of their analytical measurements and interpretation.. Precision of field sampling methods was estimated by taking duplicate samples for analysis for at 10% of all samples from the same sampling methodology. Field blanks also address precision via measurement of an air sample that has undergone field handling protocols. Field blanks were collected for 5% of all air samples collected. Both labs performed lab blanks and duplicates as part of their standard QA/QC. Moreover, during sample analyses, accuracy of measurements was checked by

measuring known standards as well as adding known spikes to samples. Both Labs performed such accuracy checks as part of their standard QA/QC.

4.9 Statistical Analysis

Statistical analyses were performed using SAS on Demand for Academics, Enterprise Guide version 4.2, Minitab, and Excel spreadsheet. Descriptive statistics, as provided via SAS PROC MEANS and PROC FREQ, were used to characterize the distributions of SNMOC (for example BTEX), particulate matters ($PM_{2.5}$), and other environmental measurements including temperature, relative humidity, wind speed and direction. The distributions of environmental factors are typically not normally distributed; therefore before proceeding further, the normality of each parameter was tested via normality test in Minitab. The measurements precision was determined by calculating standard deviations and relative standard deviations (i.e., coefficients of variation) to facilitate comparison of precision between devices and among different conditions.

Relative Percent Difference (RPD %) was also calculated to estimate the measurement precision for duplicate samples. Limits of detection were also estimated using calibration curves and variability among field blanks. Method detection limits for SNMOC were determined according to EPA guidance specified in “Definition and Procedure for the determination of the Method Detection Limit” (FR 1984). Limits of Detection (LOD) for $PM_{2.5}$ results were calculated based on the field blanks. The limit of quantification was also determined by multiplying the given MDL/LOD by 5 (EPA guidance). A correlation coefficient concept was used to determine if there was any

association between the meteorological data and $PM_{2.5}$ levels. T- Test was also used to assess whether the means of BTEX concentrations between current study and the previous study are statistically different from each other.

For hypotheses 1, analysis of variance (ANOVA), based on SAS PROC GLM, was used to statistically evaluate the variation in SNMOC and $PM_{2.5}$ concentrations both among the different sites and among the different days; the statistical significance of interaction terms was also tested within the two way analysis of variance procedure.

CHAPTER 5: RESULTS AND DISCUSSION

RESULTS

This section summarizes and interprets the SNMOC, PM_{2.5}, TVOC and meteorological data collected at two locations nearby a private residential area (Upstream of the house (UP), Downstream of the house (DN)) close to Watson Ranch Pad (WRP), Battlement Mesa, Colorado. These parameters were also measured at the fire station (FR) of Battlement Mesa as a background samples.

5.1 Speciated Non-Methane Organic Compounds (SNMOCs)/VOCs Data

During this study, SNMOC samples were collected on 4 days during winter. These samples were analyzed for concentrations of 78 organic compounds (all hydrocarbons) as well as for the concentration of total NMOC and total SNMOC. Valid sampling results were obtained on all 4 of those days. The completeness of the SNMOC sampling, defined as the attempted sampling events that were valid (EPA), was 100 percent at all three locations. The high completeness figures for all three sampling sites suggest that samples were collected and handled efficiently at the UP, DN, and FR throughout the study.

Data Summary

Four data summary parameters: prevalence, concentration range, central tendency, and variability were used to provide a complete but concise overview of the ambient air concentrations that were measured during this study. Tables 5.1, 5.2, 5.3 in appendix 5 summarize the SNMOC data collected at UP, DN, and FR respectively. An overview of the data summary parameters follows:

Prevalence: As the data summary tables show, 62 of the 78 hydrocarbons identified by the SNMOC sampling and analytical method were detected in more than 90 percent of the samples collected at UP, DN, and FR during the sampling period. The summary statistics for these compounds, many of which had a prevalence of 100 percent, are believed to be highly representative of air quality during the four sampling days, since few non-detect observations were recorded. On the other hand, there were some compounds that were detected in fewer than 50 percent of the sampling events. Those compounds should be interpreted carefully because the analytical methods do not quantify concentrations at levels below the detection limits.

Concentration range: Not surprisingly, ambient air concentrations of the 78 SNMOC varied greatly among the samples collected at the three monitoring sites in Battlement Mesa. As tables 5.1, 5.2, and 5.3 in Appendix 5 indicate, the majority of the compounds were never measured at concentrations exceeding $10 \mu\text{g}/\text{m}^3$ at the private house area. At the UP monitoring site, 3 compounds had at least one ambient air

concentration greater than $10 \mu\text{g}/\text{m}^3$, and the highest concentrations were observed for ethane ($78.0 \mu\text{g}/\text{m}^3$), propane ($43 \mu\text{g}/\text{m}^3$), and isobutene ($14 \mu\text{g}/\text{m}^3$). Also, at DN only 3 compounds had at least one concentration greater than $10 \mu\text{g}/\text{m}^3$, and the highest concentrations were observed for ethane ($96.0 \mu\text{g}/\text{m}^3$), propane ($52 \mu\text{g}/\text{m}^3$), and isobutene ($18 \mu\text{g}/\text{m}^3$). Finally, at FR site, four compounds had at least one concentration greater than $10 \mu\text{g}/\text{m}^3$ and the highest levels were observed for ethane ($90.0 \mu\text{g}/\text{m}^3$), propane ($49 \mu\text{g}/\text{m}^3$), isobutane ($16 \mu\text{g}/\text{m}^3$), and isopentane ($12 \mu\text{g}/\text{m}^3$).

Central tendency: Tables 5.1, 5.2, and 5.3 in appendix 5 present three different measures of central tendency concentrations (the median, arithmetic mean, and geometric mean) for the 78 hydrocarbons identified by the SNMOC sampling and analytical method. Due to the high prevalence for most SNMOC, the three measures of central tendency are expected to accurately represent actual central tendency levels for most compounds. The following observations are apparent from the central tendency data listed in the data summary tables (tables 5.1 through 5.3). Most of the 78 compounds identified by the SNMOC sampling and analytical method had geometric mean concentrations lower than $5 \mu\text{g}/\text{m}^3$. More specifically, about 74 of the 78 compounds at UP, DN, and FR had geometric mean concentrations lower than $5 \mu\text{g}/\text{m}^3$. For insight into trends among the central tendency levels, Table 5.4 lists the compounds with the four highest geometric mean concentrations UP, DN, and FR. As the table 5.4 shows, the following compounds have geometric mean concentrations that rank among the four highest at all three sampling sites in the Battlement Mesa area: ethane, propane, isobutane, and isopentane. Thus, a small subset of the 78 SNMOC was

consistently measured at elevated levels at the three sites. In other words, even though the ambient air in Battlement Mesa contains a wide range of hydrocarbons, a small number of these compounds (light alkanes) comprise a large portion of the airborne SNMOC. Despite the similarities between the compounds with the highest concentrations at the three locations, Table 5.4 clearly demonstrates a slight difference in the magnitude of ambient air concentrations among the three sites, but they are not statistically significant. The highest geometric mean concentrations were observed at UP, and with similar values between DN and FR site. Overall, the central tendency data provide useful insight into the relative quantities of individual SNMOC.

Variability: According to Tables 5.1, 5.2, and 5.3 in Appendix 5 most SNMOC at UP, DN, and FR have coefficients of variation lower than 1.0, suggesting that most compounds' ambient air concentrations have comparable variability in the Battlement Mesa area during the four sampling days.

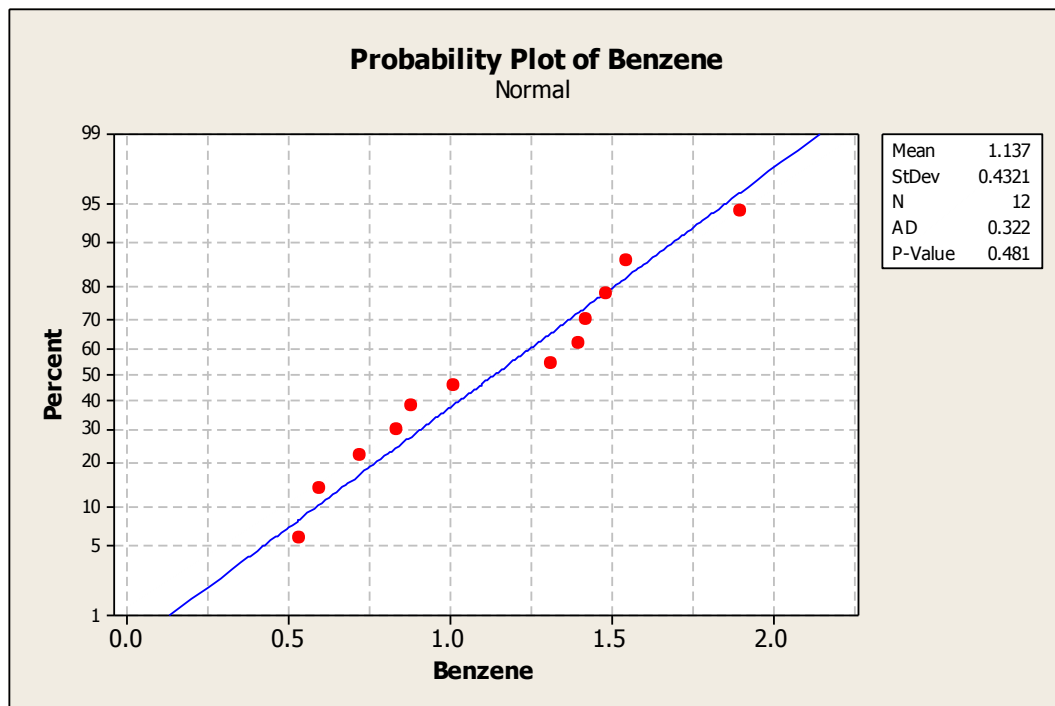
Table 5.4 SNMOC with the Highest Geometric Mean Concentrations ($\mu\text{g}/\text{m}^3$)

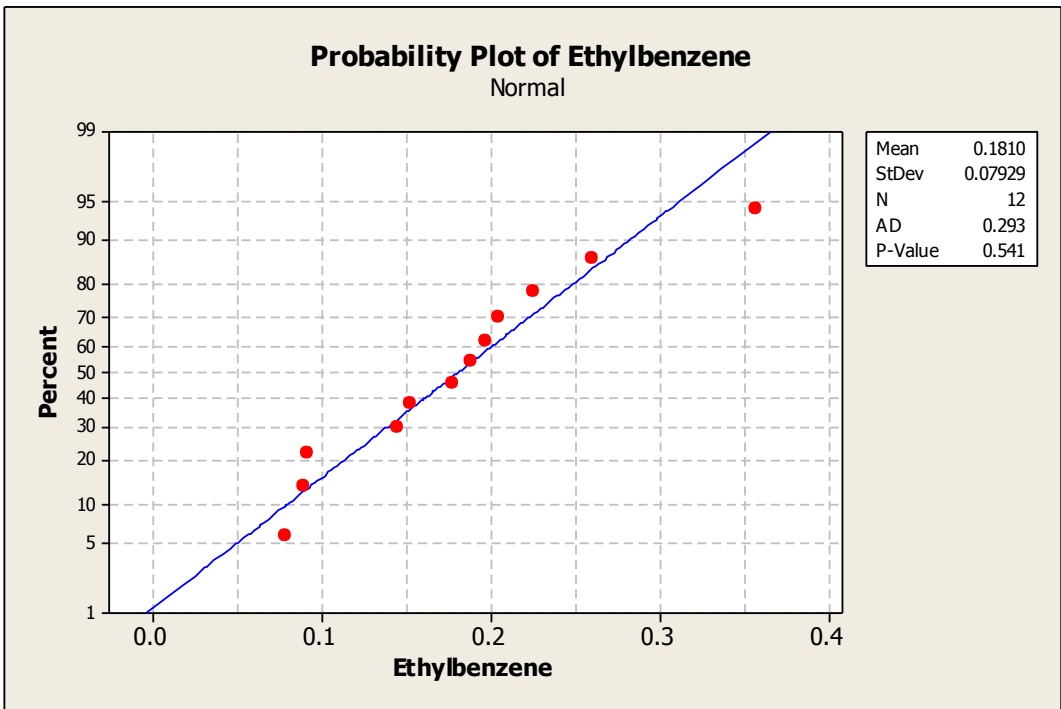
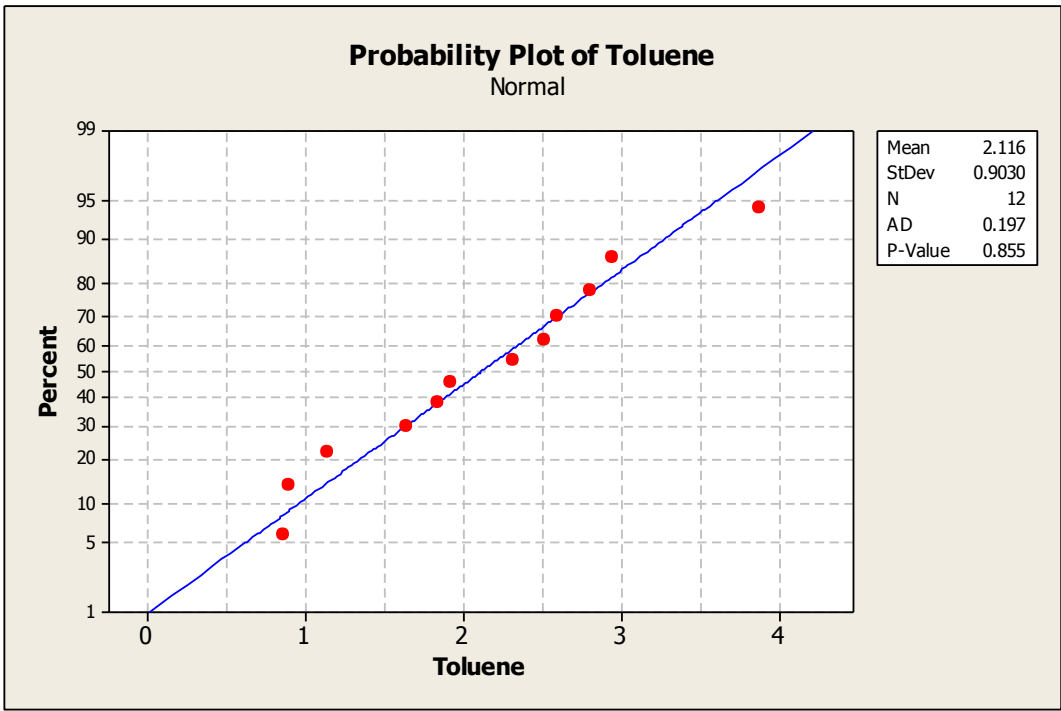
Upstream		Downstream		Fire Station	
Compound	Geometric Mean	Compound	Geometric Mean	Compound	Geometric Mean
Ethane	71	Ethane	51	Ethane	49
Propane	39	Propane	30	Propane	28
Isobutane	13	Isobutene	10	Isobutene	10
Isopentane	8	Isopentane	7	Isopentane	7

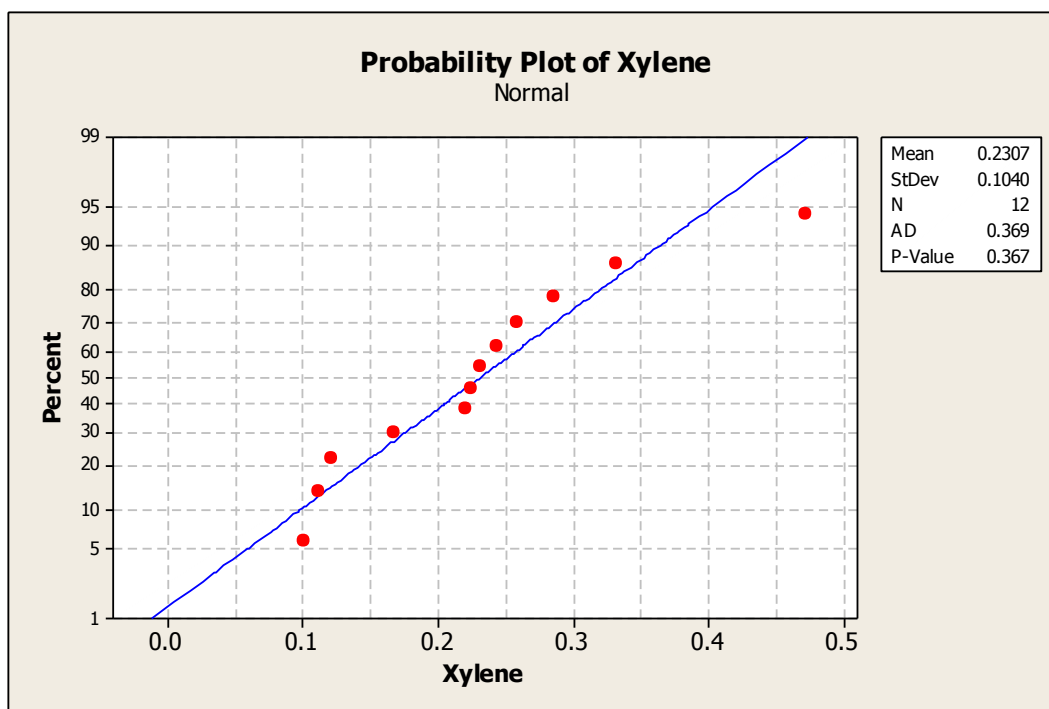
BTEX Normality Test

The assumption of normality was met for BTEX compounds as shown on the probability plots below (Figure 5.1). The primary concern of probability plots is the p value in the top right corner of the graph, which in our case is $p > 0.05$ (greater than alpha level α) for all of the BTEX compounds. The null hypothesis states that there is no difference between our data and the generated normal data so that we would not reject the null hypothesis as the p value is greater than alpha level ($\alpha=0.05$); the data is normal. The straight line on the graph is the null hypothesis of normality, so that the data is supposed to be as close to that line as possible in order to assume normality. As we can see from the probability plots the BTEX data are close to the straight line as it's approved by the p value since the p value tells us whether our data are significantly different from this line or not.

Figure 5.1: Probability Plots of BTEX Compounds (Normality Test)







5.2 BTEX Concentrations Profile

To identify the emissions sources that have the strongest effect on local air quality, many researchers have compared the relative quantities of benzene, toluene, ethylbenzene, and the xylene isomers (BTEX) compounds in ambient air to the relative quantities of these compounds emitted by different sources such as motor vehicle emissions.

Tables 5.5, 5.6, and 5.7 summarize the results and statistics of BTEX compounds collected at UP, DN and FR respectively. An overview of the BTEX data summary parameters follows:

Prevalence: As the BTEX data summary tables show, all BTEX compounds identified by the SNMOC sampling and analytical method were detected at 100 percent of the samples collected at UP, DN, and FR during four-day sampling period. On the

other hand, for the concentration range, the ambient air concentrations of the selected SNMOC compounds (i.e. BTEX) do not vary greatly among the samples collected at the three monitoring sites in Battlement Mesa. Generally, as Table 5.8 indicates, the concentration differences of those compounds are statistically significant per day; however, the statistic test shows that most of those compounds are not significantly different per site. Moreover, the interactions between the days and sites are not statistically significant.

As summary Tables 5.5, 5.6, and 5.7 indicate, all of the BTEX compounds were never measured at concentrations exceeding $5 \mu\text{g}/\text{m}^3$ in the Battlement Mesa area. Clearly, the highest BTEX compounds concentrations were observed at the FR site. Toluene had the highest concentrations among the BTEX compounds in all sites. At the UP monitoring site, benzene has the second highest ambient air concentration among the BTEX group with an arithmetic mean $1.12 \mu\text{g}/\text{m}^3$, and the maximum concentration for benzene was $1.90 \mu\text{g}/\text{m}^3$ that was measured at FR site. However, the lowest concentrations were observed for ethylbenzene ($0.206 \mu\text{g}/\text{m}^3$). Although the benzene concentration difference was not statistically significant between sites, it was close to significant ($P=0.083$) as Table 5.8 has shown above. Figures 5.2-5.4 illustrates the BTEX compounds concentrations at each site. The average benzene concentrations were higher at UP than DN site.

Central tendency: Tables 5.5, 5.6, and 5.7 present three different measures of central tendency concentrations (the median, arithmetic mean, and geometric mean) for the BTEX compounds identified by the SNMOC sampling and analytical method.

Once more, due to the high prevalence for BTEX compounds, the three measures of central tendency are expected to accurately represent actual central tendency levels for BTEX compounds. The following observations are apparent from the central tendency data listed in the data summary tables (5.5, 5.6, and 5.7): the majority of BTEX compounds identified by the SNMOC sampling and analytical method had geometric mean concentrations lower than $2 \mu\text{g}/\text{m}^3$. More specifically, only one measurement exceeded $2 \mu\text{g}/\text{m}^3$ and that was for the toluene at the FR site. Among the central tendency levels, the highest geometric mean concentrations were observed at FR. As summary Tables 5.5, 5.6, and 5.7 indicate that the highest geometric means of the BTEX compounds were as follow: toluene, benzene, Xylene and ethylbenze respectively. Despite the similarities between the BTEX compounds with the highest concentrations at the three locations, Figures 5.2-5.4 clearly demonstrate a slight difference in the magnitude of ambient air concentrations among the three sites, and they are statistically significant, except benzene which is not statistically significant as seen on table 5.8.

Variability: According to Tables 5.5, 5.6, and 5.7 all of the BTEX compounds at UP, DN, and FR have coefficients of variation lower than 1.0, suggesting that most compounds' ambient air concentrations have comparable variability in the Battlement Mesa area during the four sampling days. The standard deviations of the BTEX compounds concentrations measured in the Battlement Mesa area reflect the shapes of the concentration distributions shown in Figures 5.2, 5.3, and 5.4: The variability was least for DN (the site with the narrowest spread in its concentration distribution) and

highest for FR (the Site with the widest spread in its concentration distribution). More specifically, toluene had the highest standard deviation among the BTEX compounds in all sites, and ethylbenzene had the lowest standard deviation. The greater variability at FR suggests that the factors that contribute to BTEX levels at this site change considerably from day to day. The lower variability at DN and UP, however, suggests that the factors that affect BTEX levels most do not vary greatly from one day to the next.

Table 5.5 Summary Statistics for (BTEX) Concentrations ($\mu\text{g}/\text{m}^3$) Measured at the Upstream (UP)

Compound	Prevalence of compound in ambient air		Range of measured concentrations		Central tendency of measured concentration			Variability in measured concentrations	
	No. of nondetects	Frequency of detections	Lowest	Highest	Median	Arithmetic mean	Geometric mean	Standard deviations	Coefficient of variation
Benzene	0	100%	0.54	1.66	1.075	1.121	1.044	0.431	0.3842
Toluene	0	100%	0.91	3.18	1.857	2.057	1.883	0.866	0.421
Ethylbenzene	0	100%	0.08	0.26	0.197	0.174	0.160	0.069	0.400
O-Xylene	0	100%	0.10	0.33	0.219	0.206	0.191	0.084	0.407

Table 5.6 Summary Statistics for (BTEX) Concentrations ($\mu\text{g}/\text{m}^3$) Measured at the Downstream (DN)

Compound	Prevalence of compound in ambient air		Range of measured concentrations		Central tendency of measured concentration			Variability in measured concentrations	
	No. of nondetects	Frequency of detections	Lowest	Highest	Median	Arithmetic mean	Geometric mean	Standard deviations	Coefficient of variation
Benzene	0	100%	0.532	1.485	1.318	1.143	1.078	0.373	0.326
Toluene	0	100%	0.904	2.809	2.341	2.087	1.961	0.693	0.332
Ethylbenzene	0	100%	0.092	0.199	0.166	0.159	0.155	0.038	0.241
O-Xylene	0	100%	0.101	0.243	0.222	0.206	0.198	0.053	0.258

Table 5.7 Summary Statistics for (BTEX) Concentrations ($\mu\text{g}/\text{m}^3$) Measured at the Fire Station

Compound	Prevalence of compound in ambient air		Range of measured concentrations		Central tendency of measured concentration			Variability in measured concentrations	
	No. of nondetects	Frequency of detections	Lowest	Highest	Median	Arithmetic mean	Geometric mean	Standard deviations	Coefficient of variation
Benzene	0	100%	0.596	1.901	1.206	1.227	1.125	0.556	0.453
Toluene	0	100%	0.872	3.870	2.258	2.315	2.025	1.256	0.543
Ethylbenzene	0	100%	0.079	0.357	0.233	0.226	0.197	0.116	0.514
O-Xylene	0	100%	0.112	0.472	0.294	0.293	0.259	0.150	0.511

BTEX Graphs

Figures 5.2 through 5.4 present summary graphs of BTEX data collected at the two sampling sites (UP and DN) and at the background site (FR) during the four consecutive days. From the summary graphs, it can be seen that toluene was the highest concentration compound detected at all sites, on average, in the 22-hour samples followed by benzene and xylene. Toluene also had the single highest 22-hour concentration sample, and that was at FR ($3.87 \mu\text{g}/\text{m}^3$)

In looking across the 22-hour sample graphs, it can also be seen that certain days had higher concentrations in general than other days. A specific example was day 4 where BTEX compounds were significantly elevated at all sites compared to other days ($P < 0.05$). For example, the average benzene levels on day 4 were much higher than other days ($P = 0.0001$). Other examples include significantly declined BTEX compounds on day 2 at all sites compared to other days. The concentration variation among the four days will be discussed in detail in the meteorological section and discussion section.

Figures 5.2 through 5.4 also compare the BTEX results for each of the three sites during the sampling period. All of the 22-hour sample graphs are presented on the same concentration scale for comparability across the sites. It can be seen that the results are relatively varied in concentration for different compounds at the three sites. An example is toluene where it is not relatively stable at all of the three sites. It can also be seen that in general the concentrations of different compounds are higher at some sites than at others, such as benzene being higher at UP site than at the DN site.

Figure 5.2: 22-hour average BTEX Concentrations comparison to Days (UP Site)

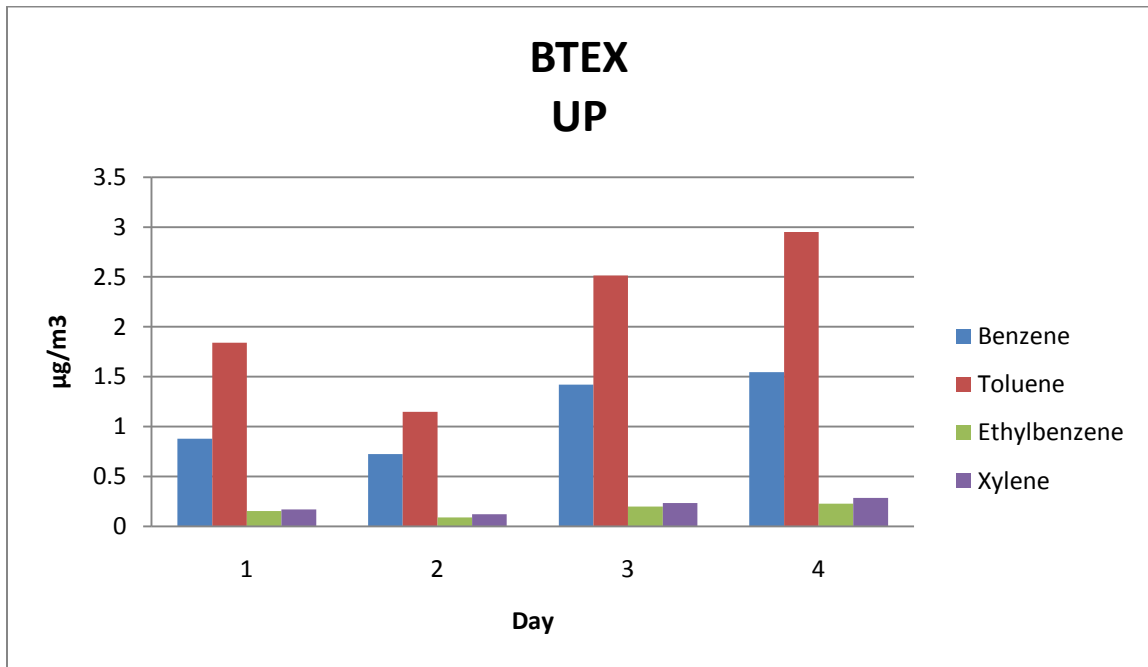


Figure 5.3: BTEX Concentrations comparison to Days (DN Site)

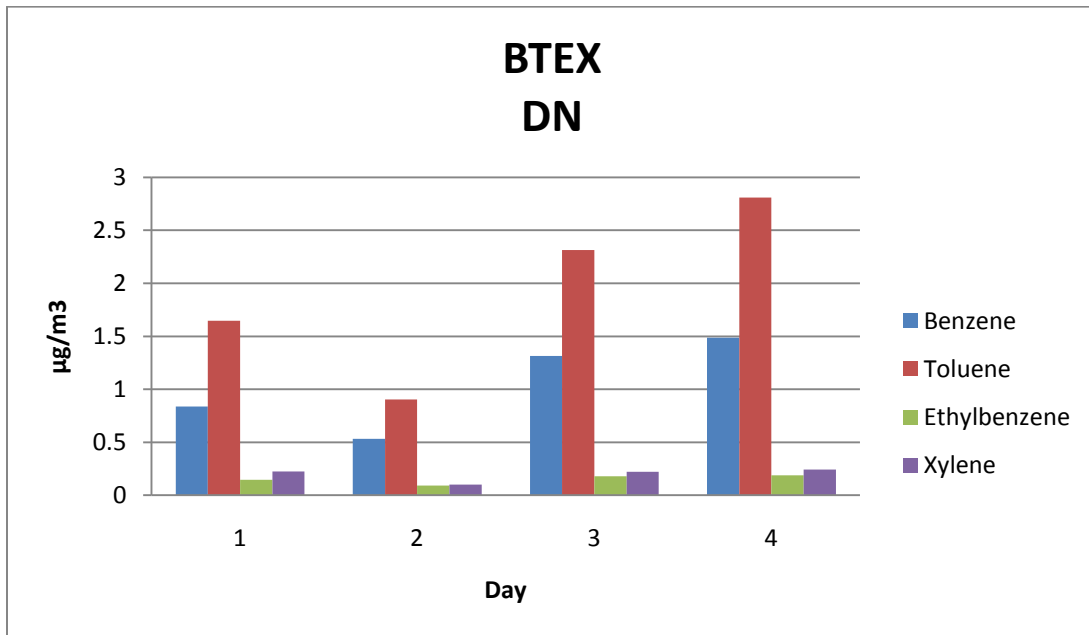


Figure 5.4: BTEX Concentrations comparison to Days (FR Site)

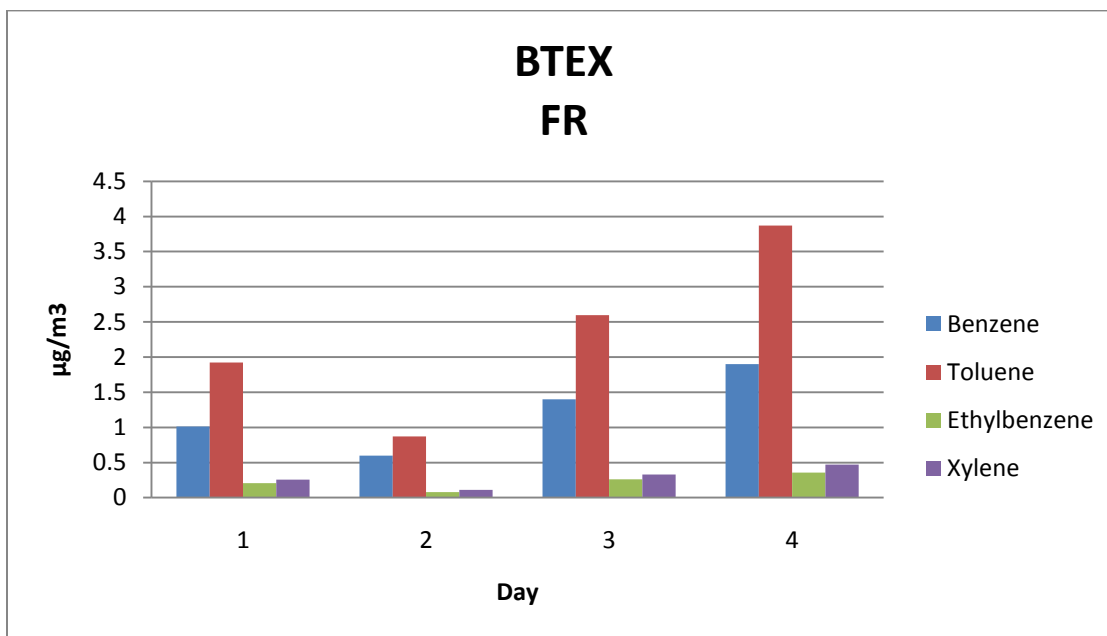


Table 5.8 shows the summary statistics for selected SNMOC compounds including BTEX compounds measured at different days and sites. Analysis of Variance (ANOVA), based on SAS PROC GLM, was used to statistically evaluate the variation in SNMOCs concentrations both among the different sites and among the different days; the statistical significance of interaction terms was also tested within the two way analysis of variance procedure. This table will be discussed in more detail in the following sections.

Table 5.8: Analysis of Variance for selected SNMOC compounds measured at different days and sites (Based on 4 days and 3 sites):

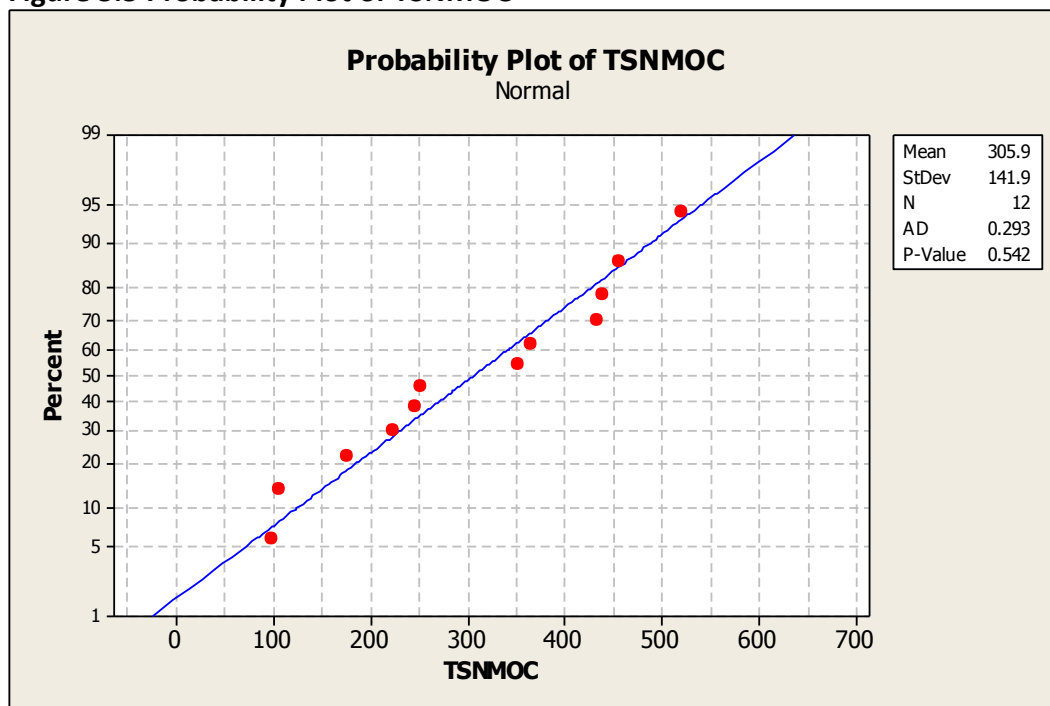
Compound	Day		Site		Day*Site	
	P	S. Significant?	P	S. Significant?	P	S. Significant?
Benzene	0.0001	Yes	0.083	No	0.420	No
Toluene	0.0001	Yes	0.041	Yes	0.107	No
Ethylbenzene	0.0011	Yes	0.017	Yes	0.114	No
O-Xylene	0.0003	Yes	0.005	Yes	0.041	Yes
TNMOC	0.0001	Yes	0.087	No	0.844	No
TSNMOC	0.0001	Yes	0.120	No	0.809	No
Ethane	0.0005	Yes	0.142	No	0.761	No

5.3 Total SNMOC

Normality Test for TSNMOC

The normality assumption for TSNMOC was met as shown on the figure 5.5 below. The p value is greater than alpha level ($0.54 > 0.05$), and the TSNMOC data is close to the straight line, so the TSNMOC data is normally distributed.

Figure 5.5 Probability Plot of TSNMOC



Once again, the four data summary parameters; prevalence, concentration range, central tendency, and variability will be used here to provide an overview of the ambient air concentrations that were measured during the sampling period. Table 5.9 provides a thorough overview of the total SNMOC concentrations measured at UP, DN, and FR during the four consecutive days. An overview of the data summary follows.

Prevalence: Total SNMOC was detected in every sample collected at UP, DN, and FR. Therefore, the prevalence of total SNMOC at these sites was 100 percent. The summary statistics presented below (table 5.9) are believed to be highly representative of total SNMOC levels in all sampling sites, since none of the statistics are biased by non-detect observations.

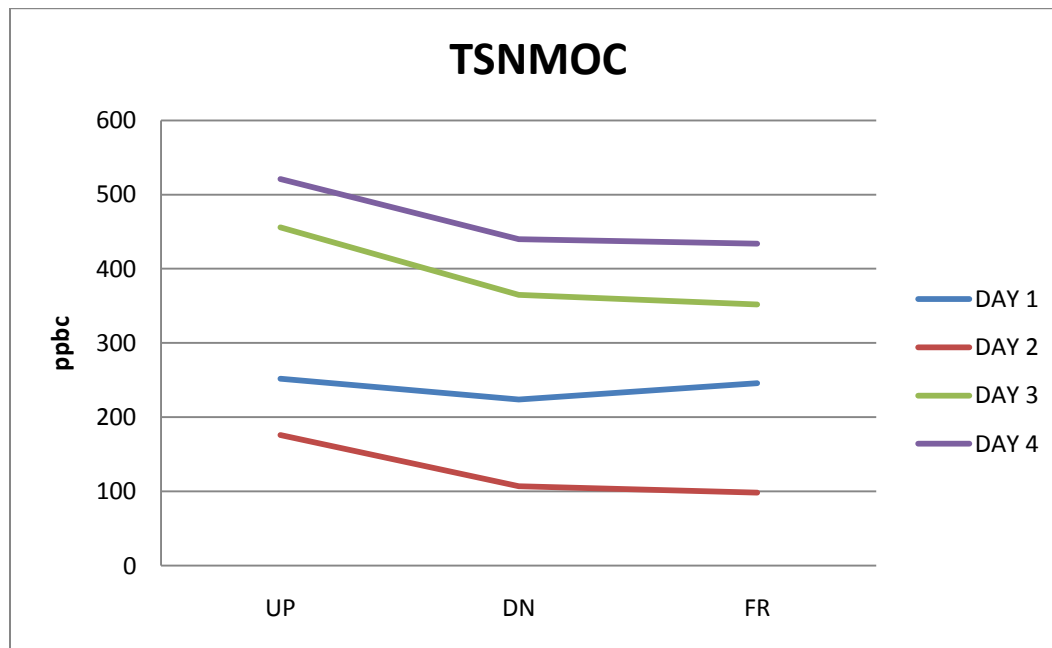
Concentration range: According to Table 5.9, the concentration ranges of total SNMOC at UP and DN were broader than that at FR. In fact, the highest total SNMOC concentration measured at FR is 434 ppbC during the four sampling days while the highest levels measured at UP and DN are 521 ppbC and 440 ppbC respectively. This trend suggests that the entire concentration distribution at UP is centered on higher total SNMOC levels than the distributions at the other two stations. To illustrate this trend, Figure 5.6 presents line a chart of the total SNMOC concentrations measured at the three sampling areas. The figure clearly shows that the concentration distribution at UP indeed has higher total SNMOC levels than the other two distributions.

When reviewing the concentration ranges, readers should remember that this air sampling project measures ambient air concentrations only during the four consecutive days taken on the beginning of February. Levels of total SNMOC during other times of year might have risen to higher or lower levels than the summary statistics indicate.

Table 5.9: Summary Statistics for Concentrations (ppbc) of Total SNMOC in all sites

Category	Parameter	Site		
		UP	DN	FR
Prevalence	Number of valid samples	4	4	4
	Number of nondetects	0	0	0
	Frequency of detection	100%	100%	100%
Concentration range	Lowest concentration	176	107	98
	Highest concentration	521	440	434
Central tendency	Median concentration	354	294	299
	Arithmetic mean	351	284	282
	Geometric mean	320	249	246
Variability	Standard deviation	164	148	145
	Coefficient of variation	0.47	0.52	0.51

Figure 5.6: TSNMOC Concentrations among the 3 Sampling Sites



Central tendency: As Table 5.9 shows, the three different measures of central tendency, the concentrations of total SNMOC at UP (i.e., the median, arithmetic mean, and geometric mean), were higher than those for DN and FR; these concentration differences were statistically significant per day, but they were not statistically significant per site as seen on table 5.9. At all three stations, concentrations of total SNMOC during the third and the fourth day were, on average, higher than those in day 1 and 2. These daily variations in central tendency levels were most pronounced at UP. Therefore, although concentrations of total SNMOC changed from one day to the next at selected locations in Battlement Mesa, the trend is possibly inconsistent and should be confirmed by additional monitoring.

Variability: The standard deviations of the total SNMOC concentrations measured in the Battlement Mesa area reflect the shapes of the concentration distributions shown in Figure 5.6: The variability was least for FR (the site with the narrowest spread in its concentration distribution) and highest for UP (the Site with the widest spread in its concentration distribution). The greater variability at UP suggests that the factors that contribute to total SNMOC levels at this site change considerably from day to day. The lower variability at DN and FR, however, suggests that the factors that affect total SNMOC levels most do not vary greatly from one day to the next.

The Relative Percent Difference (RPD)

As discussed on the methods section, compounds with relatively low measurement variability will have lower RPD and then better precision and vice versa.

Many sampling and analytical methods suggest that the monitoring program should be able to achieve RPDs of 30 % or better (less than 30%), if methods are applied correctly.

During the four sampling period, 5 SNMOC samples were collected in duplicate; 3 at UP site and 2 at DN site; results from these samples and analyses indicate that the SNMOC sampling and analytical method generated highly precise results. As tables 5.10 through 5.12 in Appendix 5 show, the precision estimates that most of the SNMOC measurements during the sampling period were less than 30%. At UP site (1st&2nd duplicate), the RPDs for 72 of the 78 SNMOC were lower than 30 percent; the six remaining compounds had concentrations lower than 1 µg/m³ and had RPDs considerably lower than 95 percent. The fourth day duplicate at UP site had only 3 compounds that exceed the 30% RPD. On the other hand, at the DN site (day 3 duplicate), the majority of the RPDs are less than 30% (73 out of 78 SNMOC). Finally, the second duplicate of the DN site had only two compound (2,3,4-trimethylpentane, m-Diethylbenzene) that had greater than 30% RPD (51%, 42% respectively).

Supporting the findings of the RPDs, the concentration differences observed in duplicate SNMOC samples were typically less than ±1 µg/m³ a level indicative of excellent measurement precision. Therefore, the SNMOC data presented in this study are of a known and high quality.

Top 1- 3 VOC's Average Compounds:

As figures 5.7 through 5.9 show, the highest three averaged compounds detected were ethane, propane and isobutane during the sampling period at all sites. These compounds are called light alkanes, which include alkanes with up to five carbon

atoms. At all three sites, concentrations of those alkanes during the third and the fourth day were, on average, higher than those in day 1 and 2, and day 2 had the lowest concentrations of all of the sampling sites. Figures 5.7-5.9 illustrate that ethane had the highest air concentrations among all the SNMOCs in all of the sampling sites during the sampling period. In general, since the compounds measured were dominated by light alkanes, we could say that these light alkanes are the primary components of natural gas in Battlement Mesa area (ARS Inc., 2010).

Figure 5.7: Top 1st – 3rd Average Compounds (UP site)

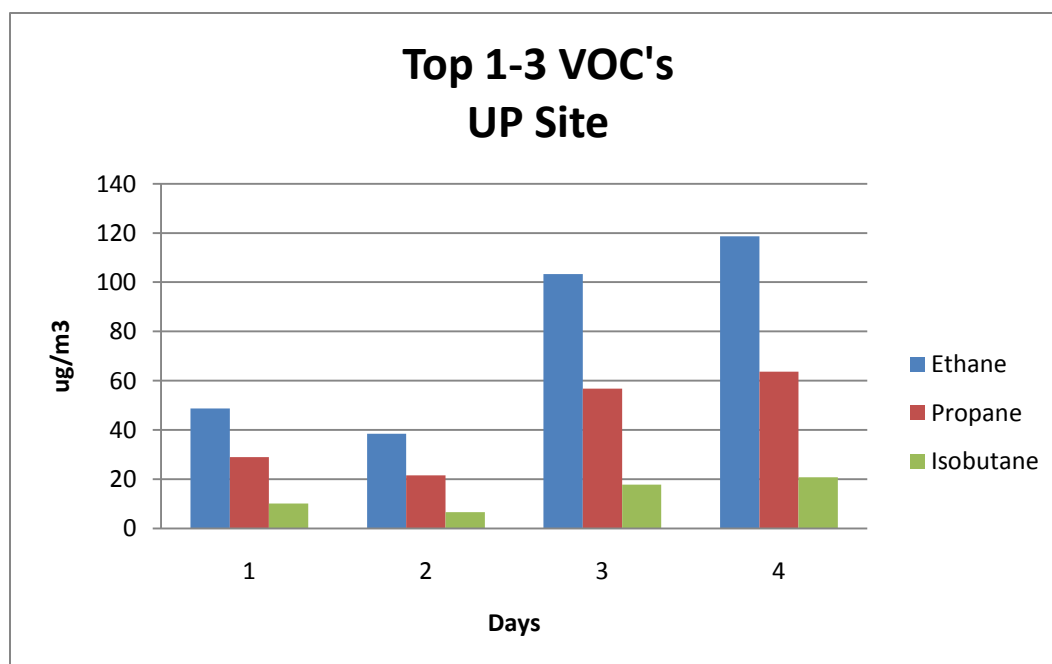


Figure 5.8: Top 1st – 3rd Average Compounds (DN site)

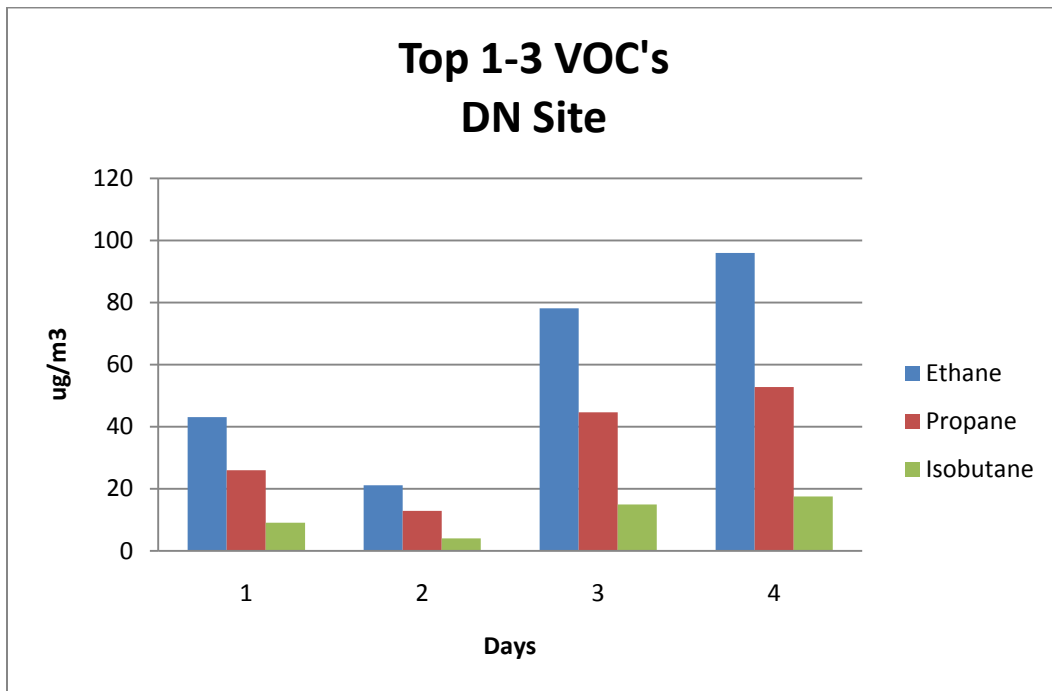
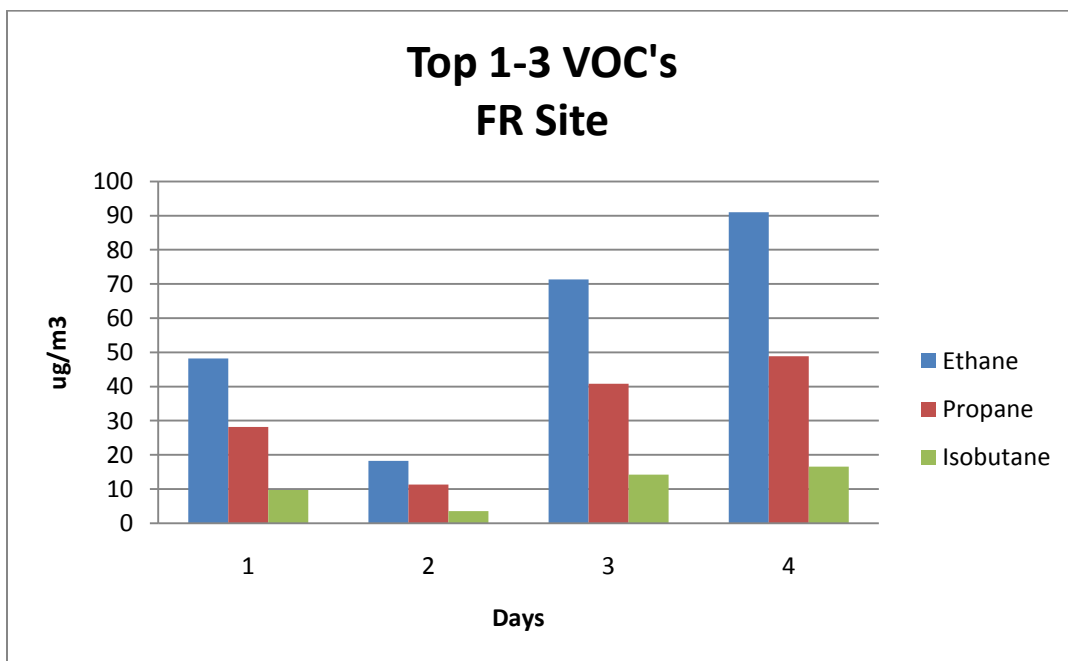


Figure 5.9: Top 1st – 3rd Average Compounds (FR site)



5.4 Fine Particulate Matter (PM_{2.5})

Analysis of variance (two-way ANOVA) was performed for PM_{2.5} data to test if there is a difference in results among the four days and three sites. As discussed previously, due to the extreme cold weather, some of the equipment didn't work for the full sampling period. More specifically, the equipment (i.e. pDR, pump) at the background site (FR) didn't take any measurements during the first and the second day. So, the PM_{2.5} data was analyzed by two different approaches: the first ignored the results from the first two days where there were no measurements collected at FR, and just analyzed PM_{2.5} data from the last two days (day 3 & 4) for comparison purpose. The second approach included all PM_{2.5} data and substituted non-detect values at FR by half value substitution (i.e. one-half detection limit). All comparisons are based on 24-hour average.

The normality assumption was met for PM_{2.5} data for the two approaches used as seen on figures 5.10 and 5.11. Both approaches have a p value that is greater than the alpha level as seen on the upper right corner of the graphs. Therefore, the null hypothesis would not be rejected.

Figure 5.10: Probability plots for PM2.5 (based on 4 days and 3 sites)

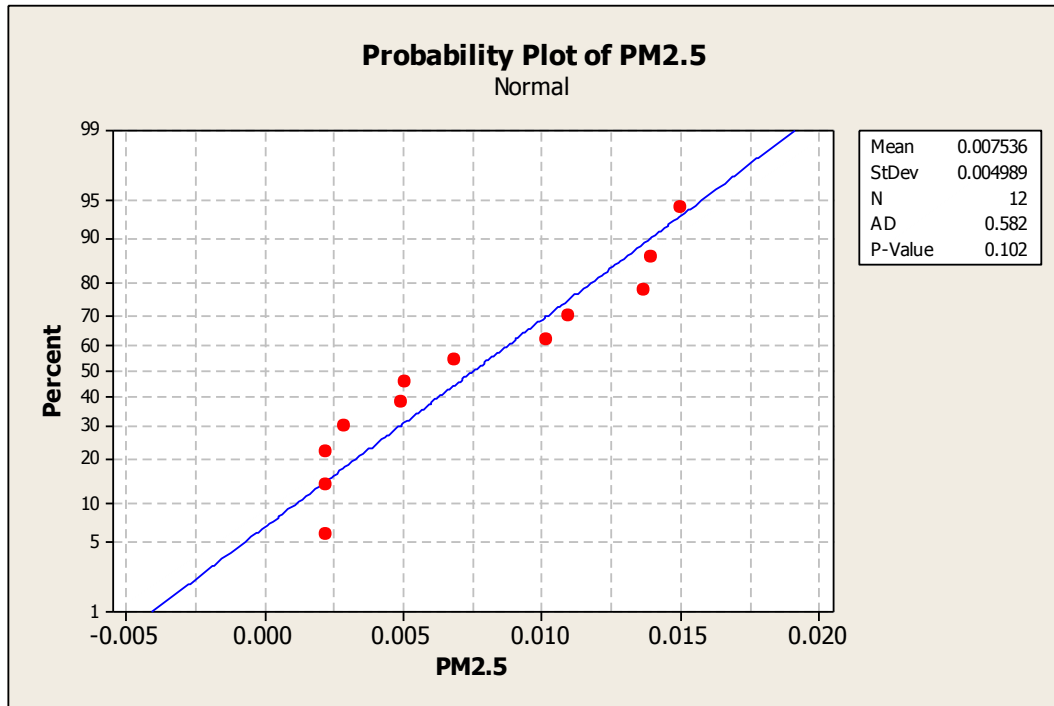


Figure 5.11: Probability plots for PM2.5 (based on 2 days and 3 sites)

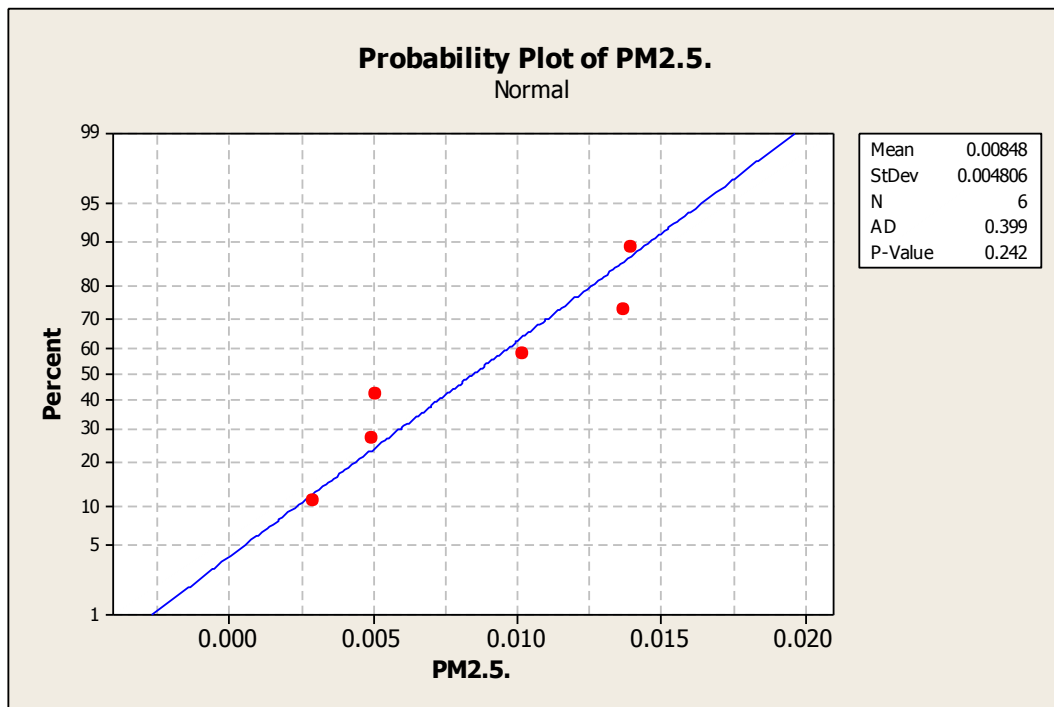


Table 5.13 provides a summary of average PM_{2.5} data from the three sites including the background (FR) during the four-day period. The National Ambient Air Quality Standards (NAAQS) for PM_{2.5} is currently set at 35 micrograms per cubic meter (µg/m³) for a 24-hour sample. No exceedances of the 24-hour NAAQS of 35 µg/m³ were observed. In general, 24-hour concentrations were 50 percent less of the NAAQS.

Table 5.13: Results Summary for PM_{2.5} (based on 4-days period)

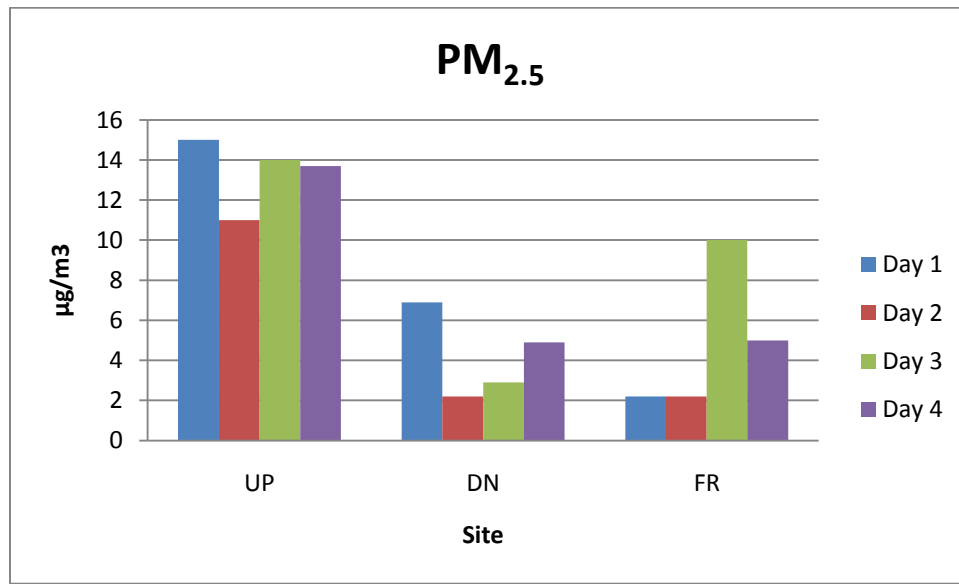
Site	Day 1	Day 2	Day 3	Day 4	Overall arithmetic average (µg/m ³)	Overall 24 hour maximum (µg/m ³)
UP	15	11	14	13.7	13.4	15
DN	6.9	2.2	2.9	4.9	4.2	6.9
FR	*2.2	*2.2	10	5	4.9	10

Note: * Missing data substituted

The fine particulate matter concentrations obtained for all sampling sites are shown in Figure 5.12. All samples were taken for 24-hours. The highest average concentration was recorded at the UP site on day 1 with a value of 15 µg/m³. The background site did not always record the lowest value, while the DN site recorded the lowest values for some days. The DN site had the lowest 24-hours average concentration at 2.2 µg/m³ and the background site (FR) value was 2.2 µg/m³ as well on day 2, but it was not the actual value or the measured value, it was the substituted value (half value substitution i.e. one half the detection limit). The overall arithmetic average concentration over the UP site (Closest to the well pad) was 13.4 µg/m³, which is larger than the concentration seen at the background site (4.9 µg/m³). All the values

obtained were below the value of the 24-hour maximum exposure EPA standard for PM_{2.5} of 35 µg/m³.

Figure 5.12: PM_{2.5} Concentrations at all sites (24-hour average)



PM_{2.5} Graphs

Figures 5.13 through 5.16 present summary graphs of the PM_{2.5} data collected at the three sampling sites over 24-hour sampling period. It is evident that the UP site has higher concentrations of particulates than DN and the background (FR), but they are not statistically significant as shown previously on table 5.13. The highest average concentrations were observed on day 4 (72 ug/m3), while day 2 recorded the lowest concentrations during the sampling period. None of the equipment ran continuously for 24-hours during the sampling period because the temperature operation conditions of the equipment were exceeded, thus the equipment did not operate under low temperatures. For example, the pDR operating environment is between -10 to 50

Celsius, and weather temperatures exceeded the limit many times as we will see in the meteorological data section. So figures 5.4 thru 5.7 do not represent a 24-hour sampling period, but they were plotted based on the measurements that were taken before the equipment turned off (Ranged from 12-18 hours).

Figure 5.13 PM_{2.5} Data over 24-Hour (Day 1)

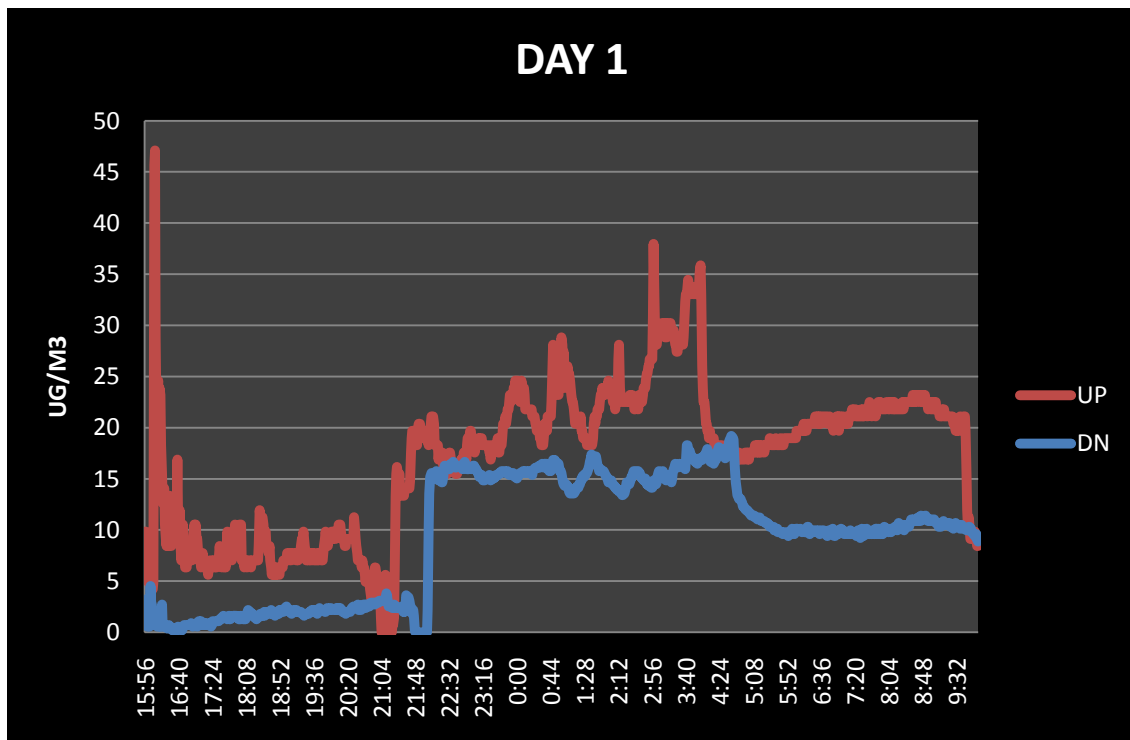


Figure 5.14: PM_{2.5} Data over 24-Hour (Day 2)

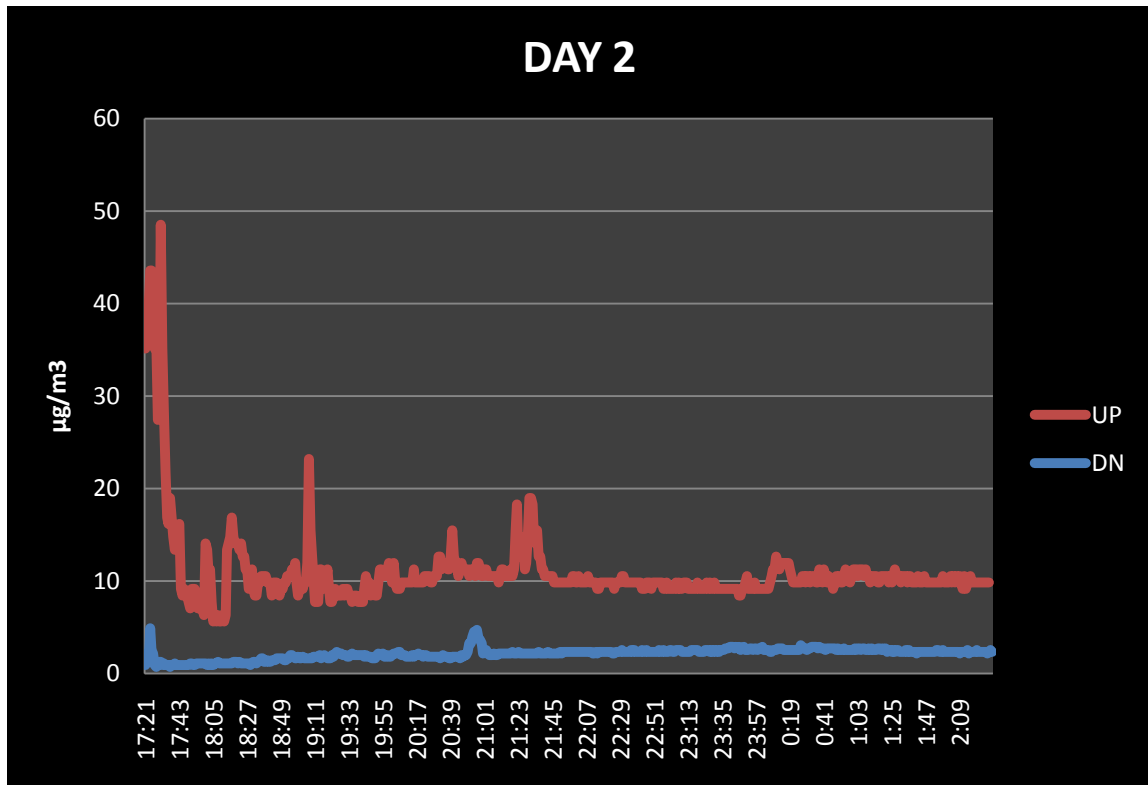


Figure 5.15: PM_{2.5} Data over 24-Hour (Day 3)

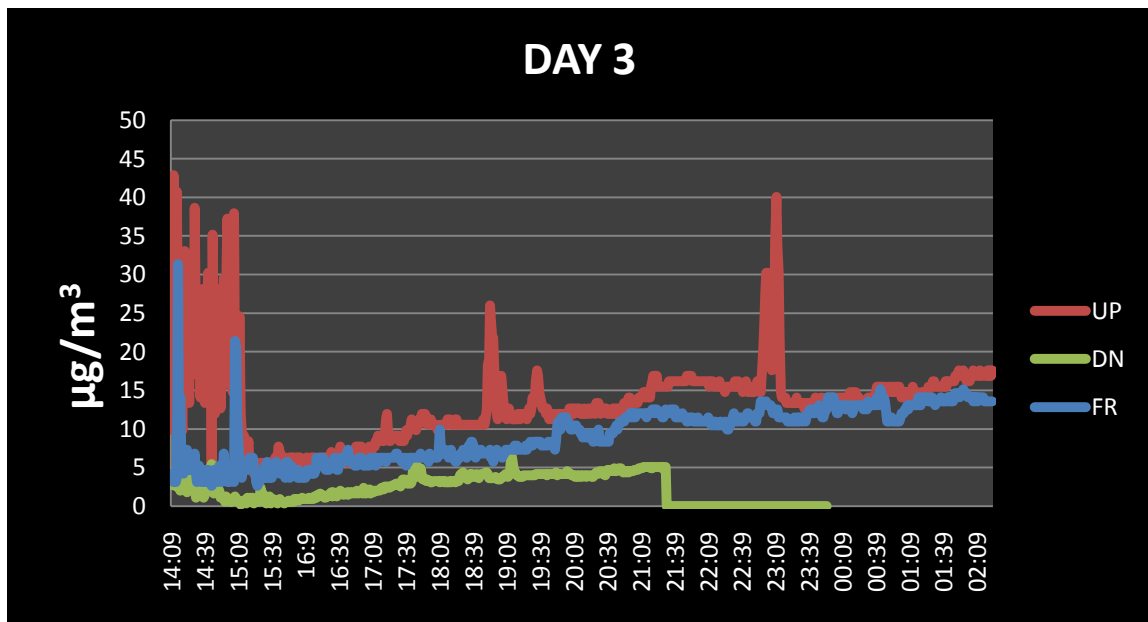


Figure 5.16: PM_{2.5} Data over 24-Hour (Day 4)

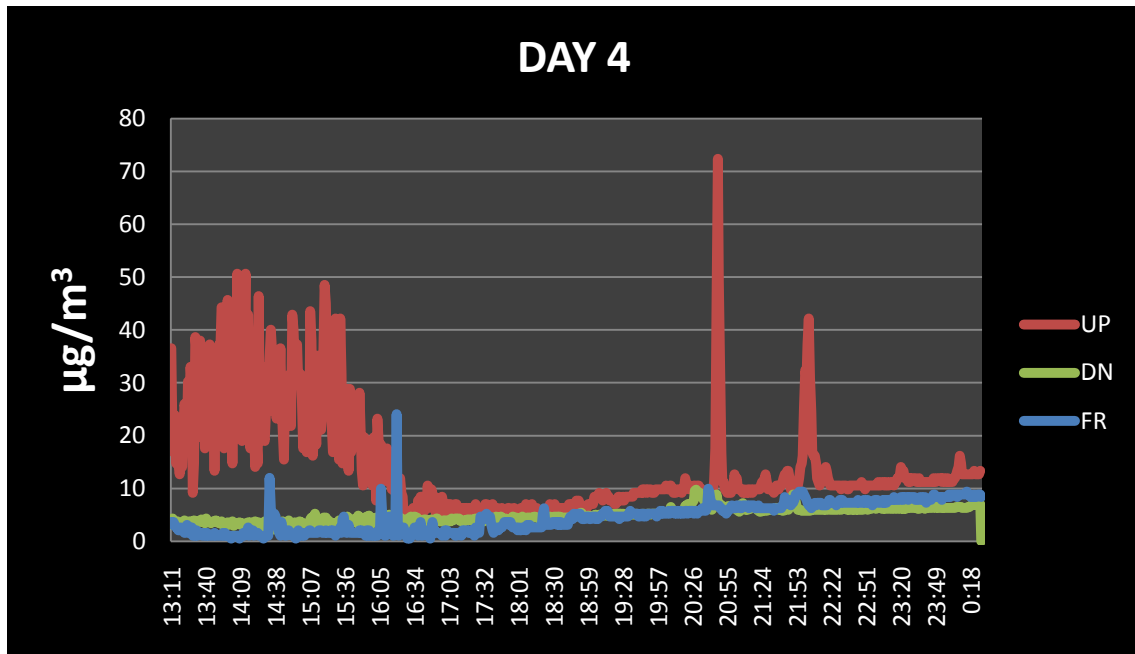


Table 5.14 provides the analysis of variance for PM_{2.5} data in two sections: one based on a 4 day period, and the second section based on only two days. As table 5.13 shows, the PM_{2.5} data are not statistically significant among the four-day sampling period, but is statistically significant between the three sites. By using the second approach, neither days nor sites are statistically significant.

Table 5.14: Analysis of variance for PM_{2.5} measured at different days and sites

Parameter	Day		Site		Day*Site	
	P	S. Significant?	P	S. Significant?	P	S. Significant?
Based on 4 days						
PM _{2.5}	0.370	No	0.004	Yes	NA	NA
Based on 2 days						
PM _{2.5}	0.653	No	0.118	No	NA	NA

5.5 Total Volatile Organic Compounds (TVOCs)

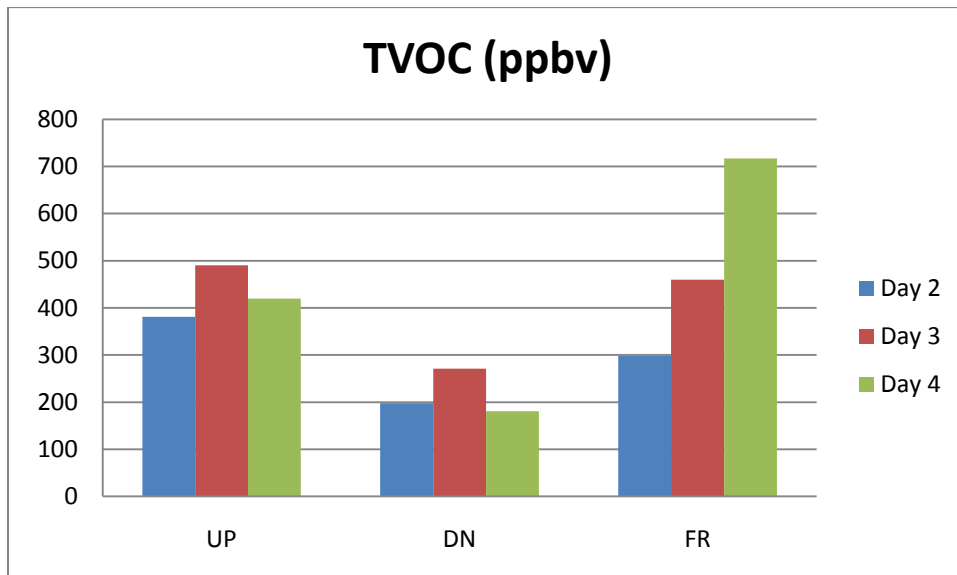
Table 5.15 provides the ten minute averaged TVOC (spot checking) measured by PID at the three sites during the sampling period. Due to equipment (PID) unavailability, the TVOC measurements for the first day couldn't be taken as shown on table 5.15.

Table 5.15: Average TVOC

DAY	Average TVOC concentration (ppbv) (Averaged over 10 minutes)		
	Site		
	UP	DN	FR
1	NA	NA	NA
2	381	298	490
3	490	271	460
4	420	181	717

Figure 5.17 shows the slight variation of the average TVOC concentrations among three sites during the four-day period. Neither the difference between the sites ($p=0.11$) nor the days ($p=0.41$) is statistically significant. The measured TVOC concentrations were as high as 717 ppbv at the background site (FR). The UP site and the FR site have higher TVOC concentrations than the DN site which is consistent with SNMOC data. Also, days 3 and 4 have higher concentrations than day 2.

Figure 5.17: Average TVOC



5.6 Metrological Data

Table 5.16 summarizes the meteorological data collected during the sampling period. Meteorological data collected during the sampling period show that, in general, the predominant wind direction was from the West/Northwest from 11:00AM to 8:00PM. The predominant wind direction was from the Northwest/Southwest from 8:00PM to 10:00AM in the first two days while the during last two days the predominant wind direction was from the Northwest/Southwest from 11:00AM to 8:00PM and Northeast/Southeast from 8:00PM to 10:00AM. As mentioned before, the sampling site was in the west side of the well pad, so the wind was mostly upwind. Wind speed was highest during the period between 6:00AM and 6:00PM during the sampling period. The highest wind speed was recorded during the first two days, averaging approximately 3.2 meter per second (m/s) and ranging from 1.2 to 8.3 m/s as shown on table 5.16. Relative humidity averaged 64%, with ranges from 34% to 93%,

with the highest percentages of humidity occurring during late evening and early morning hours. Precipitation (snow) was accumulated during days 1 and 2, but there was not any precipitation on days 3 and 4. The weather during the sampling period was extremely cold, and the lowest temperatures were recorded on days 2 and 3 (-18 C)

Table 5.16: Summary Statistic for Metrological Data

Day	Precipitation	Wind Direction	Wind Speed(m/s)			Humidity%			Temperature C		
	YES/NO	Cardinal Direction	Avg.	Hi	Lo	Avg.	Hi	Lo	Avg.	Hi	Lo
1	YES	NW/SW	3.0	8.3	1.2	73	93	57	-3	-0.2	-9
2	YES	W/NW	3.4	7.9	1.3	60	69	50	-13	-13	-18
3	NO	NW/NE	1.4	4.0	0.7	63	79	35	-12	-12	-18
4	NO	SW/SE	1.2	3.4	0.6	62	82	34	-8	-8	-15

Discussion

5.7 SNMOC data

As mentioned in the results section, 60 out of 78 compounds were detected in all sites during the sampling events. The fact that 60 compounds were detected in most samples indicates that ambient air in Battlement Mesa contains a wide range of pollutants. On the other hand, for the compounds that were detected in fewer than 50 percent of the sampling events at the three sampling sites, summary statistics for these compounds should be interpreted with caution, since they are likely to be biased by the frequent non-detect observations. The non-detect values were replaced in the SNMOC air monitoring database with an estimated concentration of one-half the method detection limit (EPA guidance). As seen in the SNMOC statistic summary tables 5.1 through 5.3 (appendix 5), 22-hour VOCs levels were generally very low.

BTEX Compounds:

As stated earlier in the result section, all BTEX compounds were detected at all sites during the sampling period, so BTEX compounds have high prevalence among SNMOCs in Battlement Mesa area. The greater variability at FR as seen in table 5.8 suggests that the factors that contribute to BTEX levels at this site change considerably from day to day. The lower variability at DN and UP, however, suggests that the factors that affect BTEX levels most do not vary greatly from one day to the next. In addition, the results show that the FR site had the highest BTEX concentrations among the three sites; this is may be an indication of association between BTEX compounds and motor vehicle emissions since the FR site is located on a traffic zone. Moreover, Next to the FR

site, there is a gas station which could be a potential interference with results at the FR site.

Comparison of Selected SNMOC data to Antero's Data

In this study, the ambient air samples were collected during the production phase (Wells on Sales) of the well development process as mentioned in the introduction section. One goal of this study is to compare the results of SNMOCs to the results that were obtained from Antero Resources during the summer through the Colorado School of Public Health (CSPH) during the well completion and flow back phase of well development process (Discussed in Literature Review section) on Watson Ranch Pad. Although Antero had collected air samples on each cardinal direction, only the west side of the well pad was chosen here to compare with our data since the private house (project location) is located on the west side of the Watson Ranch Pad. As discussed in the literature review section, the west side had the highest VOCs concentrations among all four cardinal directions. Table 5.17 shows the UP site (800ft) and Antero's (350&500ft) results. Clearly, Antero's SNMOC's results are much higher than the results obtained in this study as seen on Table 5.17.

T-Tests were performed between the three different measurements to test the concentrations difference, and the T-tests show no statistically significant difference between the measurements. For example, the air concentrations at the UP site during the production phase is not statistically significant different from the air concentrations measured during the well completion, fracking and flowback phases of well development process conducted by Antero's at both distances (i.e. 500ft&350ft)

($p=0.22$ & 0.18 respectively at $\alpha=0.05$). O-xylene is the only isomer of the xylene isomers that was detected during the production phase of this study while o-xylene and m,p-xylene were detected during the well completion and fracking/flowback phases in Antero's study. Moreover, m,p-xylene compound recorded high concentrations during the well completion and fracking processes of Antero's study as seen on Table 5.17. Seasonal variations play an important role in VOCs levels: during the winter the VOCs concentrations tend to be higher than summer season (ASR Inc., 2010). The differences of the temperature are the main reason for seasonal variations, as VOCs diminish faster during the summer due to higher reactivity at higher temperatures (ASR Inc., 2010). It could be inferred that if the Antero's data was collected during the winter season, the VOCs levels would be much higher than the summer season; therefore, the measurement here are between two different seasons are not directly comparable.

Table 5.17: Comparison of Selected SNMOC levels ($\mu\text{g}/\text{m}^3$) to Antero's data

Chemical	*UP's Results N=4	Antero's Results (West side) N=1	
	800 ft	500 ft	350 ft
Benzene	1.1	6.2	7.6
Toluene	2.1	24.7	31.4
Ethylbenzene	0.2	2.4	3.2
o-Xylene	0.2	5.1	6.8
m,p-Xylene	0	36.5	45.2
Ethane	77.3	220.0	271.0
Propane	43.0	97.4	118.4
Isobutane	14.0	31.3	38.0

Note:

*Average of 4-day period

N= number of samples

5.8 SNMOCs/VOCs Rules and Regulations:

Although there are no NAAQS or any other ambient air standards for SNMOCs/VOCs, emissions limits on industrial sources have been set by different agencies such as the EPA and California Ambient Air Quality Standards (CAAQS). Occupational exposure limits have also been set to protect human health and safety; those limits are either advisory such as NIOSH and ACGIH limits or regulatory such as OSHA limits. The EPA has developed a set of risk factors for both acute and chronic exposures. One approach that has been developed by the EPA is a Risk Based Concentration (RBC) table (also called Regional Screening Level (RSLs)) to determine potential risks from exposures to VOCs. Residential air regional screening level was used here to evaluate air pollutants. RSLs are considered by the EPA to be protective for humans over a life time.

As seen in Table 5.18, all of the maximum reported concentrations for carcinogenic and non-carcinogenic BTEX compounds except benzene are below their corresponding RBC values, based on a non-cancer hazard index of 1.0. The maximum detected concentration of benzene ($1.9\mu\text{g}/\text{m}^3$), a carcinogenic chemical, was found to be within a range of risk generally considered acceptable by the EPA. Because benzene was detected at a concentration above that equivalent to a 1 per million risk ($1\text{E}-06$), this chemical may warrant further review pertaining to exposure scenario assumptions and typical exposure concentrations. This indicates that concentrations measured within

the Battlement Mesa pose significant health risks to area residents based on this very limited pilot study. Comparison of the maximum detected concentration of benzene ($1.90 \mu\text{g}/\text{m}^3$) to the risk-based range (0.31 to $31 \mu\text{g}/\text{m}^3$), shows that the measured maximum concentration lies between the lower end of the range ($0.31 \mu\text{g}/\text{m}^3$), based on a cancer risk of one per million, and the higher end of the range ($31 \mu\text{g}/\text{m}^3$), based on a non-cancer hazard index (HI) of 1.0 as shown on Table 5.18.

Table 5.18 Comparison of BTEX Concentrations to Risk Based Screening Levels (EPA, RSL Table Nov. 2010)

Chemical	Maximum Detected Concentration $\mu\text{g}/\text{m}^3$	Risk Based Ambient Air Concentration $\mu\text{g}/\text{m}^3$		Basis	Does Maximum Detected Concentration Exceed Risk Based Concentration?
		Carcinogenic SL TR=1.0E-6	Non-Carcinogenic SL HI=1		
Benzene	1.90	0.31	31	C	Yes
Toluene	3.87	NA	5200	N	No
Ethylbenzene	0.36	0.97	1000	C	NO
O-Xylene	0.47	NA	100	N	NO

Note:

C: Cancer N: Non-Cancer TR: Target Risk HI: Hazard Index

Based on California Ambient Air Quality Standards (CAAQs), Reference Exposure levels (RELs) were developed to assess the potential risks of air pollutants. Table 5.19 lists the maximum detected BTEX concentrations ($\mu\text{g}/\text{m}^3$) and their corresponding RELs.

As seen on the table 5.19, none of the BTEX compounds have exceeded the RELs, yet they are way low from their RELs.

Table 5.19: Comparison of Maximum BTEX Concentrations to RELs

Compound	CalEPA RELs			Maximum Detected ³ Concentration $\mu\text{g}/\text{m}^3$
	Acute ³ ($\mu\text{g}/\text{m}^3$)	8-hour	Chronic ³ ($\mu\text{g}/\text{m}^3$)	
Benzene	1,300	NA	60	1.90
Toluene	37,000	NA	2,000	3.87
Ethylbenzene	NA	NA	300	0.36
O-Xylene	22,000	NA	700	0.47

. As mentioned in the literature review chapter, previous studies conducted by the EPA have proven that mobile source emissions are the major source of BTEX compounds. Since the BTEX compounds were detected on all of the sampling sites during the sampling period (100% frequency of detection), and the background site had the highest BTEX concentrations, this strongly suggests that the aromatic compounds (i.e. BTEX) originate from the mobile emissions, rather than from site-specific emissions sources (well pad). Meanwhile, since the UP site (the closet to the well pad) recorded the highest concentrations for the light alkanes (i.e. ethane, propane), it is also an

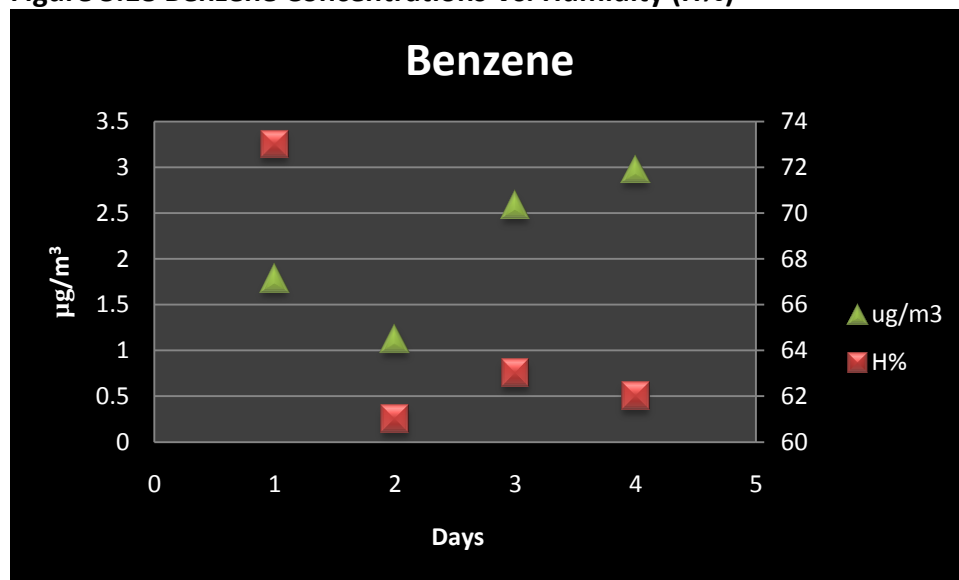
indication of association between oil and gas development processes (Production phase in our case) and SNMOCs elevation in general.

BTEX Comparison to Selected Meteorological Conditions

After performing the statistics analysis for BTEX compounds, the concentration difference from day to day was statistically significant, so the meteorological data was used here to possibly determine if there was a specific source or abnormal conditions that may have caused the results. Since the BTEX compounds behave correspondingly, benzene will be used here as a representative for BTEX compounds and SNMOCs to compare with meteorological data.

Humidity: As summarized on table 5.16, the average percent humidity of the four days period was about the same except day one, which had a higher value than the other three days. According to Figure 5.18, concentrations of benzene during the four-day period on average tended to be slightly higher with lower relative humidity. It should be noted, however, that the difference in concentrations for the two are not statistically significant. Therefore, the data collected during the four-day period are not sufficient for determining the association between relative humidity and levels of benzene. Analysis of future monitoring data is needed to characterize data trends between these parameters.

Figure 5.18 Benzene Concentrations Vs. Humidity (H%)

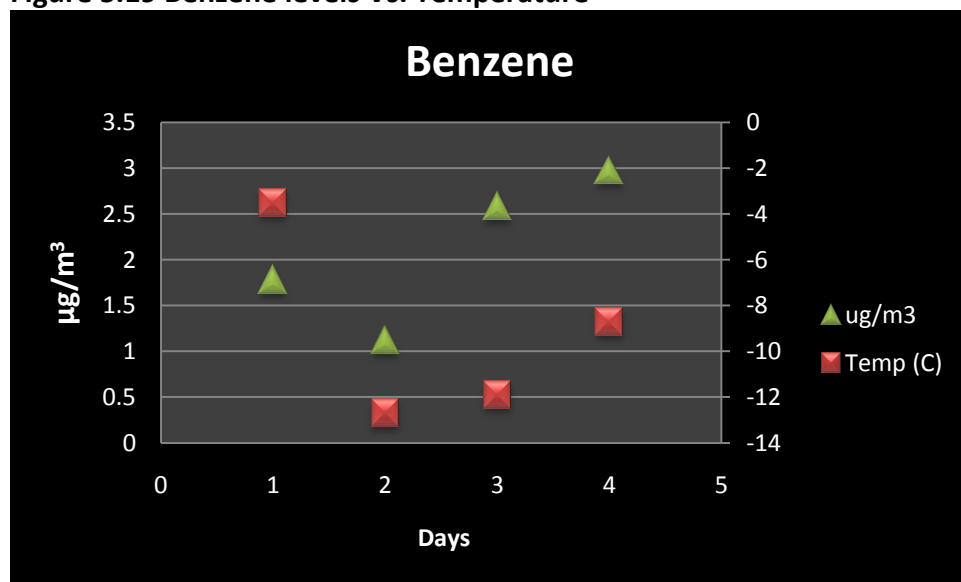


Precipitation: Snow was recorded at Battlement Mesa during only the first two days. As a result, statistically significant trends were observed between Benzene concentration on snowy days and benzene concentrations on days with no measurable precipitation, as seen earlier on table 5.5. It is clear that benzene levels were lower on snowy days than non-snowy days and this could be due to the atmospheric dispersion (i.e. aerosol particles absorption onto snowflakes).

Temperature: It is not one of the most pronounced features of the meteorological conditions during the sampling period in this study. The average temperatures during the sampling events were approximately less than -3 degrees Celsius. Day 2 has the lowest average temperature (-13C) during the sampling period. As one indication of how

temperature relates to air quality, Figure 5.19 indicates how benzene concentrations, on average, varied with temperature. Clearly, for the categories of temperature ranges selected, the temperature during a sampling event seemed to have little effect on the magnitude of the benzene concentration ($r < 0.1$ $P = 0.072$). Clearly, the temperature is weakly associated with benzene levels during the sampling period in Battlement Mesa. However, we cannot generalize our findings because temperature actually can affect the air concentration if there was a long term sampling period such as annual sampling. Then the air concentrations will have a large variability between summer and winter days.

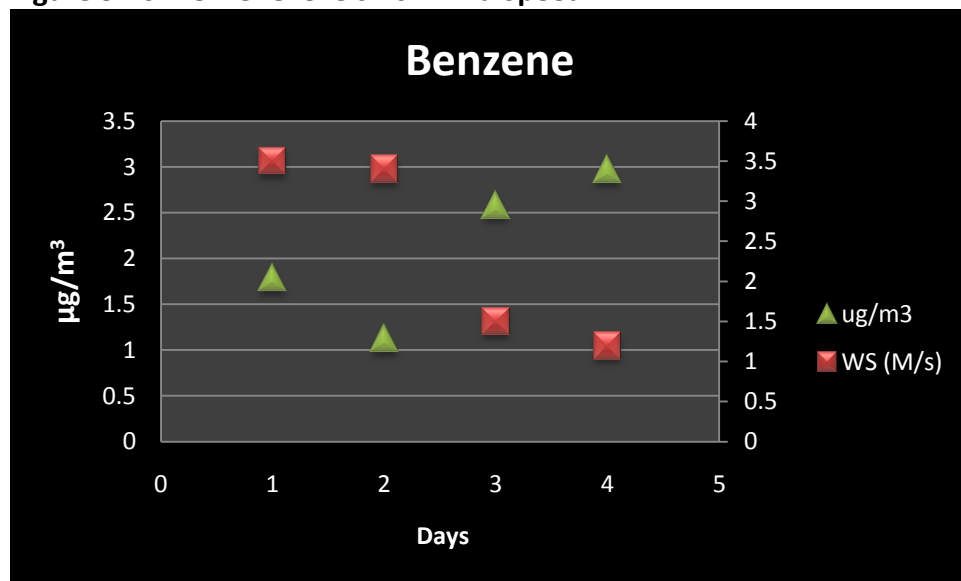
Figure 5.19 Benzene levels Vs. Temperature



Wind Speed. As Figure 5.20 illustrates, ambient air concentrations of benzene during the sampling events on windy days tended to be lower than those on days with calm or light winds. Moreover, the concentration differences for most wind speed categories shown in the figure were statistically significant. The Pearson correlation

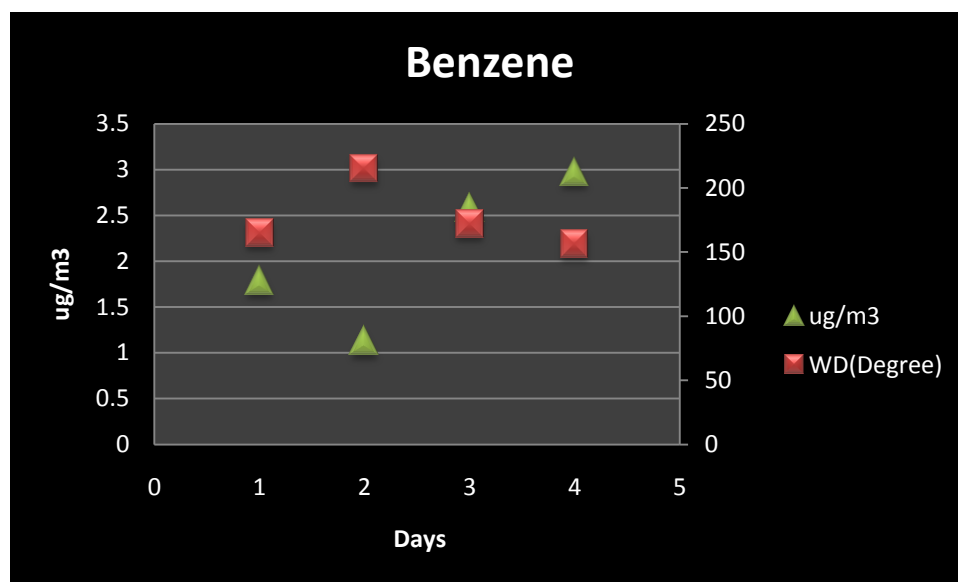
coefficients between wind speed and benzene concentration are generally consistent with the data trends indicated in Figure 5.20. The correlation coefficient was -0.93 ($P=0.07$). This negative correlation coefficient indicates that benzene levels during the sampling period tended to be lower when wind speeds were higher, and vice versa. This is generally consistent with air dispersion modeling algorithms, which predict that higher wind speeds enhance dispersion of pollutants in the atmosphere (USEPA, 1995).

Figure 5.20: Benzene levels Vs. Wind Speed



Wind Direction. The scatter plots in Figure 5.21 show how benzene varied with wind direction. The plots do not include results from the four valid samples that were collected when winds were either variable or calm.. The magnitude of benzene concentrations during the sampling event appeared to be largely independent of the wind direction.

Figure 5.21: Benzene levels Vs. Wind Direction (WD).



5.9 Particulate Matter (PM_{2.5})

Fine particulate matter (PM_{2.5}) is one criterion of the six criteria “pollutants” that the EPA has for National Ambient Air Quality Standards (NAAQS). No exceedances of federal NAAQS were recorded for PM_{2.5} in any of the sampling days or sites. As we have seen in the statistics summary table for the meteorological data (Table 5.16), the weather got too cold for instruments to operate. So, the sampling periods were limited to 12 to 18 hours per day. PM_{2.5} data should be interpreted carefully here since an instrumentation bias could be introduced. Clearly, higher concentrations at the UP site could be an indication of association between oil and gas development and PM_{2.5}.

elevated concentrations. However, Motor vehicles and other man-made activities are likely the largest contributors to PM_{2.5} in the area. For example, wood smoke from household fireplaces and stoves could be another source of particulate elevation at the sampling site since the sampling took place around the residential house.

PM_{2.5} Levels Comparisons to Other Area

Comparisons were made to another area in Garfield County for PM_{2.5}: Rifle, which is about 18 miles from Battlement Mesa. This provides a comparative look at urban area (Rifle) and oil and gas/urban area (Battlement Mesa). Both Rifle and Battlement Mesa PM_{2.5} data were collected simultaneously. Data are presented in Table 5.20 and show that PM_{2.5} levels, on average, in Battlement Mesa are generally similar to or higher than concentrations in Rifle. However, the UP site has higher PM_{2.5} concentrations than Rifle site. This could be because of the proximity of the UP site to the well pad, and that's another indication of the association of elevated PM_{2.5} levels and oil and gas development process.

Table 5.20: PM_{2.5} Comparisons to Other Area

Day	*Rifle		Battlement Mesa				
	Overall 24-hour arithmetic average (µg/m ³)	Overall 24-hour maximum	UP	DN	FR	Overall arithmetic average (µg/m ³)	Overall maximum
1	8	18	15	6.9	2.2	8	47
2	9	15	11	2.2	2.2	5	49
3	13	72	14	2.9	10	9	43
4	11	41	13.7	4.9	5.1	8	72

* Data obtained from Garfield County website.

Comparisons of PM_{2.5} data to Selected Meteorological Data

Figure 5.21 and figure 5.22 show that there were similar particulate concentrations recorded at day 1, day 3 and day 4. With primary winds, on average, from the south to southeasterly area approximately most of the time, and sometimes from the west, theoretically the largest particulate concentrations should have been seen at the sampling locations when the wind direction comes from east/northeast (downwind). But the graph cannot demonstrate whether there was elevation of PM_{2.5}

levels when the wind comes from the downwind because the graph is based on 24-hour average wind direction. There appears to be little effect of wind speed on the particulate data at the sampling location. Precipitation (snow) was covering the sampling location during the sampling period, and this could reduce the particulate that would be generated from activity on the pad or from wind.

Figure 5.21 comparison of PM_{2.5} Concentration to Wind Direction (WD)

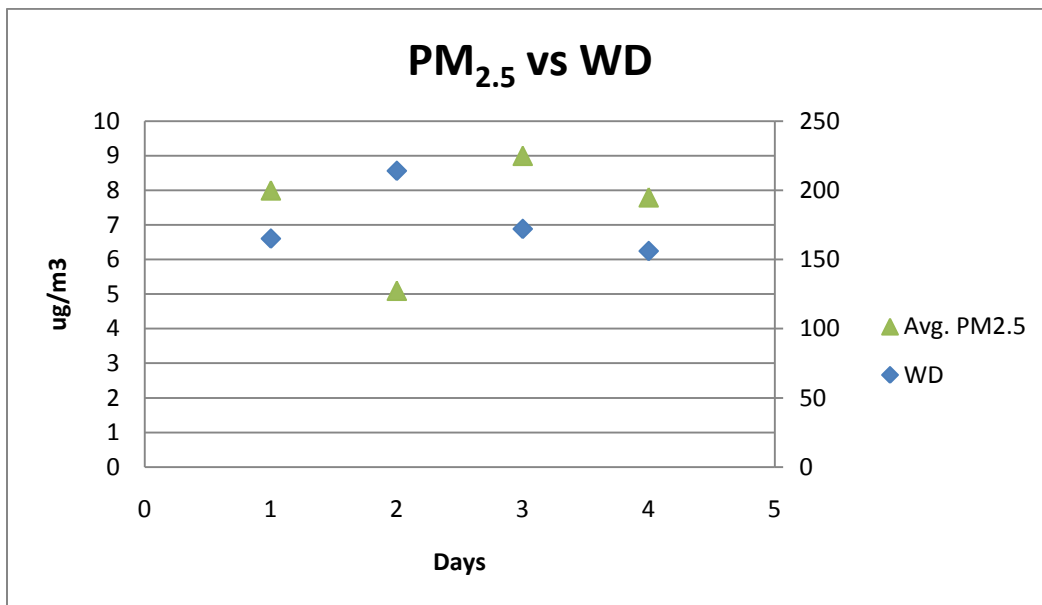
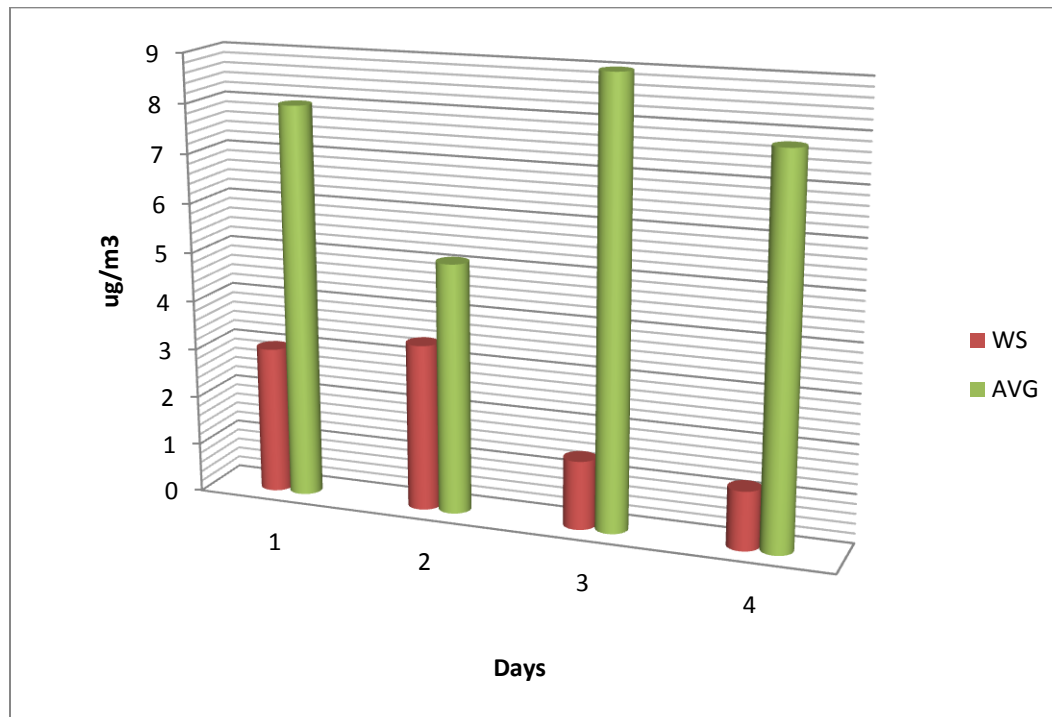


Figure 5.21 comparison of PM2.5 Concentration to Wind Speed



5.10 Total Volatile Organic compounds (TVOCs)

As mentioned in the methods section, the equipment (PID) used to measure TVOC concentrations did not provide information on concentrations of individual VOCs, but instead it detects the sum of all volatile carbon compounds in the C1 to C10 range (excluding methane). The aim of collecting TVOC was simply to enhance the canister sampling and identify whether emissions from the various sites in the private house may be creating an unhealthy level of VOCs. The background site (FR) had relatively higher TVOCs concentrations than others, but they are not statistically significant. This finding

is consistent with BTEX compounds results which were higher at the background site than other sites. The TVOCs levels elevation at the background site could be an indication of other factors that affect the ambient air of Battlement Mesa area such as mobile source emissions and stationary sources (commercial facilities). Also, as mentioned in the SNMOC section, there is a gas station right next to the fire house which could be another factor of having higher concentrations at the background site.

In August 2008 the Colorado Department of Public Health and Environment (CDPHE) conducted an air toxic study, and TVOCs was one parameter that was measured during the study. TVOCs samples were collected at north site of Battlement Mesa (close to our sampling location) and the results are presented in the TVOCs comparison table below (table 5.23). The background site had the highest total average VOC and UP site came next while CDPHE result had the lowest value. In the CDPHE study, the average VOC concentrations over the entire sampling period (24-hour), as well as the maximum value observed, are 166 and 1,116 ppbv, respectively. CDPHE study recorded the highest TVOC concentration (1,116 ppbv) compared to all sites in our study. It is not surprising to see TVOCs maximum value is higher during the summer season as seen on CDPHE study than the winter season (our study) because of the higher emissions during the winter season.

Table 5.23: TVOCs Comparisons to CDPHE study

SITE	Total Average VOC (ppbv)	Maximum VOC concentration (ppbv)
UP	430	653
DN	250	349
FR	556	890
North BM(CDPHE)	166	1,116

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

The sampling events of SNMOC, PM_{2.5}, and TVOCs were conducted in this pilot study to test the following research hypothesis and address the following specific goals:

H₀: *there are no measurable VOCs, Particulates on the resident property area (approximately 800- 1200 feet) affected by production activities of 12 producing wells on Watson Ranch Pad site compared to the background levels.*

Based on the results obtained, we would be inclined to reject the null hypothesis. There were measurable VOCs, and particulates on the resident property area (approximately 800-1200 feet) affected by production activity of 12 producing wells on WRP *compared to the background levels.*

Specific goals:

1. *Determine air concentrations of speciated non-methane organic compounds (SNMOCs/VOCs, including benzene, toluene, ethylbenzene, and xylenes), total VOCs, and particulate matter (PM_{2.5}) which is about 800-1200 feet from a well pad that has 12 wells producing natural gas.*

This first goal of this pilot study was achieved successfully, and the main findings are discussed in the following paragraphs:

The high completeness of SNMOCs sampling by getting valid sampling results during the entire sampling period suggest that samples were collected and handled efficiently at all sites throughout the study. The variability in ambient air concentrations in the Battlement Mesa area among the three sampling sites is similar (i.e. coefficients of variation lower than 1.0 or 100%) during the sampling period. Supported by the findings of the Relative Percent Differences (RPDs), the concentration differences observed in duplicate SNMOC samples were typically less than $\pm 1 \mu\text{g}/\text{m}^3$, a level indicative of excellent measurement precision. Therefore, the SNMOC/VOCs data presented in this study are of a known and high quality. All parameters: SNMOC, $\text{PM}_{2.5}$, and TVOC were tested for normality and data were normally distributed.

The Battlement Mesa area has a wide range of pollutants, based on the evidence that 62 compounds of the 78 SNMOCs were detected in most samples. Meanwhile, since the compounds measured were dominated by light alkanes, we could say that these light alkanes are the primary components of natural gas in the Battlement Mesa area. As the majority of the compounds in general were never measured at concentrations exceeding $10 \mu\text{g}/\text{m}^3$, and all of the BTEX compounds were never measured at concentrations exceeding $5 \mu\text{g}/\text{m}^3$, those are considered to be low concentrations compared to standards and suggested guidelines.

The BTEX group was detected on all of the sampling sites during the sampling period (100% frequency of detection i.e. high prevalence). Moreover, the background site recorded higher BTEX and TVOCs concentrations than the sampling sites (UP and DN sites). This could be an indication of other factors that cause the BTEX and TVOCs elevations such as mobile sources emissions rather than site-specific emissions sources (well pad). However, relatively high BTEX measurements, not just at the background site but at all sites in the Battlement Mesa area, may indicate more localized sources for these BTEX parameters, which have primarily gasoline and diesel combustion sources that include motor vehicles, oil and gas development activities (such as drill rigs and compressor engines) as well as oil and gas production equipment such as condensate tanks. On the other hand, TSNMOCs, TNMOCs, light alkanes, and most of the SNMOCs individual compounds were more pronounced at UP, DN sites than the background site (FR), so this could be an indication of strong association between oil and gas development processes and the elevations of these compounds due to the fact that UP and DN sites are closer to the well pad than the FR site.

In general, certain days had higher VOCs concentrations than other days, and the difference was statistically significant. As a result, the meteorological data was used to determine if there was a specific source that may have caused the results. The humidity, temperature, and wind directions are weakly associated with ambient air concentrations of SNMOCs/VOCs levels, but we cannot generalize our findings since we sampled in certain days for a short time period. In contrast, there is an association between the precipitation and the VOCs levels. VOCs concentration during the sampling

period tended to be lower when precipitation occurred. Also, the levels of VOCs tended to be lower when the wind speeds were higher, so the VOCs levels and wind speeds were strongly correlated during the sampling period. There also appears to be little effect of wind speed on the particulate data at sampling location.

Comparing to advisory ambient air standards (i.e. RELs and RBC), none of the VOCs had exceeded the recommended limits. Only one carcinogen, benzene, was measured in air at risk levels during this study, but it was slightly higher than the recommended limits for RBC and it did not exceed the RELs. No exceedances of federal NAAQS were recorded for $PM_{2.5}$ in any of the sampling days or sites. As a result of the comparison of $PM_{2.5}$ data between Battlement Mesa (oil and gas development area) and Rifle (urban area) from previous data, oil and gas areas recorded slightly higher $PM_{2.5}$ levels than the urban area.

2. *Determine if air concentrations of SNMOCs, $PM_{2.5}$ and TVOCs levels are higher than background concentrations/levels during the production phase of well development process.*

Briefly, most of the SNMOCs and $PM_{2.5}$ levels were higher at the sampling sites than the background site, but the difference was not statistically significant. On the other hand, TVOCs and BTEX group recorded higher concentrations at the background site than the sampling sites, but again they were not statistically different. It can be concluded that the fire station is not a good background site since it is affected by other emissions sources such as the fire truck engines and the gas station nearby the FR.

3. *Determine if air concentrations of SNOMCs, $PM_{2.5}$ and TVOCs decrease with setback distance (i.e. between UP and DN site).*

In general, despite the fact that the UP site (800ft) recorded higher concentrations than the DN site (1200ft), the air concentrations of SNMOCs, PM_{2.5}, and TVOCs were not statistically different between the UP site and the DN site. But there was a trend for air concentrations of those parameters to decrease with setback distance.

4. The air quality data and lessons learned from conducting this first field pilot study can be used to plan future research for a comprehensive project.

There is no doubt that the collected air data from this study would be very beneficial to plan future research for a comprehensive project. One of the most important outcomes of this study is that the fire station is not a good representative background site. Therefore, Garfield County should rethink about the selection of the background site for Battlement Mesa area. Another useful finding is that the information obtained about data variability in the sampling area could be helpful for sample size calculations.

Another lesson learned from this pilot study is that the direct reading photometer, Personal Data RAM (pDR1200), is not a recommended method to use for collecting particulates, predominantly during the winter season due to instrument-related temperature bias. Method IO-1.3 using TEOM Monitor could be the best alternative method to collect particulate matter since it operates at any weather condition (EPA, 1999), and there is no need for external equipment, such as the personal pump, that also gets affected by the weather conditions.

Pilot Study Recommendations for Future Studies

Placing VOC monitors, PM equipment, and meteorological equipment at close distances to the well pad, and in the four cardinal directions around the well pad, as well as at the background site would be the most beneficial to determining where and how far the compounds are transported. Placement of monitors at various distances from the well pads in the primary wind direction would also help provide a clearer picture of the transport issue.

Analysis of future monitoring data is needed to characterize data trends between the meteorological parameters (Humidity, temperature, wind speed, wind directions, and precipitation) to determine exactly how much the concentrations are affected by each of those parameters in order to fully understand the localized effects that such drilling and completion activities could possibly have on the public at large..

There should be some follow up information developed on nearby benzene emission sources near the private house and the background site and the Battlement Mesa area in general. The presence of mobile and area source emissions certainly need to be evaluated.

Based on our findings of VOC and PM, it is advised that action should be made by the agencies (such as GCPHD) to identify and monitor the concentrations of those parameters in the air in Battlement Mesa, Colorado. Not only may individual VOCs, such as benzene, be contributing to health problems in the area, the VOCs may also be contributing to the formation of ground-level ozone, which is also a health hazard. In

future research, it is also recommended to examine the PM chemical speciation to identify the potential sources of PM emissions (i.e. the origin of PM emissions) at the oil and gas industry.

Since some of the VOCs individuals (i.e. benzene) recorded a potential health hazard, it is recommended to sample during other natural gas explorations activities, such as fracking and flow back operations besides the production phase in the winter season and other seasons (all other sampling has been in the summer except year-round ambient monitoring) to see if there is a statistically different concentration between the production phase and other operations of natural gas development at different seasons. It is also suggested that VOCs monitoring occur not only in residential areas, but also in the area of oil and gas operations. This will help to get closer to the emissions source that may be emitting large volumes of VOCs due to fugitive emissions, venting, or VOC emissions due to incomplete combustions of waste gas during flaring operations.

Limitations:

The primary limitation of this pilot study is the weather conditions such as extreme cold temperature and precipitations. The sampling days recorded very cold temperatures (-18C) that affected the sampling equipment. For example, the pDR could not measure any particulate levels during the first two days at the background site due to the cold temperature. Snow was also an issue during the sampling period since some

of the equipment cannot operate when there is a precipitation. Therefore, the equipment was kept inside a cooler to avoid the precipitation.

Recommendations to reduce air pollution in the area:

In order to promote the air pollution reduction at the private house and Battlement Mesa, high-quality management practices should be used during the next phase of drilling and completions at the well pad. The followings are some examples of the best management practices that may be used to reduce air pollution (Witter wt. al, 2008):

- All venting emissions from the production tanks should be routed through a VOC combustor.
- Vapor recovery technology could be a substitution for the combustion to further reduce air pollution.
- COGCC green completion practices and EPA's natural gas STAR program should be obeyed in order to have best air pollution reduction technology.

REFERENCES

- California Air Resources Board. "Toxic Air Contaminants Monitoring" (page updated March, 2011) Available from URL: <http://www.arb.ca.gov/aaqm/toxics.htm>
- "Volatile Organic Compounds | Indoor Air Quality | US EPA." *US Environmental Protection Agency*. Web. 20 Mar. 2011. <<http://www.epa.gov/iaq/voc.html>>.
- CDPHE, 2006. Oil and Gas Exploration & Production Condensate Tanks, an Overview of Air Quality Regulations. Colorado Department of Public Health and Environment. March 2006.
- "State and County Emission Summaries | Air Emission Sources | US EPA." *US Environmental Protection Agency*. Web. 20 Mar. 2011. <http://www.epa.gov/cgi-bin/broker?_service=data&_debug=0&_program=dataprog.dw_do_all_emis_2005.sas&pol=229&stfips=08>.
- "Oil and Gas Extraction: Impacts, Risks, and Regulations." *ECM Home*. Web. 20 Mar. 2011. <<http://ecm.ncms.org/ERI/new/IRRoilgas.htm#quant>>.
- Pollack, A., Russell, J., Grant, J., Friesen, R., Fields, P. and Wolf, M. August, 2006. *Ozone Precursors Emission Inventory for San Juan and Rio Arriba Counties, New Mexico*. Prepared for New Mexico Environment Department. p. 2-19. Available from URL: http://www.nmenv.state.nm.us/aqb/projects/San_Juan_Ozone/NM_Area_Emissions_report.pdf
- U.S. Environmental Protection Agency. AP-42, CH 13.5: Industrial Flares. Available from URL: <http://www.epa.gov/ttn/chief/ap42/ch13/final/c13s05.pdf>
- Stroscher, M. Alberta Research Council. 1996. *Investigations of Flare Gas Emissions in Alberta*. Report prepared for Environment Canada, the Alberta Energy and Utilities Board and the Canadian Association of Petroleum Producers. 157 pp.
- Oklahoma Department of Environmental Quality. 2004. *Calculation of Flashing Losses/VOC Emissions from Hydrocarbon Storage Tanks*. Fact sheet. Available from URL: <http://www.deq.state.ok.us/factsheets/air/CalculationLosses.pdf>

The Endocrine Disruption Exchange (TEDX). November 17, 2006. *Chemicals Used in Natural Gas Development and Delivery*. Available from URL:
<http://www.earthworksaction.org/publications.cfm?pubID=162>

Colorado Department of Public Health and Environment. Oct, 2002. *A Community-based Short-term Ambient Air Screening Study in Garfield County for Oil and Gas Related Activities*. Available from
URL:<http://oilgas.state.co.us/Library/piceancebasin/GarfieldFinalReport10-31.pdf>

Pierce, G. (CO Dept. of Public Health and Env't). Nov. 2002. *Garfield County Air Monitoring Results*. Available from URL:
<http://oilgas.state.co.us/Library/piceancebasin/GarfieldCountyMonitoring.pdf>

"TERC - Project H051C." *TERC - TERC Projects*. Web. 20 Mar. 2011.
<<http://projects.terc.airquality.org/AQR/H051C>>.

Rada, J. April, 2006. *Status of Garfield County's Air Quality Monitoring Program*. Power point presentation. Available from URL:
http://www.garfieldcounty.com/docs/air_quality_study__4.6.06.ppt

Colorado Department of Public Health and Environment. Oct, 2009. *Garfield County Emissions Inventory Report 2009* Available from URL: <http://www.garfieldcountyaq.net/>

AIR SPECIALISTS RESOURCES. "GARFIELD COUNTY 2009 AIR QUALITY MONITORING SUMMARY." *Garfield County Air Quality*. 8 Dec. 2010. Web. 23 Mar. 2011.
<<http://www.garfieldcountyaq.net/>>.

California Air Resources Board. "Toxic Air Contaminants Monitoring" (page updated February 15, 2005) Accessed Jan. 2, 2006. Available from URL:
<http://www.arb.ca.gov/aaqm/toxics.htm>

Knox, E.G. 2005. "Childhood cancers and atmospheric carcinogens," *Journal of Epidemiology and Community Health*. 2005;59:101-105. p. 101,

Witter, Roxana. "Potential Exposure-Related Human Health Effects of Oil and Gas Development." *NRDC Document Bank*. 1 Aug. 2008. Web. 24 Mar. 2011.
<http://docs.nrdc.org/health/hea_08091702.asp>.

U.S. Environmental Protection Agency. Technology Transfer Network Air Toxics Website. 1,3- Butadiene. "Hazard Summary" (revised January, 2000). Available from URL:
<http://www.epa.gov/ttn/atw/hlthef/butadien.html>

Canadian Association of Petroleum Producers. 2006. *Best Management Practices - Control of Benzene Emissions from Glycol Dehydrators*. p. 65 Available from URL: http://www.capp.ca/default.asp?V_DOC_ID=763&PubID=80610

National Center for Environmental Assessment, Office of Research and Development. Available from URL: <http://www.epa.gov/iris/subst/0276.htm>

Canadian Association of Petroleum Producers. 2006. *Best Management Practices - Control of Benzene Emissions from Glycol Dehydrators*

Garfield County. "Garfield County - Energy Advisory Board." *Garfield County, Colorado*. 15 Aug. 2007. Web. 03 Apr. 2011. <http://www.garfield-county.com/oil-gas/energy-advisory-board.aspx>

Colorado Department of Public Health and Environment (CDPHE) - Air Pollution Control Division. Analysis of Data Obtained for the Garfield County Air Toxics Study Summer 2008, October. In: Health P, ed.; 2009

U.S. Environmental Protection Agency. *Health Effects Notebook for Hazardous Air Pollutants*. Available from URL: <http://www.epa.gov/ttn/atw/hlthef/hapindex.html>

U.S. Environmental Protection Agency. *Health Effects Notebook for Hazardous Air Pollutants*. Available from URL: <http://www.epa.gov/ttn/atw/hlthef/hapindex.html>

California Office of Environmental Health Hazard Assessment. "Chronic Reference Exposure Levels Adopted by OEHHHA as of Dec. 2008." Available from URL: http://www.oehha.ca.gov/air/chronic_rels/AllChrels.html

California Environmental Protection Agency (CalEPA). *Air Toxics Hot Spots Program Risk Assessment Guidelines: Part III. Technical Support Document for the Determination of Noncancer Chronic Reference Exposure Levels. SRP Draft*. Office of Environmental Health Hazard Assessment, Berkeley, CA. 1999. Available from URL: http://www.oehha.ca.gov/air/chronic_rels/pdf/relsP32k.pdf

All data from the U.S. Environmental Protection Agency. *Health Effects Notebook for Hazardous Air Pollutants*. Available from URL: <http://www.epa.gov/ttn/atw/hlthef/hapindex.html>

Chang, O.M.C. and England, G.C., "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Update: Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles."

Pope et al. Lung Cancer, Cardiopulmonary Mortality, and Long-Term Exposure to Fine Particulate Air Pollution. *Journal of the American Medical Association*. 287: pp 1132-1141, March 6, 2002.

Gauderman et al. The Effect of Air Pollution on Lung Development from 10 to 18 Years of Age. *The New England Journal of Medicine*. Volume 351: pp 1057–1067, Number 11, September 9, 2004.

Kunzli et al. Ambient Air Pollution and Atherosclerosis in Los Angeles. *Environmental Health Perspectives*. Volume 113, 2: pp 201-206, February 2005;
<http://ehp.niehs.nih.gov/members/2004/7523/7523.pdf>.

U.S. Environmental Protection Agency. Review of the National Ambient Air Quality Standards for Particulate Matter: Policy Assessment of Scientific and Technical Information. EPA-452/R-05-005, June 2005;
http://www.epa.gov/ttn/naaqs/standards/pm/data/pmstaffpaper_20050630.pdf.

Samet, J. M., F. Dominici, F. C. Curriero, I. Coursac and S. L. Zeger (2000). Fine particulate air pollution and mortality in 20 US Cities, 1987-1994. *New England Journal of Medicine* 343(24): 1742-1749.

Schwartz, J., D. W. Dockery and L. M. Neas (1996). Is daily mortality associated specifically with fine particles? *Journal of the Air & Waste Management Association* 46(10): 927-939.

Lipfert, F. W., S. C. Morris and R. E. Wyzga (2000). Daily mortality in the Philadelphia metropolitan area and size-classified particulate matter. *Journal of the Air & Waste Management Association* 50(8): 1501-1513.

Aunan, K. (1996). Exposure-response functions for health effects of air pollutants based on epidemiological findings. *Risk Analysis* 16(5): 693-709.

Pope, C. A. (2000). Epidemiology of Fine Particulate Air Pollution and Human Health: Biological Mechanisms and Who's at Risk? *Environmental Health Perspectives Supplement* 108(S4): 713-724.

Abbey, D.E., Nishino, N., McDonnell, W.F., Burchette, R.J., Knusten, S.F., Beeson, W.L., Yang, J.X. (1999) Long-Term Inhalable Particles and Other Air Pollutants Related to Mortality in Nonsmokers; *Am. J. Respir. Crit. Care Med.* 159, 373- 382.

Hoek, G., B. Brunekreef, S. Goldbohm, P. Fischer and P. A. van den Brandt (2002). Association between mortality and indicators of traffic-related air pollution in the Netherlands: a cohort study. *Lancet* 360(9341): 1203-1209.

CDPHE. "Garfield County Air Quality." *Garfield County, Colorado*. Garfield County Public Health, 21 Oct. 2009. Web. 28 May 2011.
http://www.garfieldcountyaq.net/default_new.aspx

Australian Institute of Energy. "AIE | Resources." *FACT SHEET 4: OIL AND GAS*. AIE, 2004. Web. 05 June 2011. <<http://aie.org.au/Content/NavigationMenu/Resources>>.

Limerick Et All. "What Every Westerner Should Know About Energy." *Center of the American West | CU-Boulder*. Center of the American West, Oct. 2003. Web. 05 June 2011.
<<http://www.centerwest.org/publications/>>.<http://www.centerwest.org/publications/pdf/energy.pdf>

Garfield County EAB. "Understanding Natural Gas Development." *Garfield County, Colorado*. Garfield County, Aug. 2007. Web. 05 June 2011. <<http://www.garfield-county.com/oil-gas/energy-advisory-board.aspx>>. Available from URL
<http://dola.colorado.gov/dlg/osg/docs/GarCoCommunityGuide.pdf>

Occupational Safety and Health Administration (OSHA). Occupational Safety and Health Standards, Toxic and Hazardous Substances. *Code of Federal Regulations*. 29 CFR 1910.1000. 1998.

U.S. Environmental Protection Agency. *Integrated Risk Information System (IRIS) on Benzene*. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 2002.

Aksoy, M.: Benzene as a leukemogenic and Carcinogenic Agent. *Am. J. Ind. Med.* 8:9-20(1985)

United States - Fact Sheet." *American FactFinder*. 2009. Web. 27 June 2011.
<http://factfinder.census.gov/servlet/ACSSAFFacts?_event=Search>.

Witter R, Stinson K, Sackett H, et al. Potential Exposure-Related Human Health Effects of Oil and Gas Development: A Literature Review (2003-2006). In. Denver, CO: Colorado School of Public Health

Bloemen, L. J., A. Youk, et al. (2004). "Lymphohaematopoietic cancer risk among chemical workers exposed to benzene." *Occupational & Environmental Medicine* 61(3): 270-4.

Collins, J. J., B. Ireland, et al. (2003). "Lymphohaematopoeitic cancer mortality among workers with benzene exposure." *Occupational & Environmental Medicine* 60(9): 676-9.

Garte, S., T. Popov, et al. (2005). "Biomarkers of exposure and effect in Bulgarian petrochemical workers exposed to benzene." *Chemico-Biological Interactions* 153-154: 247-51.

Fevotte, J., B. Charbotel, et al. (2006). "Case-control study on renal cell cancer and occupational exposure to trichloroethylene. Part I: Exposure assessment." *Annals of Occupational Hygiene* 50(8): 765-75.

Glass, D. C., C. N. Gray, et al. (2003). "Leukemia risk associated with low-level benzene exposure.[see comment]." *Epidemiology* 14(5): 569-77.

Knox, E. G. (2005). "Oil combustion and childhood cancers.[see comment]." *Journal of Epidemiology & Community Health* 59(9): 755-60.

Seniori Costantini, A., M. Quinn, et al. (2003). "Exposure to benzene and risk of leukemia among shoe factory workers." *Scandinavian Journal of Work, Environment & Health* 29(1): 51-9.

Bardodej Z, Bardodejova E, Malek B: [Value and application of exposure tests—XI. Exposure test for styrene.] *Cesk Hyg.* 6(9):546-52, 1961 (Cze)

Carpenter CP, Kinkead ER, Geary DL Jr, Sullivan LJ, King JM [1975]. Petroleum hydrocarbon toxicity studies. IV. Animal and human response to vapors of rubber solvent. *Toxicol Appl Pharmacol* 33:526-542.

Paxton MB, Chinchilli VM, Brett SM, Rodricks JV. Leukemia risk associated with benzene exposure in the pliofilm cohort. II. Risk estimates. *Risk Anal.* 1994 Apr;14(2):155–161

Crump K. 1994. "Risk of benzene induced leukemia: a sensitivity analysis of the pliofilm cohort with additional follow-up and new exposure estimates." *J. Toxicology and Environmental Health*, vol.42, 219-242.

Campagna, D., Stengel, B., Mergler, D., Limasset, J. C., Diebold, F., Michard, D., et al. (2001). Color vision and occupational toluene exposure: *Neurotoxicology and Teratology* Vol 23(5) Sep-Oct 2001, 473-480.

APPENDICES

Appendix 4.1: Sampling Periods

UP site

Start Sampling date	Start Time	End Sampling Date	End Time
2/7/2011	12:33	2/8/2011	10:35
2/8/2011	10:40	2/9/2011	8:55
2/9/2011	14:10	2/10/2011	12:10
2/10/2011	13:55	2/11/2011	11:55

DN site

Start Sampling date	Start Time	End Sampling Date	End Time
2/7/2011	12:55	2/8/2011	10:55
2/8/2011	11:25	2/9/2011	9:20
2/9/2011	14:30	2/10/2011	12:20
2/10/2011	13:30	2/11/2011	11:25

FR site

Start Sampling date	Start Time	End Sampling Date	End Time
2/7/2011	13:27	2/8/2011	11:55
2/8/2011	12:10	2/9/2011	9:50
2/9/2011	14:50	2/10/2011	12:50
2/10/2011	13:10	2/11/2011	11:45

Appendix 4.2: Target SNMOCs

ANALYTE	CAS- NUMBER	MDL ($\mu\text{g}/\text{m}^3$)
1,2,3-Trimethylbenzene	526-73-8	0.150
1,2,4-Trimethylbenzene	95-63-6	0.180
1,3,5-Trimethylbenzene	108-67-8	0.190
1,3-Butadiene	106-99-0	0.190
1-Decene	872-05-9	0.200
1-Dodecene	112-41-4	0.430
1-Heptene	592-76-7	0.440
1-Hexene	592-41-6	0.330
1-Nonene	124-11-8	0.250
1-Octene	111-66-0	0.260
1-Pentene	109-67-1	0.130
1-Tridecene	2437-56-1	0.430
1-Undecene	821-95-4	0.200
2,2,3-Trimethylpentane	564-02-3	0.260
2,2,4-Trimethylpentane	540-84-1	0.160
2,2-Dimethylbutane	75-83-2	0.140
2,3,4-Trimethylpentane	565-75-3	0.150
2,3-Dimethylbutane	79-29-8	0.210
2,3-Dimethylpentane	565-59-3	0.440
2,4-Dimethylpentane	108-08-7	0.230
2-Ethyl-1-butene	760-21-4	0.330
2-Methyl-1-butene	563-46-2	0.190
2-Methyl-1-pentene	763-29-1	0.330
2-Methyl-2-butene	513-35-9	0.190
2-Methylheptane	592-27-8	0.130
2-Methylhexane	591-76-4	0.220
2-Methylpentane	107-83-5	0.150
3-Methyl-1-butene	563-45-1	0.190
3-Methylheptane	589-81-1	0.160
3-Methylhexane	589-34-4	0.140
3-Methylpentane	96-14-0	0.170
4-Methyl-1-pentene	691-37-2	0.330
Acetylene	74-86-2	0.080
a-Pinene	80-56-8	0.200
Benzene	71-43-2	0.220
b-Pinene	127-91-3	0.200
cis-2-Butene	590-18-1	0.170
cis-2-Hexene	7688-21-3	0.330
cis-2-Pentene	627-20-3	0.180
Cyclohexane	110-82-7	0.190
Cyclopentane	287-92-3	0.120
Cyclopentene	142-29-0	0.190
Ethane	74-84-0	0.090

Ethylbenzene	100-41-4	0.180
Ethylene	74-85-1	0.290
Isobutane	75-28-5	0.160
Isobutene/1-Butene	115-11-7/106-98-9	0.130
Isopentane	78-78-4	0.180
Isoprene	78-79-5	0.190
Isopropylbenzene	98-82-8	0.200
m-Diethylbenzene	141-93-5	0.200
Methylcyclohexane	108-87-2	0.180
Methylcyclopentane	96-37-7	0.160
m-Ethyltoluene	620-14-4	0.170
m-Xylene/p-Xylene	108-38-3/106-42-3	0.240
n-Butane	106-97-8	0.190
n-Decane	124-18-5	0.200
n-Dodecane	112-40-3	0.430
n-Heptane	142-82-5	0.190
n-Hexane	110-54-3	0.180
n-Nonane	111-84-2	0.210
n-Octane	111-65-9	0.230
n-Pentane	109-66-0	0.110
n-Propylbenzene	103-65-1	0.190
n-Tridecane	629-50-5	0.430
n-Undecane	1120-21-4	0.200
o-Ethyltoluene	611-14-3	0.190
o-Xylene	95-47-6	0.170
p-Diethylbenzene	105-05-5	0.120
p-Ethyltoluene	622-96-8	0.250
Propane	74-98-6	0.100
Propylene	115-07-1	0.090
Propyne	74-99-7	0.100
Styrene	100-42-5	0.260
Toluene	108-88-3	0.280
trans-2-Butene	624-64-6	0.140
trans-2-Hexene	4050-45-7	0.330
trans-2-Pentene	646-04-8	0.140

Appendix 4.3

Standard Operating Procedure for Filter Weighing

1. Summary:

In order to determine the concentration of an aerosol sample, filters must be weighed before and after the sampling to provide the best estimate of the true total mass of the sample. The 37 mm filter will be used to calibrate the concentration estimates of for the direct reading device; personal Data RAM (pDR). Using the pre-weight and the post-weight of the filters and the known volume pulled through the filter by the personal sampling pump, the concentration (mg/m^3) of the sample will be determined.

2. Equipments and Materials

- An analytical microbalance (Mettler-Toledo MX5, Columbus, OH)
- A Polonium-210 anti-static device
- 37 mm filter
- Desiccating chamber
- Forceps
- Filter Samplers (37 mm cassettes).
- Zip-lock bags

3. Filter Weighing Procedure

3.1 Purchase filters and store them in room 111.

3.1.1 Only “in use” filters should be unwrapped from its original packing.

3.1.2 Open filter containers should be kept in the “clean” desiccators for temporary storage.

3.2 Wash hands, don gloves.

3.3 Turn on balance if not already on, re-calibrate using internal calibration.

3.3.1 After internal calibration is complete, re-zero the balance.

3.3.2 Balance indicator should read 0.000.

3.3.3 A periodic check using a type-S mg weight can be used to reconfirm correct calibration.

3.4 Use forceps to handle both the filter and its backing support at all times.

3.4.1 Place each side of the desired filter on a Polonium-210 anti-static device for at least ten seconds.

3.5 Open and close the wind screen by using the motion sensitive pad.

3.6 Weigh the filter to the nearest 0.001 mg, allowing the measurement to stabilize for 10 seconds before recording (this may take 30-45 seconds). If measurement will not stabilize, return the filter to the anti-static device for at least ten more seconds and retry to weigh filter.

3.7 Record all weights in laboratory notebook.

3.7.1 Indicate filter type and batch number.

3.7.2 Each filter should be weighed twice.

3.7.2.1 If the second weight is more than 0.005 mg different than the first measurement, the filter should be weighed a third time and all three measurements should be averaged.

3.7.2.2 If the balance does not return to zero when the filter is removed, this measurement should be discarded and the filter should be reweighed.

3.8 Place filter in 37 mm cassette.

3.8.1 Seal, label, and plug ends using appropriate sealing plugs.

- 3.9 Store all devices in individual zip-loc or similar type bags during transport to sampling site.
- 3.10 At the field site, follow the SOP for the pDR units.
- 3.11 After sampling, seal, label, and plug ends using appropriate sealing plugs and return to transport bag.
- 3.12 After returning from sampling site, remove samplers from bags. Remove plugs and place filter upright (filter side up). Keep filters/samplers in desiccant chamber overnight (at least twelve hours).
- 3.13 After at least 12 hours, remove filters/samplers from desiccant chamber and post weigh according to steps 3.2 through 3.7.
- 3.14 Transfer all laboratory notebook information to excel spreadsheet for sample concentration (mg/m^3) determination.

4. Material Handling

- 4.1 Following sampling event, place the sealed 37 mm cassettes in a ziplock bag.
- 4.2 Place the ziplock bag containing the 37 mm cassettes in a storage container that minimizes the ability of the cassette to be jostle during transport.
- 4.3 Upon arrival at the laboratory, place the 37 mm cassettes in the desiccant chamber.

5. Safety and Health

Sampling pumps, pDRs and cassettes will be contaminated during field sampling events. Workers should wear gloves when handling these devices and the devices must be cleaned appropriately after each field visit.

Appendix 4.4:

Standard Operating Procedure for Particulate Matter (PM_{2.5})

1. Summary:

In order to assess particulate matter (PM_{2.5}) concentrations present during fracing and flow back processes, the MIE personal Data RAM 1200 (pDR) will be used at the drilling site. The pDR is a direct reading instrument and PM levels will be logged at 1-minute intervals. Using the pDR, data logging software, and the total mass determined by the back-up filter, the concentration of PM_{2.5} will be determined on a near real time basis.

2. Equipments and Materials

- Personal Data RAM (pDR)
- SKC Leland Legacy pump operating at a 4 lpm flow rate
- Zeroing filter cartridge
- PM_{2.5} cyclone
- 37-mm filter holder and pre-weighed filter
- 9V batteries (lithium type)
- Tripods to hold the pDR units
- Coolers to protect pDR units
- Tubing to connect pDR to pump
- 37-mm cassette opener

3. Sample Collection and Procedure

3.1 Charge personal air sampling pumps fully prior to field visit.

3.2 Pre-weigh desiccated 37 mm filters according to filter weighing SOP prior to field visit.

- 3.3 Place pre-weighed filter into 37 mm cassette, and place sampler into a ziplock bag for transport into field.
- 3.4 Remove 37 mm cassette from ziplock bag.
- 3.5 Attach the filter in 37 mm cassette and personal air sampling pump to the pDR by means of tubing to the hose fitting on the pDR filter holder attached to sensing chamber.
- 3.6 Calibrate the pump, using a primary calibration device, to 4 Lpm and record the final average flow rate on the sample collection form.
- 3.7 Zero the pDR-1200 by:
 - 3.7.1 Connecting the green zeroing filter cartridge to the inlet.
 - 3.7.2 Run the pDR in the Zeroing mode with the attached pump for at least one minute.
 - 3.7.3 Once the CALIBRATION:OK message appears on the pDR display, stop the pump and disconnect the zeroing filter.
 - 3.7.4 The pDR is now zeroed and ready to use.
- 3.8 Attach the metal cyclone to the inlet of the pDR.
- 3.9 Press ON/OFF button, and the NEXT, and finally ENTER to run the pDR.
- 3.10 Record the exact start time on the sample collection form.
- 3.11 Place pDR in the cooler with the inlet pointing out the opening in the side of the cooler. The cooler is intended to protect the unit from changes in temperature and precipitation events.
- 3.12 At the end of the sampling period Post-calibrate the personal air sampling pump, using a primary calibration device, and record the final average flow rate on the sample collection form.
- 3.13 Stop the personal air sampling pump and record the exact stop time.

- 3.14 Stop the pDR by pressing EXIT, ENTER, ON/OFF and ENTER button sequentially. Logged data is saved automatically.
- 3.15 Remove the 37 mm cassette, cap, and place in ziplock bag.
- 3.16 Post-weigh the 37mm filter according to filter weighing SOP and record.
- 3.17 Connect the pDR to the laptop and download the data, and save in spreadsheet file.

4. Material and Data Handling

- 4.1 Following sampling event, place the filter sample holders in a ziplock bag.
- 4.2 Place the ziplock bag containing the filter sample holders in a storage container that minimizes the ability of the cassette to be jostle during transport.
- 4.3 Upon arrival at the laboratory, place the filter sample holders in the desiccant chamber.
- 4.4 Download data from pDR-1200 and save data to the shared network drive.

5. Safety and Health

- 5.1 Sampling pumps, pDRs and cassettes will be contaminated during field sampling events. Workers should wear gloves when handling these devices and the devices must be cleaned appropriately after each field visit.

Appendix 4.5: Sample Collection Form

Environmental and Health Monitoring Pilot Study

SAMPLING NOTES

CIRCLE LOCATION:

UPSTREAM

DOWNSTREAM

FIRE
STATION

DATE: _____

OPERATOR(s): _____

RECORD TIME ON 24 HR CLOCK (e.g. 2400)!

SUMMA

SAMPLE IDENTIFIER*	INITIAL PRESSURE	START TIME	END TIME	END PRESSURE
CANISTER ID		VERIFIED (☐)		

PDR (PM_{2.5})

SAMPLE IDENTIFIER	FLOW RATE	START TIME	ZERO START	END TIME
FILTER VERIFIED(☐)			POST FLOW	

ONLY FOR UPSTREAM LOCATION!

NOISE

SAMPLE IDENTIFIER	START TIME	END TIME

WINDY? _____ PRECIPITATION? _____ ODORS? _____

NOTES/OBSERVATIONS:

NOTES APPROVED BY _____

DATE _____

* Site identifier: Site ID, date, direction, distance, method, QC

For example, a sample collected for SNMOCs on February 7, 2011 at the west side of the well pad and at the upstream of the house would be assigned the following unique identifier: Normal sample:

WR20110207-UPSN, Field duplicate: WR20110207-UPSF, Blank: WR20110207- UPSB

Appendix 4.6: Chain of Custody Form

 ERG Lab ID # _____				
TOXICS/SNMOC SAMPLE CHAIN OF CUSTODY				
Lab Pre-Sampling	Site Code: _____ City/State: _____ AQS Code: _____ Collection Date: _____ Options SNMOC (Y/N): _____ TOXICS (Y/N): _____ Relinquished by: _____	Canister Number: _____ Lab Initial Can. Press. ("Hg): _____ Date Can. Cleaned: _____ Cleaning Batch #: _____ Duplicate Event (Y/N): _____ Duplicate Can #: _____ Date: _____		

	Field Setup	Received by: _____ Operator: _____ Sys. #: _____ Setup Date: _____ Field Initial Can. Press. ("Hg): _____	Date: _____ MFC Setting: _____ Elapsed Timer Reset (Y/N): _____ Canister Valve Opened (Y/N): _____	

		Field Recovery	Recovery Date: _____ Field Final Can. Press. ("Hg): _____ Status: Valid Void (Circle one) Relinquished by: _____	Sample Duration (3 or 24 hr): _____ Elapsed Time: _____ Canister Valve Closed (Y/N): _____ Date: _____

	Lab Recovery		Received by: _____ Status: Valid Void (Circle one) If void, why: _____	Date: _____ Lab Final Can. Press. ("Hg): _____

Comments: _____ _____ _____ _____ _____ _____ _____ _____ _____ _____				

White: Sample Traveler

Canary: Lab Copy

Pink: Field Copy

Appendix 5.0

5.1 Summary Statistics for SNMOC Concentrations ($\mu\text{g}/\text{m}^3$) Measured at Upstream

(Based on 4 Days with Valid Samples)

Analyte	No# of detections	Frq. of Detection	Lo	Hi	Median	Arithmetic mean	Geometric mean	Std. Dev.	Cof. Of Variation
Ethylene	4.00	100.00	0.82	1.48	1.28	1.22	1.18	0.30	0.24
Acetylene	4.00	100.00	0.60	1.09	0.87	0.86	0.83	0.24	0.27
Ethane	4.00	100.00	38.60	119.00	78.10	78.45	70.67	39.05	0.50
Propylene	4.00	100.00	0.21	0.43	0.36	0.34	0.33	0.09	0.27
Propane	4.00	100.00	21.60	63.90	43.40	43.08	39.15	20.49	0.48
Propyne	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isobutane	4.00	100.00	6.61	20.80	13.95	13.83	12.54	6.59	0.48
Isobutene/1-Butene	4.00	100.00	1.32	1.81	1.49	1.53	1.52	0.21	0.13
1,3-Butadiene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Butane	4.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
trans-2-Butene	4.00	100.00	0.04	0.09	0.07	0.07	0.06	0.02	0.33
cis-2-Butene	3.00	75.00	0.10	0.11	0.11	0.11	0.11	0.01	0.05
3-Methyl-1-butene	4.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Isopentane	4.00	100.00	4.27	13.90	9.61	9.35	8.43	4.51	0.48

1-Pentene	4.00	100.00	0.10	0.20	0.15	0.15	0.14	0.05	0.31
2-Methyl-1-butene	4.00	100.00	0.23	0.34	0.29	0.29	0.28	0.05	0.16
n-Pentane	4.00	100.00	3.26	10.60	7.39	7.16	6.47	3.41	0.48
Isoprene	4.00	100.00	0.07	0.12	0.11	0.10	0.10	0.02	0.22
trans-2-Pentene	3.00	75.00	0.08	0.11	0.09	0.09	0.09	0.02	0.16
cis-2-Pentene	3.00	75.00	0.07	0.10	0.09	0.09	0.09	0.02	0.18
2-Methyl-2-butene	3.00	75.00	0.09	0.13	0.11	0.11	0.11	0.02	0.18
2,2-Dimethylbutane	4.00	100.00	0.27	0.79	0.59	0.56	0.52	0.23	0.41
Cyclopentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Methyl-1-pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyclopentane	4.00	100.00	0.36	0.81	0.60	0.59	0.56	0.22	0.37
2,3-Dimethylbutane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methylpentane	4.00	100.00	1.68	5.36	3.80	3.66	3.33	1.68	0.46
3-Methylpentane	4.00	100.00	0.95	3.07	2.11	2.06	1.87	0.97	0.47
2-Methyl-1-pentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Hexene	4.00	100.00	0.09	0.18	0.14	0.14	0.13	0.05	0.36
2-Ethyl-1-butene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Hexane	4.00	100.00	1.93	6.59	4.43	4.35	3.91	2.10	0.48
trans-2-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

cis-2-Hexene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methylcyclopentane	4.00	100.00	1.07	3.43	2.31	2.28	2.06	1.08	0.48
2,4-Dimethylpentane	4.00	100.00	0.21	0.49	0.39	0.37	0.35	0.13	0.34
Benzene	4.00	100.00	0.73	1.55	1.25	1.20	1.15	0.37	0.31
Cyclohexane	4.00	100.00	1.21	4.09	2.75	2.70	2.43	1.31	0.48
2-Methylhexane	4.00	100.00	0.73	1.91	1.38	1.35	1.27	0.53	0.39
2,3-Dimethylpentane	4.00	100.00	0.31	0.69	0.53	0.51	0.49	0.17	0.33
3-Methylhexane	4.00	100.00	0.76	2.09	1.32	1.37	1.26	0.64	0.46
1-Heptene	4.00	100.00	0.41	1.09	0.77	0.76	0.71	0.30	0.40
2,2,4-Trimethylpentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Heptane	4.00	100.00	0.98	3.11	2.14	2.09	1.91	0.94	0.45
Methylcyclohexane	4.00	100.00	2.51	8.34	5.58	5.50	4.99	2.59	0.47
2,2,3-Trimethylpentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3,4-Trimethylpentane	3.00	75.00	0.11	0.14	0.11	0.12	0.12	0.02	0.14
Toluene	4.00	100.00	1.15	2.96	2.19	2.12	2.00	0.79	0.37
2-Methylheptane	4.00	100.00	0.28	0.81	0.61	0.58	0.53	0.23	0.40
3-Methylheptane	4.00	100.00	0.23	0.66	0.48	0.46	0.43	0.19	0.41
1-Octene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

n-Octane	4.00	100.00	0.69	1.94	1.38	1.35	1.26	0.53	0.40
Ethylbenzene	4.00	100.00	0.09	0.23	0.21	0.18	0.17	0.06	0.34
m-Xylene/p-Xylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Styrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
o-Xylene	4.00	100.00	0.12	0.29	0.23	0.22	0.20	0.07	0.33
1-Nonene	4.00	100.00	0.09	0.12	0.11	0.11	0.11	0.02	0.14
n-Nonane	4.00	100.00	0.38	0.84	0.60	0.60	0.58	0.20	0.33
Isopropylbenzene	1.00	25.00	0.04	0.10	0.05	0.03	0.51	0.04	0.06
a-Pinene	4.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Propylbenzene	4.00	100.00	0.06	0.10	0.06	0.07	0.07	0.02	0.29
m-Ethyltoluene	4.00	100.00	0.08	0.88	0.16	0.32	0.21	0.38	1.17
p-Ethyltoluene	4.00	100.00	0.09	0.15	0.14	0.13	0.13	0.03	0.21
1,3,5-Trimethylbenzene	4.00	100.00	0.13	0.23	0.18	0.18	0.18	0.04	0.23
o-Ethyltoluene	4.00	100.00	0.07	0.14	0.11	0.11	0.10	0.03	0.28
b-Pinene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2,4-Trimethylbenzene	4.00	100.00	0.18	0.28	0.21	0.22	0.21	0.04	0.20
1-Decene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Decane	4.00	100.00	0.29	0.51	0.37	0.38	0.37	0.10	0.25
1,2,3-	2.00	50.00	0.04	0.08	0.06	0.02	0.37	0.06	0.06

Trimethylbenzene									
m-Diethylbenzene	4.00	100.00	0.07	0.12	0.10	0.10	0.09	0.03	0.30
p-Diethylbenzene	2.00	50.00	0.07	0.11	0.09	0.09	0.09	0.03	0.31
1-Undecene	4.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Undecane	4.00	100.00	0.20	0.36	0.23	0.25	0.25	0.07	0.29
1-Dodecene	4.00	100.00	0.15	0.40	0.29	0.28	0.27	0.11	0.38
n-Dodecane	4.00	100.00	0.13	0.20	0.18	0.17	0.17	0.03	0.20
1-Tridecene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Tridecane	1.00	25.00	0.08	0.10	0.09	0.01	0.11	0.10	0.10

**5.2 Summary Statistics for SNMOC Concentrations ($\mu\text{g}/\text{m}^3$) Measured at Downstream
(Based on 4 Days with Valid Samples)**

Analyte	No# of detections	Frq. of Detection	Lo	Hi	Median	Arithmetic mean	Geometric mean	Std. Dev.	Cof. Of Variation
Ethylene	4	100	0.687	1.410	1.261	1.155	1.112	0.333	0.289
Acetylene	4	100	0.555	1.022	0.982	0.885	0.860	0.222	0.250
Ethane	4	100	21.217	96.417	60.798	59.808	51.301	33.924	0.567
Propylene	4	100	0.159	0.366	0.318	0.290	0.276	0.095	0.327
Propane	4	100	12.910	52.833	35.393	34.132	29.855	18.064	0.529
Propyne	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Isobutane	4	100	4.002	17.557	12.020	11.400	9.887	6.066	0.532
Isobutene/1-Butene	3	75	0.039	1.262	1.150	0.900	0.503	0.577	0.641
1,3-Butadiene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Butane	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
trans-2-Butene	3	75	0.050	0.080	0.073	0.069	0.068	0.013	0.191
cis-2-Butene	4	100	0.070	0.122	0.090	0.093	0.091	0.022	0.232
3-Methyl-1-butene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Isopentane	4	100	2.701	12.069	8.494	7.940	6.896	4.109	0.518
1-Pentene	4	100	0.083	0.150	0.108	0.112	0.109	0.028	0.254
2-Methyl-1-butene	3	75	0.179	0.428	0.273	0.288	0.274	0.105	0.366
n-Pentane	4	100	2.268	9.288	8.399	7.088	6.204	3.263	0.460
Isoprene	3	75	0.098	0.150	0.108	0.116	0.114	0.024	0.203

trans-2-Pentene	3	75	0.074	0.800	0.098	0.267	0.152	0.356	1.331
cis-2-Pentene	3	75	0.069	0.098	0.074	0.079	0.078	0.013	0.171
2-Methyl-2-butene	2	50	0.100	0.136	0.115	0.117	0.116	0.015	0.133
2,2-Dimethylbutane	4	100	0.181	0.713	0.459	0.453	0.400	0.237	0.523
Cyclopentene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4-Methyl-1-pentene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cyclopentane	4	100	0.201	0.769	0.496	0.490	0.435	0.251	0.513
2,3-Dimethylbutane	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Methylpentane	4	100	1.158	4.858	3.194	3.101	2.701	1.670	0.539
3-Methylpentane	4	100	0.633	2.777	1.819	1.762	1.528	0.954	0.542
2-Methyl-1-pentene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Hexene	3	75	0.108	0.150	0.124	0.126	0.125	0.018	0.139
2-Ethyl-1-butene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	4	100	1.277	5.832	3.712	3.633	3.136	1.998	0.550
trans-2-Hexene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
cis-2-Hexene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Methylcyclopentane	4	100	0.692	3.101	1.892	1.894	1.627	1.084	0.572
2,4-Dimethylpentane	4	100	0.105	0.460	0.259	0.271	0.237	0.151	0.558
Benzene	4	100	0.534	1.488	1.077	1.044	0.967	0.438	0.419
Cyclohexane	4	100	0.805	3.694	2.272	2.261	1.934	1.303	0.576
2-Methylhexane	4	100	0.560	1.752	1.141	1.148	1.047	0.537	0.467
2,3-Dimethylpentane	4	100	0.254	0.774	0.480	0.497	0.457	0.227	0.457
3-Methylhexane	4	100	0.363	1.744	1.277	1.165	0.985	0.655	0.562
1-Heptene	4	100	0.271	1.108	0.643	0.667	0.589	0.356	0.534

2,2,4-Trimethylpentane	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Heptane	4	100	0.692	2.883	1.772	1.780	1.549	0.985	0.554
Methylcyclohexane	4	100	1.710	7.532	4.449	4.535	3.914	2.590	0.571
2,2,3-Trimethylpentane	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2,3,4-Trimethylpentane	3	75	0.073	0.110	0.094	0.093	0.091	0.018	0.190
Toluene	4	100	0.905	2.815	1.986	1.923	1.768	0.830	0.431
2-Methylheptane	4	100	0.247	0.765	0.495	0.500	0.454	0.240	0.481
3-Methylheptane	4	100	0.164	0.627	0.402	0.399	0.353	0.208	0.521
1-Octene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Octane	4	100	0.538	1.786	1.123	1.142	1.023	0.583	0.511
Ethylbenzene	4	100	0.101	0.207	0.177	0.166	0.160	0.048	0.288
m-Xylene/p-Xylene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Styrene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
o-Xylene	4	100	0.102	0.244	0.222	0.198	0.187	0.065	0.328
1-Nonene	4	100	0.076	0.087	0.082	0.082	0.082	0.005	0.059
n-Nonane	4	100	0.322	0.744	0.478	0.506	0.470	0.216	0.428
Isopropylbenzene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
a-Pinene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Propylbenzene	3	75	0.065	0.090	0.080	0.079	0.078	0.012	0.157
m-Ethyltoluene	4	100	0.080	0.146	0.110	0.112	0.109	0.030	0.268
p-Ethyltoluene	4	100	0.085	0.121	0.115	0.109	0.108	0.017	0.155
1,3,5-Trimethylbenzene	4	100	0.085	0.206	0.143	0.145	0.134	0.063	0.436

o-Ethyltoluene	4	100	0.076	0.103	0.091	0.090	0.090	0.012	0.138
b-Pinene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,2,4-Trimethylbenzene	4	100	0.132	0.210	0.179	0.175	0.172	0.039	0.224
1-Decene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Decane	4	100	0.240	0.388	0.304	0.309	0.302	0.076	0.247
1,2,3-Trimethylbenzene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
m-Diethylbenzene	1	25	0.055	0.068	0.055	0.058	0.058	0.007	0.113
p-Diethylbenzene	2	50	0.076	0.100	0.088	0.088	0.088	0.012	0.132
1-Undecene	2	50	0.050	0.150	0.100	0.100	0.092	0.044	0.439
n-Undecane	4	100	0.165	0.208	0.182	0.184	0.183	0.022	0.119
1-Dodecene	4	100	0.085	0.476	0.235	0.258	0.217	0.162	0.630
n-Dodecane	4	100	0.087	0.164	0.120	0.123	0.120	0.033	0.271
1-Tridecene	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Tridecane	0	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000

5.3 Summary Statistics for SNMOC Concentrations ($\mu\text{g}/\text{m}^3$) Measured at Fire Station (Based on 4 Days with Valid Samples)

Analyte	No# of detections	Frq. of Detection	Lo	Hi	Median	Arithmetic mean	Geometric mean	Std. Dev.	Cof. Of Variation
Ethylene	4.000	100.000	0.816	1.527	1.305	1.239	1.201	0.337	0.272
Acetylene	4.000	100.000	0.620	1.100	0.901	0.880	0.854	0.457	0.519
Ethane	4.000	100.000	18.267	90.914	59.835	57.213	48.917	31.257	0.546
Propylene	4.000	100.000	0.211	0.509	0.357	0.358	0.340	0.222	0.620
Propane	4.000	100.000	11.313	48.999	34.580	32.368	28.293	27.263	0.842
Propyne	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Isobutane	4.000	100.000	3.548	16.630	11.996	11.043	9.514	9.664	0.875
Isobutene/1-Butene	3.000	75.000	0.039	1.844	1.300	1.120	0.587	1.379	1.231
1,3-Butadiene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Butane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
trans-2-Butene	4.000	100.000	0.068	0.164	0.129	0.123	0.116	0.074	0.599
cis-2-Butene	4.000	100.000	0.080	0.181	0.151	0.141	0.135	0.075	0.531
3-Methyl-1-butene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Isopentane	4.000	100.000	2.622	12.006	8.945	8.130	7.029	7.018	0.863
1-Pentene	4.000	100.000	0.092	0.176	0.142	0.138	0.134	0.062	0.447
2-Methyl-1-butene	4.000	100.000	0.248	0.431	0.340	0.340	0.332	0.141	0.416
n-Pentane	4.000	100.000	2.512	9.167	6.799	6.319	5.672	4.939	0.782
Isoprene	4.000	100.000	0.065	0.119	0.090	0.091	0.089	0.043	0.467

trans-2-Pentene	3.000	75.000	0.020	0.173	0.129	0.113	0.087	0.127	1.122
cis-2-Pentene	3.000	75.000	0.010	0.130	0.086	0.078	0.055	0.094	1.211
2-Methyl-2-butene	3.000	75.000	0.050	0.172	0.147	0.129	0.117	0.138	1.069
2,2-Dimethylbutane	4.000	100.000	0.201	0.666	0.521	0.477	0.433	0.356	0.747
Cyclopentene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4-Methyl-1-pentene	1.000	25.000	0.020	0.095	0.020	0.039	0.030	0.083	2.136
Cyclopentane	4.000	100.000	0.197	0.733	0.521	0.493	0.441	0.411	0.834
2,3-Dimethylbutane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Methylpentane	4.000	100.000	1.124	4.949	3.545	3.291	2.873	2.813	0.855
3-Methylpentane	4.000	100.000	0.617	2.751	2.006	1.845	1.605	1.586	0.860
2-Methyl-1-pentene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Hexene	4.000	100.000	0.096	0.150	0.118	0.120	0.118	0.042	0.349
2-Ethyl-1-butene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	4.000	100.000	1.216	5.734	4.010	3.742	3.236	3.280	0.876
trans-2-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
cis-2-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Methylcyclopentane	4.000	100.000	0.631	3.068	2.062	1.956	1.680	1.820	0.931
2,4-Dimethylpentane	4.000	100.000	0.124	0.396	0.305	0.282	0.259	0.233	0.825
Benzene	4.000	100.000	0.595	1.903	1.209	1.229	1.127	1.046	0.851
Cyclohexane	4.000	100.000	0.683	3.591	2.375	2.256	1.912	2.167	0.960
2-Methylhexane	4.000	100.000	0.522	1.913	1.335	1.276	1.143	1.046	0.819
2,3-Dimethylpentane	4.000	100.000	0.259	0.728	0.495	0.494	0.461	0.341	0.690
3-Methylhexane	4.000	100.000	0.542	2.107	1.272	1.298	1.163	1.103	0.850
1-Heptene	4.000	100.000	0.279	1.026	0.705	0.679	0.611	0.551	0.812

2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Heptane	4.000	100.000	0.607	3.280	1.918	1.931	1.631	1.921	0.995
Methylcyclohexane	4.000	100.000	1.496	7.754	4.830	4.728	4.026	4.600	0.973
2,2,3-Trimethylpentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2,3,4-Trimethylpentane	3.000	75.000	0.070	0.147	0.129	0.119	0.114	0.116	0.980
Toluene	4.000	100.000	0.874	3.877	2.264	2.320	2.030	2.332	1.006
2-Methylheptane	4.000	100.000	0.217	0.918	0.561	0.564	0.497	0.504	0.894
3-Methylheptane	4.000	100.000	0.183	0.801	0.482	0.487	0.425	0.450	0.924
1-Octene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Octane	4.000	100.000	0.488	2.222	1.249	1.302	1.133	1.245	0.956
Ethylbenzene	4.000	100.000	0.087	0.392	0.256	0.248	0.217	0.214	0.865
m-Xylene/p-Xylene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Styrene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
o-Xylene	4.000	100.000	0.112	0.473	0.295	0.294	0.260	0.276	0.940
1-Nonene	3.000	75.000	0.060	0.158	0.111	0.110	0.104	0.117	1.060
n-Nonane	4.000	100.000	0.305	1.030	0.571	0.619	0.564	0.523	0.844
Isopropylbenzene	2.000	50.000	0.043	0.103	0.055	0.064	0.059	0.093	1.468
a-Pinene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Propylbenzene	3.000	75.000	0.010	0.140	0.088	0.082	0.057	0.107	1.310
m-Ethyltoluene	4.000	100.000	0.078	0.293	0.177	0.181	0.163	0.163	0.900
p-Ethyltoluene	4.000	100.000	0.066	0.215	0.151	0.145	0.134	0.112	0.768
1,3,5-Trimethylbenzene	4.000	100.000	0.098	0.352	0.186	0.206	0.186	0.194	0.944
o-Ethyltoluene	4.000	100.000	0.071	0.238	0.142	0.148	0.136	0.126	0.850

b-Pinene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,2,4-Trimethylbenzene	4.000	100.000	0.142	0.437	0.300	0.295	0.273	0.222	0.754
1-Decene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Decane	4.000	100.000	0.282	0.683	0.407	0.445	0.422	0.295	0.662
1,2,3-Trimethylbenzene	3.000	75.000	0.009	0.090	0.076	0.063	0.046	0.076	1.209
m-Diethylbenzene	3.000	75.000	0.020	0.186	0.148	0.126	0.094	0.159	1.266
p-Diethylbenzene	4.000	100.000	0.010	0.085	0.077	0.062	0.047	0.073	1.175
1-Undecene	1.000	25.000	0.010	0.260	0.010	0.073	0.023	0.227	3.120
n-Undecane	4.000	100.000	0.172	0.465	0.282	0.300	0.280	0.222	0.741
1-Dodecene	4.000	100.000	0.231	0.356	0.306	0.300	0.295	0.099	0.330
n-Dodecane	4.000	100.000	0.156	0.353	0.202	0.228	0.216	0.154	0.676
1-Tridecene	4.000	100.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Tridecane	4.000	100.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Analyte	No# of detections	Frq. of Detection	Lo	Hi	Median	Arithmetic mean	Geometric mean	Std. Dev.	Cof. Of Variation
Ethylene	4.000	100.000	0.816	1.527	1.305	1.239	1.201	0.337	0.272
Acetylene	4.000	100.000	0.620	1.100	0.901	0.880	0.854	0.457	0.519
Ethane	4.000	100.000	18.267	90.914	59.835	57.213	48.917	31.257	0.546
Propylene	4.000	100.000	0.211	0.509	0.357	0.358	0.340	0.222	0.620
Propane	4.000	100.000	11.313	48.999	34.580	32.368	28.293	27.263	0.842
Propyne	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Isobutane	4.000	100.000	3.548	16.630	11.996	11.043	9.514	9.664	0.875
Isobutene/1-Butene	3.000	75.000	0.039	1.844	1.300	1.120	0.587	1.379	1.231
1,3-Butadiene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

n-Butane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
trans-2-Butene	4.000	100.000	0.068	0.164	0.129	0.123	0.116	0.074	0.599
cis-2-Butene	4.000	100.000	0.080	0.181	0.151	0.141	0.135	0.075	0.531
3-Methyl-1-butene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Isopentane	4.000	100.000	2.622	12.006	8.945	8.130	7.029	7.018	0.863
1-Pentene	4.000	100.000	0.092	0.176	0.142	0.138	0.134	0.062	0.447
2-Methyl-1-butene	4.000	100.000	0.248	0.431	0.340	0.340	0.332	0.141	0.416
n-Pentane	4.000	100.000	2.512	9.167	6.799	6.319	5.672	4.939	0.782
Isoprene	4.000	100.000	0.065	0.119	0.090	0.091	0.089	0.043	0.467
trans-2-Pentene	3.000	75.000	0.020	0.173	0.129	0.113	0.087	0.127	1.122
cis-2-Pentene	3.000	75.000	0.010	0.130	0.086	0.078	0.055	0.094	1.211
2-Methyl-2-butene	3.000	75.000	0.050	0.172	0.147	0.129	0.117	0.138	1.069
2,2-Dimethylbutane	4.000	100.000	0.201	0.666	0.521	0.477	0.433	0.356	0.747
Cyclopentene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4-Methyl-1-pentene	1.000	25.000	0.020	0.095	0.020	0.039	0.030	0.083	2.136
Cyclopentane	4.000	100.000	0.197	0.733	0.521	0.493	0.441	0.411	0.834
2,3-Dimethylbutane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Methylpentane	4.000	100.000	1.124	4.949	3.545	3.291	2.873	2.813	0.855
3-Methylpentane	4.000	100.000	0.617	2.751	2.006	1.845	1.605	1.586	0.860
2-Methyl-1-pentene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Hexene	4.000	100.000	0.096	0.150	0.118	0.120	0.118	0.042	0.349
2-Ethyl-1-butene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Hexane	4.000	100.000	1.216	5.734	4.010	3.742	3.236	3.280	0.876
trans-2-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
cis-2-Hexene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Methylcyclopentane	4.000	100.000	0.631	3.068	2.062	1.956	1.680	1.820	0.931
2,4-Dimethylpentane	4.000	100.000	0.124	0.396	0.305	0.282	0.259	0.233	0.825
Benzene	4.000	100.000	0.595	1.903	1.209	1.229	1.127	1.046	0.851
Cyclohexane	4.000	100.000	0.683	3.591	2.375	2.256	1.912	2.167	0.960
2-Methylhexane	4.000	100.000	0.522	1.913	1.335	1.276	1.143	1.046	0.819
2,3-Dimethylpentane	4.000	100.000	0.259	0.728	0.495	0.494	0.461	0.341	0.690
3-Methylhexane	4.000	100.000	0.542	2.107	1.272	1.298	1.163	1.103	0.850
1-Heptene	4.000	100.000	0.279	1.026	0.705	0.679	0.611	0.551	0.812
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Heptane	4.000	100.000	0.607	3.280	1.918	1.931	1.631	1.921	0.995
Methylcyclohexane	4.000	100.000	1.496	7.754	4.830	4.728	4.026	4.600	0.973
2,2,3-Trimethylpentane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2,3,4-Trimethylpentane	3.000	75.000	0.070	0.147	0.129	0.119	0.114	0.116	0.980
Toluene	4.000	100.000	0.874	3.877	2.264	2.320	2.030	2.332	1.006
2-Methylheptane	4.000	100.000	0.217	0.918	0.561	0.564	0.497	0.504	0.894
3-Methylheptane	4.000	100.000	0.183	0.801	0.482	0.487	0.425	0.450	0.924
1-Octene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Octane	4.000	100.000	0.488	2.222	1.249	1.302	1.133	1.245	0.956
Ethylbenzene	4.000	100.000	0.087	0.392	0.256	0.248	0.217	0.214	0.865
m-Xylene/p-Xylene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Styrene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
o-Xylene	4.000	100.000	0.112	0.473	0.295	0.294	0.260	0.276	0.940

1-Nonene	3.000	75.000	0.060	0.158	0.111	0.110	0.104	0.117	1.060
n-Nonane	4.000	100.000	0.305	1.030	0.571	0.619	0.564	0.523	0.844
Isopropylbenzene	2.000	50.000	0.043	0.103	0.055	0.064	0.059	0.093	1.468
a-Pinene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Propylbenzene	3.000	75.000	0.010	0.140	0.088	0.082	0.057	0.107	1.310
m-Ethyltoluene	4.000	100.000	0.078	0.293	0.177	0.181	0.163	0.163	0.900
p-Ethyltoluene	4.000	100.000	0.066	0.215	0.151	0.145	0.134	0.112	0.768
1,3,5-Trimethylbenzene	4.000	100.000	0.098	0.352	0.186	0.206	0.186	0.194	0.944
o-Ethyltoluene	4.000	100.000	0.071	0.238	0.142	0.148	0.136	0.126	0.850
b-Pinene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1,2,4-Trimethylbenzene	4.000	100.000	0.142	0.437	0.300	0.295	0.273	0.222	0.754
1-Decene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Decane	4.000	100.000	0.282	0.683	0.407	0.445	0.422	0.295	0.662
1,2,3-Trimethylbenzene	3.000	75.000	0.009	0.090	0.076	0.063	0.046	0.076	1.209
m-Diethylbenzene	3.000	75.000	0.020	0.186	0.148	0.126	0.094	0.159	1.266
p-Diethylbenzene	4.000	100.000	0.010	0.085	0.077	0.062	0.047	0.073	1.175
1-Undecene	1.000	25.000	0.010	0.260	0.010	0.073	0.023	0.227	3.120
n-Undecane	4.000	100.000	0.172	0.465	0.282	0.300	0.280	0.222	0.741
1-Dodecene	4.000	100.000	0.231	0.356	0.306	0.300	0.295	0.099	0.330
n-Dodecane	4.000	100.000	0.156	0.353	0.202	0.228	0.216	0.154	0.676
1-Tridecene	4.000	100.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Tridecane	4.000	100.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 5.10 Precision Estimates for SNMOC Measurements at UP Site

(Note: RPD: Relative percent Difference)

Analyte	Day 1 RPD (%)	Day 2 RPD (%)	Day 3 RPD (%)
Ethylene	8	23	3
Acetylene	12	11	6
Ethane	7	70	20
Propylene	22	40	NA
Propane	3	59	18
Propyne	NA	NA	NA
Isobutane	NA	53	16
Isobutene/1-Butene	6	183	5
1,3-Butadiene	NA	NA	NA
n-Butane	NA	NA	NA
trans-2-Butene	13	55	12
cis-2-Butene	26	NA	11
3-Methyl-1-butene	NA	NA	NA
Isopentane	16	49	13
1-Pentene	67	11	6
2-Methyl-1-butene	81	99	104
n-Pentane	72	44	13
Isoprene	23	30	17
trans-2-Pentene	25	NA	10
cis-2-Pentene	11	NA	NA
2-Methyl-2-butene	10	NA	31
2,2-Dimethylbutane	34	20	16
Cyclopentene	NA	NA	NA
4-Methyl-1-pentene	NA	59	NA
Cyclopentane	22	44	19
2,3-Dimethylbutane	NA	NA	NA
2-Methylpentane	8	35	10
3-Methylpentane	7	36	10
2-Methyl-1-pentene	NA	NA	NA

1-Hexene	88	12	5
2-Ethyl-1-butene	NA	NA	NA
n-Hexane	5	37	10
trans-2-Hexene	NA	NA	NA
cis-2-Hexene	NA	NA	NA
Methylcyclopentane	13	35	10
2,4-Dimethylpentane	32	27	4
Benzene	20	30	7
Cyclohexane	16	34	11
2-Methylhexane	17	16	3
2,3-Dimethylpentane	15	14	8
3-Methylhexane	8	19	14
1-Heptene	18	28	3
2,2,4-Trimethylpentane	NA	NA	NA
n-Heptane	17	25	1
Methylcyclohexane	22	23	7
2,2,3-Trimethylpentane	NA	NA	NA
2,3,4-Trimethylpentane	55	NA	0
Toluene	1	23	7
2-Methylheptane	34	11	6
3-Methylheptane	32	9	4
1-Octene	NA	NA	NA
n-Octane	31	14	4
Ethylbenzene	33	12	12
m-Xylene/p-Xylene	NA	NA	NA
Styrene	NA	NA	NA
o-Xylene	26	18	13
1-Nonene	40	33	22
n-Nonane	14	3	5
Isopropylbenzene	NA	NA	NA
a-Pinene	NA	NA	NA
n-Propylbenzene	45	45	10
m-Ethyltoluene	149	13	0
p-Ethyltoluene	NA	25	7
1,3,5-Trimethylbenzene	57	8	20
o-Ethyltoluene	29	13	13

b-Pinene	NA	NA	NA
1,2,4-Trimethylbenzene	5	18	NA
1-Decene	NA	NA	NA
n-Decane	6	3	2
1,2,3-Trimethylbenzene	7	6	13
m-Diethylbenzene	35	15	40
p-Diethylbenzene	15	25	15
1-Undecene	62	NA	57
n-Undecane	21	5	36
1-Dodecene	91	13	71
n-Dodecane	17	8	58
1-Tridecene	NA	NA	NA
n-Tridecane	NA	NA	92

Table 5.11: Precision Estimates for SNMOC Measurements at DN Site

Analyte	Day 3 RPD(%)	Day 4 RPD(%)
Ethylene	3	2
Acetylene	3	4
Ethane	0	15
Propylene	6	10
Propane	0	12
Propyne	NA	NA
Isobutane	0	8
Isobutene/1-Butene	4	28
1,3-Butadiene	NA	NA
n-Butane	NA	NA
trans-2-Butene	14	20
cis-2-Butene	1	34
3-Methyl-1-butene	NA	NA
Isopentane	1	6

1-Pentene	2	8
2-Methyl-1-butene	36	23
n-Pentane	2	5
Isoprene	21	11
trans-2-Pentene	4	17
cis-2-Pentene	12	8
2-Methyl-2-butene	36	4
2,2-Dimethylbutane	0	1
Cyclopentene	NA	NA
4-Methyl-1-pentene	NA	NA
Cyclopentane	3	6
2,3-Dimethylbutane	NA	NA
2-Methylpentane	2	3
3-Methylpentane	1	1
2-Methyl-1-pentene	NA	NA
1-Hexene	4	1
2-Ethyl-1-butene	NA	NA
n-Hexane	3	0
trans-2-Hexene	NA	NA
cis-2-Hexene	NA	NA
Methylcyclopentane	0	3
2,4-Dimethylpentane	7	17
Benzene	4	12
Cyclohexane	1	3
2-Methylhexane	0	5
2,3-Dimethylpentane	5	26
3-Methylhexane	12	5
1-Heptene	1	9
2,2,4-Trimethylpentane	NA	NA

n-Heptane	5	8
Methylcyclohexane	2	1
2,2,3-Trimethylpentane	NA	NA
2,3,4-Trimethylpentane	10	51
Toluene	7	17
2-Methylheptane	1	10
3-Methylheptane	8	9
1-Octene	NA	NA
n-Octane	5	7
Ethylbenzene	10	19
m-Xylene/p-Xylene	NA	NA
Styrene	NA	NA
o-Xylene	10	16
1-Nonene	6	33
n-Nonane	4	5
Isopropylbenzene	NA	NA
a-Pinene	NA	NA
n-Propylbenzene	26	12
m-Ethyltoluene	3	3
p-Ethyltoluene	7	12
1,3,5-Trimethylbenzene	7	8
o-Ethyltoluene	17	3
b-Pinene	NA	NA
1,2,4-Trimethylbenzene	4	16
1-Decene	NA	NA
n-Decane	1	12
1,2,3-Trimethylbenzene	NA	19
m-Diethylbenzene	38	42
p-Diethylbenzene	NA	NA

1-Undecene	NA	17
n-Undecane	17	31
1-Dodecene	70	7
n-Dodecane	37	17
1-Tridecene	NA	NA
n-Tridecane	NA	NA

The Annual Wind Rose in Parachute (Garfield County, 2011)

Garfield County - Colorado
Parachute

Wind Rose

01/01/2008 - 03/31/2010

